

INTERNATIONAL
SYMPOSIUM ON

Isotope Hydrology

Revisiting Foundations
and Exploring Frontiers

Vienna, Austria
11–15 May 2015

BOOK OF EXTENDED
SYNOPSSES

Poster session 3



Water
Resources
Programme



IAEA-CN-225

The material in this book has been supplied by the authors and has not been edited. The views expressed remain the responsibility of the named authors and do not necessarily reflect those of the government of the designating Member State(s). The IAEA cannot be held responsible for any material reproduced in this book.

POSTER SESSION 3

Atmosphere-Hydrosphere Interactions Paleoclimate and Paleohydrology Isotopes in Precipitation Environmental Studies Surface Water Isotopic Studies

Atmosphere-Hydrosphere Interactions

Factors controlling isotopic composition of water vapor over a paddy field, Mase, Japan: using a high frequency in-situ isotope observation and isotope enabled GCM (IAEA-CN-225-056).....	1
<i>Wei, Z.</i>	
Arctic water cycle: new constraints from water vapor isotope observations (IAEA-CN-225-067)	4
<i>Steen-Larsen, H.</i>	
Combining multiple types of datasets of water isotopic composition: insights from the analysis of the summer 2012 Greenland heat wave (IAEA-CN-225-101)	6
<i>Bonne, J.</i>	
Implementation of tritium in the LMDZ-iso General Circulation Model for the study of the relationships between stratospheric air inputs into the lower troposphere, water cycle and climate (IAEA-CN-225-181)	9
<i>Cauquoin, A.</i>	
Combining isotopic measurements of atmospheric vapor and lagoon water for analysing isotope fractionation during evaporation (IAEA-CN-225-250)	11
<i>Vallet-Coulomb, C.</i>	
The sensitivity of simulated water isotope distributions to differing climate model cloud parameters (IAEA-CN-225-255).....	12
<i>Nusbaumer, J.</i>	
ENSO and Indo-Pacific water isotopes: observations, modeling, and implications for proxy reconstructions (IAEA-CN-225-294).....	15
<i>Konecky, B</i>	
Evapotranspiration flux partitioning with real time stable isotope monitoring of water vapor in the monsoon region of northwestern México (IAEA-CN-225-299)	17
<i>Yépez González, E.</i>	

Paleoclimate and Paleohydrology

The ice-core stable isotope records from Svalbard glaciers as proxies of climate and environmental changes (IAEA-CN-225-130)	21
<i>Martma, T.</i>	
An online search and visualization tool for water stable isotope records from natural archives (IAEA-CN-225-138)	24
<i>Masson-Delmotte, V.</i>	
The Eemian sea and follow palaeo-hydrology of Baltic – White Sea region evidence from groundwater stable isotope ($\delta^2\text{H}$, $\delta^{18}\text{O}$) composition (IAEA-CN-225-139)	27
<i>Tokarev, I.</i>	
Weighting alternatives (precipitation vs. accumulation) for water stable isotopes – implications for ice core records (IAEA-CN-225-188).....	31
<i>Hatvani, I.</i>	
Coupling ^2H and ^{18}O biomarker analyses in palaeoclimate research: potential, conceptual model and validation (IAEA-CN-225-240)	35
<i>Zech, M.</i>	
Reconstructed isotopic composition of leaf water provides new insight into hydrological changes in east Africa during the last glacial (IAEA-CN-225-283)	38
<i>Hepp, J.</i>	

Isotopes in Precipitation

Key drivers controlling daily stable isotope variations in precipitation of Costa Rica: Caribbean Sea versus eastern Pacific Ocean moisture sources (IAEA-CN-225-019)	42
<i>Sanchez-Murillo, R.</i>	
Use of environmental isotopes for the assessment of snow water resources in the Moroccan high Atlas mountains: contribution to surface and groundwater recharge (IAEA-CN-225-022).....	44
<i>Nda, B.</i>	
Tritium time series in precipitation of Rm. Valcea, Romania (IAEA-CN-225-023)	47
<i>Varlam, C.</i>	
New isotopic data on precipitation and river water in the Central African Republic (GNIP and GNIR stations at Bangui) (IAEA-CN-225-031).....	51
<i>Djebebe-Ndjiguim, C.</i>	
A new network for isotopes in precipitation of Corsica (France) (IAEA-CN-225-033)	53
<i>Huneau, F.</i>	

Stable isotopes of daily precipitation in Singapore: a preliminary result (IAEA-CN-225-061) <i>He, S.</i>	56
Distribution of stable isotopes (^{18}O & ^2H) in precipitation in Iraq (IAEA-CN-225-068) <i>Al-Paruany, K.</i>	60
Tritium in precipitation in the southern North Sea: a marker for local formed water vapour (IAEA-CN-225-071) <i>Sueltenfuss, J.</i>	64
Stable isotope composition of the precipitation in Croatia (IAEA-CN-225-078) <i>Hunjak, T.</i>	67
The daily ^{18}O and ^2H pattern of rainfalls in Addis Ababa and their link to IWV, moisture residence time and recycling (IAEA-CN-225-095) <i>Kebede Gurmessa, S.</i>	71
Isotopic composition of precipitation in north-west Slovenia for the period 2010–2013 (IAEA-CN-225-096) <i>Vreča, P.</i>	72
9 year long moisture source diagnostic for the precipitation in Debrecen, east Hungary: implications for the changes in the climate regime (IAEA-CN-225-108) <i>Bottyán, E.</i>	76
Establishing the local meteoric water line in the El Cajon reservoir, Honduras (IAEA-CN-225-115) <i>Contreras, T.</i>	78
Of the importance of d-excess in understanding recharge process in two case studies of France (IAEA-CN-225-116) <i>Gourcy, L.</i>	81
Stable isotopes in precipitation across Japan based on the intensive observation in 2013 (IAEA-CN-225-127) <i>Ichiyonagi, K.</i>	83
Stable isotopes in precipitation in Romania – a first overall map (IAEA-CN-225-144) <i>Persoiu, A.</i>	87
Water vapor and precipitation isotope variability associated with western tropical pacific convective storms (IAEA-CN-225-149) <i>Conroy, J.</i>	88

The transfer of the isotope signal in precipitation to surface water and groundwater in Switzerland (IAEA-CN-225-158).....	91
<i>Schotterer, U.</i>	
Isotopic study of rainfall in Douala-Cameroon (GNIP station no. 6491001) (IAEA-CN-225-202)	93
<i>Ketchemen Tandia, B.</i>	
Spatial and temporal variabilities in stable isotope compositions of precipitation and air moisture sources in Hungary (IAEA-CN-225-207)	94
<i>Czuppon, G.</i>	
RCWIP2 – an improved regionalized cluster-based precipitation isoscape ($\delta^{18}\text{O}$, $\delta^2\text{H}$) (IAEA-CN-225-229)	95
<i>Terzer, S.</i>	
Recent developments in the Global Network of Isotopes in Precipitation (IAEA-CN-225-231)	98
<i>Terzer, S.</i>	
Variogram analysis of precipitation $\delta^{18}\text{O}$ in the Great alpine region - implications for isoscape modelling (IAEA-CN-225-253).....	99
<i>Kern, Z.</i>	
Disentangling the effect of climatic controls on rainfall ^{18}O variability in eastern India (IAEA-CN-225-281).....	103
<i>Basu, S.</i>	
Vienna GNIP – ANIP – station: a unique station with 40 years of dual Measurements (IAEA-CN-225-291)	104
<i>Kralik, M.</i>	
Chemical and isotopic characteristics of rain waters in Senegal north coastline (IAEA-CN-225-306)	107
<i>Diaw, M.</i>	
Variation in isotopic composition of precipitation with identification of vapors source using deuterium excess parameter as a tool: isotopic study at Tarbela dam site in Pakistan (IAEA-CN-225-320).....	108
<i>Butt, S.</i>	
Verification of a regional isotope circulation model throughout Japan (IAEA-CN-225-354)	109
<i>Tanoue, M.</i>	
A 10-yr record of stable isotope variations in precipitation across Chile (IAEA-CN-225-357)	113
<i>Aguirre Dueñas, E.</i>	

Analysis of long-term stable isotopic composition in German precipitation and rivers (IAEA-CN-225-361)	114
<i>Stumpp, C.</i>	
¹⁸ O/ ² H composition in Danish precipitation (IAEA-CN-225-374)	115
<i>Mueller, S.</i>	

Environmental Studies

Tracing organic matter sources and carbon burial in a tropical lagoon of the Caribbean Sea (IAEA-CN-225-001)	117
<i>Alonso-Hernández, C.</i>	
Geochemical, mineralogical and isotopic investigation of Inle Lake (Southern Shan State, Myanmar): preliminary results (IAEA-CN-225-004)	118
<i>Thin, M.</i>	
Use of geochemical tracers for characterization and quantification of water leakage at the Joumine dam site, Tunisia (IAEA-CN-225-015)	122
<i>Ben Hamouda, M.</i>	
Exploring the use of gamma-ray spectrometry as non-destructive method to reconstruct short-term environmental changes (IAEA-CN-225-052)	126
<i>Mikalauskiene, R.</i>	
Isotopic and chemical study for the surface and ground water interaction in the south of Iraq (IAEA-CN-225-064)	127
<i>Al-Naseri, S.</i>	
The isotopic history of lake Ontario (IAEA-CN-225-065)	131
<i>Hladyniuk, R.</i>	
Stable isotopes as tracers of anthropogenic activities in a tropical river system (IAEA-CN-225-073)	132
<i>Trinh, A.D.</i>	
Interaction between groundwater and wetlands caused by open pit mining in southeast Buenos Aires, Argentina (IAEA-CN-225-104)	133
<i>Bocanegra, E.</i>	
Groundwater interactions in Babitonga bay hydrologic complex and salinity inversions in the estuarine zone: evidences for submarine groundwater discharge (SGD) (IAEA-CN-225-105)	137
<i>Barros Grace, V.</i>	

Geothermal reservoir characteristics (T and depth) of Ayub Peighambar and Shafa hot springs using geothermometers and environmental ^2H and ^{18}O isotopes (IAEA-CN-225-132)	141
<i>Mohammadzadeh, H.</i>	
Variability in oxygen and hydrogen isotopes in human hair and limitations to geolocation (IAEA-CN-225-156).....	145
<i>Reynard, L.</i>	
Stable isotopic fingerprint of water from <i>vitis vinifera</i> plants growing in different environmental conditions (IAEA-CN-225-164)	146
<i>Costinel, D.</i>	
Application of isotopic techniques for water resource management in an arid region of western Argentina (IAEA-CN-225-213)	150
<i>Gomez, M.</i>	
Assessing the effects of land use conversion in tropical mountains through hydrological, hydro chemical and isotopic monitoring: insights and preliminary observations (IAEA-CN-225-217).....	152
<i>Villegas, J.</i>	
Assessment of water use in Brazilian sugarcane crops through stable isotopes (IAEA-CN-225-218)	154
<i>Cruz Da Silva, G.</i>	
Isotope-hydrology investigation of groundwater in the Namib desert, Namibia (IAEA-CN-225-233)	158
<i>Wanke, H.</i>	
Monitoring of stable isotopes in river water and precipitation in the Tajik Pamirs (IAEA-CN-225-245).....	159
<i>Meier, C.</i>	
Environmental isotopes studies in wetland researching: Fuente de Piedra lagoon (Malaga, Spain) (IAEA-CN-225-251).....	161
<i>Heredia, J.</i>	
The use of hydrochemistry and stable isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$) to investigate surface water and groundwater quality in the Lower Volta basin of Ghana (IAEA-CN-225-265)	165
<i>Dampare, S. B.</i>	
^{129}I and stable iodine in natural waters from Lower Saxony, Germany (IAEA-CN-225-329)	169
<i>Osman, A.</i>	

Surface Water Isotopic Studies

Human impacts on large river systems of eastern Canada: isotopic insights (IAEA-CN-225-029)	172
<i>Helie, J.</i>	
Water balance assessment across Canada (IAEA-CN-225-035).....	173
<i>Yi, Y.</i>	
Investigation of hydrology of catchment area of small river in Karelia (Russia) by high-resolution record of ^2H and ^{18}O in precipitations and river water, including experimental evaluation of evaporation (IAEA-CN-225-081)	174
<i>Borodulina, G.</i>	
Distribution of stable isotopes of liquid water in freshwater resources within Cagayan Valley river basin, Northern region Philippines (IAEA-CN-225-087)	177
<i>Mendoza, N.</i>	
Stable isotope of water as a tool to design constructed wetlands (IAEA-CN-225-111)	180
<i>Ronkanen, A.</i>	
Stable isotope transfer functions for vadose zone soils: the role of ecohydrologic routing in determining runoff and evaporation isotope composition (IAEA-CN-225-112)	183
<i>Good, S.</i>	
Distribution of stable isotopes of liquid water in freshwater resources within water resources Region X, southern Philippines (IAEA-CN-225-114)	185
<i>Racadio, C.</i>	
Flow formation in streams at high latitudes: do isotopes and catchment properties reveal patterns of groundwater dominance? (IAEA-CN-225-117)	190
<i>Marttila, H.</i>	
The residence time of water in rivers: implications on water transfer routes (IAEA-CN-225-122)	192
<i>Niinikoski, P.</i>	
Review of stable isotope studies of water done in Finland (IAEA-CN-225-125).....	196
<i>Eskelinen, R.</i>	
Using stable water isotopes in capture zone characterization of boreal springs (IAEA-CN-225-129)	200
<i>Rossi, P.</i>	

Characterization of groundwater-surface water mixing processes using environmental isotopes and geochemical models (IAEA-CN-225-133).....	202
<i>Becher Quinodoz, F.</i>	
Radon and geochemical preliminary model to assess interactions between groundwater and surface water in a Pampean stream (IAEA-CN-225-141)	206
<i>Blarasin, M.</i>	
Assessment of the role of snow in hydrological cycle of the Borjomula-Gudjareti-Tskali rivers basin, Georgia, using stable isotope approaches (IAEA-CN-225-154)	210
<i>Melikadze, G.</i>	
Partitioning evapotranspiration in sparsely gauged basins utilizing iso-hydrological modelling (IAEA-CN-225-155).....	213
<i>Smith, A.</i>	
The oxygen and hydrogen isotopic composition of Ugandan waters (IAEA-CN-225-189)	215
<i>Gebremichael, M.</i>	
⁷ Li for detecting ground water contributions and underground passages of river water (IAEA-CN-225-208).....	217
<i>Meier, C.</i>	
Groundwater and surface water interaction in the area of Podunajska Nizina lowland and Trnavska Pahorkatina hills (IAEA-CN-225-211)	219
<i>Michalko, J.</i>	
A 50 years' isotope record of Danube water – long- term trends and short-term signals (IAEA-CN-225-214).....	220
<i>Wyhlidal, S.</i>	
Hydrochemical environmental isotope study of the aquifer on the Gulf of Urabá – Colombia (IAEA-CN-225-215).....	224
<i>Villegas, P.</i>	
Application of hydrochemistry and stable isotopes (² H, ¹⁸ O, ¹³ C-DIC, ³⁴ S-SO ₄ , ¹⁸ O-SO ₄) for river/groundwater interaction in Velez river aquifer, Spain (IAEA-CN-225-219).....	225
<i>Vadillo, I.</i>	
Use of stable and radioactive isotopes to unravel surface water groundwater interactions in a developed catchment (IAEA-CN-225-227)	226
<i>Andersen, M.</i>	
Natural and induced surface groundwater exchange pathways revealed using 222-Rn and hydrochemical parameters (IAEA-CN-225-228).....	227
<i>Rau, G.</i>	

Simulation of the hydrological and isotopic balance of an endorheic lake at a monthly time step (Azigza lake, Middle Atlas, Morocco) (IAEA-CN-225-248)	228
<i>Adallal, R.</i>	
Human-driven enrichment of water stable isotopes (^{18}O , ^2H) in an intensive agriculture area (Guadalhorce basin, southern Spain) (IAEA-CN-225-260)	230
<i>Vadillo, I.</i>	
Identification of recharge sources of shallow groundwater and its interaction with surface water in a part northwestern India, using environmental isotope (IAEA-CN-225-285)	231
<i>Rai, S.</i>	
Seasonal variability of groundwater contribution to watershed discharge in discontinuous permafrost in the north Klondike river valley, Yukon (IAEA-CN-225-286)	234
<i>Lapp, A.</i>	
A time series of ^{129}I and hydrogeochemistry in a discontinuous permafrost watershed: insights from multivariate statistical methods (IAEA-CN-225-290)	238
<i>Herod, M.</i>	
A classical water balance of the Iberá wetland validated by GRACE satellite data (IAEA-CN-225-296)	242
<i>Valladares, A.</i>	
Streamflow component separation by tracer- and non-tracer-based methods (IAEA-CN-225-302)	244
<i>Stewart, M.</i>	
Multi-decadal observations of water isotopes impacting the urban Salt Lake valley (USA) – from montane sources through tapwater to the Great Salt Lake terminus (IAEA-CN-225-315)	248
<i>Ehleringer, J.</i>	
Application of the ratio of tritium concentrations in precipitation/surface water ratios to estimate timescales for historical surface water tritium data (IAEA-CN-225-337)	252
<i>Michel, R.</i>	
Origins of waters in the Australian tropics using ^{18}O and ^2H values (IAEA-CN-225-338)	255
<i>Tweed, S.</i>	
Controls on seasonal $\delta^2\text{H}$ - $\delta^{18}\text{O}$ patterns in large rivers from eastern Canada (IAEA-CN-225-358)	260
<i>Rosa, E.</i>	

ID: 56

FACTORS CONTROLLING ISOTOPIC COMPOSITION OF WATER VAPOR OVER A PADDY FIELD, MASE, JAPAN: USING A HIGH FREQUENCY IN-SITU ISOTOPE OBSERVATION AND ISOTOPE ENABLED GCM

Z. WEI,

Atmosphere and Ocean Research Institute, University of Tokyo, Tokyo, Japan.

E-mail address: weizw@rainbow.iis.u-tokyo.ac.jp

A. OKAZAKI

Atmosphere and Ocean Research Institute, University of Tokyo, Tokyo, Japan.

Wonsik KIM

National Institute for Agro-Environmental Sciences, Tsukuba Japan.

Masaharu YOKOI

SANYO TRADING CO., LTD., Tokyo, Japan.

Keisuke ONO

National Institute for Agro-Environmental Sciences, Tsukuba Japan.

K. YOSHIMURA

Atmosphere and Ocean Research Institute, University of Tokyo, Tokyo, Japan.

Abstract: Stable isotopes in precipitation and atmospheric water vapor are observed over a paddy field, Mase, Japan, from June to October of 2013. We use observed isotope ratios, in combination with an isotope-enabled GCM (IsoGSM) to investigate the major processes governing water vapor isotopic variability in the region. The results show that the water vapor is slightly affected by the local evapotranspiration but significantly related to large scale air mass advection. The different characteristics of observed isotopic dynamic variability primarily depend on the advection of water from different source regions.

1. INTRODUCTION

Isotope method has been regarded as a robust tool for tracing the origin and movement of atmospheric water [1]. Recent development in high-frequency laser spectrometer in situ technology has made it possible to measure water vapor isotopic ratios at high temporal resolution and on a continuous basis [2]. Such a measurement offers unique opportunities to examine the temporal variation in water vapor isotopic ratios and gains insights into the involved mechanisms [2]. Although the ground-based monitoring of water vapor isotopes is important, temporally continuous water vapor isotopic measurement remains sparse [1]. Furthermore, in spite of sophisticated in-situ based estimated of water vapor isotopes, it is difficult to evaluate the contribution of particular source of precipitation and water vapor with merely in-situ observation. To diagnose water cycle in respect of both isotopic variation and water origins, spatial variations of isotope should also be quantified. Given the inherently spatial and temporal complexities associated with the evolution of the vapor source, isotope-enabled GCM provide a tool to interpret the cause of isotopic variability that accounts for

large scale mixing thus minimizing the reliance on the problematic assumption of single water source [3]. Therefore, to provide a more deep understanding of the factors controlling water vapor isotopes, both in situ isotope measurement and isotope-enabled modelling are necessary.

2. METHODS

The study site (36°03' 14.3" N, 140°01' 36.9" E) is located in a rectangular paddy field (with an area of about 100m × 50m) in Mase, Tsukuba, which is 50 km northeast away from Tokyo. The water vapor isotopes are measured by in situ high-frequency laser spectrometer (Picarro, L2120-i). Precipitation samples are collected on a six hourly basis by a wet-only automatic sampling system. We use observed isotope ratios, in combination with an isotope-enabled GCM (IsoGSM, Yoshimura et al. [2008]) to investigate the major processes governing water vapor isotopic variability in the region. IsoGSM is a global spectral model equipped with water isotope tracers, which is developed to constrain predicted pattern of precipitation and water vapor transport.

3. RESULTS

The observed results show that during rainy days, the water vapor is primarily influenced by precipitation. The significant correlation ($R^2=0.66$) between measured water vapor δD and the predicted one from precipitation indicates that water vapor δD during the precipitation event can approach an equilibrium state with precipitation water. By applying Keeling plot approach with IsoGSM simulation, the contribution of local land is found to have a minor effect (about 20%) on water vapor during the fine days. Furthermore, lack of correlation between water vapor δD and local weather variability such as temperature and relative humidity, reflects the small influence of local evapotranspiration and the important contribution of air mass advection. Based on significant difference of water mixing ratios and d-excess, we divide the observation into two periods as JJA (Jun-Jul-Aug) and SO (Sep and Oct). The different characteristics of isotopic dynamic variability between JJA and SO primarily depend on the advection of water from different source regions. IsoGSM simulation shows that the circulation pattern in JJA is associated with Japan sea water vapor flow, whereas Pacific Ocean water vapor flow plays a dominant role in SO (Figure 1).

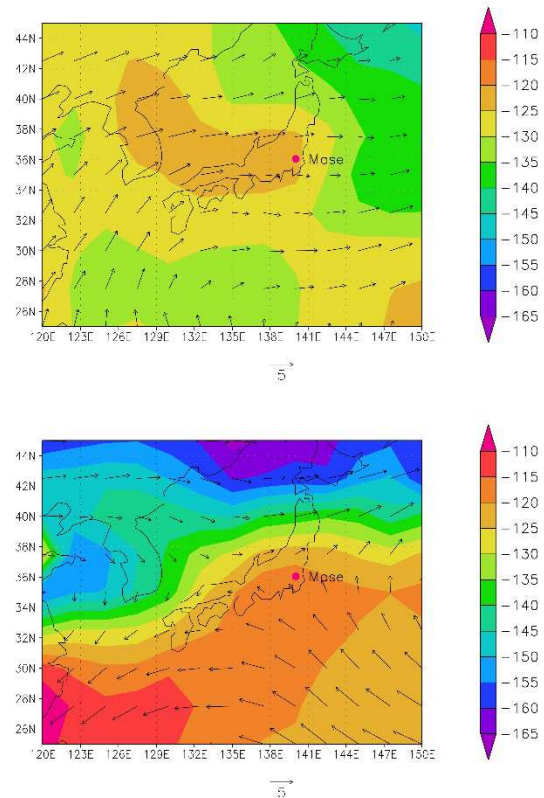


Figure 1. The mean wind field (arrow) and 850 hPa isotope ratios (color field) at 850 hPa in JJA and SO.

4. CONCLUSIONS

In this study, we use observed water vapor and precipitation isotope ratios, in combination with IsoGSM to investigate the major processes governing water vapor isotopic variability over a paddy field. The results show that the water vapor is greatly dependent on large scale air mass advection while less affected by the local evapotranspiration. The advection of water from different source regions is responsible for the diverse characteristics of observed isotopic dynamic variability. Our results demonstrate the robustness of combining isotope-enabled GCM simulation with in-situ isotopic observations to study atmospheric water circulation processes.

REFERENCES

- [1] FARLIN, J., LAI, C. T., AND YOSHIMURA, K., Influence of synoptic weather events on the isotopic composition of atmospheric moisture in a coastal city of the western United States, *Water Resour. Res.*, **49** (2013) 3685-3696.
- [2] LEE, X., SMITH, R., AND WILLIAMS, J., Water vapour $^{18}\text{O}/^{16}\text{O}$ isotope ratio in surface air in New England, USA, *Tellus B*, **58** (2006) 293-304.
- [3] BERKELHAMMER, M., STOTT, L., YOSHIMURA, K., JOHNSON, K., AND SINHA, A., Synoptic and mesoscale controls on the isotopic composition of precipitation in the western United States, *Clim. Dynam.*, **38** (2011) 433-454.

ID: 67

ARCTIC WATER CYCLE: NEW CONSTRAINTS FROM WATER VAPOR ISOTOPE OBSERVATIONS

H. C. STEEN-LARSEN, J. L. BONNE, J. JOUZEL, V. MASSON-DELMOTTE,
Laboratoire des Science du Climat et de l'Environnement, Gif-Sur Yvette, France
E-mail address: hanschr@gfy.ku.dk

A. SVEINBJORNSDOTTIR,
Institute of Earth Science, University of Iceland, Iceland

M. WERNER,
Alfred-Wegener-Institut für Polar- und Meeresforschung, Bremerhaven, Germany

V. ZAKHAROV,
Climate and Environmental Physics Laboratory, Ural Federal University, Russian Federation

Abstract: Due to the role of water vapor and clouds in positive feedback mechanisms, water vapor is a key player in the future Arctic climate. Ecosystems and human societies are vulnerable to climate change through even minor changes in precipitation patterns, including the occurrence of extreme events. It is therefore essential to monitor, understand and model correctly the mechanisms of transport of moisture, at the regional scale.

The relative abundance of heavy and light water in the atmospheric moisture is affected by each phase change, because of their molecular properties (diffusivity and saturation vapor pressure). As a result, the isotopic composition of water vapor provides an integrated tracer of water cycle processes involved in evapo-transpiration, moisture transport, and cloud formation. Second order processes such as deuterium excess can carry a signal related to moisture origin. A correct representation of these water cycle processes is expected to play a key role in the future Arctic climate. Because water stable isotopes are incorporated in a growing number of regional to general circulation atmospheric models, such data can be used to benchmark atmospheric model results with a focus on the Arctic hydrological cycle.

We present here results from international efforts to obtain water vapour measurements in the Arctic, using a network of land stations and ships. We highlight the specificities and complementarities of observations so far obtained from different sites (Greenland, Iceland, Svalbard, Siberia and research ships), calling for an international coordinated monitoring. Moreover, we report results from comparison with isotope-enabled general circulation models (nudged to re-analysis products), showing that they fail to correctly represent several key processes associated with the spatio-temporal variability of deuterium excess. The comparison of different stations, and calculations based on Lagrangian back trajectories are used to diagnose the spatial footprint of each station, arguing for an expanded and structured water vapor isotope-monitoring network in the Arctic.

REFERENCES

- [1] BASTRIKOV, V., STEEN-LARSEN, H. C., ET AL. (2014). Continuous measurements of atmospheric water vapour isotopes in western Siberia (Kourovka). *Atmospheric Measurement Techniques*, 7(6), 1763–1776.
- [2] BINTANJA, R., & SELTEN, F. M. (2014). Future increases in Arctic precipitation linked to local evaporation and sea-ice retreat. *Nature*, 509(7501), 479–482.
- [3] BONNE, J. L., MASSON-DELMOTTE, V., et al. (2014). The isotopic composition of water vapour and precipitation in Ivittuut, southern Greenland. *Atmospheric Chemistry and Physics*, 14(9), 4419–4439.
- [4] BONNE, J. L., STEEN-LARSEN, H. C. ET AL (in review), The summer 2012 Greenland heat wave: in situ and remote sensing observations of water vapour isotopic composition during and atmospheric river event, *Journal of Geophysical Research*.
- [5] GRYAZIN, V., RISI, C., ET AL. (2014). To what extent could water isotopic measurements help us understand model biases in the water cycle over Western Siberia. *Atmospheric Chemistry and Physics*, 14(18), 9807–9830.
- [6] STEEN-LARSEN, H. C., MASSON-DELMOTTE, V., (2014). What controls the isotopic composition of Greenland surface snow? *Climate of the Past*, 10(1), 377–392.
- [7] STEEN-LARSEN, H. C., JOHNSEN, S. J., ET AL. (2013). Continuous monitoring of summer surface water vapor isotopic composition above the Greenland Ice Sheet. *Atmospheric Chemistry and Physics*, 13(9), 4815–4828

ID: 101

COMBINING MULTIPLE TYPES OF DATASETS OF WATER ISOTOPIC COMPOSITION: INSIGHTS FROM THE ANALYSIS OF THE SUMMER 2012 GREENLAND HEAT WAVE

J. L. BONNE, H. C. STEEN-LARSEN,
LSCE Laboratoire des Sciences du Climat et de l'Environnement, Gif-Sur-Yvette Cedex,
France
Email address: jean-louis.bonne@lsce.ipsl.fr

C. RISI,
LMD, Paris, France

M. WERNER
Alfred Wegener Institute Helmholtz-Center for Polar and Marine Research Bremerhaven,
Bremerhaven, Germany

H. SODEMANN
ETH Zurich, Zurich, Switzerland

J. L. LACOUR
Universite Libre de Bruxelles, Brussels, Belgium
UPMC Univ. Paris 06; Universite Versailles St-Quentin, LATMOS-IPSL, Paris, France

M. DELMOTTE,
LSCE Laboratoire des Sciences du Climat et de l'Environnement, Gif-Sur-Yvette Cedex,
France

C. CLERBAUX,
UPMC Univ. Paris 06; Universite Versailles St-Quentin, LATMOS-IPSL, Paris, France

A. E. SVEINBJORNSDOTTIR
University of Iceland, Institute of Earth Sciences, Reykjavik, Iceland

V. MASSON-DELMOTTE,
LSCE Laboratoire des Sciences du Climat et de l'Environnement, Gif-Sur-Yvette Cedex,
France

Abstract: Water stable isotopes have been widely used as tracers of the atmospheric hydrological cycle, especially in palaeoclimatological studies based on ice cores to quantify past climate and the water cycle changes.

During the past decades, the mechanisms controlling the precipitation isotopic composition have been investigated thanks to precipitation sampling and laboratory analyses, with a crucial contribution of the IAEA/GNIP network. In situ observations of water vapour isotopic composition used to be limited to cold trap methods (Jacob and Sonntag, 1991). During the last decade, new laser based techniques of high precision continuous in situ measurements of water vapour isotopic composition have become field deployable, allowing investigation of variations at very short time scales.

Moreover, satellite or surface based remote sensing techniques now allow measurements of vertical profiles of the water vapour isotopic composition, with different vertical sensitivities and with a wide spatial coverage for satellite measurements.

In parallel, a growing number of regional to general circulation atmospheric models are being implemented with the explicit representation of water stable isotopes. The nudging techniques developed to guide such models with atmospheric analyses products provide a framework in which model results can be directly compared with water stable isotope measurements.

All those techniques provide multiple information on the water vapour isotopic composition, but the heterogeneous precisions, horizontal or vertical coverages of these observations complicate their common use for documenting atmospheric processes.

The extreme warm event observed in July 2012 over all Greenland (Neff et al., 2014) is an opportunity to combine the use of in situ and satellite measurements as well as model data to track the evolution of water vapour isotopic composition along transport from subtropical Atlantic to Greenland ice sheet (Bonne et al., in review). This case study allows to investigate the mechanisms relating isotopic signals and the origin of moisture, with implications for the interpretation of ice core records (e.g. similar warm events during the middle age period or in 1889).

This warm event led to surface melt over almost all the Greenland ice sheet. It was recorded in the isotopic composition of water vapour measured by the IASI satellite along the transport pathway (Lacour et al., 2012) and at two sites where continuous in situ surface vapour isotopic measurements were conducted: at Ivittuut, a coastal station of South Greenland (Bonne et al., 2014) and at NEEM camp, further north on top of the ice sheet (Steen-Larsen et al., 2013, 2014). These observations allowed us to monitor the isotopic composition of the air mass at different stages of its advection towards Greenland, which can inform on processes along this trajectory, such as cloud properties and moisture sources. In addition, two simulations of this event, using the AGCMs LMDZiso and ECHAM5wiso equipped with water stable isotopes and nudged towards large scale wind fields, are investigated.

Furthermore, a regional high-resolution model was used to study the moisture transport to Greenland during this event using tagged water tracers of the North Atlantic ocean and coastal land evaporation.

Using moisture source diagnostic based on the Lagrangian particle dispersion model Flexpart, we show that this 2012 heat wave event corresponds to moisture sources located over the subtropical Atlantic Ocean, where intense evaporation was caused by dry air masses associated with the US intense summer drought. This moisture was then advected northward along a narrow band, due to a very stationary surface cyclone southwest of Greenland. It reached southern Greenland (at Ivittuut on July 9th), travelled along the west coast of Greenland and was pushed continued eastwards above the ice sheet (arrived above NEEM on July 11th).

Surface isotopic observations during the event show larger variations at NEEM than in Ivittuut, strongly reducing the isotopic and deuterium excess latitudinal gradient usually observed between South and North Greenland. This feature clearly deviates from a simple

Rayleigh distillation process. LMDZiso and ECHAM5iso correctly simulate the magnitude of humidity and temperature peaks in both surface sites, associated with a strong isotopic enrichment and a deuterium excess decrease all over Greenland. Small biases are observed on temperature, humidity as well as isotopes, with an underestimation of deuterium excess variability, which is typical for these models at those sites. IASI observations are compared to model outputs along the transport path in the free troposphere (3-6 km) where the remote sounder is most sensitive to δD variations.

These combined measurements and simulations demonstrate that the low deuterium excess of the initial subtropical air mass is preserved along transportation, contrasting with high deuterium excess levels associated with Arctic air masses.

REFERENCES

- [1] BONNE, J. L., MASSON-DELMOTTE, V., ET AL. (2014). The isotopic composition of water vapour and precipitation in Ivittuut, southern Greenland. *Atmospheric Chemistry and Physics*, 14(9), 4419–4439.
- [2] BONNE, J. L., STEEN-LARSEN, H. C. et al (in review), The summer 2012 Greenland heat wave: in situ and remote sensing observations of water vapour isotopic composition during and atmospheric river event, *Journal of Geophysical Research*.
- [3] JACOB, H. SONNTAG, C.: An 8-year record of the seasonal variation of 2H and ^{18}O in atmospheric water vapour and precipitation at Heidelberg, Germany, *Tellus B*, 43, 291–300, doi:10.1034/j.1600-0889.1991.t01-2-00003.x, 1991.
- [4] LACOUR, J.L. C. RISI, L. CLARISSE, S. BONY, D. HURTMANS, C. CLERBAUX, & P.-F. COHEUR. Mid-tropospheric δD observations from IASI/MetOp at high spatial and temporal resolution. *Atmos. Chem. Phys.*, 12(22) :10817–10832, Nov. 2012. ISSN 1680-7324. doi : 10.5194/acp-12-10817-2012.
- [5] NEFF, W. G. COMPO, F. M. RALPH, & M. D. SHUPE. Continental heat anomalies and the extreme melting of the Greenland ice surface in 2012 and 1889. *Journal of Geophysical Research : Atmospheres*, page 2014JD021470, Apr. 2014. ISSN 2169-8996. doi: 10.1002/2014JD021470.
- [6] STEEN-LARSEN, H. C., MASSON-DELMOTTE, V., (2014). What controls the isotopic composition of Greenland surface snow? *Climate of the Past*, 10(1), 377–392.
- [7] STEEN-LARSEN, H. C., JOHNSEN, S. J., ET AL. (2013). Continuous monitoring of summer surface water vapor isotopic composition above the Greenland Ice Sheet. *Atmospheric Chemistry and Physics*, 13(9), 4815–4828.

ID: 181

IMPLEMENTATION OF TRITIUM IN THE LMDZ-ISO GENERAL CIRCULATION MODEL FOR THE STUDY OF THE RELATIONSHIPS BETWEEN STRATOSPHERIC AIR INPUTS INTO THE LOWER TROPOSPHERE, WATER CYCLE AND CLIMATE

A. CAUQUOIN,

Laboratoire de Météorologie Dynamique (LMD-UPMC), Université Paris 6. 4 place Jussieu, F 75252 Paris Cedex 05. Tour 45-55, 3rd floor.

Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Ormes des Merisiers, 91191 Gif-sur-Yvette, France.

E-mail address: Alexandre.Cauquoin@lmd.jussieu.fr.

P. JEAN-BAPTISTE,

Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Ormes des Merisiers, 91191 Gif-sur-Yvette, France.

C. RISI,

Laboratoire de Météorologie Dynamique (LMD-UPMC), Université Paris 6. 4 place Jussieu, F 75252 Paris Cedex 05. Tour 45-55, 3rd floor.

É. FOURRÉ, A. LANDAIS,

Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Ormes des Merisiers, 91191 Gif-sur-Yvette, France.

B. STENNI

Dipartimento di Scienze Ambientali, Informatica e Statistica. Università Ca' Foscari Venezia, Calle Larga Santa Marta 2137, 30123 Venezia

Abstract: Water stable isotopes (H_2^{16}O , H_2^{18}O , HDO , H_2^{17}O) are well-known tracers of the past and present-day hydrological cycle. In contrast, in spite of the global monitoring of its concentration in precipitation (IAEA database) and a substantial dataset concerning polar ice ([1] and references therein) tritium (HTO) has received little attention so far in atmospheric sciences. The main reasons for this are the relative complexity of its natural production by cosmic radiations, which requires a sophisticated cosmogenic production model [2, 3] and, above all, the lack of details concerning its massive injection by the nuclear atmospheric tests of the 1950's and early 1960's. However things have changed following the end of the "Cold War", and the detailed information on individual nuclear tests (date, location, altitude, yield...) have been released by the governments, thus allowing to build a realistic atmospheric bomb tritium input function and to revisit the issue of tritium in the atmospheric water cycle. Tritium has indeed been shown to be an appropriate tracer for the intrusion of stratospheric air masses into the lower troposphere. After its production, it enters in the hydrological in the form of tritiated water molecules and has a radioactive half-life of 4500 ± 8 days. Tritium is thus a good tool to study the links between the stratospheric injections, the hydrological cycle and the climate.

In an approach combining data and model, we have first implemented natural tritium in the coupled Laboratoire de Météorologie Dynamique Zoom (LMDZ) Atmospheric General Circulation Model developed at IPSL [4]: LMDZ-iso. Its implementation uses the same model architecture as for the other water isotopes, after a correct description of associated

cosmogenic production terms [3]. The model is used in a configuration dedicated to the simulation of the stratosphere, with 39 layers. We are currently implementing the anthropogenic tritium in the model using the individual nuclear tests list and the distribution of tritium at the surface of the ocean from [5]. It was necessary to make this implementation in two steps to firstly study the transport of tritium and its spatial/seasonal variability under equilibrium conditions, without the masking effect of the dominant transient thermonuclear signal.

In this presentation, we will firstly focus on the modeling of spatial and temporal natural variations of tritium content in precipitation. The model is validated against a compilation of available data for natural tritium. We show that the continental and latitudinal effects are well reproduced by the model. We will then present the ongoing work on the simulation of bomb tritium and its temporal evolution since the 1950's in LMDZ-iso.

REFERENCES

- [1] FOURRÉ, E., JEAN-BAPTISTE, P., DAPOIGNY, A., BAUMIER, D., PETIT, J.-R., JOUZEL, J., Past and recent tritium levels in Arctic and Antarctic polar caps, *Earth Planet. Sci. Lett.* **245**, 56-64 (2006).
- [2] MASARIK, J., BEER, J., Simulation of particle fluxes and cosmogenic nuclide production in the Earth's atmosphere, *J. Geophys. Res.* **104**(D10), 12,099-12,111 (1999).
- [3] MASARIK, J., BEER, J., An updated simulation of particle fluxes and cosmogenic nuclide production in the Earth's atmosphere, *J. Geophys. Res.* **114**, D11103 (2009).
- [4] RISI, C., BONY, S., VIMEUX, F., JOUZEL, J., Water-stable isotopes in the LMDZ4 general circulation model: Model evaluation for present-day and past climates and applications to climatic interpretations of tropical isotopic records, *J. Geophys. Res.* **115**, D12118 (2010).
- [5] BROECKER, W. S., PENG, T. H., OSTLUND, G., The distribution of bomb tritium in the ocean, *J. Geophys. Res.* **91**(C12), 14,331-14,344 (1986).

ID: 250

COMBINING ISOTOPIC MEASUREMENTS OF ATMOSPHERIC VAPOR AND LAGOON WATER FOR ANALYSING ISOTOPE FRACTIONATION DURING EVAPORATION

C. VALLET-COULOMB, H. DELATTRE, C. SONZOGNI

CEREGE, Aix-Marseille Université, CNRS, IRD, Europôle méditerranéen de l'Arbois BP 80
13545 Aix-en-Provence cedex 4, France

E-mail address: vallet@cerege.fr

Y. CHERAIN

Réserve Nationale de Camargue, Société Nationale de protection de la nature, La Capelière,
13200 Arles, France

O. BOUTRON

Fondation Tour du Valat, Centre de recherche pour la conservation des zones humides
méditerranéennes, Le Sambuc, 13200 Arles, France

Abstract: The increasing use of laser spectrometry to measure isotopes in atmospheric water vapor has evidenced that the signal is submitted to high temporal variations. The relation between these atmospheric variations and the behaviour of isotope fractionation during a daily cycle of evaporation has to be better understood. We combine isotopic measurements in atmospheric and surface water during a summer period in a Mediterranean coastal wetland with high evaporation rates (Rhône River delta, France). Atmospheric isotopic ($\delta^{18}\text{O}$, δD) and climatic (temperature, humidity, wind speed and direction) data are interpreted at different time scales, while lagoon and canal data ($\delta^{18}\text{O}$, δD , surface temperature, water level, canal discharges) are used to calculate the average isotopic composition of evaporation flux, through the combined water and isotope budgets. This approach is used to evaluate the application of available schemes of kinetic fractionation that occur during evaporation of natural systems (Craig and Gordon 1965; Merlivat and Jouzel, 1979), which actually rely on a stationary state conceptualization. Data are analyzed with a specific focus on the slope of the evaporation line.

REFERENCES

- [1] CRAIG H., GORDON L. I. (1965) Deuterium and oxygen 18 variations in the ocean and marine atmosphere. In *Stable Isotopes in Oceanographic Studies and Paleotemperatures* (ed. E. Tongiorgi). Lab. Geologia Nucleare, Pisa, pp. 9–130.
- [2] MERLIVAT L., JOUZEL J. (1979) Global climatic interpretation of the deuterium-oxygen 18 relationship for precipitation. *Journal of Geophysical Research*. 84, 5029–5033.

ID: 255

THE SENSITIVITY OF SIMULATED WATER ISOTOPE DISTRIBUTIONS TO DIFFERING CLIMATE MODEL CLOUD PARAMETERS

J. NUSBAUMER,

Atmospheric and Oceanic Sciences Department, University of Colorado, Ekeley Sciences Room W225, UCB 216, Boulder, Colorado, United States of America.

E-mail address: <mailto:nusbaume@colorado.edu>

D. C. NOONE

College of Earth, Ocean, and Atmospheric Sciences, Oregon State University, Burt 308, 2651 SW Orchard Avenue, Corvallis, Oregon, United States of America.

1. INTRODUCTION

Stable water isotope ratios are used extensively in proxy records to help reconstruct past climate. However, in order to determine the climatological and hydrological variables of interest from isotope ratios, numerous assumptions must be made [1]. One possible way to get around these assumptions is to use isotope-enabled climate and earth system models, which can allow one to directly generate isotope values from the simulated climate, and can thus allow for a more direct comparison with observations [2]. There are also new measurement systems which can allow for a better understanding of isotope ratios in current environmental conditions [3]. This provides the opportunity to use isotopes to improve the models themselves. One particularly interesting opportunity is in the parameterizations of clouds and precipitation, which are difficult to simulate given the relatively small spatial and temporal scales of the actual processes involved. Given that we know isotopes are sensitive to such processes [4-6], one could use isotopic observations to better constrain and tune the parameterizations in the models, and eventually create completely new parameterizations which would improve the models' accuracy and physical realism. This study examines this possibility by testing the sensitivity of simulated water isotope ratios in an IPCC-class climate model to changes in cloud parameters, including changes in the isotopic physics itself. By comparing the model output to observations, it can be determined which parameters isotopes are most sensitive to, and which physics choices result in the most accurate simulations. This knowledge will eventually be used to make improvements to the model itself. Ultimately, this line of research could have numerous scientific benefits, including increased understanding of the earth system, better paleoclimate reconstructions due to more robust model/proxy comparisons, and better future climate projections, which would have a direct impact on any policy decisions that need to take into account changes in climate due to either shorter-term natural climate variability or longer-term influences such as global warming.

1. METHODS

This study will use the isotope-enabled National Center for Atmospheric Research Community Atmosphere Model Version 5 (iCAM5) coupled to the isotope-enabled Community Land Model Version 4 (iCLM4), both of which are components of the fully-coupled isotope-enabled Community Earth System Model (iCESM) [7,8], whose base model was used in the latest IPCC report. Figure 1 shows the precipitation-weighted long-term average of $\delta^{18}\text{O}$ in precipitation as simulated by the model at $1.9^\circ \times 2.5^\circ$ resolution. Numerous simulations will be done with modern SST and sea ice forcing, in order to produce

a climate that should match up well with current observations. One control simulation will be generated, and then numerous other model runs will be branched off the control simulation, with each new run having a different value for a cloud or isotope parameter, or even an entirely different isotopic parameterization. This will allow for one to determine the sensitivity of the simulated isotopic distributions to the cloud, precipitation, and isotopic parameterizations, and to determine if a specific combination or set of parameter values results in the best comparison to observations.

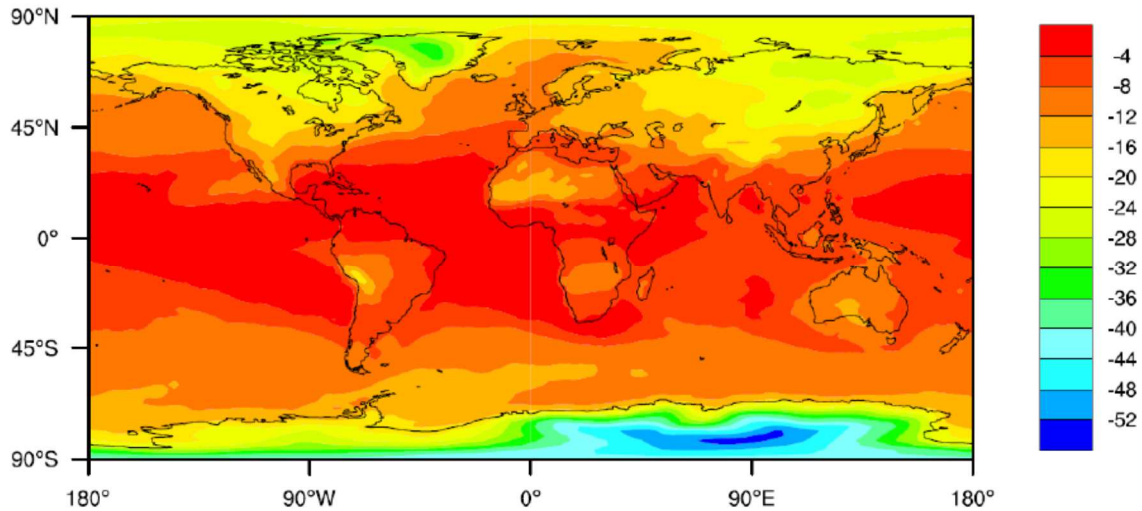


Figure 1. Long-term precipitation-weighted average $\delta^{18}\text{O}$ of precipitation as simulated by iCESM, with prescribed modern-day sea surface temperatures and sea ice.

2. RESULTS

It is found that stable water isotope ratios, at least as simulated by the climate model used in this study, are quite sensitive to numerous cloud and precipitation parameter choices. In particular, it is found that how one models or parameterizes rain re-evaporation has a strong influence on the isotope ratios of precipitation, particularly the d-excess. The same is true for the super-saturation during the formation of cloud ice, which has a strong control on the kinetic fractionation during the deposition of vapor onto ice. Water isotope ratios also appear to be sensitive to quantities that also influence the radiation budget, such as the grid-cell relative humidity cut-off for the formation of clouds.

3. CONCLUSIONS

Climate models have the capability to test hypotheses related to the distribution of stable water isotopes in our environment that would be difficult to examine otherwise, including the impact of atmospheric cloud and precipitation processes on measured isotope ratios. In order to help guide those experiments, and to help determine if current climate models have the ability to simulate such processes accurately, the isotope-enabled CESM model is used to test the sensitivity of the modeled water isotope ratios to changes in cloud and isotope physics parameters. It is found that sensitivity to such parameters does exist, and provides a way to not only improve our understanding of isotopes in the earth system, but also are ability to model the climate and earth system in general. This improvement in modeling could lead the way to better paleoclimate reconstructions and better future climate projections, which is one of the major goals of climate science as a whole.

REFERENCES

- [1] NOONE, D. C., Kink in the thermometer, *Nature* 462 (2009) 295-296.
- [2] SIME, L. C., RISI, C., TINDALL, J. C., SJOLTE, J., WOLFF, E. W., MASSON-DELMOTTE, V., CAPRON, E. Warm climate isotopic simulations: what do we learn about interglacial signals in Greenland ice cores?, *Quaternary Science Reviews* 67 (2013) 59-80.
- [3] WORDEN, J., BOWMAN, K., NOONE, D. C., BEER, R., CLOUGH, S., ELDERING, A., FISHER, B., GOLDMAN, A., GUNSON, M., HERMAN, R., KULAWIK, S. S., LAMPEL, M., LUO, M., OSTERMAN, G., RINSLAND, C., RODGERS, C., SANDER, S., SHEPARD, M., WORDEN, H., Tropospheric Emission Spectrometer observations of the tropospheric HDO/H₂O ratio: Estimation approach and characterization, *Journal of Geophysical Research - Atmospheres* 111 (2006) 1984-2012.
- [4] STEWART, M. K., Stable isotope fractionation due to evaporation and isotopic exchange of falling waterdrops: Applications to atmospheric processes and evaporation of lakes, *Journal of Geophysical Research* 80 (1975) 1133-1146.
- [5] FEDERER, B., BRICHET, N., JOUZEL, J. Stable Isotopes in Hailstones. Part I: The Isotopic Cloud Model, *Journal of Atmospheric Science* 39 (1982) 1323-1335.
- [6] JOUZEL, J., MERLIVAT, L., Deuterium and oxygen 18 in precipitation: Modeling of the isotopic effects during snow formation, *Journal of Geophysical Research - Atmospheres* 89 (1984) 11749-11757.
- [7] NUSBAUMER, J., NOONE D. C., BARDEEN, C., The atmospheric distribution of water isotopes as simulated by the isotope-enabled Community Atmosphere Model Version 5 (iCAM5) (in prep).
- [8] WONG, T., NUSBAUMER, J., NOONE, D. C. The isotope-enabled Community Land Model Version 4: Results from observationally forced single-column and global coupled simulations (in prep).

ID: 294

ENSO AND INDO-PACIFIC WATER ISOTOPES: OBSERVATIONS, MODELING, AND IMPLICATIONS FOR PROXY RECONSTRUCTIONS

B. KONECKY, D. NOONE

Cooperative Institute for Research in Environmental Sciences, University of Colorado-Boulder, 216 UCB, Boulder, CO 80309-0216, USA

College of Earth, Ocean, and Atmospheric Sciences, Oregon State University, 104 CEOAS Administration Building, Corvallis, OR, 97331-5503, USA

E-mail address: bronwen.konecky@colorado.edu

J. NUSBAUMER

Cooperative Institute for Research in Environmental Sciences, University of Colorado-Boulder, 216 UCB, Boulder, CO 80309-0216, USA

K. COBB

School of Earth & Atmospheric Sciences, Georgia Institute of Technology, 311 Ferst Dr, Atlanta, GA, 30332-0340

Abstract: Water isotope ratios ($\delta^{18}\text{O}$, δD) in precipitation, surface waters, and seawater comprise the vast majority of paleo-hydroclimate proxies in the tropical Indo-Pacific. The δD and $\delta^{18}\text{O}$ of precipitation and water vapor are powerful tracers of atmospheric circulation processes, and can help to illuminate fundamental interactions between ENSO and the atmospheric water cycle. Throughout the tropics, past changes in δD and $\delta^{18}\text{O}$ are often attributed to ENSO-driven changes in rainfall amount (via the tropical “amount effect”) and related circulation processes. However, recent studies have revealed that ENSO’s impact on rainfall δD in many Indo-Pacific locations deviates substantially from the classic “amount effect,” with other fractionation and circulation processes becoming more important (e.g. Conroy et al., 2013). In order to accurately reconstruct past changes in Indo-Pacific hydroclimate using water isotopes, an improved understanding is required of the dynamical and microphysical processes controlling $\delta^{18}\text{O}_{\text{precip}}$ and $\delta\text{D}_{\text{precip}}$ and their relationships with ENSO and other climate phenomena.

In this study, we examine the controls on $\delta\text{D}_{\text{precip}}$ and $\delta\text{D}_{\text{vapor}}$ in the Indo-Pacific and their relationships to ENSO in ground observations, data from the Tropospheric Emission Spectrometer (TES) on NASA’s Aura satellite, and a new simulation with the isotope-equipped Community Atmosphere Model v. 5 (iCAM5). In both the model and in observations, we find that the dominant processes driving monthly to interannual $\delta\text{D}_{\text{vapor}}$ anomalies differ substantially across the Indo-Pacific. Prominent differences are evident between the Indo-Pacific Warm Pool and the Central/Eastern Pacific (CEP), particularly in the relative importance of precipitation efficiency, detrainment, and rain evaporation on water isotope ratios. The dominant influence of the classic “amount effect” is spatially variable, with other processes playing important roles especially in the CEP. ENSO’s influence on $\delta\text{D}_{\text{precip}}$ and $\delta\text{D}_{\text{vapor}}$ reflects the different controls on fractionation in each region. These findings may challenge the interpretation of some proxy records simply in terms of precipitation amount, while also opening up the possibility for novel reconstructions of other key aspects of atmospheric circulation.

REFERENCES

- [1] STEPHENSON, R., Introduction to Nuclear Engineering, 2nd edn, McGraw-Hill, New York (1958) 491 pp.
- [2] GEYH, M.A., Messungen der Tritium-Konzentration in Salzlaugen, Kali Steinsalz **5** (1969) 208.
- [3] INTERNATIONAL COMMISSION ON RADIOLOGICAL PROTECTION, Evaluation of Radiation Doses to Body Tissues from Internal Contamination due to Occupational Exposure, Publication 10, Pergamon Press, Oxford and New York (1968).
- [4] GUTHRIE, F.E., PERRY, J.J. (Eds), Introduction to Environmental Toxicology, Blackwell, Oxford (1980).
- [5] HOWLAND, G.P., HART, R.W., "Radiation biology of cultured plant cells", Applied and Fundamental Aspects of Plant Cell, Tissue, and Organ Culture, 2nd edn (REINERT, J., BAJAJ, Y.R.S., Eds), Springer-Verlag, Berlin (in press).
- [6] BURKE, S.D., HOWELL, J.P., "Impact of prolonged wet storage of DOE reactor irradiated nuclear materials at the Savannah River Site", Proc. Topical Mtg on DOE Spent Nuclear Fuel — Challenges and Initiatives, Salt Lake City, 1994, USDOE, Washington, DC (1994) 118–124.
- [7] COCHRANE, M.P., DUFFS, C.M., Endosperm cell number in barley, Nature **289** (1981) 399.
- [8] BLOUNT, E.I., Symmetry properties of triplet superconductors, Phys. Rev., B: Condens. Matter **32** (1985) 2935.
- [9] TEPPER, L., Suboptimal control study of a nuclear power plant, IEEE Trans. Nucl. Sci. **NS-22** (1975) 812.
- [10] PEACOCK, K.L., Design of discrete bandpass filters for petroleum exploration, Oil Gas J. **83** 42 (1985) 121.

EVAPOTRANSPIRATION FLUX PARTITIONING WITH REAL TIME STABLE ISOTOPE MONITORING OF WATER VAPOR IN THE MONSOON REGION OF NORTHWESTERN MÉXICO

E.A. YÉPEZ, T. TARIN J. GARATUZA-PAYAN, A. ROBLES-MORUA
 Instituto Tecnológico de Sonora, 5 de Febrero 818 Sur, Cd. Obregon, Sonora, Mexico
 E-mail address: enrico.yeppez@itson.edu.mx

Abstract: We aimed to partitioning ET at half- hourly time steps during the peak monsoon season Aided by a real time field monitoring scheme of stable isotopes of water vapor to produce Keeling plots and micromet-driven modeling of the isotopic composition of soil evaporation (E) and transpiration (T) of representative species of a subtropical shrubland. The study was conducted in the state of Sonora Mexico a legume-rich shrubland that gets 550 mm of rain yearly with 70% of the total occurring during the summer monsoon season. Preliminary results indicate that on a daily scale during the peak of the monsoon season in this ecosystem T is the dominant component of ET (T/ET 0.66 to 0.91) which suggests that the vegetation uses the available precipitation efficiently during the growing season.

1. INTRODUCTION

The evapotranspiration flux (ET) is a fundamental ecosystem process that transfers large amounts of water from the surface to the atmosphere via soil evaporation (E) and plant transpiration (T). The combination of hydrometeorological (eddy covariance, EC) and stable isotope techniques to study ecosystem-level processes is an attractive alternative since this combination of techniques allows partitioning ET into E and T at scales congruent for ecosystem studies (Williams *et al.*, 2004; Tarin *et al.*, 2014). The isotopic model to estimate the ratio of T/ET has a fundamental base in a mass balance (Yakir and Sternberg, 2000):

$$\frac{T}{ET} = \frac{(\delta_{ET} - \delta_E)}{(\delta_T - \delta_E)} \quad [\text{Eq. 1}]$$

where, T/ET represents the T fraction that corresponds to the total ET flux; δ_{ET} is the isotopic composition of ET which is determined by the *Keeling* plot approach using isotopic measurements of water vapor and vapor concentrations within a gradient; δ_T is the isotopic composition of transpiration and δ_E is the isotopic composition of the vapor from soil evaporation (Craig and Gordon, 1965). The isotope value of transpiration δ_T can be assumed to equal the xylem water isotopic values if plants are transpiring at ISS. However, δ_T is often not under steady state over short time scales (Farquhar and Cernusak, 2005). Over diurnal time scales, changes in environmental factors, such as relative humidity and vapor pressure deficit, influence isotopic steady state. Under these non-steady state conditions, the main method for determining δ_T is to use the modified Craig-Gordon model:

$$\delta_T = [\alpha_{eq}\delta_L - h\delta_a - \varepsilon_{eq} - (1-h)\varepsilon_K]/[(1-h) + (1-h)\varepsilon_K/1000] \quad [\text{Eq. 2}]$$

where the subscripts, *L* and *a* stand for liquid water body and atmosphere, respectively; α_{eq} is the temperature dependent equilibrium factor, $\varepsilon_{eq} = (1 - \alpha_{eq}) 1000$, ε_K is the kinetic isotope effect, and *h* is relative humidity. In this expression δ_L can be approximated by:

$$\delta_{en}(t) = \delta_{ss}(t) - [\delta_{ss}(t) - \delta_{en}(t - 1)] \exp\left(\frac{-\Delta t}{\tau \zeta}\right) \quad [\text{Eq3}]$$

where $\delta_{en}(t)$ and $\delta_{en}(t - 1)$ are the non-steady state isotope compositions of the leaf water at predicted time t and at time $(t - 1)$ respectively; Δt is an interval time in seconds; $\delta_{ss}(t)$ is the steady state isotope composition of leaf water at time t taking that (Yakir and Stenberg, 2000):

$$\delta_{ss} = \delta_s + \varepsilon_{eq} + \varepsilon_k + h(\delta_a - \varepsilon_k - \delta_s) \quad [\text{Eq. 4}]$$

where, most of these symbols were described above (Eq. 1). In equation 3, Δt is a time interval in seconds, $\tau = W/T_{\text{leaf}}$ and represents the turn over time of water in the leaf; where W is the molar concentration of leaf water and T_{leaf} is the leaf transpiration rate ($\text{mmol m}^{-2} \text{s}^{-1}$) of species leaves. The ζ term relates $\alpha^* \alpha_k (1 - h)$ where α_k is the kinetic fraction factor (1.023), α^* and h are as in Eq. 1. Thus, the isotopic composition of T under non-isotopic steady state (NISS) conditions can be estimated considering $\delta_{en}(t)$ in as δ_L with Eq. 2. Despite that δ_{ss} does not estimate the isotopic enrichment at the sites of evaporation, it does represent the instantaneous condition of the leaf water and therefore is useful to represent the isotopic changes at the leaf through time (Farquhar and Cernusak, 2005) and therefore the non-isotopic steady state (NISS) model values of transient leaf water enrichment are a robust approximation of the isotopic composition of leaf water to estimate δ_T .

In this study we used isotopic measurements of water samples from stems, soils and atmospheric vapor in a multispecies shrubland in the North American monsoon Region combined with continuous measurements of ET from the EC method to partition the ET flux over the growing season.

2. METHODS

The isotopic measurements of water vapor were carried over a water vapor concentration gradient throughout the ecosystem boundary layer in a subtropical shrubland in north western Mexico. Air was pumped from 5 tower heights (0.1, 2, 4.5, 6, 9 m) through low absorption Teflon tubing to a manifold system to automatically change between levels and divert the air to a cavity ring down spectroscopy (DLT 100, LGR Inc.) to determine the $^{18}\text{O}/^{16}\text{O}$ ratios and the water vapor concentration of canopy vapor. Using the isotope and moisture gradients we determined δ_{ET} using the Keeling plot method. We calibrated the instrument every 1.5 hours using standard vapor. Stems were collected from four species representative of the shrubland: *Prosopis sp.*, *Fouquieria sp.*, *Acacia sp.*, *Parkinsonias sp.* and *Mimosa sp.* The soil samples were collected from 0.05 to 0.1 m depths in two different microsites at bare soil and under canopies for a total of 6 samples per microsite on each collection day. Daily values of δ_T were calculated using Eq. 2 for each species and then averaged while d_E was approximated by simply using the isotopic composition of soil water as δ_L in Eq. 2. Water from soils and stems was extracted at the laboratory using the cryogenic distillation method described by West *et al.* (2006) accepting extractions that confirmed that more than 95% of the water by weight was obtained. Water samples were analyzed in a cavity ring down spectroscopy (DLT-100, LGR Inc.). The accuracy of the isotope analysis was 0.4‰ in ^{18}O with respect to the LGR standards #1 and #5 from Los Gatos (LGR, 2008).



Figure 1. Field deployment for water vapor monitoring at a subtropical shrubland in northwestern Mexico.

3. RESULTS

Real time monitoring of atmospheric moisture and the isotopic composition of water vapor ($\delta^{18}\text{O}$) permitted the generation of *Keeling plots* of water vapor at half hour intervals on two days during the peak of the monsoon growing season of 2012. Taking the y-intercepts from Keeling plots we observed that the δ_{ET} values over both days varied in the range of 4.9 and -7.6 ‰ Figure 2.

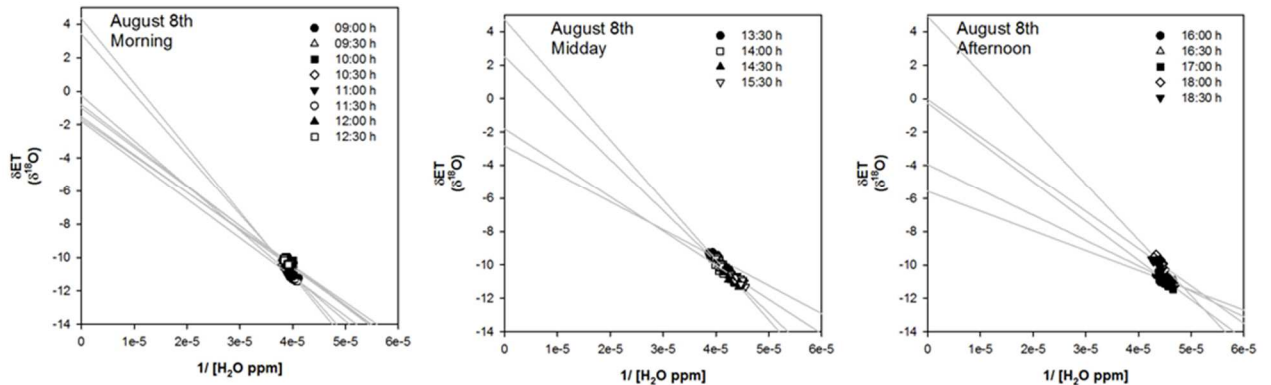


Figure 2. Half-hour integrated Keeling plots of water vapor ($\delta^{18}\text{O}$) in a subtropical shrubland in northwestern Mexico.

The mean isotopic composition of the transpiration flux on August 8th, 2012 was 8.39 ± 2.1 ‰ (Table 1) while the daily mean isotopic composition of the evapotranspiration flux was -32.16 ± 1.7 ‰ this difference permitted a mass balance to estimate the T/ET ratio on this day (Eq. 1.). Considering the range of variation of δ_{ET} during the morning (4.3 to -1.6 ‰), midday (4.7 to -1.8 ‰) and afternoon (4.9 to -5.56 ‰) (see figure 2) the T/ET during these periods would vary from 0.61 to 0.90 in the morning, from 0.66 to 0.91 and 70 to 91 in the afternoon, during the afternoon period. This observation is contrasting with previous observations based on Keeling plots and the isotopic composition of contributing sources to the ET flux where, a marked variation in the T/ET ratio was reported for the morning and afternoon periods (Tarin et al., 2014).

Table 1. Mean daily values of the isotopic composition ($\delta^{18}O$) of transpiration (δ_T) under non-isotopic steady state conditions (Eq 2.) for species representative of a subtropical shrubland in northwestern Mexico during August 8th, 2012. Standard deviation expresses the range of variation for of δ_T or each species over the diurnal cycle.

Species	δ_T species	S.D.
<i>Acacia</i>	9.6	2.5
<i>Fouquieria</i>	3.0	4.3
<i>Parkinsonia</i>	6.5	6.5
<i>Prosopis</i>	15.5	5.6
<i>Mimosa</i>	7.3	7.0
δ_T ecosystem		8.39 ± 2.1

REFERENCES

- [1] CRAIG H., GORDON L.I., Deuterium and oxygen-18 variations in the ocean and marine atmosphere. In: Tonyiorgi, E. (Ed.), Proceedings of the Conference on Stable Isotopes in Oceanographic Studies and Paleotemperatures. *Laboratory of Geology and Nuclear Science*; Pisa, Italy (1965) 9.
- [2] FARQUHAR G.D., CERNUSAK L.A. On the isotopic composition of leaf water in the non-steady state. *Functional Plant Biology*; 32 (2005) 293
- [3] LGR. Liquid-Water Isotope Analyzer, *Automated Injection* California, Los Gatos Research, USA (2008)
- [4] TARIN, T., YÉPEZ, E.A., GARATUZA-PAYÁN, J., WATTS, C.J., RODRÍGUEZ, J.C., VIVONI, E.R., MÉNDEZ-BA-RROSO, L.A. Partición de la evapotranspiración usando isótopos estables en estudios ecohidrológicos. *Tecnología y Ciencias del Agua*. **3**, (2014), 97.
- [5] WEST A.G., PATRICKSON S.J., EHLERINGER J.R. (2006). Water extraction times for plant and soil materials used in stable isotope analysis. *Rapid Communication in Mass Spectrometry* **20** (2006) 1317.
- [6] WILLIAMS D.G., CABLE W., HULTINE K., HOEDJES J.C.B., YÉPEZ E.A., SIMONNEAUX V., ER-RAKI S., BOULET G., BRUIN DE H.A.R., CHEHBOUNI A., HARTOGENSIS O.K., TIMOUK F.. Evapotranspiration components determined by stable isotope, sap flow and eddy covariance techniques. *Agricultural and Forest Meteorology*; **125** (2004) (41
- [7] YAKIR D., STERNBERG L.S. (2000). The use of stable isotopes to study ecosystem gas exchange. *Oecologia* **123** (2000) 297.

ID: 130

THE ICE-CORE STABLE ISOTOPE RECORDS FROM SVALBARD GLACIERS AS PROXIES OF CLIMATE AND ENVIRONMENTAL CHANGES

T. MARTMA,
Institute of Geology at Tallinn University of Technology,
Ehitajate tee 5, 19086 Tallinn, Estonia
E-mail address: tonu.martma@ttu.ee

E. ISAKSSON, J. KOHLER
Norwegian Polar Institute, Fram Centre, Hjalmar Johansens gt.14, 9296 Tromsø, Norway.

V. A. POHJOLA, C. P. VEGA
Department of Earth Sciences, Uppsala University, Villavägen 16, SE-752 36 Uppsala, Sweden.

R. VAIKMÄE
Institute of Geology at Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia.

Abstract: New shallow ice core and snow pit records from Svalbard (in the Norwegian high Arctic) provide an overview of the spatial and temporal distribution of water stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) over the last decade. Snow pit samples were taken from the Lomonosovfonna ice cap and from the Ny-Ålesund area glaciers. The results give an idea of the spatial variation of water stable isotopes in Svalbard winter precipitations. Post-depositional phenomena may additionally modify the ice core isotope and chemistry data. To date the shallow ice cores, seasonal cycles were counted by means of the water isotope data, using the winter minima as an annual reference.

1. INTRODUCTION

Stable water isotopic composition ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) of ice cores is commonly known as one of the most valuable paleo-climate proxies for temperature conditions of the precipitation formation in the past. The observed relationship between air temperature and isotopic content of the precipitation both geographical and temporal has been robustly confirmed experimentally and explained theoretically. Isotopic data extracted from the deep ice cores in the polar ice sheets have contributed to much of the information on climate variability both on inter-annual and ice ages time scales. However, most of the ice core records available from the northern hemisphere are from the cold dry firn zone in interior Greenland.

Ice cores from the glaciers outside the main ice fields have not received much attention, partly because of the surface melting during the summer season which could alter the original isotopic signal. In order to get a more comprehensive view of the climatic and environmental changes on a more global or hemispherical scale, the data from other locations outside large ice sheets is needed.

In the Norwegian High Arctic, Svalbard archipelago, 3 cores were sampled at a resolution of 5 cm or less in the lower part to account for glacial thinning towards the bedrock and studied in great detail with focus on the $\delta^{18}\text{O}$, $\delta^2\text{H}$ and major water soluble ion records.

Two ice cores have been drilled on Lomonosovfonna, one in 1997 (1250 m asl, 121 m long, covering ~1200 years), the other about 4.6 km further south in 2009 (1202 m asl, 149 m long, covering ~800 years). The ice core drilled in 1997 has been studied in great detail [1, 2] and confirmed that Lomonosovfonna is less affected by melting than other Svalbard glaciers [3].

The ice core drilled in 2005 was sampled for the analysis of water soluble major ions, $\delta^{18}\text{O}$, $\delta^2\text{H}$ [4]. Further studies are in progress.

An ice core extracted from Holtedahlfonna ice cap (1150 m asl, 125 m long, covering ~300 years), was analyzed for major ions, $\delta^{18}\text{O}$, $\delta^2\text{H}$ [5] and for tritium [6].

2. METHODS AND RESULTS

To illustrate the site-specific climatic and glaciological factors and to better estimate the local influence of environmental factors on Svalbard ice core records, a snow pit study was conducted in Svalbard. From 2001 to 2013, samples were taken with the aim of analysing the one year winter snow pack for $\delta^{18}\text{O}$ and $\delta^2\text{H}$. Samples were taken from Lomonosovfonna and from Ny-Alesund area and measured at the Institute of Geology, Tallinn University of Technology by mass spectrometer Delta V Advantage or Laser Analyzer Isotope Analyser L2120-i. All isotopic measurements were calibrated on a two-point scale against the international standards VSMOW (Vienna Standard Mean Ocean Water) and VSLAP (Vienna Standard Light Antarctic Precipitation).

The results give an idea of the spatial variation of water stable isotopes in Svalbard winter precipitations. Alteration by post-depositional processes, in particular seasonal melt in the ice core isotope and chemistry data was studied using shallow cores.

3. CONCLUSIONS

Svalbard is positioned in a climatically interesting area in the Eurasian Arctic since the climate over the archipelago is very sensitive to changes in the North Atlantic Current, being situated at the turning point of the oceanic conveyor. In addition, the atmospheric circulation conditions also make Svalbard a suitable place for the study of anthropogenic influences from Europe. Comparison of all the obtained data has shown that despite the fact that atmospheric records in these ice cores probably have been to some degree altered by melt, these records still provide information about the major trends in atmospheric variability of both climate parameters and pollution history. Thus we believe that with careful site selection, high resolution sampling and multiple isotopic and chemical analyses ice cores from small Arctic ice caps are extremely useful for a wide range of environmental studies.

REFERENCES

- [1] ISAKSSON, E., DIVINE, D., KOHLER, J., MARTMA, T., POHJOLA, V., MOTOYAMA, H., WATANABE, O., Climate oscillations as recorded in Svalbard ice core $\delta^{18}\text{O}$ records between 1200-1997. *AD, Geografiska Annaler* **87A**(1) (2005) 203-214.
- [2] DIVINE, D., ISAKSSON, E., MARTMA, T., MEIJER, H.A.J., MOORE, J., POHJOLA, V., van de WAL, R.S.W., GODTLIEBSEN, F., Thousand years of winter surface air temperature variations in Svalbard and northern Norway reconstructed from ice core data, *Polar Research* **30** (7379) (2011) 1-12.
- [3] POHJOLA, V. A., MOORE, J. C., ISAKSSON, E., JAUHIAINEN, T., van de WAL, R. S. W., MARTMA, T., MEIJER, H. A. J., VAIKMAE, R., Effect of periodic melting on geochemical and isotopic signals in an ice core from Lomonosovfonna, Svalbard, *JGR*, **107**(D4) (2002) 4036.

- [4] WENDL, I. A., EICHLER, A., ISAKSSON, E., MARTMA, T., SCHWIKOWSKI, M., 800 year ice-core record of nitrogen deposition in Svalbard linked to ocean productivity and biogenic emissions, *Atmos. Chem. Phys. Discuss.* **14**, (2014) 24667-24700.
- [5] BEAUDON, E., MOORE, J., MARTMA, T., POHJOLA, V., van de WAL, R., KOHLER, J., ISAKSSON, E., Lomonosovfonna and Høltedahlfonna ice cores reveal east–west disparities of Spitsbergen environment since 1700 AD, *Journal of Glaciology* **59** (218) (2013) 1069-1083.
- [6] van der WEL, L. G., STREURMAN, H. J., ISAKSSON, E., HELSEN, M. M., van de WAL, R. S. W., MARTMA, T., POHJOLA, V. A., MOORE, J. C., MEIJER, H.A.J., Using high resolution tritium profiles to quantify the effects of melt on two Spitsbergen ice cores, *Journal of Glaciology* **57** (206) (2011) 1087-1097.

AN ONLINE SEARCH AND VISUALIZATION TOOL FOR WATER STABLE ISOTOPE RECORDS FROM NATURAL ARCHIVES

V. MASSON-DELMOTTE, T. BOLLIET, P. BROCKMANN and IPSL participants
LSCE (CEA-CNRS-UVSQ/IPSL), Bat 701, l'Orme des Merisiers,
CEA Saclay, 91 191 Gif-sur-Yvette cédex, France
E-mail address: valerie.masson@cea.fr

Abstract: In order to facilitate the navigation within the wealth of water stable isotope records extracted from natural climate archives, a meta-database has been developed, and source records have been standardized, including information on age models. A user-friendly online visualization tool has been developed. The focus has been placed (i) on the past 200 years in order to allow overlap with IAEA/GNIP records, and provide a pre-industrial background; (ii) on the mid-Holocene, 6 000 years ago, the Last Glacial Maximum, 21 000 years ago, and the Last Interglacial, about 125 000 years ago, which are target periods of the Paleoclimate Modelling Intercomparison Project [1]. This database will strengthen the use of past records of water stable isotopes for model-data comparisons.

1. INTRODUCTION

During the past decades, thousands of water stable isotope records have been retrieved from a variety of natural archives, thereby providing key information on past changes in climate and the water cycle. In parallel, water stable isotopes are being implemented in a growing number of climate models, which perform simulations of key past climates. Model-data comparisons are crucial to expand the use of water stable isotopes to benchmark climate models beyond the IAEA era of direct measurements, to exploit water stable isotopes as fingerprints of climate feedbacks, and to understand the mechanisms of past changes in climate and water cycle. This strengthens the need for user-friendly tools to navigate within a standardized database of stable isotope records of past climate changes.

2. METHODS

Existing oxygen, hydrogen and carbon stable isotope records have been investigated for different types of archives: lake and marine sediments, speleothems, ice cores and tree ring cellulose, with a focus on the last two glacial-interglacial periods and selected target periods: the past 200 years, the mid-Holocene, Last Glacial Maximum and Last Interglacial. The first period provides an overlap with IAEA/GNIP data and meteorological instrumental records, and gives access to the climate response to large volcanic eruptions of the 19th century. The other periods correspond to targets of the Paleoclimate Modelling Intercomparison Project [1] for systematic simulations, model intercomparisons, and model-data comparisons. The mid-Holocene and Last Interglacial correspond to different orbital configurations, with warmer conditions in mid to high latitudes of the northern hemisphere driven by enhanced summer insolation. The Last Glacial Maximum is a cold extreme driven by the expansion of continental ice sheets and reduced concentrations of atmospheric greenhouse gases.

Existing records from the NOAA [2] and PANGEA [3] online databases have been compiled as well as the internal database from LSCE and requests to authors of publications. Raw data were transferred into a standardized format and stored in individual files, as well as age model information. Age control quality flags were integrated in the single metafile also

providing essential information on each dataset (geolocalization, archive and proxy type). Altogether, this corresponds to ~ 1500 dated records for $\delta^{18}\text{O}$ (with an additional set of 2600 non dated marine sediment records), and 800 $\delta^{13}\text{C}$ dated records. Figure 1 illustrates the geographical distribution of screened records, identified by type of archive. Figure 2 illustrates the number of records from different sources for each past period.

An open-access online platform is being built to provide dynamic and interactive browsing, visualization and downloading facilities for compiled data [4].

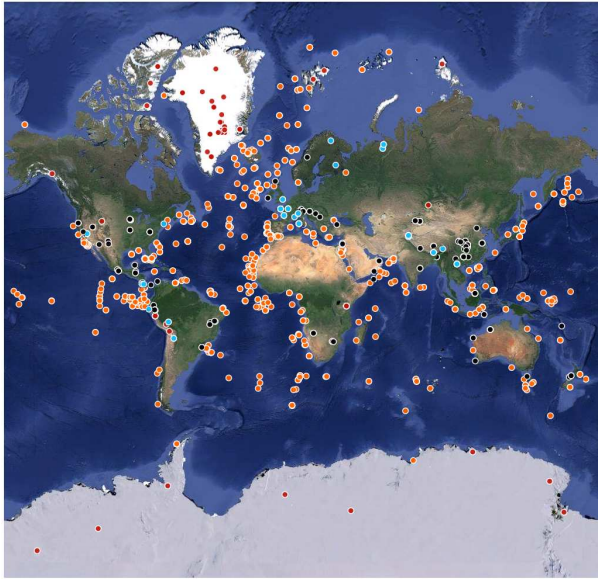


Figure 1: Map of dated records. The color of each symbol represents one type of archive (orange, marine sediment cores; red, ice cores; black, speleothems; blue, tree rings).

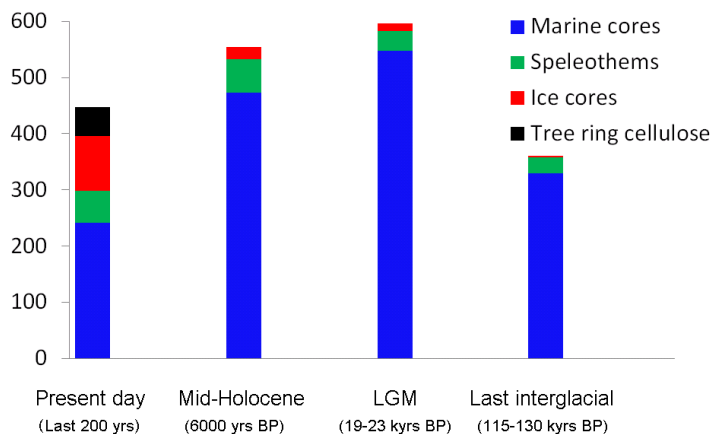


Figure 2: number of $\delta^{18}\text{O}$ records from marine cores, speleothems, ice cores, and tree ring cellulose for each PMIP time slice.

3. RESULTS

The database reflects significant enhancement of the quality of the age models during the last two decades, although information exists from old records albeit with poor age control.

Information from marine sediment cores is however limited by uncertainties for marine sediment core tops, and therefore the reference present-day for which differences for past periods are calculated.

The geographical coverage of records still remains heterogeneous (Figure 1), due to the limited number of continental records and the distribution of tree, cave, glacier and lake sediment records. Marine sediment information is also limited due to dissolution issues in the deep Indian and Pacific Oceans. For the most recent period, the number of stable isotope records covering the last 1 to 2 decades remains limited, as many archives were recovered in the mid to late 20th century. This is a caveat for the use of stable isotope data and simulations for detection and attribution, and for temporal calibration studies. Nevertheless, these records from natural archives complement IAEA/GNIP datasets both in space and time.

The significant offset between glacial and present conditions is virtually recorded all over the globe. Anomalies between the Mid-Holocene and present-day are equivocal and characterized by regional fingerprints, as the magnitude of the signal and sometimes difficult to distinguish from the noise associated with the archiving process and the background variability. As a result, the number of datasets indicating a clear (positive or negative), weak, or no significant offset between these two periods is of the same order. Anomalies for the Last Interglacial period are stronger, but age scale uncertainties also much larger.

4. CONCLUSIONS

This effort has been accomplished thanks to support from LABEX L-IPSL. An international framework is necessary to maintain this momentum, integrate new proxy records, build tools to facilitate calculations using outputs of simulations performed using isotopically-enabled climate models, and therefore allow user-friendly model-data comparisons.

REFERENCES

- [1] <https://pmip3.lsce.ipsl.fr/>
- [2] <http://www.ncdc.noaa.gov/data-access/paleoclimatology-data>.
- [3] <http://www.pangaea.de/>
- [4] <http://webportals.ipsl.jussieu.fr/ClimateProxiesFinder/latest/>

ID: 139

THE EEMIAN SEA AND FOLLOW PALAEO-HYDROLOGY OF BALTIC – WHITE SEA REGION EVIDENCE FROM GROUNDWATER STABLE ISOTOPE ($\delta^2\text{H}$, $\delta^{18}\text{O}$) COMPOSITION

I. TOKAREV, I. AVRAMENKO,

Resource center “Geomodel”, Research park, Saint-Petersburg state university,

Ul’yanovskaya 1, Petergof, Saint-Petersburg, Russian Federation, 198504

E-mail address: tokarevigor@gmail.com

G. VORONYUK

Open Joint Stock Company Saint-Petersburg Complex Geological Expedition

grigory.voronuk@yandex.ru

Abstract: Level of the regional drainage basis for surface and groundwater repeatedly has been changed in last 120 Ka on the north-west margin of Eurasia. Eemian sea have occupied aquatories of modern Baltic and White seas and part of theirs watersheds. In this time the sea water intrusions in the continental aquifers could be formed near palaeo-shoreline. During the last ice age the sea level was significantly lower than modern one, therefore part of the deep aquifers in periglacial area of the Scandinavian ice sheet could be discharge on surface and the regional level of groundwater was lower, than before and after. Together with the underglacial hydrology all these changes should be formed the complex image of the groundwater chemistry in Baltic region. This complex situation could be decrypted by the environmental isotope tracers, which are archive of the paleohydrology conditions, and by groundwater dating. Aquifers of the stratified sediments and water of the crystalline basement on contact of Russian platform and Fennoscandian shield were studied in this work by the stable isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$). Modern water was obtained in the quaternary sediments and in the bedrock aquifers, as it was expected. This water is very close to the modern atmospheric precipitation by chemistry and the isotope composition. Groundwater of Cambrian-Vendian aquifer system (CVAS) with depletion by oxygen-18 and deuterium (lightweight water) has been observed from the several sampling sites in Estonia and Finland [1, 2]. The depleted water we also found in catchments of the Ladoga Lake and the Gulf of Finland in Russia. But in some cases water from CVAS has a very high deviation of the stable isotope composition from the Global Meteoric Water Line (GMWL). This shift could be look like as depletion and also as enrichment of water by oxygen-18 and deuterium. Our interpretation of these data is follow. The lightweight water, which lies on GMWL, is the relict water of the Baltic Ice Lake as it has been proven to Tallinn water-intake [2, 3]. Water, which has the enriched isotope composition and simultaneously is shifted to right from GMWL, actually is water, which was re-formed from thawed permafrost. Depleted water, which isotope composition is shifted to left from GMWL, is the residual water. This water was extruded down from the earth surface due to slow moving of freezing front in the geological strata during climate cooling. Taking into account position of the enriched and depleted water in the geological section, it could be concluded, that lower edge of permafrost was on depth about 80–100 m from modern earth surface.

1. INTRODUCTION

In the northern part of the Baltic Artesian Basin (BAB) groundwater of the multilayered hydrogeological system (mainly the Cambrian and Vendian aquifers – CVAS) is the principal and most plentiful source for the public water supply in Russia and Estonia. But there are

problems with the water quality, which often do not conform the sanitary limits due to high salinity and/or the specific components abundance, such as the natural origin nuclides (Ra, Rn) or microelements (B, F, Fe, Mn), etc. The BAB is characterized by the limited knowledge about the hydraulic boundaries and conductivities. Taking into account the complex geological history of the Baltic region in the Pleistocene and Holocene, the isotope archive ($\delta^2\text{H}$, $\delta^{18}\text{O}$ and other environmental tracers) is significant for the groundwater flow and mass-transport understanding.

2. METHODS AND RESULTS

The stable isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$), chemistry (major components and microelements) and in some cases tritium, helium, radium and radon were studied in groundwater near the north-east margin of the BAB in terrigenous and carbonate aquifers from a crystalline basement up to Earth surface (left panel of Figure). Also surface water was sampled and monitoring of stable isotope in atmospheric precipitations was done.

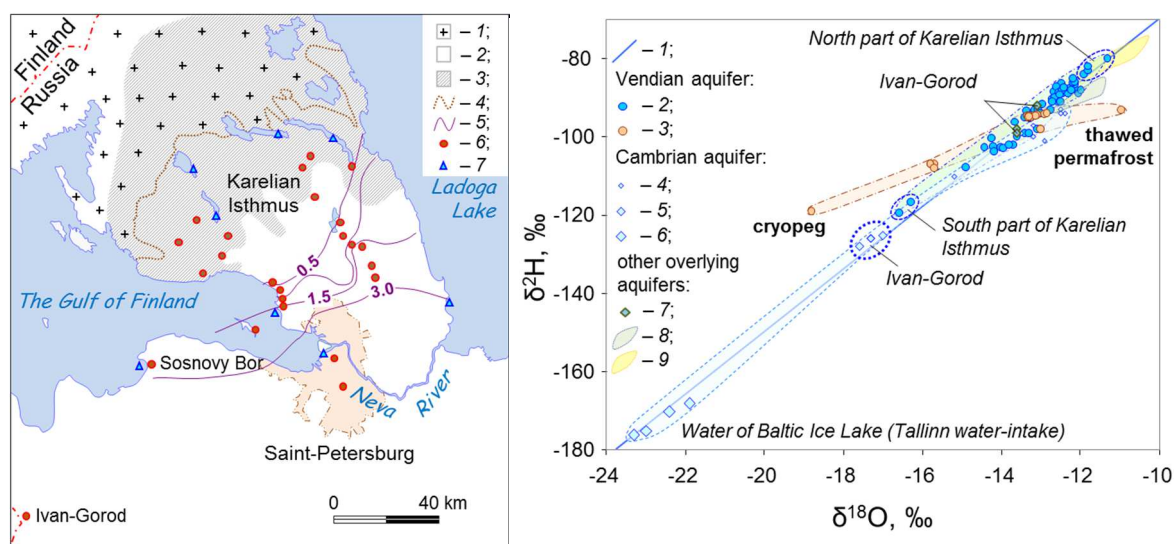


Figure. Scheme of water sample collection (left: 1 – crystalline bedrock; 2 – stratified terrigenous sediments; 3 – modern recharge area of Vendian aquifer on Karel'ian Isthmus; 4 – north boundary of Vendian aquifer; 5 – isolines of water salinity in Vendian aquifer; 6 – sampling points for groundwater; 7 – sampling points for surface water) and groundwater isotope composition (right: 1 – GMWL; 2, 3 – Vendian aquifer on Karel'ian Isthmus and near Sosnovy Bor town, respectively; 4, 5, 6 – Cambrian aquifer near Sosnovy Bor, Ivan-Gorod and Tallinn [2], respectively; 7 – Cambrian-Ordovician aquifer near Ivan-Gorod; 8 – Devonian aquifer; 9 – groundwater of Quarter sediments).

Modern water was obtained in the bedrock aquifers on the Karel'ian Isthmus and in the quaternary sediments everywhere, as it was expected. This water is very close to the modern atmospheric precipitation by chemistry, the isotope composition and tritium contents. In these water-bearing rocks and sediments the fresh bicarbonate groundwater is encountered throughout the drill hole. Sometimes radon exceeds the sanitary limits in water from fissured granitoids. Mainly modern water is observed in Cambrian-Ordovician aquifer. Hardness and anthropogenic pollution is problem for exploitation of this groundwater.

Water of the Baltic Ice Lake is clearly fixed for Cambrian aquifer in Tallinn water-intake (Estonia) due to high depletion in oxygen-18 and deuterium abundance (right panel of Figure). The lightest stable isotope composition of groundwater for Europe, which good fits on GMWL, was found here $\delta^2\text{H} = -160\text{‰}$, $\delta^{18}\text{O} = -21\text{‰}$ [2]. Noble gases composition and radiocarbon dating are agreed with the stable isotopes for Kopli Peninsula [3]. Cambrian aquifer is raised to Earth surface to the east direction from Tallinn. Following this raising the isotope composition of water is gradually enriched by oxygen-18 and deuterium and stable isotope composition is increased to $\delta^2\text{H} = -125\text{‰}$, $\delta^{18}\text{O} = -17\text{‰}$ near the boundary between Estonia and Russia, and up to $\delta^2\text{H} = -100\text{‰}$, $\delta^{18}\text{O} = -13\text{‰}$ (that is like to modern precipitation) near Sosnovy Bor (Saint-Petersburg district), where Cambrian aquifer is provided on surface.

The relict water (probably due to the Eemian sea intrusion) was opened in Vendian aquifer near town Sosnovy Bor and in Saint-Petersburg (south part of studied area). It is salty ($M = 4\text{--}6\text{ g/L}$) and isotopically fractionated water. This secondary fractionation of water could be look like as depletion and also as enrichment of water by oxygen-18 and deuterium (right panel of Figure). Water, which has the enriched isotope composition and simultaneously is shifted to right from GMWL, actually is water, which was re-formed from thawed permafrost. Depleted water, which isotope composition is shifted to left from GMWL, is the residual water. This water was extruded down from the earth surface due to slow moving of freezing front in the geological strata during climate cooling. Taking into account position of the enriched and depleted water in the geological section, it could be concluded, that lower edge of permafrost was on depth about 80–100 m from modern earth surface.

Vendian aquifer is raised to Earth surface to the north direction, where modern recharge area is located. In this direction salinity of water is decreased, isotope composition is became closer to modern precipitation and tritium is appeared in water. On the north part of studied area Vendian aquifer is the principal and most plentiful source for the public water supply for Saint-Petersburg and satellite towns and villages. However, quality of water often do not conform the sanitary limits here due to specific components abundance, such as the natural origin nuclides (Ra, Rn) or microelements (B, F, Fe, Mn).

4. CONCLUSIONS

Isotope composition of water in terrigenous and carbonate aquifers on north-east part of Baltic Artesian Basin (BAB) reflects the complex geology history of Baltic and White sea watersheds. Sampling of ground and surface water, and monitoring of stable isotope in atmospheric precipitations were done near Saint-Petersburg. Extreme depletion of groundwater by oxygen-18 and deuterium (lightweight water) indicate on the glacial meltwater intrusion in aquifers during Baltic Ice Lake existence. Secondary fractionation of hydrogen and oxygen isotopes is result of the permafrost emergence and thawing. Aquifers, wich have these isotope fingerprints, content the relict water with high age (minimum several tens of thousands of years). There are modern water in aquifers, which lays the earth surface, including shallow groundwater of quaternary sediments and water in more ancient aquifers. These circumstances should be taken into account, when exploitation of aquifers for drinking water supply is organized.

REFERENCES

- [1] BLOMQVIST, R. Hydrogeochemistry of deep groundwaters in the central part of the Fennoscandian Shield. Report YST-101. Espoo (1999) 41 p.
- [2] RAIDLA, V., KIRSIMÄE, K., VAIKMÄE, R., JÕELEHT, A., KARRO, E., MARANDI, A., SAVITSKAJA, L. Geochemical evolution of groundwater in the Cambrian-Vendian aquifer system of the Baltic Basin. *Chemical Geology* (2009) 258, 219–231 pp.
- [3] VAIKMÄE, R., MARANDI, A. RAIDLA, V. Isotopically light meltwater from Scandinavian Ice Sheet in the Cambrian-Vendian aquifer system in northern Estonia: further study prospects. *Proceedings of the 4th Mini Conference on Noble Gases in the Hydrosphere and in Natural Gas Reservoirs* held at GFZ Potsdam, GERMANY, 28.02.-02.03.2007.

WEIGHTING ALTERNATIVES (PRECIPITATION VS. ACCUMULATION) FOR WATER STABLE ISOTOPES – IMPLICATIONS FOR ICE CORE RECORDS -

I.G. HATVANI, Z. KERN

Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, MTA, Budaörsi út 45, H-1112 Budapest, Hungary

E-mail address: hatvaniig@gmail.com, zoltan.kern@gmail.com

Abstract: It is a generally accepted notion that amount-weighted stable isotope signals are archived in ice cores. Therefore, in dealing with the current and important question of whether to use precipitation or accumulation when calculating weighted annual averages, it is unavoidable. In the present study monthly measured accumulation, calculated effective-accumulation, precipitation, air temperature (T), $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values acquired from the Halley Bay (1972-2012) and Vernadsky (1964-2008) stations in Antarctica and annual $\delta^{18}\text{O}$ and $\delta^2\text{H}$ stable isotope records from ice cores in the vicinity of the stations were used. According to the different weighting schemes, (i) the alternatively weighted time series of $\delta^{18}\text{O}$ and T from the stations; and (ii) all the time series of the variables measured at the stations and in the nearby ice core records were correlated with each other. Results indicate that post-depositional processes have a much more determining effect in isotopic composition of the firn than expected.

1. INTRODUCTION

According to the classical interpretation, [1] precipitation weighted isotope signals are archived in ice cores. It is worth exploring whether a stronger link may exist between amount weighted stable isotope records [2], and ice cores, or not. Furthermore, when weighting with accumulation, drift-snow should be taken into account [3]. Therefore, the calculation of effective-accumulation weighted annual averages should be prepared and considered in the analysis.

Two questions were raised: (i) to what extent do the different weighting approaches (precipitation, accumulation, effective-accumulation or arithmetic means) improve the $\delta - T$ relationship at precipitation monitoring stations in Antarctica, and (ii) which weighting approach approximates the actual signal stored in the nearby ice cores better.

2. METHODS

For the calculation of the weighted annual averages, monthly records of primary isotopic- and climatological parameters were acquired from GNIP ISOHIS [4] and the British Antarctic Survey (BAS) for the Vernadsky and Halley Bay stations (Antarctica) respectively. For the comparison of the results with external stable isotope records, nearby ice cores were used (Table 1, for details see [5]).

Only monthly precipitation totals were available at Vernadsky. However, two types of accumulation were used at Halley Bay station. The raw accumulation data (Acc) and effective accumulation (eff-Acc; Figure. 1).

Table 1. Acquired data with time intervals of availability

	Stations			Ice cores				
	Halley Bay	Vernadsky		c61	c17	c34	c54	c55
Lat (S), Lon (W)	75.58; 26.56	65.07; 63.97	Lat (S), Lon (W)	64.2; 57.68	78.31; 39.43;	74.85; 8.49	72.65; 16.63	73.6; 12.43
Elevation (m)	30.8	1	Elevation	1392	76	2578	42	773
Prec. (mm)	-	1964-2008	Distance from HB (km)	1750	450	530	455	480
Acc (mm)			Distance from VK(km)	330	1730	2335	2080	2215
eff-Acc			Original source	[6]		www.pangaea.de		
T (°C)	1972-2012							
$\delta^{18}\text{O}$ (‰)		1964-2008	$\delta^{18}\text{O}$ (‰)	-	-	1972-1997	1972-1991	1972-1990
$\delta^2\text{H}$ (‰)			$\delta^2\text{H}$ (‰)	1964-2005	1972-1989	-	-	-

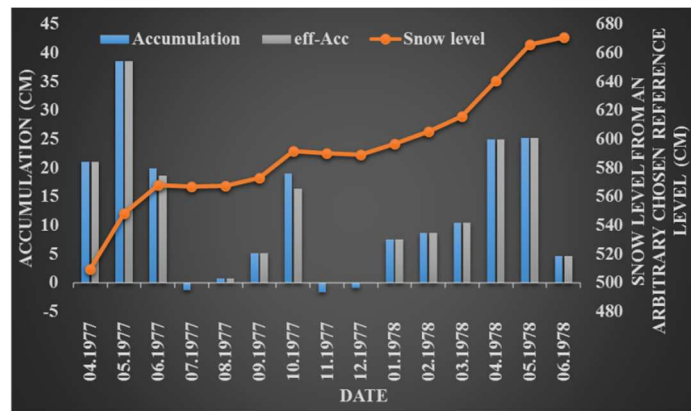


Figure 1. Acc, calculated Snow level and eff-Acc. When there was a decrease in Acc (e.g. 11&12.1977) the eff-Acc represented the Acc preceding the months of decrease (10.1977) minus the “blown away snow”. Gaps in eff-Acc represent the years of negative Acc.

The main path of the approach consisted in (i) calculating the alternatively weighted time series of $\delta^{18}\text{O}$ and T and correlating them to each other at each station separately; then (ii) the time series of all the available variables at the stations were weighted and correlated to the stable isotope records of the nearby ice core records (Table 1).

The assumption is that the most realistic scheme of weighting is the one which gives the highest correlation ($p < 0.05$) (i) between the similarly weighted $\delta^{18}\text{O}$ and T and/or (ii) with the ice core stable isotope records.

The amount-weighted annual averages were calculated according to general practice (Eq. 1).

$$am. w. ann. avg. = \frac{wtd_i * weight_i}{weight_{ann} - weight_{no.d}} \quad (1)$$

where $i = 1-12$; wtd represents the weighted variable ($\delta^{18}\text{O}$, $\delta^2\text{H}$ or T), while weight is the variable which was used for weighting (Acc, eff-Acc, Prec or arithmetic mean (i.e. weighting with one)). In the denominator $weight_{ann}$ is the annual sum of the weight, while $weight_{no.d}$ is the sum of the weight for those months where no corresponding wtd was measured. To avoid major bias, if the number of missing values for a year exceeded 50% for either wtd or the weight, then that particular year was omitted.

3. RESULTS

The amount-weighting approach indicated a stronger linear δ - T dependence at the stations, while the annual arithmetic means gave a significant and influential coefficient only at Vernadsky station (Table 2).

Table 2. Correlation coefficients between $\delta^{18}O$ and T for the same type of weighting; significant values are shown in italics

	Halley Bay			Vernadsky	
	T ₁	T _{Acc}	T _{eff-Acc}	T ₁	T _{Prec}
$\delta^{18}O_1$	0.30	-	-	0.67	-
$\delta^{18}O_{Acc}$	-	0.64	-	-	-
$\delta^{18}O_{eff-Acc}$	-	-	0.61	-	-
$\delta^{18}O_{Prec}$	-	-	-	-	0.69

Regarding the comparison of the weighted time series of all the available variables at the stations and the stable isotope records of the nearby ice cores, it turned out that at Halley Bay only the arithmetic means of T had a significant correlation with the $\delta^{18}O$ records of core c55. Although, the T did not have a significant correlation with $\delta^{18}O$ from the other nearby cores (c17 & c34), the arithmetic mean temperatures showed the relatively highest coefficients ($r > 0.37$). Correlating the other variables, measured at the station and in the ice cores, did not give any meaningful results.

At Vernadsky the weighting of δ^2H with precipitation did not give an explicitly better r with δ^2H at core c61 than the arithmetic means. However, in the case of weighted T from the station and δ^2H from the core, the arithmetic mean showed a stronger, yet still insignificant, linear relationship to the δ^2H at core c61 than the precipitation-weighted ones (Table 3).

Table 3. Correlation coefficients between differently weighted T and δ^2H from Vernadsky station (VNK) and δ^2H records from nearby ice core c61

	Arithmetic		Precipitation	
	T _{VNK}	δ^2H_{VNK}	T _{VNK}	δ^2H_{VNK}
δ^2H_{c61}	0.31	0.32	0.21	0.31

4. CONCLUSIONS

The strong correlation between the arithmetic means of T records measured at the stations and the isotope records from the cores reinforce the notion that post depositional processes exercise a stronger influence on the stable isotope content of the firn. Taking T conditions between precipitation events into account can indeed improve the statistical link. A plausible explanation could be the continuous replacement of interstitial-, with atmospheric water vapor [7] transferring the temperature signal into the firn.

Although, additional cores should be included in further analysis, ones even closer to the stations than the present one, the results obtained indeed concur with the higher importance of post depositional processes and highlight the fact that in this case amount weighting did not improve the expected linear relationships any further.

ACKNOWLEDGEMENTS

We would like to give special thanks to John King & Steve Colwell (BAS), Denis Pishniak (NASC) providing access to their data and researchers who archived their ice core data in PANGAEA. Thanks for the support of the MTA “Lendület” program (LP2012-27/2012). This is contribution No. 22 of 2ka Palæoclimatology Research Group.

REFERENCES

- [1] STEIG, E. J., GROOTES, P. M., STUIVER, M., Seasonal precipitation timing and ice core records, *Science*, **266** (1994) 1885–1886
- [2] PERSSON, A., LANGEN, P. L., DITLEVSEN, P., VINTHER, B. M., The influence of precipitation weighting on interannual variability of stable water isotopes in Greenland, *Journal of Geophysical Research: Atmospheres* **116** (2011) D20120.
- [3] BARRAL, H., GENTHON, C., TROUVILLEZ, A., BRUN, C., AMORY, C., Blowing snow in coastal Adélie Land, Antarctica: three atmospheric-moisture issues, *The Cryosphere* **8** (2014) 1905-1919.
- [4] IAEA, Global Network of Isotopes in Precipitation. The GNIP Database (2014) <http://www.iaea.org/water> (Last accessed on 19.11.2014)
- [5] HATVANI, I.G., LEUENBERGER, M., KERN, Z., Statistical assessment of ice core derived stable water isotope records to improve temporal synchronization for further geostatistical analysis in an Antarctic macro region, *Polar Research* (in revision; 2014)
- [6] MULVANEY, R., ABRAM, N. J., HINDMARSH, R. C. A., ARROWSMITH, C., FLEET, L., TRIEST, J., SIME, L. C., ALEMANY, O., FOORD, S., Recent Antarctic Peninsula warming relative to Holocene climate and ice-shelf history. *Nature* **489** (2012) 141-44.
- [7] STEEN-LARSEN, H. C., MASSON-DELMOTTE, V., HIRABAYASHI, M., WINKLER, R., SATOW, K., PRIÉ, F., BAYOU, N., BRUN, E., CUFFEY, K. M., DAHL-JENSEN, D., DUMONT, M., GUILLEVIC, M., KIPFSTUHL, S., LANDAIS, A., POPP, T., RISI, C., STEFFEN, K., STENNI, B., SVEINBJÖRNSDOTTÍR, A. E., What controls the isotopic composition of Greenland surface snow? *Clim. Past* **10** (2014) 377-392.

ID: 240

COUPLING ^2H AND ^{18}O BIOMARKER ANALYSES IN PALAEOCLIMATE RESEARCH: POTENTIAL, CONCEPTUAL MODEL AND VALIDATION

M. ZECH, J. HEPP, M. TUTHORN

Soil Biogeochemistry, Martin-Luther University of Halle-Wittenberg,

Von-Seckendorff-Platz 3, Halle (Saale), Germany

E-mail address: michael_zech@gmx.de.

R. ZECH

Institute of Geography, University of Bern, Hallerstr. 12, Bern, Switzerland.

K. ROZANSKI

Faculty of Physics and Applied Computer Science, AGH University of Kraków, Al.

Mickiewicza 30, Kraków, Poland.

Abstract: Disentangling variable $\delta^2\text{H}_{\text{precipitation}}$ versus variable isotopic evaporative leaf water enrichment in paleoclimate research using leaf wax $\delta^2\text{H}_{\text{n-alkane}}$ records alone is challenging. Here we propose a coupled $\delta^2\text{H}_{\text{n-alkane}}$ and $\delta^{18}\text{O}_{\text{sugar}}$ biomarker approach offering a possible solution. Accordingly, the biomarkers are used to reconstruct the leaf water isotopic composition. The deuterium-excess of leaf water may then serve as proxy for relative air humidity. Furthermore, using a Craig-Gordon model, the reconstructed isotopic composition of leaf water also allows calculating the isotopic composition of plant source water ($\sim\delta^2\text{H}_{\text{precipitation}}$ and $\delta^{18}\text{O}_{\text{precipitation}}$).

1. INTRODUCTION

During the last ~15 years, compound-specific $\delta^2\text{H}$ analyses of biomarkers, especially of leaf wax-derived *n*-alkanes, have become a popular tool in paleohydrology and –climate research [1]. By contrast, a method for compound-specific $\delta^{18}\text{O}$ analyses of (hemi-) cellulose-derived sugar biomarkers extracted from plants, soils and sediments was proposed only recently [2-4]. Still, a major challenge when interpreting $\delta^2\text{H}$ or $\delta^{18}\text{O}$ records obtained from biomarkers is to differentiate between climatically controlled variations of plant source water ($\sim\delta^2\text{H}_{\text{precipitation}}$ and $\delta^{18}\text{O}_{\text{precipitation}}$) and climatically controlled variations of evaporative ^2H and ^{18}O enrichment of leaf water during transpiration.

2. METHODS

Here we propose a conceptual model which allows overcoming this limitation by a coupled $\delta^2\text{H}$ or $\delta^{18}\text{O}$ biomarker approach (Fig. 1). Accordingly, the isotopic composition of leaf water can be reconstructed from $\delta^2\text{H}$ or $\delta^{18}\text{O}$ of sedimentary leaf wax-derived and (hemi-)cellulose biomarkers (*n*-alkanes and sugars, respectively) by applying biosynthetic fractionation factors. The deuterium(d)-excess of leaf water may then serve as proxy for evaporative enrichment and allows calculating relative air humidity using a Craig-Gordon model. Furthermore, also the isotopic composition of palaeoprecipitation can be calculated as intersect of the evaporation lines (EL) with the Global Meteoric Water Line (GMWL).

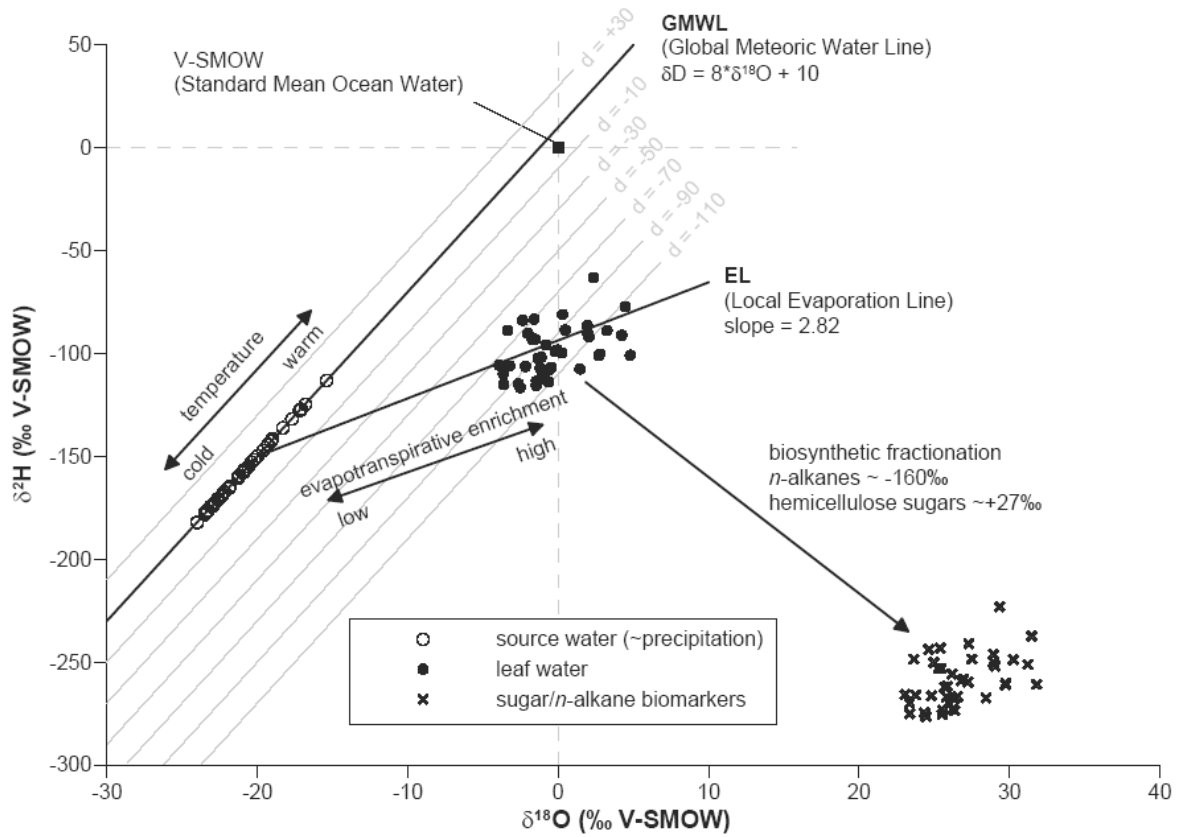


Figure 1. $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ diagram illustrating the conceptual model for a coupled $\delta^2\text{H}$ - $\delta^{18}\text{O}$ biomarker approach. GMWL = Global Meteoric Water Line, EL = Evaporation Line [5].

3. RESULTS

The proposed conceptual model can be validated by applying it to modern climate and topsoil transects. This enables the comparison of actual humidities and isotope precipitation values with “biomarker-based” reconstructed humidities and isotope precipitation values. First respective results from an Argentinean climate transect show that the model-based reconstructed $\delta^{18}\text{O}_{\text{precipitation}}$ values systematically underestimate the actual values (Fig. 2). However, they also show a highly significant correlation of reconstructed and actual values.

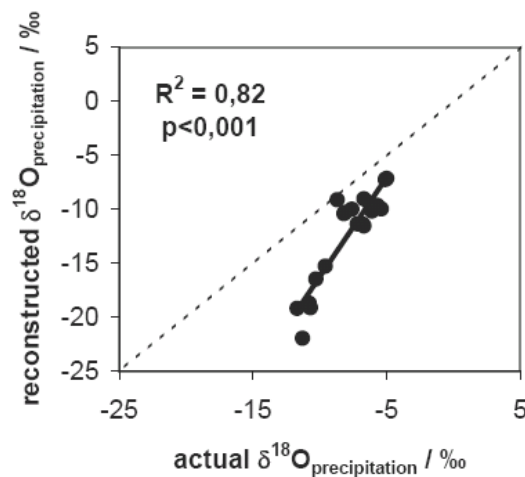


Figure 2. Correlation of “biomarker-based” reconstructed $\delta^{18}\text{O}_{\text{precipitation}}$ values with actual $\delta^{18}\text{O}_{\text{precipitation}}$ values for a Argentinean climate/topsoil-transect [6].

4. CONCLUSIONS

It can be concluded that the proposed coupled $\delta^2\text{H}_{\text{n-alkane}}$ and $\delta^{18}\text{O}_{\text{sugar}}$ biomarker approach is a promising innovative tool in palaeoclimate/-hydrology research offering the potential

- (i) to reconstruct relative air humidities and
- (ii) the isotopic composition of palaeoprecipitation.

Last but not least, the proposed coupled $\delta^2\text{H}_{\text{n-alkane}}$ and $\delta^{18}\text{O}_{\text{sugar}}$ biomarker approach can also promisingly be adopted in palaeolimnologic studies [7].

REFERENCES

- [1] SACHSE, D. et al., Molecular paleohydrology: interpreting the hydrogen isotopic composition of lipid biomarkers from photosynthetic organisms. *Annu Rev. Earth Planet Sc* **40** (2012) 221.
- [2] ZECH, M., GLASER, B., Compound-specific $\delta^{18}\text{O}$ analyses of neutral sugars in soils using GC-Py-IRMS: problems, possible solutions and a first application, *Rapid Commun Mass Spec* **23** (2009) 3522.
- [3] ZECH, M. et al., Absence of oxygen isotope fractionation/exchange of (hemi-)cellulose derived sugars during litter decomposition, *Org Geochem* **42** (2012) 1470.
- [4] ZECH, M. et al., Oxygen isotope ratios ($^{18}\text{O}/^{16}\text{O}$) of hemicellulose-derived sugar biomarkers in plants, soils and sediments as paleoclimate proxy I: Insight from a climate chamber experiment, *Geochim Cosmochim Acta* **126** (2014) 614.
- [5] ZECH, M. et al., A 220 ka terrestrial $\delta^{18}\text{O}$ and deuterium excess biomarker record from an eolian permafrost paleosol sequence, NE-Siberia, *Chem Geol* **360-361** (2013) 220.
- [6] TUTHORN, M. et al., Coupled isotopes of plant wax and hemicellulose markers record information of relative humidity and isotopic composition of precipitation, *BGD* **submitted** (2014).
- [7] HEPP, J. et al., Reconstructing lake evaporation history and the isotopic composition of precipitation by a coupled $\delta^{18}\text{O}$ - $\delta^2\text{H}$ biomarker approach, *Hydrology* **in press** (2014).

RECONSTRUCTED ISOTOPIC COMPOSITION OF LEAF WATER PROVIDES NEW INSIGHT INTO HYDROLOGICAL CHANGES IN EAST AFRICA DURING THE LAST GLACIAL

J. HEPP, M. TUTHORN, B. GLASER, M. ZECH

Institute of Agronomy and Nutritional Sciences, Soil Biogeochemistry, Martin-Luther University Halle-Wittenberg, von-Seckendorff-Platz 3, D-06120 Halle, Germany.

E-mail address: johannes-hepp@gmx.de.

R. ZECH,

Geological Institute, ETH Zurich, Sonneggstrasse 5, CH-8092 Zurich, Switzerland. Now at: Institute of Geography, Group of Biogeochemistry and Paleoclimate, University of Bern, Hallerstrasse 12, CH-3012 Bern, Switzerland.

K. ROZANSKI,

Faculty of Physics and Applied Computer Science, AGH University of Science and Technology in Kraków, Al. Mickiewicza 30, 30-059 Kraków, Poland.

W. ZECH,

Department of Soil Physics and Chair of Geomorphology, University of Bayreuth, Universitätsstrasse 30, D-95440 Bayreuth, Germany.

Abstract: We couple compound-specific $\delta^2\text{H}$ results of leaf wax-derived *n*-alkanes with compound-specific $\delta^{18}\text{O}$ results of hemicellulose-derived sugars extracted from the loess-paleosol-sequence Maundi on Mt. Kilimanjaro. This coupling allows the reconstruction of a ca. 100 ka record of isotopic composition of leaf water. This in turn allows reconstructing (i) the deuterium-excess of leaf water which may serve as proxy for palaeohumidity and (ii) the isotopic composition of precipitation. Our results suggest that sedimentary $\delta^2\text{H}_{\text{leaf wax}}$ records should not be interpreted directly in terms of reflecting $\delta^2\text{H}_{\text{prec}}$ because variable leaf water evaporative enrichment can strongly overprint the $\delta^2\text{H}_{\text{prec}}$ signal. Furthermore, our deuterium-excess record as proxy for palaeohumidity does not support the interpretation of $\delta^2\text{H}_{\text{prec}}$ in terms of an “amount-effect” in East African palaeoclimate studies.

1. INTRODUCTION

The isotopic composition of precipitation ($\delta^2\text{H}_{\text{prec}}$ and $\delta^{18}\text{O}_{\text{prec}}$) is largely climatically controlled. In order to contribute to the reconstruction of climate history of East Africa, we investigate a 6.5 m loess-paleosol-sequence of the Maundi crater (3°10'27.5"S, 37°31'05.8"E) located on the south-east slopes of Mt. Kilimanjaro at ~ 2780 m above sea level.

2. METHODS

A detailed description of the study site including sedimentological characterization as well as the age-depth model of the Maundi sediments is already given by [1]. The recent climate conditions at the study site are dominantly controlled by the seasonal migration of the inner tropic convergence zone (ITCZ), which causes pronounced rainfall maxima in spring and fall [2]. For the here presented palaeoclimate study we measured compound-specific $\delta^2\text{H}$ values of leaf wax-derived *n*-alkanes ($\delta^2\text{H}_{n\text{-alkane}}$) and compound-specific $\delta^{18}\text{O}$ values of

hemicellulose-derived sugar biomarkers ($\delta^{18}\text{O}_{\text{sugar}}$). The coupled $\delta^{18}\text{O}_{\text{sugar}}$ and $\delta^2\text{H}_{n\text{-alkane}}$ approach allows reconstructing an approximately 100 ka record of the isotopic composition of leaf water. Furthermore, this allows (i) using the reconstructed deuterium-(d)-excess of leaf water as proxy for relative air humidity and (ii) reconstructing the isotopic composition of palaeoprecipitation (by using the slope the local evaporation line (LEL) derived from a simple Craig-Gordon model) (Figure 1).

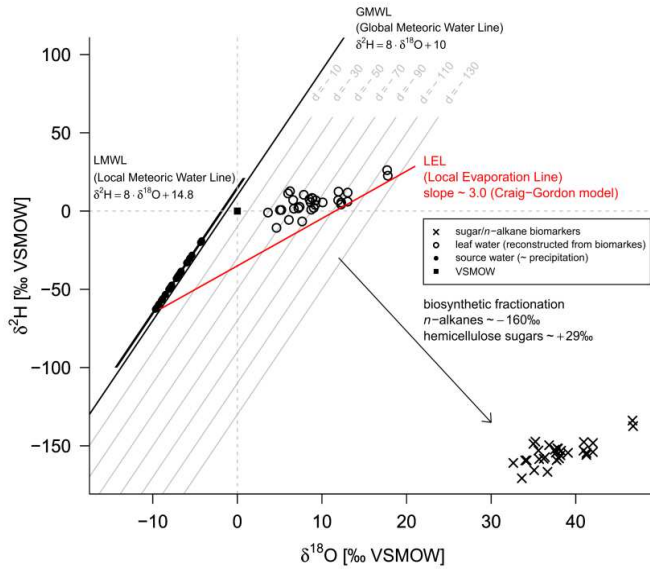


Figure 1. Conceptual model for coupling $^2\text{H}_{n\text{-alkane}}$ and $^{18}\text{O}_{\text{sugar}}$ results [3].

3. RESULTS AND DISCUSSION

The $\delta^{18}\text{O}_{\text{sugar}}$ record (weighted mean of arabinose, fucose and xylose) and the $\delta^2\text{H}_{n\text{-alkane}}$ record (weighted mean of $n\text{-C}_{29}$ and $n\text{-C}_{31}$) show basically the same trends (Figure 2).

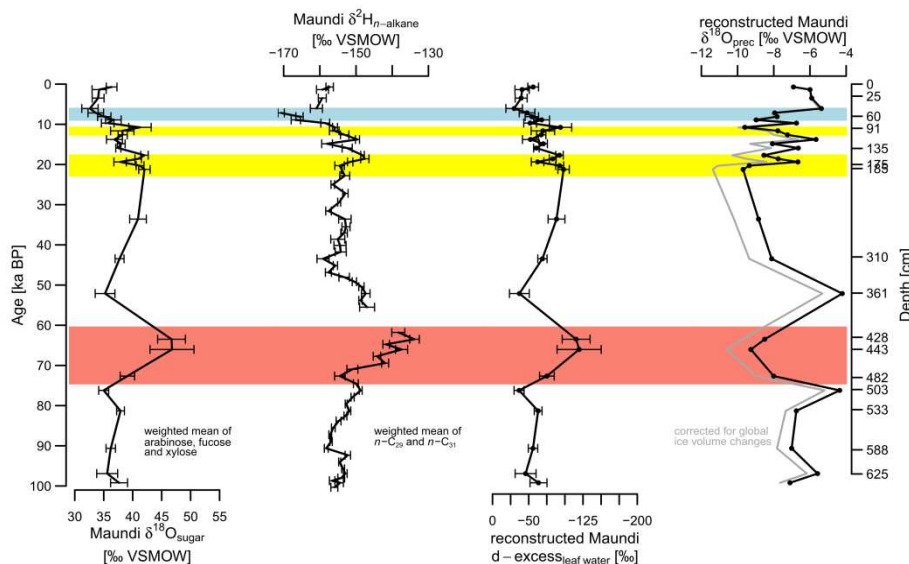


Figure 2. $\delta^2\text{H}_{n\text{-alkane}}$, $\delta^{18}\text{O}_{\text{sugar}}$, d-excess of leaf water and $\delta^{18}\text{O}_{\text{prec}}$ Maundi.

The Maundi $\delta^2\text{H}_{n\text{-alkane}}$ can be compared with $\delta^2\text{H}_{\text{wax}}$ records from Lake Challa, Lake Tanganyika and Lake Malawi (Figure 3). Accordingly, the Maundi $\delta^2\text{H}_{n\text{-alkane}}$ record is

generally in good agreement with the Lake Challa and the Lake Tanganyika $\delta^2\text{H}_{\text{wax}}$ records [5, 6]. However, a clear altitude effect can be seen in the $\delta^2\text{H}$ records (Maundi: 2780 m a.s.l.; Lake Challa: 880 m a.s.l.; Lake Tanganyika: 773 m a.s.l. [6]; Lake Malawi: 474 m a.s.l. [7]). Moreover, the Maundi $\delta^2\text{H}_{n\text{-alkane}}$ record reveals a clear smaller range compared to the other $\delta^2\text{H}_{\text{wax}}$ records. Finally, Figure 3 also illustrates clear different features amongst the available $\delta^2\text{H}_{\text{wax}}$ records, especially with the Lake Malawi $\delta^2\text{H}_{\text{wax}}$ record [7]. These differences resulted in different interpretations of the $\delta^2\text{H}_{\text{wax}}$ records (amount effect vs. source effect) [5-7].

Our coupled $\delta^{18}\text{O}_{\text{sugar}}$ and $\delta^2\text{H}_{n\text{-alkane}}$ approach sheds new light into this discussion:

- On the one hand, a reconstructed weak d-excess of leaf water during the African Humid Period (AHP) indicates humid climatic conditions. By contrast, strong d-excess of leaf water indicates that arid climatic conditions prevailed during the Younger Dryas (YD), the Last Glacial Maximum (LGM) and during a mega drought period (MD) having occurred $\sim 70\text{-}60$ ka BP [4] (Figure 2).
- On the other hand, the reconstructed isotopic composition of precipitation for the Maundi sediments ($\delta^2\text{H}_{\text{prec}}/\delta^{18}\text{O}_{\text{prec}}$) would result in a clear contradiction to d-excess when interpreting $\delta^2\text{H}_{\text{prec}}$ in terms of an amount-effect. This suggests that the amount effect is not the only driver of variable isotopic composition of palaeoprecipitation.

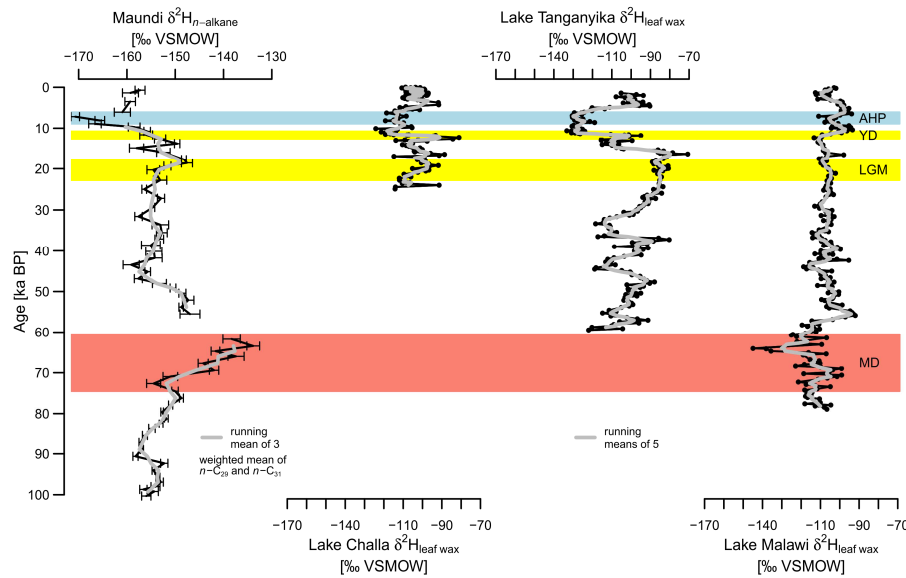


Figure 3. Comparison of Maundi $\delta^2\text{H}_{n\text{-alkane}}$ with other $\delta^2\text{H}_{\text{wax}}$ records.

4. CONCLUSIONS

Our results from the coupled $\delta^{18}\text{O}_{\text{sugar}}$ and $\delta^2\text{H}_{n\text{-alkane}}$ approach show that:

- variable evaporative enrichment hinders a direct interpretation of $\delta^2\text{H}_{\text{wax}}$ as $\delta^2\text{H}_{\text{prec}}$.
- reconstructed d-excess of leaf water may serve as valuable proxy for palaeohumidity.
- reconstructed isotopic composition of precipitation does not support a solely “amount-effect” interpretation for palaeoclimate studies in East Africa.

Including the Maundi precipitation record in a circum pacific comparison may help to identify the drivers of the past isotopic composition on east equatorial Africa. This study demonstrates the great potential of the coupled biomarker approach. However, in future studies also the uncertainties of the conceptual model should be investigated in more detail.

REFERENCES

- [1] SCHÜLER, L., HEMP, A., ZECH, W., BEHLING, H., Vegetation, climate and fire-dynamics in East Africa inferred from the Maundi crater pollen record from Mt Kilimanjaro during the last glacial-interglacial cycle, *Quaternary Science Reviews* **39** (2012) 1-13.
- [2] NEW, M., LISTER, D., HULME, M., MAKIN, I., A high-resolution data set of surface climate over global land areas, *Climate Research* **21** (2002) 1-25.
- [3] ZECH, M., TUTTHORN, M., DETSCH, F., ROZANSKI, K., ZECH, R., ZÖLLER, L., ZECH, W., GLASER, B., A 220 ka terrestrial $\delta^{18}\text{O}$ and deuterium excess biomarker record from an eolian permafrost paleosol sequence, NE-Siberia, *Chemical Geology* **360-361** (2013) 220-230.
- [4] SCHOLZ, C.A., et al., East African megadroughts between 135 and 75 thousand years ago and bearing on early-modern human origins, *PNAS* **104** (2007) 16416-16421.
- [5] TIERNEY, J.E., RUSSELL, J.M., DAMSTE, J.S.S., HUANG, Y., VERSCHUREN, D., Late Quaternary behavior of the East African monsoon and the importance of the Congo Air Boundary, *Quaternary Science Reviews* **30** (2011) 798-807.
- [6] TIERNEY, J.E., RUSSELL, J.M., HUANG, Y., DAMSTE, J.S.S., HOPMANS, E.C., COHEN, A.S., Northern Hemisphere Controls on Tropical Southeast African Climate During the Past 60,000 Years, *Science* **322** (2008) 252-255.
- [7] KONECKY, B.L., RUSSEL, J.M., JOHNSON, T.C., BROWN, E.T., BERKE, M.A., WERNE, J.P., HUANG, Y., Atmospheric circulation patterns during late Pleistocene climate changes at Lake Malawi, Africa, *Earth and Planetary Science Letters* **312** (2011) 318-326.

ID: 19

KEY DRIVERS CONTROLLING DAILY STABLE ISOTOPE VARIATIONS IN PRECIPITATION OF COSTA RICA: CARIBBEAN SEA VERSUS EASTERN PACIFIC OCEAN MOISTURE SOURCES

R. SÁNCHEZ-MURILLO

University of Idaho, Moscow, Idaho, USA, 83844-3006

Universidad Nacional, Heredia, Costa Rica, 86-3000

Email: sanc7767@vandals.uidaho.edu

WELSH, K.

University of Idaho, Moscow, Idaho, USA, 83844-3006

Centro Agronómico Tropical de Investigación y Enseñanza, Turrialba, Costa Rica, 30501

C. BIRKEL

Escuela de Geografía, Universidad de Costa Rica, Costa Rica, 11501-2060

Northern Rivers Institute, University of Aberdeen, Aberdeen, Scotland, AB24 3UF

G. ESQUIVEL-HERNÁNDEZ, J. CORRALES-SALAZAR

Universidad Nacional, Heredia, Costa Rica, 86-3000

J. BOLL, E. BROOKS

University of Idaho, Moscow, Idaho, USA, 83844-3006

O. ROUPSARD

Centro Agronómico Tropical de Investigación y Enseñanza, Turrialba, Costa Rica, 30501

CIRAD, Montpellier, France, 34398

O. SÁENZ-ROSALES

Universidad Nacional, Heredia, Costa Rica, 86-3000

I. KATCHAN

Centro Nacional de Alta Tecnología, San José, Costa Rica, 1174-1200

R. ARCE-MESÉN

Escuela de Geografía, Universidad de Costa Rica, Costa Rica, 11501-2060

C. SOULSBY

Northern Rivers Institute, University of Aberdeen, Aberdeen, Scotland, AB24 3UF

Abstract: Costa Rica is located on the Central American Isthmus, which receives moisture inputs directly from the Caribbean Sea and the Pacific Ocean. While this location includes unique mountainous and lowland microclimates, only limited knowledge exists about the impact of relief and regional atmospheric circulation patterns on precipitation origin, transport, and isotopic composition. Therefore, the main scope of this project is to identify the key drivers controlling variations in meteoric waters of Costa Rica using stable isotopes based on daily sample collection for the year 2013. The monitoring sites comprise three strategic locations across Costa Rica: Heredia (Central Valley), Turrialba (Caribbean slope), and Caño Seco (South Pacific slope). Sporadic dry season rain is mostly related to isolated enriched events ranging from -5.8‰ $\delta^{18}\text{O}$ up to -0.9‰ $\delta^{18}\text{O}$. By mid-May, the Intertropical Convergence Zone develops over Costa Rica resulting in a notable depletion in isotope ratios (up to -18.5‰ $\delta^{18}\text{O}$). HYSPLIT back air mass trajectories indicate the

strong influence on the origin and transport of precipitation of two main moisture transport mechanisms, the Caribbean Low Level Jet and the Colombian Low Level Jet as well as localized convection events. Multiple linear regression models constructed based on Random Forests of surface meteorological information and atmospheric sounding profiles suggest that Lifted Condensation Level and surface relative humidity are the main factors controlling isotopic variations. These findings diverge from the recognized ‘amount effect’ in monthly composite samples across the tropics. Understanding of stable isotope dynamics in tropical precipitation can be used to enhance groundwater modeling efforts in ungauged basins where scarcity of long-term monitoring data drastically limit current and future water resources management.

ID: 22

USE OF ENVIRONMENTAL ISOTOPES FOR THE ASSESSMENT OF SNOW WATER RESOURCES IN THE MOROCCAN HIGH ATLAS MOUNTAINS: CONTRIBUTION TO SURFACE AND GROUNDWATER RECHARGE.

B. NDA, E.H. BERAAOUZ, L. BOUCHAOU

Applied Geology and Geo-Environment Laboratory, Ibn zohr University, Faculty of Sciences, Agadir, Morocco.

E-mail address: beraaouz@gmail.com.

L. HANICH,

FST, Cadi Ayyad University, Marrakech, Morocco

J.L. MICHELOT

IDES, CNRS - Paris Sud Université, France

Abstract: The monthly monitoring of snowmelt carried out in High Atlas Mountains from January 2012 till May 2014 shows variable isotope contents, ranging from -14.5 to -1‰ VSMOW and from -119 to -20 ‰ VSMOW for oxygen-18 and deuterium respectively. The majority of the samples shows evaporation by sublimation during the sampling period, but the final monthly samples collected by the sampling design (wicks) chosen are not evaporated and thus close to the GMWL. The isotopic signatures of spring water and reservoir water are similar for the monthly samples indicating a clear contribution of the snowmelt to the recharge of these reservoirs. In all studied cases, the study proves that snow melt plays an important role in recharging groundwater and reservoir water in both borders of the High Atlas Mountains. The results have clearly shown that the isotopic composition of snowmelt varies due to melting progresses. Therefore, a characterization of the snowmelt using the average stable isotopes (oxygen-18 or deuterium) composition obtained from snow cores is limited.

1. INTRODUCTION

The High Atlas Mountains in Morocco represent important water storage because of the orographic effect, i.e. increasing rainfall with elevation. Given the large range of elevation (700 to 4200 m.a.s.l.) in this area, precipitation occurs as rain as well as snow. A common global practice in arid zones is upstream water storage in dammed reservoirs that captures mountainous snowmelt, and downstream agriculture irrigation. The snow cover shows large variations in the High Atlas Mountains during the winter. The covered surface varies from year to year and in space. This snow cover melts completely by summer and constitutes the main recharge and support of flow of springs, rivers and groundwater in the area toward the northern and southern parts of the Atlas Mountains. The main objective is to characterize the isotopic signature of snowmelt and assessment of its contribution to the recharge of Surface water and groundwater in the borders of the High Atlas Mountains.

2. METHODS

The sampling in Souss upstream catchment was carried out in 15 sites along the river from the High altitude (2248 m.a.s.l.) in Ifni area towards the Souss plain (600 m). In the Oukaïmeden area the snow cover is very important. The access is easy and the equipment is available in the Oukaïmeden station (meteorological data). 5 sites are monitored since 2011:

2 snow sites, 1 lake site, 2 springs and one river. The altitude of these sites varies between 1194 to 3244 m.a.s.l.

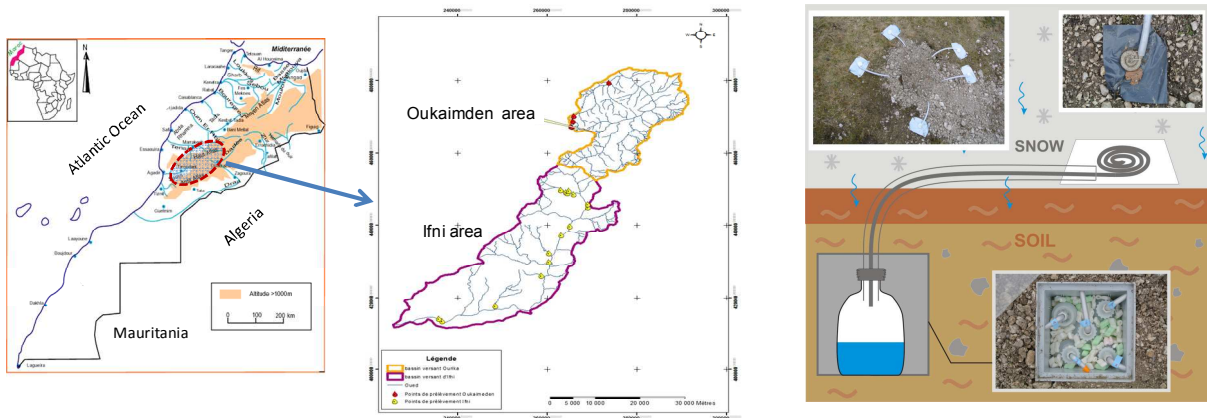


Figure 1: Sampling points in Oukaïmeden and Ifni sites with drawings and photos of the passive capillary sampler showing details (Wicks design, [4]).

3. RESULTS

The monthly monitoring of snowmelt carried out in High Atlas Mountains from January 2012 till May 2014 shows variable isotope contents, ranging from -14.5 to -1‰ V-SMOW and from -119 to -20 ‰ V-SMOW for oxygen-18 and deuterium respectively. The very negative values are observed in March 2013 at high elevation (3230 m.a.s.l.). The snowmelt waters collected by passive capillarity sampler are not evaporated comparing to the ones sampled directly from snow cover.

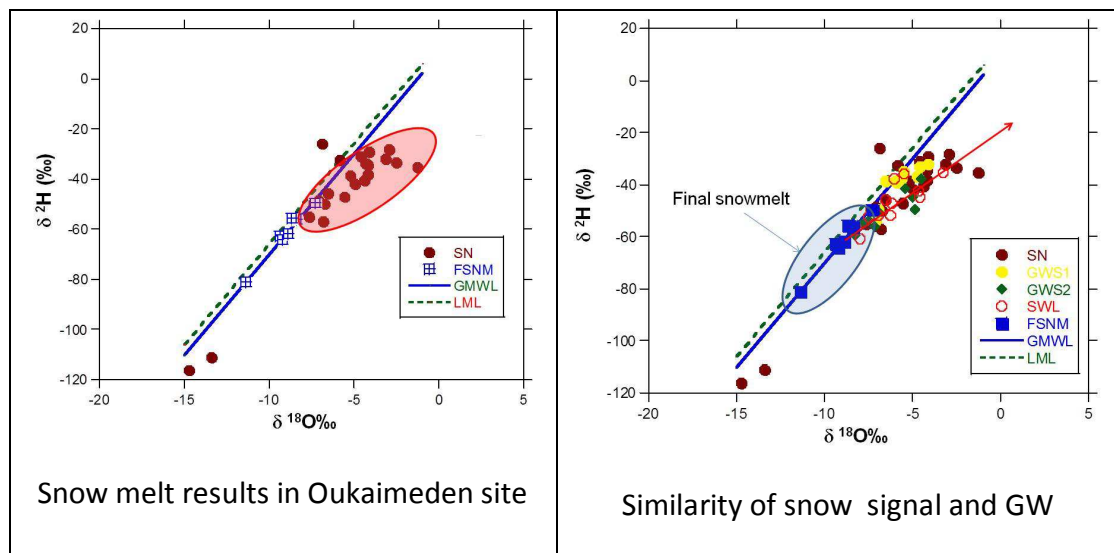


Figure 2: Isotopic signature of snow, surface water and GW in Oukaïmeden sub-catchment.

4. CONCLUSIONS

According to the isotopic signature of snowmelt from the Atlas Mountains, we notice in all cases that the snowmelt contributes both quantitatively and qualitatively to the recharge of stream flow and groundwater. Toward downstream of the studied catchments, the contribution of fresh water coming from snowmelt reduces the salinity of water resources

[1-3]. Using the model balance, the quantitative rate contribution varies from 40 to 80% in some cases. Stable isotopes show a clear mixing between rain water and snow precipitation, which is consequence of the same origin of the air masses of these inputs. Stream water can also be more or less evaporated, depending on the sub-catchment of provenience. An altitude gradient is observed for every sub-catchment. The characterization of the snowmelt using the average stable isotopes (oxygen-18 or deuterium) composition obtained from snow cores is limited.

REFERENCES

- [1] WARNER, N, LGOURNA, Z, BOUCHAOU, L, BOUTALEB S., TARIK T, HSAISSOUNE M., VENGOSH, A., Integration of geochemical and isotopic tracers for elucidating water sources and salinization of shallow aquifers in the sub-Saharan Drâa Basin, Morocco. *Applied Geochemistry* 34 (2013) 140–151.
- [2] BOUCHAOU, L., MICHELOT, J.L., VENGOSH, A., HSISSOU, Y., QURTOBI, M., GAYE, C.B., BULLEN, T.D., ZUPPI, G.M., Application of multiple isotopic and geochemical tracers for investigation of recharge, salinization, and residence time of water in the Souss-Massa aquifer, Southwest of Morocco. *J. Hydrol.* Vol. 352, (2008), 267-287.
- [3] BOURAGBA, L., MUDRY, J., BOUCHAOU, L., HSISSOU, Y., KRIMISSA, M., TAGMA, T., MICHELOT, J.L, Isotopes and groundwater management strategies under semi-arid area: Case of the Souss upstream basin (Morocco). *Applied Radiation and Isotopes*, Volume 69, Issue 7, 2011, 1084-1093.
- [4] PENNA, D., AHMAD M., BIRKS S. J., BOUCHAOU, L., BRENČIČ, M., BUTT, S., HOLKO, L., JEELANI, G., MARTÍNEZ, D. E., MELIKADZE, G., SHANLEY, J. B., SOKRATOV, S. A., STADNYK, T., SUGIMOTO, A. VREČA, P., A new method of snowmelt sampling for water stable isotopes. *Hydrol. Process.* (2014) Published online in Wiley Online Library (wileyonlinelibrary.com). DOI: 10.1002/hyp.10273

ID: 23

TRITIUM TIME SERIES IN PRECIPITATION OF RM. VALCEA, ROMANIA

C. VARLAM,

Institute of Cryogenics and Isotopic Technologies, Uzinei Street, no. 4, 240050 Rm. Valcea, Romania

E-mail address: carmen.varlam@icsi.ro

O.G. DULIU

Department of Structure of Matter, Earth and Atmospheric Physics and Astrophysics,
University of Bucharest, 405, Atomistilor str., 077125 Magurele, Ilfov, Romania

I. FAURESCU, I. VAGNER, D. FAURESCU,

Institute of Cryogenics and Isotopic Technologies, Uzinei Street, no. 4, 240050 Rm. Valcea, Romania.

Abstract: Following tritium concentration records in precipitation for the period 1999-2013, and tritium behavior during this period for Rm. Valcea location, the individual precipitations of the late spring and summer for 2009-2013 periods were investigated. Despite good correlation between monthly mean tritium concentration and monthly mean precipitation for the 15-year period of observations (Pearson coefficient, 0.87), individual precipitations had no linear correlation between tritium concentration and amount of precipitation.

1. INTRODUCTION

Tritium is produced naturally in the atmosphere as a result of thermal neutron interaction with nitrogen-14 nuclei. The cosmogenic production is estimated to be between 3.4 and 15 TU (1 Tritium Unit = 1 tritium atom to 10^{18} hydrogen atoms), prior to 1953 [1]. Atmospheric testing weapons between 1954 and 1970s produced additional tritium leading to dramatic increase of annual tritium average levels in mid-continental precipitation of few thousands TU [2]. Its application in groundwater hydrology, especially in dating groundwater, uses the peak bomb in precipitation as a tracer in hydrological system. Tritium atmospheric pulse gradually decayed and washed out from the atmosphere by the 80's and 90's. By 1997 and 1998, tritium in precipitation in Europe had reached low levels that have since remained more or less stable near 10 TU in Vienna [3]. The tritium input value to groundwater, represented as volume-weighted mean tritium concentrations in precipitation, diminished, and it is strongly dependent on the local average tritium level in post-bomb-pulse precipitation [4].

Although the Global Network of Isotopes in Precipitation (GNIP) was established in the 60's by IAEA and WMO, many areas in the world lack long term monitoring tritium in precipitation, or due to a variety of reasons many of the data sets are not complete. Romania reports now by Rm. Valcea location isotopes in precipitation, but the records period start with 1999 for tritium and 2011, for stable isotopes. Regarding the tritium level in precipitation at Rm. Valcea location there was identified a particularity for the monthly tritium average and monthly precipitations average of long term period of observations: the months with maximum concentration are also months with maximum quantity of precipitations [5]. In order to investigate this particularity there was collected and measured individual precipitation of the warm months during the period 2008-2013. Here we present the results of

tritium concentration in individual precipitation with the aim of provide a relation between tritium concentration with the amount of the precipitation.

2. METHODS

Atmospheric parameters, including the amount of precipitation, were recorded using a weather station Davis Vantage Pro2. Precipitation sampling at our Institute was performed with a typical rainwater collector [6]. It was decided to collect each individual precipitation in a month, the quantity corresponding to the collecting interval to be recorded, to be stored at low temperatures and at the end of the month to prepare both the individual precipitations and weighted mean of monthly precipitation for tritium concentration determination. They were measured in the same batch using the same conditions. The tritium concentration mean of the individual precipitation was calculated and compared with tritium concentration determined in the monthly composite precipitation. All the recorded values during the 2008-2013 periods were practically the same, taking into account the associated uncertainty of the tritium measurements.

The samples were measured by liquid scintillation method [7] with a Quantulus 1220 spectrometer for 500 min/samples. The liquid scintillation cocktail was UltimaGold uLLT (PerkinElmer). The ratio sample:scintillate was 8:12 ml, in PerkinElmer polyethylene vials of 20 ml volume. The counting efficiency varied during the period reported here between 24.67% and 25.90% (at the best figure of merit). The background recorded for the tritium free water sample also varied, from 0.547 CPM (counts per minutes) to 0.684 CPM. The deuterium depleted water with a concentration below 15 ppm D/D+H was used as tritium free water. The limit of detection [7, paragraph 8.4] was evaluated to be around 4 TU. The variation of tritium level presented below was calculated both for the annual arithmetic mean and for volume weighted annual mean according to WMO/IAEA recommendations [8].

3. RESULTS

The annual maximum value of tritium concentration varied during 1999-2013 from May to August, Figure 1.

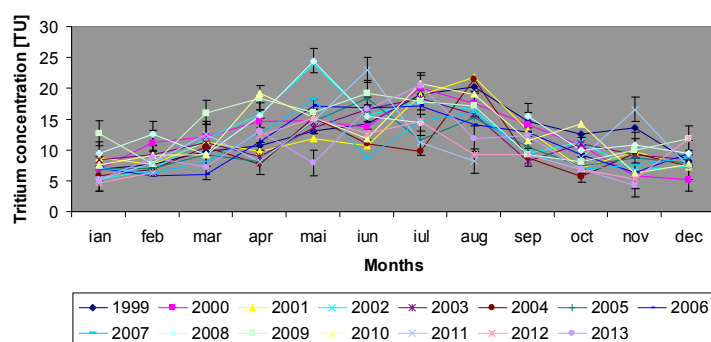


Figure 1. Annual tritium concentration variation during 1999-2013 periods in precipitation at Rm. Valcea location

May, June, July, and August are months that could have maximum values for one year period, according to recorded observations. Their tritium concentration values varied between 15.1 ± 2.1 TU (May 2012) to 24.4 ± 2.1 TU (May 2008). Annual arithmetic mean of tritium concentration in precipitation for period 1999-2013 showed a variation between 9 ± 2 TU (2012) and 13.7 ± 2.1 TU (2009). Values of volume weighted tritium mean ranged between 10.9 ± 2.1 TU and 15 ± 2.2 TU (2008). Analyzing the monthly calculated averages of tritium

concentration and precipitations for the period 1999-2013, Figure 2, one can observe the same behavior: the months with maximum values of precipitations are the same months with maximum values of tritium concentration. Pearson coefficient of these parameters rises from 0.81(1999-2009 periods) to 0.87 for 15 years of observations.

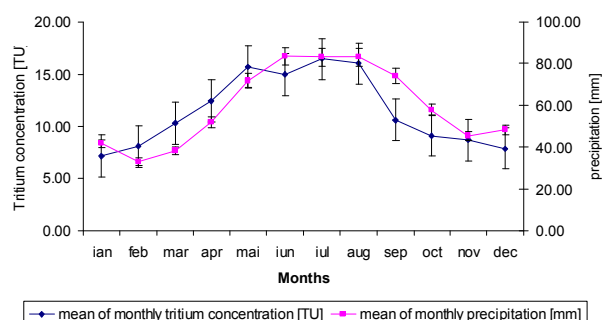


Figure 2. Monthly mean value of tritium concentration and mean value of monthly precipitation for 1999-2013 period in Rm. Valcea, Romania

This behavior was investigated by sampling and analyzing the individual precipitations of the months: May, June, July and August. May is the month with the widest range of tritium concentration, from 4.7 ± 1.8 TU (26-27.05.2013) to 33.9 ± 2.7 TU (12.05.2008), Figure 3. Tritium mean for 2008-2013, of 14.9 ± 2.2 TU is close as that established for 15 years of observation (15.9 ± 2.2 TU). The precipitation mean for the same period was 84.1 mm, higher than that for 1999-2013 periods of 71.9 mm.

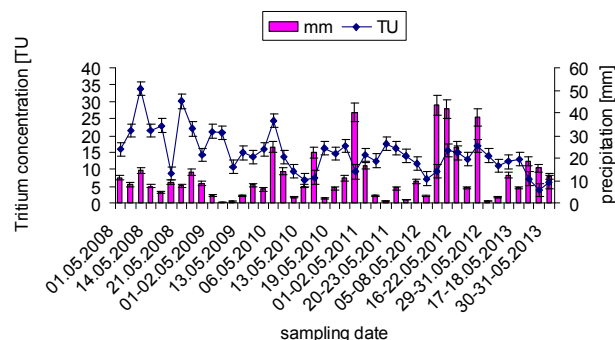


Figure 3. Tritium concentration and amount of individual precipitation for May, period 2008-2013

June of 2008-2013 period had tritium concentration in precipitation between 8 ± 2.1 TU and 26.8 ± 2.4 TU, Figure 4. The calculated mean of 16.2 ± 2.2 TU was slightly higher than 14.9 ± 2.2 TU, mean of 1999-2013 periods. The precipitation amount of June for the same period was 75.1 mm, lower than that of 15 years of observations (83.6 mm). The same behavior was recorded for July and August, 2008-2013. Tritium concentration in individual precipitation didn't have values below 9 TU, and didn't exceed 28 TU. Even if the tritium concentration means were near of those calculated for 15 years of observations (15.8 ± 2.2 TU for July, and 16.1 ± 2.2 for August), the amount of precipitations were well below the usual recorded quantities, only 52.5 mm for July (against 83.5 mm, mean for 1999-2013) and 46.1 mm for August (against 83.2 mm, mean for 1999-2013). In fact August didn't have any precipitation for the year 2008.

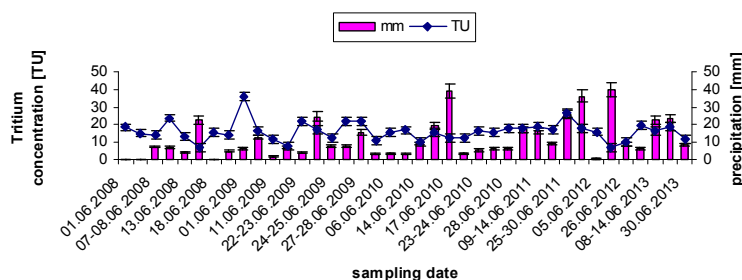


Figure 4. Tritium concentration and amount of individual precipitation for June, 2008-2013 periods

4. CONCLUSIONS

Despite the good correlation between monthly mean tritium concentration and monthly mean precipitation for 1999-2013 period (Pearson coefficient, 0.87), individual precipitations of the late spring and summer didn't present the same characteristics. Pearson coefficients were: -0.09 (May), -0.07 (June), -0.2 (July), and -0.21 (August), values that didn't show a linear correlation between studied parameters.

In order to build a tritium time series for Rm. Valcea location longer than fifteen years, it will be much easier to use GNIP stations data and different methods for reconstruction of tritium time series [9]. The established characteristics could be considered criteria in choosing the appropriate GNIP station.

ACKNOWLEDGEMENT

This paper was prepared in connection with the work done for Experimental Cryogenic Pilot for Tritium and Deuterium Separation.

REFERENCES

- [1] CLARK, I., FRITZ, P., Environmental Isotopes in Hydrology, Lewis Publishers, New York, (1997) 175pp.
- [2] MICHEL, R.L., "Tritium in hydrological cycle", Isotopes in the Water Cycle, Past Present and Future of Developing Science, (Pradeep K. Aggarwal, Joel R. Gat and Klaus F.O. Froehlich, Eds), Springer, Dordrecht Netherlands, (2005) 53-66.
- [3] International Atomic Energy Agency, Global Network of Isotopes in Precipitation, GNIP, database, http://www-naweb.iaea.org/naweb/ih/IHS_resources_isohis.html.
- [4] EASTOE, C.J., WATTS, C.J., PLOUGHE, M., WRIGHT, W.E., Future use of tritium in mapping pre-bomb groundwater volumes, Ground Water **50** 1 (2012), 87-93pp.
- [5] VARLAM, C., STEFANESCU, I., DULIU, O.G., FAURESCU, I., BOGDAN, D., SOARE, A., "Tritium level in Romanian precipitation", Proc. Isotopes in Hydrology, Marine Ecosystem and Climate Change Studies, Monaco 2011, IAEA Vienna (2013), 139-146pp.
- [6] IAEA, International Atomic Energy Agency, Measurement of Radionuclide in food and the environment, Technical Reports Series no. 295, Vienna, (1989), 15pp.
- [7] ISO 9698, International Standard Organization, Water Quality - Determination of tritium activity concentration - Liquid scintillation counting method, 2nd edn, ISO, Geneva, (2010).
- [8] IAEA, International Atomic Energy Agency, Statistical Treatment of Data on Environmental Isotopes in Precipitation, Technical Reports, Series no. 331, IAEA, Vienna, (1992), 781pp.
- [9] ZHAI, YZ., WANG, JS, GUO, H., CAO, Y., TENG, YG., Reconstruction and optimization of the tritium time series in precipitation of Beijing, China, Radiocarbon, **55** 1 (2013), 67-79.

ID : 31

NEW ISOTOPIC DATA ON PRECIPITATION AND RIVER WATER IN THE CENTRAL AFRICAN REPUBLIC (GNIP AND GNIR STATIONS AT BANGUI)

C. L. DJEBEBE-NDJIGUIM, E. FOTO, S. BACKO, E. BASSE-KEKE, B. NGUEREKOSI, N. ZOUDAMBA, O. ALLADIN, J. MABINGUI

University of Bangui, Lavoisier Hydrosociences Lab., Faculty of Sciences, avenue des Martyrs, BP 908, Bangui, Central African Republic

E-mail: ndjiguimlaure@yahoo.fr

F. HUNEAU, E. GAREL

University of Corsica, Hydrogeology Dept., UMR 6134 CNRS, Campus Grimaldi, BP 52, F-20250 Corte, France

H. CELLE-JEANTON

Clermont University, UMR 6524 CNRS LMV, 5 rue Kessler, F-63038 Clermont-Ferrand, France

Abstract: New isotope data are available for the Central African Republic. Through the IAEA CAF8003 and CAF7001 two GNIP stations and one GNIR station on the Ubangi River have been settled in the Bangui urban area. Since August 2009, precipitation and the Ubangi River stable isotopes of the water molecule are monthly sampled providing unique scientific information for the central African region. In a first attempt, the isotope data are presented and discussed, the local meteoric water line is defined and the mean weighted composition of rain water is computed.

1. INTRODUCTION

Two GNIP stations have been installed in the Bangui city urban area in the framework of IAEA CAF8003 and CAF7001 projects. These GNIP stations are located in the Bangui plain (GNIP-Bangui-Université) and in the hills surrounding the city (GNIP-Bangui-SODECA). One GNIR station (GNIR-Ubangi) has also been installed along the Ubangi River, major tributary of the Congo River basin. The three stations are operating since August 2009.

2. METHODS

Here are the exact geographic coordinates of the Bangui GNIP and GNIR stations:

- GNIP-Bangui-Université : N04°22'37.5'' ; E18°33'44.9'' ; 363 m asl.
- GNIP-Bangui-SODECA : N04°21'56.5'' ; E18°35'14.1'' ; 386 m asl.
- GNIR-Ubangi : N04°21'51.3'' ; E18°35'42.6'' ; 341 m asl.

Precipitation and river water are sampled monthly (end of the month) in rainwater collectors designed according the IAEA recommendations. Samples are stored and refrigerated before being sent to the IAEA laboratory for isotope analysis at the end of each year.

3. RESULTS

Precipitation data in Bangui doesn't show any significant evaporation and are plotted along the World Meteoric Water Line. For both GNIP-Bangui-Université and GNIP-Bangui-

SODECA the Local Meteoric Water Line has been defined and the mean weighted composition of rainwater has been computed for the 2009-2013 period (Table 1).

Table 1. Mean weighted stable isotope composition of precipitation and Local Meteoric Water Lines for Bangui GNIP stations.

Station	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	LMWL
GNIP-Bangui-Université	-2.47	-7.09	$\delta^2\text{H} = 7,69 \delta^{18}\text{O} + 11,92$
GNIP-Bangui-SODECA	-2.22	-4.78	$\delta^2\text{H} = 7,52 \delta^{18}\text{O} + 12,36$

Concerning the GNIR-Ubangi stable isotope data, a very clear seasonal oscillation is noted with depleted values at the end of the rainy season and enriched values at the end of the dry season (Figure 1).

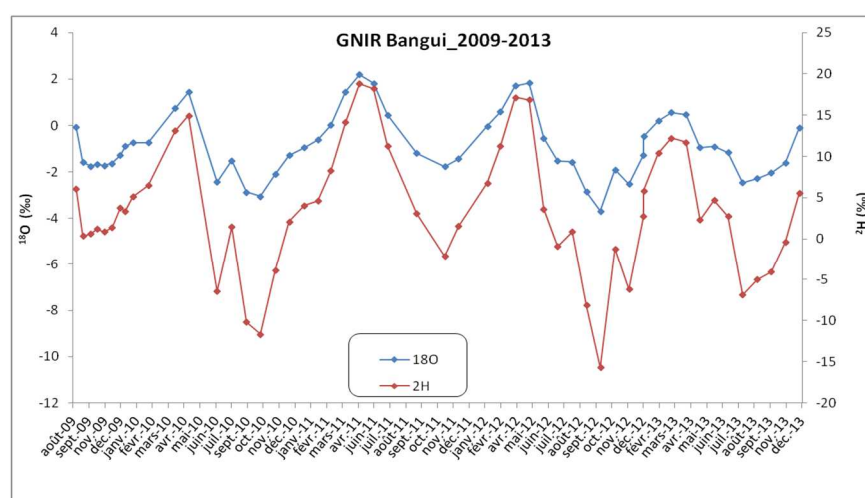


Figure 1. Seasonal stable isotope evolution of the Ubangi River waters at GNIR-Ubangi station (2009-2013).

4. CONCLUSIONS

The data set is only slightly influenced by evaporation processes occurring during the sampling procedure which can be considered as a validation of the sampling protocol. The two GNIP stations of Bangui don't show significant isotopic variations despite their different locations. Strong isotopic contrasts are registered all along the hydrological year in relation with the dry/rainy season cycles both for GNIP and GNIR stations. The amount effect is also particularly well documented through this chronicle. The GNIP and GNIR stations of Bangui provide unique isotope information for the central African region and will be strategic key tools for further isotope hydrology studies in the whole African continent for both climate and hydrogeological surveys.

ID: 33

A NEW NETWORK FOR ISOTOPES IN PRECIPITATION OF CORSICA (FRANCE)

F. HUNEAU, E. GAREL, S. SANTONI

University of Corsica, Hydrogeology Department, CNRS UMR 6134 SPE, Campus Grimaldi, BP 52, F-20250 Corte, France

E-mail address: huneau@univ-corse.fr.

J. JAUNAT

University of Reims Champagne-Ardenne, EA 3795–GEGENAA, 2 esplanade Roland Garros, F-51100 Reims, France.

H. CELLE-JEANTON

Clermont University, CNRS IRD UMR 6524 LMV , BP 10448 , F-63038 Clermont-Ferrand, France.

Abstract: Corsica is a French island of the Occidental Mediterranean with a mean elevation of 568 m and a mountain barrier oriented N-S reaching more than 2700 m in altitude. To characterize the stable isotopic signal of the precipitation, a network of 10 stations has been established since February 2013 all over the island. The first preliminary results show strong isotopic contrasts in relation with the physiography and the elevation of the stations. For each station, the mean weighted composition of precipitation is computed and the local meteoric water line for Corsica is proposed. This network provides fundamental observations for the definition of isotope patterns in precipitation for the western Mediterranean.

1. INTRODUCTION

Corsica is a French island of the Occidental Mediterranean which is situated 160 km from the French mainland and 80 km from the Italian coast. The Corsica has an area of 8680 km² with a maximum altitude of 2706 m at Monte Cintu and a mean elevation of 568 m. The mountainous barrier is oriented N-S and plays a dominant role on the contrasted hydroclimatic conditions of the island. For a proper management and evaluation of the water resources, a characterization of the stable isotopic signal of the precipitation has been carried out since February 2013 on 10 stations spread all over the island.

2. METHODS

A network of 10 rainfall collector stations has been established all over the island (Figure 1) with 5 coastal stations (Bastia, Ile-Rousse, Ajaccio, Bonifacio and Aleria), 3 inner stations (Corte 750 m asl, Campana 500 m asl and Palneca 850 m asl), and 2 intermediate stations (Pirio and Sartene). Rainfall collectors are designed according to IAEA recommendations to prevent evaporation during the sampling. Each station is sampled at the end of the month.

The analyses of the stable isotope (^{18}O , ^2H) content of precipitation are carried out with a LGR laser spectrometer DT-1000 at the Hydrogeology Dept. of the University of Corsica.



Figure 1. Location of the 10 precipitation stations of the Corsican network. (Sartene station is in square grey because no isotopic data of this station is available for the moment)

3. RESULTS

The monthly stable isotopic compositions of the precipitation for 2013 are plotted on the Figure 2 along the West Mediterranean Meteoric Water Line (WMMWL) and the Global Meteoric Water Line (GMWL). A slight evaporation effect is detected for the precipitation collected during the summer period. The rainfall isotopic signal of the inner stations is more depleted than the coastal stations in relation with the altitude elevation. A variation of the isotopic signal according the geographic position for the coastal stations is also observed, with a more enriched signal for stations located in the northern part than for these placed in the south.

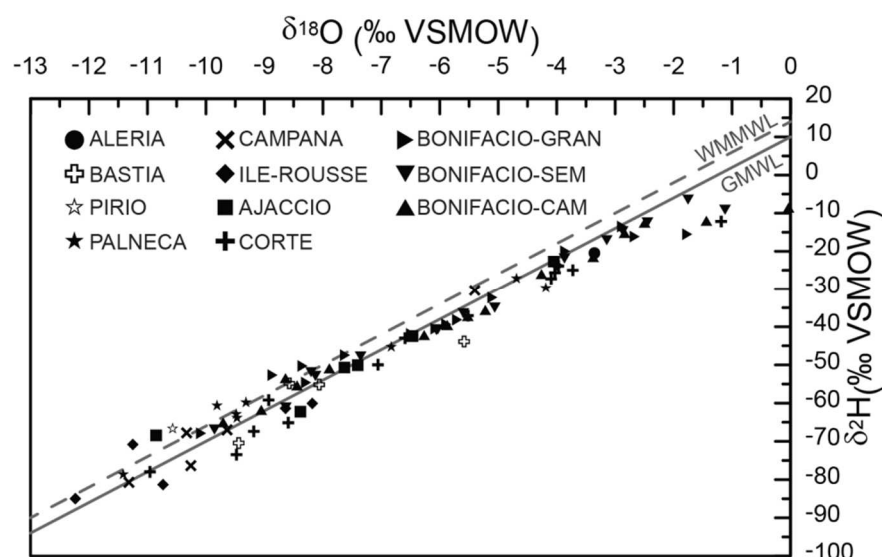


Figure 2. Monthly stable isotopic composition of precipitation in Corsica for 2013, the GMWL and the WMMWL.

4. CONCLUSIONS

The isotopic signature of precipitation in Corsica is governed by intricate geomorphological and microclimatological conditions. The main obstacle made by the central mountain range give rise to very different exposure conditions for the main valleys and hence favors very much contrasted isotopic signatures. This network is a first step to accurately define the local isotopic signature of recharge waters and to understand and manage the water resources from the island which are the object of an ever increasing demand.

ID: 61

STABLE ISOTOPES OF DAILY PRECIPITATION IN SINGAPORE: A PRELIMINARY STUDY

S. HE, N. GOODKIN, K. NIEZGODA, X. WANG, C. M. RUBIN

Earth Observatory of Singapore, Nanyang Technological University, Singapore

E-mail address: snhe@ntu.edu.sg

Q. DING

Department of Atmospheric Sciences, University of Washington, USA.

S. WATTS

Department of Chemistry, National University of Singapore, Singapore.

Abstract: We analyzed stable isotopic composition of 708 daily precipitation samples taken from Singapore rain stations. These data provide valuable information about the major drivers of δ -values of daily precipitation in the area; regional atmospheric circulation and moisture sources. The samples with the lowest δ -value in the Early Northeast (NE) Monsoon are closely related to cold surges from subtropical regions, which likely brought low δ -value moisture to the region. Regional organized convection or local convection is largely responsible for a periodic shift in $\delta^{18}\text{O}$ -values to lower ones in the Southwest (SW) Monsoon. Amount effect is not observed in the study area but evaporative enrichment of raindrops during condensation is a minor driver of δ -values of daily precipitation in Singapore.

1. INTRODUCTION

Drivers of variations in stable isotopic compositions of precipitation in the tropics are highly uncertain and controversial, but knowledge of such drivers will help us to interpret paleoclimate archives, understand regional climate dynamics and thus to predict the future climate change. In 2013, the IAEA launched a new Coordinated Research Project (CRP) “Stable Isotopes in Precipitation and Paleoclimatic Archives in Tropical Areas to Improve Regional Hydrological and Climatic Impact Models (2013-2016)” with a focus on present precipitation in the tropics. As part of this international effort, our project targets the tropical regions of Southeast Asia, i.e., Singapore and surrounding countries. In this paper, we present the preliminary results of stable isotopic analyses of daily precipitation collected over one year at rain stations in Singapore (Fig. 1). The correlation between stable isotopic compositions of precipitation and various climate factors is discussed.



Figure 1. Locations of Singapore rain stations. Figure 2. Rain collector at Changi airport.

2. METHODS

Rain collectors for precipitation were designed by IAEA and distributed by PALMEX [1]. They were normally installed in open spaces to prevent rainfall from being blocked by high buildings or trees (Fig. 2). The stable isotopic composition of rain samples was analyzed using a Picarro water analyzer L2130-i. The memory correction was done following van Geldern and Barth [2]. The stable isotopic data are reported in the standard δ -notation relative to Vienna Standard Mean Ocean Water (VSMOW) for oxygen and hydrogen, and normalized on scales such that the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of Standard Light Antarctic Precipitation (SLAP) are -55.5‰ and -428‰ , respectively [3]. The long-term precision of our QA standard is 0.04‰ for $\delta^{18}\text{O}$ and 0.2‰ for $\delta^2\text{H}$.

3. RESULTS AND DISCUSSIONS

Singapore samples show a large range of variation with $\delta^{18}\text{O}$ values from 1.41 to -17.52‰ , and $\delta^2\text{H}$ values from 11.92 to -126.70‰ . They define well a local meteoric water line (LMWL), which is close to the global meteoric water line (GMWL) (Fig. 3).

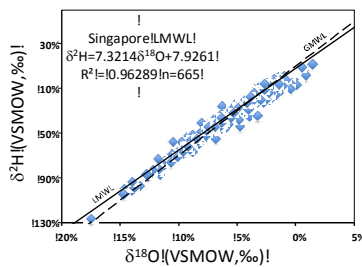


Figure 3. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of one year's daily precipitation samples ($n=665$) from Singapore stations.

The time series of $\delta^{18}\text{O}$ values of daily precipitation samples from Singapore shows the variation of their $\delta^{18}\text{O}$ values versus time through one year (Fig. 4). The samples with the lowest δ -values were collected during the early NE Monsoon. During the SW Monsoon and inter-monsoon period, the $\delta^{18}\text{O}$ values periodically shifted to more negative values, although not as low as those observed during the NE Monsoon.

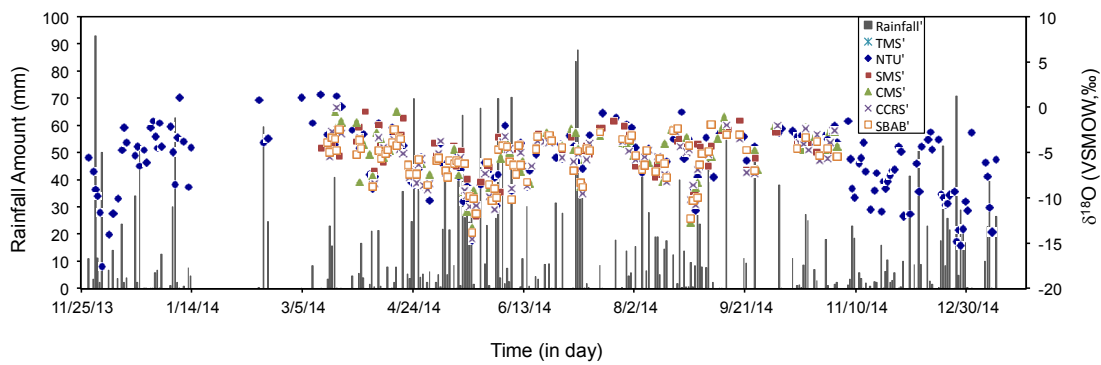


Figure 4. The time series of rainfall amount and $\delta^{18}\text{O}$ values of daily precipitation samples ($n=708$) from all rain stations in Singapore.

An “amount effect” is seemingly not a major control of stable isotopic compositions of daily precipitation because no correlation is observed between the $\delta^{18}\text{O}$ values and rainfall amount (Fig. 5). A weak negative correlation between the $\delta^{18}\text{O}$ values and relative humidity implies some evaporation enrichment in raindrop during condensation, particularly over dry seasons, during which rainwater generally shows the highest $\delta^{18}\text{O}$ values (Fig. 6).

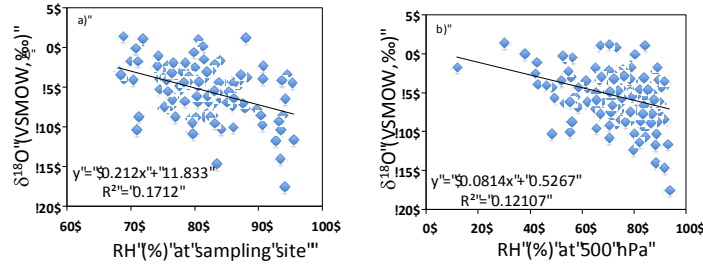


Figure 5. Correlation between $\delta^{18}\text{O}$ values of precipitation samples and relative humidity (RH) at (a) sampling site and (b) at 500hPa.

During the NE Monsoon, the dominant moisture source of the region is from the North or Northeast due to the prevailing winds (Fig. 6a). The rainwater with the lowest $\delta^{18}\text{O}$ values collected in the early NE Monsoon is likely related to cold surges that might bring moisture with very low $\delta^{18}\text{O}$ values here from subtropical regions over the South China Sea. Less negative $\delta^{18}\text{O}$ values during the 2014 NE Monsoon is probably because of some contribution of moisture from local tropic oceans (Fig. 6b)

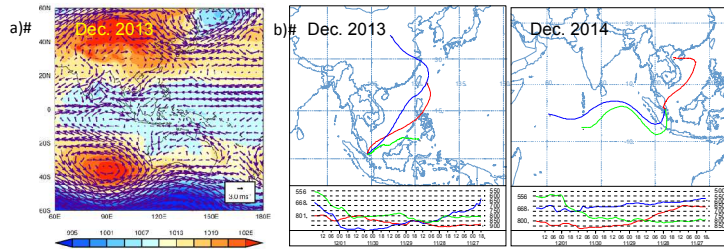


Figure 6 (a) NCEP atmospheric re-analysis at 850 hPa (December 1 to 10, 2013); (b) Average back trajectories (5 days) of air masses at NTU site of December 2013 and December 2014 calculated using HYSPLIT model.

During the SW Monsoon, moisture sources also change with winds to the South, Southwest or Southeast according to atmospheric re-analysis and back-trajectory (Fig. 7a and 7b). The periodical drift to more negative values of the precipitation during this time is not due to the moisture source in the tropical oceans, which generally has very constant isotope values. The negative shift in stable isotope values is likely related to the local convection activities.

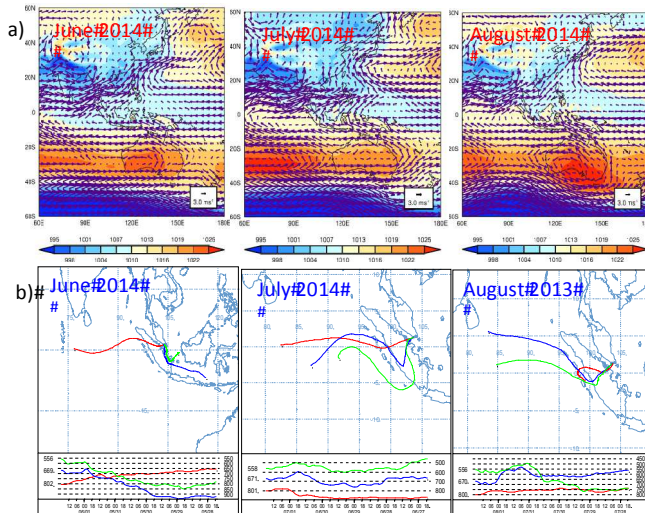


Figure 7. a) NCEP atmospheric re-analysis at 850 hPa (June to August 2014); b) Average monthly back trajectories (5 days) of air masses at NTU site (June to August 2014) calculated using HYSPLIT model.

Outgoing longwave radiation (OLR) has been used as a proxy of deep tropical convection, and OLR values correspond to cold and high clouds [4-6]. However, the shifts in $\delta^{18}\text{O}$ to more negative values during the SW Monsoon do not directly correspond to the lowest values of OLR (Fig. 8). A more significant correlation exists between the $\delta^{18}\text{O}$ values and OLR when it is averaged over 4 days preceding the event ($r = 0.52$; $p < 0.01$) whereas the

instantaneous correlation is low ($r = 0.21$). This integration of local convective activity is attributed to the progressive isotopic depletion of low-level water vapor during convections [6]. It is therefore reasonable to conclude that regional organized convection is the cause of lower $\delta^{18}\text{O}$ values observed in some samples during the SW Monsoon.

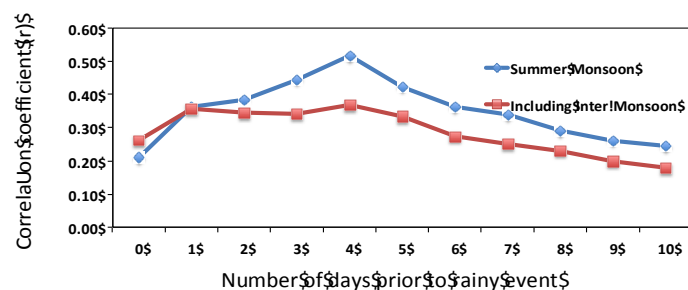


Figure 8. Correlation coefficient (r) between OLR and $\delta^{18}\text{O}$ values of the precipitation over 10-days preceding the rainy event.

4. CONCLUSIONS

This preliminary study indicates that regional atmospheric circulation also plays an important role in moisture transport. During the NE Monsoon, moisture from Northeast South China Sea is dominant whereas the moisture from Indian Ocean is dominant during the SW Monsoon. It is likely that subtropical intra-seasonal systems invaded the tropics to bring moisture with very low δ -values during the NE Monsoon, especially in the early Monsoon. The periods with low δ -value during the SW Monsoon are closely related to regional organized convection. Further studies are needed to investigate the relationship between stable isotopes and convections. Rain amount is not a driver of daily precipitation $\delta^{18}\text{O}$ values in the region, as there is no close correlation between $\delta^{18}\text{O}$ values and rainfall amount. A weak, inverse correlation between $\delta^{18}\text{O}$ values and relative humidity suggests that evaporation enrichment of raindrops during condensation affects δ -values of precipitation.

REFERENCES

- [1] GROENING M., LUTZ H.O., ROLLER-LUTZ Z., KRALLIK M., GOURCY L., AND POLTENSTEIN L., A simple rain collector preventing water re-evaporation dedicated for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ analysis of cumulative precipitation samples, *Journal of Hydrology* 448-449 (2012) 195.
- [2] VAN GELDERN R., BARTH J.A.C., Optimization of instrument setup and post-run corrections for oxygen and hydrogen stable isotope measurements of water by isotope ratio infrared spectroscopy (IRIS), *Limnology and Oceanography: Methods* 10 (2012)1024.
- [3] COPLEN T.B., Reporting of stable hydrogen, carbon and oxygen isotopic abundance (Technical report), *Pure Applied Chemistry* 66 (1994) 273.
- [4] LEKSHMY P.R., MIDHUN M., RAMESH R., AND JANI R.A., ^{18}O depletion in monsoon rain relates to large scale organized convection rather than the amount of rainfall, *Scientific Report* 4 (2014) 5661, doi:10.1038/srep05661.
- [5] GAO J., MASSON-DELMOTTE V., RISI C., HE Y., AND YAO T., What controls precipitation $\delta^{18}\text{O}$ in the southern Tibetan Plateau at seasonal and intra-seasonal scales? A case study at Lhasa and Nyalam, *Tellus B* 65 (2013) 20143.
- [6] VIMEUX F., TREMOY G., RISI C., AND GALLAIRE R., A strong control of the South American SeeSaw on the intra-seasonal variability of the isotopic composition of precipitation in the Bolivian Andes, *Earth and Planetary Science Letters* 307 (2011) 47.

ID: 68

DISTRIBUTION OF STABLE ISOTOPES (^{18}O AND ^2H) IN PRECIPITATION IN IRAQ

K. ALPARUANY. S. AL-NASERI,
Ministry of Science and Technology, Al-Jadiriya, Baghdad, Iraq
E-mail address: kamalalparuany@yahoo.com.

Abstract: The study investigated the concentrations of stable isotopes of ^{18}O and ^2H in samples of precipitation in Iraq. Eighteen sampling stations were used to collect rainwater samples during (December 2011, and January to March 2012). Results show a linear correlation between Temperature and isotopes concentration. The same was found between altitude and isotopes concentration but with a negative trend. Finally local meteoric water line (LMWL) was obtained by fitting the results of deuterium with oxygen-18 to find the deuterium excess. The obtained equation shows higher deuterium excess value (13.81‰) that reflects the continental nature of Iraq with high temperature and low humidity.

1. INTRODUCTION

Iraq is suffering a drastic water shortage caused by a long dry weather period engulfed the entire Middle East countries and reducing the Iraqi share of fresh surface water. Therefore, new techniques to manage water resources are necessary for supporting sustainability in water resources management. Environmental isotope technique is one of such technique and it has been used successfully by several countries starting from obtaining the meteoric water characteristics using stable isotopes, and tritium isotope to obtain the origin [1-4].

Iraq mainly consists of desert, but near the two major rivers (Euphrates and Tigris) are fertile alluvial plains. The north of the country is mostly composed of mountains; the highest point being at 3,611 m in Al-Sulaimaniya in the north of Iraq, while the lowest point is 8 m in Al-Basrah in the south.

The climate of the study area is of continental arid, characterized by a cool winter and a dry summer. Summer temperatures average above 40 °C, while winter temperatures infrequently exceed 21 °C. Typically, precipitation is low; most places receive less than 250 mm annually, with maximum rainfall occurring during the winter months. Rainfall during the summer is extremely rare, except in the far north of the country. The aim of the study is to characterize rainwater in Iraq using stable environmental isotopes (^{18}O and ^2H). The study will cover the effects of temperature and altitude on the concentration of the stable isotopes.

2. METHODS

Water samples were collected from 18 sampling location to cover the area of Iraq (Figure 1). Samples were collected as an incident base from December 2011, January to March 2012. The samples were analyzed for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ using laser spectroscopy type LGR-100 at the Iraqi ministry of science and technology, and the Turkish accreditation Agency.

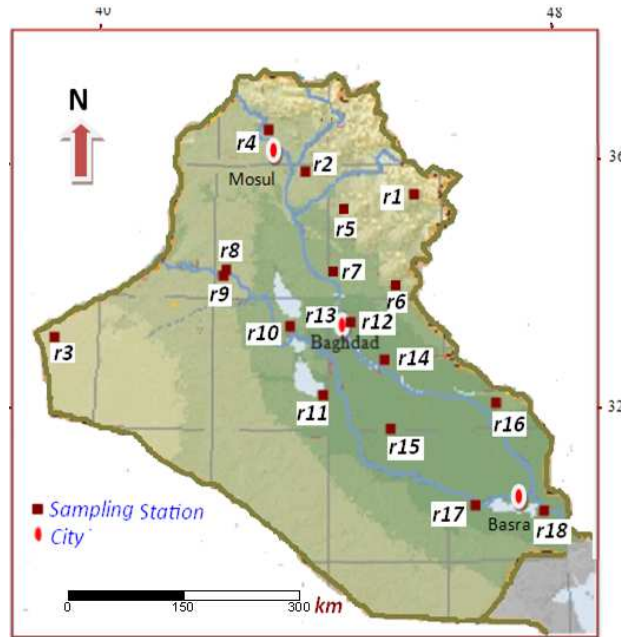


Figure 2. Rainwater sampling stations throughout Iraq.

3. RESULTS

a- Effect of temperature

The relation between temperature and isotopes concentration is shown Figure 2. It can be seen that the higher air temperature at Basrah station, shows the highest stable isotope concentration, and the lowest temperature at Sulaimaniya shows the lowest concentrations. The result shows a linear correlation between the measured values and temperature, which indicates that temperature, is one of the major parameters controlling the behavior of the isotopic composition in precipitation.

b- Effect of Altitude

The relation between stable isotopes concentration with altitude is shown in Figure 3. The relation is, as expected, an inverse behavior than that shown in Figure 2 because temperature reduces as altitude increases. It is fit in the range by in which the gradient $\delta^{18}\text{O}$ between (-0.15‰) and (-0.5‰) per 100 m rise in altitude and the gradient in δD is between (-1‰) and (-4‰) per 100m.

c- Meteoric Water Line

The relationship between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ was plotted in order to find the equation of the local meteoric water line (LMWL). The slope of the line was fixed to 8 and deuterium excess was fitted to the experimental data and the result is ($d=13.82$ ‰). This value is higher than the GMWL value (10) due to the continental effect that characterizes Iraq with less humidity and high temperature. The obtained LMWL equation is:

$$\delta^2\text{H} (\text{‰}) = 8 \times \delta^{18}\text{O} (\text{‰}) + 13.82$$

The equation is close to former study results for Baghdad [5], and it was plotted together with the experimental results and the global meteoric water line in Figure 4.

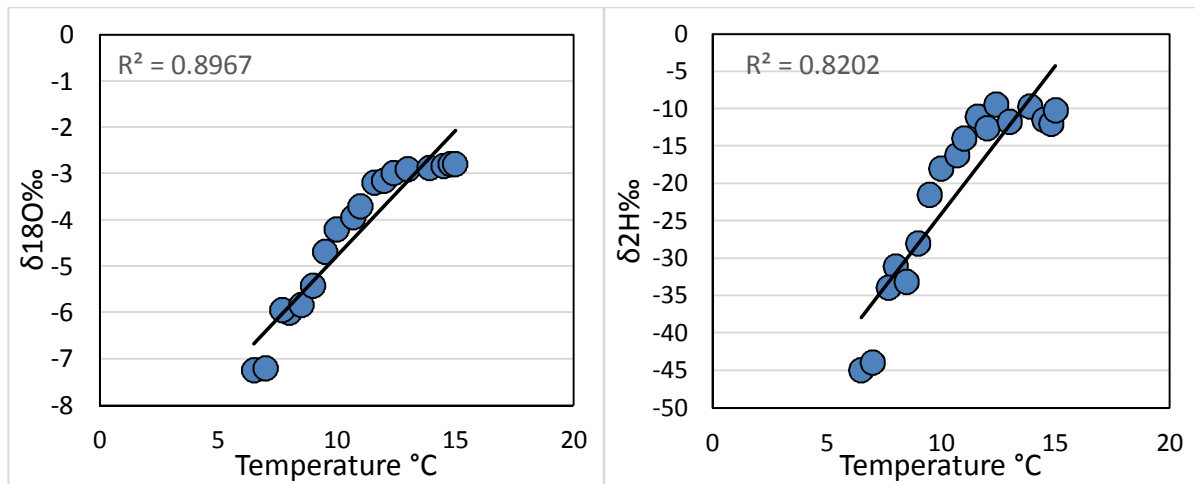


Figure 2. Relation between stable isotopes concentration and temperature

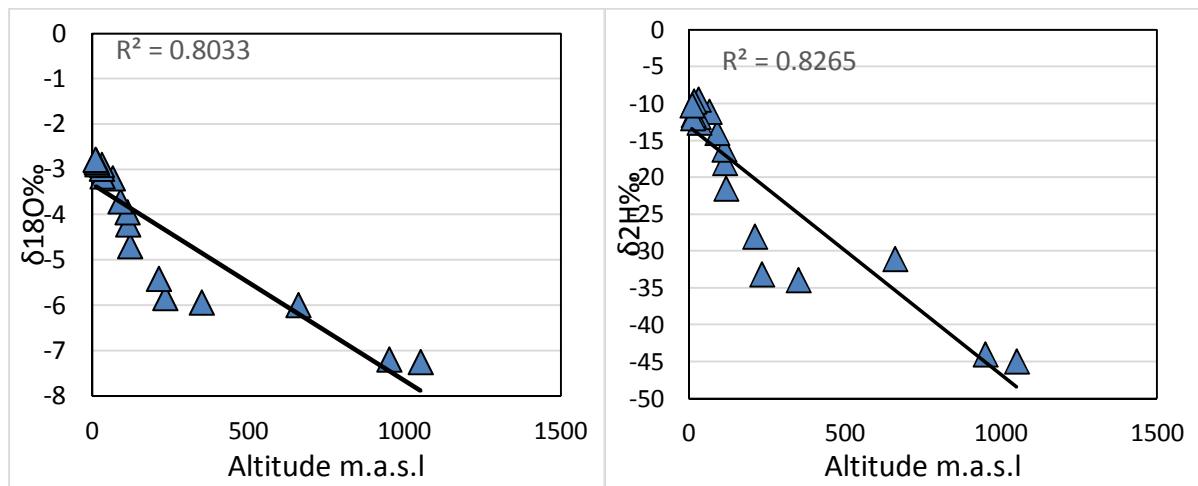


Figure 3. Relation between stable isotopes concentration and altitude

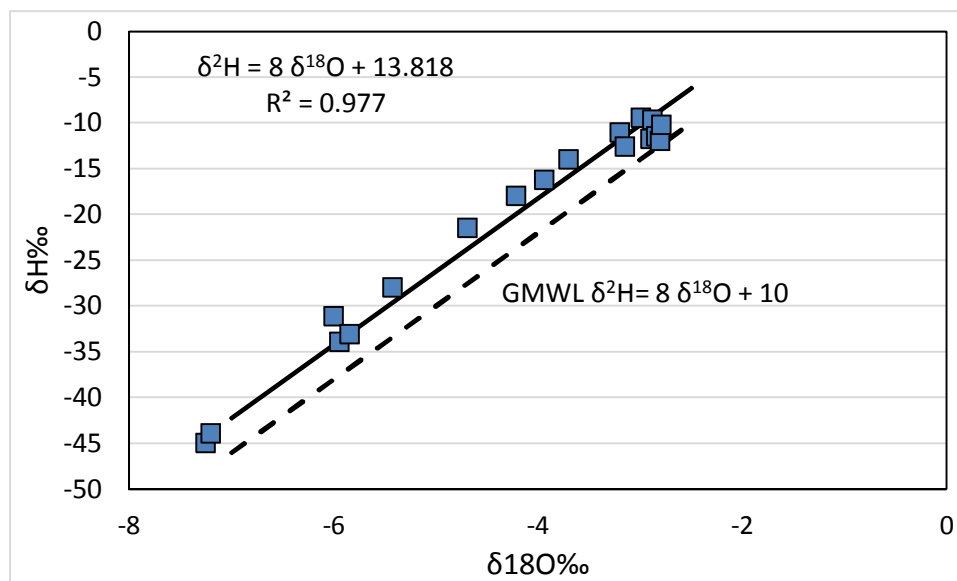


Figure 4. Relation between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ to obtain LMWL

4. CONCLUSIONS

Positive linear relationship was found between temperature and stable isotopes concentration for both $\delta^2\text{H}$ and $\delta^{18}\text{O}$, while the relation was negative linear relationship with altitude. The LMWL equation was found and compared with the GMWL equation. The determined equation shows higher deuterium excess that reflects the continental nature of Iraq with high temperature and low humidity.

REFERENCES

- [1] CRAIG, H., Isotopic Variations in Meteoric Waters. *Science*, 133, (1961)1702-1703.
- [2] CLARK, I. D., AND P. FRITZ, Environmental isotopes in hydrogeology, 328 pp., (1997), CRC Press/Lewis Publishers, Boca Raton, FL.
- [3] GAT, J.R. AND CARMI, I. , Evolution of the Isotopic Composition of Atmospheric Waters in the Mediterranean Sea Area. *Journal of Geophysical Research.*, (1970)75(15) 3039-3048.
- [4] DANSGAARD, W. Stable isotopes in precipitation. *Tellus*, (1964) 16, 436-468.
- [5] AL-NASERI, S. Determination of the meteoric water line using Stable isotopes in precipitations at several locations in Baghdad, Iraqi J. of Science and Technology, (2013), vol.4, No.1.

TRITIUM IN PRECIPITATION IN THE SOUTHERN NORTH SEA: A MARKER FOR LOCAL FORMED WATER VAPOUR

J. SUELTFUSS,
University of Bremen, Institute of Environmental Physics,
Otto-Hahn-Allee, Bremen, Germany
E-mail address: suelten@uni-bremen.de

Abstract: Cumulated data of tritium concentrations in groundwater of East-Frisian islands (German Bight) are elevated with respect to tritium concentration in precipitation of inland locations. Tritium concentrations in ocean water are high along the Southern shore of the North Sea because an eastward current carries tritium from the nuclear reprocessing plant in La Hague, France. This contribution compares time series of precipitation data and North Sea waters, leading to the hypothesis that tritium from the Southern North Sea surface waters evaporates and contributes to the precipitation of the islands and coastal location. Here, an unique setting can be found: high tritium levels of a confined but large enough area to mark the source of evaporating water, and combined with prevailing westerly winds, leading to a deposition of elevated tritium levels on land.

1. INTRODUCTION

The reservoir providing tritium to the hydrological cycle primarily is the lower stratosphere [1]. Mid latitude stratospheric-tropospheric exchange of water vapour in spring refills the tritium levels of the troposphere. The ocean surface generally acts as the sink for tritium. The so called continental effect is attributed to this feature [2]. But also nuclear facilities provide tritium in various amounts to the environment. Local tritium sources from nuclear reprocessing plants and nuclear power plants contribute to tritium in rivers and shore-near ocean areas.

In the German Bight tritium concentration in ocean water are elevated up to 40 TU (in 2000). An eastward current carries tritium from the nuclear reprocessing plant in La Hague, France. Additionally, tritium is released to the Southern North Sea from the rivers Rhein, Ems, Weser and Elbe. All these rivers carry a tritium load from nuclear power plants.

2. RESULTS

Tritium concentrations in groundwater samples from the East Frisian Islands Spiekeroog and Langeoog were elevated compared to samples from more inland locations of Northern Germany. The tritium concentration of groundwater samples were reconstructed from analysis of tritium and tritiogenic ^3He . From the ratio of both tracers the infiltration period (calendar year in Fig. 1) is calculated and the sum is a measure for the infiltrated tritium concentration, sometimes called 'initial tritium'.

A comparison of initial tritium with tritium in precipitation indicates dilution of recent recharged water with old and therefore tritium-free water. But here, all groundwater samples fall above all available data from monthly mean tritium concentration in entire Germany.

A separated examination of tritium in precipitation from the coastal station Cuxhaven clearly shows that Cuxhaven data are at the upper limit of all Germany data since the late 1990s.

Until the mid-1990s Cuxhaven concentrations are at the lower side of all German tritium data, as would be expected when assuming that the continental effect applies. An interesting feature in the general decline of tritium in precipitation at all stations is the slight increase in 1996 and 2006/2007. During these years the solar activity shows minima. This leads to reduced shielding of cosmic radiation and increased stratospheric tritium production.

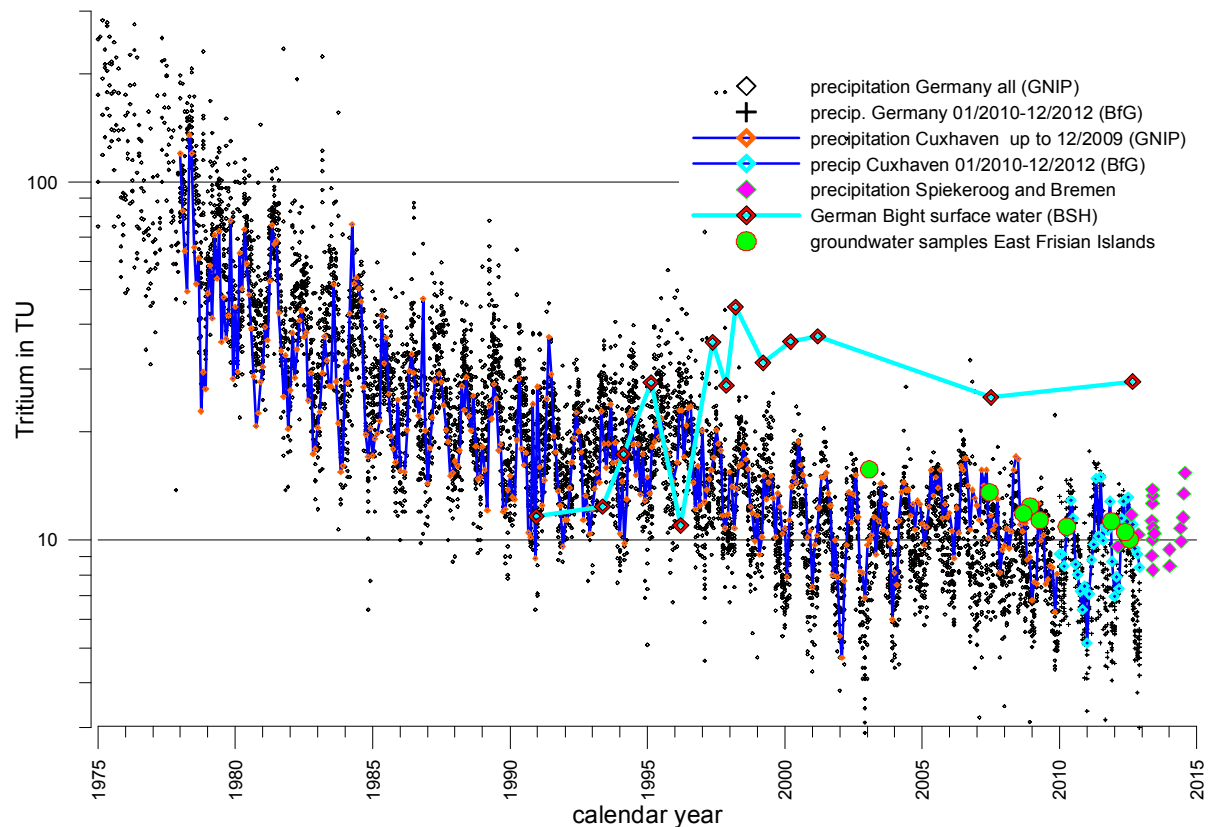


Figure 1. Tritium concentration in precipitation (data: IAEA GNIP up to 2010, data 2010 – 2012: Bundesanstalt für Gewässerkunde, Koblenz), tritium concentration in surface water in the German Bight (data: Bundesamt für Seeschifffahrt und Hydrographie, Hamburg) and tritium concentration of groundwater samples from the East Frisian Islands Spiekeroog and Langeoog.

A (not complete) record of tritium concentrations of ocean surface waters in the German Bight [3] is shown in Fig. 1. These values increase significantly after the mid-1990s. In the period from 1990 to 1998 the release of tritium from the nuclear reprocessing plant in La Hague, France, increased from about 2 PBq to about 10 PBq. As the ocean currents in the Southern North Sea display a cyclonic structure La Hague may have caused this tritium increase in the German Bight.

3. CONCLUSIONS

An increase of tritium in the surface layer of the waters in the German Bight after the late 1990ies clearly correlates with higher tritium concentrations in precipitation in the nearby locations on land. Hence, a fraction of the precipitation at these coastal locations therefore must have been evaporated from the nearby surface ocean waters. As the tritium concentration in surface waters falls off on a length scale of about 100 km perpendicular to the

direction of the current, i.e. to the North, tritium serves as a tracer for the location of the evaporation process.

The portion of locally evaporated water will depend on weather conditions. So, the records of tritium in precipitation on the islands or coastal station like Cuxhaven should correspond to single weather events. A monitoring program should also include stable isotopes and better resolution of the tritium distribution in the German Bight surface waters. Hence, tritium can be used as tracer for a study of regional evaporation processes. Numerical atmospheric models could be challenged by implementing tritium distribution in water vapour.

REFERENCES

- [1] ZAHN, A., BARTH, V., PFEILSTICKER, K., PLATT, U., Deuterium, Oxygen-18, and Tritium as Tracers for Water Vapour Transport in the Lower Stratosphere and Tropopause Region, , J Atmosph. Chem **30**, 1998, 25-47
- [2] WEISS W., BULLACHER, J., ROETHER, W., Evidence of Pulsed Discharges of Tritium from Nuclear Energy Installations in Central European Precipitation, IAEA-SM-232/18, Behaviour of Tritium in the Environment (1979) 17-30
- [3] HERRMANN, J., Bundesamt für Seeschifffahrt und Hydrographie, personal communication (2014)

THE LOCAL METEORIC WATER LINES AND THE D-EXCESS OF PRECIPITATION IN CROATIA

T. HUNJAK,

Stable Isotope Laboratory, Medical Faculty, Rijeka University, 51000 Rijeka, Croatia

H. O. LUTZ,

Stable Isotope Laboratory, Medical Faculty, Rijeka University, 51000 Rijeka, Croatia

Faculty of Physics, Bielefeld University, 33615 Bielefeld, Germany

Z ROLLER-LUTZ

Stable Isotope Laboratory, Medical Faculty, Rijeka University, 51000 Rijeka, Croatia

E-Mail address: roller@medri.uniri.hr

Abstract: At the Stable Isotope Laboratory at Rijeka University (*SILab Rijeka*) we monitor the stable isotope composition ($\delta^{18}\text{O}$, $\delta^2\text{H}$) of precipitation in Croatia. Our data base contains about 50 stations distributed all around the country. Their different latitudes, longitudes and altitudes give information in great detail, including the influence of the topographic structure on the precipitation in this south-eastern part of Europe, as well as the complex interplay of the different climate conditions in the area. Within a few hundred kilometers, the stable isotope values display a significant change from the maritime character in the South (mean $\delta^{18}\text{O}$ around -6 to -8 ‰) to the continental behavior in the North (mean $\delta^{18}\text{O}$ around -8 to -11 ‰). In addition, depending on the location, the mean $\delta^{18}\text{O}$ values vary with altitude at a rate between approximately $-0.2\text{‰}/100\text{m}$ to $-0.4\text{‰}/100\text{m}$, respectively. Particular attention is given to the correlation between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (the Local Meteoric Water Line, LMWL), as well as the d-excess $d = \delta^2\text{H} - 8 \cdot \delta^{18}\text{O}$.

1. INTRODUCTION

The precipitation as the input into the water system and its stable isotope composition has to be known for the proper use and management of water resources. The stable isotopes of oxygen (^{16}O , ^{17}O , ^{18}O) and hydrogen (^1H , ^2H) are natural tracers in the water cycle, therefore, they serve as powerful tools for the understanding of many meteorological, hydrological and climatic processes. Average distributions of the O and H isotope content in precipitation are available in the literature (e.g. [1]). They are mostly based on the GNIP compilation (Global Network of Isotopes in Precipitation [2]); particularly since Croatia is not well represented in this data base, such global data are often not really useful if it comes to the treatment of hydrological processes in an actual local setting. For example, besides latitude, longitude and altitude, important parameters to be considered include the orographic structure, the climate, the prevailing winds etc. A particularly sensitive situation is also found in Croatia: the country is under the influence of at least three climate zones (Mediterranean; Atlantic; continental), and the topography is quite complex (in the North the Pannonian plain; in the middle part the Dinaric hills and mountains with altitudes of up to approximately 2000 m; in the South it borders on the Adriatic Sea with a coast line of about 1800 km length).

Therefore, in recent papers [3, 4] we discussed some general aspects and the mapping of the isotopic composition of the meteoric precipitation in Croatia. Prompted by a renewed interest in rather detailed information, we have now reanalyzed the available country-wide data on the

stable isotope (^{16}O , ^{18}O , ^1H , ^2H) composition of precipitation. While in the previous papers we concentrated mainly on yearly averages of the meteoric isotopic composition in some representative sampling stations, the present more detailed analysis is based on original (monthly averaged) data of the Local Meteoric Water Lines (LMWL, the dependence of the isotopic amount ratios $^{18}\text{O}/^{16}\text{O}$ on $^2\text{H}/^1\text{H}$) and the deuterium excess $d = \delta^2\text{H} - 8 \cdot \delta^{18}\text{O}$. The data are presented in “delta” notation

$$\delta = (r_{\text{sample}}/r_{\text{standard}} - 1) \cdot 10^3 \text{ ‰}; \quad (1)$$

r_{sample} is the molar ratio of heavy-to-light isotopes in a sample, relative to that in Vienna Standard Mean Ocean Water (V-SMOW), r_{standard} .

2. METHODS

The analysis is based on data from more than 50 stations. Most stations are part of a network that has been established by the Stable Isotope Laboratory Rijeka (*SILab Rijeka*); it includes some stations which are served by Croatian schools in the GLOBE program (Global Learning and Observation to Benefit the Environment), a worldwide primary and secondary school-based science and education program for students and teachers). In addition, we use data from GNIP stations [2].

According to the GNIP protocol sampling is made on a monthly basis. Each sample should represent precipitation for at least one entire one-month period, beginning on the first day of the month and continuing until the end of the month. In the sampling stations served directly by *SILab Rijeka* we used collectors in which a layer of paraffin prevents evaporation, as well as a newly developed type of collector [5] with a practically identical performance (though easier to handle). The complete results of the sampling campaigns will be made available in the GNIP data tables.

Samples have been analyzed for their isotopic composition in the Stable Isotope Laboratory *SILab* at Rijeka University. $\delta^2\text{H}$ and $\delta^{18}\text{O}$ were measured in a Thermo-Finnigan Delta^{plus}XP isotope ratio mass spectrometer using a combination of dual inlet and equilibration unit as periphery. The precision of the δ -values thus determined is better than 1‰ for $\delta^2\text{H}$ and 0.1‰ for $\delta^{18}\text{O}$.

3. RESULTS AND DISCUSSION

3.1. The Local Meteoric Water Lines (LMWLs):

As an example, Figure 1 displays the LMWL using the averaged data of all stations in Croatia. Closer inspection of the data shows that the individual LMWLs are not very sensitive to the details of the local conditions: The average slopes show an only slight dependence on the locality (c.f. Table 1), indicating the transition from the continental conditions in the East to the more Atlantic climate in the West and to the Mediterranean influence on the coast. All slopes are smaller than 8, i.e., smaller than the slope of the Global Meteoric Water Line (GMWL), $\delta^2\text{H} = 8 \cdot \delta^{18}\text{O} + 10$, suggesting enhanced evaporation below the cloud base [6, 7].

The d-excess:

An example for the d-excess $d = \delta^2\text{H} - 8 \cdot \delta^{18}\text{O}$ is shown in Figure 2. In the warm season the d-excess is smaller than in the cold season in agreement with our earlier work [3, 4]. This is due to a prevailing Mediterranean influence in autumn and winter [6, 7]. The general behavior is consistent with the one known for the northern hemisphere [8].

Table 1. Slopes of the LMWLs in Croatia and the three main climate regions.

Coast	7.01
Croatian Dinarides	7.61
Pannonia	7.32
All stations	7.54

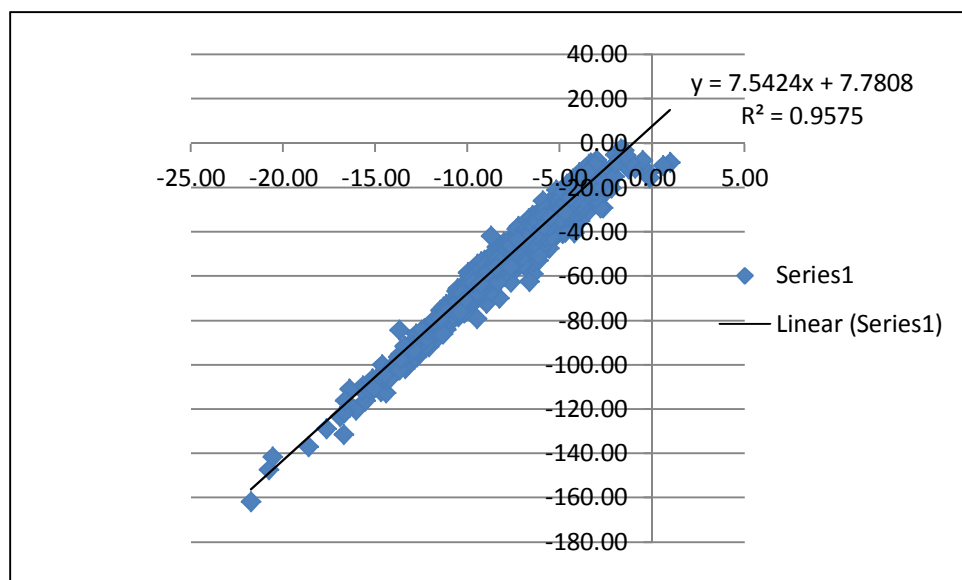


Figure 1. The LMWL for Croatia, averaged over all stations in the network (abscissa: $\delta^{18}O$; ordinate: δ^2H).

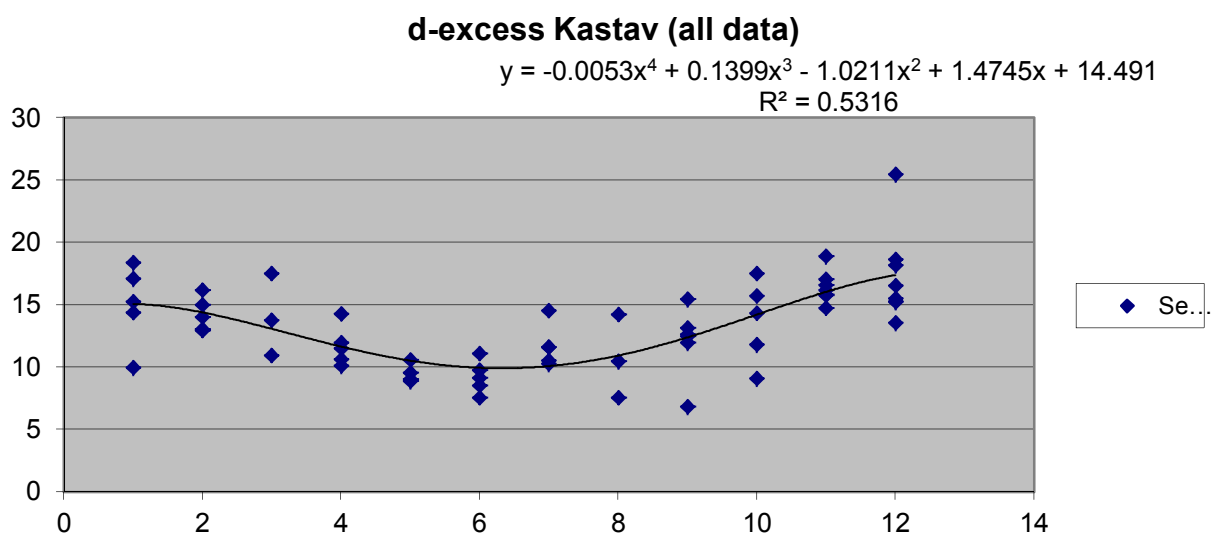


Figure 2. Seasonal variation (abscissa) of the d-excess (ordinate) in Kastav (altitude 350 m a.s.l., close to Rijeka on the coast). The data points represent different years.

4. CONCLUSIONS

The slopes of the LMWL are smaller than 8, the slope of the Global Meteoric Water Line, suggesting enhanced evaporation. The d-excess is larger in the cold season if compared to the warm season. It increases with increasing altitude and the difference between d in the warm and the cold season is smaller for increasing altitude. Therefore, the general tendency is clear; however, if accurate values are required, measurements of the relevant data are necessary. The sensitivity of the d-excess to the origin of the precipitating air mass will be discussed in a forthcoming paper.

REFERENCES

- [1] MOOK, W.G. Environmental Isotopes in the Hydrological Cycle: Principles and applications, Technical documents in Hydrology (2001), UNESCO/IAEA, Paris, France
- [2] GNIP, available at http://www.naweb.iaea.org/napc/ih/documents/other/GNIP%20station%20operation%20manual_Feb13_EN.pdf
- [3] ROLLER-LUTZ, Z., MANCE, D., HUNJAK, T., LUTZ, H.O. On the Isotopic Altitude Effect of Precipitation at the Northern Adriatic (Croatia). Isotopes in Hydrology, Marine Ecosystems and Climate Change Studies, Proceedings of the International Symposium, Wien, IAEA (2013). 99-105.
- [4] HUNJAK, T., LUTZ, H. O., ROLLER-LUTZ, Z. Stable isotope composition of the meteoric precipitation in Croatia. Isotopes in environmental and health studies, 49, 3 (2013); 336-345.
- [5] GROENING, M., LUTZ, H.O., ROLLER-LUTZ, Z., KRALIK, M., GOURCY, L., POELTENSTEIN, L. A simple rain collector preventing water re-evaporation dedicated for delta 18O and delta 2H analysis of cumulative precipitation. Journal of Hydrology, 448/449, 2 (2012); 195-200.
- [6] FROELICH, K., GIBSON, J.J., AGGARWAL, P. Deuterium excess in precipitation and its climatological significance, Study of environmental change using isotope techniques, C&S Paper Series 13/P, pp. 54-65, International Atomic Energy Agency, Vienna, Austria (2002), ISBN 92-0-116402-5.
- [7] PENG, H., MAYER, B., HARRIS, S. KROUSE, H.R. The influence of below-cloud secondary effects on the stable isotope composition of hydrogen and oxygen in precipitation at Calgary, Alberta, Canada. Tellus, 59 (2007), 698-704
- [8] ROZANSKI, K., ARAGUAS-ARAGUAS, L., GONFIANTINI, R. Isotopic patterns in modern global precipitation. Geophysical Monograph, 78 (1993); 1-36

THE DAILY ^{18}O AND ^2H PATTERNS OF RAINFALL IN ADDIS ABABA AND THEIR LINK TO IWV, MOISTURE RESIDENCE TIME AND RECYCLING

S. KEBEDE GURMESSA, S

School of Earth Sciences, Addis Ababa University, Ethiopia

Email Address: seifukebede@yahoo.com

T. TUJUBA, B. ELIAS

Post graduate program, Addis Ababa University, Ethiopia

Abstract: Meteoric waters in Ethiopia are the most $\delta^{18}\text{O}$ - $\delta^2\text{H}$ enriched. Origin of the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signal of rainfall waters of the Addis Ababa and Ethiopia has been widely debated over the last four five decades. The earlier explanations attribute the enriched signals to the isotope effects. Nevertheless isotope effects could not explain for instance as to why rainfalls in the high altitude in Ethiopia are still highly enriched and as to why amount effect is non-existent in high rainfall seasons. Other explanations attribute the signals to the sources of the moisture. This is faced by the challenge that one tracer cannot give full information on multiple source reservoirs- as the region is sitting in a zone where multiple moisture sources converge. The purpose of the current study is to investigate the linkage between the stable isotope variations and the atmospheric vapor derivation processes including a) residence time, b) recycling and c) integrated water vapor content of the atmosphere as an attempt to find mechanistic explanation for origin of the isotope signals. Daily rainwaters and intermittent atmospheric vapor have been sampled between March 15 and October 15, 2014 at Addis Ababa and three other stations in Ethiopia for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ measurement. The atmospheric moisture properties were investigated using Geodetic GPS applications. The general seasonal pattern of the moisture properties matches well the seasonal isotope pattern. This work will show the linkage between IWV content, atmospheric mean residence time and moisture recycling at daily time scale.

ISOTOPIC COMPOSITION OF PRECIPITATION IN NORTH-WEST SLOVENIA FOR THE PERIOD 2010–2013

P. VREČA

Jožef Stefan Institute, Department of Environmental Sciences,
Jamova 39, Ljubljana, Slovenia

E-mail address: polona.vreca@ijs.si

Abstract: Isotopic composition of precipitation at 5 new GNIP stations located in NW Slovenia is presented for the period 2010–2013. Oxygen isotopic composition was determined by different techniques (IRMS and LAS) and deuterium excess was calculated by using both sets of results. The estimated differences indicate the need for caution in future application of different stable isotope analytical techniques in hydrological investigations.

1. INTRODUCTION

Geographical diversity (complex topography, geology, geomorphology, varied vegetation, etc.) and geographical position considerably influence the climate of Slovenia [1]. It is well known that precipitation is of major interest in the hydrological cycle and that understanding of temporal and spatial variations in the amount and mode of precipitation as well as information about the isotopic composition can help in basin-wide balance studies. Some European countries have established networks of stations where isotopic composition of precipitation is regularly determined on monthly basis [e.g. 2]. In Slovenia, the precipitation monitoring program is performed in the framework of the regular activities of the Environmental Agency of the Republic of Slovenia (ARSO). However, monitoring of isotopic composition of precipitation is not included into the regular national monitoring program but has been performed in the past by the Jožef Stefan Institute (JSI) in cooperation with other institutions in the frame of Global Network of Isotopes in Precipitation (GNIP) organized jointly by the IAEA and WMO. In the beginning of 2010 was isotopic monitoring in Slovenia performed at 4 locations: Ljubljana (Reaktor), Portorož, Postojna and Dvor. None of those sampling locations is situated in NW Slovenia (Julian Alps and Karavanke), an area that falls within the mountain climate zone according to climatic division of Slovenia [1] and represents the upper catchment area of river Sava, the longest water course in Slovenia and a transnational watershed. In addition, NW Slovenia represents an important water resource, therefore, we focused on more detailed investigations of isotopic composition of water cycle components in this area in the frame of IAEA CRP F3.20.06, including establishment of new isotope in precipitation monitoring network.

2. METHODS

We started with monthly sampling of precipitation in 2010 in co-operation with the ARSO at 5 locations in NW Slovenia. Four of them (i.e. Kredarica, Rateče, Bohinjska Češnjica and Zgornja Radovna) are situated in Julian Alps while Podljubelj is located in Karavanke. Basic information about sampling locations is presented in Table 1. Monthly composite precipitation samples were collected according to IAEA technical procedures for GNIP stations.

The oxygen stable isotopic composition ($\delta^{18}\text{O}$) was determined on isotope ratio mass spectrometer (i.e. IsoPrime with MultiFlow-Bio module or Varian MAT 250) at the Jožef

Stefan Institute (JSI) by means of water-CO₂ equilibration technique. All measurements are carried out against laboratory standards that are periodically calibrated against international standards recommended by the IAEA. In addition, reference materials provided by IAEA were used for daily quality control. Precipitation samples were sent for isotope analyses also to Isotope Hydrology Laboratory (IHL) at IAEA. The oxygen ($\delta^{18}\text{O}$) and hydrogen ($\delta^2\text{H}$) stable isotopic composition was determined by laser absorption spectroscopy (LAS) according to IAEA laboratory procedures.

Table 1. Basic information about sampling locations.

	Kredarica	Rateče	B. Češnjica	Podljubelj	Z. Radovna
Station type	Synoptic	Synoptic	Climatological	Precipitation	Precipitation
Latitude	46°23' N	46°30' N	46°18' N	46°24' N	46°26' N
Longitude	13°51' E	13°43' E	13°57' E	14°17' E	13°57' E
GNIP code	1400800	1400700	1400601	1401001	1400801
Altitude (m a. s. l.)	2514	864	595	681	750
Mean annual temperature (°C)*	-1,7	5,9	7,5	n.d.	n.d.
Annual amount of precipitation (mm)*	2164	1547	2088	1725	1850

Legend: n.d. – not determined; * – period 1961–1990

3. RESULTS

The results of isotopic composition of oxygen show different patterns in particular year (Figure 1) that are related to different climate conditions during observation period. The lowest mean $\delta^{18}\text{O}$ values are observed at Kredarica and the highest at Bohinjska Češnjica (Table 2). The different climate conditions in February and March 2012 are distinctly recorded (Figure 1). February 2012 was very cold, dry and windy [3] while March 2012 was very mild and dry [4]. The average air temperatures at Kredarica were -12.6 and -2.7°C in February and March 2012, respectively, and differed considerably from long-term averages. Comparison of results for $\delta^{18}\text{O}$ determined at Kredarica and Bohinjska Češnjica by different analytical techniques is presented in Figure 2 indicating slight differences in the frame of analytical error. Comparison of mean values calculated from results obtained either by IRMS analyses or by LAS analyses is presented in Table 2. Isotopic composition of hydrogen is changing parallel to oxygen isotopic composition. Both isotopes are highly correlated and the results are distributed along the global meteoric water line.

Table 2. Mean isotopic composition of precipitation for the period from April 2010 to March 2013. Legend: JSI – analyses performed at JSI, IAEA – analyses performed at IAEA.

Location	$\delta^{18}\text{O}_{\text{JSI}}$	$\delta^{18}\text{O}_{\text{IAEA}}$	$\delta^2\text{H}_{\text{IAEA}}$	d_{JSI}	d_{IAEA}	$(d_{\text{JSI}} - d_{\text{IAEA}})$
Kredarica	-11.3	-11.0	-76	14.5	12.4	2.1
Rateče	-10.6	-10.5	-74	11.1	10.2	0.9
B. Češnjica	-8.7	-8.6	-59	10.6	10.3	0.3
Podljubelj	-9.4	-9.2	-65	9.7	8.8	0.9
Z. Radovna	-9.7	-9.5	-66	11.5	9.8	1.7

Deuterium excess was calculated taking into account oxygen data obtained either by IRMS analyses or by LAS analyses (Table 2). The differences in mean d values for all 5 locations

are summarized in Table 2 and comparison of calculated values for Kredarica is presented in Figure 3. Mean d values at all stations in Julian Alps exceed 10 ‰, while at Podljubelj which is located in Karavanke we observed slightly lower d values (Table 2). Some data at Podljubelj might indicate the influence of evaporation or some sampling error. In addition, it has to be stressed that at JSI we performed analyses prior to analyses performed at IAEA and that some leaking from bottles sent to IAEA was observed. Comparison of different techniques continues and more attention is paid to proper storage and transport of samples.

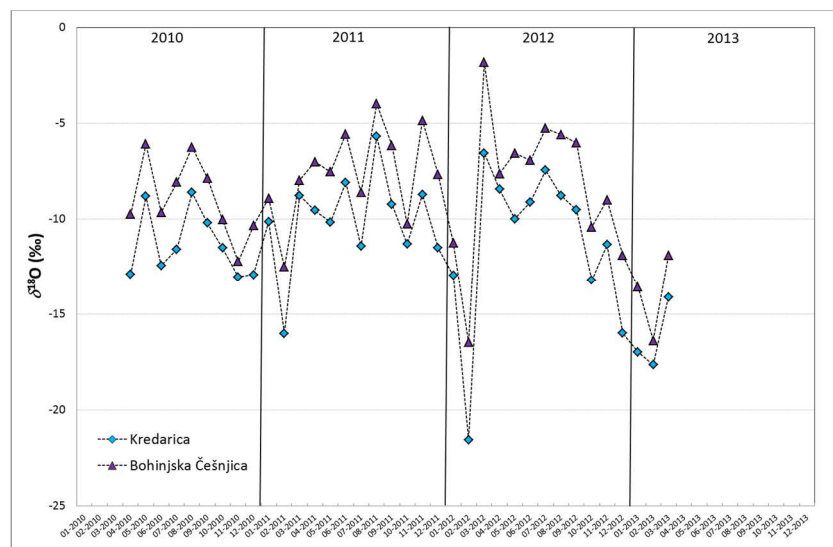


Figure 1. Isotopic composition of oxygen at locations Kredarica and Bohinjska Češnjica determined at JSI.

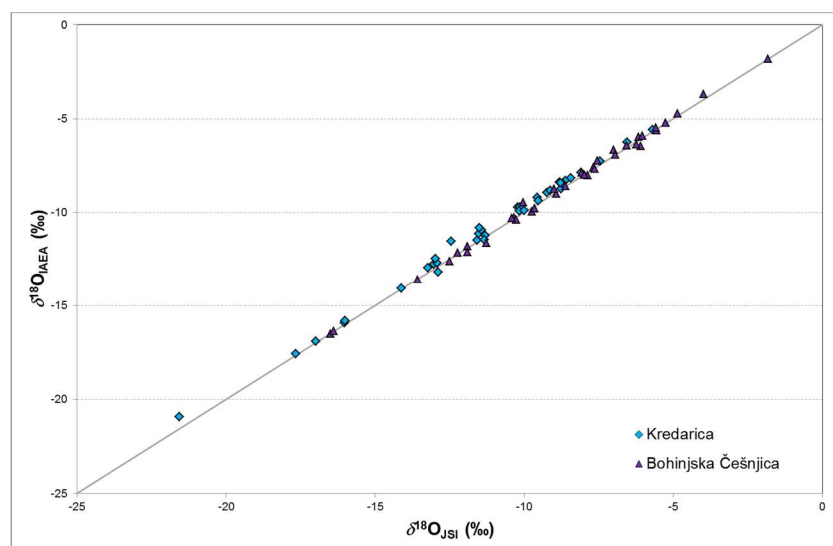


Figure 2. Comparison of results for $\delta^{18}\text{O}$ determined at IAEA vs. JSI.

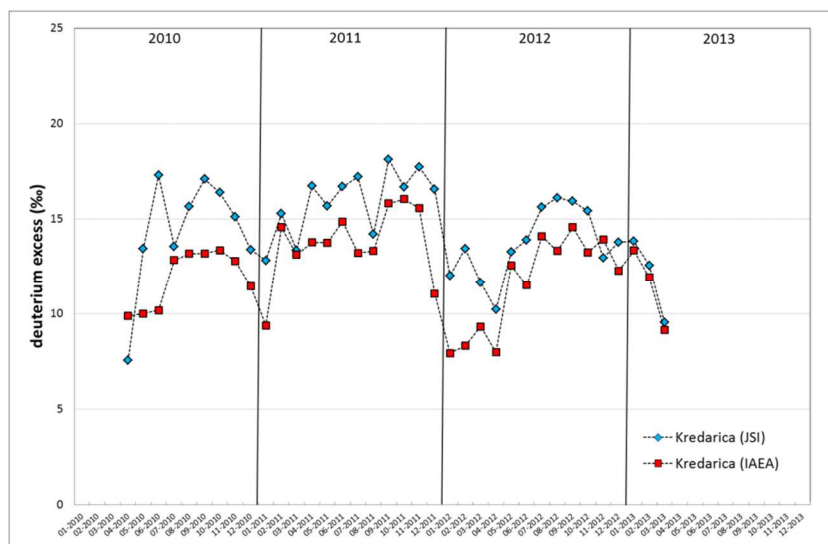


Figure 3. Comparison of results for deuterium excess calculated by taking into account $\delta^{18}\text{O}$ determined at JSI (Kredarica (JSI)) and at IAEA (Kredarica (IAEA)).

4. CONCLUSIONS

We established new isotope in precipitation monitoring network in NW Slovenia in the frame of IAEA CRP F3.20.06. Oxygen isotopic composition was determined using different analytical techniques and results show that further calculations can lead to different conclusions especially when deuterium excess is used for determination of air mass sources. The data will be submitted to GNIP database where it is necessary to add also information about analytical techniques used for determination of isotopic composition.

5. ACKNOWLEDGEMENT

This study was supported by research program P1-0143 and IAEA project 16199/R0. I thank the staff of the meteorological stations for their invaluable help with sampling and S. Žigon for help with isotope analyses. The help the staff of Isotope Hydrology Section at IAEA is also gratefully acknowledge.

REFERENCES

- [1] PUČNIK, R., Velika knjiga o vremenu, Cankarjeva založba, Ljubljana, (1980) 368 pp.
- [2] SCHÜRCH, M., KOZEL, R., SCHOTTERER, U., TRIPET, J.P., Observation of isotopes in the water cycle – the Swiss National Network (NISOT), Environmental Geology **45** (2003) 1–11.
- [3] CEGNAR, T., Naše okolje, Bilten Agencije RS za okolje **XIX/3** (2012).
- [4] CEGNAR, T., Naše okolje, Bilten Agencije RS za okolje **XIX/4** (2012).

ID: 108

9 YEAR LONG MOISTURE SOURCE DIAGNOSTIC FOR THE PRECIPITATION IN DEBRECEN, EAST HUNGARY: IMPLICATIONS FOR THE CHANGES IN THE CLIMATE REGIME

E. BOTTYÁN,

Department of Meteorology, Eötvös Loránd University, H-1117 Budapest, Pázmány P. sétány 1/A, Hungary,

E-mail address: emese.bottyan@gmail.com

G. CZUPPON,

Institute for Geological and Geochemical Institute, RCAES, Hungarian Academy of Sciences, H-1112 Budapest, Budaörsi út 45., Hungary

L. PALCSU,

Hertelendy Laboratory of Environmental Studies, Institute for Nuclear Research of The Hungarian Academy of Sciences, H-4026 Debrecen, Bem tér 18/C, Hungary

K. KÁRMÁN,

Institute for Geological and Geochemical Institute, RCAES, Hungarian Academy of Sciences, H-1112 Budapest, Budaörsi út 45, Hungary

T. WEIDINGER,

Department of Meteorology, Eötvös Loránd University, H-1117 Budapest, Pázmány P. sétány 1/A, Hungary

L. HASZPRA

Hungarian Meteorological Service, H-1675 Budapest, P.O.Box, 39, Hungary, also at Geodetic and Geophysical Institute, Hungarian Academy of Sciences, H-9400 Sopron, Csatkay Endre u. 6-8., Hungary

Abstract: In the last few years, the analysis of backward trajectories has become a common use for identifying moisture uptake regions for the precipitation of a given region (Sodemann and Zubler, 2010, Krklec and Domínguez-Villar, 2014). Our examination focuses on the air moisture source regions for the precipitation in Debrecen (East-Hungary) from January 2006 to December 2014. In addition, for this period, there is an event-based stable isotopic data set for the precipitation in Debrecen, so these data were also involved to the analysis. Beside the determination of the origin of the water vapour, we tracked the moisture variability for relative long time period. Additionally, we evaluated the relation between the isotopic composition of the precipitation and its source region, as well as their seasonal and interannual variability during the examined period.

For the determination of the moisture source regions, we applied the NOAA HYSPLIT model based on GDAS database with 1° spatial and 6 hours temporal resolution. The backward trajectories were calculated for every day and every hour when precipitation was observed, for heights of 500, 1500 and 3000 m. The evaluation of the right time interval of the precipitation event was carried out by applying a threshold for relative humidity of 80% for

every height for the starting point. Only these trajectories were considered for further calculation.

The evaporative regions along the trajectories were determined by calculation of the specific humidity along the trajectories. If the amount of the humidity rose between two time intervals at least 0.1 g/kg, then the area overpassed in the time interval was considered as moisture source area.

We determined five moisture source regions based on the trajectories: Atlantic, North European, East European, Mediterranean and continental. We also evaluated the ratios of the water originated from the different regions so we could give the first long-term quantitative estimation for the precipitation supply of Hungary. We examined the statistics of the stable isotope data for every region and looked forward to find relation between the source region and the stable isotope composition of the precipitation samples.

REFERENCES

- [1] KRKLEC K., DOMÍNGUEZ-VILLAR D., (2014) Quantification of the impact of moisture source regions on the oxygen isotope composition of precipitation over Eagle Cave, central Spain. *Geochim. Cosmochim. Acta* **134**, 39–54.
- [2] SODEMANN H., ZUBLER E. (2010) Seasonal and inter-annual variability of the moisture sources for Alpine precipitation during 1995–2002. *Int. J. Climatol.* **30**, 947–961.

ID: 115

ESTABLISHING THE LOCAL METEORIC WATER LINE IN THE EL CAJON RESERVOIR, HONDURAS

T. CONTRERAS,

Hydrogeologist, MOS Project, El Cajón, Santa Cruz de Yojoa, Honduras

E-mail address: tirza.contreras@gmail.com

E.SOTO

Chief of the Chemical Laboratory of ENEE, Tegucigalpa, Honduras

Abstract: El Cajon hydroelectric power plant is located in the central part of Honduras; between 3 important departments and it is the most important project for the country, generating 300 MW. The reservoir has an extension of 8600 km². The geology of the area is basically conformed of limestone and volcanic rocks. A few years ago the civil engineering department found that in the right side of the dam where the galleries are not concrete filled some infiltrations of water have begun, because of this and with the support of the IAEA in 2003 ENEE start a project named “Filtrations in the El Cajon Reservoir”. The main objective of the study was to know using hydro chemical and isotope techniques the origin of these filtrations, meanwhile the campaign covered piezometers and hydrometers all over the dam, which allows us to differentiate the main local water groups. The results show that the water of the filtrations on the right side galleries belongs to the reservoir, although the results of lower elevation of the dam indicate a different source of the water that probably belong to a regional aquifer. To have a better understanding of the hydrogeological behavior of the area is that in 2012, 7 meteoric water stations were installed all over the basin to evaluate the ¹⁸O and ²H contents with the main objective of establish the local meteoric water line.

1. INTRODUCTION

In the General Francisco Morazán hydropower plant known as El Cajón, in Honduras, Central America, the stable isotopes of ¹⁸O and ²H have been used since 2003 when the civil engineering department with the support of the IAEA started the Project “Filtrations in the El Cajon Reservoir” using hydrochemical and isotope techniques with the main objective of characterize the water flowing thru the filtrations in the right drainage gallery.

The stable isotopes of ¹⁸O and ²H in the water have been used as tracers to know the origin of groundwater. Its content depends on various factors and processes such as: the water history, the precipitation conditions, geographical and climatological factors, the evaporation processes, geothermal and metamorphic processes, and human activity.

Its content is expressed in ‰ respect to a global meteoric water line that has been defined by Craig (1961) as: $\delta^2\text{H} = \delta^{18}\text{O} + 10$. This value correspond to a global meteoric water line and is used worldwide as references to correlate information obtain of isotopic analysis, however this value change under different circumstances so it's different for every country and to each study area. This is why on 2012 it has been decided to installed 7 meteoric water stations all over the basin to evaluate ¹⁸O and ²H composition of the meteoric water with the objective of establish the local meteoric water line of El Cajón basin in Honduras.

2. METHODS

A monitoring network has been located all over the basin, the location of the stations was chosen according to general conditions as: facility of access, safety and care of the stations and the representativeness of the study area.

General information of the stations is shown in table 1 and the geographic location is shown on figure 1.

Table 1: General information of the sampling stations.

Station	Code	Elevation (masl)	East (m)	North (m)	Department
Los Planes	E1-PL	840	415161	1659626	Cortés
Puente Bailey	E2-PB	92	419865	1662308	Cortés
Puerto Escondido	E3-PE	769	423232	1662871	Yoro
Tapiquillares	E4-TA	429	414403	1652172	Cortés
Terreritos	E5-TE	485	423608	1657927	Comayagua
Cabecera	E6-CA	736	433011	1653397	Comayagua
Lajas	E7-LA	1.045	438194	1646539	Comayagua

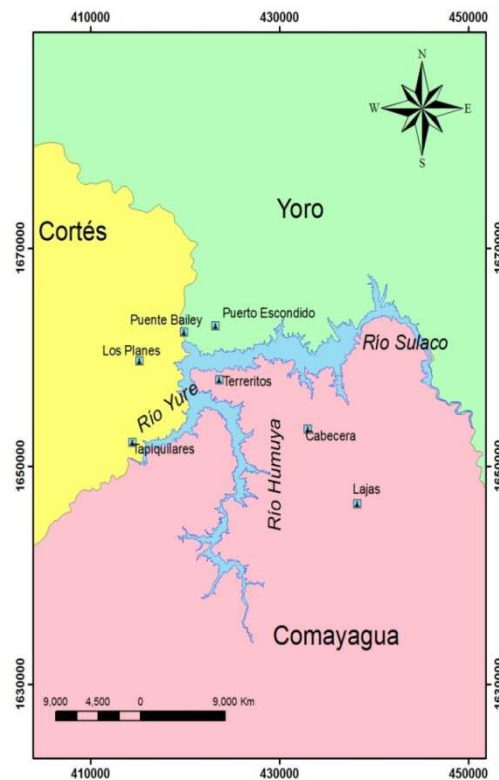
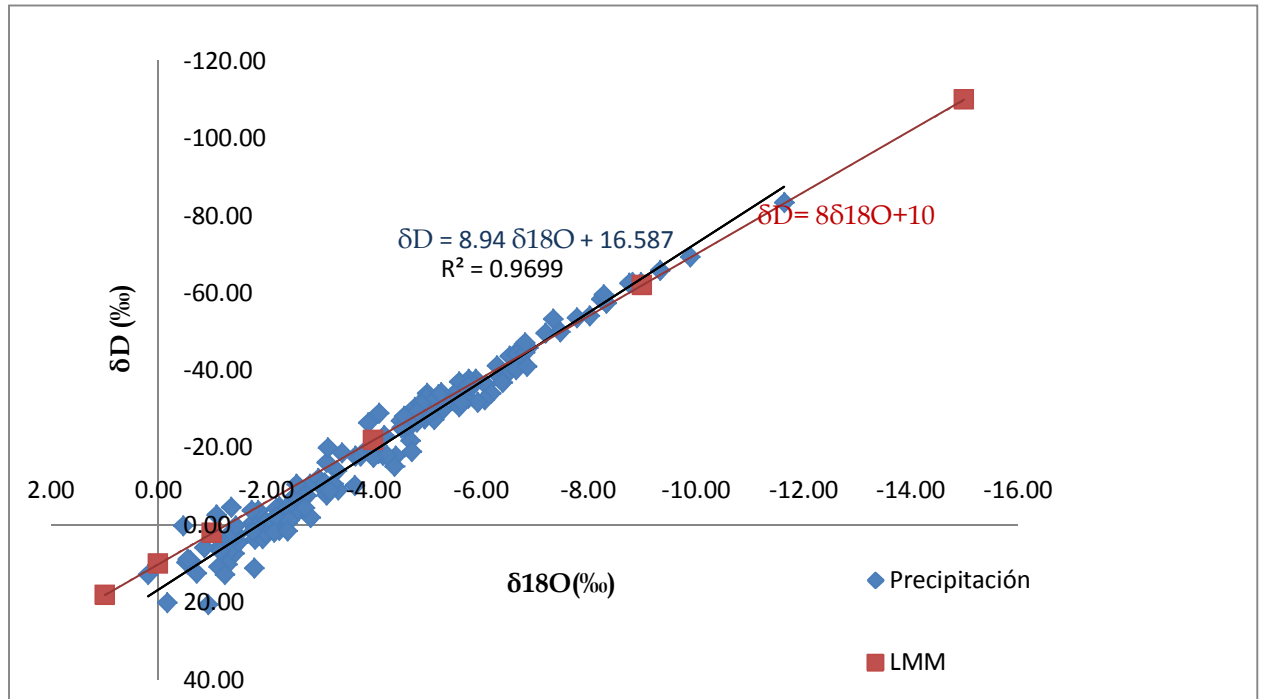


Figure 1: Geographical location of the stations.

3. RESULTS

The isotopic composition of the precipitation in the study area is under the range of 0.2 - -8.82 ‰ for the $\delta^{18}\text{O}$ and 20.9 - -59.54 ‰ for the $\delta^2\text{D}$. The equation of the local meteoric water line is:

$$\delta\text{D} = 8.94\delta^{18}\text{O} + 16.587$$



4. CONCLUSIONS

1. According to the results the dominant control on the temporal variations on rainfall is the precipitation amount, showing more negative values on humid station and more positive on the dry season.
2. The local meteoric water line moves above the global meteoric water line which according with Clark & Fritz is an indication that the moisture source of the study area has a humidity percentage lower than 50%.

REFERENCES

- [1] CLARK, I., & FRITZ, P., 1997: Environmental Isotopes in Hydrogeology. - 328 pages.

OF THE IMPORTANCE OF D-EXCESS IN UNDERSTANDING RECHARGE PROCESS IN TWO CASE STUDIES OF FRANCE

L. GOURCY¹, L. ARNAUD, D. SALQUEBRE
BRGM, Orleans, France
E-mail address: L.Gourcy@brgm.fr

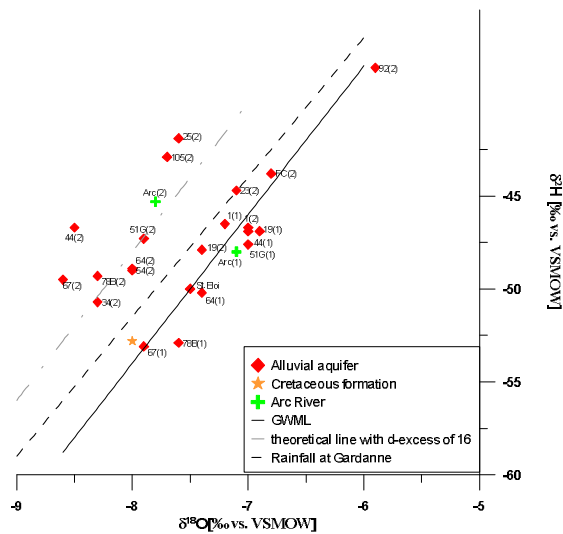
Abstract: Stable isotopes of water ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) are classical tools for determining hydrogeological parameters ea. recharge area, flow directions, groundwater-surface water exchanges, (Mook et al. 2008). However the successful use of the isotope techniques depends on local or regional hydrogeological characteristics. Meteorological and hydrological conditions leading to contrasting isotope composition of the water bodies are required.

The relation between these two elements in precipitation from various part of the world is $\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 10$. The so called Global Meteoric Water Line (GMWL) is characterised by a slope of 8 and an intercept with the ^2H axis of 10‰. This intercept is more generally called d-excess and may vary from 10 depending on the humidity and the temperature of the evaporation region. Then depending on the existing conditions during the formation of precipitation (=evaporation) and mostly at the site of sea-air interaction the d-excess may vary. The d-excess is then highly variable from one precipitation station of another and may reflect various so-called “effect” (continental, seasonal, altitude effects) as well as other processes such as re-evaporation of rain droplets. In two recent studies carried out in south of France and in the Martinique French overseas the d-excess has proven to be a valuable tool giving additional and more evident information than the stand alone $\delta^2\text{H}$ and $\delta^{18}\text{O}$.

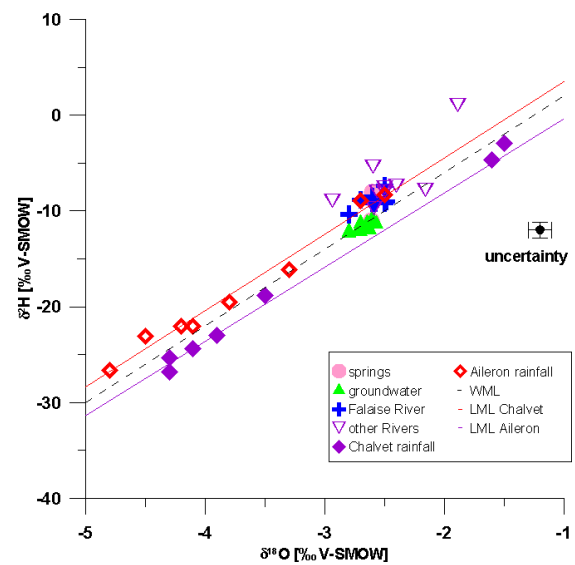
In Berre plain, near Marseille, two sampling campaigns were carried out in October and in April. Samples from the deep calcareous aquifer, the alluvial aquifer, the Arc River and the water supply channel were analysed for $\delta^2\text{H}$ and $\delta^{18}\text{O}$. The samples from October (1) plot quite well along the local precipitation line (Gardanne, Celle 2000) having a d-excess between 7.9 and 10‰. Part of the samples from the second sampling campaign (high stage water, 2 in the below figure) has a quite different d-excess, usually close to +16‰.

For the water having a similar d-excess in April and October, the aquifer is considered as less vulnerable as recharge process is quite slow. For the other points, as well as for the River Arc, the seasonal variation can be clearly seen showing high sensitivity to direct recharge processes (by surface water or precipitation).

At Martinique (French West Indies), a study was performed during a short period of time (Dec. 2011 up to August 2012). The sampling site, at the North-Eastern part of the island, covered a great part of the basin area of the Falaise River. Altitudes of the river basin range from 30m (Chalvet groundwater sampling points) up to 1230m (Pele Mountain). A difference in d-excess was observed between high altitude precipitation (Aileron, 800m) and low altitude rainfall (Chalvet, 30m) (see Figure). This was observed in the past for example by Gat and Dansgaard (1972) for the Jordan River System. This difference can be used to determine mean recharge altitude of groundwater and surface water basin in the studied site while $\delta^2\text{H}$ and $\delta^{18}\text{O}$ variation were more difficult to interpret.



Isotope composition of ground- and surface water collected in April and October in Berre plain (South of France)



δ^2H vs $\delta^{18}O$ at Falaise River Basin, Martinique

REFERENCES:

- [1] MOOK W.G. (2008) - Introduction to Isotope Hydrology - Stable and Radioactive Isotopes of Hydrogen, Oxygen and Carbon. International Association of Hydrogeologists/IAEA/UNESCO, Taylor&Francis/Balkema, 226p.
- [2] CELLE H. (2010) - Caractérisation des précipitations sur le pourtour de la Méditerranée occidentale. Approche isotopique et chimique, thèse, université d'Avignon, 222 p.
- [3] GAT J., DANSGAARD W. (1972) - Stable isotope survey of the fresh water occurrences in Israel and the Northern Jordan Rift System. Journal of Hydrology, 16, pp.177-212.

ID: 127

STABLE ISOTOPES IN PRECIPITATION ACROSS JAPAN BASED ON THE INTENSIVE OBSERVATION IN 2013

K. ICHIYANAGI,
Graduate School of Science and Technology,
Kumamoto University, 2-39-1 Kurokami, Kumamoto, Japan
E-mail address: kimpei@sci.kumamoto-u.ac.jp

M. TANOUE,
School of Engineering, The University of Tokyo, 2-11-16 Bunkyo-ku, Tokyo, Japan

T. YOSHIKUNI
Graduate School of Science and Technology, Kumamoto University, 2-39-1 Kurokami,
Kumamoto, Japan

Abstract: Spatial and seasonal variations of stable isotopes in precipitation across Japan were observed based on the intensive observation throughout 2013. Annual mean values in oxygen-18 show the strong altitude effect from -13‰ in the north part to -6‰ in the southwest part of Japan. Annual mean values in d-excess ranged from 7‰ in the southwest part to 22‰ in the northeast part of Japan. The d-excess values in the north part and along the Japan Sea coast are relatively higher than those along the Pacific coast of Japan. Monthly oxygen-18 values ranged from -15‰ to -5‰ and those values were relatively high in spring months and low in winter months. On the other hand, the monthly d-excess values show strong seasonal variations from 0‰ to 40‰ observed both in the north and southwest parts of Japan. Especially in the north part of Japan, monthly d-excess values were extremely high in the winter month.

1. INTRODUCTION

Stable isotopes in precipitation (oxygen-18 and deuterium) are useful natural tracers for understanding the hydrological cycle and reconstructing paleo-climates. There are a lot of observational studies of stable isotopes in precipitation in Japan [1, 2]. However, most observations on the local scale were conducted only one point or less than several points. Seasonal variation and spatial distribution of stable isotopes in precipitation across Japan was revealed by the integration of previous studies at 48 stations which observed within one year or less than several years in the different periods [3]. There have not been conducted precipitation samplings all across Japan during the same period. It means that the spatial and temporal variation of stable isotopes in precipitation across Japan is still not well understood. The Isotope Mapping Working Group of the Japanese Association of Hydrological Sciences (JAHS-IMWG) conducted the intensive observation of stable isotopes in precipitation across Japan throughout 2013 (IOP2013). In this study, seasonal variation and spatial distribution of oxygen-18 and d-excess more than 60 stations across Japan was shown from the preliminary result of the IOP2013.

2. METHODS

More than 100 stations all over Japan were conducted precipitation isotope sampling every 10 days to every month. Ball-in-funnel type collector was used to prevent evaporation in the plastic bottle. Isotope sampling points across Japan conducted in IOP2013 was shown in Figure 1. Precipitation sampling at 56 points were conducted in this study, but not conducted

at 5 points. Also precipitation sampling and analyzing stable isotopes were conducted at 39 points by other research projects and were conducted at 24 points by each university and/or institute. More than 2,000 water samples from more than 60 stations were collected and were analyzing oxygen-18 and deuterium values by using the Isotope Ratio Mass Spectrometer (Delta-V) in the Hydrology Laboratory of Kumamoto University. This is the first study that stable isotopes in precipitation were observed across Japan in the same period. Annual and monthly mean oxygen-18 and deuterium values were calculated weighted by the precipitation amount in each point.

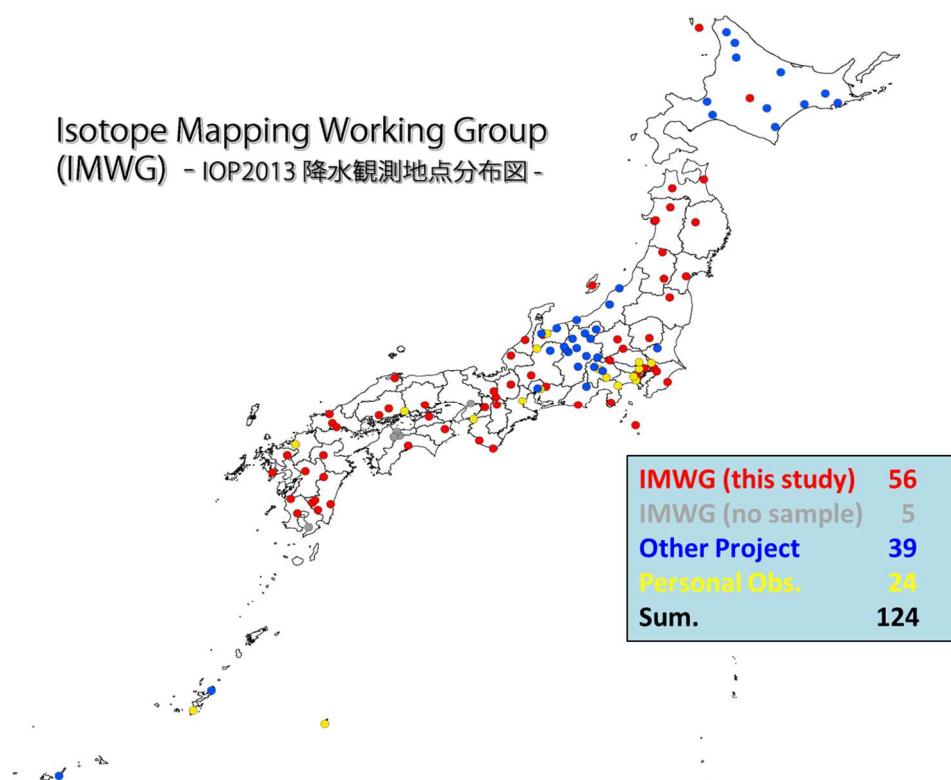


Figure 1. Locations of the isotope sampling points across Japan conducted in IOP2013.

3. RESULTS

Spatial distributions of annual mean values in Oxygen-18 and d-excess observed in the IOP2013 are shown in Figure 2. Annual mean values in Oxygen-18 show the strong altitude effect from -13‰ in the north part to -6‰ in the southwest part of Japan. The oxygen-18 values along the Pacific coast and the Japan Sea coast of Japan are more and less than -8‰, respectively. Annual mean values in d-excess ranged from 7‰ in the southwest part to 22‰ in the northeast part of Japan. The d-excess values in the north part and along the Japan Sea coast are relatively higher than those along the Pacific coast of Japan. The differences in d-excess values between the Pacific coast and the Japan Sea coast are mentioned in the previous studies [3].

Seasonal variations of monthly oxygen-18 and d-excess observed in the IOP2013 are shown in Figure 3. Stations located only in the northeast and southwest parts of Japan are shown in it. Most of the monthly oxygen-18 values ranged from -15‰ to -5‰ observed in the north part of Japan, and those values were relatively high in the spring months (March-June) and low in

the winter months (December to February). Most of the monthly Oxygen-18 values ranged from -10‰ to -5‰ in the southwest part of Japan, the seasonal variation is small. On the other hand, the monthly d-excess values show strong seasonal variations observed both in the north and southwest parts of Japan. Those values ranged from 0‰ to 40‰ in the north part and from 0‰ to 30‰ in the southwest part of Japan. Especially in the north part of Japan, monthly d-excess values were extremely high in the winter month (December to February). The high d-excess values are caused by the strong evaporation from the Japan Sea in the winter months [4].

4. CONCLUSIONS

This is the first study that stable isotopes in precipitation were observed more than 60 stations across Japan in the same period throughout 2013. Seasonal variation and spatial distributions of annual and monthly mean Oxygen-18 and Deuterium values were revealed. Annual mean values in Oxygen-18 show the strong altitude effect, while the d-excess values in the north part and along the Japan Sea coast are relatively higher than those along the Pacific coast of Japan. The monthly d-excess values show strong seasonal variations observed both in the north and southwest parts of Japan. Especially in the north part of Japan, monthly d-excess values were extremely high in the winter month.

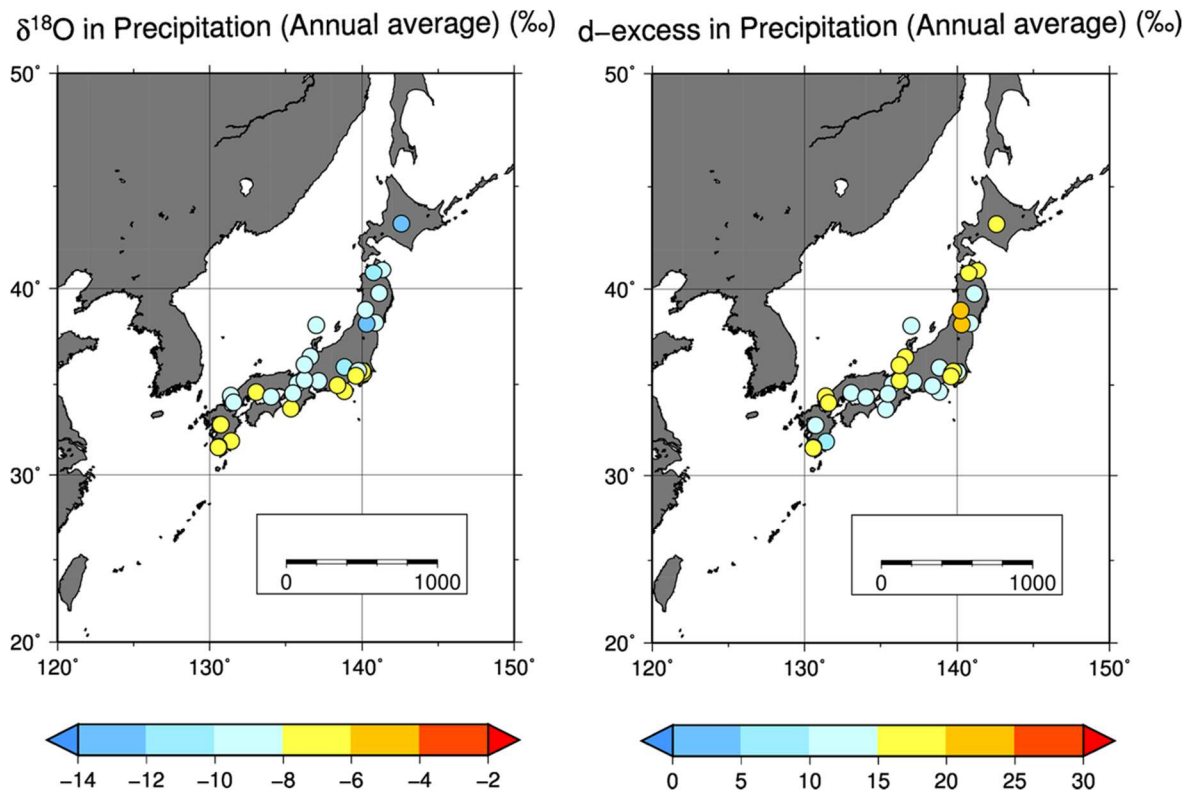


Figure 2. Spatial distributions of annual mean values in Oxygen-18 (left panel) and d-excess (right panel) observed in the IOP2013.

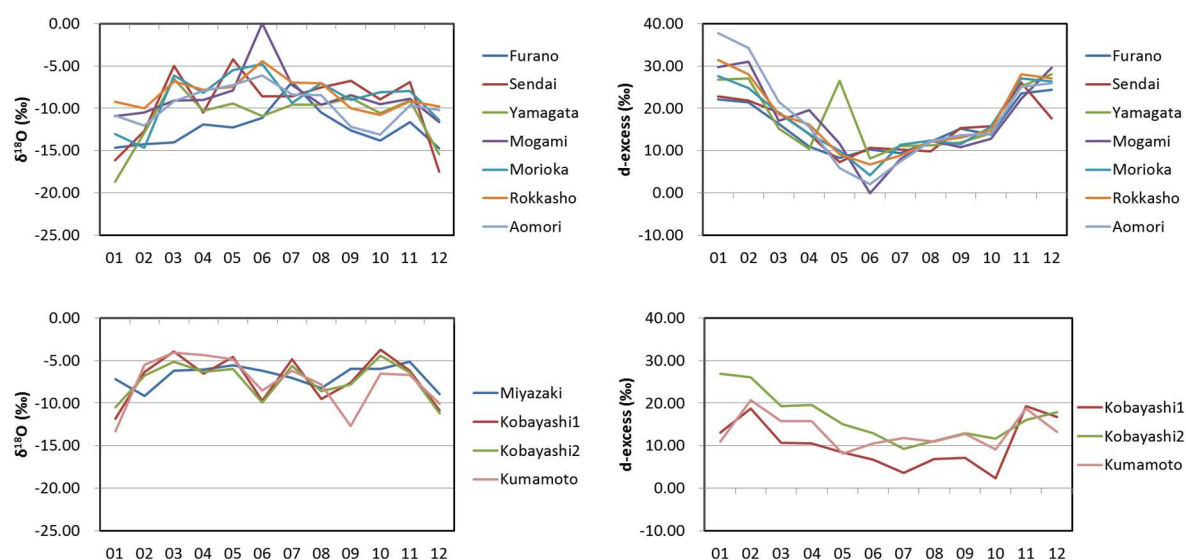


Figure 3. Seasonal variations of monthly Oxygen-18 (left panels) and d-excess (right panels) observed in the IOP2013. Stations located only in the northeast part (upper panels) and southwest part (lower panels) of Japan are shown in it.

REFERENCES

- [1] MATSUBAYA, O., KAWARAYA, H., Hydrogen and oxygen isotopic characteristics of precipitation in coastal areas of Japan determined by observations for 23 years at Akita and for 1–2 years at other several localities, *Geochem. J.* **48** (2014) 397-408.
- [2] HASEGAWA, H., AKATA, N., KAWABATA, H., SATO, T., CHIKUCHI, Y., HISAMATSU, S., Characteristics of hydrogen and oxygen stable isotope ratios in precipitation collected in a snowfall region, Aomori Prefecture, Japan, *Geochem. J.*, **48** (2014), 9-18.
- [3] TANOUE, M., ICHIYANAGI, K., SHIMADA, J., Seasonal variation and spatial distribution of stable isotopes in precipitation over Japan, *Jap. Assoc. Hydrol. Sci.*, **43** (2013) 73-91. (in Japanese)
- [4] WASEDA, A., NAKAI, N., Isotopic compositions of meteoric and surface waters in Central and Northeast Japan, *Chikukagaku*, **17** (1983) 83–91. (in Japanese)

STABLE ISOTOPES IN PRECIPITATION IN ROMANIA – A FIRST OVERALL MAP

A. PERSOIU, V. NAGAVCIUC, C. BADALUTA,
Stefan cel Mare University Suceava, Romania
E-mail address: aurel.persoiu@gmail.com

Abstract: Stable isotopes in precipitation in Romania have been measured only sporadically with no long-term monitoring project existing so far. Here we present the results of a 3-year, ongoing, monitoring study of stable isotope distribution in precipitation in 20 stations from Romania (East-Central Europe), spread throughout the country, at altitudes between 0 and 1150 m a.s.l. The general Meteoric water line is described by the equation $\delta^2\text{H} = 7.7 \cdot \delta^{18}\text{O} + 6.9$. The monthly $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values range between -12 and -6 ‰, and -40 and -90 ‰, respectively, being higher at high altitudes and in NW Romania, and lower in the W and SE Romania. No clear continentality trend could be discerned in the distribution of $\delta^{18}\text{O}$ and $\delta^2\text{H}$. Altitude, latitude and local factors (rain shadow, foehn effects, high evaporative plains) seems to be the most important factors in the spatial pattern of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ distribution. While most of the precipitation is derived from moisture originating in the North Atlantic, SW Romania receives supplemental amounts of precipitation from the Eastern Mediterranean, as clearly seen in the higher than average (16-18‰, compared to ~10‰) d-excess values in precipitation from this region (mainly during the autumn and early winter months).

ID: 149

WATER VAPOR AND PRECIPITATION ISOTOPE VARIABILITY ASSOCIATED WITH WESTERN TROPICAL PACIFIC CONVECTIVE STORMS

J.L. CONROY,

Department of Geology, Department of Plant Biology, The University of Illinois Urbana-Champaign, 605 E Springfield Ave, Champaign, IL, United States of America

E-mail address: jconro@illinois.edu

K.M. COBB,

School of Earth and Atmospheric Sciences, Georgia Institute of Technology, 311 Ferst Dr, Atlanta, GA, United States of America

D. NOONE

College of Earth, Ocean, and Atmospheric Sciences, Oregon State University, 101 SW 2th St, Corvallis, OR, United States of America

Abstract: Understanding the controls on the stable isotopic composition of water in the west Pacific warm pool is vital for accurate representation of convective processes in climate models and accurate interpretation of the numerous water isotope-based paleoclimate proxies located in this region. Measurements of the stable isotopic composition of precipitation and water vapor at Manus Island (2.06°S, 147.42°E, 4 meters above sea level) in April-May 2013 show that at the sub-event scale, precipitation isotope values are strongly correlated with surface vapor isotope values. Vapor and precipitation isotope values progressively increased throughout the period of measurement, coincident with a transition from a period of low to high Madden Julian Oscillation values. Vapor isotope values approached calculated values of vapor in equilibrium with seawater during the quiescent part of the measurement campaign. Abrupt drops in vapor and precipitation isotope values lag behind maximum precipitation rates, although precipitation d-excess values were related to humidity, surface temperature and cloud base height. Our results support the interpretation of western tropical Pacific water isotope values as indicators of large-scale convective activity and conditions at the moisture source and condensation height.

1. INTRODUCTION

High-frequency precipitation isotope measurements through individual events are extremely useful for parsing convective processes and provide useful information on isotopic exchange between vapor and precipitation, precipitation height, and intraseasonal oscillations [1-3]. Coupled vapor-precipitation datasets through individual storms, which are becoming more common with new technology [3-4], can provide even more insight into the microphysical processes that define convective activity in observations, isotope-based paleoclimate records, and model simulations. Ultimately, the hope is that paleo and present-day isotopic data can be used to improve model simulations of convection, a source of uncertainty in future hydroclimate projections [5]. Here we present the results of paired vapor-precipitation measurements through 7 rain events on Manus Island, Papua New Guinea. Manus, a small island in the heart of the west Pacific warm pool, the world's largest zone of deep convection [6] is ideally situated to investigate convective processes, as atmospheric measurements taken here reflect regional, oceanic conditions [7].

2. METHODS

We measured the stable isotopic composition of near-surface water vapor and precipitation at the highly instrumented U.S. Department of Energy Atmospheric Radiation Management (ARM) facility on Manus Island from April 28 to May 8, 2013. Vapor measurements were performed on a Picarro L1102-*i* water isotope analyzer. Heated copper tubing drew ambient air from a height of 3m into the instrument at a rate of 1 L/minute. Resulting data are reported in 10 minute averaged intervals. A total of 162 precipitation samples were collected at timed intervals throughout 7 rain events. All samples were taken immediately and sealed in 3.5mL crimp top vials. Precipitation samples were measured on a Picarro L2120-*i* water isotope analyzer. Each instrument was calibrated with NIST-VSMOW, NIST-GISP, and NIST-SLAP and three internal lab standards. Cross-instrument calibration indicates no instrument-specific isotopic offsets in the calibrated results. Precision is 0.1‰ for $\delta^{18}\text{O}$ and 1.0‰ for δD values. Memory and drift corrections were applied using internal standards. Isotope data were then compared to surface meteorological data, including temperature, relative humidity, vapor mixing ratios, precipitation rate, wind speed and direction, pressure, and cloud base height.

3. RESULTS

Mean δD_v values of near-surface water vapor (δD_v) were $-108.6 \pm 39.3\text{‰}$ during the period of measurement, ranging from -224.9‰ to -71.0‰ . A gradual transition from lower to higher δD_v values over time coincided with a transition through a Madden-Julian Oscillation event into a quiescent period, when measured δD_v was equilibrium with seawater δD . Of all surface meteorological variables, δD_v was most strongly correlated with specific humidity ($r=0.67$, $N=1407$, $p<0.001$). During precipitation events, δD_v dropped abruptly following maximum precipitation rates, then gradually returned to pre-event values.

Intra-event δD values of precipitation (δD_p) were most strongly correlated with δD_v ($r=0.98$, $N=50$, $p<0.001$) and only weakly correlated with surface meteorological variables. We did not observe an amount effect through all precipitation events, as the lowest δD_p values often lagged maximum rain rates. Precipitation deuterium excess (d-excess) values were significantly correlated with surface relative humidity ($r=0.54$, $N=50$, $p<0.001$) and temperature ($r=-0.44$, $N=50$, $p<0.001$), as well as cloud base height measurements ($r=0.61$, $N=28$, $p<0.001$), with higher d-excess values corresponding to higher cloud altitudes (Figure 1).

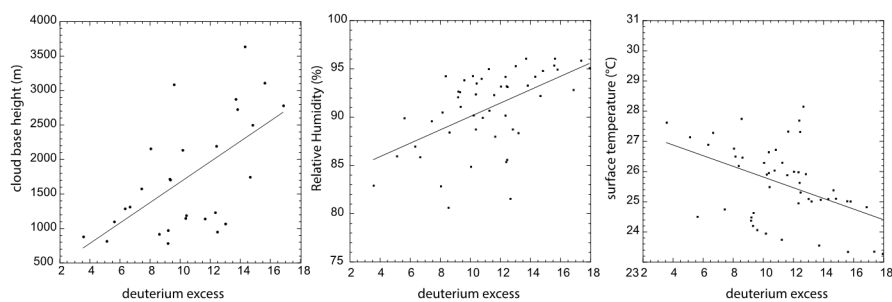


Figure 1: Precipitation d-excess versus cloud base height (left), surface relative humidity (middle) and surface temperature (right).

4. CONCLUSIONS

Our data suggest that δD_v and δD_p are tightly linked on event timescales. The lagged relationship between δD_v , δD_p and precipitation rate highlights the importance of rain evaporation and mesoscale subsidence in controlling vapor and precipitation isotope values. Low δD_v and δD_p values coincident with the passage of an MJO event support the interpretation of δD_p values as a proxy for large-scale convective activity in the western Pacific [8]. The lack of a local ‘amount effect’ at sub-monthly timescales also supports recent findings elsewhere in the western tropical Pacific [8-10]. However, at the intraevent timescale, precipitation d-excess responds to both variability in climate at the moisture source as well as processes related to condensation.

REFERENCES

- [1] MIYAKE, Y., MATSUBAYA, O., NISHIHARA, C. An isotopic study on meteoric precipitation. *Papers in Meteorology and Geophysics* **19** (1968) 243-266.
- [2] COPLEN, T.B. et al. Extreme changes in stable hydrogen isotopes and precipitation characteristics in a landfalling Pacific storm. *Geophysical Research Letters* **35** (2008) doi:10.1029/2008GL035481.
- [3] KURITA, N. et al. Intraseasonal isotopic variation associated with the Madden Julian Oscillation. *Journal of Geophysical Research-Atmospheres* **116** (2011) doi: 10.1029/2010JD015209.
- [4] TREMOY, G. et al. A 1-year long delta O-18 record of water vapor in Niamey (Niger) reveals insightful atmospheric processes at different timescales. *Geophysical Research Letters* **39** (2012) doi:10.1029/2012GL051298
- [5] RYBKA, H., TOST, H. Uncertainties in future climate predictions due to convection parameterisations. *Atmospheric Chemistry and Physics*, **14** (2014) 5561-5576.
- [6] CHIANG, J.C.H. The Tropics in Paleoclimate. *Annual Review of Earth and Planetary Sciences* **37** (2012) 263-297.
- [7] RIIHIMAKI L.D. and LONG, C.N. Spatial variability of surface irradiance measurements at the Manus ARM site. *Journal of Geophysical Research-Atmospheres*, **119** (2014) 5475-5491.
- [8] KURITA, N. et al. The relationship between the isotopic content of precipitation and the precipitation amount in tropical regions. *Journal of Geochemical Exploration*, **102** (2009) 113-122.
- [9] MOERMAN, J.W. et al. Diurnal to interannual rainfall $\delta^{18}O$ variations in northern Borneo driven by regional hydrology. *Earth and Planetary Science Letters*, **369-370** (2013) 108-119.
- [10] CONROY, J.L., COBB, K.M., NOONE, D. Comparison of precipitation isotope variability across the tropical Pacific in observations and SWING2 model simulations. *Journal of Geophysical Research-Atmospheres* (20013) 1-26.

ID: 158

THE TRANSFER OF THE ISOTOPE SIGNAL IN PRECIPITATION TO SURFACE WATER AND GROUNDWATER IN SWITZERLAND

U. SCHOTTERER,

Climate and Environmental Physics, Physics Institute, University Bern,
Sidlerstrasse 5, 3012 Bern, Switzerland.

E-mail address: schotterer@climate.unibe.ch

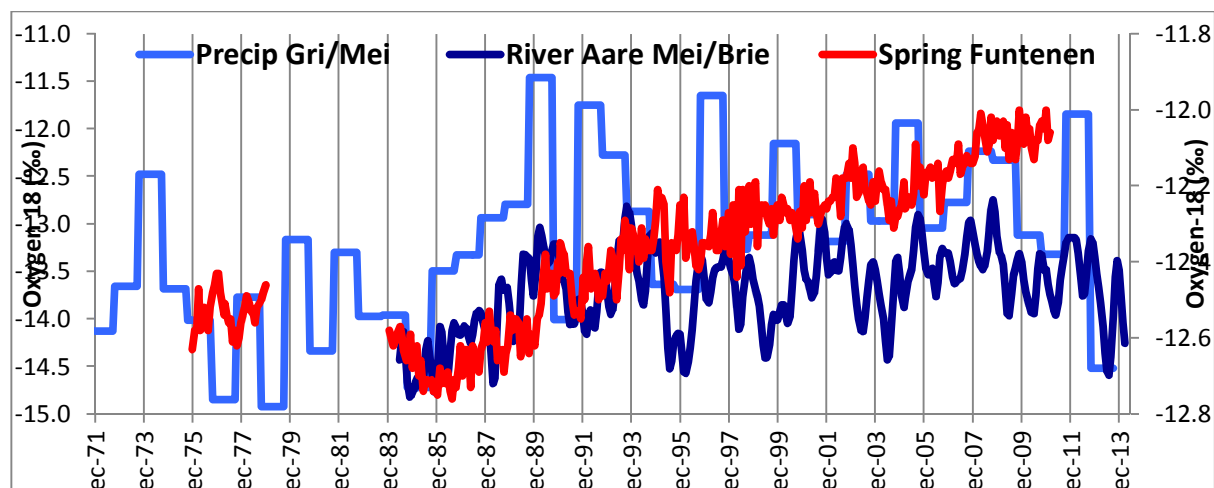
R. KOZEL, M. SCHÜRCH

Federal Office for the Environment, Papiermühlstrasse 172, 3063 Ittigen, Switzerland.

R. RICKLI

Geographic Institute, University Bern, Hallerstrasse 12, 3012 Bern, Switzerland.

Abstract: The stable water isotopes in precipitation transfer area-wide hydro-climatic changes to surface water and groundwater. Regular data collection started in 1971. Today the isotope network of the Swiss Federal Office for the Environment provides data from precipitation, river, and groundwater from important hydro-climatic regions for scientific and public use. Precipitation stations, although limited in number, are situated close to stations of the Swiss National Basic Climatological Network [1]. Despite differences in altitude and seasonality the monthly δ -values are fairly well correlated, thus allowing the estimation of regional δ -input data. The longest time series capture the warming trend since the early 1980s; however, during the last decade this trend has changed. On a seasonal basis the air masses contributing moisture originate from different oceanic and continental sectors and this mix may have changed [2, 3], with consequences for using δ -values as temperature proxies, although this does not affect the use of the δ -values as natural tracer input data for hydrogeological studies. In addition, the spot collection of these precipitation data is confirmed by the corresponding river runoff δ -values that integrate large regional areas. In Figure 1 we present an example of combined precipitation – river – spring data from the alpine area of the Berner Oberland. Precipitation data are mean amount-weighted yearly averages from Meiringen (600 masl) and Grimsel (1950 masl) to better characterize the supposed recharge area of the Spring Funtenen and to account for the recharge of the spring. River and spring data are low-pass filtered to smooth variability in the spot measurements and to pronounce the seasonal variations according to snow melt (one to two samples per month). The river data also average two stations approximately 10 km apart. Both precipitation and river δ -values, scaled on the left side of the graph, depict the increase in the 1980s, followed by a high inter-annual variability. As mentioned, during the last decade the trend seems to reverse to more negative values, especially in winter, in contrast to the generally rising δ -values from Funtenen spring scaled on the right side of the graph. This steady increase probably indicates a large reservoir and the isotope data may be used as boundary conditions for model considerations. In the paper we will present more details together with similar examples from other Swiss regions.



REFERENCES

- [1] BEGERT, M., Die Repräsentativität der Stationen im Swiss Basic Climatological Network (Swiss NBCN), Arbeitsberichte der MeteoSchweiz, **217** (2008)
- [2] SCHOTTERER, U., SCHÜRCH, M., RICKLI, R., STICHLER, W., Wasserisotope in der Schweiz, neue Ergebnisse und Erfahrungen aus dem nationalen Messnetz ISOT, (2010). gwa 12/20/10.
- [3] SODEMANN, H., ZUBLER, E., Seasonal and inter-annual variability of the moisture sources for Alpine precipitation during 1995-2002, *Int. J. Climatol.* 30 (2010) 947-

ID: 202

ISOTOPIC STUDY OF RAINFALL IN DOUALA-CAMEROON (GNIP STATION NO. 6491001)

C. KETCHEMEN TANDIA, B. Y. NLEND, S.. NGO BOUM NKOT, H. EMVOUTOU,
The University of Douala, Douala, Cameroon
E-mail address: beatrice_tandia@yahoo.fr

Abstract: A study of ^{18}O and ^2H isotopes in the monthly rainfall in Douala (GNIP station No. 6491001) was conducted from July 2006 to December 2012. The ultimate goal, to get the isotopic signature of rainwater that infiltrate in groundwater. This can also be used to improve atmospheric circulation models applied in the study of climate change. The data obtained from the analyses of ^{18}O and ^2H isotopes of rainwater yielded a local Meteoric Water Line (MWL) with d-excess values of 11‰ that fall between the Atlantic (10‰) and western Mediterranean (14‰) values. The isotopes in meteoric water are influenced by heavy rainfall values ($>3471\text{mm/year}$) in the Douala area, typical of the Equatorial rainforest zone. Mass effect is also noticed to show two trends, however, temperature show insignificant effects on the isotopic composition in the precipitations. This can be explained by low thermal variations observed in Douala. Despite the heavy rainfall the $\delta^{18}\text{O}$ -values of the rainwater still follow a seasonal trend with a maximum in February (-0.22‰) related to high temperatures observed at this time of the year (dry season) and a minimum in October (-4.75‰) which corresponds to the end of the rainy season, and a change in the wind direction.

The deuterium-excess values obtained permitted an identification of the air masses that causes rain events in the Douala area. Using the Inter-tropical Convergent Zone and the stable isotopes in the rainwater we noted the influences of the African Easterly Jet (SE trade wind) and the Tropical Easterly jet (NE trade wind).

Four different stations within the Gulf of Guinea, show large differences in d-excess values ranges from 11‰ to 13‰, indicating the influence of local geographic factors.

ID: 207

SPATIAL AND TEMPORAL VARIABILITIES IN STABLE ISOTOPE COMPOSITIONS OF PRECIPITATION AND AIR MOISTURE SOURCES IN HUNGARY

G.Y. CZUPPON

Institute for Geological and Geochemical Institute, Hungarian Academy of Sciences, H-1112 Budapest, Budaörsi út 45, Hungary.

E-mail address: czuppon@geochem.hu

E. BOTTYÁN, T. WEIDINGER

Department of Meteorology, Eötvös Loránd University, H-1117 Budapest, Pázmány P. sétány 1/A, Hungary.

K. KÁRMÁN

Institute for Geological and Geochemical Institute, Hungarian Academy of Sciences, H-1112 Budapest, Budaörsi út 45., Hungary.

L. HASZPRA

Geodetic and Geophysical Institute, Hungarian Academy of Sciences, H-9400 Sopron, Csatkay Endre u. 6-8., Hungary.

Abstract: This study evaluates the regional differences in stable isotope compositions of precipitation in the Pannonian Basin based on hydrogen and oxygen isotope analyses of daily rainwater samples collected in seven distinct meteorological stations in Hungary (Farkasfa, Kecskemét, Szeged, Pécs, Kékes, Budapest, Siófok) since April 2012. Thus, this work provides the first “comprehensive map” of isotopic composition of precipitation for Hungary. Additionally, we present an investigation about the determination of air moisture source regions for each location during the studied period. To reconstruct the path of the air moisture from the source region, we ran the NOAA HYSPLIT trajectory model using the GDAS database with 1° spatial and 6 hours temporal resolution for every precipitation event, for heights of 500, 1500 and 3000 m. We determined the location where water vapor entered into the atmosphere by calculating specific humidity along the trajectories. Five possible moisture source regions for precipitation were defined: Atlantic, North European, East European, Mediterranean and continental (local/convective).

Stable isotope variations show systematic and significant differences between the regions, especially large differences in the local meteoric water line were observed between the stations in West and East Hungary. The variability of moisture source shows also systematic distribution. Interestingly, the most dominant among the identified source regions in all stations is the Mediterranean area; while the second is the Atlantic region. The ratio of the precipitations originated in Eastern and Northern Europe seem to correlate with the geographic position of the meteorological station. Additionally, the ratios of the different moisture sources show intra annual variability. In each location, the amount weighted d-excess values were calculated for the identified moisture sources. The precipitation originated in the Mediterranean regions has systematically higher d-excess values than that originated in the Atlantic sector, independently from the absolute value which apparently changes from station to station. The precipitation fraction attributed to the Northern European sector has also relatively elevated d-excess values that might be related to the cold-season domination of moisture transport from this region.

RCWIP2 – AN IMPROVED REGIONALIZED CLUSTER-BASED PRECIPITATION ISOSCAPE ($\delta^{18}\text{O}$, $\delta^2\text{H}$)

S.TERZER, L.I.WASSENAAR, L. ARAGUÁS-ARAGUÁS

Isotope Hydrology Section, International Atomic Energy Agency, Vienna, Austria

E-mail address: s.terzer@iaea.org

Abstract: For 20 years, isoscapes (high-resolution gridded spatial datasets of precipitation isotopes) have been used for numerous hydrological, climatological and ecological studies. Prediction models combining multiple regression and subsequent interpolation of the residuals remain the state-of-the-art technique for isoscape generation at global and regional level, yet suffer from constraints imposed by either a global parameter forcing, or a reduction of the geographical domain. Bridging the gap between these two approaches, a regionalized prediction model framework was previously developed based on fuzzy climatic clusters (RCWIP). Here we present improvements to the existing approach, including an expansion of the models application domain using the most up-to-date data from the Global Network of Isotopes in Precipitation (GNIP), and advanced regression selection based on the Akaike's Information Criterion (AIC).

1. INTRODUCTION

The Global Network of Isotopes in Precipitation (GNIP, [1]), a joint endeavour pioneered by the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO) and currently in its 6th decade of operation, continues to be an indispensable source of basic data for stable ($\delta^{18}\text{O}$, $\delta^2\text{H}$) isotope ratios in global precipitation for various disciplines. However, due to the inherent spatial disparities of GNIP sampling station coverage, and since the provision of precipitation samples or isotope data by governmental or academic institutions is voluntary, large spatial and or temporal gaps are found inherent to the GNIP database (e.g. [2], [3]). To help overcome these spatial gaps, a number of prediction techniques were employed, including simple interpolation (e.g. [4]), Cressman objective analysis ([5]), and finally models combining multiple regression and subsequent interpolation of the residuals (e.g. [6], [7]). The variety of models has quickly amplified, establishing isoscapes for specific regions (incorporating regionally specific corollaries, e.g. [8], [9], [10], and [11]) or particular elements of the water cycle (e.g. groundwater, cf. [2], [12] or [13]). Any of these models suffers from either a global parameter forcing ignoring e.g. regionally differing altitudinal gradients (cf. [14]), or from a constrained spatial domain limiting its applicability to other parts of the world.

In [15] we sought to bridge the gap between regional and global models by establishing a regionalization framework based on like climatic clusters with fuzzy boundary delineation [16], resulting in 36 distinctive regions. For these climatic clusters, specific regression equations were derived based on multi-annual means of monthly and annual precipitation $\delta^{18}\text{O}$ and $\delta^2\text{H}$ GNIP data against an array of available spatial and climatic covariates, through automated testing of their combinations and ranking them by their coefficient of determination (R^2). Residuals of the best-performing regression equations were weighted according to their cluster membership and subsequently interpolated onto the regression surface, resulting in significantly improved kriging performance indicators and overall reduced interpolation uncertainty compared to previous globally parameterized approaches. The resulting isoscape grids reasonably reproduced the global $\delta^{18}\text{O}$ and $\delta^2\text{H}$ distribution in

modern precipitation; however, preliminary efforts to compare the resulting isoscape grids to established proxy datasets (e.g. shallow groundwaters) as well as to downscale the approach to regional patterns, occasionally resulted in diverging trends for the two isotopic species, particularly exemplified by the 2nd-order parameter of d excess [17].

Here we attempt to remediate these deficiencies by establishing a more robust selection of covariate combinations using Akaike's Information Criterion (AIC, [18]). In addition to that, new isotopic data were added for some regions previously not sufficiently covered by the RCWIP model could now be predicted using regionalized regressions (as opposed to the 2009 snapshot used in [15]). Additional data was derived from concerted efforts over the past few years to improve the GNIP spatial coverage [19].

2. METHODS

While globally parameterized or regional multiple regression based prediction models can be built with a fairly small number of regressors, RCWIP required the testing of almost 20,000 combinations of dependent and explanatory variables for their suitability. This task was performed using the R statistical computing language [23]. Previously, regressor combinations were considered to be useful only if they had an $R^2 > 0.50$ and the ratio of the remaining degrees of freedom and the number of regressors used were > 7.5 ; from which the combination with the highest R^2 was chosen as the best model. The computations were run separately for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, which was subsequently identified as one factor contributing to the partial divergence of the two isoscapes since it was possible that $\delta^{18}\text{O}$ and $\delta^2\text{H}$ predictions could be based on slightly different regression equations. To address this statistical vulnerability, additional statistical assessments were implemented in the regression decision tree, including but not limited to AIC. Moreover, automated regression selections were conducted for both isotopic species simultaneously, tightly coupling the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isoscapes and rejecting a covariate combination if the discrepancy of any statistical testing was more than 10 % between the two isotopes. Hypothesizing that this approach would result in a reduced number of erroneous d excess patterns, we examined the deviation of the predicted deuterium excess \hat{d} from the observed for both the previous and the current methods using the Root Mean Square Error (RMSE) as simple diagnostics tool.

3. RESULTS

As a new benchmark for the improvement of RCWIP regression selection, we present improved RMSE statistics for a substantial number of RCWIP cluster-month-species combinations. It must be kept in mind that smaller residuals result in a lower kriging sill, which is one of the driving parameters for the interpolation uncertainty. Notwithstanding ongoing discussions about the uncertainty quantification of isoscapes (cf. [24]), the reduction of *any* uncertainty component of isoscape grids can be considered as desirable.

REFERENCES

- [1] INTERNATIONAL ATOMIC ENERGY AGENCY / WORLD METEOROLOGICAL ORGANIZATION, Global Network of Isotopes in Precipitation. The GNIP Database. Available via <http://www.iaea.org/water> (2014)
- [2] WASSENAAR L.I. et al., A groundwater isoscape (δD , $\delta^{18}\text{O}$) for Mexico, *J. Geochem. Explor.* 102, 123-136 (2009)
- [3] BOWEN, G.J., Statistical and geostatistical mapping of precipitation water isotope ratios, in: WEST, J.B. et al., *Isoscapes: Understanding movement, pattern, and processes on Earth through isotope mapping*, Springer, London, 139-178 (2010)

- [4] YURTSEVER, Y. and J.R. GAT: Atmospheric Waters, in: GAT, J.R. and R. GONFIANTNI, Stable Isotope Hydrology (Tech. Rep. Series 210), International Atomic Energy Agency, Vienna, 103-142 (1981).
- [5] BIRKS, S. et al., Maps and animations offer new opportunities for studying the global water cycle, EOS T. Am. Geophys. Un., 83, 406 (2002)
- [6] BOWEN, G.J. and B.M. WILKONSON, Spatial distribution of $\delta^{18}\text{O}$ in meteoric precipitation, Geology, 30, 315-318 (2002)
- [7] BOWEN, G.J. and J. RVENAUGH, Interpolating the isotopic composition of modern meteoric precipitation, Water Resour. Res., 39, 1299 (2003)
- [8] LIEBMINGER A. et al., Correlation of the isotopic composition in precipitation with local conditions in alpine regions, J.Geophys.Res., 111, D05104 (2006)
- [9] LYKOUDIS, S. P. and A.A. ARGIRIOU, Gridded data set of the stable isotopic composition of precipitation over the eastern and central Mediterranean, J.Geophys.Res.-Atmos., 112, D18107 (2007).
- [10] LIU, Z. et al., A model-based determination of spatial variation of precipitation $\delta^{18}\text{O}$ over China, Chem. Geol., 249, 203–212 (2008)
- [11] DELAVAU, C., T. STADNYK and J. BIRKS, Model Based Spatial Distribution of Oxygen-18 Isotopes in Precipitation Across Canada, Can. Water Resour. J., 36, 313–330, (2011)
- [12] WEST, A.G., E.C. FEBRUARY, and G.J. BOWEN, Spatial analysis of hydrogen and oxygen stable isotopes (“isoscapes”) in ground water and tap water across South Africa, J. Geochem. Explor., 145, 213-222 (2014)
- [13] MEZGA, K., J. URBANC and S. CERAR, The isotope altitude effect reflected in groundwater: a case study from Slovenia, Isot. Env. Health Stud., 50 (1), xx-xx, (2014)
- [14] POAGE, M.A. and C.P. CHAMBERLAIN, Empirical Relationships between Elevation and the Stable Isotope Composition of Precipitation and Surface Waters: Considerations for Studies of Paleoelevation Change, Am. J. Sci., 301, 1-15 (2001)
- [15] TERZER, S. et al., Global isoscapes for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in precipitation: improved prediction using regionalized climatic regression models, Hydr. Earth Sys. Sci., 17, 4713-4728 (2013)
- [16] BEZDEK, J.: Pattern Recognition With Fuzzy Objective Function Algorithms, Plenum, New York, (1981)
- [17] DANSGAARD, W.: Stable isotopes in precipitation, Tellus, 5, 436–468 (1964).
- [18] BURNHAM, K.P. and D.R. ANDERSON, Model selection and inference: a practical information-theoretic approach. Springer-Verlag, New York, 353 pp. (1998)
- [19] TERZER, S. et al., "GNIP meets WISER" - Recent developments and data dissemination in the Global Network of Isotopes in Precipitation (working title, this symposium)
- [20] DUTTON, A. et al., Spatial distribution and seasonal variation in $^{18}\text{O}/^{16}\text{O}$ of modern precipitation and river water across the conterminous USA, Hydrol. Process., 19, 4121–4146 (2005)
- [21] HALDER, J. et al., The Global Network of Isotopes in Rivers (GNIR) - global spatial and temporal patterns of riverine stable water isotopes (working title, in preparation)
- [22] JASECHKO, S. et al., The pronounced seasonality of global groundwater recharge, Wat. Resour. Res. (accepted manuscript, 2014)
- [23] R DEVELOPMENT CORE TEAM, R: A language and environment for statistical computing, R Foundation for Statistical Computing, Vienna, available at: <http://www.R-project.org/> (2014).
- [24] BOWEN, G.J. et al., Leveraging GNIP and investigator research to map isotopic climate: Two decades of precipitation isoscapes (working title, submitted to this symposium)

ID: 231

RECENT DEVELOPMENTS IN THE GLOBAL NETWORK OF ISOTOPES IN PRECIPITATION

S. TERZER, L. ARAGUAS,

Isotope Hydrology Section, International Atomic Energy Agency, Vienna, Austria\

E-mail address: S.terzer@iaea.org

A. PUCHER, K. KRIZ

Dept. of Geography & Regional Research, University of Vienna, Vienna, Austria

Abstract: For more than five decades, the Global Network of Isotopes in Precipitation (GNIP) has been a unique source of baseline data for stable ($\delta^{18}\text{O}$, $\delta^2\text{H}$) and radioactive (^3H) isotope ratios in global precipitation, with an increasing variety of applications in numerous disciplines. New and less resource-intensive analytical techniques on one side and the growing demand for up-to-date isotope data on the other side impose new challenges for the operation of the GNIP, but also for the data dissemination cyberinfrastructure. The Water Isotope System for Data Analysis, Visualization and Electronic Retrieval (WISER), a web-based platform for geospatial presentation and distribution of GNIP data, has been in operation since 2004 and has been subject to a major technical overhaul based on a recently conducted user survey. Here we present both a status update concerning the coverage of the GNIP, highlighting recent developments, as well as the renewed WISER platform, which excels with a modernized interface and shorter update intervals.

ID: 253

VARIOGRAM ANALYSIS OF PRECIPITATION $\delta^{18}\text{O}$ IN THE GREAT ALPINE REGION - IMPLICATIONS FOR ISOSCAPE MODELING

Z. KERN,

Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, MTA, Budaörsi út 45, H-1112 Budapest, Hungary

E-mail address: kern@geochem.hu; zoltan.kern@gmail.com.

B. KOHÁN, A. CZINDER, D. CSONKA

Eötvös University, Pázmány sétány 1/c, H-1117, Budapest, Hungary

M. LEUENBERGER

University of Bern, Physics Institute, Climate and Environmental Physics, Sidlerstrasse 5 and Oeschger Centre for Climate Change Research, Falkenplatz 16, CH-3012, Bern, Switzerland

Abstract: An accurate picture of the spatial distribution of water stable isotopes of modern precipitation is a crucial prerequisite for many hydrological, ecological and paleoclimatological applications. The main aim of our research is to develop a gridded data set of monthly stable oxygen isotope composition of precipitation ($\delta^{18}\text{O}_p$) for the Alps and the adjacent regions. However, as a pre-processing step, it is necessary to assess the spatial dependence structure of the isotopic parameters of the Alpine precipitation in order to tune the interpolation method to improve the performance of a derived isoscape model. $\delta^{18}\text{O}_p$ of 88 stations distributed in the 45.5-49N, 5.5-17E domain have been gathered and analysed. The main spatial trends related to the rain-out process (altitude and continentality effects) were estimated by multivariate regression for each month using the mean long-term (1992-2000) monthly $\delta^{18}\text{O}_p$ values and the basic 3D geographical coordinates (latitude, longitude, altitude) as independent variables. Then the monthly model estimates were removed from the original measured $\delta^{18}\text{O}_p$ values and the residuals were entered into the variogram analysis. Gaussian models with ~70-90 km range could be fitted to the ‘normal’ experimental semivariograms. Based on this preliminary range estimate (80 km) and assuming isotropy for the Alpine $\delta^{18}\text{O}_p$ range ellipses could be drawn around each monitoring stations. The obtained ellipsoids showed multiple overlaps over the Berner Alps and Tirol. While the current network seems to be unable to provide accurate information over large regions of the Southern Alps.

1. INTRODUCTION

The stable isotopes of past and present precipitation are important natural tracers of the hydrological cycle on global, regional and local scales. The Alps host the oldest and densest network monitoring stable isotopes of precipitation compared to any other mountainous area of the world owing to the good representation of international (GNIP) and national (Switzerland and Austria) networks (Fig.1).

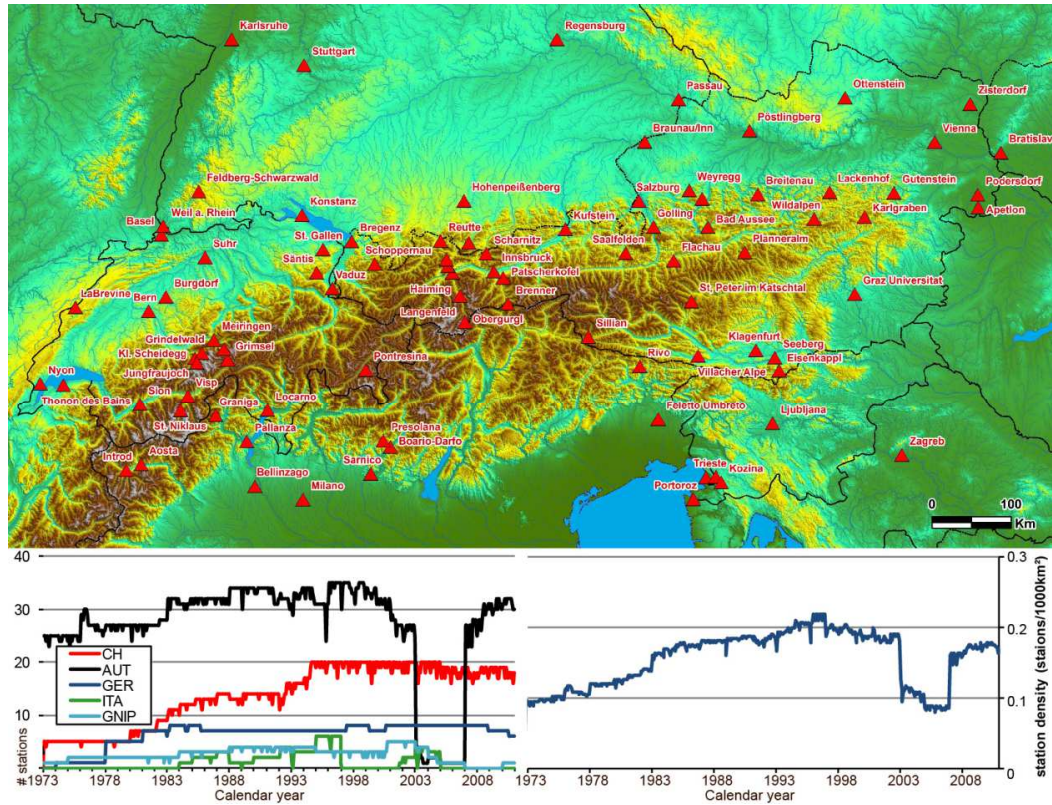


Figure 1. Spatial and temporal distribution of the 88 stations with available records of monthly stable oxygen isotope ratio of precipitation over the Alpine domain. Temporal distribution is shown between 1973 and 2010. (Data sources: Switzerland: NISOT [4] and the network run by the Division of Climate and Environmental Physics, Physics Institute, University of Bern, Austria: ANIP [5], Germany: [6], N-Italy [7,8], and GNIP-ISOHIS [9] for France, Slovenia, Croatia and Slovakia.

The main aim of our research is to develop a gridded data set of monthly oxygen isotope ratios in precipitation ($\delta^{18}\text{O}_p$) for the Alps and the adjacent regions. The derived data product will most probably provide a better calibration target for modern high-resolution terrestrial proxies than the traditional practice using the “nearest”, sometimes 100s of km away, and usually discontinuous station record. However it is a crucial prerequisite to assess the spatial dependence structure of the isotopic parameters of the Alpine precipitation.

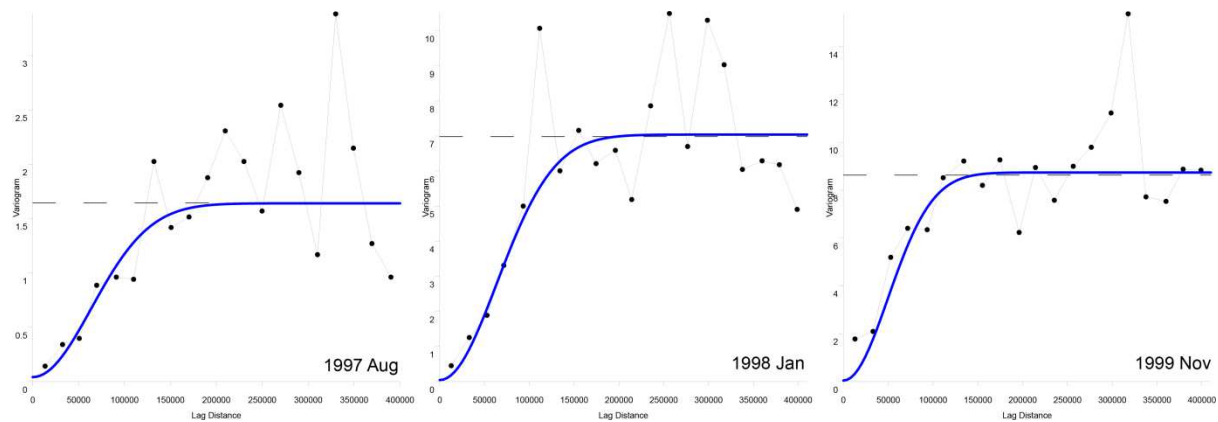


Figure 2. Examples of omnidirectional experimental semivariograms (black dots) and fitted Gaussian models (blue line) of the Alpine $\delta^{18}\text{O}_p$. Total variance is indicated by a dashed horizontal line. Lag width = 20.5°km, no. of lags = 20.

2. METHODS

Measurements of $\delta^{18}\text{O}_p$ started as early as 1961 in Vienna (Austria) and 1965 in Thonon des Bains (France) in the Alpine region. The network was very sparse during the first years. We have gathered $\delta^{18}\text{O}_p$ of 88 stations distributed in the 45.5-49N, 5.5-17E region (Fig.1). A multivariate regression model has been calibrated for each month for the long-term (1992-2000) mean monthly $\delta^{18}\text{O}_p$ values using the basic 3D geographical coordinates (latitude, longitude, altitude) as independent variables. The main well-known spatial trends related to the rain-out processes (such as the altitude effect and the continentality effect [1] and the influence of the seasonal differences in the dominant air mass/moisture sources [2] were to remove from the original measured $\delta^{18}\text{O}_p$ values by subtracting the corresponding monthly model estimates. Afterwards the residuals were entered into the variogram analysis. As earlier studies indicated the seasonal discrepancies of the vertical isotopic trend of the Alpine precipitation [3] variogram analyses were conducted on monthly basis.

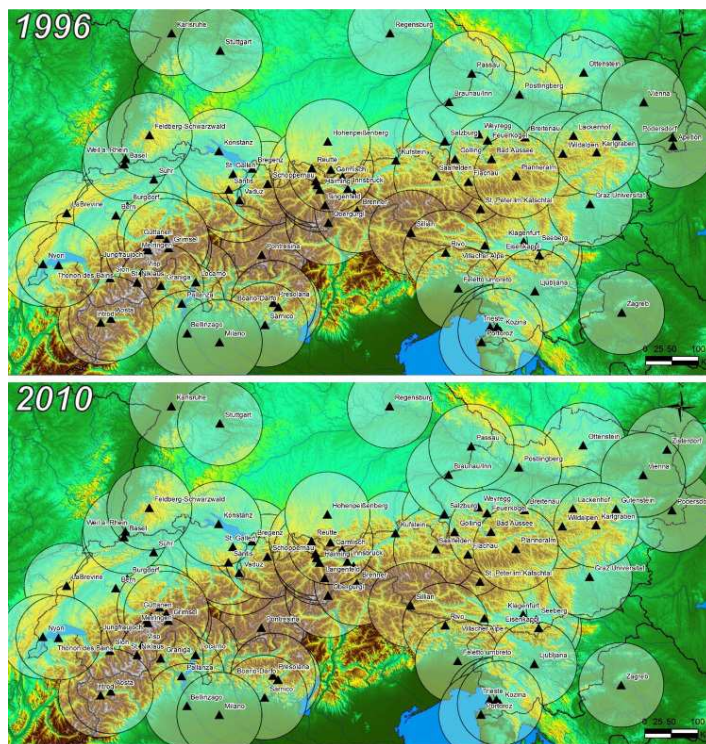


Figure 3. The Alpine $\delta^{18}\text{O}_p$ monitoring network available in 1996 (top) and in 2010 (bottom). Spatial representativeness of the network can be characterized by the halos of range ellipses [e.g. 10].

3. RESULTS

Station density significantly improved only from 1973 when more Swiss and Austrian stations were involved (Fig.1). Station density is around $0.2 \text{ station}/10^3 \text{ km}^2$ from 1992 to 2000 peaking at 1996 ($0.22 \text{ station}/10^3 \text{ km}^2$).

Only ~30% of the derived 108 experimental semivariograms showed optimal pattern as defined in literature: rising tail and wiggling around the mean variance over large distances. Gaussian models were fitted indicating a ~70-90 km range regularly (Fig.2). The rests were so-called nugget type variograms lacking the rising tail. Random tests suggested that sometimes only a sole anomalous value biases these semivariogram functions. Checking the variogram clouds for each nugget type semivariograms will be a next major task.

Based on this preliminary range estimate (80 km) and assuming isotropy for the Alpine $\delta^{18}\text{O}_p$ range ellipses could be drawn around each monitoring stations. Despite the remarkable reduction of the station density compared to the densest network of 1996, the network available in 2010 still provided a good coverage for most of the Alpine region (Fig.3). The range ellipsoids show multiple overlap over the Berner Alps and the region of Tirol. While the current Alpine $\delta^{18}\text{O}_p$ monitoring network seems to be unable to provide accurate information over large regions of the Southern Alps. The most desired places for two new stations are i) Trento, east from the Garda Lake, ii) Piedmont, at the southern part of the Gran Paradiso group.

4. CONCLUSIONS

Preliminary results from the variogram analysis of the Alpine $\delta^{18}\text{O}_p$ network suggests that a Gaussian empirical variogram function with a 80 km range can be used in the future geospatial models for the precipitation stable water isotopes for the Alpine region. The map derived using this preliminary range estimate pointed to insufficient station density over the Southern Alps.

ACKNOWLEDGEMENTS

Thanks for the support of the MTA “Lendület” program (LP2012-27/2012). This is contribution No.23. of *2ka Palaeoclimate* Research Group.

REFERENCES

- [1] ROZANSKI, K., ARAGUAS-ARAGUAS, L., GONFIANTINI, R., Isotopic patterns in modern global precipitation, in: *Climate Change in Continental Isotopic Records – Geophysical Monograph* **78** (1993) 1.
- [2] SJOSTROM, D. J., WELKER, J. M., The influence of air mass source on the seasonal isotopic composition of precipitation, eastern USA, *J. Geochem. Explor.* **102** (2009), 103.
- [3] KERN Z. KOHÁN B. LEUENBERGER, M., Precipitation isoscape of high reliefs: interpolation scheme designed and tested for monthly resolved precipitation oxygen isotope records of an Alpine domain, *Atmos. Chem. Phys.* **14** (2014) 1897
- [4] SCHÜRCH, M., KOZEL, R., SCHOTTERER, U., TRIPET, J. P. Observation of isotopes in the water cycle – the Swiss National Network (NISOT). *Environ. Geol.* **45** (2003) 1.
- [5] KRÁLIK, M., PAPESCH, W., STICHLER, W., Austrian Network of Isotopes in Precipitation (ANIP): Quality assurance and climatological phenomenon in one of the oldest and densest networks in the world - Isotope Hydrology and Integrated Water Resource Management, *C&S Paper series* **23** (2003) 146-149,
- [6] SCHÜRCH, M., KOZEL, R., SCHOTTERER, U., TRIPET, J. P. Observation of isotopes in the water cycle – the Swiss National Network (NISOT). *Environ. Geol.* **45** (2003) 1.
- [7] LONGINELLI, A., SELMO, E., Isotopic composition of precipitation in Italy: a first overall map, *J. Hydrol.* **270** (2003) 75.
- [8] LONGINELLI, A., SELMO, E., Isotopic composition of precipitation in Northern Italy: Reverse effects of anomalous climatic events. *J. Hydrol.* **329** (2006) 471.
- [9] IAEA: Global Network of Isotopes in Precipitation. The GNIP Database – (2010) www.isohis.iaea.org.
- [10] HATVANI I G, MAGYAR N, ZESSNER M, KOVÁCS J, BLASCHKE A P., The Water Framework Directive: Can more information be extracted from groundwater data? A case study of Seewinkel, Burgenland, eastern Austria. *Hydrogeol. J.* **22** (2014) 779.

DISENTANGLING THE EFFECT OF CLIMATIC CONTROLS ON RAINFALL $\delta^{18}\text{O}$ VARIABILITY IN EASTERN INDIA

S.BASU, P. SANYAL,

Department of Geology and Geophysics, Indian Institute of Technology, Kharagpur, India

E-mail address: sayak.geo@gmail.com

Abstract: Variability in the oxygen isotopic composition of rainfall ($\delta^{18}\text{O}$) at low latitude tropics are contributed by numerous parameters like moisture transport mechanism, raindrop reevaporation, moisture mixing along the trajectories, changes in the vapor source condition. Owing to sporadic dataset of rainfall $\delta^{18}\text{O}$ values and in absence of temporally and spatially dense meteorological network, characterization of climatic controls on the rainfall $\delta^{18}\text{O}$ variability mostly remain unknown in India. Due to course spatial coverage of IAEA-GNIP stations (only three IAEA-GNIP stations are employed in India), no long-term record is available in eastern India from where the BoB branch of vapor enters the Indian landmass. In this study, daily-resolved 3-year time series of rainfall $\delta^{18}\text{O}$ from Mohanpur, located in eastern India (22.9°N, 88.5°E) is presented and the role of different climatic variables has been identified. Rain samples were collected at daily time-series from 2011 to 2013. The $\delta^{18}\text{O}$ values of daily rainfall vary from 6.7 to -17.5‰ with an average value of $-5 \pm 4.3\text{‰}$ (1σ , $n=201$) and exhibit poor correlation with rainfall amount ($R = -0.2$, $p < 0.01$). However, daily rainfall $\delta^{18}\text{O}$ shows better correlation ($R = -0.4$, $p < 0.05$) with amount in dry season (Jan to Apr) and suggests a higher amount effect during dry season than wet season (Jun-Sep time). The correlation between rainfall $\delta^{18}\text{O}$ and amount enhances with increased temporal averaging which can be seen at monthly intervals ($R = -0.5$, $p < 0.05$) or at annual scale ($R = -0.9$, $p < 0.05$). This reflects the time integrative nature of rainfall $\delta^{18}\text{O}$ values. Slope versus amount range plot reveals that samples below 5 mm amount has suffered post-condensation evaporation. Filtering of such samples ($n=51$) improves LMWL from $\delta\text{D} = 7.3\delta^{18}\text{O} + 2.9$ to $\delta\text{D} = 7.9\delta^{18}\text{O} + 7.2$ and the reevaporation of falling rain-drops is more pronounced in dry season. Back-trajectory computation (HYSPLIT-4) has revealed the change in the moisture sources from dry to wet season, which also been supported by d-excess value. Based on the specific humidity change along the trajectory path, the regions of moisture entertainment have been located. Rainfall during Indian Summer Monsoon is dominantly fed by the Bay of Bengal (BoB), whereas continental water bodies are also significant contributor. The most depleted rainfall $\delta^{18}\text{O}$ days were supplied by continental water bodies. The contribution pattern of each moisture source almost remains similar in 3-year time-scale. Present study disentangles the effect of different climatic parameters and hence, provides support to the accurate interpretation of paleo-archives present in this region. In future, incorporation of this rainfall $\delta^{18}\text{O}$ dataset to the atmospheric general circulation model would be helpful to understand the regional hydrological system at a finer spatial resolution.

ID: 291

VIENNA GNIP-ANIP – STATION: A UNIQUE STATION WITH 40 YEARS OF DUAL MEASUREMENTS

M. KRALIK,

Environment Agency Austria, Spittelauer Laende 5, 1090 Vienna, Austria

E-mail address: martin.kralik@umweltbundesamt.at

S.TERZER

Isotope Hydrology Section, International Atomic Energy Agency,

Vienna International Centre P.O. Box 100, Vienna, Austria

S.WYHLIDAL

AIT, Austrian Institute of Technology, Konrad Lorenz-Str. 24, A-3430 Tulln, Austria.

Abstract: The Vienna GNIP-station is also part of the Austrian Network of Isotopes in Precipitation (ANIP) and as a result of this, monthly precipitation samples were measured both by the IAEA and the Arsenal research, now Austrian Institute of Technology (AIT). This presents a unique opportunity to estimate the variability and errors of a long term precipitation monitoring data set spanning over forty years. Starting in 1973 only 8 monthly data of $\delta^{18}\text{O}$ -measurement are missing in both data sets. The difference in the results is only greater than 0.3‰ in 20% of the 462 monthly values. Moreover in only 6% of the data are the differences greater than 1 ‰. However, the mean difference per decade decreases from 0.18 to 0.01 ‰ over 40 years. The mean $\delta^{18}\text{O}$ -values increase, as is the case in most stations, from -10.33 to -9.52 ‰ over the four decades.

1. INTRODUCTION

The Vienna GNIP-station (Global Network of Isotopes in Precipitation, [1]) is also part of the Austrian Network of Isotopes in Precipitation (ANIP, [2]). The Isotope Hydrology Section of the International Atomic Energy Agency (IAEA) started to measure the isotope composition since February 1961 in Vienna. Since January 1973 the Bundesversuchs- und Forschungsanstalt (predecessor organisation of AIT) started to measure $\delta^{18}\text{O}$ in the ANIP-stations including Vienna. The data of both laboratories present a unique data set spanning more than forty years allowing us to estimate the variability and errors of this long term precipitation monitoring.

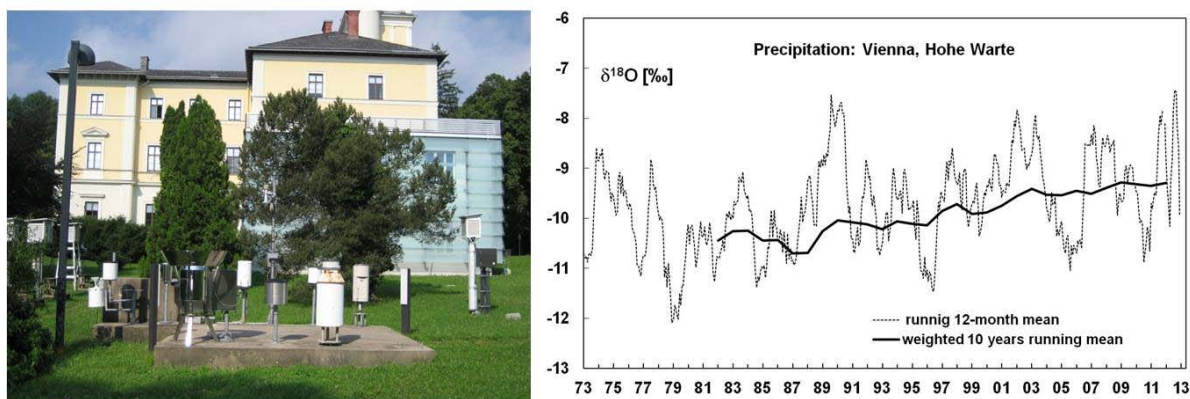


Figure 1. Vienna (Hohe Warte) precipitation collection site and long-term $\delta^{18}\text{O}$ variation at the sampling site

2. METHODS

At the Vienna (Hohe Warte, 198 m altitude) main meteorological station (Figure 1) the daily precipitation is collected in a standard Hellmann – Ombrometer and combined to a monthly sample. From this normally 1 L is sent to the IAEA and the AIT-laboratory for analysis. The amount of precipitation and the mean monthly temperature is measured by the meteorological station in immediate vicinity.

The available data [1, 2] were compared by forming mean values by decades and by calculating the difference of every single pair of values. From these differences a mean value and the standard deviation was calculated for the decades 1973-1982, 1983-1992, 1993-2002 and 2003-2013 (Table 1).

3. RESULTS

From the 492 month during 41 years 467 (95%) and 481 (98%) $\delta^{18}\text{O}$ -values have been measured by IAEA and AIT, respectively. From just 8 month (1.6%) no values are available.

Table 1. Mean $\delta^{18}\text{O}$ -values and mean difference of the $\delta^{18}\text{O}$ -values of the IAEA and AIT laboratories per decade

	2003-2013	1993-2002	1983-1992	1973-1982
IAEA mean $\delta^{18}\text{O}$	-9.52	-9.62	-9.56	-10.15
AIT mean $\delta^{18}\text{O}$	-9.57	-9.61	-9.78	-10.33
Mean diff. IAEA - AIT	-0.01	0.05	0.18	0.09
Std.Dev. diff. IAEA - AIT	0.11	1.05	1.92	0.72

From 462 month (94%) two values for comparison are available. The frequently accepted difference between two laboratories 0.3 ‰ is however exceeded in 20.8% of the cases. The exceedance of the extreme difference of 1 ‰ still occurred in 6.5 % of cases (Figure 2). The mean values increase from -10.33 to -9.52 ‰ over for decades. The mean difference and their standard deviation decreased from 0.18 to -0.01 ‰ and 1.92 to 0.11, respectively from 1983 to 2013. In the decade 1973-1982 the mean difference and standard deviation was already smaller by 0.09 and 0.72 ‰ respectively (Table 1 and Figure 2).

4. CONCLUSIONS

This unique data set of dual measurements of the same precipitation is a good opportunity to estimate the frequency of not sampling the exact aliquot of rain, analytical errors mix up of samples etc. in a routine monitoring process. The differences up to 0.3 ‰ can be regarded as standard analytical error between two laboratories. Errors above the 0.3 ‰ must be related to not sampling well mixed aliquots, evaporation effects, transcription and analytical errors. Differences of more than 1 ‰ can only explained by mixing up samples, transcription and major analytical errors.

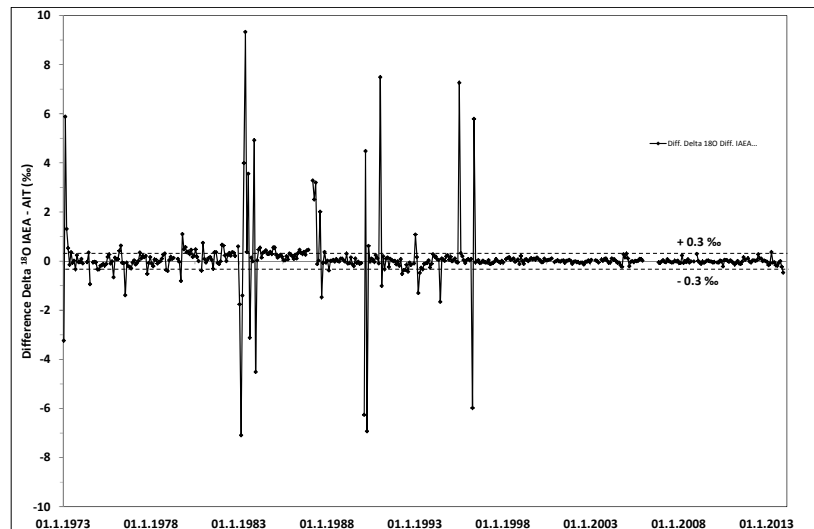


Figure 2. Difference of monthly $\delta^{18}\text{O}$ -values ($n=462$) of the IAEA and AIT laboratory from the Vienna (Hohe Warte) GNIP-ANIP station since 1973.

REFERENCES

- [1] GNIP Global Network in Precipitation and Isotope Hydrology Information System. International Atomic Energy Agency (IAEA), Vienna.
<http://nucleus.iaea.org/CIR/CIR/GNIPIHIS.html> (2014).
- [2] ANIP: Austrian Network of Isotopes in Precipitation. Environment Agency Austria. (Umweltbundesamt), Vienna (2014)
<http://www.umweltbundesamt.at/en/umweltschutz/wasser/isotopen/>

CHEMICAL AND ISOTOPIC CHARACTERISTICS OF RAIN WATERS IN SENEGAL NORTH COASTLINE

M. DIAW, I. MALL I, C.B GAYE

Geology Department, Faculty of Sciences and Techniques, University Cheikh Anta Diop (UCAD), PO Box 5005, Dakar, Senegal

E-mail address: mkdiaw@ucad.edu.sn

Abstract: This study falls within the framework of the overall problematic of chemical and isotopic characterization of rainwater in the West African Sahel. It was initiated with the aim of first bearing to a lack of quantitative and qualitative characterization of the input signal rainwater yet very useful for hydrological and hydrogeological studies of the hydrosystem the northern coast of Senegal. The stable isotope composition and the tritium content of precipitation analysed within the framework of the IAEA/WMO Global Network for Isotopes in Precipitation (GNIP) have been evaluated for the Senegalese stations located in the arid Sahel region characterized by semi arid coastal Sahelian climate that offers enough features particularized in Dakar, often continentalized in Pout and sub-desert climate in Louga. The daily composite samples of rain have been collected at these stations. The samples were analysed for the isotopic ratios of the stable isotopes ($^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$) and the radioactive isotope tritium ($^3\text{H}/^1\text{H}$). The latter is given in tritium units TU (1TU = 0.118 Bq/l), and the former as δ values (relative to VSMOW in per mille).

The rainfalls in Senegal are controlled by moving Monsoon which is humid equatorial wind, and low generator rain from the south-southwest sometimes becoming northwest in the coastal area. Monsoon gradually covers the entire West Africa and moves between the 4th and 20th parallel north it reached in July and in January. In the Sahelian fringe precipitations depend almost exclusively on the latitudinal position of the ITCZ (Leroux, 1983). The advance of the ITCZ to the north, facilitated by the continental depression centered over the Sahara allows the invasion of monsoon rains which brings intense convective small scale. Monsoon with diverse routes and variable transit times over the land subsequent to their recovery is responsible of the variation of rainy season duration and of chemical and isotopic compositions. The evaluation of the chemical and isotope data of the three stations provided specific information on the moisture source of the Monsoon rains. The chemical composition and the average isotope ratios clearly represent an imprint of oceanic and continental moisture during the summer monsoon period. Furthermore, the isotope data indicate a lack of correlation between monthly $\delta^{18}\text{O}$ and rainfall and guessed the importance of atmospheric circulation pattern. The large isotopic variation over the rainy months and the rain water isotope line slopes observed in these station rains could be explained by combination rain-forming mechanisms and moisture source changes (continental and oceanic). Rainfall in Dakar station show a linear correlation with a slope 8.0 features condensation that always occur at saturation. Oceanic vapor precipitation which gives a d -excess value equal to 8. In the other stations, evaporation leads in linear correlations for contents $\delta^{18}\text{O}$ and $\delta^2\text{H}$ with slopes equal to 7.2 and 5.7 respectively in Pout and Louga stations where deuterium excess increasingly negative. Values for $\delta^{18}\text{O}$ range from -8.4 to -2.2 ‰ and for δD , from -57.8 to -5.5 ‰ in Dakar; values for $\delta^{18}\text{O}$ range from -7.4 to 0.09 ‰ and for δD , from -55.7 to -0.65 ‰ in Pout and in Louga values for $\delta^{18}\text{O}$ range from -9.42 to -0.6 ‰ and for δD , from -73.24 to 5.13 ‰.

ID: 320

**VARIATION IN ISOTOPIC COMPOSITION OF PRECIPITATION
WITH IDENTIFICATION OF VAPORS SOURCE USING DEUTERIUM
EXCESS PARAMETER AS A TOOL: ISOTOPIC STUDY AT TARBELA
DAM SITE IN PAKISTAN**

S. BUTT, M. A. TASNEEM, M. ALI, F. MUHAMMAD,
Pakistan Institute of Nuclear Science & Technology, Islamabad, Pakistan
E-mail address: sairaasloob@yahoo.com

Abstract: In this paper we report isotopic data of 10 years (1988-1997) of rain samples collected at Tarbala dam site in Pakistan. Isotopic data is used to explain the origin of vapor source responsible for precipitation in this region. Seasonal variations in the isotopic composition of rain in addition to deuterium excess parameter particularly associated with winter/summer rain are observed and co linked with vapor source. The variations are clearly associated with different source regions of vapors i.e. Arabian Sea/Bay of Bengal in summer and Mediterranean Sea in winter. It is also related with the transportation trajectories of vapor masses responsible for precipitation. Inverse relation is observed between humidity and temperature at the site of precipitation.

ID: 354

VERIFICATION OF A REGIONAL ISOTOPE CIRCULATION MODEL THROUGHOUT JAPAN

M. TANOUE

School of Engineering, the University of Tokyo, Tokyo, Japan

E-mail address: masatano@sogo.t.u-tokyo.ac.jp

K. ICHIYANAGI

Graduate School of Science and Technology, Kumamoto University, Kumamoto, Japan

Abstract: Isotopic composition ($\delta^{18}\text{O}$ and δD) in precipitation simulated by a regional isotope circulation model with 10 km horizontal resolution was compared with observed that at 56 sites throughout Japan. The model could capture both seasonal variation and spatial pattern of the isotopic composition through a year, except for January along Pacific side in eastern and western Japan. The simulated isotopic composition in January overestimated anomaly $\delta^{18}\text{O}$ values by 8.1 ‰ and 3.4 ‰ in eastern and western Japan, respectively. The reason of the overestimation was caused by that simulated sea level pressure in the center of an extratropical cyclone in 14 January 2013 was higher by 10 hPa than that derived from Japanese 55-year reanalysis data.

1. INTRODUCTION

The isotopic composition in precipitation ($\delta^{18}\text{O}$ and δD) exhibits a broad range of spatiotemporal variations because of atmospheric hydrological processes, such as moisture transportation and complex phase changes of water (e.g., Dansgaard, 1964). That is used for estimations of origin, transport pathway, mixing process, and age in water. Many studies incorporated the water isotopes into atmospheric general circulation model, and compared the simulated isotopic composition with observed that (e.g. Yoshimura et al., 2008). However, the scale of the comparison was more than country or global scale. The problem is caused by two reasons; a lack of observation data with fine spatial resolution (less than country scale) and few regional isotope circulation models. We carried out intensive observation of isotopic composition in precipitation at 56 sites throughout Japan in 2013. In this study, the isotopic composition simulated by a regional isotope circulation model with 10 km horizontal resolution was compared with obtained that. We summarized imperfect points of reproduction by a regional isotope circulation model.

2. METHODS

Precipitation samples were observed at 56 sites throughout Japan in 2013 (see Figure 1). The Isotope Ratio Mass Spectrometer (Thermo Fisher Scientific, Delta-V) was used to measure $\delta^{18}\text{O}$ and δD of precipitation samples with a $\text{CO}_2/\text{H}_2\text{O}$ equivalent method for $\delta^{18}\text{O}$ and a platinum catalyst equivalent method for δD . Isotopic ratios are expressed by convention as parts per thousand (‰), deviations relate to Vienna Standard Mean Ocean Water. The analytical errors for standard measurements of $\delta^{18}\text{O}$ and δD are better than ± 0.05 ‰ and ± 0.5 ‰, respectively.

The isotopic regional spectral model (IsoRSM; Yoshimura et al., 2010) was used in this study. Major physical processes were included: the relaxed Arakawa–Schubert scheme, the Noah land surface model, the Chou radiation scheme, and a planetary boundary scheme. Isotopic

physical schemes were included: the parameterization of equilibrium fractionation among vapor, liquid, and ice, kinetic fractionation for surface evaporation from open water, condensation from vapor to ice under super-saturated conditions at temperatures lower than -20°C , and evaporation and isotopic exchange between falling raindrops and vapor in surrounding air. The domain of the IsoRSM simulation in this study is shown in **Error! Reference source not found.** The simulation domain sufficiently covers all observation sites of stable isotopes in precipitation over Japan. The simulation domain had 289×350 horizontal grid points and 28 vertical layers. The horizontal grid size was approximately 10 km. The IsoRSM simulation run in 2013. The initial and lateral boundary conditions were taken from the global nudged isotope simulation (Yoshimura et al., 2008). The sea surface and ice distributions were taken from the National Oceanic and Atmospheric Administration Optimum Interpolation Sea Surface Temperature V2.

In order to check spatial patterns of sea level pressure (SLP), we utilized Japanese 3-hourly 55-year Reanalysis (JRA-55) data in 2013.

3. RESULTS

Comparison of seasonal variations of simulated and observed regional averaged anomaly $\delta^{18}\text{O}$ in precipitation are shown in Figure 2. The regional averaged values were calculated by anomaly $\delta^{18}\text{O}$ from the averaged value weighted by precipitation amount at each site, because latitude effect of $\delta^{18}\text{O}$ in precipitation throughout Japan (Tanoue et al., 2013). There are clear seasonal variations of observed $\delta^{18}\text{O}$ in precipitation in each region; positive anomaly in the Northern Japan (Pacific side and Japan Sea side) from March to July, and Eastern and Western Japan (Pacific side and Japan Sea side) from March to May. However, seasonal amplitude of observed $\delta^{18}\text{O}$ throughout Japan (approximately 6 ‰) was lower than that in the other monsoonal region (Araguás-Araguás et al., 1998). Seasonal variation of simulated $\delta^{18}\text{O}$ by the IsoRSM agrees with observed that. However, the simulated values in January are overestimated in Pacific side in Eastern and Western Japan.

Relationship between monthly mean $\delta^{18}\text{O}$ in precipitation weighted by precipitation amount and latitude of stations are shown in Figure 3. The Simulated and the observed $\delta^{18}\text{O}$ in precipitation show latitude effect (values decrease with increasing latitude of observation site), except from June to September. The IsoRSM can capture the intensity of latitude effect of observed $\delta^{18}\text{O}$ values, however simulated absolute values were higher than observed that in latitude from between 30°N and 40°N , especially in January. The low observed $\delta^{18}\text{O}$

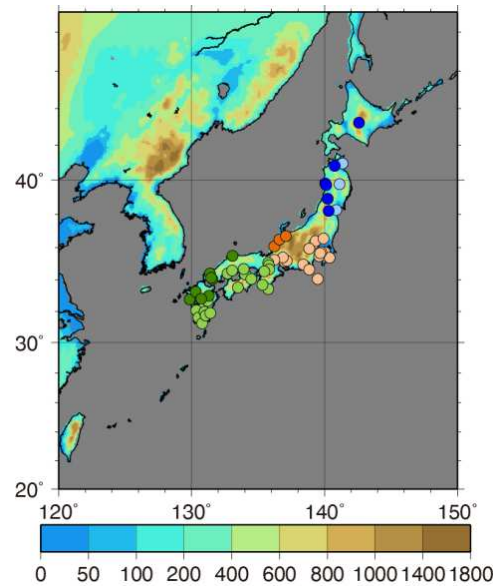


Figure 1: Domain of the IsoRSM simulation and geo-potential height (shaded; gpm) in this study. Light blue, dark blue, light brown, dark brown, light green, and dark green indicated stations on the Northern Japan/Pacific side, Northern Japan/Japan Sea side, Eastern Japan/Pacific side, Eastern Japan/Japan Sea side, Western Japan/Pacific side, and Western Japan/Japan Sea side, respectively.

values (less than -20 ‰) was brought by the enhanced extratropical cyclone in middle January 2013. Spatial SLP patterns in 14 January are shown in

Figure 4. We found that simulated SLP in the center of the enhanced extratropical cyclone (approximately 1000 hPa) was higher than that derived from JRA-55 (less than 990 hPa). Generally, $\delta^{18}\text{O}$ values do not have physical connection to SLP. However, underestimated SLP cause suppressed cyclone system, leading to change precipitation amount and condensation level. We will further numerical simulation with different convective scheme.

4. CONCLUSIONS

We verified the isotopic composition in precipitation simulated by the IsoRSM with fine horizontal resolution using by intensive observation data throughout Japan. The IsoRSM can capture seasonal variation and spatial pattern of the observed isotopic composition in precipitation, however simulated isotopic composition overestimated in the case of precipitation event by the enhanced extratropical cyclone. In order to adjust SLP pattern, we will run further numerical simulation with different convective scheme.

REFERENCES

- [1] ARAGUAS-ARAGUAS, L., ET AL., Stable isotope composition of precipitation over southeast Asia southeast. J. Geophys. Res. **103** (1998) 28721.
- [2] DANSGAARD, W., Stable isotopes in precipitation, Tellus **XVI** (1964) 436.
- [3] TANOUE, M., K. ICHIYANAGI, J. SHIMADA, Seasonal variation and spatial distribution of stable isotopes in precipitation over Japan (in Japanese). J. Jpn. Assoc. Hydrol. Sci., **43** (2013) 73.
- [4] YOSHIMURA, K., M. KANAMITSU, D. NOONE, T. OKI, Historical isotope simulation using Reanalysis atmospheric data. J. Geophys. Res. **113** (2008).
- [5] YOSHIMURA, K., M. KANAMITSU, M. DETTINGER, Regional downscaling for stable water isotopes: A case study of an atmospheric river event. J. Geophys. Res. **115** (2010).

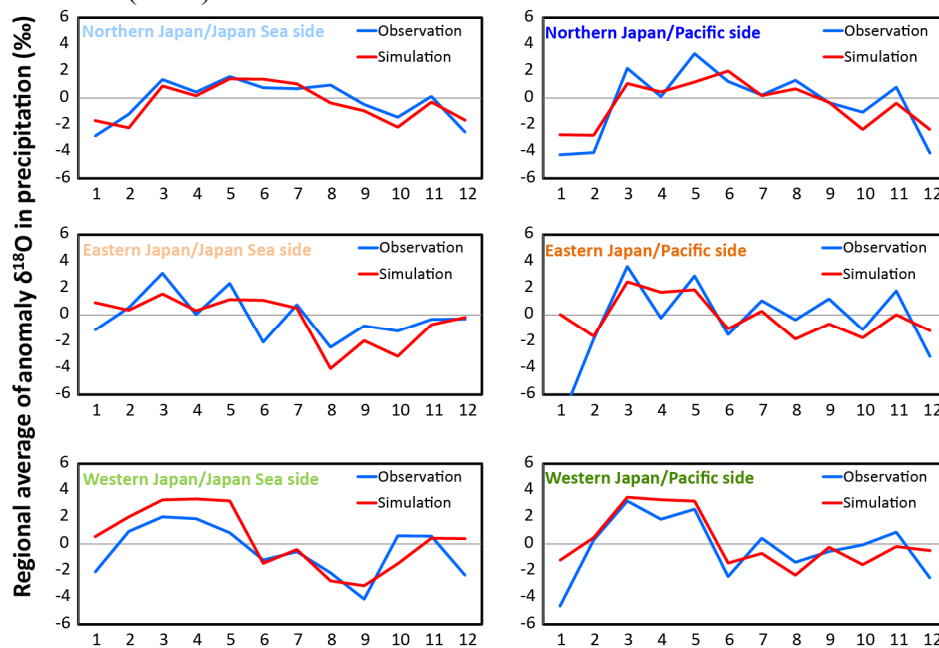


Figure 2: Comparison of seasonal variations of simulated (red) and observed (blue) regional averaged anomaly $\delta^{18}\text{O}$ in precipitation in the regions.

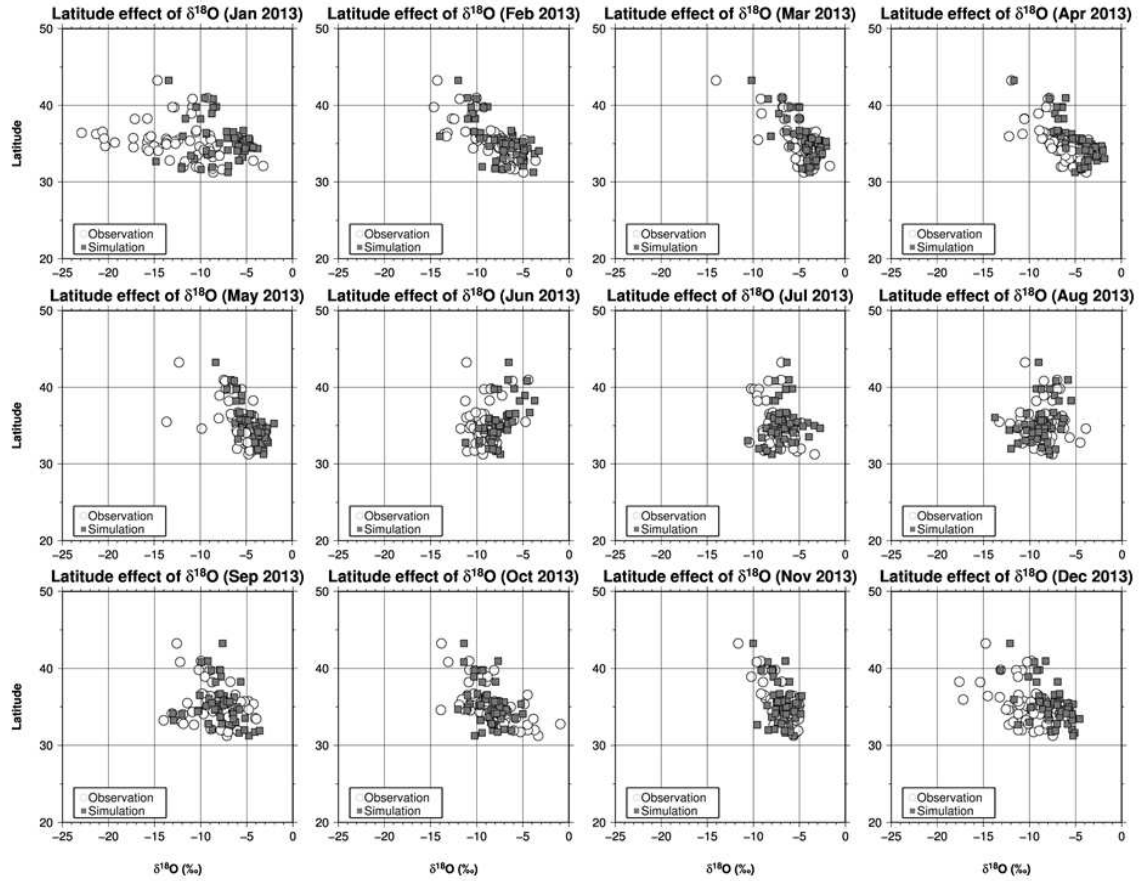


Figure 3: Relationship between monthly mean $\delta^{18}\text{O}$ in precipitation weighted by precipitation amount and latitude of stations. Circles and squares indicate observation and simulation, respectively.

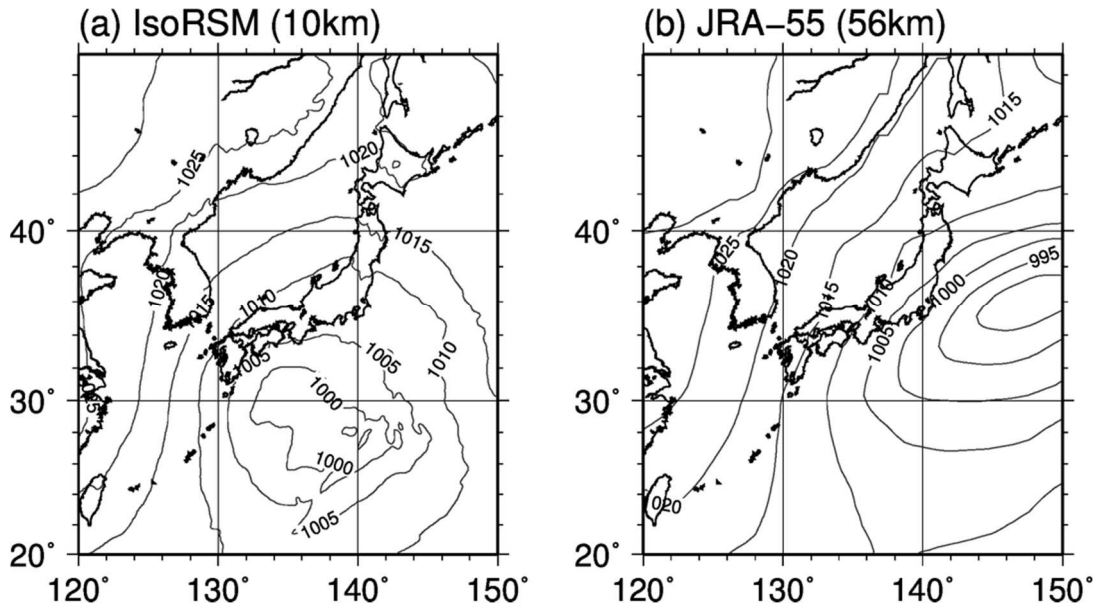


Figure 4: Spatial SLP patterns derived from (a) IsoRSM simulation and (b) JRA-55 data in 13 January 2013.

A 10-YR RECORD OF STABLE ISOTOPE VARIATIONS IN PRECIPITATION ACROSS CHILE

E. AGUIRRE DUEÑAS,
Comisión Chilena de Energía Nuclear, Santiago, Chile
E-mail address: eaguirre@cchen.gob.cl

R. SANCHEZ-MURILLO,
National University of Costa Rica, San Jose, Costa Rica

M. GALLARDO AMESTICA, P. MOYA VEGA,
Comisión Chilena de Energía Nuclear, Santiago, Chile

Abstract: Chile is located within a latitudinal range (17° S to 56 ° S) has wide range of weather conditions due the geographic characteristics, offer an interesting opportunity to study stable isotope variations in a region bounded by the South Pacific Ocean (west side) and the Andes Cordillera (east side); this large geographic spectrum turns in a wide range of climatic scenarios from desert in the north, to alpine tundra in the east and southeast, Mediterranean climate in the central region, and humid subtropical in the Eastern Island, Oceanic climate in the south and Polar climate in the Antarctic Territory . Here, we present 10-year of monitoring (2004-2013) archive (N= 435; monthly composite samples) of five GNIP stations administrated by the Environmental Isotope Laboratory of Chilean Commission of Nuclear Energy: La Serena (northern semi-arid region, 142 m.a.s.l), Santiago (central region, 520 m.a.s.l), Eastern Island (South Pacific region, 42 m.a.s.l), Puerto Montt (southern coastal region, 81 m.a.s.l), and Punta Arenas (Patagonia region, 37 m.a.s.l). The maritime meteoric water line of Eastern Island is described as: $\delta^2\text{H} = 6.68 \cdot \delta^{18}\text{O} + 5.76$ ($r^2=0.81$) with an average d-excess of +8.7 (‰). No significant correlations were found between precipitation volume ($r^2=0.08$), surface temperature ($r^2=0.01$), and ^{18}O composition at Eastern Island suggesting that other oceanic or atmospheric processes may play a significant role controlling the isotopic variations at this site. The continental meteoric water line of Chile is described as: $\delta^2\text{H} = 6.72 \cdot \delta^{18}\text{O} - 5.46$ ($r^2=0.90$) with a mean d-excess of +2.96‰. In the semi-arid region of Serena, a moderate ($r^2=0.22$) relationship between the precipitation amount and the $\delta^{18}\text{O}$ (‰) was observed. Contrary to the other continental monitoring sites (Santiago, Puerto Montt and Punta Arenas, i.e. lower slopes and intercepts), the meteoric water line at Serena is particularly similar ($\delta^2\text{H} = 8.02 \cdot \delta^{18}\text{O} + 10.8$; $r^2=0.92$) to the Global Meteoric Water Line with d-excess values ranging from +4.42‰ up to +19.2‰. The isotope data registered will provide a fundamental baseline for future hydrological modeling studies in Chile.

ANALYSIS OF LONG-TERM STABLE ISOTOPIC COMPOSITION IN GERMAN PRECIPITATION AND RIVERS

C. STUMPP, P. MALOSZEWSKI, W. STICHLER

Helmholtz Zentrum München, Institute of Groundwater Ecology,

Ingolstädter Landstrasse 1, 85764 Neuherberg, Germany

E-mail address: christine.stumpp@helmholtz-muenchen.de.

Abstract: Stable water isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) have been frequently used as environmental tracers to understand processes and timescales in hydrology and climate research. Capturing changes of isotopic composition over time and investigating long-term processes requires long-term data set analysis. In Germany, we have one of the world's densest national networks for long-term isotopic analysis (i) in precipitation covering up to 36 years of time series at 28 locations and (ii) in rivers covering between 13 and 26 years of time series at 9 locations. These data allow to answer the following research questions: (i) how and why does the isotopic composition in precipitation change over time and space?, (ii) how and why does the isotopic composition in rivers change over time and space?, (iii) are spatiotemporal changes in precipitation and rivers following same trends? Water isotopes in precipitation show increasing trends over time in most locations in Germany which is associated with temperature increases [1]. However, not all of these trends are significant [2]. Similar trends were found for rivers too with some exceptions in the Weser and Rhine catchments. Next to temporal trends, the isotopic composition of the nine investigated rivers has a clear variability in space. Average and seasonal dynamics can reflect the location (latitude, longitude, elevation of recharge area) and the size of catchment area (small, little tributaries vs. many tributaries).

REFERENCES

- [1] STUMPP, C., KLAUS, J., STICHLER, W., "Analysis of long-term stable isotopic composition in German precipitation", *Journal of Hydrology* 517 (2014) 351-361
- [2] KLAUS, J., CHUN, K. P., STUMPP, C., " Temporal trends in $\delta^{18}\text{O}$ composition of precipitation in Germany: insights from time series modeling and trend analysis", *Hydrological Processes* (in press) DOI: 10.1002/hyp.10395

ID: 374

$^{18}\text{O}/^2\text{H}$ COMPOSITION IN DANISH PRECIPITATION

S. MÜLLER, K. S. LARSEN, S. JESSEN,
University of Copenhagen, Department of Geosciences and Natural Resource Management,
Øster Voldgade 10, Copenhagen, Denmark.
E-mail address: samu@ign.ku.dk

T. J. POPP
Centre for Ice and Climate, Niels Bohr Institute, University of Copenhagen, Juliane Maries
Vej 30, 2100 Copenhagen, Denmark

J. H. SØRENSEN, N.W. NIELSEN
Danish Meteorological Institute, Lyngbyvej 100, DK-2100 Copenhagen Ø, Denmark

Abstract: The regional distribution of stable isotopes of water in precipitation and groundwater, both of which is traditionally, a priori, often assumed to be geographically invariant on the small scale. Yet, stable isotopes have been proven to be a useful tool as a tracer for the hydrological studies. Precipitation defines the input function to the hydrological cycle. Due to increasing temperatures over the next century this input function will be subject to significant changes in its isotopic composition. A four degrees Celsius increase will yield 2.4 to 3.6 ‰ increase. In the near future this will create a very significant contrast in most aquifers between "pre-climate change" and "post-climate change" water. Little is known about the spatial distribution and yearly variation of precipitation in Denmark, but has been assumed to be constant in recent years. Within the small country area of Denmark the spatial variation of precipitation and Temperature is large, which certainly produces an effect on the isotopic composition in rain. Furthermore, could atmospheric studies from Denmark have shown that air masses delivering rain have different geographical origin during a single rain event and are not necessarily dominated by moisture sources from west, but rather originate from north or south as well[1].

The aim of this study is to *a)* characterize the $^{18}\text{O}/^2\text{H}$ composition of monthly accumulated precipitation across Denmark and detect major trends and factors causing such isotopic variation. Thereby a "Danish meteoric waterline" will be developed. *b)* Investigate the isotopic composition throughout specific rain events in different seasons and find major formation conditions for such $^{18}\text{O}/^2\text{H}$ signal development.

Rain water was collected over three years on a monthly basis on eight stations across Denmark. Rain event sampling was carried out between October 2013 and June 2014 for 8 rain events at a sampling location north of Copenhagen. The collection device for the monthly samples is developed and described by [2]. Event-based sampling was carried out with a funnel construction where evaporation loss from funnel was minimized due to the high manual sampling frequency. Samples were analyzed with a Picarro 2130-i analyzer.

The data shows a 1‰ change in isotopic composition over a short distance (70 km) over land with average $\delta^{18}\text{O}$ of -7.8‰ at the coast to -8.7‰ 70 km inland. Accordingly, variation within a year also increases with distance from the ocean. The most western station has an $\delta^{18}\text{O}$ -standard deviation ($\delta^{18}\text{O}$ -Stdv.) of 1.2 ‰ whereas the station 70 km east of the coast has an $\delta^{18}\text{O}$ -Stdv. of 2.6‰ throughout the year (Fig.1). Preliminary results show that the effect

of temperature can be neglected due to the small difference between each station, hence; an altitude effect cannot be seen. A decrease in the regression slope(s) between each station is not observed. Yet, a lower d -excess compared to the GMWL in all stations indicates higher humidity conditions during formation of vapor masses.

From the event samples $\delta^{18}\text{O}$ maximum range from -5 ‰ to -14 ‰ throughout an event could be observed. Common observed $\delta^{18}\text{O}$ trends are V-shape and descending trends (defined in [3]). According to rain trajectories V-shape trends can be explained by the delivery of new vapor masses with different travel passes over sea and land. Descending trends result from the amount effect.

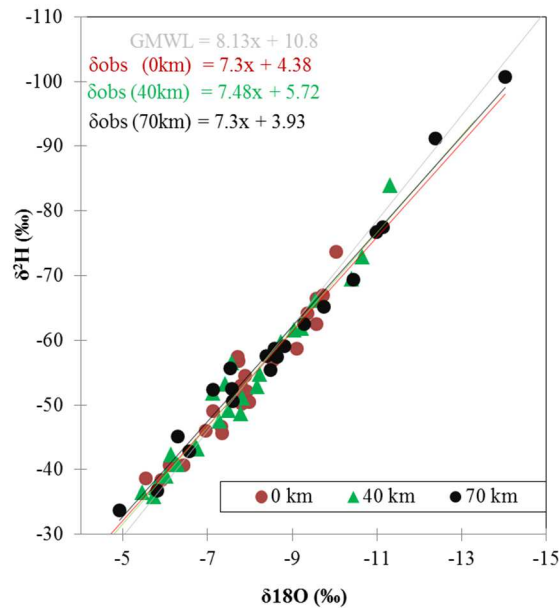


Fig.1. Showing the continental effect across Denmark at three stations with different distance to coast.

REFERENCES

- [1] ŠANTL TEMKIV, T., FINSTER, K., MUNK HANSEN, B., HARTMANN, S., GOSEWINKEL KARLSON, U., The relevance of outer membrane vesicles derived from airborne *Pseudomonas* SPP. And entire cells for ice nucleation in the atmosphere, In: Šantl Temkiv, T. *Bacteria in Clouds*, PhD Thesis, Aarhus University, (2015).
- [2] GRÖNING, M., LUTZ, H. O., ROLLER-LUTZ, Z., KRALIK, M., GOURCY, L., PÖLTENSTEIN, L. , A simple rain collector preventing water re-evaporation dedicated for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ analysis of cumulative precipitation samples, *Journal of Hydrology*, 448-449, 195–200 (2012).
- [3] CELLE-JEANTON, H., GONFIANTINI, R., TRAVI, Y., SOL, B., Oxygen-18 variations of rainwater during precipitation: application of the Rayleigh model to selected rainfalls in Southern France, *Journal of Hydrology*, 289(1-4) (2004).

ID: 1

TRACING ORGANIC MATTER SOURCES AND CARBON BURIAL IN A TROPICAL LAGOON OF THE CARIBBEAN SEA

C. M. ALONSO-HERNÁNDEZ,
Centro de Estudios Ambientales de Cienfuegos, Cuba
E-mail address: carlos@ceac.cu

Abstract: The natural protected lagoon of Guanaroca, located between Cienfuegos Bay and the Arimao River, Cuba, has been heavily impacted by human-induced environmental changes over the past century. Sources and burial patterns of organic matter in the Guanaroca lagoon were investigated in a sediment core. Analyses included: variation in total organic carbon (C_{org}), total nitrogen (TN), stable carbon isotopic composition ($\delta^{13}C$ and $\delta^{15}N$) and ratio of total organic carbon to total nitrogen (C_{org}/TN). On such a basis, the environmental evolution and the primary productivity changes of the lagoon were revealed, and the impacts of human activities identified. Downcore variation patterns of the parameters representing sources and burial flux of organic matter were predominantly related to the impacts of human activities. Up to the nineteenth century, the principal sources of organic matter to sediments (more than 80%) were a mixing of terrestrial vascular plants (~43%) and freshwater phytoplankton (~41%), with minimal contribution from the marine component. In the period 1900–1980, due to the strong influence of human activities in the catchment area of the Arimao River, the water exchange capacity of the lagoon declined substantially, as indicated by the relatively high proportion and burial flux of organic matter originated from marine sources. Since 1980, as a result of management actions in the protected area, the lagoon has regained gradually his capability to exchange freshwater, showing sources and burial fluxes of organic matter similar to the natural conditions recorded previous to 1900.

ID: 4

**GEOCHEMICAL, MINERALOGICAL AND ISOTOPIC
INVESTIGATION OF INLE LAKE (SOUTHERN SHAN STATE,
MYANMAR): PRELIMINARY RESULTS**

M. M. THIN

Department of Physics, University of Mandalay, Mandalay, Myanmar

E-mail address: demomyatmonthin.edu@gmail.com.

E. SACCHI, M. SETTI

Department of Earth and Environmental Sciences, University of Pavia, Via Ferrata 1, Pavia, Italy.

H. HLAING

University of Lashio, Lashio, Myanmar.

Abstract: This paper reports some preliminary results obtained on waters and sediments from the Inle Lake. Carbonate equilibria dominate the lake water hydrochemistry. During the summer season, strong evaporation affects the water body, coupled to intense photosynthetic activity. These processes favour authigenic carbonate precipitation, as indicated by the high calcite content detected in the lake sediments. Isotopes of the water molecule indicate a residence time shorter than one year. The short residence time and calcite precipitation likely prevent the accumulation of anthropogenic contaminants and nutrients within the lake.

1. INTRODUCTION

Inle Lake, situated in Naung Shwe Township, Southern Shan State (20°27'–20°40' N, 96°52'–96°57' E, 870 m a.s.l.) is the second largest and the most important lake in Myanmar. Its average length is 18 km and the width is 11 km [1]. The Inle Lake region is characterized by a large, flat valley running N to S, surrounded by mountain ranges. The basin is located in the Shan Plateau, mainly constituted by limestone, about 50 km E of the tectonically active Sagaing fault and faults along the Shan scarp [2]. The lake is fed by several streams, the main contributor being the Nanlit Chaung, which flows from N to S with headwaters 16 km north of the inlet to the lake. The lake outlet flows to the S, entering the Thanlwin River [3]. The drainage area and storage capacity of the lake have been estimated at 5.612 km² and 3.5 x 10⁷ m³, respectively, while annual inflow and water residence time are estimated as 1.1 x 10⁸ m³ year⁻¹ and 0.32 year [4, 5]. The climate in the lake area is tropical monsoon with three seasons: hot dry, rainy and winter season. Approximately 70% of the annual rainfall occurs during the months of July, August, and September: the mean annual rainfall is 920 mm, generally occurring on 70–75 individual days. Mean air temperature near the lake ranges from 16.9°C to 31.5°C. The depth of the lake fluctuates with the seasons ranging from four meters in summer and seven meters in the rainy season [3].

The lake is a vital part of the broader ecosystem and economy of Shan State, providing many goods and services to its surrounding communities. Over 200 villages surround the lake and inhabit the immediate watershed. The lake is a main water resource for Law Pi Ta hydroelectricity power plant, a major tourist attraction upon which many in the local economy rely, a provider of agricultural products, and a habitat for rich biodiversity and traditional culture.

Inle lake is severely threatened by anthropogenic activities on the lake sides and in its drainage basin, causing an increase in sedimentation, with a consequent shrinking of the open water surface, and a change in water quality [6, 7]. The objectives of this study are to investigate present day water dynamics and sedimentation processes, to reconstruct its environmental evolution and assess the anthropogenic impact.

2. METHODS

During the one-year sampling period, water and sediment samples were collected from 5 study sites, selected based on their environmental setting (Table 1 and Figure 1).

Table 1. Sampling stations.

Station	Environmental setting	Characteristics
1	Natural biodiversity fishes and birds	Wildlife Sanctuary
2	Input from the main inflow	Inflow Stream
3	Water at the center of lake	Wide View Area
4	Influence of agrochemicals and anthropogenic pollution	Floating Cultivation Area
5	Output from the lake	Outflow Stream

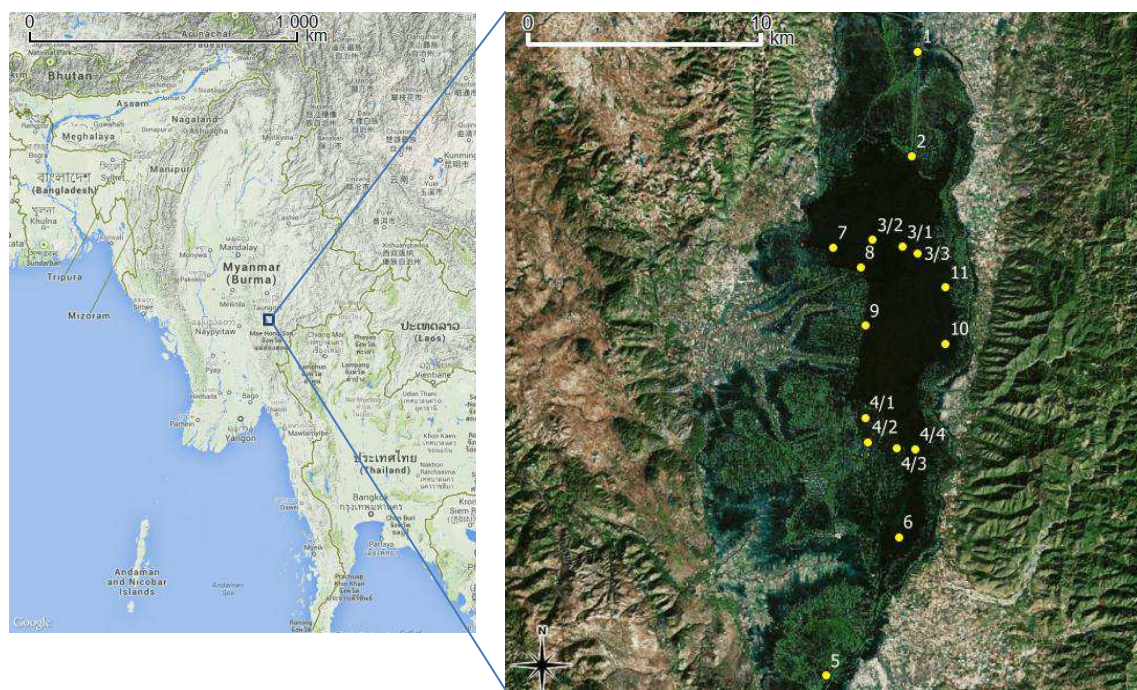


Figure 1. Location of the Inle Lake in Myanmar with water and sediment collection stations.

Sampling campaigns were performed in August, September and October 2013 (monsoon), in November and February 2014 (winter), and in May 2014 (summer) for hydrochemical and isotopic monitoring. Nine sediment cores were also collected in October 2013. A more detailed sampling campaign was carried out in March 2014 (summer), increasing the number of sampling stations (Figure 1) and collecting surface and bottom water, together with dredged bottom sediment, and sediment cores. During this campaign, water depth, surface temperature, pH, Eh, and alkalinity were measured in the field. In the laboratory, all water samples were (re)analyzed for pH, electrical conductivity and alkalinity (by titration). The

major ion contents were determined by ion chromatography. Stable isotopes of the water molecule were analyzed by WS-CRDS. Water samples from the March 2014 campaign were also analyzed for $\delta^{13}\text{C}_{\text{DIC}}$ using the gas evolution technique [8]. Sediment samples were dried at room temperature for 2-3 days. Major shells were eliminated by manual picking and the sediment was ground to fine powder in an agate mortar. The mineralogical composition of sediment samples were measured by XRD powder diffraction.

3. RESULTS

Water stable isotopes range from -8.23 to -0.76‰ in $\delta^{18}\text{O}$ and from -63.55 to -18.06‰ in $\delta^2\text{H}$. In the rainy season, the isotopic compositions align parallel to the Global Meteoric Water Line (GMWL), but with a lower d-excess (Figure 2). At the end of winter, but mostly during the summer season, with rising temperatures, the lake water is subject to strong evaporation under low relative humidity conditions. In all sampling campaigns, the most enriched isotopic value is displayed by Station 3 at the center of the lake. Also, at the onset of the rainy season, this station maintains an enriched isotopic composition, whereas at the end of the rainy season it displays a composition in agreement with that of precipitation. This observation indicates that, during the rainy season, the lake water is fully flushed by the inflow water, and therefore the residence time is < 1 year. As a reference, the isotopic composition of precipitation in Yangon (retrieved from the Global Network of Isotopes in Precipitation - GNIP database) is also shown in Figure 2.

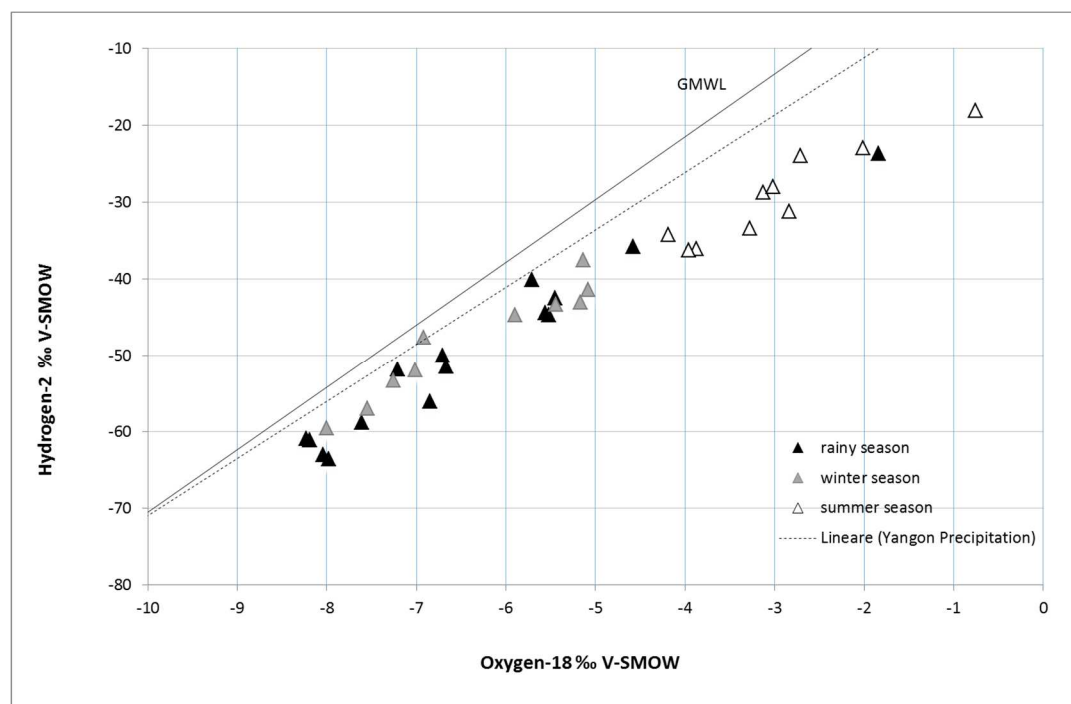


Figure 2. Stable isotope composition of water samples collected during one hydrological year, the GMWL and the regression line for Yangon precipitation data (GNIP database).

Lake waters are characterized by relatively low conductivities (range 257 to 486 $\mu\text{S}/\text{cm}$ during the annual monitoring, with higher conductivities characterizing samples from the summer season), neutral to alkaline pH (range 6.51 to 8.37) and oxidizing conditions (range 122 to 250 mV). The most abundant cation is calcium, followed by magnesium, sodium and potassium, whereas bicarbonate is the most abundant anion, followed by chloride, sulphate and carbonate. Therefore carbonate equilibria dominate the lake water hydrochemistry.

The isotopic composition of dissolved carbonates ($\delta^{13}\text{C}_{\text{DIC}}$), measured during the March 2014 campaign, ranges from -7.74 to -1.86‰ PDB, with the most depleted values characterizing inflow water and the most enriched values recorded in open lake water. Depleted DIC could derive from the dissolution of soil CO_2 in areas dominated by C4 vegetation, while in open lake waters, DIC could be enriched as a result of photosynthetic activity.

In the bulk sediment, the most abundant mineral is calcite, followed by quartz, mica/illite, kaolinite, aragonite and traces of dolomite. The clay fraction is mostly composed by kaolinite with lower mica and chlorite, and traces of smectite. Calcite is not evenly distributed in the lake area: samples collected at the inflow and outflow show a percentage of about 50%, rising up to 90% in samples collected within the lake. This observation suggests that authigenic calcite precipitation could significantly contribute to sedimentation.

Preliminary isotope data obtained on sediment calcite range from -1.34 to +4.67‰ in $\delta^{13}\text{C}$. Based on $\delta^{13}\text{C}_{\text{DIC}}$, the more depleted values could correspond to authigenic calcite precipitated from open lake waters, whereas enriched values could correspond to detrital calcite.

4. CONCLUSIONS

Preliminary results indicate that carbonate equilibria dominate the lake water hydrochemistry. During the summer season, strong evaporation affects the water body. The increase in temperature, coupled to intense photosynthetic activity, induces authigenic carbonate precipitation, as testified by the high calcite content detected in the sediments. Isotopes of the water molecule indicate a residence time shorter than one year. The relatively short residence time and calcite precipitation likely prevent the accumulation of anthropogenic contaminants and nutrients within the lake. The characterization of sediment core samples will allow for the reconstruction of the environmental evolution in time and assess the anthropogenic impact on this valuable ecosystem.

REFERENCES

- [1] MA, T.D.W., Floating island agriculture Ye-chan of Inle Lake, MA thesis, University of Yangon, Yangon (1996).
- [2] VIGNY, C., SOCQUET, A., ET AL., Present-day crustal deformation around Sagaing fault, Myanmar. *J. Geophys. Res.* **108 B11** (2003) 2533.
- [3] BUTKUS, S., MYINT, S., Pesticide use Limits for Protection of Human Health in Inle Lake Watershed, Myanmar. Living Earth Institute Olympia, Washington, DC (2001).
- [4] VOLK, P., HEYMANN, J., ET AL., Mapping and land use planning for watershed management. Final Rep. for the Gov. of Myanmar, Ministry of Forestry, GAF, Munich (1996).
- [5] NGWE, S.U., CATALAN, I., Preliminary survey on potentiality of reforestation under clean development mechanism in Myanmar with particular reference to Inle region. Unpublished report by Karamosia Intl, Yangon (2000).
- [6] SIDLE, R.C., ZIEGLER, A.D., VOGLER, J.B., Contemporary changes in open water surface area of Lake Inle, Myanmar, *Sustain Sci* **2** (2007) 55-65.
- [7] AKAISHI, F., SATAKE, M., OTAKI, M., Surface water quality and information about the environment surrounding Inle Lake in Myanmar, *Limnology* **7** (2006) 57-62.
- [8] ATEKWANA, A. E., KRISHNAMURTHY, R. V., Seasonal variations of dissolved inorganic carbon and $\delta^{13}\text{C}$ of surface waters: Application of a modified gas evolution technique. *J. Hydrol.* **205** (1998) 265-278.

ID: 15

USE OF GEOCHEMICAL TRACERS FOR CHARACTERIZATION AND QUANTIFICATION OF WATER LEAKAGE AT THE JOUMINE DAM SITE, TUNISIA

M.F. BEN HAMOUDA, S. SARI, M. KHOUATMIA, T. AOUADI

Isotope Hydrology and Geochemistry Unit, CNSTN, UMTN,

Technopark of Sidi Thabet, 2020, Tunisia

E-mail: f.benhamouda@cnstn.rnrt.tn

L. ARAGUAS

Isotope Hydrology Section, International Atomic Energy Agency, Vienna, Austria

Abstract: The Joumine reservoir, located in the north west of Tunisia and constructed in the early 1980s, has an upstream watershed area of 418 km² and the reservoir capacity is 130 Mm³. The dam presented a water leakage immediately after its construction. Shortly after the first filling of the reservoir in 1987, an important water leak was detected at the dam toe. The emerging flow rate at the maximum level in the reservoir was close to 500 L/s. An important sinkhole was detected in a limestone block outcropping in the left abutment, at a short distance from the uptake tower. The emergency work aimed at stopping the sinkhole by the injection of mine tailings lowered down the flow-rate of the leakage to about 120 L/s. The flow-rate of the leakage was monitored in two drains D1 and D2, located at the dam toe. The decrease of the flow-rate of the leakage due to emergency work was accompanied by an increasing of the salinity in the drain D2, which was interpreted as a risk to the integrity of the dam. A combined hydrogeological, geochemical and isotopic investigation (²H, ¹⁸O, ³H and ¹³C) was carried out afterwards in 2013 to determine the origin, flow path and other characteristics of leakage, integrating water level data from monitoring piezometers, water temperature and electrical conductivity, as well as hydro-chemical and environmental isotopes. Flow-rates measured in drains D1 and D2 by means of the tracer dilution technique were 45 and 58 L/s, respectively. The study carried out at the Joumine reservoir is a good example illustrating the usefulness of geochemical tracer methods for obtaining more precise and rapid information of the main features of water leakages, which if ignored may result in great repair costs or even affect the stability of a dam.

1. INTRODUCTION

In arid and semi-arid regions, the growing water demand for irrigation, industrial uses and domestic water supply is often satisfied by the combined use of a network of irrigation systems feed by reservoirs and local groundwater. In the case of Tunisia, water transfer systems consist of pipe lines and canals constructed to transfer surface water from dams in the north part of the country to the coastal urban and farming areas, where the demand for water is high. The ratio of water supply from surface and groundwater is about 50/50. About 97% of available surface runoff in Tunisia has already been used through the construction of reservoirs or planned to exploit. Due to the difficulties to develop new surface water resources it is necessary to optimize existing infrastructures to minimize water losses through leaks in dams and reservoirs. Therefore, sedimentation and leak control is an important issue in the sense of sustainable surface water resource management. Millions of people depend on dams and reservoirs for domestic, industrial and agricultural water supply, for flood protection and for electricity.

One of the most efficient and least costly methods of detecting and characterizing leaks from dams and canals is the use of geochemical and isotope tracers to delineate the source and movement of water [1]. These methods will often reveal the flow path of the leak and will help in adopting engineering approaches to reduce the safety risks and water losses, instead of the costly, yet common, trial and error method of repair. Such tests may also reveal that sudden changes in flow-rates downstream are not necessarily due to a leak from the reservoir, but may actually be the result of natural groundwater discharges unconnected with the dam.

The Joumine reservoir, located in the north-west of Tunisia, constitutes an important water resource for the region and the sedimentation and leaks in the dam site have been the subject of previous studies [2]. The dam presented a water leakage immediately after its construction. The reservoir has an upstream watershed area of 418 km² and the capacity is 130 Mm³ which ranks 5th in water storage capacity among all the water reservoirs in Tunisia. Water salinity in the reservoir is lower than most reservoirs in Tunisia, and due this property, water stored in the Joumine is utilized not only for drinking purposes and irrigation (about 1800 ha) but also, is mixed with water from other reservoirs to produce water of lower salinity. The Joumine reservoir has been in use since 1987.

The objective of the study is to illustrate the crucial role of isotope hydrology and related geochemical tools in characterizing the origin and flow paths of leaks from dams, contributing to the adoption of corrective measures leading to reduce water losses and/or minimize safety risks.

2. METHODS

The first part of this investigation on the leakage problem in the Joumine reservoir was carried out in 1998 within the framework of an international workshop on dam leakage studies organized in Tunis by the International Atomic Energy Agency (IAEA) and the National Centre of Nuclear Science and Technology of Tunisia. The figure 1 present, respectively, the results obtained from the measurements of potentiometric levels, conductivity and temperature profiles in all accessible piezometers at the dam site. For simplicity, the individual values of these parameters obtained at each borehole have been omitted. The flow rates measured in drains D1 and D2 by means of the tracer dilution technique were, respectively, 45 and 58 L/s.

Previous hydrochemical data of surface and ground water in the area was obtained as part of a reconnaissance study in 1964. For this study, the geographical position, depth to the water table, pH, electrical conductivity and temperature were measured in 62 sampling points in the study area during field campaigns carried out in 1998, 2013 and 2014. Samples were also collected for analysis of major ions, stable isotopes of water (²H, ¹⁸O), carbon-13 in total dissolved inorganic carbon (TDIC), and tritium. Isotope analysis of the water samples (²H, ¹⁸O, ¹³C and ³H) were conducted at the Isotope Hydrology Laboratory (IAEA), Vienna, Austria through the technical cooperation project RAF/8/028 and at the DEVIL: Duke Environmental Stable Isotope Laboratory, Duke University, NC, USA.

3. RESULTS

Water level measurements at boreholes provide valuable information on the local groundwater flow and hydraulic connections in the dam and in the surrounding areas. The potentiometric contour lines shown in Figure 1 indicate that the subsurface waters emerging at both drains are related to the infiltration occurring at a zone of the reservoir close to the uptake tower, that is, from the zone where the sinkhole was initially found. The piezometric high observed in the zone of piezometer P57 is explained by the infiltration of local precipitation into the two affected piezometers. Local precipitation remained stored inside the casing of these piezometers due to the partial clogging of their screens, which are located at the bottom. The piezometric level outside

this casing was normal. The low conductivity of the waters of these piezometers confirms the previous statement. The arrows marked in the figure show the direction of the preferential pathway of the water escaping from the reservoir.

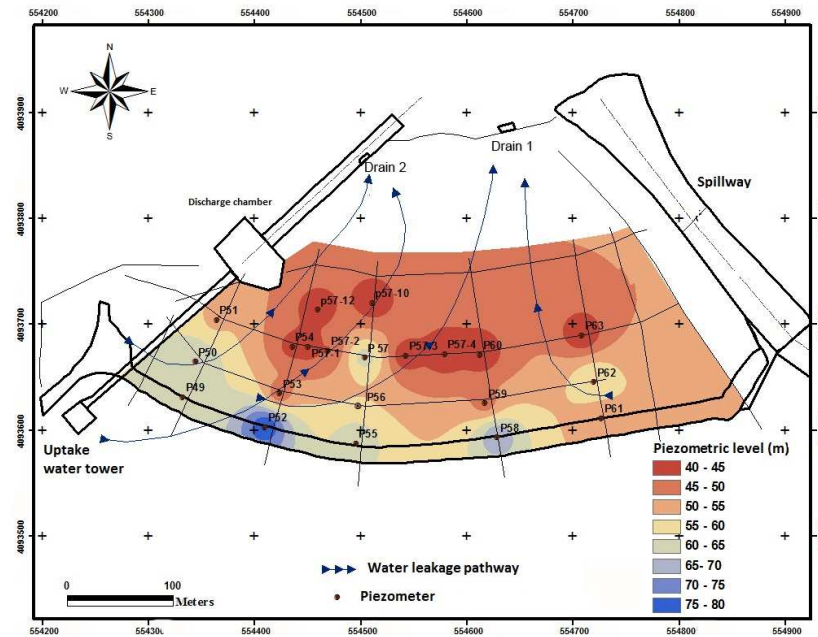


Figure 1. Piezometric map and sampling sites.

Stable isotopes of hydrogen and oxygen are very suitable tracers for hydrogeological investigations because (1) they are part of the water molecule and follow their behavior through the hydrological cycle; (2) they are conservative in most low-temperature environments [2], [3], [4], [5]. The plot of $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ (Fig. 2) reveals that groundwater close to the reservoir has a stable isotope composition which is indicative of an appreciable contribution of water coming from reservoir (P57, P17, P21, P22 and P55). Moving away from the reservoir the δ values become more depleted, owing to the contribution of infiltrating precipitation which also recharges the local groundwater system of piezometers P42, P41, P12 and P49.

Leakage water in D1 and D2, in addition to reservoir water R with piezometers: P57, P17, P57-2 and P55 that show a similar isotopic composition and hence, reflecting the same origin. Regression line that best fit the aforementioned group has a slope of 4.36, which reflects the effect of evaporation and/or mixing on δ values. This cluster P57, P17, P57-2 and P55 represents the first end member which is the surface water suffering from partial evaporation. The second end-member P42, P41, P24 and P49 (which is more depleted in stable isotope contents) and whose $\delta^{18}\text{O}$ contents vary between -5.41 and -4.96 ‰, thus less than -4.41 ‰, the weighted average of rain in Tunis-Carthage, is mainly composed by the local groundwater system which shows a different isotopic composition that has ruled out of theory that the reservoir water is only source of water in the piezometers (Fig 2). This separate cluster plot to the left of meteoric water line is indicative of non-local recharge. The points located between the two end members in Fig 2 (P22, P57) represent a mixture of the reservoir water and the local groundwater with different mixing proportions.

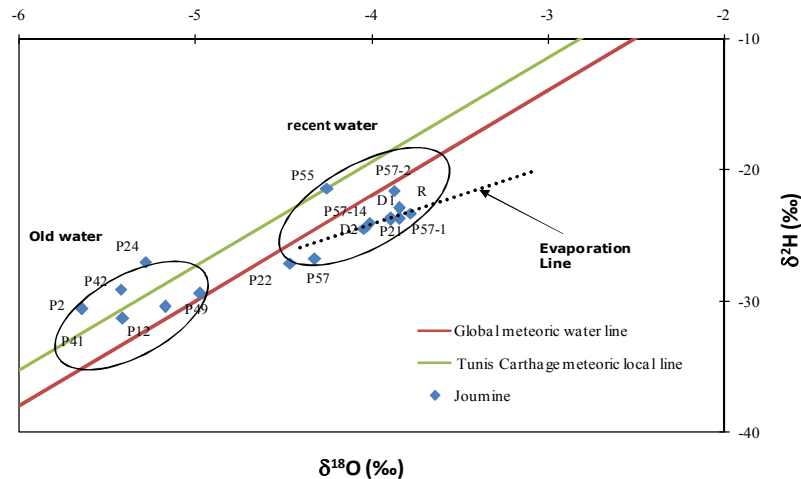


Figure 2. Plot δ^2H vs $\delta^{18}O$.

4. CONCLUSIONS

The results presented in this paper have provided a deeper insight into the nature and characteristic of the leaks and discharge of local groundwater in the vicinity of the Joumine dam. The main results are:

- 1) Water leakage from the reservoir mainly occurs in the karstic area situated in the left bank foundation and abutment and moves towards the middle part of the downstream toe of the dam, then dissipates into two main flows that join through the drainage system drains D1 and D2.
- 2) The spatial distribution of temperature, electrical conductivity and the chemical composition of water in the piezometers and in D1, D2 shows that the origin of leakage occurs through a perched aquifer situated in the left abutment and has a direct impact on the water quality in D2 by increasing the salinity and has no influence about the stability of the dam.
- 3) Finally, the change in the salinity of water observed in D2 is due to the contribution of brackish water from the mound on the Triassic formations in the left bank. Hydrological maps were produced showing the water leakage paths at the dam site. Many of the conclusions presented in this paper could not have been obtained using exclusively classical hydrological methods.

REFERENCES

- [1] CONTRERAS, I.A., HERNÁNDEZ, S.H., "Techniques for Prevention and Detection of Leakage in Dams and Reservoirs". Collaborative Management of Integrated Watersheds, 30th Annual USSD Conference Sacramento, California, April 12-16, 2010, (2010), 785-814.
- [2] PLATA, B.A., ARAGUÁS, L., Detection and Prevention of Leaks from Dams. A.A. Balkema Publishers, (2000) p. 419.
- [3] CLARK, I.D., FRITZ, P., Environmental isotopes in hydrogeology. CRC Lewis Publishers, New York, (1997) p 328.
- [4] PENG, T.R., WANG, C.H., Identification of sources and causes of leakage on a zoned earth dam in northern Taiwan: Hydrological and isotopic evidence, Applied Geochemistry. (2008) 2438–2451.
- [5] AGGARWAL, P K, FROELICH K, GONFIANTINI, R., Contributions of the International Atomic Energy Agency to the development and practice of isotope hydrology. Hydrogeol J 19 (2010), 5-8.

ID: 52

EXPLORING THE USE OF GAMMA-RAY SPECTROMETRY AS NON DESTRUCTIVE METHOD TO RECONSTRUCT SHORT-TERM ENVIRONMENTAL CHANGES

R. MIKALAUSKIENĖ, J. MAŽEIKĀ, I. BAUŽIENĖ

Nature Research Centre, Laboratory of Nuclear Geophysics and Radioecology,
Akademijos str. 2, Vilnius, Lithuania

E-mail address: renata.mikalauskiene@gmail.com

Abstract. The aim of this research is based on applying a gamma-ray spectrometry using natural archives, such as peat bogs, where information about the past conditions can be preserved. We used isotopes for radiometric dating of the recent peat record. We are seeking to reconstruct ages in Holocene period using measurements by gamma-spectrometry. For this research, the isotopes ^{210}Pb and ^{137}Cs have been used as time indicators. ^{210}Pb used to date surficial peat deposits providing chronology on a 100-150 year scale. ^{137}Cs widely used as supportive information in ^{210}Pb dating techniques.

The four peat cores were collected in a 2 m x 2 m area from the two peat bogs of Lithuania - Čepkeliai and Žudiškės in September 2013 for treatment in the laboratory. The peat cores were sub-sampled at 0.01-0.02 m layers. ^{210}Pb and ^{137}Cs specific activities were measured using well calibrated gamma-spectrometry based on HpGe detector. The gamma transmission used for activity calculations was 46.5 keV for ^{210}Pb and 662 keV for ^{137}Cs . Sequential isotopes data were processed to obtain peat ages using an appropriate CRS (Constant Rate of Supply) model of radioactive decay through time. CRS model is known to produce reasonable results for most environments, including recent peats.

Modern spectroscopy equipment base and research methodology allow for much greater precision than in the past to measure the activity of radionuclides in natural or artificial matrices. However, in order to achieve greater accuracy and reliability of the research allowing sufficient resolution to investigate chronologically related samples sequences we need to create a single chronological scale and improve the existing research methodologies and to time-series models.

ID: 64

ISOTOPIC AND CHEMICAL STUDY FOR THE SURFACE AND GROUND WATER INTERACTION IN THE SOUTH OF IRAQ

S. AL-NASERI,

Ministry of Science and Technology, Al-Jadiriya, Baghdad, Iraq,

E-mail address: saadikadhum@gmail.com.

M. ABDULRAZZAQ,

Ministry of Water Resources, Baghdad, Iraq

Abstract: This study focalizes on the area between Al-Samawa and Al-Shinafiya cities in the southern of Iraq. Chemical and isotopic analysis was used to characterize the groundwater and its relationship to the surface water in Al-Atshan River (A branch from the Euphrates River). The chemical study showed that ground water is characterized by its high salinity, and the presence of two layers of ground water; one with high total dissolved solids (50-100 g/L) and one with medium salinity (4-25 g/L). The study also showed that the salinity of Al-Atshan River increases with the path of the river from north to south. The study found weak relationship between surface and ground water. The results of the stable isotopes concentration (^{18}O and ^2H) confirmed the presence of the two layers of the groundwater, and the weak relationship between surface and groundwater.

1. INTRODUCTION

The study area lies in the south of Iraq, between Al-Samawah and Al-Shinafiyah cities (about 220 km south of Baghdad). It is bounded from the east by Al-Atshan River; a branch from Euphrates River. To the west of the study area, there is the western plateau with a simple inclination tendency toward the river. In the middle of the study area, there is a saline water natural lake (named Sawa), with a TDS of about 70 g/L. The detailed description of the geological formation can be found in [1-4]. In general, the area is considered semi-arid area with an annual average temperature of 24 °C and a relative humidity of 35-40%. The annual evaporation rate is about 3.5 m, while the annual rainfall rate is 75-100 mm. The area is important for its large agricultural usage. River water is normally used for irrigation, and its drain is returned back to the river column. The study aims to characterize groundwater and surface water in the area from the chemical and isotopic point of view and define the relationship between them.

2. METHODS

Water samples were collected from 12 artesian wells and 14 monitoring wells. Surface water samples were collected from 10 sampling points along the riverbank in the study area. Water samples from Sawa Lake were also collected. Stable isotopes (^{18}O and ^2H) were analyzed using laser spectrometer type LGR-100, while chemical analysis were implemented using conventional analysis for dissolved solids in water samples.

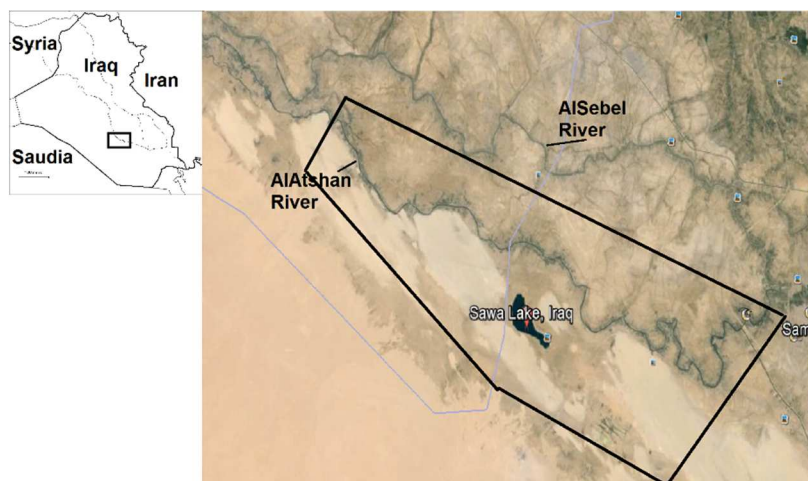


Figure 1. Study area aerial view.

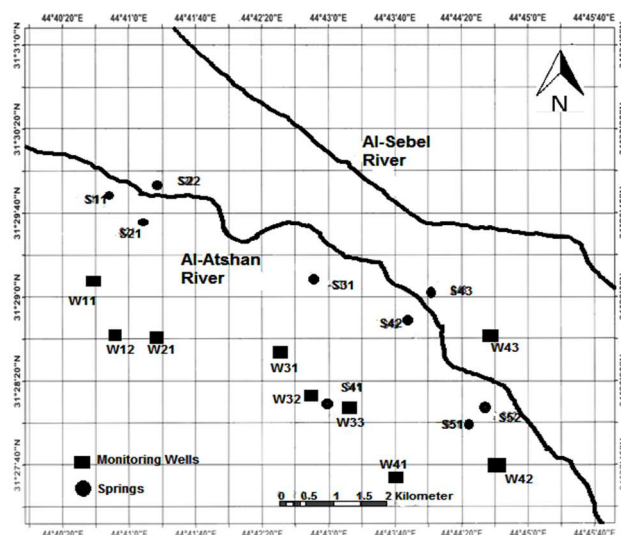


Figure 2. Sampling locations for wells and springs

3. RESULTS

Chemical analysis for the ground water showed that TDS range from about 4 to 100 g/L. Well water was characterized by high chloride concentration (0.7-70 g/L) and Boron (1.5-54 mg/L). River water, on the other hand, shows relatively high sulphate (170-780 mg/L) and low boron concentration (0.3-0.8 mg/L). A conclusion arises that there is weak interaction between groundwater and surface water.

Isotopic analysis for ^{18}O and ^2H are shown in Figure 3 together with the Global meteoric Water line (GMWL) and the local one (LMWL). The results showed three different fingerprints. Ground water samples can be classified accordingly into two groups; one is highly depleted (Group2) and the other is slightly depleted (Group1). Group1 is characterized by its high water TDS values (50-100 g/L), which points to the source of the water from the south with the ability to dissolved salts from rock formation. Group2, with less TDS values (4-25 g/L) indicates that water source is from Al-Damam formation with relatively low recharge activity. Figure 4 shows the relationship between ^{18}O concentration and TDS in

water samples, and shows the same two groups of groundwater. Both groups have stable isotopes concentration higher than that of the river water samples, which confirms the previous conclusion of weak interaction between ground and surface water in the area.

4. CONCLUSIONS

Chemical and isotopic analysis for samples showed weak interaction between ground and surface water. The TDS buildup of Al-Atshan River water can be attributed to the effect of the agricultural drainage on the river.

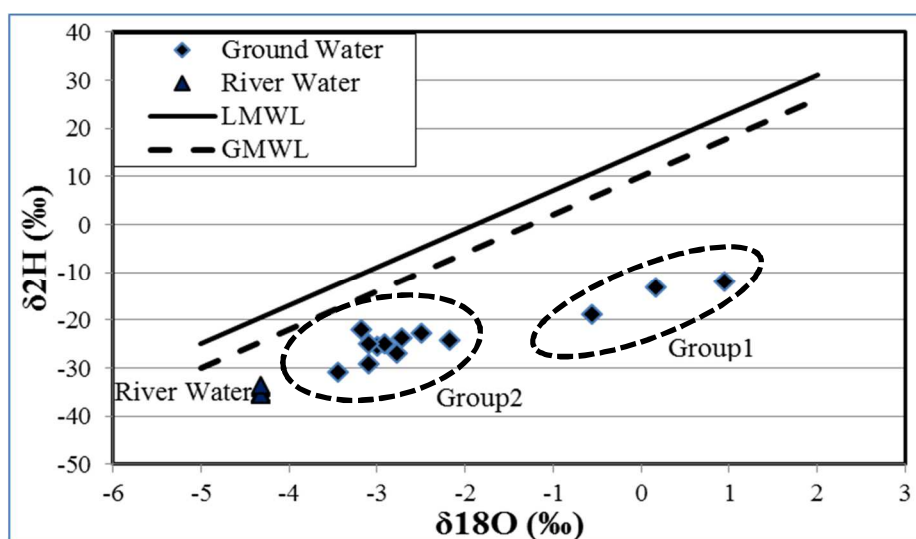


Figure 3. Relationship between δ^2H and $\delta^{18}O$

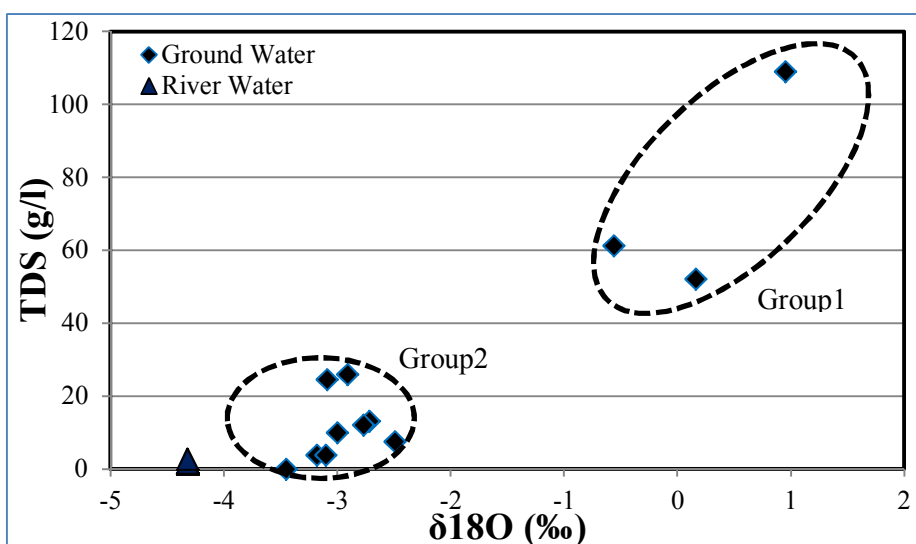


Figure 4. Relationship between $\delta^{18}O$ and water samples TDS

REFERENCES

- [1] BUDAY, T, AND JASSIM, S.Z, The Regional Geology of Iraq, Vol.2: Tectonism, magmatism and Metamorphism publication of GEOSURV, Baghdad, (1987), p. 352.
- [2] JASSIM, S.Z AND GOFF, J.C, Geology of Iraq First edition/ printed in the Czech Republic. (2006)
- [3] MOHAMMED I. ABDUL RAZZAQ, AND SUA'D A. RIDHA, The using of Geo-Electrical Method to study the effect of Ground Water on Al-Atshan River. Local scientific report submitted to the Ministry of water Resources, (2011).
- [4] MOHAMMED I. ABDUL RAZZAQ, KHALID S. DAWOAB, DUNIA I. DANNASH, The study of the effect of ground water on Al-Atshan River in the area between Al-Shanafiya-AlSamawa. Local scientific report submitted to the Ministry of water Resources, (2013).

THE ISOTOPIC HISTORY OF LAKE ONTARIO

R. HLADYNIUK, F. J. LONGSTAFFE

The University of Western Ontario, Department of Earth Sciences, 1151 Richmond Street,
London, Ontario, Canada, N6A3K7

E-mail address: rhladyn@uwo.ca

Abstract: Proxies from lake sediments can be used to infer paleoclimate in the absence of long-term climate and environmental monitoring data. More specifically, stable isotopes (carbon, nitrogen, oxygen) have become an essential part of paleolimnological studies. In lacustrine systems, variations in the oxygen-isotope composition of biogenic carbonates arise from changes in temperature, precipitation/evaporation ratios and/or water sources, whereas changes in carbon- and nitrogen-isotope compositions and abundances of organic matter generally reflect changes in productivity and/or source inputs. We have analyzed proxies from three piston cores located from west to east across Lake Ontario to reconstruct the climate/environmental/water balance history of the basin from ~16,000 to 3,500 cal BP. In addition, we are using benthos cores from the same locations to compare results for such proxies, at high-resolution, with archival climate records available from 1850 to 2008 A.D, and with modern lakewater isotopic records collected since 2006. This has allowed us both to validate the proxy method and to observe how well sediment proxies from Lake Ontario have responded to recent climatic, hydrological and environmental changes. During the glacial period (>13,000 cal BP) lakewater oxygen-isotope composition (–17‰, VSMOW), inferred from ostracodes valves, indicates significant involvement of glacial meltwater. The low abundances of organic carbon (~0.25%) and carbon-isotope compositions of ~ –27‰ (VPDB) and other biomarkers in the glacial sediments suggest a dominantly allochthonous organic matter source. In postglacial sediments, the lakewater oxygen-isotope composition initially increases from ~ –14 to –9‰ from 12,500 to 12,300 cal BP, marking cessation of meltwater influx and hydrologic closure of the basin. By 10,500 cal BP, the lakewater oxygen-isotope composition increases to –6‰, reflecting greater evaporation under cold and dry conditions. C/N ratios and increasing carbon-isotope compositions of bulk organic matter (–29.5 to –27.5‰, VPDB) during postglacial times indicate rising primary lacustrine productivity. Pb-210 chronology for the most recent sediment record has allowed us to establish a robust age-depth model over the last ~200 years. Initial proxy results demonstrate a strong correlation with measured climatic and environmental changes in Lake Ontario during that time.

ID: 73

STABLE ISOTOPES AS TRACERS OF ANTHROPOGENIC ACTIVITIES IN A TROPICAL RIVER SYSTEM

A. D. TRINH,

Institute of Chemistry, Viet Nam Academy of Science and Technology, Viet Nam

E-mail address: trinhanhduc@yahoo.com

T. P. Q. LE,

INPC, Viet Nam Academy of Science and Technology, Viet Nam

D. L. VU,

ICH, Viet Nam Academy of Science and Technology, Viet Nam

T. T. TA,

Faculty of Chemistry, Hanoi National University, Viet Nam

Abstract: The Red River network in northern part of Vietnam is vital to the socio-economic development of this region. The development has, however, created profound hydro-environmental changes to the River (e.g. discharge reduction; nutrients load increase, salinity intrusion in delta area). Our preliminary results have shown great variation of stable isotopes between different sites. Those sites were selected based on the difference of anthropogenic activities and water regime change. This variation after a well calibration with additional data could be integrated with water quality data to give a quantitative picture of anthropogenic impacts to the lower section of Red River.

ID: 104

INTERACTION BETWEEN GROUNDWATER AND WETLANDS, CAUSED BY OPEN PIT MINING IN SOUTHEAST BUENOS AIRES, ARGENTINA

E. BOCANEGRA.

Universidad Nacional de Mar del Plata. Instituto de Geología de Costas y del Cuaternario.
Mar del Plata, Argentina.

E-mail address: emilia.bocanegra@gmail.com

M. QUIROZ LONDOÑO.

Instituto de Geología de Costas y del Cuaternario – Instituto de Investigaciones Marinas y
Costeras. Mar del Plata, Argentina.

J. DEL RÍO, M. FARENGA

Universidad Nacional de Mar del Plata. Instituto de Geología de Costas y del Cuaternario.
Mar del Plata

Abstract: This paper proposes to characterize the interactions between groundwater and the anthropogenic wetlands resulting from mining activities in Buenos Aires province, Argentina. The methodology consisted of measuring levels, hydrochemical and isotopic sampling, and construction of diagrams. Wetlands located on quartzites have a higher level than the groundwater in the transition zone to the porous aquifer. Wetlands have an isotopic enrichment relative to groundwater, suggesting the occurrence of evaporation processes. The origin of wetlands is water from the fractured aquifer whose thickness corresponds to the quarry face, and also from runoff.

1. INTRODUCTION

The production of aggregates from mining is one of the main socio-economic activities of peri-urban areas of Mar del Plata, head of the General Pueyrredón County in the southeast of Buenos Aires Province, Argentina (Figure 1). From the hydrogeological point of view, the exposed rock formations are quartzites (Balcarce Formation) arranged in horizontal layers with a thickness between 0.30 and 1 meter. These layers are affected by systems of high-grade fractures, crossed by faults with NE-SW [1], which constitute a system of low permeability. Overlying these rocks, there is a sequence of silty-like loess Quaternary sediments. These constitute the Pampean aquifer, source of water supply to urban, agricultural and industrial purposes.

In the peri-urban area, 18 quarries have been developed since 1960 as a result of mining activity. In 8 of them (Pétrea, Paso de Piedra, Don Mariano, La Gloria, Minera, Cerámica, Silex y Castillo), (Figure 1), the existence of wetlands has been ascertained, whose surface varies between 2100 and 14000 m² and their depth ranges from 6 to 12 m.

Wetlands located in areas of quarries are facilitators of local development, by providing various services to human welfare, including the provision of water for mining, development of aquaculture for the rehabilitation of environmental liabilities resulting from mining activity, and cultural services (tourism, landscape, identity and sense of belonging) [2].

The aim of this work is to characterize the wetlands – groundwater interactions in the fractured / porous media transition of peri-urban areas, and establish the importance of these water bodies as a source of recharge to the main aquifer.

2. METHODOLOGY

A water sampling was conducted in 6 wells and 2 wetlands in summer 2013 and in 4 wells and 3 wetlands in spring 2014, for the determination of physicochemical parameters and content of stable isotopes ^2H and ^{18}O . Information on groundwater levels was collected and physicochemical analysis in the study area were performed. Chemical and isotope hydrology diagrams were used.

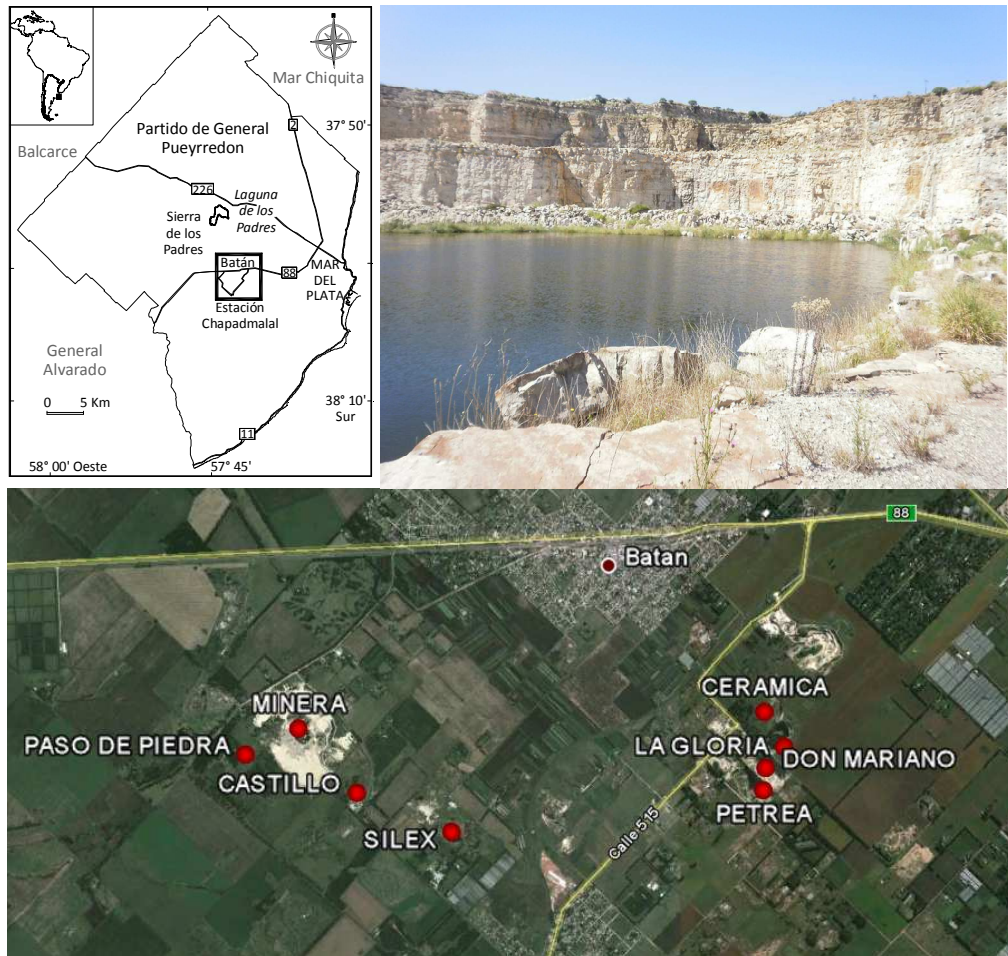


Figure 1. Location map

3. RESULTS

The flow patterns indicate that wetlands resulting from mining activities in quartzites rocks have a higher level than the groundwater in the transition zone to the porous aquifer; a level in a wetland of up to 24 m above the water table has been recorded in a well located within 200 m of the wetland (Figure 2). The flux passing through the fractured aquifer recharges the porous aquifer. This flow has been estimated in an average annual contribution of 5 hm^3 [3] through the numerical simulation of the aquifer for supply of Mar del Plata.

Ion analysis establishes two types of water: calcium - magnesium bicarbonate or sodium bicarbonate. The electrical conductivity varies in a range between 1720 $\mu\text{S}/\text{cm}$ and 142 $\mu\text{S}/\text{cm}$, with mean value of 854 $\mu\text{S}/\text{cm}$ in groundwater and 221 $\mu\text{S}/\text{cm}$ in wetlands. The conductivity increases as the topographic heights decrease, associated to water recharge and transit areas [4].

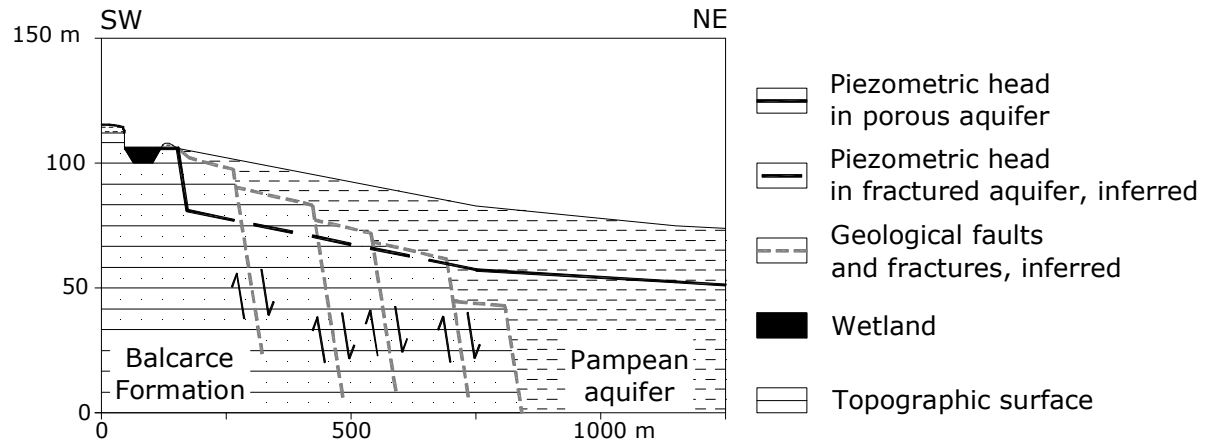


Figure. 2. Flow diagram in the fractured – porous media transition

The isotopic composition shows that groundwater is practically on the local meteoric line (Figure 3), suggesting that rain water is the source of recharge. In spring wetlands have a certain isotopic enrichment relative to groundwater; in summer, they are strongly evaporated. The mean values of the isotopic contents are shown in Table 1.

The relationship between concentration of Cl^- and $\delta^{18}\text{O}$ is shown in Figure 4. Groundwater presents homogeneous isotopic values, but an increase of Cl^- in the direction of flow. Wetlands, isotopically enriched, show a low Cl^- content, similar to groundwater from wells in quarries.

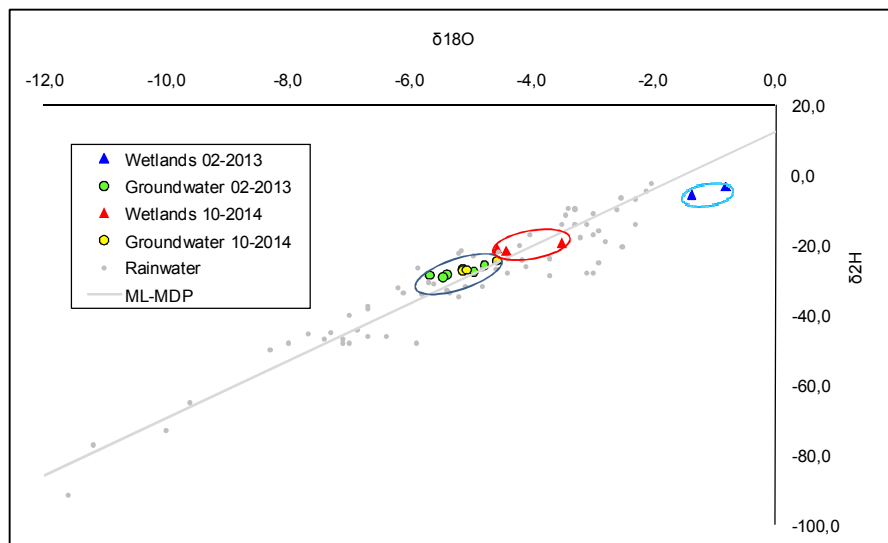


Figure. 3. Diagram $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ of groundwater and wetlands

4. CONCLUSIONS

The origin of wetlands is water from the fractured aquifer whose thickness corresponds to the quarry face. Runoff is another source of wetlands. Studies including seasonal isotopic monitoring will allow quantifying the mass balance. The flux passing through the fractured aquifer recharges the porous aquifer.

The functional model of the environment shows that anthropogenic wetlands are supporting productive activities such as intensive aquaculture, and sites of social recognition for their amenity associated to recreation. Concerning the groundwater, it has a direct role as a water source.

Table 1. Mean isotopic contents

	Rain water	Groundwater	Wetlands 10-2014	Wetlands 02-2013
$\delta^2\text{H}$	-29,85	-27,41	-20,6	-4,48
$\delta^{18}\text{O}$	-5,03	-5,12	-4,17	-1,09

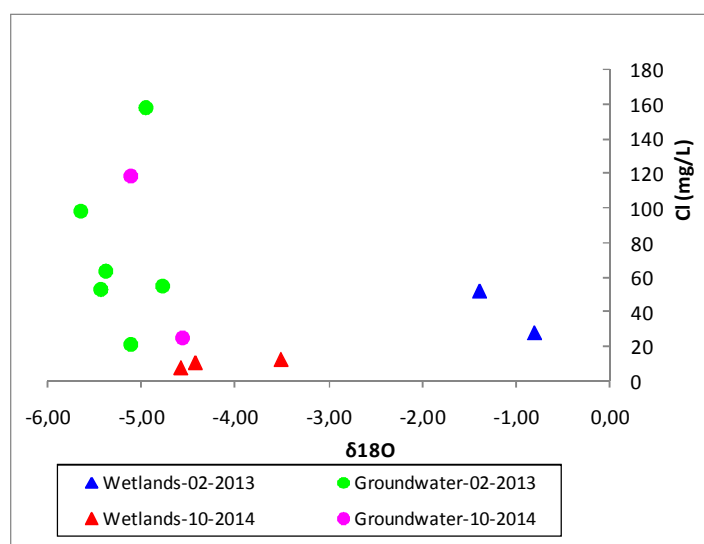


Figure 4. Relationship between concentration of Cl^- and $\delta^{18}\text{O}$

REFERENCES

- [1] TERUGGI, M., KILMURRAY, J. Tandilia. Geología de la provincia de Buenos Aires. Relatorio, *VI Cong. Geol. Arg. Bahía Blanca*, (1975). 55-77.
- [2] BOCANEGRA E., DEL RÍO, J. L., QUIROZ LONDOÑO, O. M, FARENGA, M. Caracterización de las interacciones humedales antrópicos- aguas subterráneas-ser humano en canteras de áridos del sudeste bonaerense. 2º Congreso Argentino de Áridos. Cámara de la Piedra de la Provincia de Buenos Aires. (2014). 12 pp
- [3] BOCANEGRA, E. Estrategias de gestión del acuífero de Mar del Plata. Modelo conceptual y simulación numérica. Tesis Doctoral. Facultad de Ciencias Exactas, Ingeniería y Agrimensura. Universidad Nacional de Rosario. (2011). Unpublished.
- [4] QUIROZ LONDOÑO, O. M., MARTÍNEZ, D. E., DAPENA, C., MASSONE, H. Hydrogeochemistry and isotope analyses used to determine groundwater recharge and flow in low-gradient catchments of the province of Buenos Aires, Argentina. *Hydrogeology Journal*, 16 (6), 1113-1127. (2008).

ID: 105

**GROUNDWATER INTERACTIONS IN BABITONGA BAY
HYDROLOGIC COMPLEX AND SALINITY INVERSIONS IN THE
ESTUARINE ZONE: EVIDENCES FOR SUBMARINE
GROUNDWATER DISCHARGE (SGD)**

V. G. BARROS,

Hydrology Laboratory, UDESC, Rua Paulo Malschitzki, s/n, Joinville - SC – Brazil.

E-mail address: virginia.barros@udesc.br

I. BANESCHI,

Institute of Geosciences and Earth Resources – CNR, Via Moruzzi 1, Pisa, Italia.

D. A. RAMOS,

Hydraulics Laboratory, UDESC, Rua Paulo Malschitzki, s/n, Joinville - SC – Brazil.

R. S. BAIL

Environmental Engineer

Abstract – The hydrologic complex of Babitonga Bay (134 km²), one of the main estuarine formations in the south of Brazil, encompasses 1.400 km². The hydrographic network is formed by carved thalwegs and strong vertical gradient that, associated to the high pluviometric index, determines a great hydraulic potential. Discharges of groundwater in coastal areas (Submarine Groundwater Discharge - SGD) occur when an aquifer (superficial or confined) is hydraulically connected with coastal areas. Responsible for transporting nutrients, they are object of study in several countries, due to the importance of mixing processes and chemical reactions that occur in these areas. SGDs are present in all coastal zones and are controlled by a series of climatological, hydrological and oceanographic processes. This work intends i) to identify evidences of the occurrence of SGDs in Babitonga Bay (BB) and ii) to characterize isotopic composition in surface and groundwaters in the region. Preliminary results of parameters such as temperature, salinity, pH, DO, and electrical conductivity from superficial and bottom water in the sampling sites of the BB where SGDs were supposed, seem to confirm the hypothesis of their presence. Moreover, determinations of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ from wells inside BB's islands, springs nearby the bay and surficial waters suggest possible sources of these phenomena in this area.

1. INTRODUCTION

The hydrologic complex of Babitonga Bay (BB), one of the main estuarine formations in the South of Brazil, is located in Santa Catarina State - southern of Brazil, and encompasses 1.400 km² including a mangrove ecosystem (130 km²). The complex is located 45 km northeast of the city of Joinville (population: 511604). The bay's drainage basin (26°02' - 26°28's and 48°28' - 48°50'w) forms a vast environmental complex, where agricultural and shellfish farming activities as well as a spectrum of industries, like textile, "metal-mechanical", foundries, etc. coexist with a unique natural area of Atlantic rain forest. According to USGS [1], Submarine Groundwater Discharge (SGD) - is a coastal characteristic present all around the world. These occurrences are controlled by a series of climatological, hydro(geo)logical and oceanographic processes, such as terrestrial hydraulic gradients that reflect climatic conditions and, in the long term, they carry surface and groundwater to the coast. In coastal waters, physical oceanographic processes such as the formation of waves, tide variation and the circulation driven by density, impact these

hydraulic gradients and thus affect rates of submarine groundwater discharge. Although only the groundwater discharge of fresh water is explained by traditional numerical simulations of coastal waters, the discharge of saline recirculated groundwaters can be even more important in terms of material transport (i.e., nutrients, metals, organic substances) through the continental/sea boundaries. Thus, SGD can encompass underground fresh water, sea water recirculated, or a composition of both. Consequently, SGD can be considered as a vector for nutrients and other substances, including pollutants, to coastal waters. An approach used to study inputs of groundwater into the oceans is the use of geochemical tracers. According to [2], geochemical tracers (such as $\delta^2\text{H}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, Cl^- , Br^- , etc.) have been used successfully to evaluate SGD influences. The use of isotopic techniques, combined with traditional geochemical tools, allows identifying different sources of waters and to trace their paths and reactions.

2. SITE DESCRIPTION

Babitonga Bay is an estuary located in the northern portion of the Santa Catarina State coast, South of Brazil ($26^\circ02' - 26^\circ28'\text{S}$ and $48^\circ28' - 48^\circ50'\text{W}$), bordered in the northwestern portion by the Serra do Mar geomorphological unit. The geomorphology discloses a vast diversity of lithological and structural aspects, including: quaternary sediments, which correspond to plains, Precambrian rocks, which correspond to the mountains area where the landscape was intensely affected by erosional processes. The basin and topography of the region generates pronounced altimetric contrasts. The principal geomorphological unit is the Serra do Mar, formed by a set of crests, peaks, uplands, mountains and scarps separated by deep “V-shaped” valleys with high declivities. In this region the highest altitudes are found, with peaks exceeding 1500 m. The altimetric amplitude can exceed 400 m, especially in the east front, where the uplands raise over the coastal plains. This Crystalline unit and the high precipitation observed (mean 2000mm/y, with large concentration in summer season) is caused by the influence of this relief, which blocks the humid winds originating in the ocean favour the hydrographic network, that shows carved thalwegs and strong vertical gradient, determines a great hydraulic potential. The occurrence of groundwater is related to three main aquifer formations: weathered crystalline rocks, fractured granite complex, and quaternary sedimentary formations. The underground discharge rate in the crystalline aquifer is up to $15 \text{ m}^3/\text{h}$.

3. METHODS

Measurements and collection of water samples followed [4] results that found salinity inversions in the water column at some points within BB. Sampling campaigns performed during the austral summer (2008) allowed for the collection of 30 samples from private wells, springs in BB islands, São Francisco do Sul (SFS) Island and continental zone near BB islands (Figure 2, oval shapes). Moreover, samples inside Cubatão River Basin were sampled as representative of the hydrologic complex [3-4]. In situ measurements involved pH, Eh, Dissolved Oxygen (DO). BB waters (surface and bottom) were also analyzed in some points. In situ measurement involved pH, Eh, DO, Electrical Conductivity, temperature and alkalinity. Samples for stable isotope analysis were collected and prepared according to standard procedures [5]. All gases were analysed on a FinninganTM MAT 250 Mass Spectrometer at ISO4 s.n.c., Turin, Italy.

4. RESULTS AND DISCUSSION

On the diagram (Figure 1), results indicate:

1. Figure 1 a): The electrical conductivity of the all collecting samples, excluding BB waters, (mean = 0.098; St Dev = 0,055 mS/cm; N=17) varied from 0.03081 mS/cm to 0.14 mS/cm

which correspond to the samples collected in the continental area (Cubatão River Basin) and a spring inside a BB island. Despite the little difference among the $\delta^{18}\text{O}$ of all the samples (mean = $-3,48\text{‰}$; St Dev = 0.41‰ ; N=17) two groups of water could be identified. a) Groundwaters related to the Cubatão River basin (CRB), characterised by lightest isotopic content and lower electrical conductivity (mean = -3.64‰ ; St Dev = 0.12‰ ; N=11). Cubatão River, during the two campaigns, presented a $\delta^{18}\text{O}$ value of -3.58‰ . b) Groundwaters characterised by heaviest isotopic content and higher electrical conductivity collected from shallow wells and springs located inside BB islands in sandy areas (mean = -2.96‰ ; St Dev = 0.12‰ ; N=6). Such correspondence can be attributed to the effective recharge of rainfall (higher during summer than winter season) and surface water to the aquifers, suggesting the harmonisation of hydrological and hydrogeological systems. Moreover, rivers sampled in SFS from low altitude water springs present $\delta^{18}\text{O}$ value of -2.96‰ . These results can suggest water inputs from different origins in wells and springs in the region.

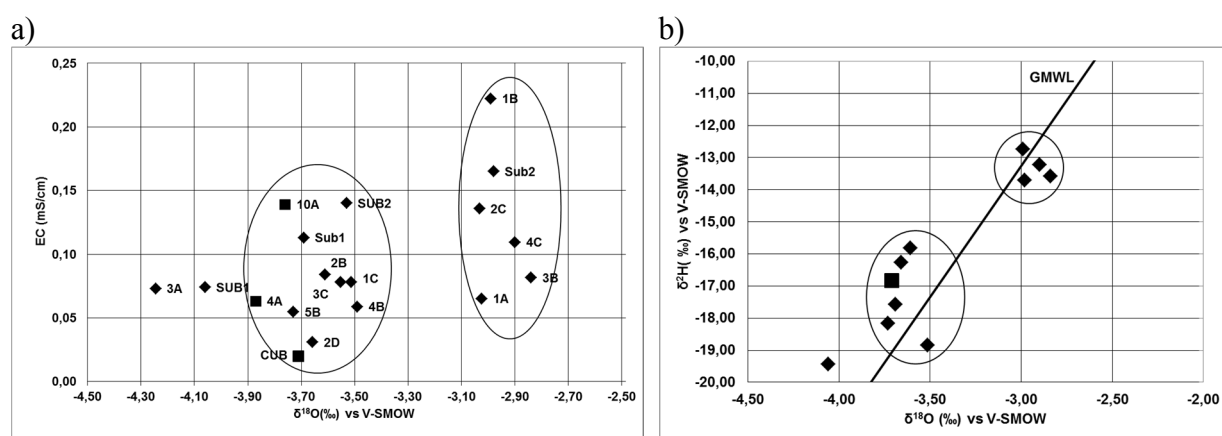


Figure 1a: Correlation between $\delta^{18}\text{O}$ and electrical conductivity in samples, presenting two groups of water. Groundwaters from CRB (left) and groundwaters from shallow springs inside BB islands (right). Figure 1b: Water stable isotope content in study area. Square highlight the isotopic composition of Cubatão River.

- Similar conclusions can be obtained observing the diagram $\delta^{18}\text{O}$ versus $\delta^2\text{H}$, Figure 1b). Water samples related to the Cubatão River basin (CRB) are characterised by lightest isotopic content. In summer season, little differentiation is observed in the isotopic composition in BB hydrologic complex [3-4], even so it is possible to distinguish two different groups. Groundwaters from plateau system present little deuterium excess, around 11-13‰, that can be attributed to discrete fractionation processes of local rainfall in summer. Evapotranspiration can be the responsible of this result. In fact the dense vegetation of the BB region can be the source of this evapotranspirative flux because of the re-evaporation of the lighter $^2\text{H}^1\text{H}^{16}\text{O}$ molecule. Very similarity is observed in waters from shallow wells and springs inside BB islands. Again, isotopic content from these samples is very similar to those coming from rivers of low altitude springs.

Table 1: Electrical conductivity (in mS/cm) measured in different point of Babitonga Bay

Point	Surface	Bottom	Point	Surface	Bottom
B9	42,7	44,0	B14	44,9	40,6
B3	43,9	41,8	B17	43.9	27.2
B12	42,9	43,5	B20	43.6	35.1

3. Inversions of salinity. Figure 2 shows points (B14, B17 and B20) where the greatest salinity inversion were found in the water column, an indication that these sites may be occurrence of SGD. Moreover Table 1 presents results of electrical conductivity from campaigns carried out in order to find these inversions.

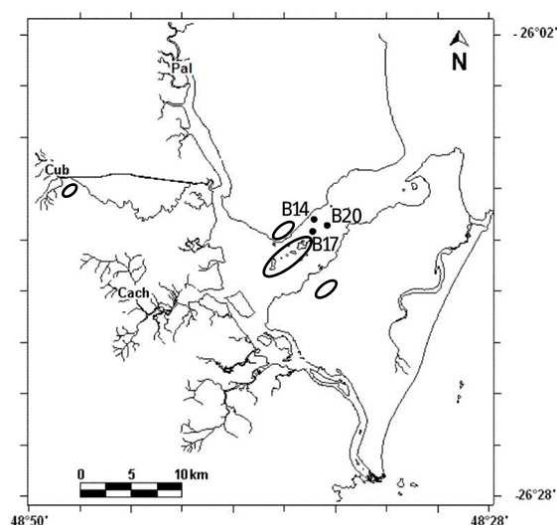


Figure 2. Study area, oval shapes indicate the sampled zone. Dots indicate points B14, B17 and B20 where salinity inversion in water column were found.

5. CONCLUSION

The potential process responsible for the inversion of salinity in BB water column can be the same by which freshwater is found in the islands inside the bay. It could mean that freshwater from the continent arrives to the Bay as free submarine discharge. The geology and hydraulic gradient formed by the strong vertical gradient could support this hypothesis. Unfortunately no samples could be collected as a function of the depth (mean 5m) and structure available. More efforts must be done to confirm SGD presence and source of these waters.

REFERENCES

- [1] United States Geological Survey - USGS, 2004. <http://coastal.er.usgs.gov/sgd/ofr_2004-1226sgd.pdf>.
- [2] DULAIIOVA, H., BURNETT, W.C., CHANTON, J.P., MOORE, W.S., BOKUNIEWICZ, H.J., CHARETTE, M.A., SHOLKOVITZ, E., Assessment of groundwater discharges into West Neck Bay, New York, via natural tracers. *Cont. Shelf Research* 26, (2006) 1971-83.
- [3] BARROS, V.G., MAS-PLA J., OLIVEIRA, T. M. N., SACCHI, E., ZUPPI, G. M., Hydrological mixing and geochemical processes characterization in an estuarine / mangrove system using environmental tracers in Babitonga Bay (Santa Catarina, Brazil). *Continental Shelf Research* 28, (2008) 682-695.
- [4] BARROS, G. V., MARTINELLI, L. A., MAS-PLA J., OLIVEIRA, T. M. N. , OMETTO, J. P. B., SACCHI, E., ZUPPI, G. M., Spatial variations of environmental tracers distribution in water from a mangrove ecosystem: the case of Babitonga Bay (Santa Catarina, Brazil). In: *International symposium on advances in isotope hydrology and its role in sustainable water resources management (IHS-2007)*, Vienna. *Advances in Isotope Hydrology and its Role in Sustainable Water Resources Management*. Viena: IAEA, (2007). v. 1. p. 131-138.
- [5] CLARK, I., FRITZ, P., *Environmental Isotopes in Hydrogeology*, Lewis Publishers, Boca Raton (1997) 328.

GEOTHERMAL RESERVOIR CHARACTERISTICS (T AND DEPTH) OF AYUB PEIGHAMBAR AND SHAFI HOT SPRINGS USING GEOTHERMOMETERS AND ENVIRONMENTAL ^2H AND ^{18}O ISOTOPES

H. MOHAMMADZADEH, M. KAZEMI

Groundwater Research Center (GRC), Department of Geology, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran, P. O. Box:91775-1436

E-mail address: mohammadzadeh@um.ac.ir

Abstract: Hot springs are evidence of geothermal field, where the internal thermal of the earth, resulted from volcanic activities and from geochemical reactions, is transferring to the land surface. Ayub Peighambar and Shafi hot springs, with temperature of about 40 °C and CaSO_4 water type, are located in Northeast of Iran. These springs due to have high temperature than other adjacent springs and are using for balneotherapy purposes, are very important. According to geothermometry and stable isotope (^{18}O and ^2H) studies, depth of Ayub Peighambar hot spring geothermal reservoir is about 4-5 kilometer and its temperature is less than 150 °C.

1. INTRODUCTION

Several factors can generate hot springs including: 1- volcanic activities; 2- geothermal gradient with deep circulation of water; 3- radioactive material (long-lived radioactive isotope) and decay process that produced heat; 4- tectonic and fault movement/earthquake; and 5-physicochemical reaction [1-6]. To estimate the temperature and the depth of geothermal reservoir, the geothermometers tools (minerals, element and chemical composition) can be applied [7].

2. METHODS

Samples were collected, each in polyethylene 25 ml bottle, from Ayub Peighambar and Shafi hot springs. All samples were filtered using 0.45 μm membrane and the cation samples were acidified with concentrated HNO_3 acid. Samples were sent to Ottawa University Geochemistry and G.G Hatch stable isotope laboratories for measuring anions, cations and stable isotope (^{18}O and ^2H) compositions. During field observation and sampling period, the field parameters (T, EC, TDS, Ph, Eh and DO) were measured. In this paper, the temperature and the depth of geothermal reservoir of Ayub Peighambar and Shafi hot springs were estimated using Na-K geothermometer, methods developed Giggenbach [8] and by Mohammadi [9], and stable isotope techniques.

3. RESULTS

Based on chemical composition, the temperature and depth of geothermal reservoir for Ayub Peighambar and Shafi hot springs were calculated and the results were tabulated in Table 1.

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ contents of samples from Ayub Peighambar and Shafi hot springs indicate origin of geothermal and meteoric waters (Figure 1). The average $\delta^2\text{H}$ values of hot springs is about -73 ‰, therefore, the source of temperature/heat for Ayub Peighambar and Shafi hot springs can't be related to volcanic activities (with $\delta^2\text{H}$ values of -20 ‰ to -30 ‰). The

temperature/heat source and the origin of water for both hot springs are geothermal gradient and meteoric waters. Meteoric water, by penetrating to the depth through existence deep faults/fractures in the study area, get the heat of the earth and altering to geothermal waters, then rising to the land surface. The depth of water circulation in Ayub Peighambar hot spring calculated using isotopic composition and the results are tabulated in Table 2.

Table 1: Temperatures and depths of hydrothermal reservoir for Ayub Peighambar and Shafa hot springs.

	Ayub Peighambar hot spring					Shafa hot spring	
	Sp8.1	Sp8.2	Sp8.3	Sp8.4	Sp8.5	Sp10.1	Sp10.2
Using Aq.QA hydrogeochemistry software							
Temperature (Na-K)	150 >	150 >	150 >	150 >	150 >	150 >	150 >
Depth (km)*	5 >	5 >	5 >	5 >	5 >	5 >	5 >
Depth (km)**	4.65	4.65	4.65	4.65	4.65	4.65	4.65
Using Mohammadi method's [9]							
Temperature (Na-K)	113	114	114.50	109.80	111	100.90	100.90
Depth (km)*	3.76	3.80	3.82	3.66	3.70	3.36	3.36
Depth (km)**	3.42	3.45	3.47	3.31	3.35	3.02	3.02
Using Giggenbach method's [8]							
Temperature (Na-K)	157	157	158	154	155	146.50	146.50
Depth (km)*	5.20	5.20	5.26	5.10	5.16	4.80	4.80
Depth (km)**	4.89	4.89	4.92	4.79	4.82	4.54	4.54

Note: *General law (0.03 °C/m) and ** Using Marques et al., method [10].

Table 2: Maximum depth of circulation of hot water in study area

Average amount in cold spring (‰)		Average amount in hot spring (‰)		Difference (‰)		Maximum depth of circulation of water (‰)	
$\delta^{18}\text{O}$	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^2\text{H}$
-9.29	-66.47	-9.97	-73	-0.68	-6.53	4.16	3.66

4. CONCLUSIONS

According to geological, hydrogeochemical and stable isotope studies of Ayub Peighambar hot spring area, the main source for fairly high temperature of water (38 °C) in this spring is the geothermal gradient and may be the underground alteration and partial melting (new deep situated material). The origin of water is meteoric water which is penetrated to the depth through existence deep fault in highly tectonized study area. According to geothermometry and stable isotope studies, depth of Ayub Peighambar hot spring geothermal reservoir is about 4-5 kilometer and its temperature is less than 150 °C.

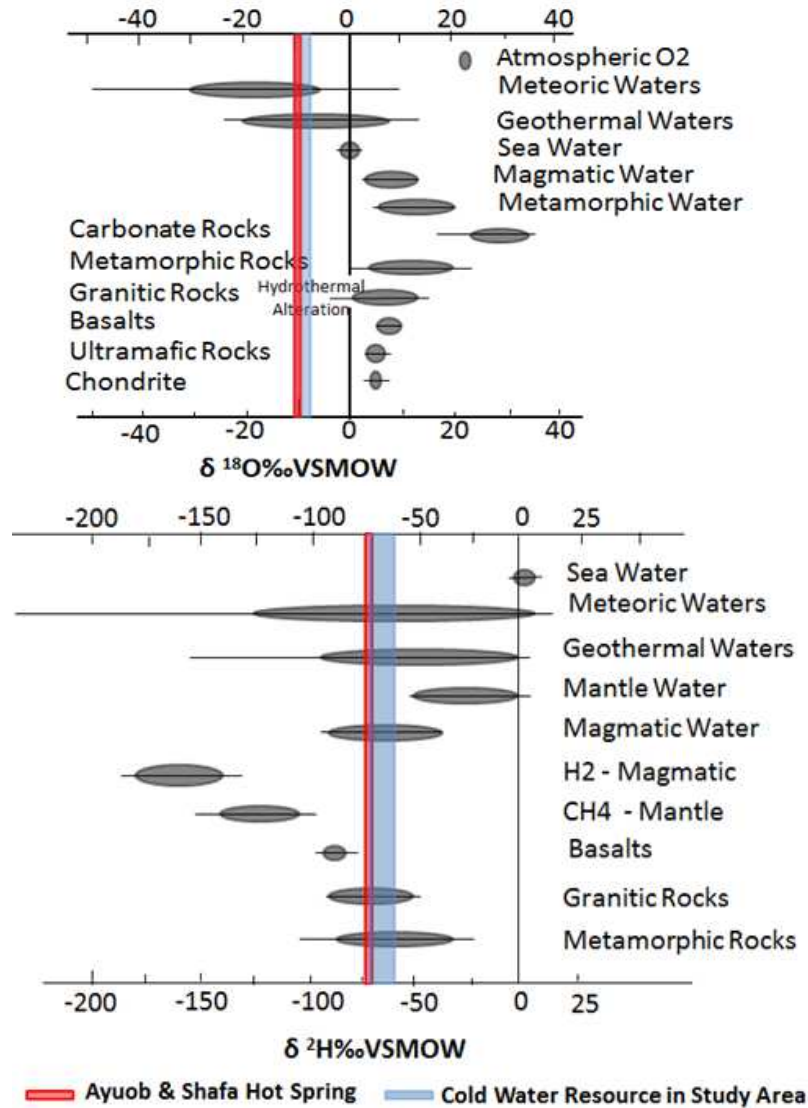


Figure 1: The range of $\delta^{18}O$ and δ^2H in various crustal rock and water type [11] and in Ayub Peighambar hot spring and other cold water resources in the study area.

REFERENCES

- [1] BARBIER, E, Nature and technology of geothermal energy: A review. Renewable and sustainable energy reviews. 1 (1997) 1-69.
- [2] DILSIZ, C., MARQUES, J.M., CARREIRA, P.M.M., The impact of hydrological changes on travertine deposits related to thermal springs in the Pamukkale area (SW Turkey). Environ Geol 45 (2004) 808–817.
- [3] BARUT, I.F., EROGAN, N., BASAK, E., Hydrogeological evaluation of Western Anatolian mineral waters. Environmental Geology, 45 (2004) 494-503.
- [4] LAMBRAKIS, N., KALLERGIS, G., Contribution to the study of Greek thermal springs: hydrogeological and hydrochemical characteristics and origin of thermal waters. Hydrogeology Journal. 13 (2005) 506-521.
- [5] VELLAYATI, S., Geography of waters. Mashhad. Iran. University Jahad press (2009).

- [6] HAILE, T., ABIYE, T.A., The interference of a deep thermal system with a shallow aquifer: the case of Sodere and Gergedi thermal springs, Main Ethiopian Rift, Ethiopia. *Hydrogeology Journal*. 20 (2012) 561-574.
- [7] ALLEN, D.M., GRASBY, S.E., VOORMEIJ, D.A., Determining the circulation depth of thermal springs in the southern Rocky Mountain Trench, south-eastern British Columbia, Canada using geothermometry and borehole temperature logs. *Hydrogeol J* 14 (2004) 159-172.
- [8] MOHAMMADI, A., Investigation hydrogeochemical and balneotrapy of Ayub hot spring (north Khorasan). Paper presented at the 15th symposium of Geological Society of Iran. Tarbiat Moalem University, 14-15 December (2011).
- [9] GIGGENBACH, W., Geothermal solute equilibria. Derivation of Na–K–Mg–Ca geosindicators. *Geochim. Cosmochim. Acta* 52 (1988) 2749–2756.
- [10] MARQUES, J., CARREIRA, P.M., MARQUES, J.E., CHAMINE, H.I., FONSECA, P.E., MONTEIRO SANTOS, F.A., EGGENKAMP H.G.M., TEIXEIRA, J., The role of geosciences in the assessment of low-temperature geothermal resources (N-Portugal): a review. *Geosciences Journal*, 14 (2010) 423 – 442.
- [11] CLARK, I.D., FRITZ, P., *Environmental Isotopes in Hydrogeology*. CRC Press LLC. United States of America (1997).

ID: 156

VARIABILITY IN OXYGEN AND HYDROGEN ISOTOPES IN HUMAN HAIR AND LIMITATIONS TO GEOLOCATION

L.M. REYNARD,

Harvard University, 11 Divinity Avenue, Cambridge, USA

E-mail address: lreynard@fas.harvard.edu.

N. BURT,

Cleveland Museum of Natural History, 1 Wade Oval Drive, Cleveland, USA

N. TUROSS

Harvard University, 11 Divinity Avenue, Cambridge, USA

Abstract: The development of isoscapes for meteoric water hydrogen and oxygen isotopic values and the reflection of the hydrologic variation in human tissues [1] has led to an exploration of these proxies in determining human migration. We present data that has considerable variation in oxygen and hydrogen stable isotope ratios between ~1 cm serial sections of human hair of co-local individuals from Boston, Massachusetts. Within individual variation reaches up to 1 ‰ in $\delta^{18}\text{O}$ and < 5 ‰ in $\delta^2\text{H}$, and a significant difference in the covariation of these isotopic pairs both within and between individuals. At this point, it is difficult to suggest a uniform sampling of hair strands to assess an “average” value in both hydrogen and oxygen isotopes, particularly in seasonal environments. In spite of this variability a significant difference is noted between Boston and Gainesville, Florida samples; however, as noted previously by others [2-3] this difference is far less than the drinking water isotopic difference.

REFERENCES

- [1] BOWEN, G.J., WASSENAAR, L.I., HOBSON, K.A., Global application of stable hydrogen and oxygen isotopes to wildlife forensics, *Oecologia* **143** (2005) 337.
- [2] EHLENGER, J.R., BOWEN, G.J., CHESSON, L.A., WEST, A.G., PODLESAK, D.W., CERLING, T.E., Hydrogen and oxygen isotope ratios in human hair are related to geography, *Proc. Natl. Acad. Sci. USA* **105** (2008) 2788.
- [3] KIRSANOW, K., TUROSS, N., Oxygen and hydrogen isotopes in rodent tissues: Impact of diet, water and ontogeny, *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **310** (2011) 9.

STABLE ISOTOPIC FINGERPRINT OF WATER FROM VITIS VINIFERA PLANTS GROWING IN DIFFERENT ENVIRONMENTAL CONDITIONS

D. COSTINEL, R.E. IONETE, R. POPESCU, I. STEFANESCU, O.R. DINCA

National Research and Development Institute for Cryogenics and Isotopic Technologies - ICSI Rm. Valcea, Uzinei Street no. 4, P.O. Box Râureni 7, 240050, Râmnicu Vâlcea, Romania;

E-mail address: diana.costinel@icsi.ro

G. BUTNARU

Banat University of Agricultural Sciences and Veterinary Medicine “Regele Mihai 1 al Romaniei” from Timisoara, 300645 - Calea Aradului, no. 119; Romania

Abstract: An investigation of the isotopic changes induced in *Vitis Vinifera* plants grown in different environmental conditions was performed in this paper by means of the isotopic analysis using continuous flow mass spectrometry (CF-IRMS). Our results showed that the geo-climatic conditions of the growing area and the plants varieties, the laboratory and greenhouse conditions respectively, greatly influence the stable isotopes fingerprint (deuterium and oxygen 18) in water and their distribution in plants.

1. INTRODUCTION

For this research we firstly performed an isotopic survey of the waters and precipitation collected during 2009-2011 from the study area, the Valea Calugareasca vineyard (Romania), continuing with an isotopic characterisation of the grape vines sap, and finally with the stable isotopic fingerprint of the wines from different *Vitis vinifera* varieties [1]. In the second part of the research we investigated the effect of deuterium depleted water (DDW) associated with Magnetic Nano Particles (MNPs) on the organogenesis evolution of the *Vitis vinifera* (L) [2].

2. METHODS

2.1. Biological materials and preparation:

For the first study, performed during 2009-2011, a number of ten different *Vitis Vinifera* varieties (white wines: Feteasca Regala (FR), Riesling Italian (R), Sauvignon (S), Chardonnay (C), Muscat Ottonel (MO); and red wines: Feteasca Neagra (FN), Cabernet Sauvignon (CS), Merlot (M), Pinot Noir (PN), Burgund Mare (B)) from Valea Calugareasca vineyard (Romania) were selected. Grape vine sap, surface waters and precipitation samples, were also collected in the same timeframe (March-April of 2009 and 2011). The wines were produced by the R&D Institute for Viticulture and Oenology Valea Calugareasca – Dealu Mare.

For the second study we used tap water (TW) as negative control (NC) and depleted water (DDW 30 ppm; positive control-PC); and mixture of each water type with Magnetic Nano Particles (MNPs) in $\theta = 0.23 \times 10^{-3} \text{ g/100cm}^3$ concentration (TW&MNPs; DDW&MNPs). The extraction of water from the plants was done by lyophilization.

2.2. Analytical methods:

The isotopic fingerprint for Deuterium and Oxygen 18 was obtained using equilibration system GasBench II (Thermo Electron) coupled at Continuous Flow Isotope Ratio Mass Spectrometer (CF-IRMS) Delta V Plus (Thermo Electron, Bremen-Germany), system supported by a robotic autosampler GC PAL and uses septum-sealed sample vials. The Deuterium and Oxygen 18 isotope ratio analysis from water are obtained after the isotope exchange of sample with equilibration mixture gas [3].

3. RESULTS

The water content in the plants depends of the species, age and type of plants tissue and can participate to regulate the body temperature of the plant. High temperatures in the spring of 2009 made the plants to enter earlier into vegetation, called “crying” period, comparative with spring 2011. In 2009, we collected the vine sap grape for each variety, given that the average temperature was $11 \div 12$ °C, comparative with 2011 (the average temperature was $8 \div 9$ °C). The slope of the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ line obtained for grape vine sap in 2009 ($\delta^2\text{H}_{\text{VSMOW}} = 2.40\text{‰} \cdot \delta^{18}\text{O}_{\text{VSMOW}} - 26.55\text{‰}$) decrease due to evaporation process who enriches the oxygen 18 more than deuterium, decay that depends also on the *Vitis Vinifera* varieties (e.g. Tamaioasa romaneasca comparative with Cabernet Sauvignon) (figure 1). The enrichment behaviour in heavy isotopes is more pronounced at Cabernet Sauvignon than other *Vitis vinifera* variety and is kept in every spring. The local meteoric water line LMWL obtained in spring 2011 ($\delta^2\text{H}_{\text{VSMOW}} = 5.98\text{‰} \cdot \delta^{18}\text{O}_{\text{VSMOW}} - 17.76\text{‰}$) compared to the same period in 2009 ($\delta^2\text{H}_{\text{VSMOW}} = 7.14\text{‰} \cdot \delta^{18}\text{O}_{\text{VSMOW}} - 4.24\text{‰}$) indicates a depletion of deuterium in rainwater, reflected by the temperature effect.

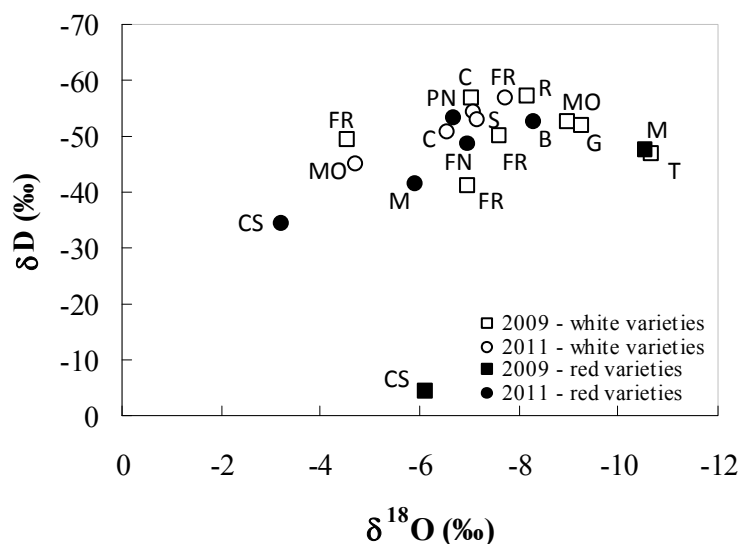


Figure 1.

Isotopic fingerprinting of water extracted from plants in various stages of development showed the concentration in heavy isotopes in evolution of plants to maturity, starting with period when plants enter earlier into vegetation, the isotopic fingerprints for vine sap grape have average $\delta^{18}\text{O} = -7.99\text{‰}$ for spring 2009 and in final product, wine vintage 2009, increase to average $\delta^{18}\text{O} = +4.65\text{‰}$.

The subject of the second study consisted in investigation the influence of the two natural factors, electromagnetic field (EMF) and water (“normal” and depleted: DDW) in organism evolution of the two *Vitis vinifera* (L) genotypes. The experiment was divided in two parts, laboratory and greenhouse conditions respectively and during one year. In this period, in the laboratory experiment no nutrients were added in experimental solutions. A total of 10 cuttings of first year shoots belonging to different Vitis Vinifera varieties were put into liquid mixtures (500 cm³ / jar) in three experimental groups and one control (C) each in four replications. In all this period the organogenesis of Vitis vinifera plants pointed out a particular behaviour. The amount of Deuterium (expressed in ppm) was evaluated on Sylvania and Socodor leaves (Figure 2) and the content of D was significant lower in both cultivars if the cutting organogenesis and plantlets growths took place in DDW with 30 ppm concentration.

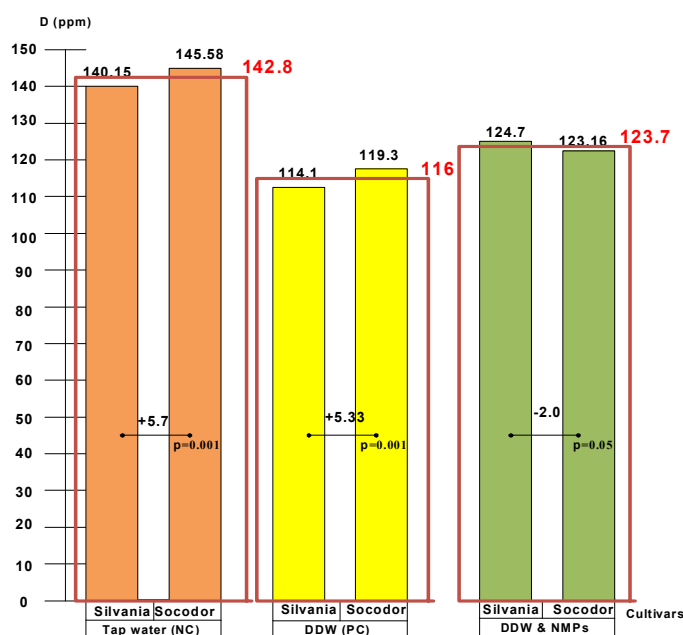


Figure 2. The amount of D (ppm) in the leave tissue of different potted vine plantlets

The majority plantlet traits were positive influenced by 30 ppm D concentration. In lab conditions the leaves and root formation was earlier and the number of surviving stocks was higher when they were kept in DDW and DDW&MNPs. On DDW-plantlets the chlorophyll content was higher and the amount of deuterium was less.

4.CONCLUSIONS

Environmental isotopes such as ¹⁸O and ²H are by their nature a good tracers of the physical processes affecting water, being the most conservative and abundant tracers used in characterizing a water source. The isotopic parameters of surface water from vineyard region, vine sap, of ethanol and water extract from wine „reflect the climatic influences which took place at different periods of plant growth”[5].

The studies pointed out the involvement of Deuterium content (ppm) and Magnetic nanoparticles (MNPs) on *Vitis vinifera* L organogenesis of cuttings and plantlets. The single

action of DDW or in association with MNPs has had a favourable influence in organogenesis, growth and synthesis of chlorophyll involved in metabolic activity.

ACKNOWLEDGEMENTS

This work was supported by PNII – TRICHOAS 52158/2008 and ARVINIZO 52162/2008.

REFERENCES

- [1] COSTINEL, D., TUDORACHE, A., IONETE, R.E., VREMERA, R., “The impact of grape varieties to wine isotopic characterisation“, Journal Analytical Letters, **44**, Issue 18 (special issue: IC-ANMBES-2010) (2011) 2856-2864.
- [2] BUTNARU, G., DOBREI, A., STEFANESCU, I., TITESCU, G., BOLEMAN, A., COSTINEL, D., “The associate effect of depleted water and magnetic particles on *Vitis vinifera* (L) organogenesis” Progress of Cryogenics and Isotopes Separation **23-24** (2009) 94-105.
- [3] COPLEN, T.B. “Reporting of stable hydrogen, carbon, and oxygen isotopic abundances”. Pure Appl. Chem. 66 (1994) 273-276.
- [4] DUNBAR, J., WILSON. A.T., “Oxygen and hydrogen isotopes in fruit and vegetable juices”, Plant Physiol. **72** (1983) 725.
- [5] MARTIN, G.J., MARTIN, M. “Climatic significance or isotope ratios”, Photochemistry Reviews **2** (2003) 179-190.

ID: 213

APPLICATION OF ISOTOPIC TECHNIQUES FOR WATER RESOURCE MANAGEMENT IN AN ARID REGION OF WESTERN ARGENTINA

L. GOMEZ, A. ALVAREZ, S. IBÁÑEZ, F. DONNA

IADIZA-CONICET. Av. Ruiz Leal s/n, Parque Gral. San Martín, Mendoza, Argentina

E-mail address: lgomez@mendoza-conicet.gov.ar

R. ARAVENA

Department of Earth and Environmental Sciences, University of Waterloo, 200 Univ. Av. West. Waterloo, Canada.

Abstract: The Carrizal Subbasin (CS), an arid region in the piedmont of the central Andes, is an area where agriculture and petroleum-related activity are superimposed. Increase of groundwater salinity in some wells has created legal conflicts between water users. Major ions and a set of isotopes analyses were carried out to provide information for evaluating the origin of the salinization in the study area. The stable isotopes, tritium and radiocarbon data shown groundwater recharge is associated to the Mendoza River and it also demonstrated that the source of groundwater salinity is associated with irrigation return flows in the agriculture areas. Evidence of the presence of water in the aquifer from re-injection from secondary oil recovery techniques is also shown in this study without any influence in groundwater salinity.

1. INTRODUCTION

In arid regions of Mendoza, groundwater recharge from local precipitation is reduced and localized [1]. Andean Rivers, with a snow and ice-melt regime, are the main source of recharge for aquifers. Hydrological modeling of the Mendoza river watershed predicts a reduction in water availability that ranges between 1 and 10% under a climate change scenarios [2]. In the CS region, groundwater is an important resource for agriculture and human consumption. Additional, oil industry demands and adds a large quantity of water. The lack of knowledge on the salinization of the water resources has created long-running legal conflicts related to groundwater quality and its source at NW of the subbasin. The available hydrogeological model does not identify the presence of additional sources of water in the aquifer. The main objectives of this study, which included the use of geochemical and isotopes tools, is to evaluate the source of groundwater salinity and to improve the knowledge of surface –groundwater interactions. The information generated is vital for water management under increasing demand of water by agriculture, industry and urban consumption in an arid zone under the influence of climate change and less availability of water resources.

2. METHODS

Surface and groundwater water samples were collected in the CS (600 km²) during August 2013. The Mendoza River was sampled in four occasions during 2013-2014. Major ions and a set of isotopes analyses ($\delta^{18}\text{O}$, $\delta^2\text{H}$, ^3H , ^{14}C , $\delta^{13}\text{C}$, $\delta^{34}\text{S}$) were carried out in the study.

3. RESULTS

Groundwater has a general NW-SE flow direction and its salinity increases from near recharge areas with values around 1000 $\mu\text{S}/\text{cm}$ to values as high as 2500 $\mu\text{S}/\text{cm}$ observed in

the middle of the basin and then the salinity decreases to values around 1500 $\mu\text{S}/\text{cm}$ toward the lower part of the study area. The highest salinity values are also correlated with high nitrate content in the groundwater. Surface water and groundwater present a mainly Ca-SO_4 composition reflecting the presence of gypsum and carbonates in the basin sediments. However, Na-SO_4 groundwater types are observed at the SW area. The environmental isotope data made possible the identification of five water groups in the area: *Group 1 (Springs)*: $\delta^{18}\text{O}$ values ranging between -8.0 a -13.2 ‰ are associated to recharge by local precipitation. They are characterized by tritium values between <0.8 and 1.2 T.U and a ^{14}C value of 70 pmC was observed in an up-gradient fresh water spring. *Group 2 (recharging water and groundwater in the recharge area)*: $\delta^{18}\text{O}$ values for the Mendoza River range between -16.7 a -18.4 ‰. Tritium values range between 2.3 and 3.4 T.U reflecting the present tritium values in precipitation. Groundwater in recharge area shows more depleted $\delta^{18}\text{O}$ values of -18.3 to -19.5 ‰ reflecting recharge during the snow melting season. Tritium values between 1.7 and 2.6 T.U show the influence of modern water. These waters are characterized by $\delta^{13}\text{C}$ and ^{14}C values of -2.0 and 56 pmC, respectively. *Group 3*: These groundwaters are located in the central part of the basin and correspond to the more saline waters with high nitrates contents. Their $\delta^{18}\text{O}$ values range between -16.5 and -18 ‰ and their depleted $\delta^{13}\text{C}$ values of around -12‰ and a high ^{14}C value of 104 pmC, compared to up-gradient groundwater, reflect the incorporation of biogenic CO_2 in the agriculture areas associated to recharge of irrigated return flow. *Group 4*: These groundwaters correspond to Na-SO_4 water type and are located near an area with oil industrial activity. The isotope data showed $\delta^{18}\text{O}$ values between -12.8 and -14.2 ‰, which are more enriched than the up-gradient groundwater. ^{14}C data showed the lowest values between 22 and 36 pmC indicating an input of old carbon into the aquifer. The isotope evidence showed the influence of re-injection water from a secondary petroleum recovery activity in the aquifer. *Group 5 (groundwater of natural evolution)*: This group included groundwater with $\delta^{18}\text{O}$ values between -19.5 and -18.9‰ typical of recharge water and tritium and ^{14}C values of <0.8 T.U and 43 and 50 pmC, indicating a moderate residence time in the system.

4. CONCLUSIONS

The chemical and isotopic evolution observed along the groundwater flow path has shown an input of water from different origins along the basin. The recharge water associated to the Mendoza River is observed near recharge areas and in different parts of the aquifer. Water recharge from precipitation at the foothills was discarded as a local recharge source. The high increase of groundwater salinity in the central part of the basin is related to water input derived from irrigations return flows in agriculture areas and evidence of input of re-injection water associated to secondary oil recovery practice was also documented in the study. The information generated in this study will contribute to resolve legal conflicts and for the application of the Integrated Water Resources Management by the Irrigation Department in the basin.

REFERENCES

- [1] JOBBÁGY, E., NOSETTO, M., VILLAGRA, P., JACKSON, R. Water subsidies from mountains to deserts: Their role sustaining groundwater-fed oases in a sandy landscape. *Ecological Applications*, 21(3). Pp. 678–694. (2011).
- [2] SCHWANK, J., ESCOBAR, R., GIRON, G., MORA N-TEJEDA, E. Modeling of the Mendoza river watershed as a tool to study climate change impacts on water availability. *Environmental Science and Policy ENVSCI-1315*; No. of Pages 7. Article in press (2014).

ID: 217

ASSESSING THE EFFECTS OF LAND USE CONVERSION IN TROPICAL MOUNTAINS THROUGH HYDROLOGICAL, HYDROCHEMICAL AND ISOTOPIC MONITORING: INSIGHTS AND PRELIMINARY OBSERVATIONS

J.C. VILLEGAS,
Universidad de Antioquia, Colombia
E-mail address: villegasjcv@gmail.com

J.D. LEÓN PELÁEZ,
Universidad Nacional de Colombia

T. BETANCUR,
Universidad de Antioquia, Colombia

C.P. FLÓREZ,
Universidad Nacional de Colombia

V. GARCÍA LEOZ,
Universidad de Antioquia

D. SUESCÚN CARVAJAL,
Universidad Nacional de Colombia

Abstract: Tropical mountain ecosystems are key for the provision of multiple ecosystem services to communities that extend beyond their geographical boundaries. Particularly important are two—seemingly competing—types of services: (1) regulation and (2) provisioning services. More specifically, food provision has traditionally required extensive land use conversion from natural ecosystems to highly disturbed agricultural systems. The dynamics of these conversions generally lead to potential loss of the regulating properties of natural ecosystems, traditionally agreed to improve hydrological and biogeochemical stabilization at multiple scales. In this study we present a monitoring protocol and preliminary observations for assessing the effects of land use conversion on three key regulation functions related to the vegetation-unsaturated soil zone domain: hydrology, nutrient cycling and sediment retention. We selected and instrumented a group of 7 plots representing a continuum of human intervention, ranging from highly intervened seasonal crops to old-growth natural ecosystems. Our measurements include regular observations of hydrological and biogeochemical measurements combining a suite of analogue and automated instrumentation, including hydrochemical and isotopic analysis. Although not yet implemented, isotopic analysis on rainfall, runoff and infiltration samples at different levels are considered as a validation tool for mass balances in different components of the hydrological system. This isotopic analysis is associated with the CRP project on ground and surface water Interactions, in collaboration with the IAEA. Preliminary observations indicate that natural vegetation types are more effective in regulating hydrological fluxes (reflected in the partitioning of rainfall into runoff and infiltration fluxes) and that the ability of ecosystems to maintain this regulation generally decreases as intervention increases. A similar response is also observed in the dynamics of water-soluble nutrients and sediment

production, highlighting the potential loss of soil fertility and the potential for nutrient transport to nearby water bodies. More generally, our preliminary results highlight the need of more informed land management tools that allow the optimization of ecosystem functions in the highly diverse, yet highly intervened tropical mountain ecosystems.

ID:218

ASSESSMENT OF WATER USE IN BRAZILIAN SUGARCANE CROPS THROUGH STABLE ISOTOPES

G. C. DA SILVA, A. L. R. WAGENER, J. M. O. GODOY.

Department of Chemistry, Laboratories of Marine and Environmental Studies (LABMAM) and of Waters Characterization (LABAGUAS), Pontifical Catholic University of Rio de Janeiro.

E-mail address: angela@puc-rio.br.

MARCELO Z. MOREIRA

Center for Nuclear Energy in Agriculture, Laboratory of Isotope Ecology (CENA), University of São Paulo.

Abstract: Sugarcane is vastly cultivated in Brazil for production of bioethanol and sugar. The present work aimed at testing the isotopic markers ^{18}O and D as tools for evaluation of regional isotopic patterns, seasonal variations and water use in four Brazilian sugarcane crop areas.

1. INTRODUCTION

Water isotopes are important tracers in hydrogeological studies, since there is no isotopic fractionation during water uptake by roots and transportation to leaves [1-3] the isotopic evaluation provides information about the water source and usage by plants. Sugarcane crops require water availability since it represents 70 % of its weight [4]. The objectives of this work were to assess oxygen and hydrogen isotopic patterns in plant-water, soil-water, rainwater, and water from reservoirs and rivers associated to four Brazilian sugarcane crop areas and evaluate regional isotopic patterns and seasonal variations.

2. METHODS

Crop areas are located in the states of Amazonas (AM, Presidente Figueiredo, North), Mato Grosso (MT, Campo Novo do Parecis, Center-West) São Paulo (SP, Ibirarema, Southeast) and Rio Grande do Sul (RS, Porto Xavier, South). Sampling campaigns were carried out during the months of August and November, 2011 (pilot study) and July and October/November, 2012. Samplings included rainwater, surface and groundwater (only 2012), plant, and soil (20-25 cm depth, only 2012). Plant- and soil-water were extracted by vacuum distillation previously to the analyses. Analyses were performed by isotope ratio infrared spectroscopy (IRIS) in a water analyzer DLT-100 (OA-ICOS; Los Gatos Research). An inter-laboratory comparison was performed for the plant-water samples using an analyzer L2130-I equipped with a micro-combustion module (WS-CRDS; Picarro Inc.).

3. RESULTS

Results for $\delta^{18}\text{O}$ and δD in 2012 sampling campaign are presented in Table 1. As plant-water analysis by IRIS can be biased due to the presence of residual methanol or ethanol after distillation procedure [5, 6], results were evaluated by statistical comparison of their variances (F test) and means (t test). This comparison showed that respectively 83% and 78% of the $\delta^{18}\text{O}$ and δD results were not statistically different at significance levels of 0.05 to 0.02.

Table 1. Results for $\delta^{18}\text{O}$ and δD for 2012 sampling campaigns

Sampling Information		$\delta^{18}\text{O}$ (‰) [♦]					δD (‰) [♦]				
		Rain	Reser- voirs	Soil- water [◇]	Plant-water A	Plant-water B	Rain	Reser- voirs	Soil- water [◇]	Plant-water A	Plant-water B
AM	Oct/12	-0.85	-4.71	-2.60	-2.47	-2.33	2.45	-27.01	-17.99	-16.10	-14.68
MT	Jul/12	-	-7.39	-5.99	-7.71	-7.34	-	-43.15	-41.73	-59.22	-56.60
	Oct/12	-1.60	-	-3.52	-4.15	-3.85	-1.80	-	-31.37	-34.48	-33.21
SP	Aug/12	-	-4.16	-5.65	-2.96	-2.73	-	-28.46	-39.87	-23.49	-20.53
RS	Jul/12	-1.13	-4.90	-4.83	-3.58	-3.38	7.97	-27.95	-37.68	-24.42	-20.28
	Oct/12	-2.74	-4.38	-9.58	-4.52	-4.47	-7.71	-26.85	-71.49	-29.52	-28.07

[♦] Mean results (plant-water combines results of several sugarcane varieties for each sampling campaign); [◇] 20-25 cm; Sampled in Sep/2014 A: OA-ICOS; B: WS-CRDS.

Assessment of data obtained in the present work included drawing of Local Meteoric Water Lines (LMWL) [7] as well as Soil and Plant Water Lines and comparison with those from GNIP rainwater database [8] (Figure 1). Except for MT, surface water results were close to $\delta^{18}\text{O}$ and δD mean values of -4.54 ‰ and -27.65 ‰ for 2011-2012 samplings.

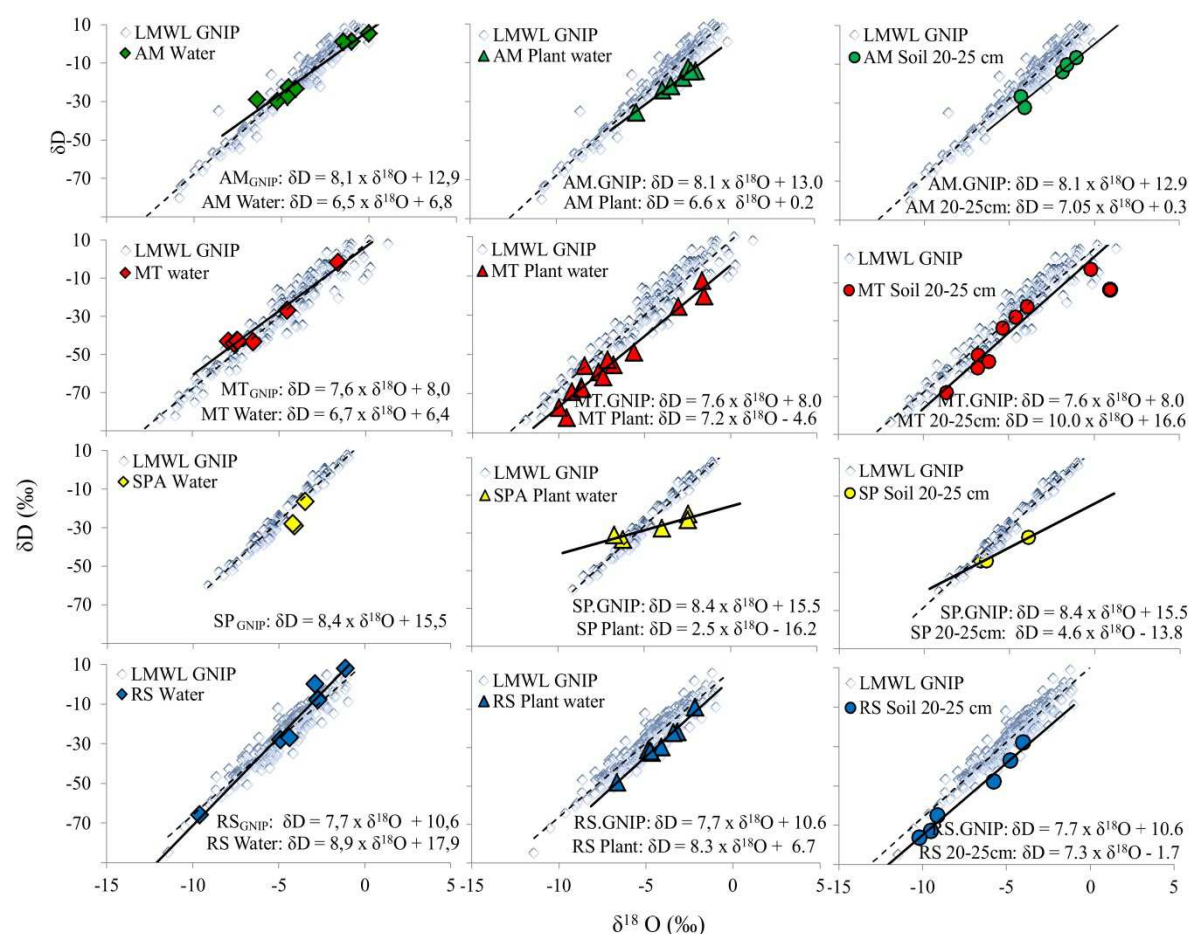


Figure 1. Local Meteoric, Soil- and Plant Water Lines and comparison with GNIP data.

Despite the variability of plant-water results (Table 1), the proximity with the weighted average for rainfall [9] evidenced groundwater plays an important role on plant- and soil-water isotopic content even in the drought period. The results point to a reasonable parity between soil-water (20-25 cm) and the respective plant-water average isotopic ratios.

Plant-water results in AM along 2011 were consistent with those from local rain samples and with the isotopic fingerprint of groundwater, represented by the weighted average for annual rainfall [9]. Plant-water results for 2012 campaign presented isotopic ratios between those for rainwater collected in the same period and groundwater. The plot of $\delta^{18}\text{O}$ versus δD for plant-water and soil-water (Figure 1) shows profiles consistent with those observed for GNIP meteoric water in the location.

Plant- and soil-water from MT were the most depleted (Table 1, Figure 2). This sampling location undergoes severe drought during all the harvest period, and the only important sources of water in August/2011 and July/2012 were the vadose zone and the phreatic. Comparison of MT results from local groundwater isotopic fingerprint with those from plant-water proved the occurrence of strongly depleted rainwater in MT location and indicated the vadose zone is the source of water for the sugarcane crop during the drought period, rather than groundwater.

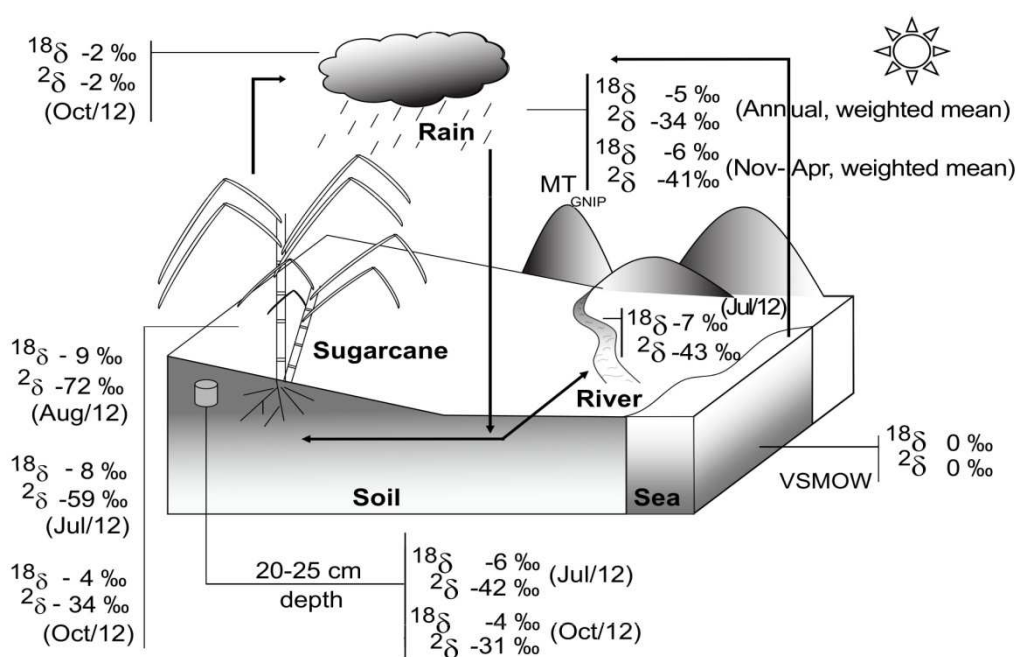


Figure 2. Graphical representation of MT results for rainwater, and waters from river, sugarcane xylem and soil.

Results in SP were atypical since only one sugarcane sample, collected on August/2011, presents results for plant-water consistent with the respective soil-water and other matrices. The considerably reduced slopes of the linear regression for both plant and soil-water versus $\text{LMWL}_{\text{GNIP}}$ indicate strong isotopic enrichment in the SP area (Figure 1).

In RS plant-water presented the most constant results, which are consistent with those for weighted average for the annual rainfall obtained from GNIP data. The depleted isotopic results for October/2012 soil-water occurred due to a recent rain event, similar to another observed in November/2011 (isotope rain values of $\delta^{18}\text{O} = -9.6$ ‰ and $\delta\text{D} = -65.9$ ‰).

4. CONCLUSIONS

In general, surface water samples reflected the weighted average isotopic ratios of annual rainwater, and consequently the isotopic fingerprint of groundwater. For plant-water the largest ^{18}O and D depletion were found in MT samples during the drought period that occurs in the middle of the year. It was evidenced that vadose zone, rather than groundwater, is the source of water for the sugarcane crop in this location. Isotopic shifts in RS were practically constant over the observation period in the present study. Isotopic ratios for AM samples, showed a robust connection with local water cycle, indicating that rainwater in this site is the main water source for the soil and crop. SPA results showed poor correlation between the different evaluated matrices, revealing also an unexpected enrichment for both plant- and soil-water when compared to the local meteoric water line. Soil-water results were considered to be in good agreement with those of the respective plant-water for the depth of 20-25 cm.

REFERENCES

- [1] EHLERINGER, J. R.; RODEN, J.; DAWSON, T. E., "Assessing ecosystem-level water relations through stable isotope ratio analyses", *Methods in ecosystem science*. SALA, O.; JACKSON, R.; MOONEY, H. A.; HOWARTH, R. (Eds), Springer, New York, (2000) 421 pp.
- [2] ALLISON, G. B.; BARNES, C. J.; HUGHES, M. W., The distribution of deuterium and ^{18}O in dry soils 2: Experimental, *J. Hydrol.* **64** (1983) 377.
- [3] CLARK, I. D.; FRITZ, P., *Environmental Isotopes in Hydrogeology*, CRC Press, New York, (1997) 352 pp.
- [4] CESNIK, R.; MIOCQUE, J. Melhoria da cana-de-açúcar. Embrapa Informação Tecnológica. Brasília, Brazil (2004) 307 pp.
- [5] SCHULTZ, N. M.; GRIFFIS, T. J.; LEE, X.; BAKER, J. M., Identification and correction of spectral contamination in $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ measured in leaf, stem, and soil water, *Rapid Commun. Mass Spectrom.* **25** (2011) 3360.
- [6] LEEN, J. B.; BERMAN, E. S. F.; LIEBSON, L.; GUPTA, M., Spectral contaminant identifier for off-axis integrated cavity output spectroscopy measurements of liquid water isotopes, *Rev. Sci. Instrum.* **83** (2012) 044305.
- [7] CRAIG, H., Isotopic variations in meteoric waters, *Science*, **133** (1961) 1702.
- [8] IAEA/WMO. Global Network of Isotopes in Precipitation. The GNIP Database, 2014, <http://www.iaea.org/water>
- [9] KENDALL, C., DOCTOR, D.H., YOUNG, M.B. "Environmental Isotope Applications in Hydrologic Studies", *Surface and groundwater, weathering and soils: Treatise on Geochemistry*, v. 7, 2nd ed., HOLLAND, H. D.; TUREKIAN, K. K. (Eds), Elsevier, Oxford (2014) 454 pp.

ISOTOPE-HYDROLOGY INVESTIGATION OF GROUNDWATER IN THE NAMIB DESERT, NAMIBIA

H. WANKE, J.T. HAMUTOKO,
University of Namibia, Namibia
E-mail address: jhamutoko@gmail.com

Abstract: Namibia is one of the driest countries in sub-Saharan Africa and water supply in the Namib deserts is very limited and relies on groundwater only. In this study, isotopic compositions of groundwater, surface water and rain water have been used to characterise recharge processes in a part of the Namib Desert. Rain samples were obtained in a monthly sum collector, while groundwater and surface water samples were collected during a field campaign in July 2014. Coordinates, altitude, temperature, and electric conductivity were measured in the field. Stable isotope analyses were conducted using a Los Gatos LGR DLT-100 at University of Namibia. The resulting isotope data were plotted together with the global meteoric water line (GMWL). Isotopic ratios for $\delta^{18}\text{O}$ range from -9.14‰ to -2.16‰ for groundwater and from -8.89 to -0.27‰ for rain water; for $\delta^2\text{H}$ from -62.9‰ to -23.6‰ for groundwater and from -55.3‰ to 8.3‰ for rain water. The rain water samples plot very close to the GMWL and the resulting local meteoric water line (LMWL) is given by $\delta^2\text{H} = 7.5 \times \delta^{18}\text{O} + 9.3$. The electrical conductivity of the samples ranges from 22.4 to 35.5 $\mu\text{S}/\text{cm}$ for rain water, from 737 – 3120 $\mu\text{S}/\text{cm}$ for the groundwater supplied for human consumption and wildlife watering and between 29000 and 37 600 $\mu\text{S}/\text{cm}$ in the samples from a mine in the driest part of the study area. The electrical conductivity increases with increasing $\delta^{18}\text{O}$ and samples with highest electric conductivity also plot furthest away from the LMWL along an evaporation line indicating that evaporation is the main source of the salinity in the groundwater in the Namib Desert. For the correlation between altitude and $\delta^{18}\text{O}$ a negative trend is observed: higher altitudes are associated with more negative $\delta^{18}\text{O}$, but data are currently insufficient to establish an altitude effect for this part of Namibia.

MONITORING OF STABLE ISOTOPES IN RIVER WATER AND PRECIPITATION IN THE TAJIK PAMIRS

C. MEIER, M. KNOCHE, R. MERZ, S. M. WEISE

UFZ – Helmholtz-Centre for Environmental Research, Catchment Hydrology, Theodor-Lieser-Str. 4, 06120 Halle (Saale), Germany

E-mail address: christiane.meier@ufz.de.

Abstract: In a dense monitoring network in the Gunt catchment in Central Asia water samples were collected each month from river water, ground water and thermal water as well as precipitation. More than 1000 samples were analyzed for their stable isotope values ^{18}O and ^2H . Our first results show $\delta^2\text{H}$ values in the range from -131.2 to -94.9‰ and $\delta^{18}\text{O}$ values from -18.0 to -14.0‰ . The stable isotope patterns in the catchment seem to follow a systematic way, dominated by an altitude effect. The observed seasonal variations can be explained by geographical aspects such as the influence of different wind systems as well as melting processes.

1. INTRODUCTION

The Central Asian lowlands receive their water from large rivers like the Syr Darya and Amu Darya, originating in the Tien Shan and the Pamir Mountains. These river systems are mainly fed from snow and glacial melt. Stable isotopes of water (^2H and ^{18}O) act as an ideal conservative tracer of water sources and mixing processes. The Global Network for Isotopes in Precipitation, which was established by the International Atomic Energy Agency (IAEA) together with the World Meteorological Organization (WMO), provides long-term isotope signals in precipitation over large parts of the world. Yet there is an almost blank spot on the map that are the Central Asian mountains, especially the Pamirs. To cover this gap and to understand the origin of precipitation and different runoff components in the Tajik Pamir, we have undertaken a stable isotope study in an exemplary drainage basin (river Gunt) in the headwaters of the Amu Darya. This ongoing study offers an insight into stable isotope patterns of surface water and precipitation in the Pamir Mountains.

2. METHODS

During several field campaigns in 2011, 2013 and 2014 water samples were collected from the main stream Gunt, its accessible tributaries, lake Yashikul as well as some additional samples from lake Bulunkul, hot springs, cold springs and wells. Since November 2011, a monthly monitoring programme was started where local technicians are involved. Each month water samples were collected at 38 sampling sites, filtered in the field through a $0.45\text{ }\mu\text{m}$ cellulose acetate filter paper and stored in clean 30 ml HDPE bottles. The bottles were filled to the top and secured tightly to prevent evaporation and exchange with atmospheric water vapour. Precipitation samples were collected at six meteorological stations either as monthly integral samples or in an event based resolution.

All water samples were shipped bimonthly to Germany to be analyzed in the laboratory for Stable Isotopes of the Department of Catchment Hydrology in the Helmholtz-Centre for Environmental Research – UFZ in Halle/Saale. The analysis of oxygen and hydrogen stable isotopes was done by a PICARRO L2120-i water isotope analyzer utilizing the cavity ringdown spectroscopy technology. All isotope measurements were calibrated in a two-point

scale against the international standards of Vienna Standard Mean Ocean Water (V-SMOW) and Vienna Standard Light Antarctic Precipitation (V-SLAP).

The calibration was controlled with third laboratory reference water (the procedural standard). For excluding any memory effects, each sample was measured by six injections while the first three injections were rejected. The isotope values are expressed as δ values in per mil notation (‰) relative to V-SMOW. The values have an overall measurement precision of ± 0.2 ‰ for $\delta^{18}\text{O}$ and ± 0.8 ‰ for $\delta^2\text{H}$.

3. RESULTS

Our first analytical results of the river water show $\delta^2\text{H}$ values in the range of -131.2 to -94.9 ‰ and $\delta^{18}\text{O}$ values from -18.0 to -14.0 ‰ due to an altitude interval from 2000 to 6700 m a.s.l. However, the precipitation data feature a more wide-spreading range ($\delta^{18}\text{O}$: -21.1 to -5.9 ‰ and $\delta^2\text{H}$: -157.0 to -48.0 ‰). The high variance in the precipitation data cannot be explained only by changes of the physical state of the precipitation, but by the different precipitation sources.

The river monitoring data show high $\delta^2\text{H}$ (-103.5 to -96.5 ‰) and $\delta^{18}\text{O}$ (-14.8 to -14.0 ‰) values far in the west of the catchment, and the lowest values in the plateau area around the lake Yashikul and in the east of the catchment ($\delta^2\text{H}$: -125.0 to -131.0 ‰, $\delta^{18}\text{O}$: -16.0 to -18.0 ‰). This effect results from the increasing altitude and continentality as well as the decreasing amount of precipitation from west to east. The eastern part of the catchment is an cold alpine desert with precipitation sums of ≤ 160 mm/a while the western part is warmer and receives a little more precipitation (~ 300 mm/a).

D-excess values (*d*) of markedly more than 10‰ indicate a precipitation source with a strong re-evaporation rate and therefore an origin in the Caspian Sea and/or the Mediterranean Sea. For the surface water samples the high *d* values must be traced back to their origins in snow and glacier melt.

An additional isotopic pattern in the catchment is a distinction between tributaries flowing from the northern boundary to the main stream and tributaries originating in the south of the catchment. The altitudes of the northern and southern mountain ranges are similar, but however the stable isotope values in $\delta^2\text{H}$ and $\delta^{18}\text{O}$ and also the *d* values figure out a clear differentiation between the subcatchments. The causes are to be found in the variously influences of northern and southern air masses, respectively.

ID: 251

ENVIRONMENTAL ISOTOPES STUDIES IN WETLAND RESEARCHING: FUENTE DE PIEDRA LAGOON (MALAGA, SPAIN)

J. HEREDIA,

Instituto Geológico y Minero de España. C/Ríos Rosas, 23. 28003, Madrid, SPAIN

E-mail address: j.heredia@igme.es

F. J. MONTALVÁN,

Instituto Geológico y Minero de España. C/Ríos Rosas, 23. 28003, Madrid, SPAIN

ETSI de Minas de Madrid, Universidad Politécnica de Madrid. C/Ríos Rosas, 23. 28003, Madrid, SPAIN

J. M. RUIZ, A. GARCÍA DE DOMINGO, E. PARDO-IGUZQUIZA,

Instituto Geológico y Minero de España. C/Ríos Rosas, 23. 28003, Madrid, SPAIN

F. J. ELORZA

ETSI de Minas de Madrid, Universidad Politécnica de Madrid. C/Ríos Rosas, 23. 28003, Madrid, SPAIN

1. INTRODUCTION

The Fuente de Piedra lagoon (Malaga, Spain) is a wetland with a high ecological value. It was one of the three first Spanish wetlands included in the Ramsar convention and was declared Integral Reserve in 1984 (Nature Reserve from 1989). The lagoon (13 km²) is located in an endorheic basin (150 km²). In the basin outcrops Miocene calcarenites that host a freshwater aquifer, and the Chaotic Subbetic Complex (CSC), which defines the Miocene aquifer bottom. The CSC is a lower to middle Miocene olistrome formed by a marly-gypson matrix of Triassic age and limestone, dolomites and marls blocks of Jurassic to Oligocene age (Mollina and Humilladero ranges, Fig. 1). A deep hyper-saline karst system was developed in the CSC evaporative levels. Genetic model of the lagoon, conceptual model of the hydrogeologic system and genetic evolution of the brine are closely related. The origin of the lagoon is related to karstification and collapse processes of the CSC gypsum-saline materials. The system presents high density contrasts: shallow freshwater, brackish water and shallow and deep brines. Traditionally, based on classic models for closed basins in semiarid climates, the brine present in the system was considered of evaporative origin and it was placed in the discharge zone. However, the investigation that IGME has developed suggests that the brines origin is not exclusively due to evaporation. Besides the hydrochemical and geophysical studies, environmental isotope research has been a fundamental contribution to define a new conceptual model of the hypersaline hydrogeological system (Kendall and Mc Donnell, 2003).

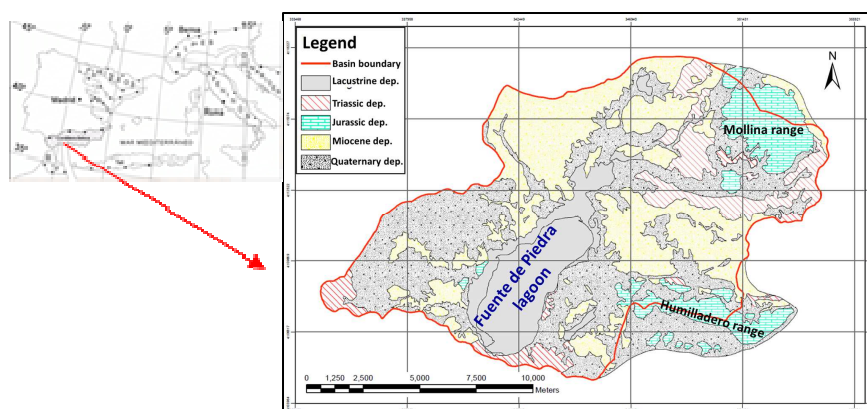


Figure 1. Geological map of the Fuente de Piedra basin

2. GEOPHYSICAL STUDIES

Several brine enclaves were identified by geo-physical technical: 10 electrical tomography profiles (38.5 km total length and 105 m deep). Brine enclaves are in the upper and middle basin. Later drillings confirmed geophysical interpretation and they founded karst levels about 65 m around the lagoon (Ruiz *et al*, 2007).

3. HYDROCHEMICAL STUDIES

Hydrochemistry shows differences according to lithological and spatial situation (Fig.2). The water in the limestone is calcium bicarbonate. The Miocene aquifer has chloride-sulphated magnesium -calcium facies. The CSC marly-gypsum matrix water shows magnesium-sodium sulphated-chloride facies. The brine enclaves in lagoon basin and hypersaline karst springs in neighbor Guadalhorce basin show only sodium-chloride facies. This suggests a similar origin: dissolution of evaporites. Shallow brine around lagoon shows sodium chloride facies and contains Mg^{2+} . Mg^{2+} increases by evaporation and dedolomitization. Deep brine around lagoon is a mixture of enclave and shallow lagoon brines (Heredia et al, 2004).

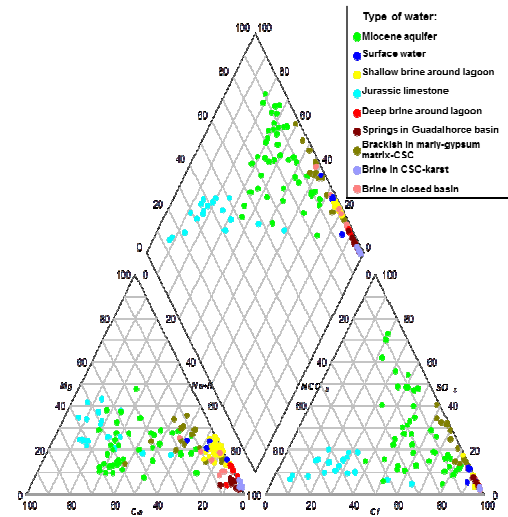


Figure. 2. Piper diagram of water and brines

4. ISOTOPIC STUDIES

A. STABLE ISOTOPES OF BRINES (TDS> 50G/L): EVAPORATION, SALINITY AND GENESIS

The $\delta^{18}O$, δD and TDS analysis (Fig. 3, Fig 4) indicates that brine enclaves in the upper and middle basin and hyper-saline Guadalhorce springs brines did not suffer evaporation. The shallow brine around the lagoon defines a mixture line from the most evaporated brine in North and East of the lagoon, to the least evaporated in W and S side. Likewise, the analysis also shows that surfaces waters and shallow brine define different slopes, which suggests that evaporation-concentration processes in the origin of both brines would be different, probably due to the existence of other water inputs. The deep brine around the lagoon is as evaporated as the most evaporated shallow brine, but their TDS are different. The deep brine is more saline than the shallow brine but is less saline than enclave brines. Enclave brines according to $\delta^{18}O$ are not evaporated, so that, its salinity could be by dissolution processes of evaporitic rocks. Therefore, this fact relates the brine enclaves with the hypersaline karst system developed in the CSC (Montalván *et al*, 2012).

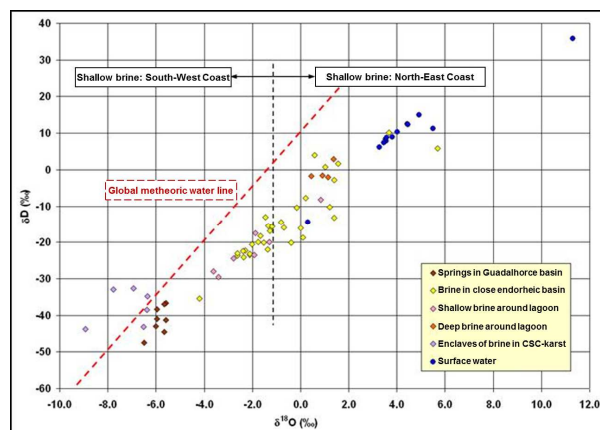


Figure 3. $\delta^{18}O$ - δD relationship

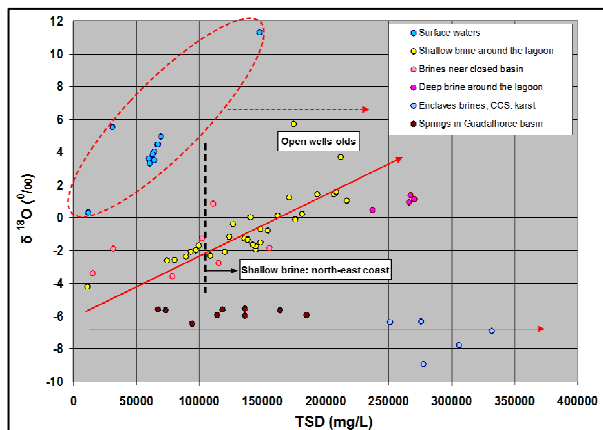


Figure 4. $\delta^{18}O$ - TDS (g/L) relationship

b. STABLE ISOTOPES ON BRINES (TDS> 50G/L): RECHARGE ZONE IDENTIFICATION

Multiple regression model that describes spatial trend of $\delta^{18}\text{O}$ in precipitation in Iberian Peninsula at wet season allows to identify areas of recharge (Heredia *et al*, 2013):

$$\delta^{18}\text{O} = b_0 + b_1 H^{-1}\sqrt{T} + b_2 P + b_3 L_0^2 \ln(L) \quad (1)$$

Where, model variables are geographical (latitude, L ; longitude, L_0) and climatological (atmospheric pressure, P ; temperature, T ; relative moisture, H). The model indicates for: 1) brine enclave samples (CSC, hypersaline karst system) that plausible geographic- climatic conditions of recharge occur in carbonated ranges at regional scale (Fig. 5); 2) if it considers that Miocene aquifer water suffers evaporation before recharge, plausible climatic-geographic conditions of recharge occur in lagoon basin in Miocene outcrops and carbonated blocks (Humilladero and Molina ranges) and 3) CSC marly-gypsiferous matrix water is a mixture between Miocene aquifer water and brine enclaves.

c. RADIOACTIVE ISOTOPES: DATING

^{14}C dating was calculated with ^{13}C chemical correction of Tamers. Also the tritium content was considered (Fig 6.). The strong pumping for urban supply causes a mixture of modern and old waters in carbonated blocks (Humilladero and Molina ranges). Miocene aquifer water is modern. The CSC marly-gypsum matrix water was dating in 800 years old at a deep borehole in upper basin and Tritium content is absent or lower than analytical error. Shallow brines around lagoon present the oldest of the basin (28,500 yr) and other ancient ones were dating between 21500 yr and 850 yr. Deep brines around lagoon were dating in 24000 yr and 14,400 yr. Brine enclaves (CSC, karst system) were dating between 8,300 yr and 800 yr. Brines around lagoon and brine enclaves lack tritium.

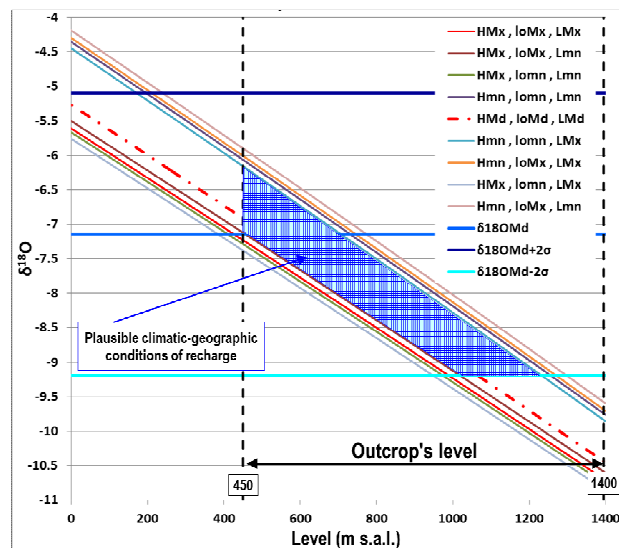


Figure 5. Brine enclaves (CSC: hyper-saline karst system): plausible climatic-geographic conditions of recharge

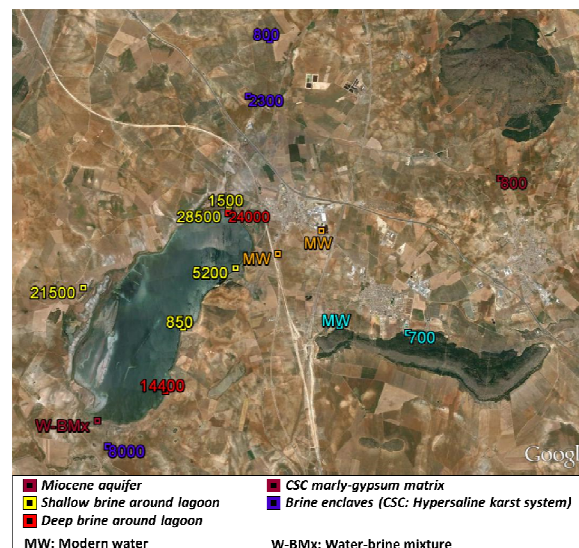


Figure 6. Radiocarbon dating of water and brine

5. CONCEPTUAL MODEL

Groundwater circulation is characterized by the existence of layered flow systems, due to a marked density contrasts between freshwater, brackish waters and brine. Miocene aquifer (freshwater) recharges in the lagoon basin (local) and discharges in lagoon. The residence time is short (months-years). CSC hypersaline karst system (brine enclaves) recharges in carbonated ranges at regional scale and discharge is both local (lagoon) and regional (Guadalhorce river). The residence time is large (thousands years). CSC marly-gypsum matrix confines karst system and brackish water is a mixture of Miocene aquifer freshwater and karst system brine.

6. CONCLUSION

Geophysical studies identified brine enclaves in Fuente de Piedra lagoon basin. Hydrochemistry allowed to define water and brine families and showed similarity between brine enclaves in basin and hypersaline karst springs in Guadalhorce river. Stable isotope analysis (^{18}O , D) allowed to discriminate different genesis of shallow and deep brine around lagoon and brine enclaves. Spatial trend of $\delta^{18}\text{O}$ model characterized recharge zone of Miocene aquifer, brine enclaves and CSC matrix. Radioactive isotopes (^{14}C , T) date freshwater and the different kinds of brines in the lagoon basin. Therefore environmental isotopes have been necessary to define a flow pattern of this complex and multilayer flow system and, finally, to propose a new conceptual model. This model point out that there are two flow system that discharge in lagoon: Miocene aquifer (freshwater, local recharge, short residence times) and CSC hypersaline karst system (brine, regional recharge, long residence times). Both system are important for Fuente de Piedra wetland but Miocene aquifer is clearly the most vulnerable of them and this is why it must be especially protected

ACKNOWLEDGEMENTS

To Director and staff of the Natural Reserve Fuente de Piedra lagoon, the Director and staff of the Laboratories of Isotopic Technical of the CEDEX who contributed to this work

REFERENCES

- [1] HEREDIA, J; ARAGUÁS, L. RUIZ, J. 2004. Delineation of groundwater dynamics and flow patterns under variable density conditions: case of the subsurface brine of Fuente de Piedra (SW Spain). 18 th Salt Water Intrusion Meeting. Ed. ARAGUÁS, CUSTODIO & MANZANO. 679:692. Cartagena, España
- [2] HEREDIA, J., PARDO-IGÚZQUIZA, E., RODRÍGUEZ-ARÉVALO, J., CASTAÑO, S., DÍAZ, M.F., CAPILLA, J.E., PRADO, A. Y BARDASANO, L. 2013. Identification of spatial models of $\delta^{18}\text{O}$ in precipitation of the wet season over Spain using genetic algorithms. 15th IAMG Conference: Mathematic of Planet Earth. Mathematics of Planet Earth. (Ed. Springer) 163-167. Madrid, Spain
- [3] KENDALL, C. J. MC DONNELL (2003): "Isotope tracers in catchment hydrology". 3th Ed. ELSEVIER. Netherlands. 839 pp.
- [4] MONTALVÁN, F.J., HEREDIA, J., ELORZA, F.J. (2012). Hydrochemical and isotopic characterization and the use of natural tracers for the flowing pattern conceptualization in a hypersaline hydrogeological system: Fuente de Piedra (Spain). 6th WWF-CHF: Ressources et gestion des aquifères littoraux, Cassis-Francia, p. 159.
- [5] RUIZ, J.M., HEREDIA, J., G. DE DOMINGO, A. 2007. Characterization of subsurface brines in Fuente de Piedra lake hydrogeological system (Málaga, Spain) using hydrogeochemical and geophysical techniques. XXXV IAH Congress. Portugal.

THE USE OF HYDROCHEMISTRY AND STABLE ISOTOPES ($\delta^{18}\text{O}$, $\delta^2\text{H}$) TO INVESTIGATE SURFACE WATER AND GROUNDWATER QUALITY IN THE LOWER VOLTA BASIN OF GHANA

S. B. DAMPARE, S. Y. GANYAGLO, S. OSAE, D. ADOMAKO, E. M. TEYE, C. D. EGBI
National Nuclear Research Institute, Ghana Atomic Energy Commission, P.O. Box LG 80,
Legon-Accra, Ghana
E-mail address: sbdampare@ug.edu.gh.

Abstract: The hydrochemistry and stable isotopes of surface and groundwater have been studied to examine the overall water quality status of the Volta River and shallow groundwater in the Lower Volta Basin (LVB). The pH values ranged from 4.9 to 7.5 for surface water (SW), demonstrating mild acidic to alkaline conditions. The pH values for the groundwaters (GW) range from 3.6 to 7.8, suggesting acidic to alkaline waters. The nitrate concentration ranges from 0 to 3.0 mg/L for surface water and 7.3 to 433 mg/L for groundwater. The nitrate values in SW are comparatively lower than nitrate values in GW for the entire area. The hydrochemical facies for the groundwater samples show four main water types, namely NaCl, (CaCl_2 , MgCl_2), CaMgHCO_3 and the non-dominant water type. The predominant hydrochemical facies is NaCl, whereas CaCl_2 , MgCl_2 and CaMgHCO_3 water types occur to a smaller extent in the area. Mineralisation (salinity) of the groundwaters, which was initially not considered in the research objective, has become a key issue worth mentioning. Possible processes responsible for the groundwater mineralization include halite dissolution, cation exchange and seawater intrusion. Stable isotope composition of the shallow groundwaters shows that GW in the north east of the study area (Sogakope), GW in the south west (Ada) and the Volta River appear to define a mixing line with multiple end-members.

1. INTRODUCTION

Freshwater quality is becoming widely and increasingly compromised due to various human influences and more so in peri-urban areas in developing countries. Surface water and groundwater play a key role both in the domestic water delivery system as well as the agricultural sector in the Lower Volta River Basin of Ghana (LVRB) where these resources are often used for irrigation purposes to support rain-fed agricultural activities.

The Lower Volta River Basin of Ghana forms part of the southern coastal belt of Ghana (537 km). The study area (Figure 1) lies approximately between longitude $0^\circ 32' - 0^\circ 42' \text{ E}$ and latitude $5^\circ 44' - 6^\circ 02' \text{ N}$ respectively. The area lies in the savannah zone and features a tropical savannah ecological climate with settlements within 5 km off either bank of the Volta River. It is interconnected with two distinct geological formations stretching from Sogarkope southward to Big Ada and Ada Foah.

Greater part of the Lower Volta River basin is underlain by tertiary and recent deposits [1]. A small section in the northern and eastern parts falls under the Dahomeyan complex rocks of Precambrian age. Groundwater in the basin occurs in fractures in highly consolidated siliciclastic aquifers overlain by a thin unsaturated zone [2].

Inhabitants in the LVB depend heavily on shallow aquifer systems, the Volta River and nearby streams for their domestic and agricultural water supply. The shallow aquifers are

tapped by hand-dug wells in various households, where sanitary conditions around the wellhead in most cases are poor. Considering the increasing population in the area, the aquifers are vulnerable to pollution from domestic waste discharge. Pollutants carried by these shallow aquifer systems may in turn be discharged into the Volta River closed by and nearby streams.

Some works have been done on different aspects of hydrogeology and water quality issues in the Volta Basin [3 - 5]. However, no serious attention has been given to the interaction of the shallow aquifer systems and the Volta River as well as nearby streams in the area to establish a link between the groundwater and surface water systems. This may partly be due to lack of knowledge on groundwater discharge areas, magnitude of groundwater discharge, quantification of fluxes of pollutants derived from groundwater discharge, assessment of origin and age of groundwater discharge. The need for greater understanding of the hydrogeologic and chemical processes in relation to the surface water and groundwater quality and interaction in the basin cannot be overemphasized.

The principal objective is to assess the water quality of the Volta River, nearby streams and shallow groundwater systems in the Lower Volta Basin, establishing the impact of the shallow groundwater discharge on the Volta River and the nearby streams. This will contribute to the assessment of sustainable management of surface water and groundwater resources in the basin since the development of climate proofed economic projects in the area is tied to these water resources.

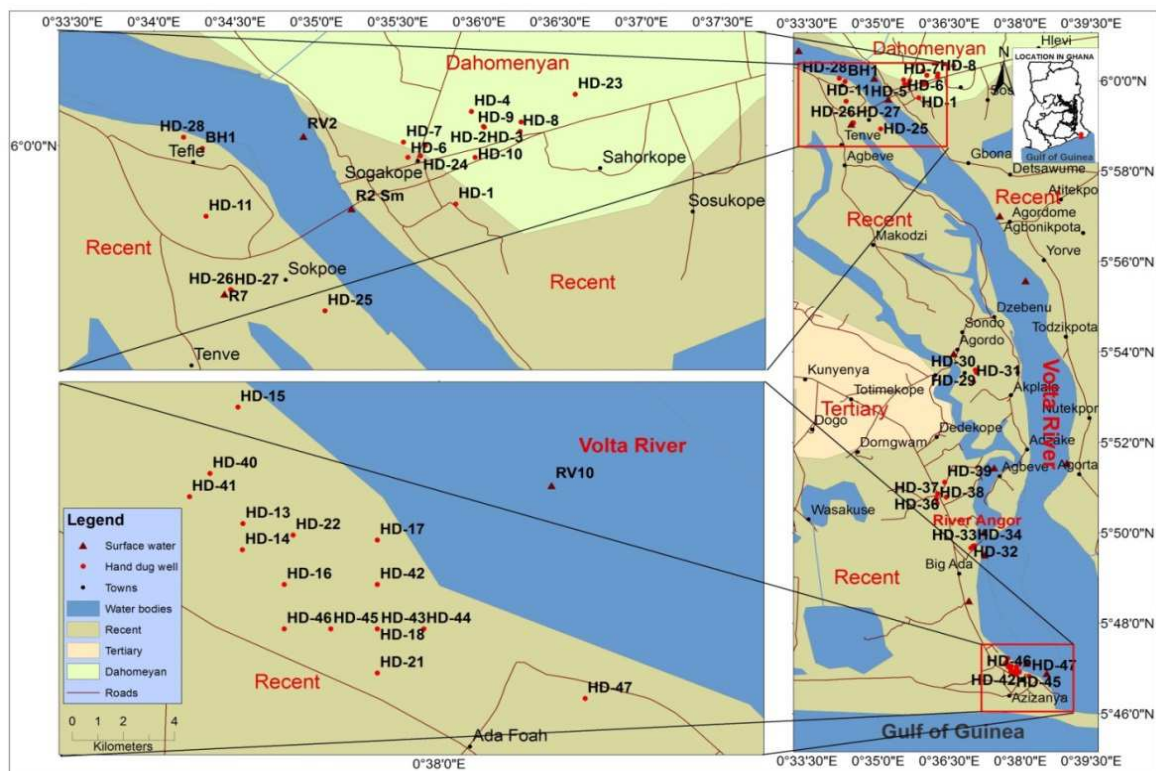


Figure 1. The geological map of the study area showing sampling points.

2. METHODS

A number of activities, including field and laboratory works, have been planned to achieve the objectives of the project. Water quality data has been collected through sampling of both

surface and groundwater. Water samples were collected in the field from hand dug wells, boreholes, and the Volta River. Groundwater samples were obtained from active water supply wells used for domestic purposes. Rainwater was also collected on event basis from the Sogakope and Ada stations for isotopic studies. Physical parameters determined *in situ* using a HACH Digital Tritator included (EC, TDS, temperature, pH, Eh, alkalinity, salinity). The chemical parameters (Na^+ , Mg^{2+} , K^+ , Ca^{2+} , SO_4^{2-} , Cl^- , HCO_3^- , NO_3^- , PO_4^{3-} , F^- , SiO_2 , Fe^{2+} , Br^- , Al^{3+}) and stable isotopes of ^{18}O and ^2H were measured at the Ghana Atomic Energy Commission using Dionex IC 90 system and LGR DLT 100 Liquid Water Isotope Analyser, respectively.

3. RESULTS

The pH values ranged from 4.9 to 7.5 for surface water, indicating mild acidic to alkaline. The pH values for the groundwaters range from 3.6 to 7.8, suggesting acidic to alkaline waters. The nitrate concentration ranges from 0 to 3.0 mg/L for surface water and 7.3 to 433 mg/L. The highest nitrate concentration in surface water occurred at sampling points R5 and R6 all located in the vicinity of a commercial rice farm. This confirms earlier observation with regards to pH –4.9 in surface water for the same sampling location, evident of point-source agricultural runoff. The nitrate values in the surface water are comparatively lower than nitrate values in groundwater for the entire area. The distribution of ions along the course of the Volta River depicts relatively high concentration value for SO_4^{2-} , compared to the other parameters.

The Piper trilinear diagram (Fig. 2) constructed for the groundwater samples shows four main hydrochemical facies, namely NaCl, (CaCl_2 , MgCl_2), CaMgHCO_3 and the non-dominant water type. The predominant chemical facies is NaCl, whereas CaCl_2 , MgCl_2 and CaMgHCO_3 water types occur to a smaller extent in the area. Mineralisation (salinity) of the groundwaters, which was initially not considered in the research objective, has become a key issue worth mentioning. Possible processes responsible for the groundwater mineralization include halite dissolution and cation exchange and seawater intrusion. Seawater intrusion needed to be carefully looked at since fresher groundwaters are obtained closer to the coast.

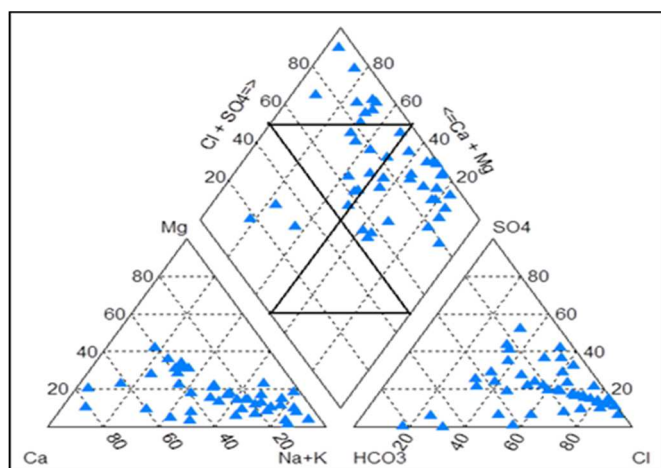


Figure 2. Piper trilinear diagram.

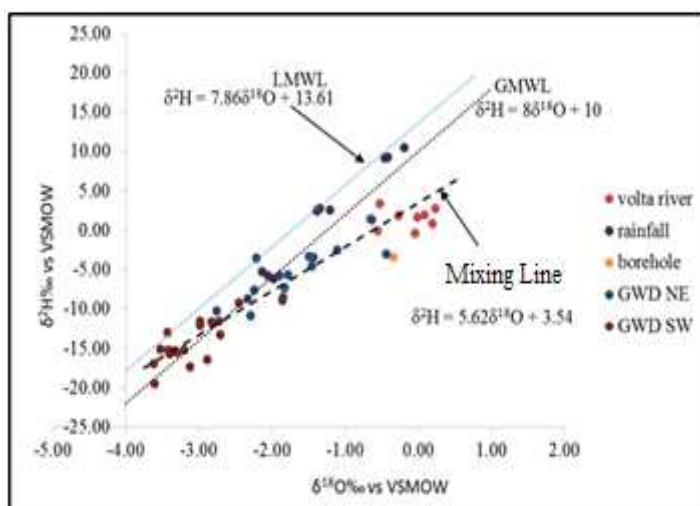


Figure 3. Stable isotope plot for water samples.

The distribution of $\delta^{18}\text{O}$ values of groundwater ranges from -3.61 to -0.43‰ and $\delta^2\text{H}$ from -19.53 to 1.29‰. The mean values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are -2.45‰ and -10.24‰, respectively. The stable isotope plot (Fig. 2) shows that shallow GW in the north east of the study area (Sogakope), GW in the south west (Ada) and the Volta River appear to define a mixing line with multiple end-members.

4. CONCLUSIONS

Agricultural and other anthropogenic activities seem to negatively impact the quality of water in the LVRB. Nitrate values in surface water are comparatively lower than in groundwater for the entire area. Relatively high concentration of sulphate is observed compared to the other parameters. Also, shallow groundwater mineralisation in the area may be caused by halite dissolution, cation exchange associated with clay minerals in the aquifer matrix and probably seawater intrusion. The graph of stable water isotopes (^{18}O and ^2H) indicate that groundwater in the study area is of meteoric origin. Further work is required to resolve the seemingly complex isotopic data and also to understand salinity issues in the area.

REFERENCES

- [1] KESSE, G.O., The mineral and rock resources of Ghana. Balkema, Rotterdam (1985) 610 pp.
- [2] ACHEAMPONG, S.Y., HESS, J.W., Hydrogeological and hydrochemical framework of the shallow groundwater system in the southern Voltaian Sedimentary Basin, Ghana. *Hydrogeology J.*, **6** (1998) 527.
- [3] WORLD VISION INC., Ghana Rural Water Project: Fiscal Year 1992 Annual Report. Report to the Hilton Foundation (1993).
- [4] HELSTRUP, T., Environmental Isotopic and Hydrochemical Characteristics of Groundwater from the Cretaceous-Eocene Limestone Aquifer in the Keta Basin, Ghana and the Coastal Sedimentary Basin of Togo Ph.D. Thesis, Geological Institute, Faculty of Science University of Copenhagen (2006).
- [5] KAKA, E.A., AKITI, T.T., NARTEY, V.K., Stable isotopes of water as indicator of Groundwater-Volta Lake interactions in the south-western margin of the Volta Lake, Ghana. *Elixir Agric.* **39** (2011) 4888.

ID: 329

^{129}I AND STABLE IODINE IN NATURAL WATERS FROM LOWER SAXONY, GERMANY

A. A. A. OSMAN,

Leibniz University of Hannover, Institute for Radioecology and Radiation Protection (IRS),
Herrenhäuserstraße 2, D-30419 Hannover, Germany

E-mail address: osman@irs.uni-hannover.de

S. BISTER, A. DAROUI, B. RIEBE, C. WALTHER

Leibniz University of Hannover, Institute for Radioecology and Radiation Protection (IRS),
Herrenhäuserstraße 2, D-30419 Hannover, Germany

Abstract: Water samples from different sources in Lower Saxony (Germany) have been analyzed for ^{127}I , ^{129}I , and their isotopic ratio ($^{129}\text{I}/^{127}\text{I}$). ^{127}I was determined directly by inductively coupled plasma mass spectrometry (ICP-MS) and ^{129}I was measured using accelerated mass spectrometry (AMS) after a chemical separation procedure. The $^{129}\text{I}/^{127}\text{I}$ isotopic ratios in the investigated groundwater samples were higher than the natural equilibrium isotopic ratio (1.5×10^{-12}), and not much lower when compared to those in other environmental materials from the same region. This means the water reservoirs in the region are already slightly affected by anthropogenic ^{129}I , most likely deriving from the European reprocessing plants (via North Sea).

1. INTRODUCTION

^{129}I , the long-lived ($T_{1/2} = 15.7$ Ma) radioisotope of iodine, occurs in the environment naturally and/or anthropogenically. The earth total inventory of ^{129}I is estimated to be 50,000 kg (326.8 TBq) which is mostly bound to the Lithosphere and only 263 kg (1.7 TBq) represent the “free” inventory in the atmosphere, hydrosphere, and biosphere [1]. After the pre-nuclear era, the anthropogenic input of ^{129}I into environment became more considerable especially from nuclear reprocessing plants in Western Europe. An example is the continuous discharges from the facilities in the La Hague (France) and Sellafield (UK) into the North Sea and Irish Sea, respectively. Due to its chemical and environmental properties, ^{129}I has been assigned as a tracer for various environmental processes and hydrological applications. For instance, it is a useful tracer of groundwater pollution from nuclear facilities. Moreover, its long half-life provides the opportunity to date groundwater in the range 2 – 80 Ma. In this framework we are aiming to assess the sensitivity of drinking water reservoirs with regard to introduction and accumulation of radioiodine.

2. METHODS

Natural water samples (surface-, ground-, and rain waters) were taken from Lower Saxony, Germany, and were preserved immediately after sampling by adding 50 mL 0.6 M caustic soda. Prior to AMS measurements, a solid phase extraction procedure was applied to all water samples to separate ^{129}I . At first, after adding 3 mg of Woodward iodine carrier, all iodine species were oxidized to iodate by using $\text{Ca}(\text{ClO})_2$ and afterwards reduced back to iodide with NH_3OHCl and NaHSO_3 . This was followed by an ion exchange separation using a DOWEX[®] 1×8 analytical grade ion exchange resin. The iodine was then eluted with concentrated potassium nitrate solution (2.25 mol/L) after rinsing the ion exchange columns with high purity water and a 0.5 mol/L potassium nitrate solution. Finally, ^{129}I was

precipitated as AgI for AMS measurement. The measurements were performed at the AMS facility in ETH Zürich, Switzerland. ^{127}I was determined directly without any chemical separation by using ICP-MS at Leibniz Universität Hannover, Germany.

3. RESULTS

^{129}I concentrations and $^{129}\text{I}/^{127}\text{I}$ isotopic ratios of the investigated waters are presented in figure 1. The $^{129}\text{I}/^{127}\text{I}$ isotopic ratios for all waters are significantly higher than the natural equilibrium isotopic ratio (1.5×10^{-12}). The investigated waters were compared to other environmental compartments in the same region as well as North Sea water as a hot spot of ^{129}I due to the continuous discharge from the neighboring reprocessing plants in France and UK. The general trend is that the rain water has the higher ^{129}I concentration and $^{129}\text{I}/^{127}\text{I}$ isotopic ratio in comparison with surface water which in turns is higher than groundwater. This is because both, precipitation and surface water bodies are open water sources in contrast to groundwater.

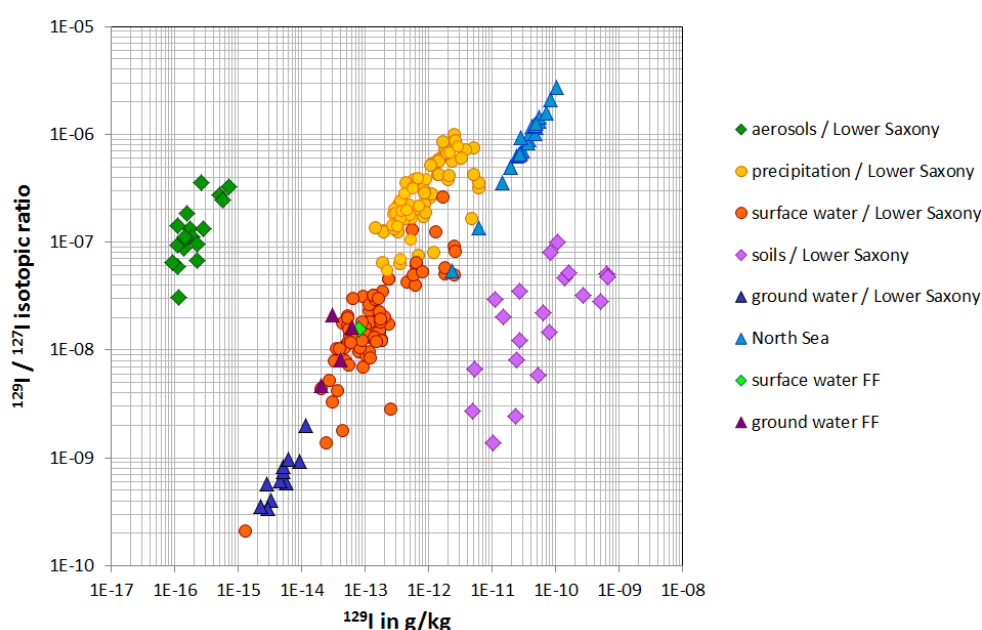


Figure 1. $^{129}\text{I}/^{127}\text{I}$ isotopic ratios versus ^{129}I for the investigated water in comparison to other environmental compartments in Lower Saxony and North Sea water

Another reason is that transfer of iodine from the North Sea as a sea-spray, CH_3I , or as volatile iodine (I_2) causes precipitation and aerosols samples have higher ratios. Although soil samples have higher ^{129}I concentrations compared to surface waters, but they still have almost the same ratios which is attributed to the higher content of stable iodine in soils than in surface waters. Groundwater samples have the least ratio comparing to others, with an exception of samples from Fuhrberger Feld (FF) reservoir which reveal the same concentration and ratio as some of the surface water samples. This is most likely due to the fast infiltration of water into the soils of that reservoir.

4. CONCLUSIONS

Our preliminary results showed a slight effect by atmospheric input of anthropogenic ^{129}I on groundwater samples from Fuhrberger Feld (FF) aquifer, which is an unconfined aquifer, and thus prone to contamination by percolating water. It is an interesting study area for assessing sensitivity of groundwater to ^{129}I and other man-made radionuclides such as ^{36}Cl and ^{90}Sr .

REFERENCES

- [1] MICHEL, R., DARAOUI, A., GORNY, M., JAKOB, D., SACHSE, R., TOSCH, L., NIES, H., GORONCY, I., HERRMANN, J., SYNAL, H. A., STOCKER, M., ALFIMOV, V., Iodine-129 and iodine-127 in European seawaters and in precipitation from Northern Germany, *Sci. Total Environ.* **419** (2012) 151.

HUMAN IMPACTS ON LARGE RIVER SYSTEMS OF EASTERN CANADA: ISOTOPIC INSIGHTS

J. F. HELIE, C. HILLAIRES-MARCEL, E. ROSA

Geotop-UQAT, Montreal, Canada

Email address: helie.jean-francois@uqam.ca

Abstract: Canada holds about 7% of the world's renewable freshwater on its territory. While many river systems drain this water to the Pacific, Arctic and Atlantic oceans, two major river systems are mainly responsible for draining Canada's freshwater to the oceans: the Mackenzie River and the St. Lawrence-Great-Lakes river system with annual water discharges of 325 km³/yr and 318 km³/yr respectively. These 2 major river systems have punctually been the focus of isotopic monitoring in the past and have been targeted by the Advisory Committee Report on an Expanded "Global Network on Isotopes in Rivers" (GNIR) Program for further monitoring. These isotopic monitoring have revealed that both the Mackenzie and St. Lawrence river systems depict evaporated signals modulated by low signature spring snow melt events through their tributaries (Yi et al., 2010, Rosa et al., in prep). The St. Lawrence carbon cycle is dominated by DIC which depicts high $\delta^{13}\text{C}$ due to equilibrium with atmospheric CO₂ in the Great Lakes during base flow and low isotopic compositions during the spring freshet due to soil drainage through the tributaries (Hélie et al., 2002). DOC mainly originates from soils, but can be influenced by autochthonous carbon during the warmer months (Hélie and Hillaire-Marcel, 2006). POC is low and mainly produced in lakes and waterways (Hélie and Hillaire-Marcel, 2006). Nitrates are dominated by inputs from the Great Lakes, but modulated by atmospheric inputs (Thibodeau et al., 2013).

ID: 35

WATER BALANCE ASSESSMENT ACROSS CANADA

Y. YI, J. GIBSON, J. BIRKS,
Alberta Innovates Technology Futures, Canada
E-mail address: yyi@uvic.ca

Abstract: Extensive campaign of sampling and archiving lake water isotopic compositions across Canada were conducted in recent years. As a practical alternative to classical hydrological monitoring for understanding water balance in often remote locations, the isotopic approach was employed to determine basic lake hydrological characteristics such as the evaporative over inflow ratio (E/I) and residence time (τ). According to the distribution of lake water isotope composition in $\delta^{18}\text{O}$ - $\delta^2\text{H}$ space and geographic locations, various scenarios for atmospheric conditions and δP - δA relations are developed to best fit the observations. The spatial pattern of these inferred hydrological characteristics were further extrapolated to gain insights on regional characteristics. In regions, where density of sampling is adequate to establish a robust local evaporation line (LEL), the LEL is extended to produce the first-order estimation of isotope compositions of precipitation for the region (δP). Inferred δP values are further tested and discussed for providing isotopic input for the GNIR-Canada network. Overall, the objective of this national wide survey is to assess the potential of isotope mass balance conducted on one sampling from individual lake to be used to generate reliable hydrological information at the regional scale and provide hydrologic insights to lake water quality and biological condition status.

ID: 81

INVESTIGATION OF HYDROLOGY OF CATCHMENT AREA OF SMALL RIVER IN KARELIA (RUSSIA) BY HIGH-RESOLUTION RECORD OF $\delta^2\text{H}$ AND $\delta^{18}\text{O}$ IN PRECIPITATIONS AND RIVER WATER, INCLUDING EXPERIMENTAL EVALUATION OF EVAPORATION

G. S. BORODULINA,

Institute of Northern Water Problems Karelian Research Centre of RAS, Petrozavodsk, Russian Federation

E-mail address: bor6805@yandex.ru

I.V. TOKAREV, I. A. AVRAMENKO.

Research Center "Geomodel" of Saint-Petersburg State University, St. Petersburg, Russian Federation

Abstract: Pronounced climate changes have lately been observed in Arctic and sub-Arctic regions. The response of hydrological systems to these changes is especially visible in small river catchments, which are also most sensitive to weather extremes. Stable water isotopes (deuterium and oxygen-18) exhibit seasonal cycles similar to air temperature variations [Gat and Gonfiantini, 1981], with enrichment of heavy isotopes during warm summer months and depletion in cold winter months. Also evaporation is evident from isotope fractionation effect due to residual water enrichment [Dansgaard, 1964]. Thus, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ can be used to partition river flow into snow and rain components, and for evaporation estimation. Hence, monitoring of the stable isotopic composition of water enables investigation and quantification of changes in the hydrological cycle at the integrated basin scale for rivers in difficult-to-access and remote northern regions [Welp et al., 2005].

The study area is the catchment of small river Neglinka, which flows to Lake Onega. The river is 14 km long and the catchment area is 46.1 km². The formerly heavily paludified upstream parts have been partially drained. The City of Petrozavodsk is located in the lower stretch of the river. The river serves as the receiver of storm water runoff. The river has an observed average annual runoff of 0.51 m³/s and about 57% of total annual flow occurs during the spring season, the peak flow rate observed in May. The share of winter discharge is 9%. The summer-autumn discharge is almost four times as much as that in winter.

The climate in the study area is transitional between maritime and continental. Annual average precipitation is about 650-750 mm, and its temporal distribution is such that 350-400 mm occurs during the warm period and 150-250 mm during the cold period. The average annual temperature is +2.5° C; mean temperature in July is +16°C, in January -12°C. Average stored moisture in snow is 100 mm. Evaporation during the winter period is around 30 mm.

Monitoring of the volumes and stable isotope composition of atmospheric precipitation in Petrozavodsk started in 2009. The temperature, electrical conductivity, stable isotope composition of the water at the Neglinka River have been monitored since 2012, and evaporation experiments were performed in 2014. We sampled precipitation and river water with weekly collections during winter and more frequent collections during the ice-free season (with diurnal sampling during spring flood). Heavy rainstorm events were sampled

individually and the pan-collector was emptied immediately following the event to minimize evaporation. The snow cover (the entire body of snow) was surveyed before melting began. Plastic vials with samples were stored upside-down in cool conditions. We analyzed water for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ on Picarro L-2120i infra-red ring-down spectrometer at the "Geomodel" (Resource Center Research park of Saint-Petersburg State University). All isotope results are presented on V-SMOW scale. We used V-SMOW-2, GISP, LASP, USGS-45 and USGS-46 standards. The measurement error was 1‰ for $\delta^2\text{H}$ and 0.1‰ for $\delta^{18}\text{O}$.

Weighted annual precipitations have $\delta^{18}\text{O} = -11.4$ ‰ and $\delta^2\text{H} = -83.3$ ‰ with minimum value in winter up to $\delta^{18}\text{O} = -30.9$ ‰ and $\delta^2\text{H} = -239$ ‰ and maximum in summer $\delta^{18}\text{O} = -4.3$ ‰ and $\delta^2\text{H} = -33$ ‰. A slight depletion (more negative values) of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ began to be detected late in winter (before the start of massive snow-melt) due to thaws. Quite heavy depletion was observed during one or two weeks in the spring high water period, when the snow cover was thawing most intensively. In this period the Neglinka river had lightest isotope composition of water $\delta^{18}\text{O} = -16.4$ ‰ and $\delta^2\text{H} = -116$ ‰. In summer the isotope composition of water was more heavy $\delta^{18}\text{O} = -9.8$ ‰ and $\delta^2\text{H} = -75$ ‰. Evaporation strongly influences the water balance, as evidenced by a declension of the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotope composition rightward from the Global Meteoric Water Line and the deuterium excess in river water reaches value $d^2\text{H} = -1.2$. A short-lived (several days) slight depletion (2 - 3 ‰ in $\delta^{18}\text{O}$) of stable isotopes occurred in September and/or October due to rain freshet. In the winter low-water period the isotope composition of river water was similar to the weighted annual precipitations ($\delta^{18}\text{O} = -11.8$ ‰ and $\delta^2\text{H} = -85$ ‰).

Precipitation of the given period (spring, summer and fall) was used in evaporation experiments. The residual volume of water in the vaporizer was measured daily, and a water sample, which was negligibly small compared to the vaporizer capacity, was collected. All results of the evaporation experiment were well fit for calculations using the Rayleigh distillation model. Thus, evaporation rate and the isotope effect of evaporation were calculated under different conditions. If daily temperature was lower than +5 °C, then physical evaporation was negligibly low and excluded from the calculations. The deuterium excess was calculated on a subset of all other samples to verify the evaporation influence on the isotope composition of water. All samples with values of d-excess less than 10 were used for estimating the evaporation loss by the Rayleigh distillation model, and relevant corrections were introduced to the experimental data.

The contributions of snow or rain input to the Neglinka river in each week of the sampling period were calculated using the two end-member mixing model. The isotope composition of snow was determined as the arithmetic mean of the snow survey in the Neglinka river catchment in spring. The isotope composition of rainfall was determined as the weighted mean. Each individual rain event or weekly sum was weighted on the measured amount of precipitation in that month. Corrections in the isotope composition and runoff volume due to the influence of evaporation were made. It was found that the water leaving the basin through the river consisted around 60 % of snow and 40 % of rainfall, on an annual basis. These values should be compared with the annual inputs of snow (43 %) and rain (57 %) to the water balance, suggesting that transpiration by vegetation is a significant factor during the growing season. A substantial proportion of moisture leaves the Neglinka river catchment through evapotranspiration during the growing season.

Quantification of the hydrological cycle and investigation of its changes related to climate fluctuations is difficult in remote northern regions. However, monitoring of the stable isotope

composition of water in Arctic rivers may potentially be a means of integrated basin-scale estimation of the water balance.

ACKNOWLEDGEMENTS

The study has been financially supported by the Russian Science Foundation №14-17-00766 and Russian Foundation for Basic Research 12-05-1004_a.

REFERENCES

- [1] DANSGAARD W. (1964) Stable isotopes in precipitation. *Tellus*. V. 16. № 4, 436–463.
- [2] GAT J.R. AND GONFIANTINI R. (1981) *Stable Isotope Hydrology: Deuterium and Oxygen-18 in the Water Cycle*, IAEA, Vienna.
- [3] WELP L.R., RANDERSON J.T., FINLAY J.C., DAVYDOV S.P., ZIMOVA G.M., DAVYDOVA A.I., AND ZIMOV S.A. (2005) A high-resolution time series of oxygen isotopes from the Kolyma River: Implications for the seasonal dynamics of discharge and basin-scale water use. *Geophysical Research Letters*. V. 32, L14401, doi:10.1029/2005GL022857.

DISTRIBUTION OF STABLE ISOTOPES OF LIQUID WATER IN FRESHWATER RESOURCES WITHIN CAGAYAN VALLEY RIVER BASIN, NORTHERN REGION PHILIPPINES

N. D. S. MENDOZA, S. S. CASTAÑEDA, C. T. RACADIO, R. J. SUCGANG, E. P. VARGAS,

Philippine Nuclear Research Institute, Commonwealth Ave., Diliman, Quezon City, 1101

Email address: ndsmendoza@outlook.com

J. R. CARDENAS,

Metro Tuguegarao Water District, Tuguegarao City, Cagayan 3500, Philippines.

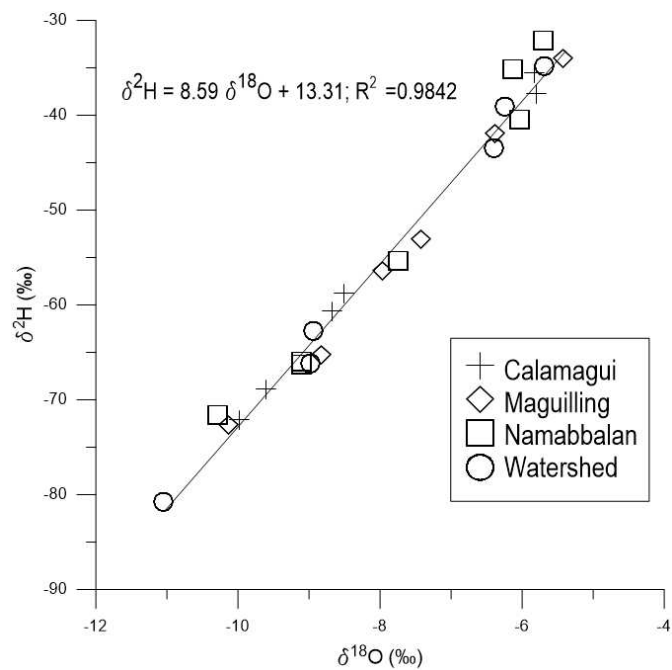
F. I. BILLONES,

National Water Resources Board, NIA Building, EDSA, Diliman, Quezon City, 1101

A.D. TORRESS,

Mines and Geosciences Bureau, North Avenue, Diliman, Quezon City 1101

Abstract: Stable isotope abundance of hydrogen ($\delta^2\text{H}$) and oxygen ($\delta^{18}\text{O}$) in liquid water from different freshwater resources in the Cagayan valley river basin were used to gain insight about the hydrological processes in the area. The data presented here were the results of the reconnaissance water sampling campaign that started from March 2012 to August 2013. Isotopic composition of rain water were used to identify the role of rainfall as an input to the river systems as well as in groundwater recharge. Rain samples collected between June to December 2012 from areas of Solana, Piat, Tuguegarao, and Nattalad watershed were found to have $\delta^{18}\text{O}$ values that range between -5.4‰ to -11.1‰ and $\delta^2\text{H}$ values of -32.1‰ to -80.7‰. The local meteoric water line (LMWL) was determined to be $\delta^2\text{H} = 8.6 \delta^{18}\text{O} + 13.3$ ($r=0.98$). The weighted annual average for $\delta^{18}\text{O}$ was found to be about -7.1‰ which was estimated based on a 2012 rain-event based sampling record available for Diliman, Quezon City area. The estimated average (i.e. -7.1‰ $\delta^{18}\text{O}$) was used as an index to demarcate possible interconnection between different freshwater resources such as rivers, springs, shallow and deep groundwater based on corresponding $\delta^{18}\text{O}$ values obtained for each water type. The $\delta^{18}\text{O}$ abundance of waters from rivers collected at high elevation areas, such as in Nueva Viscaya, Mountain Province, Kalinga and Ifugao, which are tributaries to the Cagayan river, showed more depleted values (data range: -5.8‰ to -10.1‰; mean: -8.47‰ and s.d.: 1.25‰; median: -8.61‰; $n=9$) as compared to the estimated index. The difference may be attributed to the depletion of oxygen-18 containing water during downpour caused by altitude effects. Consequently, groundwater driven from boreholes (production wells) in these areas had more depleted average $\delta^{18}\text{O}$ values (mean: -7.52‰; s.d.=0.8‰; $n=5$) as compared to index value which may indicate local recharge process. On the other hand, $\delta^{18}\text{O}$ values for both river waters and groundwater obtained at lower elevation areas particularly in Isabela and Cagayan, showed values ranging from -3.3‰ to -7.7‰ and exhibited more enriched mean $\delta^{18}\text{O}$ values (6.4‰ (s.d.:1.4; $n=9$) and -6.6 ‰ (s.d.: 0.9; $n=99$) for rivers and boreholes, respectively) as compared to the estimated index of -7.1‰ which may be due to evaporative enrichment. For the first time, isotopic data for freshwater resources in the Cagayan river basin is reported.



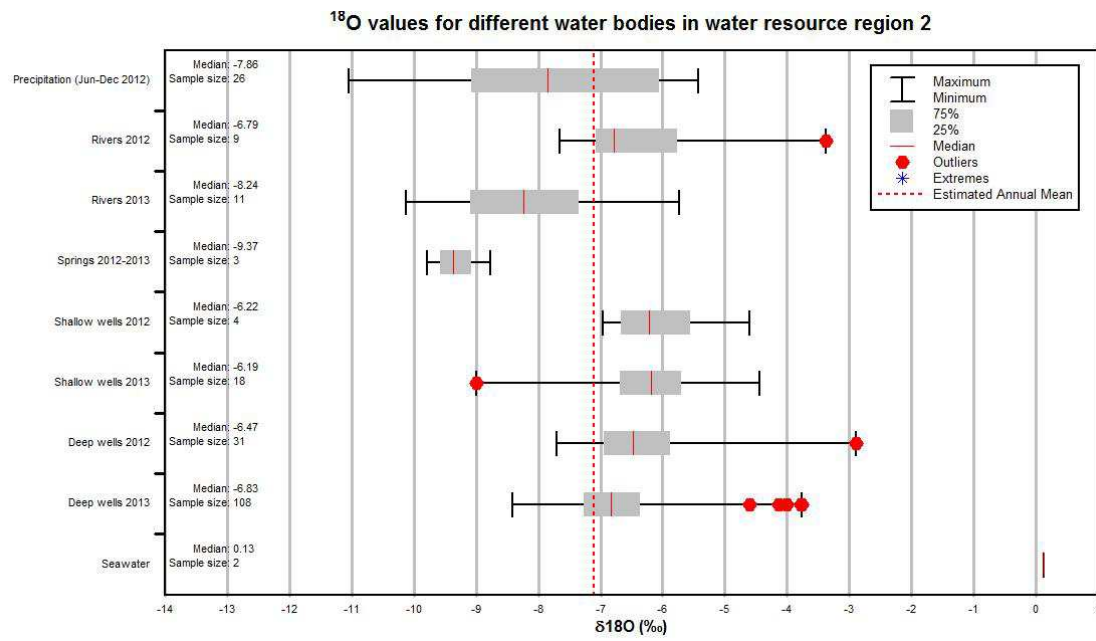


Figure 3. Box and whisker plot of oxygen-18 values from different water resources in Cagayan River Basin

STABLE ISOTOPES OF WATER AS A TOOL TO DESIGN CONSTRUCTED WETLANDS

A-K. RONKANEN, E. ISOKANGAS, K. PALMER, R. ESKELINEN
Water Resources and Environmental Engineering Research Group, P.O. Box 4300,
FIN-90014 University of Oulu, Finland
E-mail address: anna-kaisa.ronkanen@oulu.fi

Abstract: The abundance of peatlands offers an opportunity to use them as treatment steps for different type of wastewaters in the boreal climatic region. In this study, stable isotopes of water ($\delta^{18}\text{O}$, $\delta^2\text{H}$) were used as a tool to determine preferential flow paths and evaporation signal in 6 treatment peatlands purifying different types of runoff and wastewaters as well as in 1 restored agricultural peatland site. The spatial distribution of $\delta^{18}\text{O}$ was determined from 16-150 surface water samples collected from each peatland. Moreover, temperature and electric conductivity were used as tracers to confirm isotope analysis results. In addition to $\delta^{18}\text{O}$ analysis, $\delta^2\text{H}$ distributions were studied in four of the peatlands. Sampling was repeated 1-3 times in each site. The results showed that the isotope method was efficient for determining preferential flow areas. Even though the other tracers provided preferential flow areas, only stable isotopes of water could be used to estimate flow velocities and transit times in constructed peatlands.

1. INTRODUCTION

The aim of this study was to determine flow paths and flow processes in treatment peatlands in cold climate region in Finland. For comparison purposes, the same methods were also applied to a restored agricultural pasture site in Iceland. Treatment peatlands are one type of constructed wetlands (CW) that are build either on pristine or on previously drained peatlands. CWs are widely used for different types of runoff and wastewaters all around the world [1-3]. One of the biggest challenges in treatment peatlands is to get evenly distributed inflow water which provides a high hydraulic efficiency and good purification results [4]. As CW is designed, selection of location, where treatment area is constructed, can be difficult and in many cases in Finland selection process has been unsuccessful. The main reason for this has been that local groundwater and surface water processes have been poorly understood, causing e.g. discharge of groundwater to the CW. This should be avoided for optimal CW functioning.

Traditionally, artificial tracers have been used to determine the residence time of water and preferential flow areas in CWs (e.g. [5-6]). However the conservative behavior of tracers and requirements of tracer injection (e.g. risk in density stratification or too low tracer concentration in outflow) are difficult to achieve in treatment peatlands which can be up to 50 ha in size. Moreover, water loss due to evapotranspiration can cause a considerable effect on purification efficiency throughout concentration processes especially in a large peatland.

Environmental tracers like stable isotopes of water ($\delta^{18}\text{O}$, $\delta^2\text{H}$), offer an effective tool to investigate flow patterns in treatment peatlands which are typically more complicated than those in other type of CWs. The use of stable isotopes also facilitates the study of possible impacts of local groundwater-surface water interactions on the suitability of an area for CW construction. Furthermore, the importance of evaporation from an area can be easily assessed by stable isotope analyses but not by traditional tracer injection. The objective of this study

was to create a comprehensive interpretation from flow processes in six treatment peatlands with varying size as well as in a restored agricultural peatland. The ultimate goal was to provide better guidelines for designing treatment peatlands.

2. METHODS

The study included peatlands treating 1) municipal wastewaters, 2) mine waters and 3) peat extraction effluents as well as 4) a restored agricultural pasture. There were two study sites in all three categories, except in the restoration category. All the treatment peatlands have been originally pristine peatlands which have been used for 1-16 years to decrease nutrient and metal load to downstream water bodies. The agricultural pasture has also been a pristine peatland, which was drained in order to improve its yield. However, it was noticed that the drainage did not bring large benefits therefore the drainage ditches were filled as restoration pilot test in 2012.

The areas of peatlands varied from 0.8 ha to 46 ha and hydraulic load from 6 to 44 mm d⁻¹. The spatial distribution of $\delta^{18}\text{O}$ in the peatlands was determined collecting 16-75 surface water samples per sampling campaign at each site. The number of samples depended on the size of the peatland. In four of the peatlands also the distribution of $\delta^2\text{H}$ was studied. Sampling was repeated 1-3 times in each site during years 2002-2014. In addition to isotopes, also other environmental tracers (like electrical conductivity and temperature) were used to confirm flow patterns and hydraulics in the studied treatment peatlands.

The isotopic composition of the water samples relative to VSMOW was analyzed using a Picarro L2120-i isotope analyzer in 2013 with the precision of 0.1 and 1.0 ‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ measurements respectively. In 2002, isotopes were analyzed at the University of Mining and Metallurgy, Cracow (Poland) and in 2004-2010 at the Dating Laboratory, Finnish museum of Natural History, Helsinki (Finland) by a mass spectrometry method. The δ distributions were interpolated from the values determined at the sampled points to the whole peatland area using standard ordinary Kriging and inverse distance weighting interpolation method.

3. RESULTS

Generally, the $\delta^{18}\text{O}$ content in the studied peatlands varied spatially. Preferential flow areas were clearly indicated in all treatment peatlands. Also at the restored peatland, in Iceland, the main flow area was detectable by stable isotope analysis and restoration action by filling ditches could be proved to be sufficient. Other tracers confirmed the different flow areas at every site. The preferential flow area was 50-90% of the total surface areas. This preferential flow area is essential for the functioning of CW as biogeochemical processes involved in contaminant retention occur mainly in this area.

Groundwater discharge to Sodankylä CW was found by isotopes. In groundwater discharging points, the $\delta^{18}\text{O}$ content was about -11.2‰ whereas in other points the $\delta^{18}\text{O}$ was around -9.9‰. Discharging groundwater might dilute mine water and falsify purification efficiency monitoring. In Rimminvuoma CW, the surface water from the catchment close to the treatment area discharged to the CW. However, these waters by pass the preferential flow area of the CW flowing along one side of the CW. Thus, the impact of those natural waters on processes involved in mine water purification is likely minor. $\delta^2\text{H} - \delta^{18}\text{O}$ plot illustrates the distribution of stable isotopic composition of treatment waters in four CWs (Fig. 1). Different flow, fractionation and mixing processes have caused the deviation to $\delta^2\text{H} - \delta^{18}\text{O}$ relationship within sites.

Table 1. The content of $\delta^{18}\text{O}$ in surface waters of studied treatment peatlands, n = number of samples.

Treatment peatland	Wastewater type	$\delta^{18}\text{O}$ (‰)	n
Kompsasuo*	Peat extraction runoff	-12.24 - -11.45	25
Puutiosuo*	Peat extraction runoff	-11.17 - -10.04	22
Rimminvuoma	Mine water	-14.33- -6.94	125
Sodankylä	Mine water	-12.11 - -9.49	40
Mellanaava*	Municipal wastewater	-12.93 - -10.79	19
Ruka*	Municipal wastewater	-14.45 - -12.45	25
Restored peatland		$\delta^{18}\text{O}$ (‰)	n
Mahvahlid, Iceland		-9.94 - -7.63	150

*Part of the data have been published in [4]

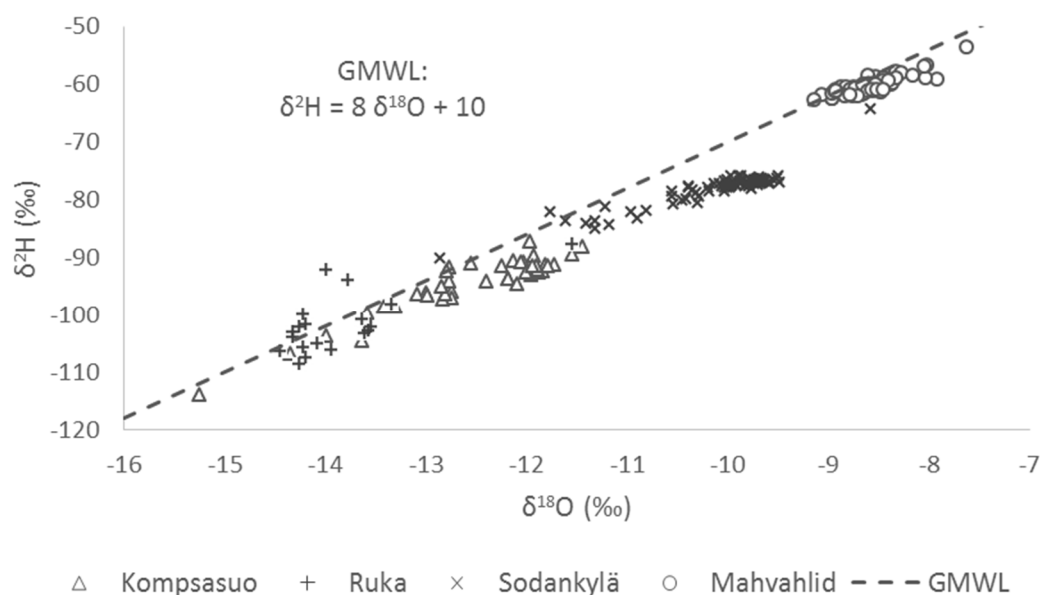


Figure 1. $\delta^2\text{H} - \delta^{18}\text{O}$ relationship for peatlands Kompsasuo, Ruka, Sodankylä and Mahvahlid.

REFERENCES

- [1] SHARMA, P.K., TAKASHI, I., KATO, K., IETSUGU, H., TOMITA, K., NAGASAWA, T., Effects of load fluctuations on treatment potential of a hybrid sub-surface flow constructed wetland treating milking parlor waste water (2013). *Ecol. Eng.* 57, 216-225.
- [2] KOSKIAHO, J., EKHOLM, P., RÄTY, M., RIIHIMÄKI, J., PUUSTINEN, M., Retaining agricultural nutrients in constructed wetlands – experiences under boreal conditions (2003). *Ecol. Eng.* 20, 89-103.
- [3] VYMAZAL, J., Constructed wetlands for wastewater treatment: five decades of experience (2011). *Environ. Sci. Technol.* 45, 61-69.
- [4] RONKANEN, A.K., KLØVE, B., Hydraulics and flow modelling of water treatment wetlands constructed on peatlands in Northern Finland (2008). *Water Res.* 42, 3826-3836.
- [5] MUÑOZ, P., DRIZO, A., HESSION, W. C., Flow patterns of dairy wastewater constructed wetlands in a cold climate (2006). *Water Research* 40 (17), 3209-3218.
- [6] WERNER, T. M., KADLEC, R. H., Application of residence time distributions to stormwater treatment systems (1996). *Ecological Engineering* 7 (3), 213-234.

ID: 112

STABLE ISOTOPE TRANSFER FUNCTIONS FOR VADOSE ZONE SOILS: THE ROLE OF ECOHYDROLOGIC ROUTING IN DETERMINING RUNOFF AND EVAPORATION ISOTOPE COMPOSITION

S. P. GOOD,

Department of Geology and Geophysics, University of Utah

Fredrick Albert Sutton Building, 115 S 1460 E, Salt Lake City, Utah 84112, United States

E-mail address: s.good@utah.edu.

G. J. BOWEN

Department of Geology and Geophysics, University of Utah

Fredrick Albert Sutton Building, University of Utah, Utah 84112, United States

D. NOONE

College of Earth, Ocean, and Atmospheric Sciences, Oregon State University

Burt Building, Oregon State University, Corvallis, Oregon 97331, United States

Abstract: The routing of precipitation through soils and into runoff, evaporation, and transpiration determines the isotopic composition of these fluxes relative to incident precipitation. Here, we present a simplified set of isotope transfer functions that estimate the isotopic composition expected within soil moisture in the vadose zone and its outward fluxes as a function of soil hydrologic connectivity and plant water use. These new theoretical relationships are explored with a large set of isotope of precipitation, runoff and evapotranspiration data as well as with stochastic simulations of synthetic rainfall which are used to examine the influence of seasonality and the precipitation amount effect on isotopic fluxes. Our results demonstrate the importance of transpiration/evaporation partitioning and the connectivity of the soil column on runoff composition. Additionally, we describe the relative importance of the correlation between precipitation amount and isotopic composition on soil moisture and associated fluxes.

1. INTRODUCTION

In terrestrial ecosystems, the relative balance between evaporation and transpiration and their respective isotopic signals determines the isotopic composition of evapotranspiration [1]. However the balance between evaporation and transpiration is poorly quantified both spatially and temporally in current hydrologic science. This problem is further complicated by the possible ecohydrologic separation between plant available waters and runoff, where mobile and immobile waters may be isotopically distinct [2]. Thus by understanding how precipitation is altered isotopically as it moves through soils and back to the atmosphere and into streams we can infer process-level information about ecohydrologic routing.

2. METHODS

A simple mass balance of the vadose zone can be written with respect to the fraction of precipitation intercepted (x), the runoff ratio (r), and the fraction of evapotranspiration that leaves the system as transpiration (f) as:

$$(1) \quad R_L N_0 + (1-x)PR_p dt = (R_L + dR_L)N_0 + rPR_Q dt + (1-x-r)fPR_T dt + (1-x-r)(1-f)PR_E dt$$

where R_L , R_Q , R_T , and R_E are the isotopic compositions of soil water, runoff, transpiration, and evaporation. Runoff can be expressed as a function of the hydrologic connectivity of soils with a parameter c , where in highly connected ($c=1$) systems R_Q is equal to soil water, and in highly disconnected ($c=0$) systems R_Q is equal to R_p . The Craig-Gordon model [3] is used to express R_E as a function of R_L , and we assume that R_T approximates R_L . Incorporation of these elements allows for equation (1) to be integrated and for soil moisture, evaporation, transpiration, and runoff isotope transfer functions to be developed. Conversely, given R_p , R_T , R_E and R_Q the manner by which precipitation is routed through ecosystems (via parameters c and f) can be explored.

3. RESULTS

Combining the isotope transfer functions derived from equation (1) with a global mass-balance of isotope ratios in precipitation and ocean fluxes, we estimate the global value of f is between 52-62% and c is approximately 58-81%. Thus, slightly over half of all evapotranspiration returns to the atmosphere through the stomatal pathway. Our assessment of the connectivity indicates that approximately 30% of runoff is direct precipitation which has not mixed with vadose zone soil moisture. Additional sensitivity tests with stochastic simulations of rainfall isotope ratios reveals that both seasonality and amount effects likely influence soil water isotopic composition due to the tendency for isotopically heavier rainfall associated with larger events to either run off or recharge soil columns.

4. CONCLUSIONS

In this study we present a series of theoretical isotope transfer functions for surface hydrologic processes. These transfer functions are used with global estimates of evapotranspiration and runoff to determine ecohydrologic routing of water through basins. This approach provides a useful framework from which further isotope studies of the soil-plant-atmosphere continuum may be based.

REFERENCES

- [1] GOOD, S., ET. AL., $\delta^2\text{H}$ isotopic flux partitioning of evapotranspiration over a grass field following a water pulse and subsequent dry down. *Water Resources Research*. **50** (2014)
- [2] BROOKS, J. ET. AL., Ecohydrologic separation of water between trees and streams in a mediterranean climate. *Nature Geoscience*, **3**(2014)
- [3] CRAIG H, GORDON, L., Deuterium and oxygen-18 variations in the ocean and marine atmosphere. *Stable Isotopes in Oceanographic Studies and Paleotemperatures* (1965)

ID: 114

**DISTRIBUTION OF STABLE ISOTOPES OF LIQUID WATER IN
FRESHWATER RESOURCES WITHIN WATER RESOURCES
REGION X, SOUTHERN PHILIPPINES**

C.T. RACADIO, S. S. CASTAÑEDA, N.D.S. MENDOZA, R.J. SUCGANG, E.P. VARGAS,
Philippine Nuclear Research Institute, Commonwealth Ave., Diliman, Quezon City, 1101
E-mail: ctracadio@pnri.dost.gov.ph

BEJA, R.M.,
Cagayan de Oro City Water District, Corrales Avenue, Cagayan de Oro City 9000

PANGAN, R.K.,
Manolo Fortich Water District, A. Ditona St., Tankulan, Manolo Fortich, Bukidnon 8703

LUZON, E.T.,
San Francisco Water District, Osmena St., Brgy. 2, San Francisco, Agusan del Sur 8501

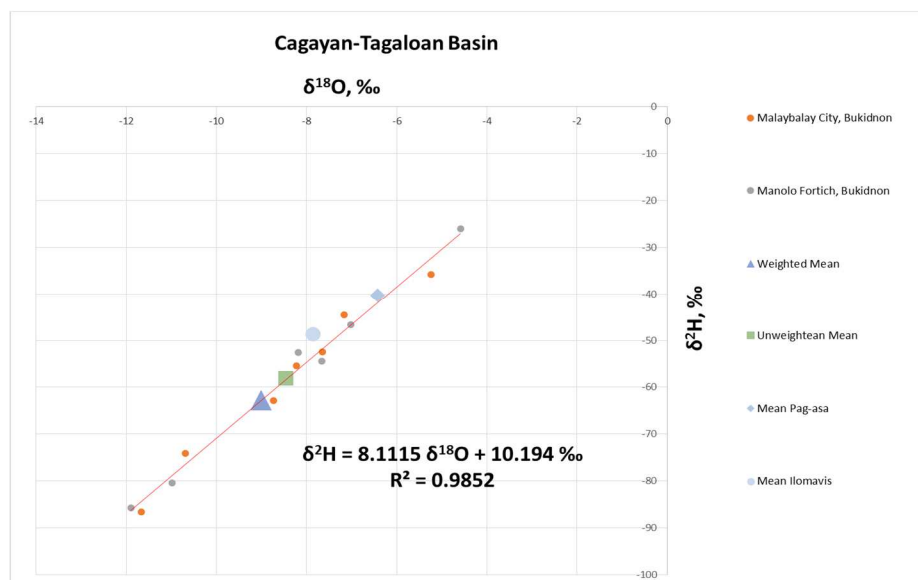
AROA, J.C.,
Malaybalay City Water District, Sayre Highway, Sumpong, Malaybalay City, Bukidnon 8700

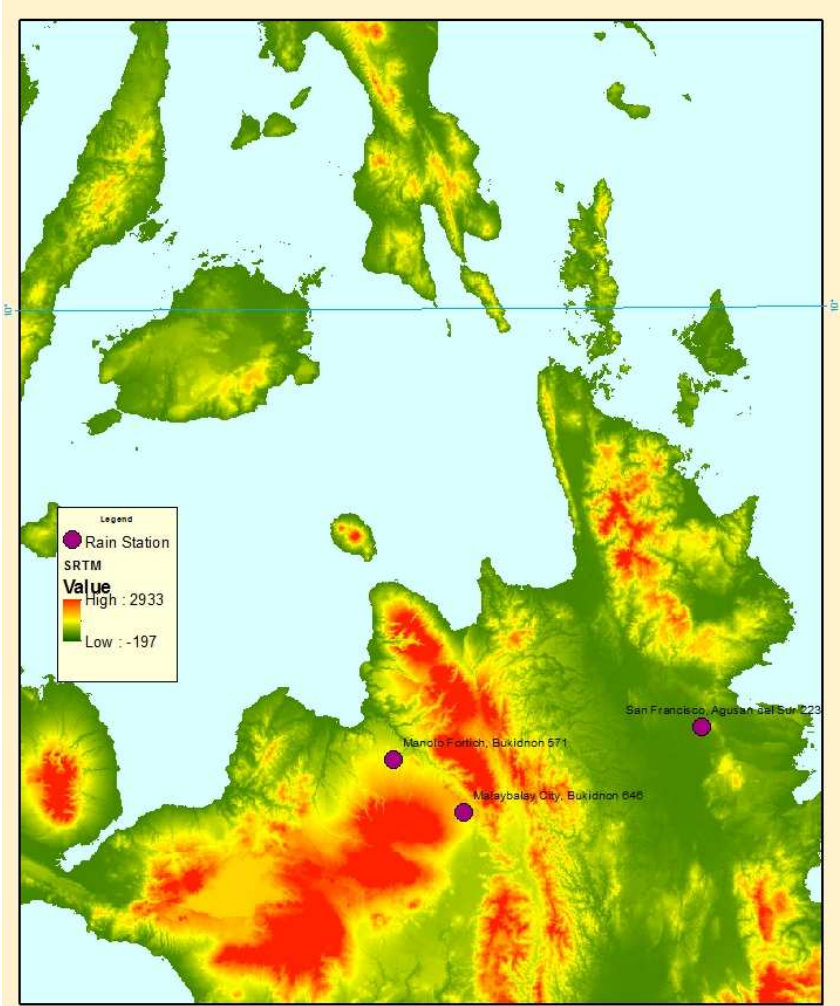
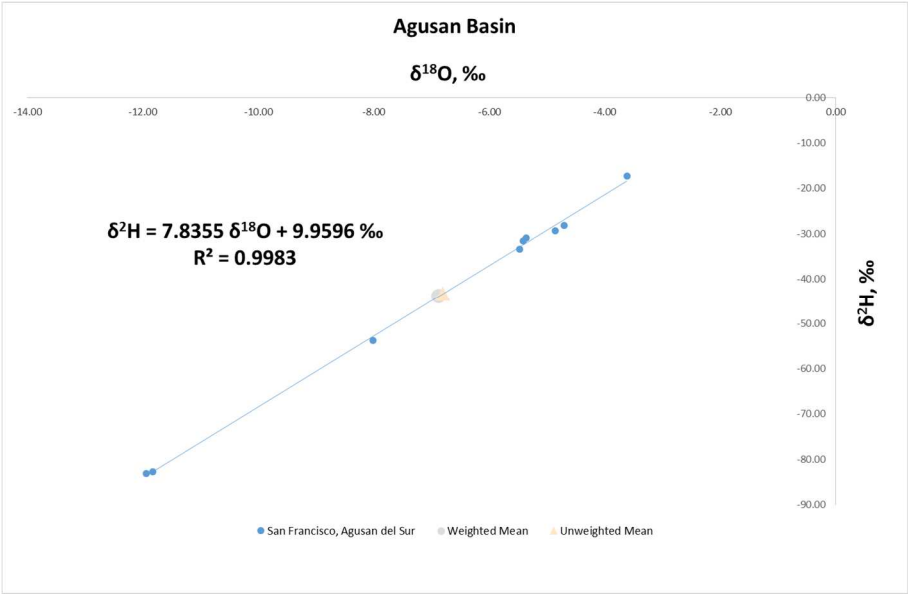
CASTRO, J.,
National Water Resources Board, NIA Building, EDSA, Diliman, Quezon City, 1101

LARAÑO, L.
Mines and Geosciences Bureau, North Avenue, Diliman, Quezon City 1101

Abstract: Stable isotope abundance of hydrogen ($\delta^2\text{H}$) and oxygen ($\delta^{18}\text{O}$) in liquid water from different freshwater resources in the Water Resources Region X, Southern Philippines were used to gain insight about the hydrological processes in the area. Water Resources Region X is divided into Cagayan-Tagaloan Basin and Agusan Basin. Cagayan-Tagaloan Basin is subdivided into Bukidnon, Cagayan de Oro East and West and MisOr. Agusan Basin is subdivided into Agusan, Surigao and Dinagat. Data presented here were the results of the reconnaissance water sampling campaign from September 2012 to August 2013. Precipitation samples were collected between October 2012 to September 2013 from areas of Malaybalay City (646 masl) and Manolo Fortich (571 m.a.s.l.), Bukidnon and San Francisco, Agusan del Sur (223 masl) to establish the local meteoric water line (LMWL) and to identify the role of precipitation as an input in groundwater and river systems. Precipitation samples were found to have $\delta^{18}\text{O}$ values ranging between -3.62‰ to -11.94‰ and $\delta^2\text{H}$ values of -17.30‰ to -86.56‰. LMWL for Agusan Basin was determined to be $\delta^2\text{H} = 7.84 \delta^{18}\text{O} + 9.96 \text{‰}$ ($r^2 = 0.998$) using rain collected from San Francisco, Agusan del Sur. LMWL for Cagayan-Tagaloan Basin was determined to be $\delta^2\text{H} = 8.11 \delta^{18}\text{O} + 10.19 \text{‰}$ ($r^2 = 0.985$) using rain collected from Malaybalay City and Manolo Fortich, Bukidnon. The weighted annual average for $\delta^{18}\text{O}$ was determined to be -6.87‰ and -9.00‰ for Agusan and Cagayan-Tagaloan Basins, respectively. Weighted average for Cagayan-Tagaloan Basins was compared with the long-term weighted average of the nearest GNIP station of almost the

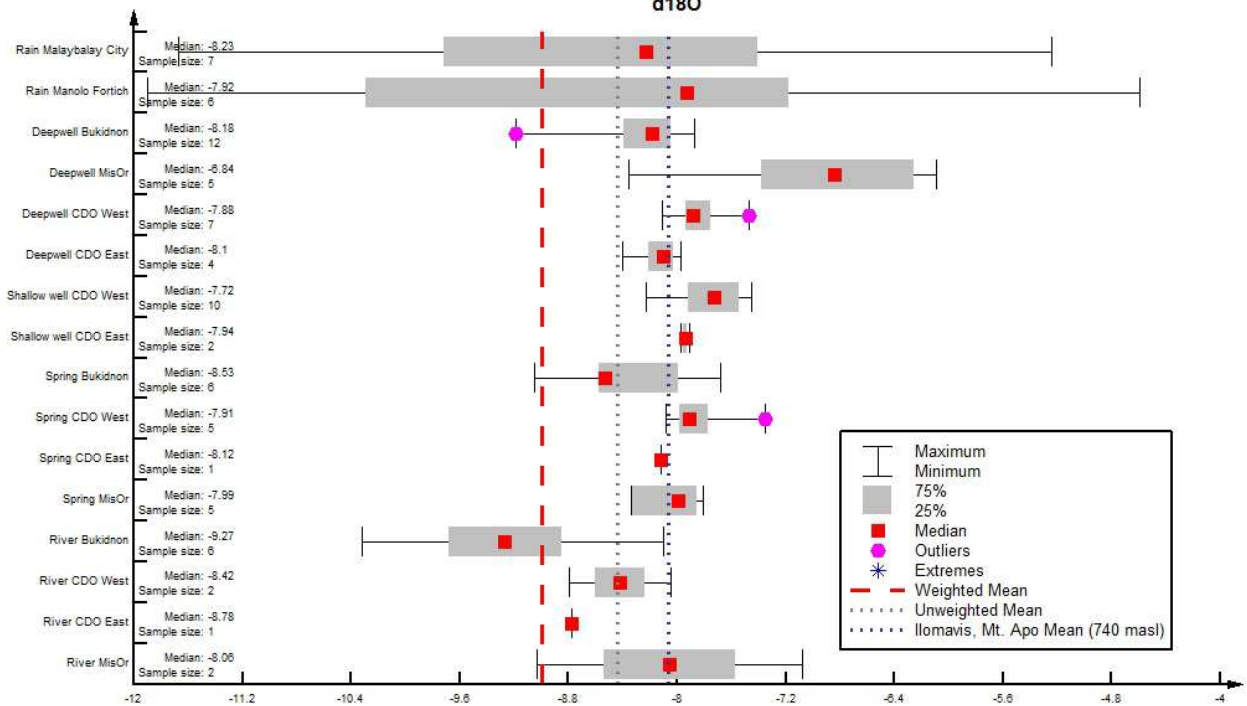
same elevation at Ilomavis, Mt. Apo, Davao City (740 masl) which is -8.06‰ for $\delta^{18}\text{O}$ and was adapted as the reference index. The estimated average (-6.87‰ and -8.06‰ for $\delta^{18}\text{O}$) was used as an index to demarcate possible interconnection between different freshwater resources such as rivers, springs, shallow and deep groundwater based on corresponding $\delta^{18}\text{O}$ values obtained for each water type. The $\delta^{18}\text{O}$ abundance of waters from rivers in Cagayan-Tagaloan Basin collected at high elevation areas, such as in Bukidnon, which are tributaries to the Tagaloan river, showed more depleted values (data range: -8.1‰ to -10.32‰; mean: -9.25‰ and s.d.: 0.78‰; median: -9.27‰; n=6) as compared to the estimated index. The difference may be attributed to the depletion of oxygen-18 containing water during downpour caused by altitude effects. Groundwater driven from deepwells and springs from these areas have more depleted average $\delta^{18}\text{O}$ values (-8.30‰ (s.d.= 0.4‰; n=12) and -8.37 (s.d.=0.52; n=6) for deepwells and springs, respectively) as compared to index value which may indicate local recharge process. On the other hand, $\delta^{18}\text{O}$ values for both deepwell and spring groundwater obtained at lower elevation areas particularly in Cagayan de Oro, showed values ranging from -7.47‰ to -8.4‰ and exhibited more enriched mean $\delta^{18}\text{O}$ values (7.95‰ (s.d.:0.25; n=11) and -7.87 ‰ (s.d.: 0.28; n=6) for deepwells and springs, respectively) as compared to the estimated index of -8.06‰ which may be recharged at lower elevations. The $\delta^{18}\text{O}$ abundance of waters from rivers in Agusan Basin (i.e. Agusan and Surigao) showed more enriched values (data range: -4.4‰ to -6.28‰; mean: -5.66‰ and s.d.: 0.45‰; median: -5.78‰; n=18) as compared to the estimated index which may indicate evaporative enrichment. On the other hand, $\delta^{18}\text{O}$ abundance for both deepwell and spring groundwater generally exhibited more enriched mean $\delta^{18}\text{O}$ values (6.17‰ (s.d.:0.50; n=7) and -5.73‰ (s.d.= 0.57; n=27) for deep wells and springs, respectively) as compared to the isotopic index of -6.87‰ which may be recharged at lower elevations. Isotopic data for freshwater resources in Water Resources Region X is reported for the first time.





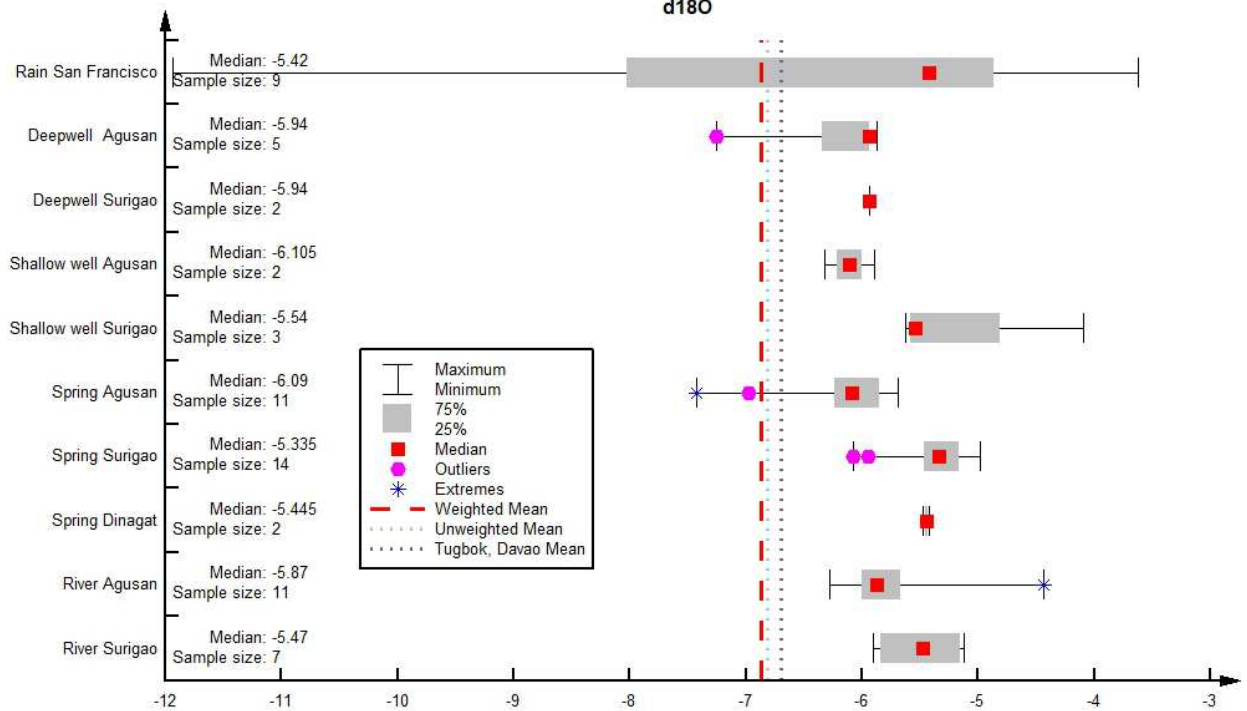
Water Resources Region X

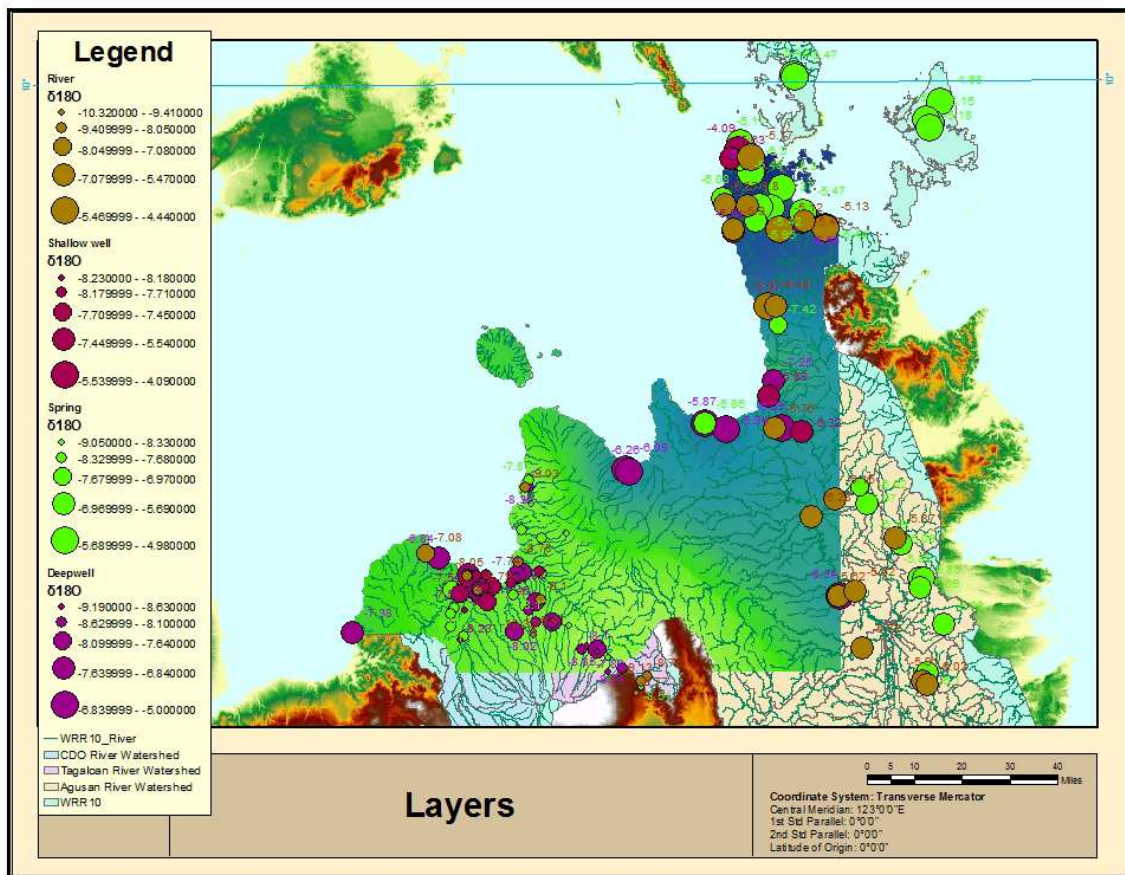
Cagayan-Tagaloan Basin
d18O



Water Resources Region X

Agusan Basin
d18O





ID: 117

FLOW FORMATION IN STREAMS AT HIGH LATITUDES: DO ISOTOPES AND CATCHMENT PROPERTIES REVEAL PATTERNS OF GROUNDWATER DOMINANCE?

H. MARTTILA

Water Resources and Environmental Engineering Research Group, P.O. Box 4300, FI-90014 University of Oulu, Finland
E-mail address: hannu.marttila@oulu.fi

P. ROSSI

Water Resources and Environmental Engineering Research Group, P.O. Box 4300, FI-90014 University of Oulu, Finland

S. PUHAKKA

University of Oulu, Department of Geography, P.O. Box 3000, FI-90014 Oulu, Finland.

K. LEINONEN

Finnish Environment Institute, Natural Environment Centre, Paavo Havaksen tie 3, P.O. Box 413, FI-90014 University of Oulu.

K. TOLONEN

Finnish Environment Institute, Natural Environment Centre, Biodiversity, Paavo Havaksen tie 3, P.O. Box 413, FI-90014 University of Oulu.

J. ERKINARO

Finnish Game and Fisheries Research Institute, Paavo Havaksen tie 3, P.O. Box 413, FI-90014 University of Oulu.

J. HJORT

University of Oulu, Department of Geography, P.O. Box 3000, FI-90014 Oulu, Finland.

J. HEINO

Finnish Environment Institute, Natural Environment Centre, Biodiversity, Paavo Havaksen tie 3, P.O. Box 413, FI-90014 University of Oulu.

Abstract: In this study, we describe flow formation and dominant flow patterns (DFP) in subarctic streams aiming to integrate hydrological and ecological connectivity. We specifically examined interactions and feedbacks between hydrology and catchment topographical and landscape characteristics using natural tracers, stable isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$) and silica (SiO_2). Our study is based on data collected from 51 streams in the River Tenojoki basin in Northern Finland and Norway. The study sites were sampled for water chemistry and tracers, such as SiO_2 , in 2013 and 2014. These tracers were used as proxies for DFP in each study catchment. Our preliminary results look promising, and the relative differences of DFP distributions (*e.g.* groundwater proportion) between the study catchments can be estimated reliably. The variation in DFP is linked to topographical settings and land cover information, aiming to provide a useful proxy variable explaining variation in ecological communities.

Our approach to separate catchments by DFP offers a cost-effective method for tracing DFP in non-gauged stations in the majority of stream at high latitudes.

1. INTRODUCTION

There is an urgent need to understand how aquatic ecosystems are connected with their catchments and how they are affected by variability in hydrological controls at high latitudes. In particular, there is a need to develop methods to predict hydrological controls in remote locations and non-gauged catchments. Changes predicted by future climatic scenarios for high latitudes include increasing precipitation and temperatures, which may lead to changes in runoff and temperature regimes in streams. We hypothesised that, in the face of climate change, streams with a high proportion of groundwater (GW) tolerate variation and regime shifts and provide a less sensitive habitat against climatic variability, especially in high latitudes. Such groundwater-fed streams may also provide stable conditions for many cold-water species, such as Arctic char.

2. METHODS

A total of 51 headwater catchments located in the River Tenojoki basin were sampled for water chemistry and tracers (e.g. SiO_2) in 2013 and 2014. For isotope analysis, daily precipitation and snow profile samples were taken from the Kevo research station. Additionally, some natural springs were sampled to obtain “groundwater signal” and lakes were sampled for “evaporation signal”. For the DFP analysis, end-member mixing (EMM, *sensu* hydrograph separation) was used to determine DFPs in our study catchments. We acknowledge the fact that estimation of DFPs is sensitive and variable when the observation period is relatively short and the number of samples is small. Therefore, the purpose of our study was to observe relative differences between the study catchments rather than estimate absolute DFPs at individual the study area. Our results are also linked to topographical settings and land cover features, aiming to find a useful proxy variable for ecological studies. Various topographical indices were calculated and compared, such as topographical wetness index (TWI), SIDE-index, aspect and HAND-index together with geological analysis.

3. RESULTS

Our preliminary results are promising. In particular, they show that the relative differences of DFP distributions (e.g. groundwater proportion) between study catchments can be estimated reliably. However, we have not yet got final results and, therefore, those results will be presented at symposium presentation.

4. CONCLUSIONS

The approach integrating tracers and catchment characteristic for DFP separation offers a cost-effective method for tracing DFP in non-gauged stations, such as the majority of high-latitude catchments.

THE RESIDENCE TIME OF WATER IN RIVERS: IMPLICATIONS ON WATER TRANSFER ROUTES

P. NIINIKOSKI

Department of Geosciences and Geography, University of Helsinki, Finland

E-mail address: paula.niinikoski@helsinki.fi

N. M. HENDRIKSSON

Geological Survey of Finland, GTK, Espoo, Finland

J. A. KARHU

Department of Geosciences and Geography, University of Helsinki

Abstract: We studied the isotopic composition of oxygen and hydrogen in two rivers, and compared the results to local precipitation by fitting sinusoidal functions on the oxygen isotope data and looking at the phase shift and amplitude damping to find out the residence times of the river waters and the routes the water travels before entering the river channels. The Kokemäenjoki River is lake dominated whereas the Vantaanjoki River has been reported having a substantial groundwater component. Spring flooding is more evident in the Vantaanjoki River making up most of its annual discharge and in this study it was found out that the duration of snow cover dictates the mean residence time of the water in the Vantaanjoki River, not the groundwater component. In the case of the Kokemäenjoki River lake storage raises the mean residence time.

1. INTRODUCTION

Determining the residence time of water in catchments can help in predicting the behavior and lifetime of possible contaminants in the catchment. It has also been suggested to be an important factor in controlling nutrient budgets [1]. The residence time is determined by the routes water travels before entering the river channel and in part also by the depth of the channel. Lake storage can extend the residence time of water to a year [2-3], whereas river waters with a significant groundwater component can be expected to have longer residence times, up to several hundreds of years.

In this study, we used the stable isotope compositions of hydrogen and oxygen in water, and their annual fluctuations to determine the residence time of water in two different rivers in southern and southwestern Finland, the Kokemäenjoki River and the Vantaanjoki River. The residence time, and other isotopic evidence was used to get information about the storage of water in the catchment of the two rivers.

The Kokemäenjoki River is located in southwestern Finland, and it has the mean discharge of 180 m³/s. It is located in a mostly forested and agricultural area with many lakes. The Vantaanjoki River is located in the most densely populated area in southern Finland. It is considerably smaller than the Kokemäenjoki River with a mean discharge of only 16 m³/s. The catchment contains mostly agricultural and urban areas with several facilities releasing purified waste water into the river. Interaction with groundwater has been observed previously, but its extent remains to be determined [4].

Snowmelt during the spring causes a considerable flooding event in both rivers. In the Kokemäenjoki River the period of higher than average discharge lasts for two to three months, in the Vantaanjoki River only for two weeks. The proportional rise in the discharge is much larger in the Vantaanjoki River, in which the flow of water 100-fold compared to the winter discharge, whereas in the Kokemäenjoki River, the discharge is only doubled or tripled during the spring flood.

2. METHODS

Monthly precipitation was collected from Espoo, southern Finland. The Kokemäenjoki River was sampled from November 2000 to February 2012 and the Vantaanjoki River from February 2010 to October 2011. From the Kokemäenjoki River the samples were collected at one site, 50 km from the mouth of the river. From the Vantaanjoki River monthly samples were collected from the mouth of the river, but, in addition to that, the length of the river was sampled at 14 different locations four times during the year. In addition, some of its main tributaries were sampled.

3. RESULTS

Isotopic time series from precipitation and river water show cyclical annual variations. Sinusoidal curves were fitted onto the time series using least squares methods (Fig. 1). The damping of the amplitudes of the curves for the river waters in comparison to that for the precipitation gives a method to estimate the mean residence time (MRT) of river water using the equation:

$$\text{MRT} = \frac{1}{2} \pi (1-C)^{1/2} / C ,$$

where C is the amplitude damping given as $C=B/A$, A is the amplitude for the precipitation and B that for the river water. MRT is given in months [5].

The amplitudes of the sine curves were 3.24‰ for the precipitation, 0.36‰ for the Kokemäenjoki and 1.50‰ for the Vantaanjoki River. This gave a mean residence time of 2.4 months for the Vantaanjoki River and 13.3 months for the Kokemäenjoki River.

The mean annual $\delta^{18}\text{O}_{\text{VSMOW}}$ value for rainfall in southern Finland varied from -12 to -11‰. The annual mean $\delta^{18}\text{O}$ value of water was -12‰ in the River Vantaanjoki and -9.5‰ in the River Kokemäenjoki. Considering also hydrogen isotope ratios, it can be inferred that the water in the Kokemäenjoki River is more evaporated in comparison to water in the Vantaanjoki River. Evaporation effects are also evident in the deuterium excess values for the rivers, which are 7.4‰ for the Vantaanjoki River, 4.9‰ for the Kokemäenjoki River and 10.8‰ for the precipitation.

The profile of the Vantaanjoki River (Fig. 2) indicates three distinct isotopic trends along the flow path. Stage I is a fall in the $\delta^{18}\text{O}$ values from the evaporatively enriched isotope values of a headwater pond. This shift may be addressed to discharge of surface and groundwater into the river. In the transition from Stage II to Stage III, a tributary adds an ^{18}O -enriched, evaporated water component into the river channel. Water in these rivers can be regarded as a three component mixture of evaporated lake water, base flow from groundwaters and surface flow. In sub-freezing temperatures during the winter, any surface flow into the river channel is prevented. Under these conditions, isotopic composition of the water can be modelled as a two component mixture of base flow and an evaporated lake water component. In Stage II, about 70% of water seems to have been derived from base flow. During spring flooding, the

mass balance is completely different. The discharge has raised 100 fold, and the isotopic composition of the river water does not differ from the average isotope value of the snow cover. Under these conditions, surface flow dominates the system and the proportion of base flow is insignificant.

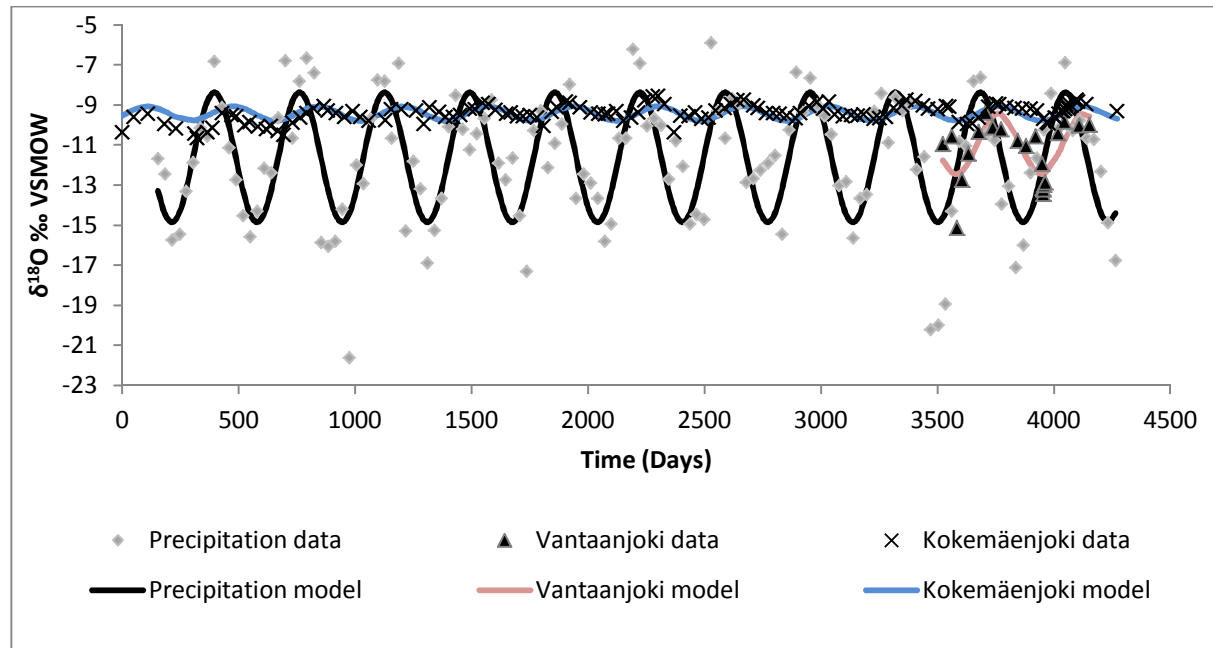


Figure 1. The $\delta^{18}O_{VSMOW}$ values of rainfall and rivers Kokemäenjoki and Vantaanjoki and the model curves fitted to the data.

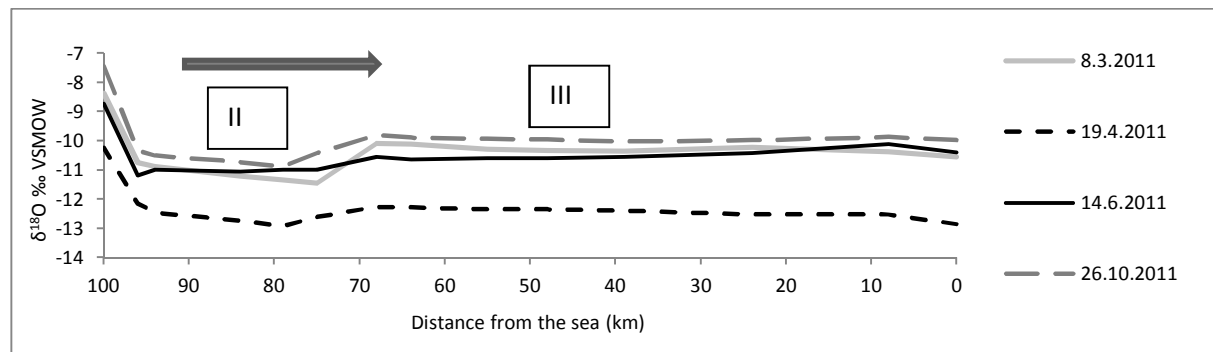


Figure 2. The $\delta^{18}O_{VSMOW}$ value profiles from the Vantaanjoki River in the winter, spring, summer and autumn in 2011. The arrow indicates the direction of flow.

4. CONCLUSIONS

The stronger enrichment in 2H and ^{18}O in water from the Kokemäenjoki River in comparison to the Vantaanjoki River can be addressed to lake storage in the catchment of the river. Lake storage results in a relatively long residence time of river water. A moderate enrichment in 2H and ^{18}O in water in the Vantaanjoki River appears to be related to water being stored in groundwater aquifers. Isotope mass balance calculations show that there is indeed a significant groundwater component in the Vantaanjoki River. The comparatively short mean residence time of the river is explained by the spring flooding event constituting 70% of its annual recharge.

REFERENCES

- [1] BOYNTON, W. R., Garber, J. H., Summers, R. and Kemp, W. M., Inputs, transformations, and transport of nitrogen and phosphorus in Chesapeake Bay and selected tributaries, *Estuaries* 18 (1995) 285-314 pp.
- [2] RUEDA, F., MORENO-OSTOS, E. ARMENGOL, J., The residence time of river water in reservoirs, *Ecological Modelling* 191 (2006) 260-274 pp.
- [3] SHEN, J., WANG, H. V., Determining the age of water and long-term transport timescale of the Chesapeake Bay, *Estuarine, Coastal and Shelf Science* 74 (2007) 585-598 pp.
- [4] KORKKA-NIEMI, K., KIVIMÄKI, A-L., LAHTI, K., NYGÅRD, M., RAUTIO, A., SALONEN, V-P. PELLIKKA, P., Observations on groundwater-surface water interactions at River Vantaa, Finland, *Management of Environmental Quality: An International Journal*, Vol. 23 Iss: 2 (2012) 222-231 pp.
- [5] BURGMAN, J. O., CALLES, B. WESTMAN, F., Conclusions from a ten year study of oxygen-18 in precipitation and runoff in Sweden, *Isotope Techniques in Water Resources Development*, IAEA-SM-299/107 (1987) 579-590 pp.

ID: 125

REVIEW OF STABLE ISOTOPE STUDIES OF WATER DONE IN FINLAND

R. ESKELINEN

Thule Institute, P.O. Box 7300, FIN-90014 OULUN YLIOPISTO, Finland

E-mail address: riku.eskelinen@oulu.fi

A-K. RONKANEN

Water Resources and Environmental Engineering Research Group, University of Oulu, P.O. Box 4300, FIN-90014 OULUN YLIOPISTO, Finland

P. ROSSI

Water Resources and Environmental Engineering Research Group, University of Oulu, P.O. Box 4300, FIN-90014 OULUN YLIOPISTO, Finland

E. ISOKANGAS

Water Resources and Environmental Engineering Research Group, University of Oulu, P.O. Box 4300, FIN-90014 OULUN YLIOPISTO, Finland

H. MARTTILA

Water Resources and Environmental Engineering Research Group, University of Oulu, P.O. Box 4300, FIN-90014 OULUN YLIOPISTO, Finland

B KLØVE

Water Resources and Environmental Engineering Research Group, University of Oulu, P.O. Box 4300, FIN-90014 OULUN YLIOPISTO, Finland

Abstract: Stable isotopes of water are a valuable tool for studying the water cycle. In our opinion the full potential of the stable isotopes of water have not been fully realized in Finland as there has been a lack of equipment and awareness how the isotopes can be used to generate new knowledge of the processes related to the water cycle. In this study we want to map how and where the stable isotopes of water have been used in Finland and form a database of the studies done so far in order to make the methods more known and available for future research(ers).

1. INTRODUCTION

The stable isotopes provide a valuable tool for researchers to study the water cycle. The purpose of this paper is to review and make metadata databank from stable isotope analysis conducted in Finland. The use of stable isotopes of water in Finland begun about 30 years ago, through a need to search for a safe location to store nuclear waste within the bedrock [1]. For this purpose samples for ^{18}O , ^2H and ^3H were taken from deep boreholes across Finland. The results helped decipher the age of groundwater at a certain level of the boreholes, which further on made it possible to give trustworthy statements how likely threat the stored nuclear waste would pose for the population.

At that time, the amount of ^{18}O and ^2H isotopes were analyzed with conventional mass spectrometers which were expensive and rare, therefore the number of samples in studies

were low. Lately new techniques in spectroscopy have succeeded in bringing the analyzer costs down and helped to popularize the isotope analysis as a standard tool in hydrology studies. However their wider use in Finland has been dragging due to lack of analyzers and the awareness of what can be studied and archived with the water isotopes.

2. METHDOS

We reviewed the published and unpublished literature about stable isotope studies done in Finland and gathered the essential sampling information to a database. So far the database contains location, coordinates, type of water sampled, starting and end time of sampling, sampling frequency and sampling quantity of approximately 11000 samples. Our goal is to bring the created database publicly available when completed.

3. RESULTS

The results of the first larger campaign for defining the isotopic composition of Finnish waters was published by Kortelainen and Karhu [2]. They monitored groundwater wells from 19 different places for six years and sampled 953 wells scattered around Finland. In addition precipitation was sampled monthly for two years. As a conclusions of the study a national meteoric water line for Finland was defined from the groundwater data as $\delta D = 8.5 \delta^{18}O + 16.55$ and $\delta^{18}O$ and the δ values were found to decrease towards the northern Finland parallel with the mean annual surface temperature. Recent and on-going studies have added detail by forming regional meteoric waterlines, which help the researchers to improve their estimates of local water cycle. In recent years at University of Oulu, the isotopes have been used in various ways for example taking spatially distributed samples across wetlands to define which the active or stagnant flow zones are[3]or for quantifying groundwater surface water- interactions[4] On-going studies also include stable isotope of water to identify groundwater dependent water bodies and groundwater recharge/discharge areas. Also continuous sampling of precipitation has been started to get knowledge about annual variation of $\delta^{18}O$ and δ^2H in precipitation. Results of data collection done up to now are plotted in Figure 1, which shows the locations of isotope studies done in Finland found from peer reviewed journals and also the known study sites from which the data has not yet been published.

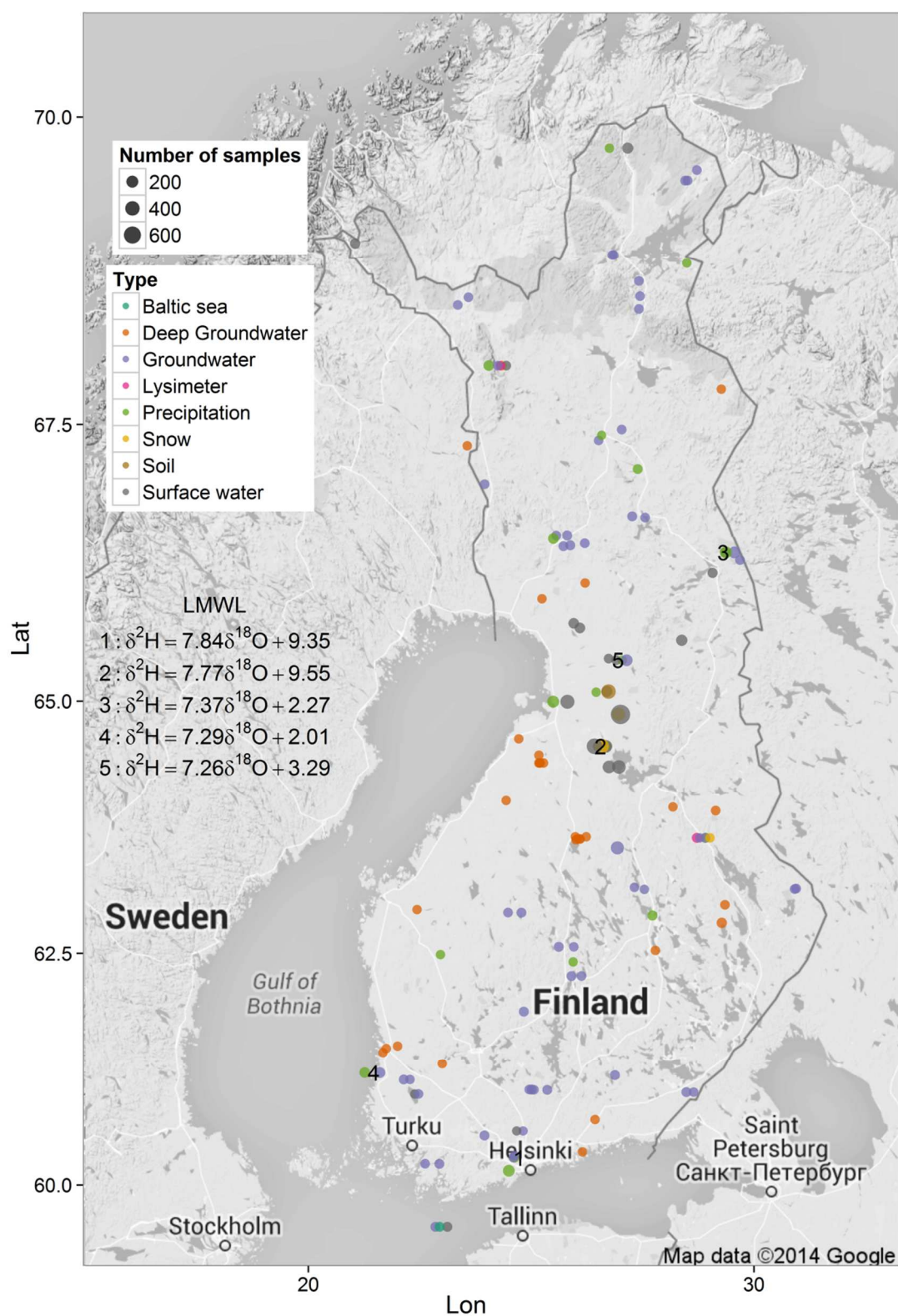


Figure 1. Plotted locations isotope studies done in Finland and estimate of their sample sizes. Sample numbers represent a total number of ^{18}O , ^2H and ^3H analysis. Figure contains data from unpublished studies and following references [1 - 11].

REFERENCES

- [1] BLOMQVIST, R., LAHTINEN, R., LAHERMO, P., HAKKARAINEN, V. & HALONEN, S. *Kalliopohjavesien geokemia: tutkimustulokset syvistä kairareitistä vuonna 1986*. 87+21 (Geological Survey of Finland, 1986).
- [2] KORTELAINE, N. & KARHU, J. Regional and seasonal trends in the oxygen and hydrogen isotope ratios of Finnish groundwaters: a key for mean annual precipitation. *Journal of Hydrology* **285**, 143157 (2004).
- [3] RONKANEN, A.-K. & KLØVE, B. Hydraulics and flow modelling of water treatment wetlands constructed on peatlands in Northern Finland. *Water research* **42**, 3826–36 (2008).
- [4] ISOKANGAS, E., ROZANSKI, K., ROSSI, P., RONKANEN, A.-K. & KLØVE, B. Quantifying groundwater dependence of a sub-polar lake cluster in Finland using an isotope mass balance approach. *Hydrology and Earth System Sciences Discussions* **11**, 9183–9217 (2014).
- [5] KIETÄVÄINEN, R. *et al.* Characterisation and isotopic evolution of saline waters of the Deep Drill Hole, Finland – Implications for water origin and deep terrestrial biosphere. *Applied Geochemistry* **32**, 3751 (2013).
- [6] LUOMA, S., OKKONEN, J., KORKKA-NIEMI, K., HENDRIKSSON, N. & BACKMAN, B. Confronting vicinity of the surface water and sea shore in a shallow glaciogenic aquifer in southern Finland. *Hydrology and Earth System Sciences Discussions* **11**, 8651–8695 (2014).
- [7] LAMMINEN, S. *Kiven ja veden välinen vuorovaikutus erilaisissa kivilajiympäristöissä*. 60 + 3 (Geologic Survey of Finland, 1995).
- [8] KORKKA-NIEMI, K., LAHTI, A.-L., NYGÅRD, M., RAUTIO, A. & PELLIKKA, V.-P. Observations on groundwater-surface water interactions at River Vantaa, Finland. *Management of Environmental Quality: An International Journal* **23**, 222231 (2012).
- [9] KORTELAINE, N. Isotopic composition of oxygen and hydrogen in Finnish groundwaters: Tables of groundwater monitoring in. (2007). at <http://arkisto.gsf.fi/p32/p32_4_2007_49.pdf>
- [10] LEPISTÖ, A. Runoff generation processes in peaty forest catchments - possibilities for regionalization. Tracer Technologies for Hydrological Systems (Proceedings of a Boulder symposium) IAHS Publ. no. 229, 1995.
- [11] IAEA/WMO (2014). Global Network of Isotopes in Precipitation. The GNIP Database. Accessible at: <http://www.iaea.org/water>

ID: 129

USING STABLE WATER ISOTOPES IN CAPTURE ZONE CHARACTERIZATION OF BOREAL SPRINGS

P. M. ROSSI, E. ISOKANGAS, H. MARTTILA, P. ALA-AHO, B. KLØVE

Water Resources and Environmental Engineering Research Group,

University of Oulu, P.O. Box 4300, 90014 University of Oulu, Finland

E-mail address: pekka.rossi@oulu.fi.

Abstract: Springs are unique and threatened groundwater dependent ecosystems. There is an urgent need for understanding the dynamics of spring capture zone and how the capture zone defines the spring ecosystem or if land use close to a spring might threaten the ecosystem. From this perspective we have collected stable water isotopes in various crystalline bedrock or glacio-fluvial soil formation springs in Northern Finland. The goal was to define what stable water isotopes can reveal from the spring capture zone. Our study shows that stable water isotopes of spring samples could be used to estimate groundwater residence time which largely determines the chemical characteristics of spring water. Isotopes also reveal if a spring is recharged by surface water.

1. INTRODUCTION

Springs are unique groundwater dependent ecosystems (GDEs) from ecological point of view [1]: their flora and fauna are highly specialized in boreal region, because of the continuous cold groundwater flux to the spring. Management of these springs should be emphasized and new indicators should be studied, which could e.g. help to classify the springs or to define the source of groundwater to the springs. On this perspective, we studied how stable water isotopes could be used as a part of the management of boreal springs in Finland.

2. METHDOS

From selected boreal sites in Northern Finland, spring water, groundwater and surface waters were sampled for chemical composition and stable isotopes of water. Springs were situated on crystalline bedrock (Fig. 1) or glacio-fluvial soil formations as esker or moraine. Samples were taken one or two times during summer period to define differences between start and end of the annual evaporation period. Isotope samples were analyzed using CRDS spectroscopy with Picarro L2120-i analyzer and isotope values were notified relative to VSMOW standard using δ notation. Statistical methods as Ward's hierarchical clustering, principal component analysis and random forest model were used to define how different spring could grouped and how much information the stable water isotope data can explain the differences between springs.

3. RESULTS

Based on the isotopic fingerprint, spring waters were mostly homogenous, but some of the spring samples were more enriched due to evaporation. These springs could be separated to have significant amount of surface water. Based on statistical analyses the stable isotopes of water have a good correlation to the chemical quality of spring water. This was probably due to the size of the capture zone of the springs. Smaller capture zone of a spring would mean a shorter residence time, which means less time for different chemical components (e.g. anions or cations) to dissolve into water. Even though the elevation differences within studied areas

were only hundreds of meters, which is not enough for elevation signal in the rain water, the temporal difference of groundwater recharge was noted and explains why stable water isotopes have a correlation with capture zone size. The smaller capture zone water could be recharged within few months and e.g. the summer rain signal could be distinguished. The springs with average groundwater signal on the other hand indicate larger capture zone where isotope signal of different times of year have time to dilute.



Figure 1. A studied boreal spring in Oulanka National Park, Finland (picture by Jussi Jyväsjärvi).

4. CONCLUSIONS

Given that water chemistry is a pivotal factor in spring biota, successful management and conservation of springs should take water chemistry into account. If the local conditions surrounding the studied springs have been initially studied, the isotopic signature of spring water can be a useful proxy for spring water chemistry. As the resources for spring management can be limited, the stable water isotopes can be nowadays a cheap indicator that can be collected from numerous sites.

REFERENCES

- [1] KLØVE, B., ALA-AHO, P., BERTRAND, G., BOUKALOVA, Z., ERTÜRK, A., GOLDSCHIEDER, N., ET AL., Groundwater dependent ecosystems. Part I: Hydroecological status and trends, *Environ.Sci.& Policy* **14** (2011) 770-781.

ID: 133

CHARACTERIZATION OF GROUNDWATER-SURFACE WATER MIXING PROCESSES USING ENVIRONMENTAL ISOTOPES AND GEOCHEMICAL MODELS

F. BECHER QUINODOZ, M. BLARASIN

CONICET, Dpto. Geología, Universidad Nacional de Rio Cuarto (UNRC)

Ruta 36 km 602 Rio Cuarto (Córdoba) Argentina

E-mail address: mblarasin@exa.unrc.edu.ar

H. PANARELLO

Instituto de Geocronología y Geología Isotópica. (INGEIS-CONICET-UBA)

Abstract: The aim of this work is to characterize the hydraulic/geochemical relationships between surface water and groundwater in the Quinto river basin (Cordoba province). The aquifer-river hydraulic relationships were effluent/influent, varying in space basically as a result of geomorphology. $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotopic values show that surface water and groundwater samples coincide in a mixing line, presenting different evaporation degrees. The isotopic results and geochemical numerical model show that in summer and winter, the water quality of Quinto River may be explained by mixing processes between surface water, greatly influenced by Chañares dam, and local, intermediate and/or regional groundwater flow. In summer, the surface water component (72%) predominates while in winter groundwater prevails (82%).

1. INTRODUCTION

Most surface water systems interact with groundwater, making it necessary to elucidate the relationships for the appropriate management of water resources. The aim of this work is to perform dynamic and geochemical (general/isotopic) characterization of the interrelationships between surface water and groundwater to establish a reliable hydrogeological model as a base for environmental planning.

2. METHODS

Climatic, geological, hydrological and land use features were analyzed and interpreted after the field work and sampling surveys in which 30 samples of surface water and groundwater were collected. Routine chemical analyses were made at the National University of Rio Cuarto (UNRC), also adding $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotopes analyses at the Instituto de Geocronología y Geología Isotópica (INGEIS). The numerical geochemical models were performed using the PHREEQC software [2].

3. RESULTS

The studied area (2,300 km²) is located in the South of Córdoba province (Argentina, Figure 1). The sandy plain of southern Córdoba is a palimpsest relief type resulting from the juxtaposition of a wind system (Pampean Sand Sea) with the Quinto river fluvial system. It has a flat to gently undulated topography, where aggradation processes dominate.

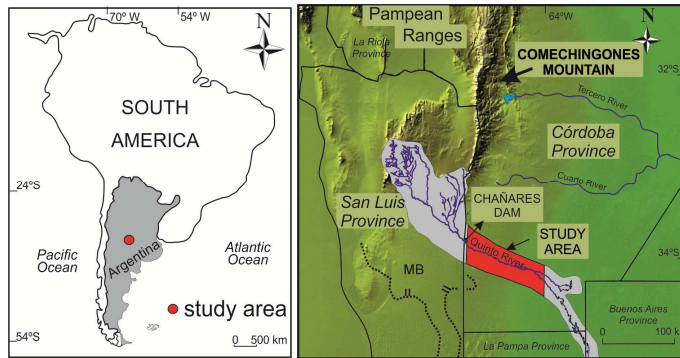


Figure 1. Study area

Longitudinal and parabolic dune systems of different origin and age distinguish the area. The dunes overlap the Quinto River alluvial palaeofan. The area is crossed by the mid-lower reach of the present Quinto River course whose headwaters are located in San Luis province (towards the West) and regulated by dams upstream of the study area. The dry sub-humid climate is characterized by an annual rainfall of 607 mm from which 85% is concentrated in spring-summer.

The river has flow variations between summer ($25.0 \text{ m}^3/\text{s}$) and winter ($4.2 \text{ m}^3/\text{s}$) with an average water velocity of 0.8 m/s . Hydraulic relationships (Figure 2) are variable but in most reaches the river is a gaining watercourse as a result of aquifer contribution. Surface water salinity increases following the flow direction (1,680 up to 1,960 in summer, and 2,289 up to 3,150 mg/L in winter). The geochemical surface water in the studied area is always and everywhere sodium sulfate type.

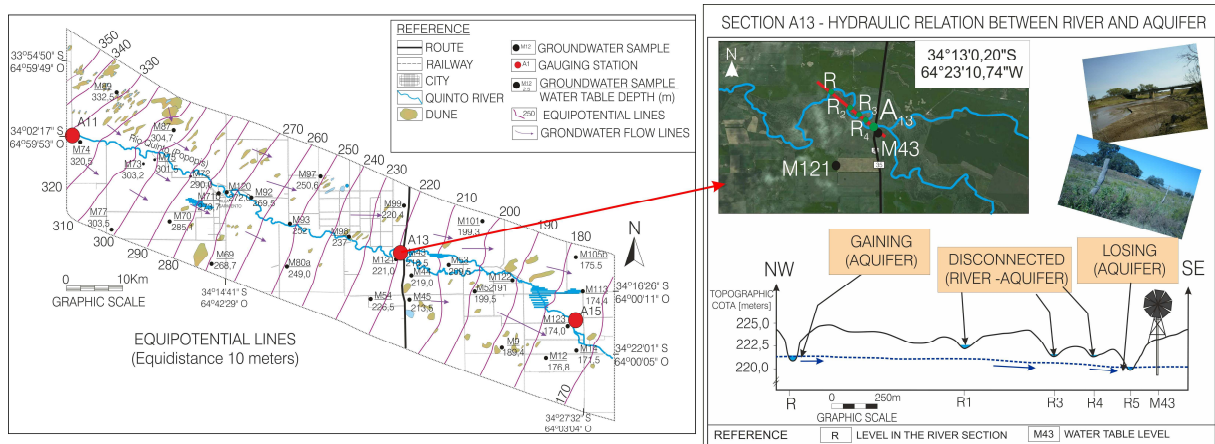


Figure 2. Section A13. Unconfined aquifer - Quinto river hydraulic relations.

The unconfined aquifer is mainly composed of Quaternary sediments, dominantly of aeolian origin (with different carbonate cementation grades), and subordinately of fluvial materials. Hydraulic conductivities are variable (1-10 m/d). The general groundwater flow direction is NW-SE (Figure 2) and groundwater flow velocities are low (0.04 up to 0.20 m/d). This unconfined aquifer exhibits a complex geochemical pattern. In fact, groundwater salinity ranges from 0.4 g/L (fresh), linked to recharge in dunes, up to 2.0-11.0 g/L (brackish to salty) associated with the rest of the aeolian plain, especially in the low hydrohalomorphic areas. In general, groundwater shows a geochemical evolution in the flow direction from fresh to salty water, changing also the geochemical type (sodium bicarbonate to sodium chloride).

Isotopic results ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) show a general enrichment in West-East direction, as a result of water flow after the recharge of surface water and groundwater bodies in the piedmont region (San Luis province, at the West area). The recharge comes from rains, isotopically depleted by continental and altitude effects, originated in a wet warm front from the Atlantic Ocean. (Figure 3A). Isotopic behavior shows that river samples, with different evaporation degrees, are aligned in a mixing line and are connected to those of the unconfined aquifer. Thus, the position of the samples indicates mixing river-aquifer processes. Using the “lever rule” (Figure 3B) and the extreme position obtained for Chañares dam sample (ARV8) and for the unconfined aquifer average value sample (M122), it was determined the mixture percentages of aquifer and dam contribution in the river water. This information confirms that at the entrance of Cordoba province, surface water dominates in summer (72%), while in winter, base flow from the aquifer predominates (82%) despite being a dam regulated river.

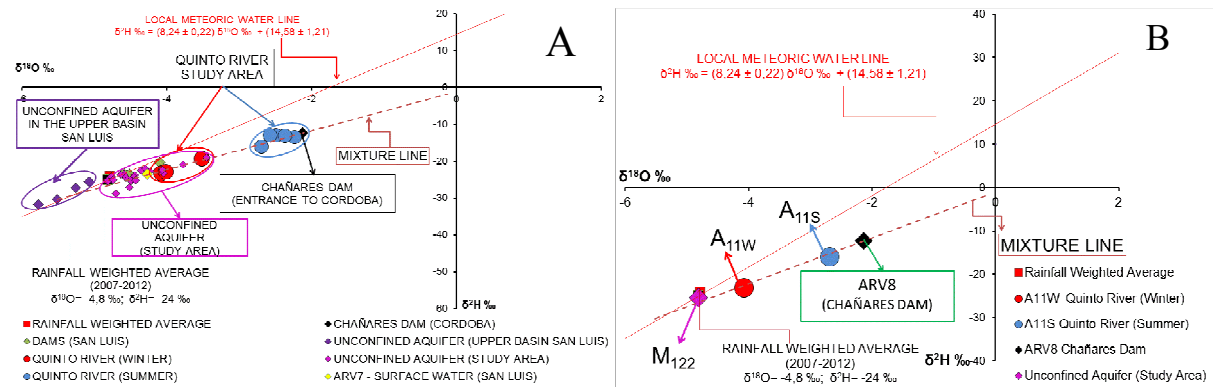


Figure 3. (A) $\delta^2\text{H}$ vs $\delta^{18}\text{O}$ for Quinto river and unconfined aquifer samples in the upper basin and in the study area. (B) $\delta^2\text{H}$ vs $\delta^{18}\text{O}$ for Quinto river water samples (A11) at the entrance of Cordoba province (summer and winter) and the relation with Chañares dam sample (ARV8) and groundwater sample (M122).

To validate this scenario, a numerical inverse geochemical model was made using PHREEQC 2.17 software [2]. The constraints were HCO_3^- , SO_4^{2-} , Cl^- , Na^+ , K^+ , Ca^{2+} , Mg^{2+} (Table 1) and the mineral phases were those identified in the river and aquifer sediments [1]. Isotopes values were considered. The hypothesis was that A₁₁ sample is the result of a mixture between ARV₇ (surface water that is flowing from the upper basin) ARV₈ (water from Chañares dam) y M_{15JD} (groundwater). Twenty one (21) models satisfy the restrictions assumed in the conceptual model. In Table 2 the model that better fits the summer season is presented. In this model, 75% is surface water and 25 % is groundwater. In the winter season, surface water contributes with 18 % and the aquifer with 82% [1].

Table 1. Chemical analysis of the samples used in the numerical modeling

SAMPLE	pH	EC μS/cm	TDS mg/L	CO ₃ ⁻² mg/L	CO ₃ H ⁻ mg/L	SO ₄ ⁻² mg/L	Cl ⁻ mg/L	Na ⁺ mg/L	K ⁺ mg/L	Ca ⁺² mg/L	Mg ⁺² mg/L
ARV _{7S} (IS)	7.9	2.240	1.568	0	293	713	251	404	15	107	25
ARV ₈ (IS)	8.2	3.100	2.170	0	325	832	337	556	18	92	57
M _{15JD} (IS)	8.2	6.300	4.410	0	440	1698	1057	1607	28	104	83
A _{11S} (FS)	8.7	2.400	1.680	12	278	643	243	450	16	84	32

4. CONCLUSIONS

These surface water-groundwater relationships show the control exerted by the relief, the lithology and the climate. The chemical composition of both hydrological systems is essentially the consequence of different water velocity in each water body. Mixing processes between surface water and local, intermediate or eventually regional groundwater result in the observed geochemical pattern.

Table 2. Results of numerical modeling carried out with PHREEQC (Model 7)

SAMPLE	Mixture fraction	NaX ₂ mol/L	CaX ₂ mol/L	MgX ₂ mol/L	CaSO ₄ ·2H ₂ O mol/L	ClNa mol/L
ARV _{7V} (IS)	0.61	2.07	-1.37	0.33	1.96	1.66
ARV ₈ (IS)	0.14	0.47	-0.32	0.07	0.45	0.38
M _{15JD} (IS)	0.25	0.85	-0.56	0.14	0.80	0.68

The chemical composition of surface water is homogeneous with freshwater from beginning to end of the study area, despite having traveled tens of kilometers and maintaining, in most sections, hydraulic connection with an aquifer that provides brackish to salty groundwater. Although the river flows through areas with different aquifer salinity and geochemical type, a preponderance of surface water in summer is evident. A larger surface water mass and the differences in water velocity between the two systems generate a scenario where solutes that come from the aquifer are diluted by hydrodynamic dispersion.

Isotopic data and numerical geochemical modeling indicate that in summer and winter, the water quality of Quinto River may be explained by mixing processes between surface water, greatly influenced by Chañares dam, and groundwater flow. In summer, the surface water component dominates (72 %) while in winter groundwater prevails (82%).

The findings in the studied basin show a typical case of natural and anthropic constraints, whose behavior does not recognize political boundaries. This would indicate the need for inter-jurisdictional studies.

REFERENCES

- [1]. BÉCHER QUINODÓZ F. Implicancias ambientales de las relaciones hidrodinámicas e hidroquímicas entre aguas superficiales y subterráneas en la planicie arenosa del Sur de Córdoba. Argentina. Ph. D. Thesis,. UNRC. (2014) 412 p. Unpublish.
- [2]. PARKHURST D. D. Y C. A. APPELO. User's Guide to PHREEQC (version 2). A computer program for ecuación, Batch-Reaction, one-dimensional transport, and inverse geochemical calculations. U.S. department of the Interior. U.S.G.S. Water-Resources Investigations Report 99-259. (1999) 326 p.

ID: 141

RADON AND GEOCHEMICAL PRELIMINARY MODEL TO ASSESS INTERACTIONS BETWEEN GROUNDWATER AND SURFACE WATER IN A PAMPEAN STREAM

M.BLARASIN

Dpto. Geología. Universidad Nacional de Rio Cuarto (UNRC)

Ruta 36 km 602 Rio Cuarto (Córdoba) Argentina

E-mail address: mblarasin@exa.unrc.edu.ar

H. PANARELLO, E. DUCOS

Instituto de Geocronología y Geología Isotópica. (INGEIS-CONICET-UBA).

F. BECHER QUINODOZ

CONICET-UNRC. Ruta 36 km 602 Rio Cuarto (Córdoba) Argentina

Abstract: The objective of this work is to characterize the hydraulic and geochemical relationships between surface water and groundwater using ^{222}Rn to validate the summer hydrological model in the Ají stream basin (Córdoba, Argentina). The aquifer-stream hydraulic relationships were effluent/influent, varying spatially as a result of geomorphology, climate and human actions. Isotopic values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ show that groundwater and stream samples lay in a mixing line. Geochemical numerical model and ^{222}Rn indicate a small contribution from the aquifer in the summer season (in the order of 2%).

1. INTRODUCTION

For the evaluation of surface water -groundwater interactions all methods have shown significant uncertainty, as usually happens when humans try to quantify nature. The objective of this research was to evaluate surface water and groundwater hydrodynamic and hydrochemical behavior and their relationships. The studied area (1,200 km², Figure 1), defined as a result of a water company requirement, is the medium-low reach of Ají stream basin, situated in the sandy plain of the South of Córdoba province (Argentina). The upper basin of this stream is located in the Comechingones Mountains (Córdoba Province). The area has a flat to gently undulated relief, with longitudinal and parabolic dune systems of different origin and age which are crossed by the Ají stream fluvial strip. Climate is subhumid, characterized by an annual rainfall of 750 mm, from which 85% is concentrated in spring-summer.

2. METHODS

Climatic, geological, hydrological and land use features were analyzed. Twenty five samples of surface and ground water were collected. Routine chemical analyses were made at National University of Rio Cuarto laboratory and ^2H and ^{18}O isotopes analyses at the Instituto de Geocronología y Geología Isotópica (INGEIS). Some samples were collected in the upper and middle basin to facilitate hydrological interpretations. The numerical geochemical models were performed using the PHREEQC software [3]. The activity of ^{222}Rn in surface water and groundwater was measured in situ in 7 samples through the RAD7 radon detector (DurrIDGE Co.) belonging to INGEIS.

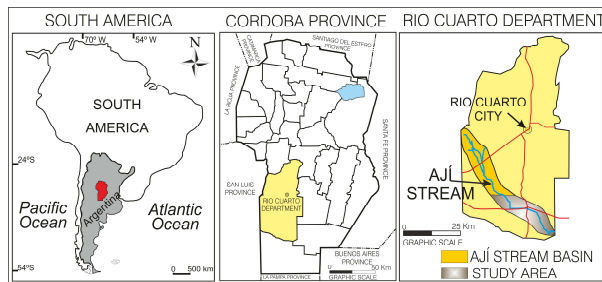


Figure 1. Study area.

3. RESULTS

The stream has flow variations between summer ($0.8 \text{ m}^3/\text{s}$) and winter ($0.46 \text{ m}^3/\text{s}$) with an average water velocity of 0.34 m/s . Hydraulic relationships (Figure 2) are variable but, in most reaches, the watercourse is a gaining stream as a result of aquifer contribution. Surface water salinity shows a notable homogeneity along the studied stream reach (848 mg/L to 987 mg/L in the flow direction) and along the year, with low salt increases in winter. The surface water is of sodium bicarbonate geochemical type (Figure 3A).

The unconfined aquifer exhibits a complex geochemical pattern, with variable salinity from 0.4 g/L (fresh water), linked to recharge in dunes, up to 11 g/L (salty water) in the hydrohalomorphic areas. Groundwater shows a normal geochemical evolution in the flow direction from fresh to salty water, changing also from sodium bicarbonate to sodium sulfate and, finally, to sodium chloride geochemical type (Figure 3A).

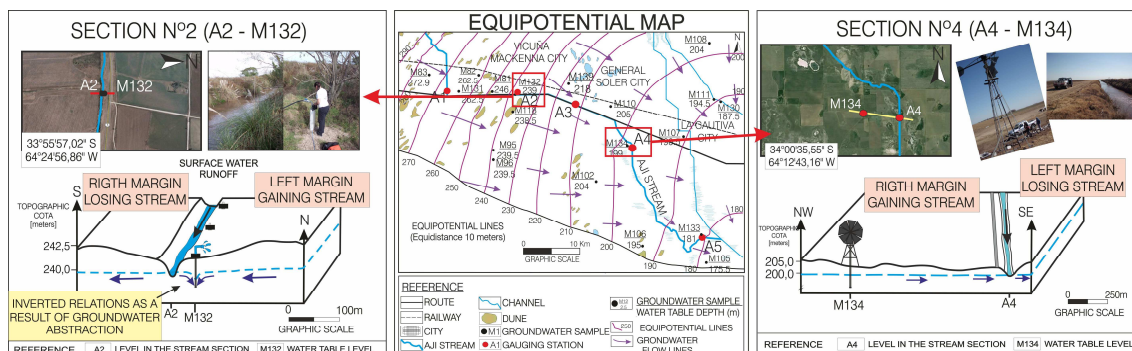


Figure 2. Hydraulic relation between stream and aquifer in sections A2 and A4.

The analyses of relationships shown that surface water exhibits marked homogeneity, with freshwater from beginning to end of the studied area, despite having traveled tens of kilometers and maintaining, in most sections, hydraulic connection with an aquifer that provides brackish to salty groundwater. The nitrate, a pollution indicator derived from cattle and fertilizers, was found in high values in groundwater, exceeding natural background. However, surface water shows low nitrate values (4.5 mg/L - 14.7 mg/L), as a result of hydrodynamic dispersion and the N use from macrophytes and algae.

Isotopic results ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) show a general enrichment in West-East direction, because the water that recharges the aquifer and surface water bodies in the piedmont area of the Comechingones Mountains (outside the study area) comes from depleted rains originated in a wet warm front from the Atlantic Ocean (continental and altitude effects) [1]. In Figure 3B it can be seen that all the samples from the stream and the aquifer lay in a mixing line, where

they show different evaporation degree. The most depleted are those surface water samples pertaining to the rainy season which are linked to the flows coming from the mountains.

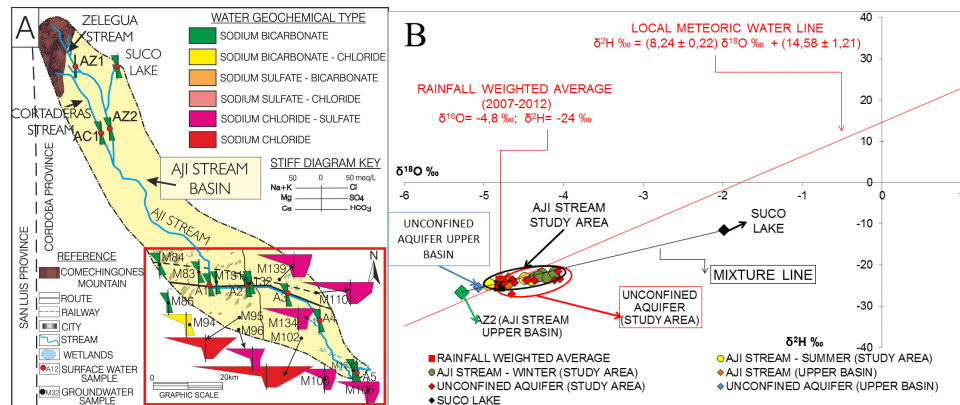


Figure 3: (A) Water geochemical type in stream and aquifer. (B) $\delta^2\text{H}$ vs $\delta^{18}\text{O}$ for Aji stream and unconfined aquifer samples

In some samples, the similarity between aquifer and stream isotopic features are closely linked to induced recharge from the stream freshwater when groundwater is abstracted in wells located at the side of the stream (Figure 2, Section A2). This holds a singular environmental positive connotation, because the induced recharge improves the groundwater status. More studies are necessary to evaluate the winter behavior, but preliminary $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotope results show more fractionation in winter stream samples as a result of evaporation and low influence from high flows from the upper basin. The numerical geochemical model of the Aji stream for the summer season, near the gauging station where ^{222}Rn was measured (A3 section), shows that sample A3 is predominantly surface water (98/2) [1]. If isotopes values are considered, the geochemical model using PHREEQC (Table 1) shows a bit lower aquifer contribution (98.5/1.5). To obtain the explained A3 sample composition, the mixture was made with 3 components (considering their position in the basin): Aji stream upper basin (AZ2), Suco Lake and aquifer (M139) samples (Figure 4A).

Table 1. Results of numerical modeling carried out with PHREEQC (Model 14)

SAMPLE	Mixture fraction	NaX mol/L	CaX ₂ mol/L	MgX ₂ mol/L	CaCO ₃ mol/L
AZ2 (Aji stream upper basin) (IS)	0.83	-0.35	0.48	-0.29	-0.30
SUCO LAKE (IS)	0.155	-0.06	0.09	-0.05	-0.05
M139 (IS)	0.0114	-0.005	0.007	-0.004	-0.004

In order to add quantitative evidence to the conceptual hydrogeological model, a preliminary characterization of the stream-aquifer relationships, using ^{222}Rn dissolved in water, was made at the end of the rainy season. The characterization of ^{222}Rn activity (in Picocurie per liter, pCi/L) of groundwater and surface water was performed by punctual water measurements in 7 sites (stream and wells) (Figure 4B) located along the entire basin. Suco Lake, located in the upper basin (outside the study area) showed results (2.2 pCi/L) which are consistent with large surface runoff contribution. On the other hand, the Aji stream (within the study area), with a flow of about 0.8 m³/s at the selected gauging station, showed low ^{222}Rn values (4.5 pCi/L), but consistent with its hydrological position, i.e. discharge zone of groundwater flow. The unconfined aquifer near the gauging station exhibited high ^{222}Rn values, typical of groundwater contained in aeolian sediments [1]. The highest value (351 pCi/L) corresponds

to a confined aquifer and is probably related to the aquifer depth and slow groundwater flow (Figure 4B). At the A3 gauging station, an estimation of groundwater contribution was performed, taking into account ^{222}Rn mass balance [2]. The ^{222}Rn regional background value in surface water was tentatively established in 1pCi/L, on the basis that generally there is no ^{222}Rn in surface water. The result indicates that, at the sampling moment, surface flow predominated and groundwater contribution would be of approximately only 2%.

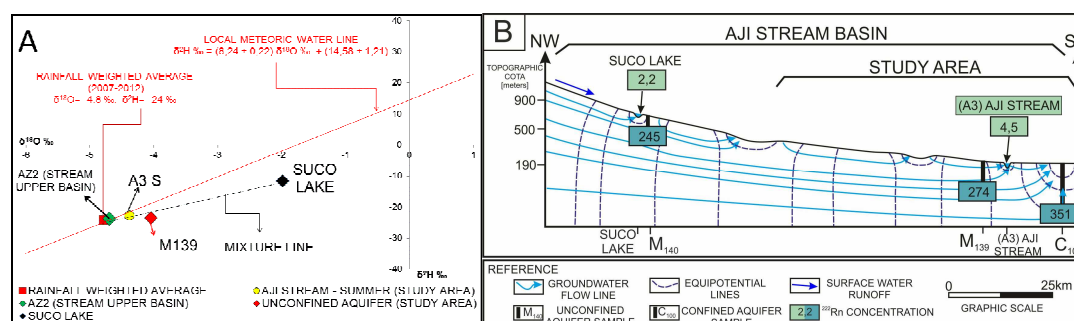


Figure 4. (A) Samples selected for the mixture model. (B) Schematic situation for ^{222}Rn

4. CONCLUSIONS

These surface water-groundwater relationships show the control exerted by the relief, the lithology and the climate. The chemical composition of both hydrological systems is essentially the result of different water velocity in each body. This situation leads to mixing processes between surface water and local, intermediate or regional groundwater giving rise to the observed geochemical pattern. The aquifer-stream relationships were effluent/influent, varying spatially as a result of geomorphology and human actions. The stream water samples and those abstracted from adjacent wells exhibit the same geochemical type (sodium bicarbonate) due to induced recharge.

The isotopic behavior ($\delta^2\text{H} - \delta^{18}\text{O}$) of both hydrological systems in the studied stream reach also indicates water mixtures. This point is validated by ^{222}Rn and the numerical geochemical modeling which indicate a small contribution from the aquifer (~2 %) in summer.

Considering that surface water flows in areas with different groundwater salinity (up to 10 mS/cm in the low basin), it was interpreted that, in summer, surface water dominates the water mixture process. As a result of its high velocity and the entering of such small groundwater quantities, salts that come from the aquifer are diluted. More studies are required; especially an extensive sampling in the two contrasting seasons if a more comprehensive description of the entire basin is attempted.

REFERENCES

- [1] BÉCHER QUINODÓZ, F. Implicancias ambientales de las relaciones hidrodinámicas e hidroquímicas entre aguas superficiales y subterráneas en la planicie arenosa del Sur de Córdoba. Argentina. Ph.D. Thesis UNRC. (2014). Unpublished 412 p.
- [2] ELLINS, K. E., ROMAN-MAS, A. and LEE, R. Using ^{222}Rn to examine groundwater/surface discharge interaction in the Rio Grande de Manati, Puerto Rico. Journal of Hydrology, 115 (1990) 319-341.
- [3] PARKHURST D. D. and C. A. APPELO. User's Guide to PHREEQC (version 2). A computer program for eciation, Batch-Reaction, one-dimensional transport, and inverse geochemical calculations. U.S. department of the Interior. U.S.G.S. Water- Resources Investigations Report 99-259. (1999) 326 p.

ID: 154

ASSESSMENT OF THE ROLE OF SNOW IN HYDROLOGICAL CYCLE OF THE BORJOMULA-GUDJARETI-TSKALI RIVERS BASIN, GEORGIA, USING STABLE ISOTOPE APPROACHES

G. MELIKADZE, N. ZHUKOVA, N. KAPANADZE

Iv. Javakhishvili Tbilisi State University, M. Nodia Institute of Geophysics, Georgia

E-mail address: melikadze@gmail.com

T. VITVAR

Czech Technical University in Prague, Faculty of Civil Engineering, Prague, Czech Republic

L. HOLKO

Institute of Hydrology, Slovak Academy of Sciences, Bratislava, Slovakia

Abstract: Role of snow in the hydrological cycle of the Borjomula-Gudjaretis-Tskali rivers basin, Little Caucasus Mountains, South-western Georgia, was assessed using stable isotope approaches since 2010. Monitoring consists of precipitation, air temperature and humidity measurements at 3 sites, and water level measurements at 2 rivers. Monthly samples for ^{18}O and ^2H were collected from 3 rain gauges, 2 rivers, 1 borehole and 2 springs at different altitudes. Additional event measurements were conducted during snowmelt periods. Although snowfall represents just about 30% of annual precipitation, snowmelt water contributes by about 50% to streamflow. Snowmelt affects river runoff at least 2-3 months.

1. INTRODUCTION AND STUDY AREA

The studied area is situated in the South-western Georgia, in the Little Caucasus Mountains, mean altitude about 1700 m a.s.l. It is drained by the Gudjareti-Tskali (316 km²) and the Borjomula rivers (168 km²). Apart from the mountains surrounding the study area, the dominant geological unit is the lava plateau between the two rivers [1]. Mean annual precipitation varies from 650 to 950 mm. This study is a pioneering work on snowmelt contribution to water resources in the Georgia-Armenia-Azerbaijan region using isotope approaches, and addresses two objectives: a) proportion of snow in the annual precipitation, and b) contribution of snowmelt to streamflow. It is supported by the IAEA-CRP F3.20.03 “The role of snow in hydrological cycle of the Borjomula-Gudjareti-Tskali rivers basin, Georgia“, and more recently by the Swiss National Foundation, Joint Research Project (Switzerland –Georgia–Czech Republic) “Snow resources and the early prediction of hydrological drought in mountainous streams”.

2. METHODS

Monitoring and sampling (since 2010) consisted of precipitation, air humidity and temperature measurements at three stations, water level measurements on the Borjomula and Gudjareti rivers, monthly sampling for ^{18}O and ^2H at 3 precipitation stations, 2 river gauges, 2 springs and 1 borehole, snow depth and water equivalent measurements at 5 sites and event-based snowmelt water sampling at 3 sites. Analyses of ^{18}O and ^2H were performed by the LGR facility at the Czech Technical University in Prague, and the Picarro facility at the Institute of Geophysics of Ivane Javakhishvili Tbilisi State University.

3. RESULTS

Fig. 1a summarizes the monthly stable isotope monitoring for 2010-2014, incl. GNIP stations in Bakuriani and Tbilisi (since 2008) and GNIR station on Mtkvari close to the study area (since 2010). Values in streams indicate appearance of lighter water, attributed to snowmelt contribution. Groundwater values indicate a well-mixed origin and are mostly higher than those in streams. This suggests a dominance of snowmelt-governed headwaters for streamflow generation along the entire river course. Daba spring and Tba borehole demonstrate the identical isotopic behavior during spring seasons, as they both are located in the same aquifer.

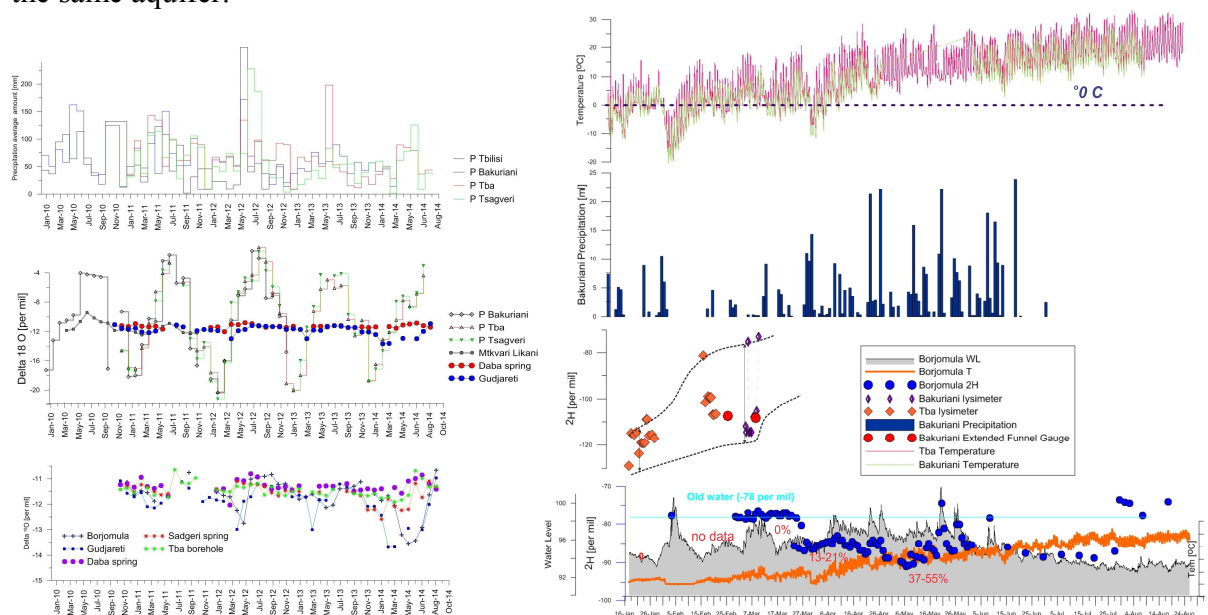


Fig. 1 – a) Isotopic monthly monitoring in the study area over the period 2010-2014, b) Snowmelt period 2014 in the area of the Borjomula river.

Fig. 1b shows that the first phase of snowmelt period 2014 started early in the middle of January and ended in the first decade of February. The second phase started in the end of February and lasted about 2 weeks. Water level in the Borjomula river increased as a response to the snowmelt in the first February decade and later the typical snowmelt diurnal variability of runoff evolved. Snow in the upper areas of the catchment melted before the river reactions on snowmelt season.

4. CONCLUSIONS

Snowfall in the Borjomula-Gudjareti catchments represents about 30% of annual precipitation, and snowmelt water is an important source of water for the rivers. It affects river runoff at least 2-3 months, thus important also for water availability in dry summer period. Groundwater supplies the streams by sustainable runoff contribution, causing an overall mean water transit time of between 2 and 3 years from precipitation to runoff. Isotopic composition of snow cover does not show an altitude gradient, but, stable water isotopes in the snowmelt water significantly differ among the sites and they are different from those in the snow cover.

REFERENCE

- [1] MELIKADZE G., CHELIDZE T., ZHUKOVA N., MALIK P., VITVAR T. (2011). “Using Numerical Modeling for Assessment of Pollution Probability of Drinking Water Resources in Borjomi Region (Southern Georgia)”, In: Climate Change and its Effects on Water

Resources, Issues of National and Global Security (Baba, A., Tayfur, G., Gunduz, O., Howard, K.W.F., Fridel, M.J., Chambel, A., eds.), NATO Science Series. Springer. ISBN:978-94-007-1145-7. Chapter 29, pp.267-275.

PARTITIONING EVAPOTRANSPIRATION IN SPARSELY GAUGED BASINS UTILIZING ISO-HYDROLOGICAL MODELLING

A. SMITH, T. STADNYK,

University of Manitoba, 15 Gillson St, Winnipeg, Canada

E-mail address: umsmi454@cc.umanitoba.ca

Abstract: Evapotranspiration is a key component of the hydrologic cycle in Canada, causing an annual runoff deficit in some regions during low precipitation years [1]. Many areas in northern Canada have limited available data, leading to the use of estimation methods and remote sensing for water management with limited validation of these estimates. This is a concern in the lower Nelson River basin (LNRB, Nelson River basin between Lake Winnipeg and Hudson Bay), where Manitoba Hydro manages six hydroelectric generating stations and relies on accurate simulations and forecasting for efficient water management. Reduction of evapotranspiration uncertainties within northern basins may be assisted with partitioning evapotranspiration to address vegetation types (transpiration) and surface water (evaporation). Partitioning evapotranspiration is also significant for non-stationarity and climate change assessments due to varying vegetation cover [2]. Stable water isotopes can be used to identify evaporation-transpiration partitioning due to differences in fractionation, useful for assessing outlet fractionation. Using stable water isotopes, partitioning of evapotranspiration for terrestrial lakes has shown a wide range of partitions, where transpiration partitions have been as high as 80% [3]. Similar concepts of partitioning may also be applied to basins through the use of iso-hydrological modelling. A lumped iso-hydrological model was previously developed to identify the primary streamflow components within select headwater basins in the LNRB [4], and identified high uncertainty with evapotranspiration rates due to the rate fractionation. The model was modified to partition evapotranspiration into the fractionating (evaporation) and non-fractionating (transpiration) components. These locations collect both discharge and isotopic compositions at the outlet, where throughout the LNRB, precipitation, evaporation pan, and soil water compositions are collected [5]. Surface water mixing slopes (3.9 – 4.3) indicate strong evaporative influence in addition to strong seasonality (minimum 7‰ annual variability) due to snowmelt. The headwater basins have limited topographic relief resulting in high wetland percentages and greater transpiration partition. Northern seasonality impacts the partition due to shortened growing seasons, where evaporation dominates the partition early and late in the ice-off period when transpiration is limited due to cold temperature effects on vegetation. Evapotranspiration estimations are difficult to quantify due to limited measurements, however validation of estimates may be facilitated through the simulation of streamflow compositions.

REFERENCES

- [1] LUI, J., CHEN, J. M., CIHLAR, J., Mapping evapotranspiration based on remote sensing: An application to Canada's landmass. *Water Resources Research*, **39** 7 (2003), doi:10.1029/2002WR001680
- [2] WRUTH, S., "Incorporation of non-stationary landcover into WATFLOOD climate change scenarios", Winnipeg: University of Manitoba, M.Sc. Thesis (2014).
- [3] JASECHKO, S., SHARP, Z. D., GIBSON, J. J., BIRKS, S. J., YI, Y., FAWCETT, P. J., Terrestrial water fluxes dominated by transpiration. *Nature*, **496** (2013) 347-350.

- [4] SMITH, A. A., STADNYK, T. A., “Development and assessment of an iso-hydrologic model through select headwaters in the Lower Nelson River Basin”, Canadian Geophysical Union Annual Conference, Banff, 2014. Poster Presentation.
- [5] SMITH, A. A., DELAVAU, C. J., STADNYK, T. A., Hydrologic Assessment of the Lower Nelson River Basin using Stable Water Isotope Investigations, Canadian Water Resources Journal (in press)

THE OXYGEN AND HYDROGEN ISOTOPIC COMPOSITION OF UGANDAN WATERS

M. GEBREMICHAEL

School of Earth Sciences, Addis Ababa University, Addis Ababa, Ethiopia

E-mail address: meregebre@gmail.com

S. JASECHKO

Department of Geography, University of Calgary, Calgary, Canada

Abstract: In this study we report a stable O and H isotopic investigation of Ugandan rivers, lakes, wetlands, rainfall and groundwaters. Surface- and ground-waters in Uganda have $\delta^{18}\text{O}$ values ranging between -4.0‰ and $+8.7\text{‰}$, $\delta^2\text{H}$ values ranging between -13.2‰ and $+55.5\text{‰}$, and deuterium excess values ranging between -17‰ and $+22\text{‰}$. The highest $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values and lowest deuterium excess values are found in Ugandan lakes; whereas, the lowest $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values and highest deuterium excess values are found in springs and river waters sourced from the Rwenzori mountains of southwest Uganda. We analyze the isotopic composition of lake waters using a stable-isotope-mass-balance to calculate the fraction of evaporation as a proportion of water inputs to 24 lakes and show that a sample of lake water analyzed for O and H isotopes, coupled to the application of a stable-isotope-mass-balance, can rapidly delineate well flushed (low evaporation/input ratio) and terminal (evaporation/input ratio of close to 1) lake systems.

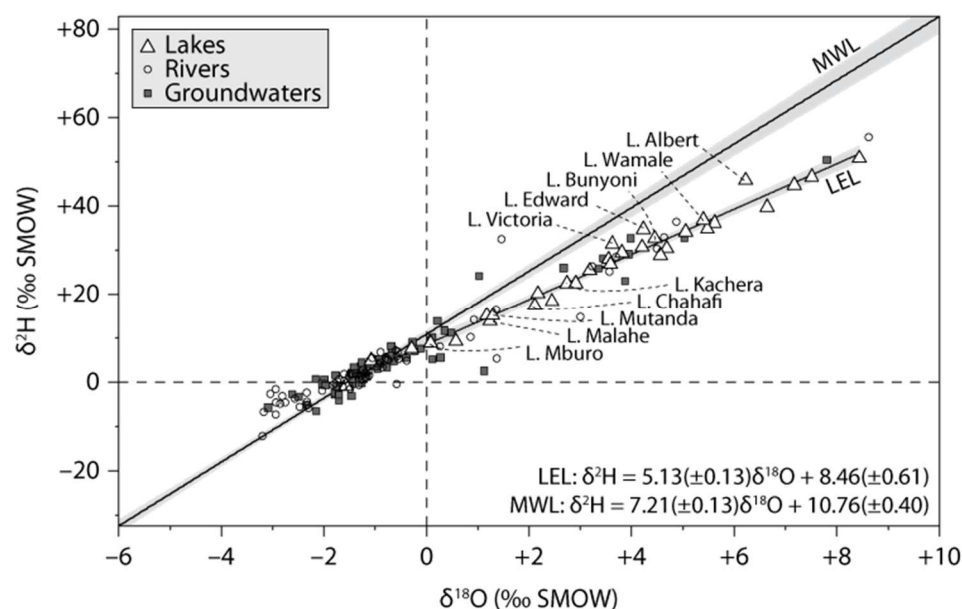


Figure 1. The isotopic composition of Ugandan waters. Regressions are shown for lakes (LEL) and meteoric waters at Entebbe (MWL, data obtained from the International Atomic Energy Agency's Global Network for Isotopes in Precipitation). Grey shading surrounding regressions mark *tthl*

Table 1. Average isotopic compositions of Ugandan water samples

Sample type	n	$\delta^{18}\text{O}$ (‰)		$\delta^2\text{H}$ (‰)		d-excess (‰)	
		Avg.	s.d.	Avg.	s.d.	Avg.	s.d.
Groundwater	75	−0.5	1.9	+6.1	10.2	+10.2	6.0
Lakes	36	+3.4	2.6	+25.9	13.3	−1.3	7.6
Rivers	67	−0.5	2.4	+5.8	12.7	+10.0	7.6
Springs	13	−2.0	1.7	−0.3	9.3	+15.5	4.7
Swamps	12	−0.3	2.0	+8.2	12.6	+10.5	6.5
Tap water	22	+0.1	2.5	+8.8	12.8	+7.9	7.5
Rainfall *	267	−2.0	2.4	−3.6	17.7	+12.3	5.3

* rainfall statistics from the combined precipitation datasets collected at Entebbe, Soroti, Jinja, Masaka, Wobulenzi and Kericho; data obtained from the International Atomic Energy Agency's Water Resources Programme: www.iaea.org/water.

ID: 208

$\delta^7\text{Li}$ FOR DETECTING GROUND WATER CONTRIBUTIONS AND UNDERGROUND PASSAGES OF RIVER WATER

C. MEIER,

UFZ – Helmholtz-Centre for Environmental Research, Catchment Hydrology, Theodor-Lieser-Str. 4, 06120 Halle (Saale), Germany

E-mail address: christiane.meier@ufz.de.

K. OSENBRÜCK,

University Tübingen, WESS – Water and Earth System Science, Keplerstr. 17, 72074 Tübingen, Germany.

H.-M. SEITZ,

j. W. Goethe-University Frankfurt, Institute of Geoscience, Altenhöferallee 1, 60438 Frankfurt a. M., Germany.

S. M. WEISE

UFZ – Helmholtz-Centre for Environmental Research, Catchment Hydrology, Theodor-Lieser-Str. 4, 06120 Halle (Saale), Germany.

Abstract: We determined the Li isotopic composition of water samples from the River Gunt catchment (Tajikistan) to identify ground water contributions and/or subsurface passages of the River Gunt and its tributaries. The Li-isotopic signatures of the water samples show big differences in their spatial distribution in the catchment ($\delta^7\text{Li}$ from +7‰ to +30‰). These variations give us a hint on the flow paths of the tributaries and possible ground water inflows.

1. INTRODUCTION

The high alpine regions in Central Asia are the headwaters for big river systems such as the Amu Darya, which is intensively used for agricultural purposes. For the local water resources management it is important to understand the key factors and processes of runoff generation. It is assumed, that the dominant factors for runoff generation are glacier and snow melt in the Pamir Mountains. However the influence of ground water to river water is also an important factor but still not well understood. We investigated the River Gunt catchment as an exemplary catchment for the Pamir Mountains to identify the origin and to quantify the portion of ground water. Thereby we analyzed water samples of river water, subsurface water, thermal water and glacier water for $\delta^7\text{Li}$.

2. METHODS

In October 2011 and September 2013, water samples were collected from rivers, thermal springs, cold springs and wells at in total 50 sampling sites. All water samples were filtered through a 0.45µm cellulose acetate filter and filled in pre-cleaned 125 and 250 mL HDPE bottles and acidified with nitric acid.

At the laboratory for isotopes at the Institute for Geosciences at the Goethe-University Frankfurt the sample preparation was modified and realized after Seitz [1] and afterwards measured by a Multi-Collector Inductively Coupled Plasma Mass Spectrometer Neptune.

The Li isotopic compositions are presented as per mil (‰) deviation from the isotopic standard NIST L-SVEC.

3. FIRST RESULTS

We detected a wide range of $\delta^7\text{Li}$ values (from +7‰ to +30‰), whereas the highest values were measured in the glacier melt water at the glacier snout ($\delta^7\text{Li} = +28.8\text{‰}$) which are similar to the $\delta^7\text{Li}$ value of sea water, the lowest values were found in the samples of thermal water and springs in solid rock ($\delta^7\text{Li}$ between +8‰ and +11‰), the samples of river water are more or less placed on a mixing line in between (Fig. 1).

We assume that tributaries showing an isotope signature similar to the glacier ones are mainly controlled by melt water while water samples with $\delta^7\text{Li}$ values comparable to the $\delta^7\text{Li}$ values of subsurface water samples pass through the underground or have a strong interaction between river water and river bed. The water samples of the main stream Gunt also show low $\delta^7\text{Li}$ values so we assume a strong contribution of subsurface water to the total runoff or an intensive water-rock-interaction in its riverbed.

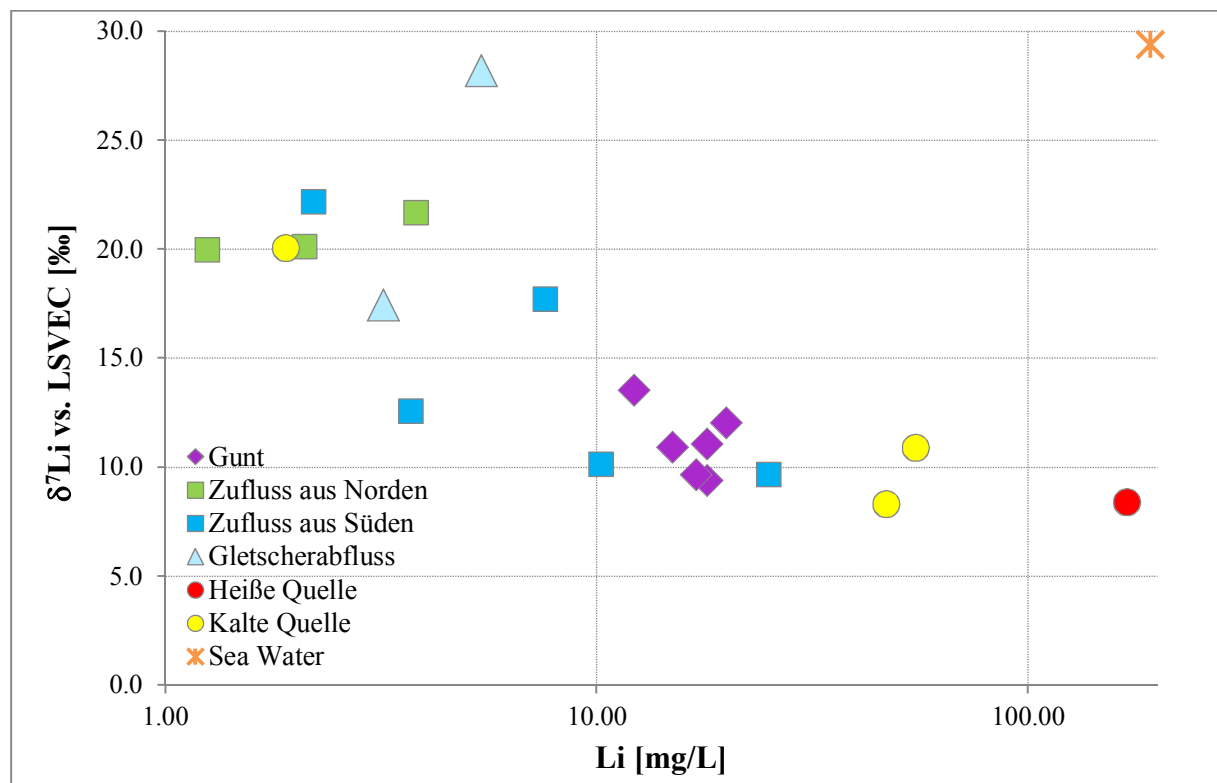


Figure 1. $\delta^7\text{Li}$ distribution in waters in the Tajik Pamir.

REFERENCES

- [1] SEITZ, H.-M., BREY, G. P., LAHAYE, Y., DURALI, S., WEYER, S., Lithium isotopic signatures of peridotite xenoliths and isotopic fractionation at high temperature between olivine and pyroxenes, Chem. Geol. **212** (2004).

ID: 211

GROUNDWATER AND SURFACE WATER INTERACTION IN THE AREA OF PODUNAJSKA NIZINA LOWLAND AND TRNAVSKA PAHORKATINA HILLS

J. MICHALKO, D. BODIŠ,

State Geological Institute of Dionyz Stur, Bratislava, Slovakia

E-mail address: juraj.michalko@geology.sk

Z. ŽENIŠOVÁ,

Department of Human Geography and Demography, Bratislava, Slovakia

P. MALÍK, Z. GROLMUSOVÁ, Zuzana

State Geological Institute of Dionyz Stur, Bratislava, Slovakia

A. LUPTÁKOVÁ,

Slovak Hydrometeorological Institute, Slovakia

J. KORDÍK, F. BOTTLIK, P. ČECH, J. ŠVASTA,

State Geological Institute of Dionyz Stur, Bratislava, Slovakia

Abstract: In the north of the Žitný ostrov, part of the Podunajská nížina Lowland, Slovakia, gradually rises as much as 2000 L/s of groundwater. Groundwater in this area is mainly formed by bank infiltration from Danube River - directly, or indirectly through the Danube left arm Malý Dunaj River. As probable potential sources of groundwater could be considered river Váh and local streams as well. Since the Danube water isotopic composition differs vastly from the water of local origin, monitoring of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ represents an appropriate tool for identification of origin of groundwater springing in Klatovské rameno stream. Results of more than one year monitoring have shown that this groundwater originates from local rivers bank infiltration and reaches seepage place by flowing under Malý Dunaj River bed without the interaction. Groundwater of similar (enriched) isotope composition is present in upper part of Quaternary sedimentary aquifers. This concept is consistent with body of groundwater of worsened quality documented in this area. Deeper situated aquifers are fed by groundwater of Danube origin. Groundwater in aquifers in underlying Neogene sediments is depleted and probably recharged in colder climatic period.

ID: 214

A 50 YEARS' ISOTOPE RECORD OF DANUBE WATER – LONG-TERM TRENDS AND SHORT-TERM SIGNALS

S. WYHLIDAL,

AIT, Austrian Institute of Technology, Konrad Lorenz-Str. 24, A-3430 Tulln, Austria.

E-mail address: Stefan.Wyhlidal@ait.ac.at

D. RANK

University of Vienna, Center for Earth Sciences, Althanstrasse 14, 1090 Wien, Austria.

M. KRALIK,

Environment Agency Austria, Spittelauer Laende 5, 1090 Vienna, Austria

Abstract: The isotope ratios of hydrogen and oxygen in Danube water at Vienna have been measured since 1963 (^3H , stable isotopes ^2H and ^{18}O since 1968). This is probably the worldwide longest isotope record of a large river. The advantage of river water sampling in comparison to precipitation sampling is that the isotopic composition in river water represents the whole catchment area, it allows drawing hydro-meteorological conclusions on a larger scale based on a relatively small number of measurements. The stable isotope time series shows significant changes in a decadal scale, e.g. a remarkable increase of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in the 1980ies mainly due to rising environmental temperature. Results of stable isotope measurements ($\delta^2\text{H}$, $\delta^{18}\text{O}$) of daily grab samples, taken from the Danube at Tulln (river km 1963) during 2012, show seasonal and short term variations depending on the climatic/hydrological conditions and changes in the catchment area (temperature changes, heavy rains, snowmelt processes). ^3H results show peaks (half-width 1-2 days, up to about 150 TU) exceeding the regional environmental level of about 9 TU, due to releases from nuclear power plants.

1. INTRODUCTION

Rivers are an important linkage in the global hydrological cycle, returning about 35 % of continental precipitation to the oceans [1]. For sustainable management of water supply, agriculture, flood-drought cycles as well as ecosystem and human health, there is a basic need to improve the scientific understanding of water cycling processes in river basins and the ability to detect and predict impacts of climate change and water resources management. The International Atomic Energy Agency (IAEA) has launched a monitoring program, the Global Network of Isotopes in Rivers (GNIR), aimed at regular analyses of the isotope composition of runoff in large rivers. Austria contributes to this global network with the long term sampling and measuring series of the sampling site “Donau/Wien”. The existing sampling program in Vienna comprises monthly grab samples. Furthermore a new sampling point was established at Tulln (river km 1963) to conduct a detailed analysis of daily data including the meteorological documentation in order to understand short-term isotopic signals in the Danube River system [2].

2. METHODS

Water samples for ^3H activity measurement were electrolytically enriched and analysed by low level liquid scintillation counting (LLSC, precision $\pm 5\%$). All $\delta^{18}\text{O}$ and $\delta^2\text{H}$ results are reported as relative abundance in per mil (‰) with respect to the international standard

VSMOW (Vienna Standard Mean Ocean Water). The accuracy of measurement is better than ± 0.1 ‰ for $\delta^{18}\text{O}$ and better than 1.0‰ for $\delta^2\text{H}$.

3. RESULTS

Long term trends

The impetus for starting isotope hydrology in the early sixties came from the marking of the atmosphere and therefore the precipitation water with tritium by the atmospheric nuclear weapons tests in the fifties and early sixties. Since 1952, the ^3H content of precipitation has been dominated by the ^3H releases of nuclear weapon tests. As a consequence the ^3H concentration of precipitation increased by about a factor 1000 in 1963 (maximum) followed by a continuous decrease. During the last decade ^3H values have approached “pre-bomb” levels again (Figure 1). The ^3H -tracer went through all hydrological systems and allowed for decades to determine reliably the age or mean residence time (MRT) of water in a hydrological system, e.g. [3]. The ^3H content of rivers follows with a certain delay on the ^3H content of precipitation, depending on the residence time of precipitation water in the catchment area.

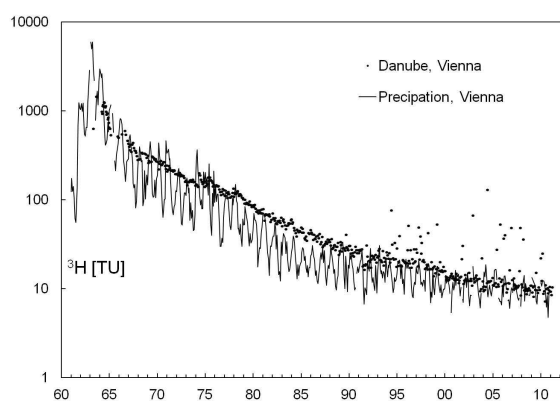


Figure 1: Long-term ^3H time series of precipitation (monthly mean values) and Danube (monthly grab samples) at Vienna.

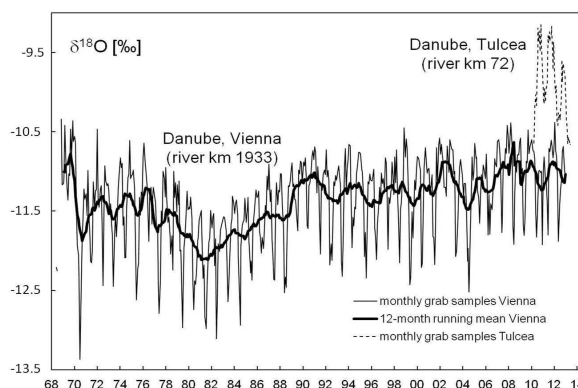


Figure 2: $\delta^{18}\text{O}$ time series of the Danube River at Vienna (monthly grab samples, 12-month running average, Rank et al. 2012, updated) and Tulcea.

Associated with the attenuation of the nuclear weapons ^3H activity in the environment local and regional ^3H releases have become more important and visible. Since 1994 some of the monthly grab samples of Danube water showed elevated ^3H content (Figure 1), obviously due to regional or local influences (mainly releases from nuclear power plants, [4, 5]). This delay in runoff leads also to an attenuation of seasonal fluctuations of ^3H concentration.

Long-term stable isotope records of precipitation water exhibit significant decadal changes in the isotopic composition [4]. As a consequence, also the stable isotope time series of rivers shows significant changes in a decadal scale, e.g. a remarkable increase of $\delta^{18}\text{O}$ in the 1980s mainly due to rising environmental temperature (Figure 2). The long-term $\delta^{18}\text{O}$ trend of several Austrian rivers – Danube tributaries and the alpine section of the Rhine – is similar to that of the Danube [5]. Thus one can conclude that this trend in the order of decades represents a general climatic long-term isotopic signal – input from precipitation – in all hydrological systems.

Short-term signals

In addition, daily grab samples of the Danube river water at Tulln through the entire year 2012, allow a detailed analysis of the seasonal, temperature and weather governed progress of stable isotope ratios in river water (Figure 3). Quick changes of the isotopic composition within a few days emphasize the necessity of at least daily sampling for the investigation of hydrological events. The isotope data of daily samples are lying close to the Global Meteoric Water Line, which leads to the conclusion that evaporation influence on the isotopic composition in river water plays only a minor role in the Upper Danube Basin. The comparison of the seasonal variation of isotope ratios in river water with that in precipitation in the catchment area shows a significant difference in the seasonal variation. While precipitation shows a maximum in $\delta^{18}\text{O}$ during summer, river water is characterised by a summer minimum due to snowmelt in the high mountainous regions of the catchment. Major changes in the isotopic composition in river water as well as in flow rates can be expected from heavy rain fall and snowmelt processes, in mountainous and/or low land regions, connected with temperature changes in the catchment area [2]. Low $\delta^{18}\text{O}$ values are associated with mountain snow melt; high $\delta^{18}\text{O}$ values are mainly related to spring and summer rainfall. High water on the Danube River occurs during warm periods in spring or early summer that experience heavy rainfall and mountain snow melt.

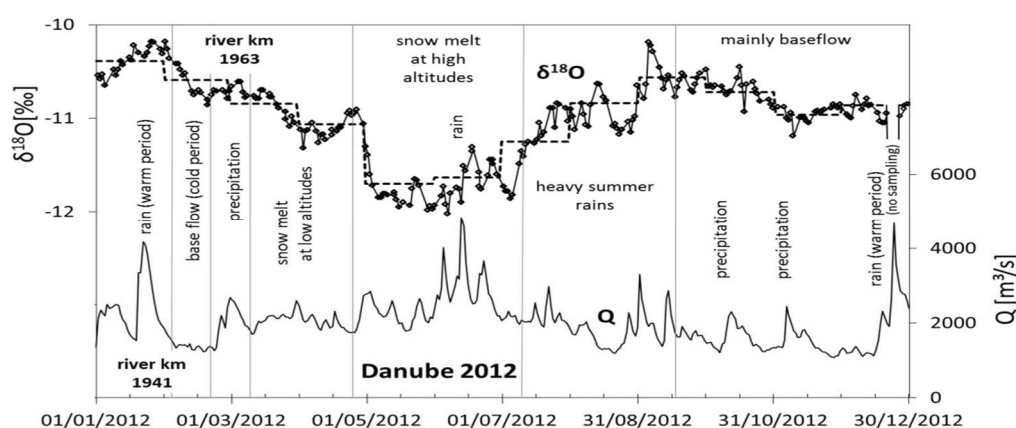


Figure 3: General interpretation of $\delta^{18}\text{O}$ variations of daily river samples (dashed line: monthly means) during 2012 with the help of flow rate data.

The 2012 record of the Danube River water at Tulln was characterised by short-term elevations of the ^3H concentration. Daily samples were analysed for those months for which

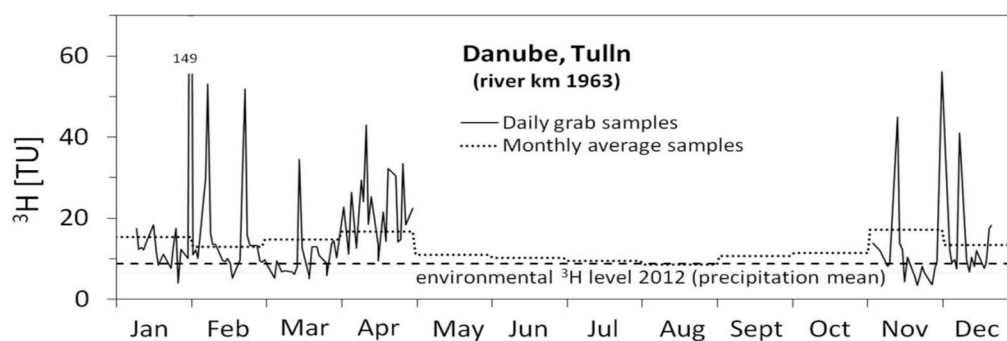


Figure 4: ^3H concentration of daily samples for months with elevated mean ^3H content.

the average sample indicated ^3H activities significantly exceeding the environmental ^3H level (Figure 4). These short term ^3H elevations may be related to releases from nuclear power plants (NPPs) in Bavaria (Isar: about 400 km upstream, Gundremmingen: about 600 km upstream).

4. CONCLUSIONS

The isotope record “Donau/Wien” (Danube at Vienna) is a unique database for hydrological and hydro climatic modelling. The isotopic composition of Danube water is mainly governed by the isotopic composition of precipitation in the catchment area, evaporation effects play only a minor role. Short-term and long-term isotope signals from precipitation are thus transmitted through the whole catchment. The isotopic composition of Danube water so provides an integrated isotope signal for climatic/hydrological conditions and changes in the upper Danube Basin. For the investigation of short-term fluctuations of the isotopic composition (^2H , ^{18}O) daily grab samples of the Danube River water were collected at Tulln. Frequently significant changes of the isotope composition occurred within a few days or even one single day. In most cases these changes could be clearly attributed to hydrological events and conditions (precipitation events, snow melt processes, base flow conditions). Snow melt processes caused minima in the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ course (summer minima are typical for alpine rivers), summer rains were responsible for maxima, and during base flow conditions the isotopic composition returned to the mean value in the system. The ^3H course of the Danube River at Tulln 2012 is characterised by several peaks in the range of 50 TU with a half width of 1-2 days. According to the Austrian Drinking Water Regulations the “indicator parameter” for ^3H is 100 Bq/L (847 TU). All ^3H values measured within this project were far below this benchmark.

REFERENCES

- [1] GIBSON, J. J., AGGARWAL, P. K., HOGAN, J. F., KENDALL, C., MARTINELLI, L. A., STICHLER, W., RANK, D., GONI, I., CHOUDHRY, M., GAT, J., BHATTACHARYA, S., SUGIMOTO, A., FEKETE, B., PIETRONIRO, A., MAURER, T., PANARELLO, STONE, H., D., SEYLER, P., MAURICE-BOURGOIN, L. and HERCZEG, A., Isotope studies in large river basins; A new global research focus. – EOS Trans. AGU, (2002) 83: 613–617.
- [2] WYHLIDAL, S., RANK, D., SCHOTT, K., HEISS, G., GOETZ, J., Analysis of isotopic signals in the Danube River water at Tulln (Austria) based on daily grab samples 2012, Isotopes in Environmental & Health Studies (2014)
- [3] MOOK, W. G., Environmental Isotopes in the Hydrological Cycle - Principles and Applications. International Hydrological Programme (IHP-V), Technical Documents in Hydrology, Paris (International Atomic Energy Agency/ UNESCO) (2000) 39/1, 280 p
- [4] RANK, D., PAPESCH, W., HEISS, G., TESCH, R., Environmental Isotope Ratios of River Water in the Danube Basin. - Monitoring Isotopes in Rivers: Creation of the Global Network of Isotopes in Rivers (GNIR), Vienna (International Atomic Energy Agency) IAEA-TECDOC-1673 (2012) 13-40
- [5] RANK, D., WYHLIDAL, S., SCHOTT, K., JUNG, M., HEISS, G., TUDOR, M., A 50 years' isotope record of the Danube River water and its relevance for hydrological, climatological and environmental research, Acta zool. bulg., Suppl. 7, (2014) 109-115

ID: 215

HYDROCHEMICAL ENVIRONMENTAL ISOTOPE STUDY OF THE AQUIFER ON THE GULF OF URABÁ - COLOMBIA

V. PAREDES; P. VILLEGAS,

Corporación para el Desarrollo Sostenible del Urabá, Apartadó, Colombia.

E-mail address: v.paredes@corpouraba.gov.co

T. BETANCUR,

Facultad de Ingeniería de la Universidad de Antioquia, Medellín, Colombia.

J.D. TAUPIN,

UMR Hydrosiences (CNRS, UM1, UM2, IRD), Montpellier, France

L. TORO,

International Atomic Energy Agency, Isotope Hydrology Section (IAEA), Vienna, Austria

Abstract: The region of Urabá is a coastal area located in the northwest of Colombia (Antioquia). The rapid growth in demand for water in the past two decades, mainly driven by agribusiness and by population growth, has been a source of concern among local authorities. The extraction of groundwater has increased exponentially as a result of agricultural expansion, consisting mainly of banana plantations. In the area there are 730 deep wells that extract annually about 23M m³.

The Autonomous Corporation for the Sustainable Development of Urabá (CORPOURABA) in 2008 began to incorporate isotope techniques in their research projects. The first phase of these studies was conducted between 2008 and 2012 and had the funding and technical assistance from the International Atomic Energy Agency (IAEA) and the Institute of Research for Development, France (IRD). The overall objective in this first phase was to obtain improved on the evolution of groundwater in the confined aquifer conceptual model as well as a first approach to the history of recharge, especially considering that some of the water exploited seems to have been recharged under climatic conditions different to the present. In conducting the investigation, 93 wells, 12 artesian wells and 3 springs were analyzed between 2008 to 2012. Of the 108 sampling points, 99 correspond to the Corpa Formation (of the Tertiary) and nine, located north of the area study belong to the Quaternary sediments. At 85 points deuterium and oxygen-18 were measured. Both isotopes were also determined in 48 monthly composite rain samples obtained from a collector installed west of the study area, in longitude and latitude coordinates -76.9624 ° + 7.652 °.

Based on chemical analysis it was established that the processes that individually or in combination influence the composition of the water include cationic exchange, dissolution of feldspar and sulphate reduction. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values along with the results obtained from the interpretation of the data of ^{14}C in the aquifer, reflect differences in climatic conditions between the recharge area and the confined part of the aquifer near the ocean. Groundwater samples, whose ^{14}C ages range from recent recharge to ~28 ka present decreasing isotope values (-6.43 to -9.14 ‰ for $\delta^{18}\text{O}$ and -43.2 ‰ to -65.7 ‰ for $\delta^2\text{H}$). Very depleted values in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ reflect a cold weather at the time of the recharge. Meanwhile $\delta^{13}\text{C}$ results reflect the occurrence of oxidation processes of organic matter whose $\delta^{13}\text{C}$ values were depleted, reflecting the presence of reducing conditions in the aquifer.

ID: 219

APPLICATION OF HYDROCHEMISTRY AND STABLE ISOTOPES (^2H , ^{18}O , ^{13}C -DIC, ^{34}S - SO_4 , ^{18}O - SO_4) FOR RIVER/GROUNDWATER INTERACTION IN VELEZ RIVER AQUIFER, SPAIN

I. VADILLO, J. BENAVENTE, B. URRESTI, P. JIMENEZ,

University of Malaga, Spain

E-mail address: vadillo@uma.es

Abstract: The in-depth knowledge of the interaction between surface water and groundwater is one of the challenges of the Water Framework Directive (WFD) in order to achieve good quantitative status of water bodies. This fact makes necessary to improve the currently held knowledge about the relationship between groundwater and surface water in recharge and discharge areas of aquifers (wetlands, rivers, lakes, etc.), the dependence by each other and the importance they have for the associated ecosystems. The Velez alluvial aquifer (Province of Malaga, Southern Spain) was selected to meet river-aquifer relationships by studying the hydrochemistry and stable isotopic content of water molecule ($\delta^2\text{H}$, $\delta^{18}\text{O}$), dissolved inorganic carbon ($\delta^{13}\text{C}$) and sulphate ($\delta^{34}\text{S}$, $\delta^{18}\text{O}$).

ID: 227

USE OF STABLE AND RADIOACTIVE ISOTOPES TO UNRAVEL SURFACE WATER GROUNDWATER INTERACTIONS IN A DEVELOPED CATCHMENT

M. S. ANDERSEN, G. RAU,
University of New South Wales, Australia
E-mail address: m.andersen@unsw.edu.au

K. MEREDITH,
Australian Nuclear Science and Technology Organisation, Australia

A. MCCALLUM,
Office of the NSW Chief Scientist and Engineer, Australia

I. ACWORTH,
University of New South Wales, Australia

Abstract: Traditionally surface water groundwater interactions are estimated using hydrometric and water balance methods. However, the hydrometric methods, based on hydraulic gradients, have huge uncertainties related to the mostly unknown and often highly heterogeneous permeability distribution. Similarly, the surface water groundwater exchange can be relatively small compared to other components of the water balance (e.g. differential stream flow gauging) and consequently its estimation is associated with large uncertainties when using a water balance method. Environmental tracers such as isotopes on the other hand integrate what has actually taken place. However, each individual isotopic tracer has particular advantages and disadvantages and therefore limited use. For instance each radioactive isotope is limited to provide residence time estimations within a certain age range whereas stable isotopes only work when different water sources have distinctly different isotopic compositions. In this study, of a highly developed catchment subject to groundwater depletion it is demonstrated that by combining different tracers (^{14}C , ^3H , ^2H and ^{18}O) a more complete picture of the surface water groundwater interactions can be obtained.

ID: 228

NATURAL AND INDUCED SURFACE GROUNDWATER EXCHANGE PATHWAYS REVEALED USING ^{222}Rn AND HYDROCHEMICAL PARAMETERS

G. RAU, H. RUTLIDGE, M. S. ANDERSEN
University of New South Wales, Australia
E-mail address: gabriel.rau@unsw.edu.au

N. UNLAND,
Monash University, Australia

H. HOFMANN,
University of Queensland, Australia

B.. GILFEDDER,
University of Bayreuth

A.. ATKINSON, I. CARTWRIGHT
Monash University, Australia

A..BAKER, Andy I. ACWORTH,
University of New South Wales, Australia

Abstract: Surface water sampling of ^{222}Rn is often used to map zones of groundwater discharge. Sampling of groundwater ^{222}Rn is less often used to estimate water residence times in shallow alluvial systems. Radon groundwater grab samples offer a discrete time snapshot of flow path integrated Rn activities. During a pumping experiment on the banks of Maules Creek (Australia) a 2.5 m flood event occurred in the stream. This offered a rare opportunity to investigate the groundwater response to two simultaneous stressors: groundwater abstraction and flooding. The stream-aquifer response was monitored with 25 observation bores, and 15 were sampled regularly for radon activities as well as hydrochemical parameters (EC, dissolved O_2 and fluorescence). Subsurface heterogeneity and distinct flow paths are revealed by analysing hydraulic heads, radon activities and hydrochemical parameters with high spatial and temporal resolution. The results show that ^{222}Rn can reveal water movement but not accurately estimate residence times, and that a dynamic surface water-groundwater system is best characterised by combining different tracers.

ID: 248

SIMULATION OF THE HYDROLOGICAL AND ISOTOPIC BALANCE OF AN ENDORHEIC LAKE AT A MONTHLY TIME STEP (AZIGZA LAKE, MIDDLE ATLAS, MOROCCO).

R. ADALLAL

CEREGE, Aix-Marseille Université, UMR 7330 CNRS-IRD-CDF, Europôle Méditerranéen de l'Arbois, BP80, 13545 Aix-en-Provence, France,
Laboratoire de Géoressources-Unité associée au CNRST (URAC 42), Université Cadi Ayyad, Faculté des Sciences et Techniques, Bd. A. Khattabi, BP 549, 40 000 Marrakech, Morocco.

E-mail address : adallal@cerege.fr

C. VALLET-COULOMB,

CEREGE, Aix-Marseille Université, UMR 7330 CNRS-IRD-CDF, Europôle Méditerranéen de l'Arbois, BP80, 13545 Aix-en-Provence, France

A. BENKADDOUR,

Laboratoire de Géoressources-Unité associée au CNRST (URAC 42), Université Cadi Ayyad, Faculté des Sciences et Techniques, Bd. A. Khattabi, BP 549, 40 000 Marrakech, Morocco.

C. SONZOGNI,

CEREGE, Aix-Marseille Université, UMR 7330 CNRS-IRD-CDF, Europôle Méditerranéen de l'Arbois, BP80, 13545 Aix-en-Provence, France

A. RHOJJATI

Laboratoire de Géoressources-Unité associée au CNRST (URAC 42), Université Cadi Ayyad, Faculté des Sciences et Techniques, Bd. A. Khattabi, BP 549, 40 000 Marrakech, Morocco.

L. VIDAL

CEREGE, Aix-Marseille Université, UMR 7330 CNRS-IRD-CDF, Europôle Méditerranéen de l'Arbois, BP80, 13545 Aix-en-Provence, France

Abstract: Stable isotopes of water (^{18}O , ^2H) and their associated isotope fractionation during water-cycle phase changes can be efficiently, used to study hydrological and climatic processes at local, regional and global scales. Understanding the seasonal and inter-annual stable isotope behaviour in a lacustrine system is a key for interpreting carbonate $\delta^{18}\text{O}$ obtained from lake sediments in order to reconstruct past changes in local hydro-climatology. The natural mountain lake system Aguelmam Azigza ($32^{\circ}58'\text{N}$, $5^{\circ}26'\text{W}$, 1470 m asl), is lying in the tectonic-karstic tabular Middle Atlas (Morocco), considered as the “water tower” of the country. A lake monitoring has been implemented since October 2012 with a monthly water sampling (precipitation, lake, well and springs) for water isotope and chemical measurements. An isotopic balance model ($\delta^{18}\text{O}$, $\delta^2\text{H}$), including the Craig and Gordon evaporation model, has been coupled with the water balance model in order to simulate the evolution of both lake water level and isotopic composition at a monthly time step. First, the estimation of the lake water balance reveals that this lacustrine system is an open system and sensitive to climatic parameters. The ratio of evaporation over inputs (E/I) of 0.19 shows that

less than 20% of the lake water is lost by evaporation. Secondly, for the dynamic water balance modelling, the water inflows from the catchment (surface and subsurface runoff) are weighted by the amount of precipitation on the lake surface. The groundwater outflows are considered as constant. Both of these estimations provide a good simulation of the monthly lake water isotopic composition. Nevertheless, assessment of evaporation outputs needs to be improved.

ID: 260

HUMAN-DRIVEN ENRICHMENT OF WATER STABLE ISOTOPES (^{18}O , ^2H) IN AN INTENSIVE AGRICULTURE AREA (GUADALHORCE BASIN, SOUTHERN SPAIN)

I. VADILLO, B. URRESTI, P. JIMENEZ, J. BENAVENTE

Department of Ecology and Geology, University of Malaga, Malaga, Spain

E-mail-address: vadillo@uma.es

Abstract: Isotopic content of water ($\delta^{18}\text{O}$, $\delta^2\text{H}$) in aquifers with significant abstraction devoted to irrigated agriculture may reflect changes in its natural signal. In the Guadalhorce river basin (South Spain) the effect of irrigation return flow and subsequent evaporation processes, modifies the isotopic signature of the global meteoric water line (GMWL), and as a result, water becomes enriched in heavy isotope content. The location of three water reservoirs in the middle sector of the basin causes a division between the waters belonging to the upper and waters belonging to the lower basin. It has been possible to distinguish two straight lines of successive evaporation processes that coincide with the gathered samples upstream and downstream of the reservoirs. The slopes of both lines range between 4 and 5. The enrichment in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ match with an increased in salinity such as electrical conductivity or the concentration of chloride and sulfate.

ID: 285

IDENTIFICATION OF RECHARGE SOURCES OF SHALLOW GROUNDWATER AND ITS INTERACTION WITH SURFACE WATER IN A PART NORTHWESTERN INDIA, USING ENVIRONMENTAL ISOTOPE

S. P. RAI, M. S. RAO, S. KUMAR, Y.S. RAWAT, R. D. SINGH,
National Institute of Hydrology, Roorkee-247667, Uttarakhand, India
E-mail address: sprai1966roorkee@gmail.com

Abstract: The study area is a part of the Saluj basin in state of Punjab of India which lies in Indo-Gangetic plain of northwest India. Northwestern (NW) India is a hotspot of groundwater depletion driven largely by intensive irrigation. GRACE satellite-based regional analysis shows that groundwater is being depleted at a mean rate of 4.0 ± 1.0 cm/yr in Rajasthan, Haryana, and Punjab (Rodell, 2009). Groundwater in northwestern India was lost at a rate of 54 ± 9 km³/yr from April 2002 to June 2008. The recent studies reveal that groundwater *loss from Northwestern India is largest in comparison to any comparable- sized region on Earth'*. However, little is known about groundwater dynamics in this region. Therefore, it becomes an urgent need to explore the groundwater recharge sources and its dynamics in part of NW India, which will be useful in developing a strategy for sustainable management of groundwater. The present study is part of the coordinated research programme of IAEA.

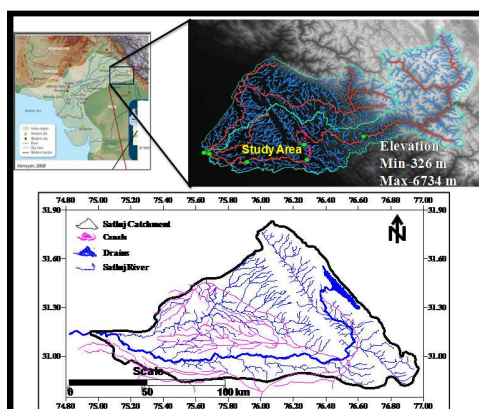


Figure 1. Study Area Map

The groundwater flow pattern analyzed using water table data which shows flow direction of groundwater in the study area is towards northeast-southwest direction. Water level data show that water level has declined up to 2 m to 10 m in last two decades. The environmental isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$ and ^3H) have been used to understand the recharge source and interaction between groundwater and surface water in the study area. About 100 groundwater samples from whole study area were collected for isotopic characterization during post-monsoon of 2013. The groundwater samples were collected from existing dug well, hand pump and tube wells. Four rain gauges were installed for the collection of water samples from the study area. Collected samples were analysed at National Institute of Hydrology, Roorkee as per standard procedure.

The overall precision, based on 10 points repeated measurements of each sample, was with the $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 1\text{‰}$ for δD .

The isotopic composition of weighted average of precipitation in study area varies from -13.3‰ to 4.2‰ for $\delta^{18}\text{O}$ and -105.2‰ to 41.4‰ for $\delta^2\text{H}$. The local meteoric water line (LMWL) developed for the study area is $\delta^2\text{H} = 7.8 \times \delta^{18}\text{O} + 5.1$; $r^2=0.98$, $n=119$. Slope and intercept is less than GMWL (Rozanski, 1993). The $\delta^{18}\text{O}$ of Rivers Satluj, flowing through the study area, varies between -12.7‰ to -8.0‰ and $\delta^2\text{H}$ from -87.9‰ to -56.3‰ , the depleted isotopic composition suggesting source of water from higher Himalayas.

The $\delta^{18}\text{O}$ of groundwater belong up to depth of 80 m varied from -12.4‰ to -4.7‰ and $\delta^2\text{H}$ from -85.1‰ to -32.4‰ (Fig. 2). The regression analysis between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ gives the best fit line (BFL) as:

$$\text{Shallow GW} : \delta^2\text{H} = 6.6 * \delta^{18}\text{O} - 2.7 \quad (n = 61, r^2 = 0.98)$$

The slope and intercept of the groundwater is less in comparison of LMWL. It indicates evaporative fractionation during recharge process of groundwater. Groundwater isotopic values fall on the LMWL, indicating local precipitation as the main recharge source, although a few depleted samples falling above the LMWL suggest recharge from river and local canal. Therefore study reveals that shallow groundwater is being recharged through local precipitation and surface water body (river and canal). Figure 2 shows spatial variation in recharge source.

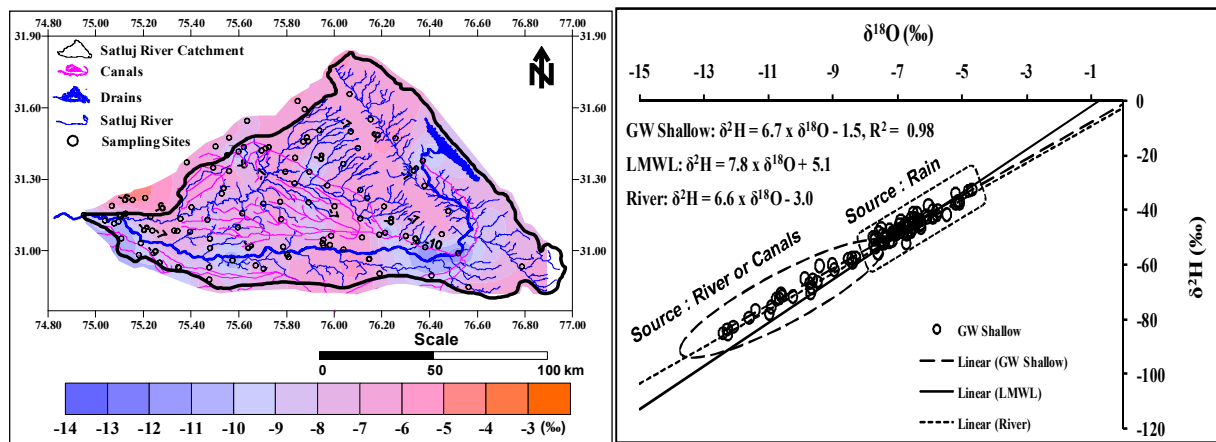


Figure 2. Isotopic variation and characterization of shallow groundwater

Interaction between river and Groundwater

To study the river - groundwater interaction, river water (on daily basis) and groundwater samples (weekly basis) were collected at five sites (i.e., Ropar, Phillaur, Sidhwan, Yusafpur and Harike), groundwater samples were collected from both bank of river and covering distance of 5 km to 6.5 km.

Figure 3 shows the variation in isotopic composition of river and adjacent groundwater on five sites. On average $\delta^{18}\text{O}$ values of Satluj river at Ropar site varied between -12.2‰ during

monsoon (July to September) and -11.5‰ post-monsoon. The isotopic composition of shallow groundwater varied from -9.5‰ to -6.1‰ during monsoon and -9.7‰ to -5.7‰ post-monsoon at right bank of river. Similarly, average $\delta^{18}\text{O}$ ranged from -11.4‰ to -6.3‰ in monsoon and -1.4‰ to -6.5‰ during post-monsoon at left bank (Fig. 3). It indicates that groundwater $\delta^{18}\text{O}$ is depleted near to the river and $\delta^{18}\text{O}$ enriches as distance of the well increases from the river. It indicates that river is recharging to groundwater and recharge ratio is more towards the left side of the river (Fig. 3). Similar results have been found on other sites also. At Sidhwan site, recharge from river is both sides.

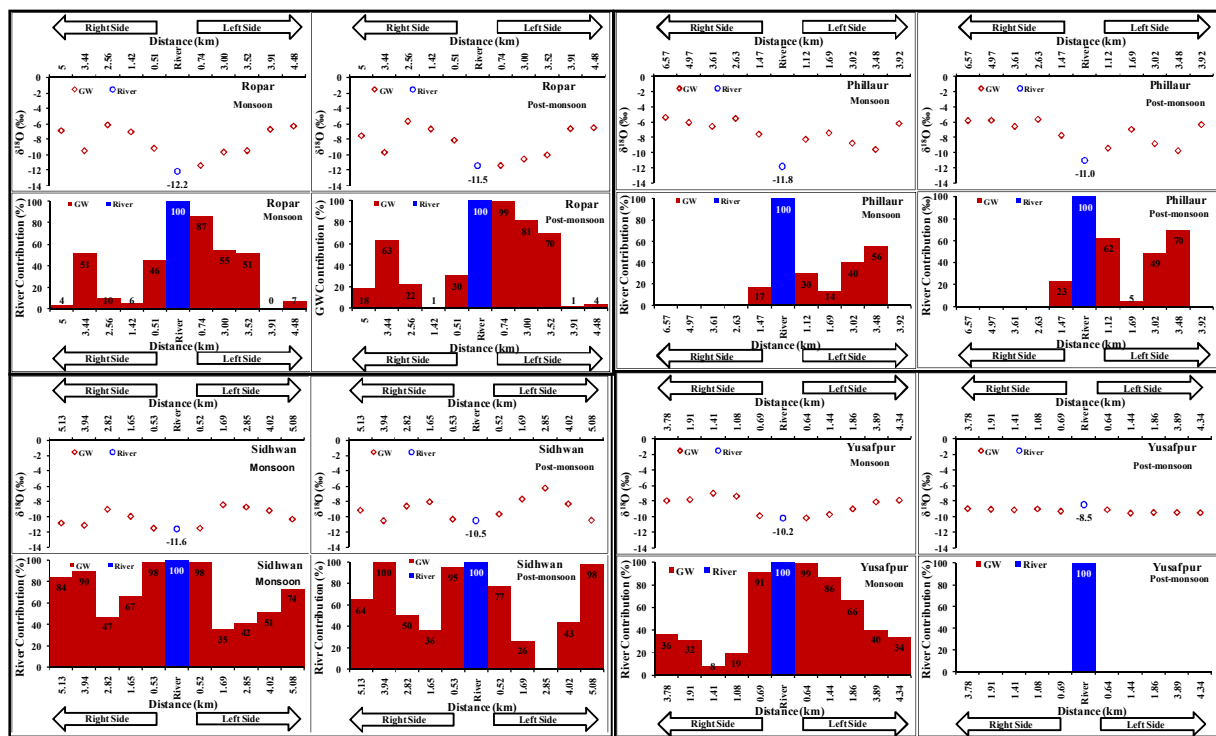


Figure 3. Isotopic variation and contribution of river to shallow groundwater

REFERENCES

- [1] RODELL, M. et al. (2009) Nature, doi: 10.1038/nature08238.
- [2] ROZANSKI, K., ARAGUAS-ARAGUAS, L., GONFIANTINI, R (1993) Isotopic patterns in modern global precipitation. In Climate Change in the Isotopic records. Monograph 78, American Geophysical Union: Washington, DC; 1-36.

ID: 286

SEASONAL VARIABILITY OF GROUNDWATER CONTRIBUTION TO WATERSHED DISCHARGE IN DISCONTINUOUS PERMAFROST IN THE NORTH KLONDIKE RIVER VALLEY, YUKON

A LAPP,

Department of Earth Sciences, University of Ottawa, Ontario, Canada.

E-mail address: anthony.lapp@gmail.com

I D CLARK,

Department of Earth Sciences, University of Ottawa, Ontario, Canada.

Abstract: Total groundwater contribution to total river discharge and its effect on river geochemistry was investigated within a subarctic catchment with discontinuous permafrost (North Klondike River, Yukon) from August 2013 to August 2014. During spring freshet, stream DOC increased rapidly, peaking prior to maximum discharge before returning to pre-baseflow levels. Carbon-14 dating shows the presence of old organic carbon within the river prior to spring freshet, with a large influx of modern carbon as the river breaks. Major solutes such as bicarbonate, calcium, magnesium, and sulphate show similar increases in concentrations prior to maximum discharge.

1. INTRODUCTION

Permafrost environments are hydrologically complex, and little is known about groundwater flow rates, pathways, and contribution to surface waters. The understanding of hydrology in permafrost environments is of the utmost importance due to recent, and predicted, climate warming in north latitudes. These areas have often been understudied due to a lack of spatial coverage of hydrometric and climatic data networks in northern regions [1-3]. Research conducted in the north has often been of short duration, lacking in measured hydrologic variables, and of limited spatial extent [2]. This project builds on previous research, using longer time-series data sets and covering a greater number of parameters. The objectives of this project were (1) to quantify seasonal groundwater contribution to total stream discharge, and (2) determine the effect of groundwater on carbon sources and pathways.

The Northern Klondike River, located in Yukon's Tombstone Territorial Park, was an appropriate site for the study of groundwater hydrology in a discontinuous permafrost zone. Logistically, the river is easily accessible from the Dempster highway by foot. The Yukon government has maintained a hydrologic monitoring station for a period of approximately 30 yr, and is one of the few gauging stations still active today. Personnel from the University of Ottawa conducted high resolution sampling during major hydrologic events, and the Yukon Government Tombstone Highway maintenance camp was enlisted to sample the North Klondike River from January 2014 to August 2014. This allowed for a robust data set monitoring eight months of dissolved carbon, geochemistry, and stable- and radio-isotope concentrations being discharged from the river.

2. METHODS

Field work was conducted between August 2013 and August 2014. This included monitoring the North Klondike River during major hydrologic events such as winter baseflow, spring freshet, and summer. Precipitation was collected from the Dawson City Airport to establish a local meteoric water line for the area. The Yukon Government Highway Tombstone

maintenance camp was able to sample bi-monthly during the winter months (starting January 2014), spring freshet, and into the summer during times when University of Ottawa personal could not be present. All water samples were analyzed at the University of Ottawa for major ion concentrations and solutes, $\delta^{18}\text{O}$ ($^{18}\text{O}/^{16}\text{O}$) and $\delta^2\text{H}$ ($^2\text{H}/^1\text{H}$), dissolved inorganic and organic carbon concentrations (DIC and DOC) including $\delta^{13}\text{C}$ ($^{13}\text{C}/^{12}\text{C}$), and tritium concentrations (TU). Select samples were also analysed for $\delta^{14}\text{C}$ ($^{14}\text{C}/^{12}\text{C}$) in DIC and DOC. Total river discharge for the North Klondike River was obtained through the Yukon government. A three component hydrograph separation was used to establish end-member contributions to total river discharge. Weather data such as maximum and minimum temperature and precipitation were collected by Dawson City Airport for Environment Canada. All climate data was obtained through the Government of Canada's Historical Climate records.

3. RESULTS

Total river discharge for 2014 in the North Klondike River combined with average temperatures recorded at Dawson City airport, Yukon, is presented in Figure 1. The discharge profile for 2014 has a much smaller maximum discharge event compared to previous years, as well as variable flow during the winter months before river break and spring freshet. In previous years the average discharge during the winter months prior to spring freshet is $\sim 2 \text{ m}^3/\text{sec}$. During the winter, average temperatures that approach 0°C are often followed by increased discharge events. These spikes in flow show little change in solute concentrations within the river. DIC and DOC concentrations and $\delta^{13}\text{C}$ values for 2014 in the North Klondike River are presented in Figure 2. $\delta^{13}\text{C}$ are reported relative to VPDB. Major solutes and their concentrations for 2014 in the North Klondike River are presented in Figure 3.

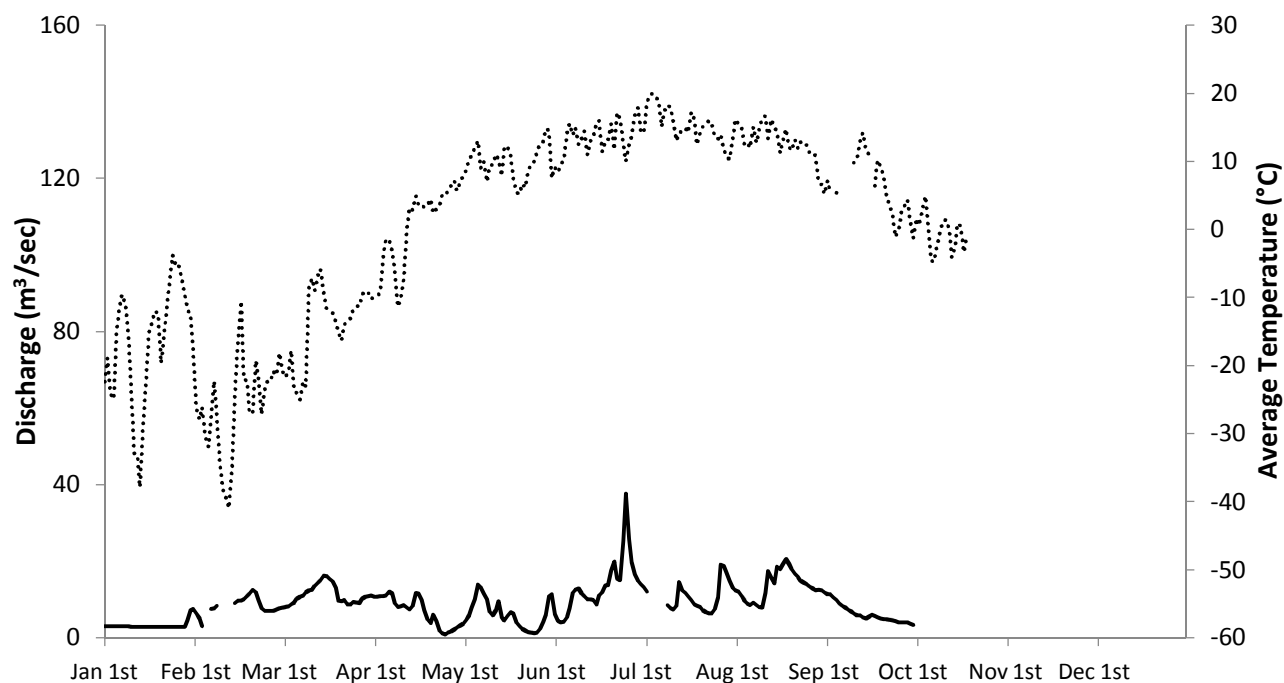


Figure 1 Annual discharge (m^3/sec) in the North Klondike River and average temperature at Dawson City airport for 2014.

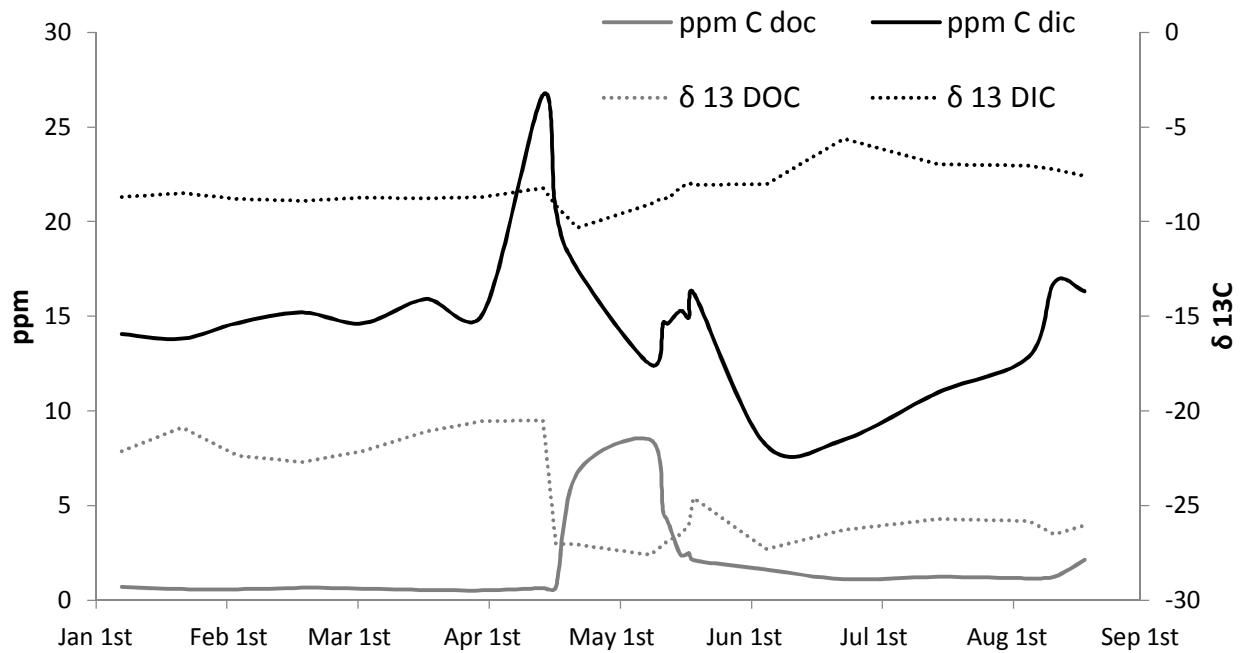


Figure 2 Time series of dissolved inorganic and organic carbon as well as $\delta^{13}\text{C}$ values in the North Klondike River during 2014.

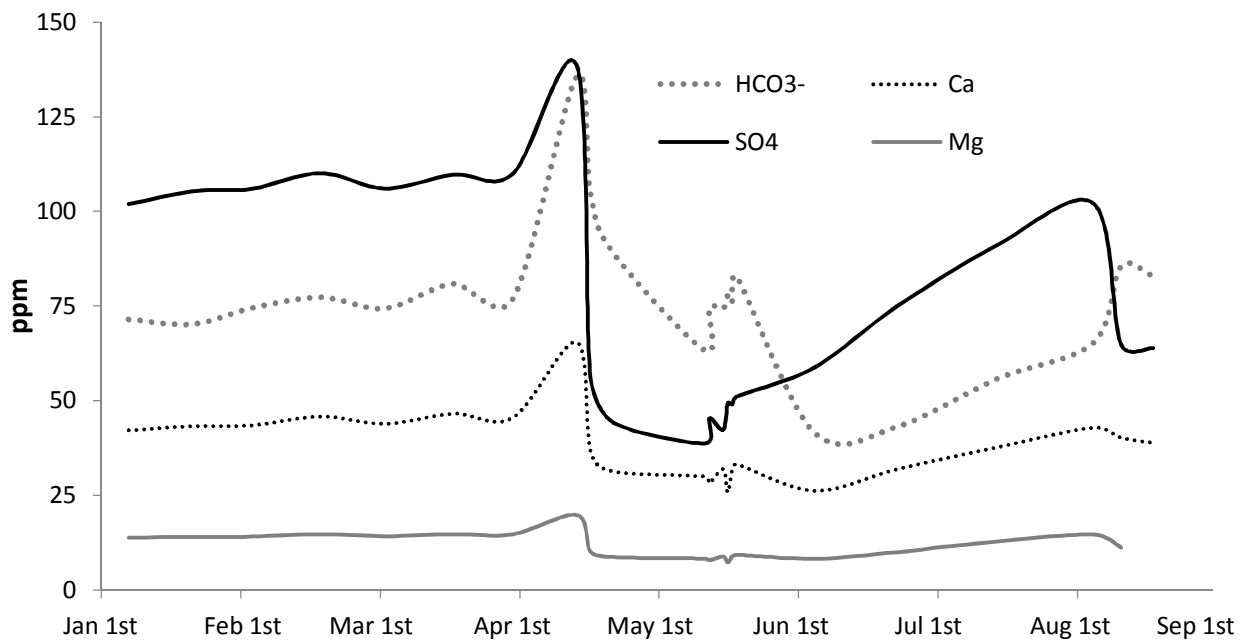


Figure 3 Time series of major solutes including bicarbonate (HCO_3^-), calcium (Ca), sulphate (SO_4^{2-}), and magnesium (Mg) in the North Klondike River during 2014.

4. CONCLUSIONS

Initial findings show an alpine catchment in a discontinuous permafrost area that is strongly dominated by groundwater. Dissolved solutes show no significant changes prior to the river break and spring freshet despite changes in total river discharge during the winter months.

During spring freshet there is a large influx of modern carbon, supported by carbon-14 activities. The months following spring freshet show a tendency for river chemistry to return to baseflow conditions.

REFERENCES

- [1] CAREY S.K., POMEROY J. W., “Progress in Canadian Snow and Frozen Ground Hydrology, 2003-2007”, Canadian Water Resources Journal, Vol: 34(2) (2009) 127-138.
- [2] WOO M.K., KANE D.L., CAREY S.K., YANG D., “Progress in Permafrost Hydrology in the New Millennium”, Permafrost and Periglacial Processes. 19: (2008) 237-254.
- [3] MUSKETT R.R., ROMANOVSKY V.E., “Groundwater storage changes in arctic permafrost watersheds from GRACE and *in situ* measurements”, Environmental Research Letters. 4 (2009) 045009 (8pp)

CYCLING OF ^{129}I IN A DISCONTINUOUS PERMAFROST WATERSHED: INSIGHTS FROM MULTIVARIATE STATISTICS AND THE POTENTIAL OF ^{129}I AS A TRACER

M. N. HEROD, T. LI, I. D. CLARK

André E. Lalonde Accelerator Mass Spectrometry Lab, Department of Earth Science, University of Ottawa, Advanced Research Complex, 25 Templeton St. Ottawa, Ontario, Canada

E-mail address: mattherod@gmail.com

1. OBJECTIVES

The objective of this work was to understand potential changes in the source of ^{129}I (half-life: 15.7 million years) in discharge over time, identify the role of ^{129}I in geochemical cycles and discover any other isotopes or elements that could be used to complement our understanding of the behaviour of ^{129}I in the watershed. Once the geochemical cycle and sources of ^{129}I have been clarified it may be possible to use it as an isotopic tracer in hydrograph separation or characterization of catchment flow paths. Furthermore, as a mobile, long lived fission product in nuclear waste a clear understanding of the cycle of ^{129}I is essential to predicting its behaviour and accurately assessing the risk of long term radioactive waste disposal.

2. SITE DESCRIPTION AND SAMPLING

The Wolf Creek Research Basin (WCRB) is a discontinuous permafrost watershed located near Whitehorse, Yukon and is a tributary to the Yukon River. Figure 1 shows the boundaries of the WCRB. The watershed is 195 km² and the discharge at the Wolf Creek outlet typically ranges from a minimum of 0.4 m³/s to a peak of 10 m³/s during spring freshet [Janowicz *et al.*, 2004]. The climate of WCRB is highly variable and temperatures range from -40°C to 25°C throughout the year with a mean annual temperature of -3°C. The mean annual precipitation is 300 to 400 mm/year with ~40% of this falling as snow [Janowicz *et al.*, 2004]. The bedrock geology of the WCRB is primarily sedimentary with limestone, sandstone, siltstone and conglomerate all present. There is also a large intrusion of andesite and basalt within the watershed (Israel *et al.*; Janowicz *et al.* 2004). Sampling of discharge began just prior to freshet in late April and concluded after freeze up in 2012. Precipitation samples were also collected over the course of the summer and soil was collected throughout the watershed. All samples were analyzed for ^{129}I and numerous other analytes, including stable isotopes, $^{14}\text{C}_{\text{DIC}}$, ^3H , cation and anions. Physical hydrology data was also collected for Wolf Creek discharge. $^{14}\text{C}_{\text{DIC}}$ and ^{129}I analyses were performed using the new 3MV accelerator mass spectrometer and other instruments at the University of Ottawa's André E. Lalonde Laboratory.

3. RESULTS

The large number of samples and analytes yielded a very complex dataset that made it difficult to distinguish the effect of hydrologic process and temporal relationships between analytes, particularly ^{129}I . In order to reduce the dataset and reveal the behaviour of ^{129}I principal components analysis (PCA) was used [Vega *et al.*, 1998; Güler *et al.*, 2002]. ^{129}I was not included in the PCA as this allows its temporal variation to be compared to the results more easily. PCA identified three water sources with distinct chemistry contributing to

Wolf Creek discharge. The first PC represents a groundwater end member with high concentrations of mineral weathering ions such as Ca, Na, Mg, Sr, Si, SO₄ and DIC. The second PC is a freshet end member that includes ¹⁸O, ²H and discharge, which suggests it is partially composed of snowmelt. However, the K:Ca ratio is also grouped into this PC suggesting that shallow soil drainage is also a significant part of this water end member as would be expected during freshet in a sub-arctic watershed [Carey *et al.*, 2012]. The third PC includes ¹³C_{DOC}, DOC and ¹²⁷I and is also identified as a soil water component. A relationship between ¹²⁹I concentration, time elapsed and the principal components was observed from the results suggesting that hydrological process and geochemistry in the watershed greatly affect ¹²⁹I sources in discharge (Figure 2).

Agglomerative hierarchical clustering (AHC) was then performed on the dataset to reveal the temporal relationships between the samples and corroborate the qualitative observations of PCA. AHC results show that samples are organized into three groups, each representing a distinct change in Wolf Creek water chemistry over time. This confirms that the conclusions made by PCA are robust and clarifies the effect of differing water sources on sample chemistry. Time constraints were placed on the influence of each water source in Wolf Creek discharge as it transitioned from groundwater dominated to shallow soil drainage and snowmelt as the temperature warmed and then to precipitation and groundwater for rest of the sampling period.

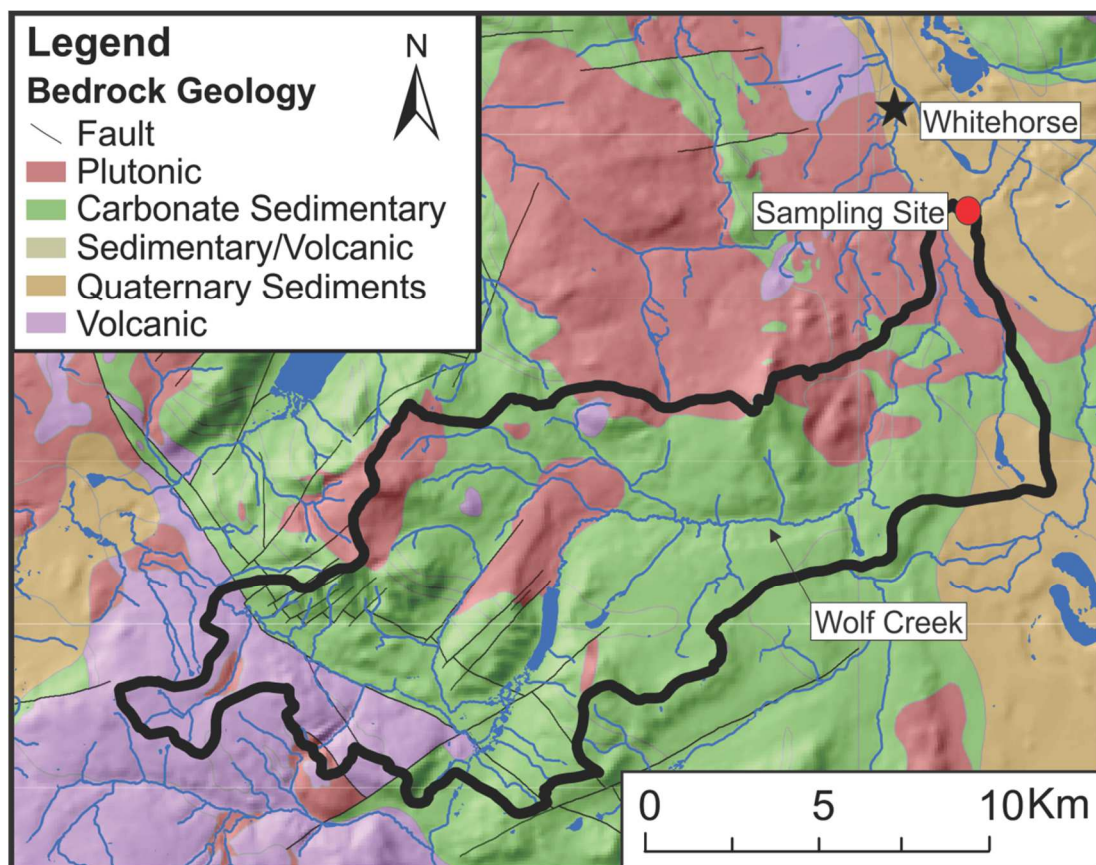


Figure 1: Hillshade map showing the boundaries of the Wolf Creek Research Basin and rock types within the watershed.

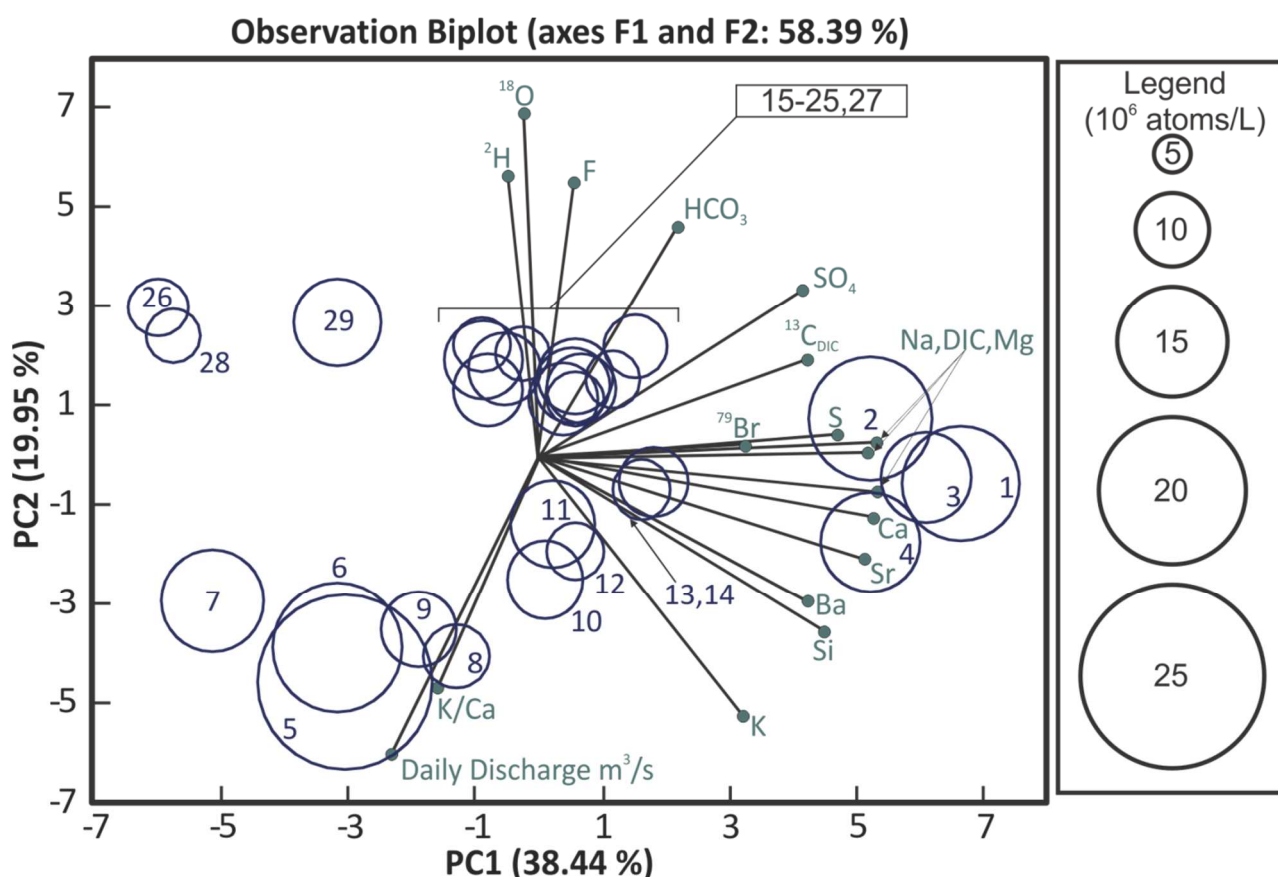


Figure 2: Observation biplot of PC1 vs. PC2 showing relative relationships between the analytes and the samples. The groupings of samples according to their chemistry is distinct as Wolf Creek evolved as samples 1-4, 5-10 and 11-27 are related. Bubble size corresponds to the concentration of ^{129}I in each sample. The legend provides scale. Sample numbers are pictured in the graph. The biplot arms begin at the origin.

The evolution of water sources to Wolf Creek over the sampling period have had a large effect on ^{129}I concentrations (Figure 2) showing that ^{129}I , which is often considered to be independent of many geochemical cycles, is in fact intrinsically linked to watershed hydrology and geochemistry as a labile fraction exists in soil water. This finding means that ^{129}I has excellent potential as a new water flow path tracer and expands our understanding about the far field behaviour of ^{129}I in the environment. Measurements of other analytes such as Ca , ^{14}C , ^{18}O , ^2H and the $\text{K}:\text{Ca}$ molar ratio corroborate this observation.

The mass flux and storage of ^{129}I was also estimated based on the influx of ^{129}I from snowfall and precipitation and the measured efflux from the Wolf Creek discharge. A mass balance suggests that there is a positive input of ^{129}I of $\sim 1.4 \times 10^{18}$ atoms/yr for the watershed, which represents 75% of the ^{129}I deposited. Soil samples measured for ^{129}I have a very strong linear correlation with the organic carbon content indicating that much of the excess ^{129}I is stored within organic soils in the watershed.

4. CONCLUSIONS

The hydrogeochemistry of the Wolf Creek Research Basin was characterized for an entire summer season in the context of the mobility and behaviour of ^{129}I . The large dataset was analyzed using multivariate statistical methods and four water sources contributing to Wolf Creek discharge were identified: groundwater, soil water, snowmelt and precipitation.

Temporal trends in water chemistry were also identified using clustering analysis and these trends corroborate the qualitative sample relationships revealed by PCA. ^{129}I behaviour was shown to be sensitive to numerous chemical and physical processes within the watershed suggesting that it has potential as a tracer of water flow paths and may be useful as a tool for hydrograph separation. The mass input and the output of ^{129}I were characterized and it was determined that the watershed acts as a net sink for ^{129}I , due to adsorption in organic rich soils.

REFERENCES

- [1] CAREY, S. K., J. L. BOUCHER, C. M. DUARTE (2012), Inferring groundwater contributions and pathways to streamflow during snowmelt over multiple years in a discontinuous permafrost subarctic environment (Yukon, Canada), *Hydrogeol. J.*, 21(1), 67–77
- [2] GÜLER, C., G. D. THYNE, J. E. MCCRAY, K. A. TURNER (2002), Evaluation of graphical and multivariate statistical methods for classification of water chemistry data, *Hydrogeol. J.*, 10(4), 455–474,
- [3] ISRAEL, S., M. COLPRON, C. ROOTS, T. FRASER (n.d.), *Overview of Yukon Geology by Ancestral North America (Laurentia)*.
- [4] JANOWICZ, J. R., N. HEDSTROM, J. POMEROY, R. GRANGER, S. CAREY (2004), Wolf Creek Research Basin water balance studies, *North. Res. Basins Water Balanc.*, 290(March), 195–204.
- [5] VEGA, M., R. PARDO, E. BARRADO, L. DEBÁN (1998), Assessment of seasonal and polluting effects on the quality of river water by exploratory data analysis, *Water Res.*, 32(12), 3581–3592

ID: 296

A CLASSICAL WATER BALANCE OF THE IBERÁ WETLAND VALIDATED BY GRACE SATELLITE DATA

A. VALLADARES,

Subsecretaría de Recursos Hídricos, Esmeralda 241, Piso 10^{mo}, Buenos Aires, Argentina.

E-mail address: andrea.valladares@gmail.com.

L. RODRÍGUEZ

Facultad de Ingeniería y Ciencias Hídricas, Universidad Nacional del Litoral, Santa Fe, Argentina

L. GUARRACINO

Observatorio Astronómico, Universidad Nacional de La Plata, La Plata, Argentina.

L. VIVES

Instituto de Hidrología de Llanuras, Universidad Nacional del Centro de la Provincia de Buenos Aires, Azul, Argentina

Abstract: The Iberá is an extensive wetland located on Corrientes Province, Argentina, where marshes and wetlands interconnect large lagoons joined by water courses. A great portion of the area is devoted to natural resources conservation. The Iberá water region, shown in Figure 1, extends for some 14000 km², with a regional NE-SW surface flow direction. The groundwater component of the water balance constitutes the biggest unknown of the hydrologic functioning of the system due to a complete lack of piezometric data. Due to this limitation, it has been generally disregarded in previous studies. In this work, the existence of a groundwater component contributing to storage variations in the Iberá wetlands is postulated, though it is a secondary component compared to the predominant surface contribution to the hydrology of the area. The contribution of the groundwater component to the water balance was analyzed comparing wetlands storage variations calculated by means of two completely independent methodologies. The first consists on calculating those variations through a classical water balance without explicitly contemplating a groundwater contribution. The calculation of each water balance components was carefully validated [1]. Those variations are later compared with data provided by a satellite technique which detect water storage variations without making a distinction between surface or groundwater origin. The Gravity Recovery and Climate Experiment (GRACE) satellite mission used in this work, whose representativeness to calculate water storage in the region was previously tested [2], has a regional scale resolution, which makes it suitable for this large area, providing data from August, 2002. Therefore, storage differences obtained by these two methodologies can be interpreted as groundwater contributions to the water balance. According to the water balance, almost all years analyzed present a negative storage variation, even if evapotranspiration estimations are considered very low compared to the expected values for a wetland of these characteristics. Storage variations estimated with GRACE were stable during the satellite data period. Consequently, the comparison between the monthly storage variation trends obtained with both methodologies highlights a groundwater contribution of around 500 mm per year to the wetlands. The mean annual value of precipitation, surface runoff and evapotranspiration were 1464 mm, 410 mm and 1570 mm, respectively. Groundwater contribution to the water balance of the wetlands will be validated by means of hydrochemical and isotopic analysis of surface as well as groundwater samples.

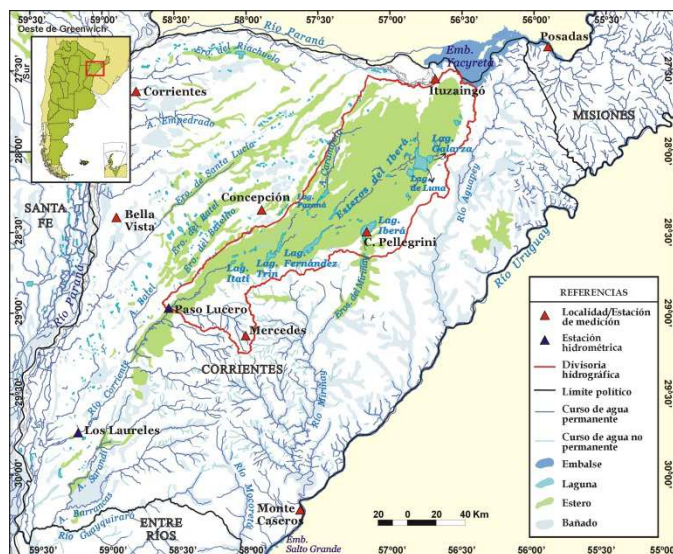


Figure 1. Location map of the Iberá wetlands.

REFERENCES

- [1] VALLADARES A.I. , RODRÍGUEZ L.B., GUARRACINO L., VIVES L.S. Análisis de Sensibilidad del Balance Hídrico a la Evapotranspiración en los Esteros del Iberá, Argentina. Proc. 2nd International Conference on Flatland Hydrology. Santa Fe, Argentina (2014). Editors: VENTURINI V., RODRÍGUEZ L. , CELLO P. E-book ISBN 978-987-692-039-1.
- [2] VALLADARES A.I., GUARRACINO L., RODRÍGUEZ L.B., VIVES L.S. Estimación de las Variaciones de Almacenamiento de Agua en los Esteros del Iberá a partir de Datos Gravimétricos Satelitales. GONZÁLEZ N., KRUSE E., TROVATTO M., LAURENCENA P. (eds.). Temas actuales de la hidrología subterránea 2013. Pág. 213:218. La Plata, EDULP (2013).

ID: 302

STREAMFLOW COMPONENT SEPARATION BY TRACER AND NON TRACER METHODS

M. K. STEWART,
GNS Science, PO Box 30 368, Lower Hutt, New Zealand
E-mail address: m.stewart@gns.cri.nz

Abstract: Tracers such as stable isotopes or chemicals continue to show that baseflow (groundwater) plays an active and often dominating role in streamflow generation, and in fact is surprisingly responsive to rainfall. Accepting this tracer evidence leads to a novel baseflow separation filter (the ‘bump and rise’ method or BRM filter) that can be applied to streamflow data of any time-step to extract the baseflow component. Application of the BRM filter to three New Zealand catchments is described below.

1. INTRODUCTION

Tracers have been used for over forty years to separate hydrographs into different flow components, commonly time source components (e.g. event and pre-event components), or geographic source components (i.e. components sourced from different parts of the catchment). The use of tracers produced a paradigm shift in thinking about runoff generation since they often showed that baseflow water dominated storm hydrographs, in addition to the lower flow periods between events.

A wide variety of non-tracer (mainly hydrometric) tracer methods of hydrograph separation have been used for much longer and continue to be used in practical applications. Among the most recently proposed methods are recursive digital filters that are applied to the streamflow record to extract the baseflow hydrograph (e.g. Eckhardt, 2005). This presentation presents a new digital filter whose shape is based on tracer separations, i.e. a digital filter that produces separations that mimic tracer separations more accurately than previous filters.

2. METHODS

The new baseflow separation method (hereafter called the bump and rise method or BRM) has an algorithm chosen to simulate tracer separations simply but accurately (Stewart 2014). Tracer separations show rapid baseflow responses to storm events (the “bump”), which is followed in the method by a steady increase (the “rise”). The steady rise is justified by increase in catchment wetness conditions and gradual replenishment of groundwater aquifers during rainy periods. The size of the bump (f) and the slope of the rise (k) are parameters of the BRM recursive digital filter that is applied to the streamflow record. The separation procedure is described by the equations:

$$\begin{aligned} B_t &= B_{t-1} + k + f(Q_t - Q_{t-1}) & \text{for } Q_t > B_{t-1} + k \\ B_t &= Q_t & \text{for } Q_t \leq B_{t-1} + k \end{aligned}$$

where f is a constant fraction of the increase or decrease of streamflow during an event. The values of f and k can be determined from tracer measurements, or if no tracer information is available, can be determined by an optimization process (Stewart, 2014). A feature of the BRM filter is that two types of baseflow response are included, a short-term response via the bump and a longer-term response via the rise.

3. RESULTS

Glendhu Catchment, Otago, NZ. The BRM filter was calibrated by fitting to tracer data, because deuterium measurements had been used to separate event and pre-event waters in the storm hydrograph (Bonell et al., 1991). The filter was fitted to the pre-event water component (Fig. 1a). A good fit is obtained (better than those obtained by other methods, Stewart 2014). Note that the BRM filter gives an event/pre-event water separation rather than a baseflow/quickflow separation, when it is calibrated in this way. The BFI (i.e. baseflow index = pre-event index for this catchment) was 0.78 for the streamflow record in 1996 (Fig. 1b).

Toenepi Catchment, Waikato, NZ. The BRM filter was applied to separate three components in the hydrograph (Fig. 2a) using the optimization method. Tritium and silica concentrations were used to identify three components in the streamflow (Morgenstern et al., 2010), and Fig. 2b shows tritium versus silica concentrations in a bivariate mixing diagram that identifies the flow components as end members: quickflow (A), fast groundwater (C) and slow groundwater (D). These components are then used to simulate the nitrate-N concentration in the stream (Fig. 2c), assuming that they have constant nitrate-N contents. Fig. 2c compares the continuous simulation of nitrate-N (based on combining the components) with nitrate-N measurements on the streamflow. The simulation results are similar to those obtained by a catchment modelling method (Woodward et al., 2011).

Tutaeuaua Catchment, Taupo, NZ. The BRM filter was applied to the Tutaeuaua runoff by optimizing the fit of the “sum” of the BRM baseflow and fast recession to the streamflow (Fig. 3a, Stewart 2014). The BRM baseflow for the 2007 discharge is given in Fig. 3b. In contrast to the other catchments, the bump fraction f obtained by fitting is very small (Table 1, Fig. 3a). Tritium measurements were available for a period of eight years for this catchment, and the BRM baseflow separation is useful in determining the makeup of the streamwater when the samples were collected since the baseflow and quickflow have very different tritium concentrations.

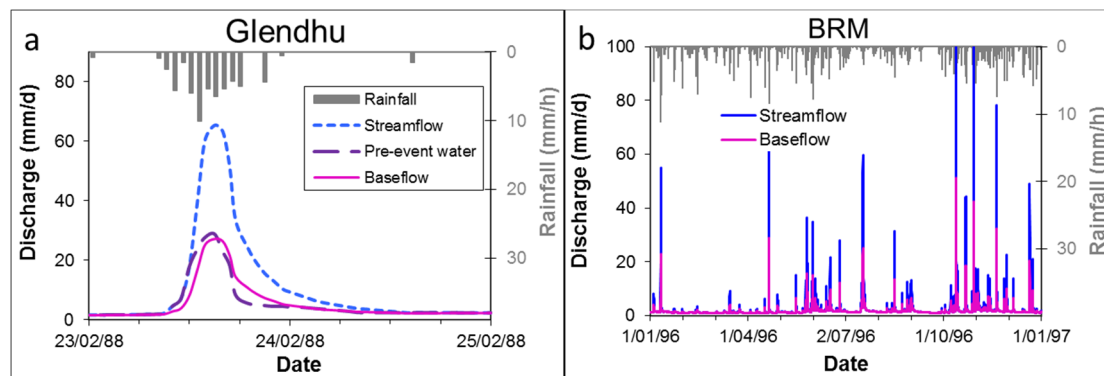


Fig. 1a, b. BRM pre-event water separation at Glendhu Catchment.

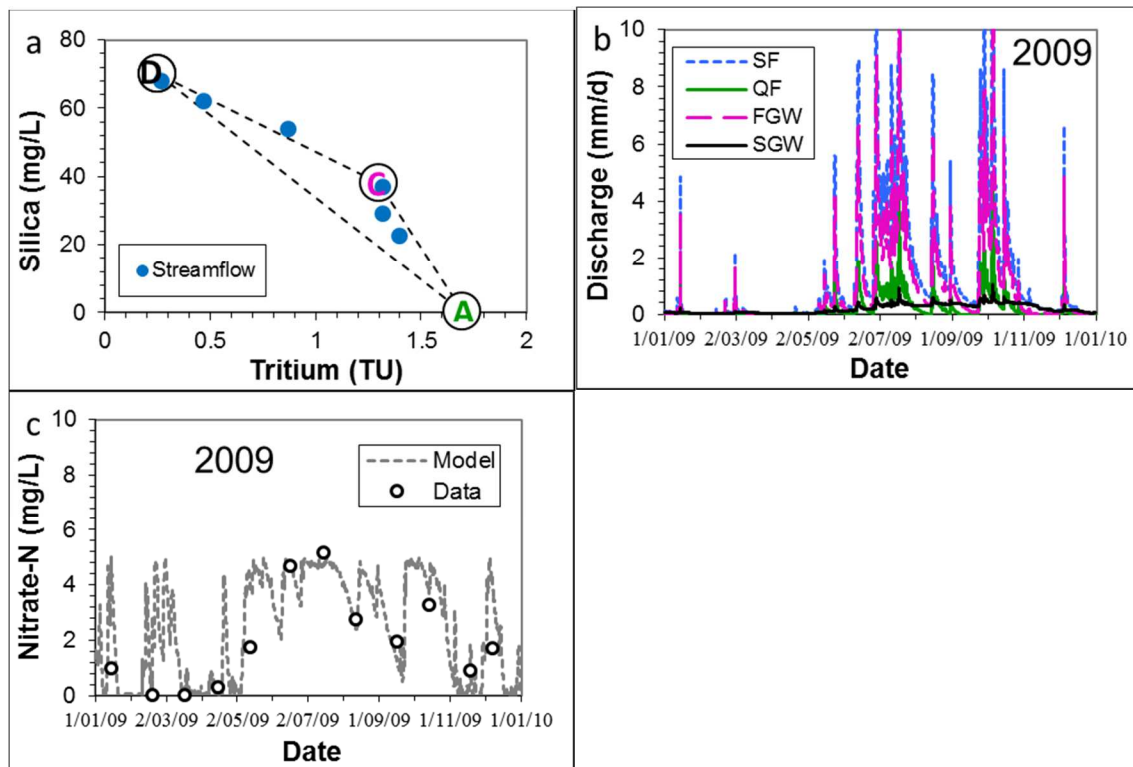


Fig. 2. Results for Toenepi Stream. (a) Bivariate mixing diagram between tritium and silica concentrations in streamflow. (b) Three component BRM separation of the streamflow hydrograph in 2009. (c) Measured and simulated nitrate concentrations in the stream in 2009. The simulation is based on the BRM component separations.

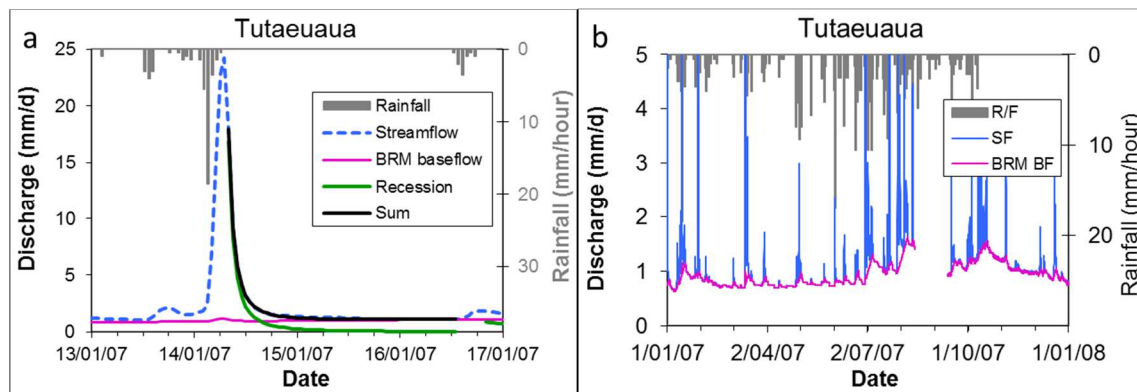


Fig. 3a, b. Application of the BRM baseflow separation method to the Tutaeuaua Catchment.

Table 1 gives information on the studied catchments and the parameters derived by fitting the BRM filter to the tracer separations or streamflow. The catchments are of similar scale, and have similar BFIs. However, the bump fraction f varies greatly, from 0.78 for baseflow at Toenepi (this includes both the fast and slow groundwater components) to 0.01 for baseflow at Tutaeuaua. This means that at Toenepi most of the storm peak is composed of baseflow (actually the fast groundwater), while at Tutaeuaua almost none of it is. This extreme difference in catchment response is considered to be due to the different subsurface permeability structures of these two catchments.

Table 1. Catchment information and BRM filter parameters for the studied catchments. f is the bump fraction, k the slope of the rise, and BFI the ratio of baseflow to streamflow.

Catchment	Rock type	Area km ²	f	k mmd ⁻¹ h ⁻¹	BFI
Glendhu	Schist	2.18	0.4	0.009	0.78
Toenepi	Volcanic ash	15.1	0.78	0.00006	0.83
Tutaeuaua	Volcanic ash	4.73	0.01	0.0029	0.83

4. CONCLUSIONS

The BRM filter for separating hydrograph components is based on mimicking the shape of the baseflow shown by tracer separations. It can be applied with or without tracer data, but if no tracer data is available, there is a subjective element in the application as with all baseflow separation methods except for the tracer method. The three case studies presented here indicate the variety of applications of the method and the wide variation in catchment responses.

REFERENCES

- [1] BONELL, M., PEARCE, A.J., STEWART, M.K., Identification of runoff production mechanisms using environmental isotopes in a tussock grassland catchment, Eastern Otago, New Zealand, *Hydrol. Process.* **4** (1990) 15.
- [2] ECKHARDT, K., How to construct recursive digital filters for baseflow separation, *Hydrol. Process.* **19** (2005) 507.
- [3] STEWART, M.K., New baseflow separation and recession analysis approaches for streamflow, *Hydrol. Earth Syst. Sci. Disc.* **11** (2014) 7089.
- [4] WOODWARD, S.J.R., STENGER, R., BIDWELL, V.J., Dynamic analysis of stream flow and water chemistry to infer subsurface water and nitrate fluxes in a lowland dairying catchment, *J. Hydrol.* **505** (2013) 299.

ID: 315

MULTI-DECADAL OBSERVATIONS OF WATER ISOTOPES IMPACTING THE URBAN SALT LAKE VALLEY (USA) – FROM MONTANE SOURCES THROUGH TAPWATER TO THE GREAT SALT LAKE TERMINUS

J.R. EHLERINGER, J.E. BARNETTE, B.J. TIPPLE, G.J. BOWEN
University of Utah, Salt Lake City, Utah USA 84112
E-mail address: jim.ehleringer@utah.edu

Abstract: For the past three decades, we have quantified the stable isotopes of water as it moves in various forms through a coupled natural-human landscape, from its montane source through regions of human activity and terminating in an interior closed basin. Within the Salt Lake Valley USA, a rapidly growing population of now more than one million individuals depend on these surface waters from the adjacent Wasatch and Uinta Mountains as their primary water resource for culinary and industrial needs. We have measured the stable isotope ratios of the hydrologic system's primary components: precipitation, surface waters, tap waters, atmospheric waters, and terminus waters. Here we present an overview of the annual and interannual stable isotope ratio dynamics of these waters and of the changes in isotopic composition that occurred spatially and temporally as water moved through this coupled natural-human system.

1. INTRODUCTION

Water is a valuable resource for human development and sustainability, especially in arid regions. Historically in the driest regions of the western USA, it was common to find populations settling and developing closest to a reliable water montane source. Over the past century, the development of long-distance water conveyances has altered this settlement pattern in some places, allowing megapolitan regions, such as Los Angeles and Phoenix, to develop as well. In the very arid state of Utah (USA), the long distance transport of water into the region was not historically available. As a consequence, we find nearly 90% of the state's 2.9 million population are clustered in only a few valleys immediately adjacent to the Wasatch and Uinta Mountains of northern Utah. In the largest of these valleys, the Salt Lake Valley (SLV), more than one million individuals depend on adjacent mountains as their primary water resource for culinary, industrial and agricultural needs. To a lesser degree, both agricultural needs and some of the communities within the SLV also utilize groundwater that has been recharged by these same montane systems.

The SLV lies within the Great Basin, an extensive interior basin where precipitation inputs flow into one of several closed saline basins or lakes. This situation provides an unusual opportunity to describe a more complete isotope hydrologic cycle, capturing inputs and outputs as well as the consequences of changes in both environmental and population drivers influencing hydrological components. For the SLV, precipitation falling in the Wasatch and Uinta Mountains terminates in the Great Salt Lake, resulting in a flow path of less than 200 km. Over the past three decades, we have collected incoming precipitation, surface waters, tap waters, atmospheric waters, and terminus waters for this coupled natural–human hydrologic system. Here we present an overview of the annual and interannual dynamics.

2. METHODS

We have sampled (a) precipitation, (b) surface waters entering into the SLV, (c) surface and tap waters within the SLV, and (d) the Great Salt Lake. Water samples were collected and stored in glass vials sealed with hand tightened, lined caps. Parafilm was used to seal the cap-vial interface to reduce the probability that the cap loosens during transport or storage. Once collected water samples were stored in a refrigerator until analysis. Over 4,500 observations are contained within the dataset, including both single-observations and temporal collections. The first collections were made in July 1988 and sampling continues through the present. A total of 126 different locations have been sampled, with 34 of these locations having been sampled >15 times (Figure 1). Since 2004, 14 of the SLV locations and 1 Great Salt Lake location have monitored on a bi-weekly to monthly basis.

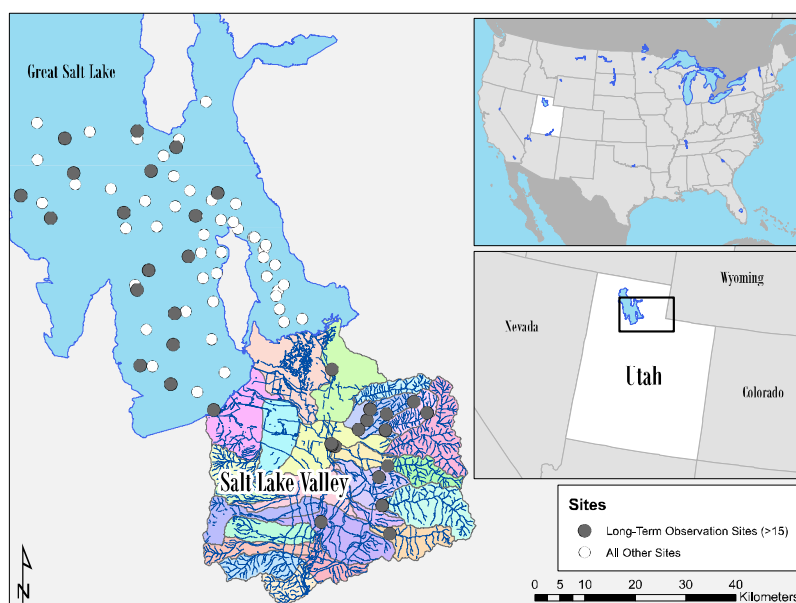


Figure 1. A map of the Great Salt Lake and the natural and urbanized landscape of the SLV and Wasatch Mountains where waters in this study have been collected for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ analyses.

All water samples have been analyzed for stable isotope ratio analyses at the Stable Isotope Ratio Facility for Environmental Research at the University of Utah (<http://sirfer.utah.edu>). Over three decades, SIRFER has progressed through multiple approaches to measure the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of water. For $\delta^2\text{H}$ analyses using IRMS analytical instrumentation, these have included zinc reduction [1] and pyrolysis [2] preparation approaches. For $\delta^{18}\text{O}$ analyses using IRMS analytical instrumentation, these have included $\text{CO}_2/\text{H}_2\text{O}$ equilibration [3] and pyrolysis [2] preparation approaches. Over the last four years, all water samples have been analyzed using a Picarro cavity ring-down spectrometer [4]. Data are expressed using δ -notation with a 2 end-member correction with laboratory reference materials that have been calibrated against IAEA reference standards. Each analytical run included blind samples of QAQC water reference materials, which indicated that the long-term analytical precision was $\sim 1\text{‰}$ for $\delta^2\text{H}$ and $\sim 0.2\text{‰}$ for $\delta^{18}\text{O}$ analyses.

3. RESULTS

Observations of incoming precipitation revealed a common meteoric water line at two sampling locations on the east side of SLV; the meteoric water line had both shallower slope and lower d -excess values than observed with the global meteoric water line (Figure 2). The stable isotope ratios of montane surface waters coming into the SLV showed similar values

(Table 1), despite differences in watershed elevations and watershed areas. In contrast, all stream waters ultimately feed into the Jordan River, an 83-km river that conveys water from Utah Lake through the Salt Lake Valley and terminates in the Great Salt Lake.

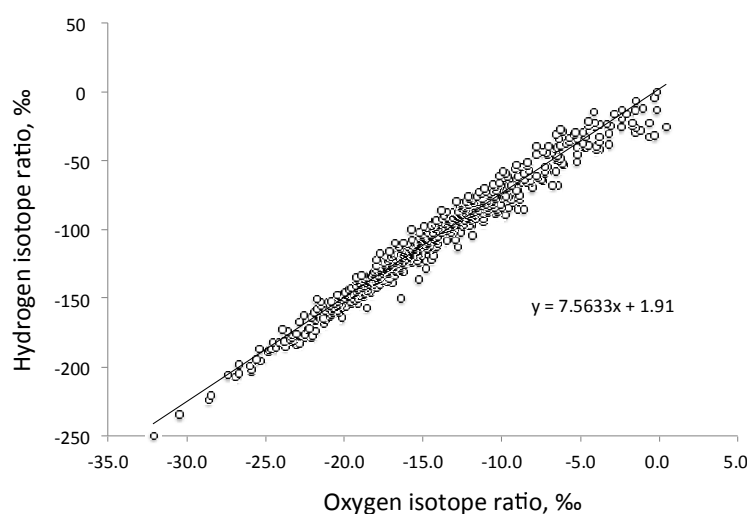


Figure 2. The meteoric water line for precipitation in the Salt Lake Valley based on two sampling locations on the eastern edge of the valley and sampled over a three-decade time period.

As the Jordan River passes through the SLV, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values decrease in value reflecting inputs from both stream and urban inputs (e.g., urban water, storm water, and sewage water). The magnitude of these impacts on the Jordan River is indicated by the directional arrow in Figure 3. Water balance studies have estimated that Utah Lake contributes ~30% of the water into the Jordan River, whereas the remainder is associated with natural and human inputs [5]. As a first approximation, this coupled natural-human inputs into the Jordan River are not quite consistent with the observed decreases in the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values as the river moves through the SLV. While future data may better constrain human inputs into the river system, it is clear that humans are having a large hydro-impact.

Table 1. Average hydrogen and oxygen isotope ratios of incoming stream waters, tap waters, the Jordan River as it passes through the Salt Lake Valley, and the terminus water in the Great Salt Lake.

	n	$\delta^2\text{H}$, ‰	$\delta^{18}\text{O}$, ‰
<i>Incoming Streams</i>			
Big Cottonwood Creek	66	-123.5 ± 4.1	-16.6 ± 0.9
Emigration Creek	154	-123.2 ± 6.8	-16.4 ± 1.3
Little Cottonwood Creek	55	-122.4 ± 4.1	-16.5 ± 0.9
Mill Creek	123	-126.3 ± 2.1	-17.0 ± 0.5
Red Butte Creek	342	-123.1 ± 3.5	-16.3 ± 0.7
<i>Drinking waters</i>			
University tap water	127	-120.3 ± 3.3	-15.8 ± 0.8
Holladay tap water	20	-123.3 ± 2.2	-16.5 ± 0.5
Salt Lake City tap water	5	-124.7 ± 1.2	-16.9 ± 0.2
<i>Jordan River</i>			
2780 South	42	-111.3 ± 6.1	-14.3 ± 1.1
10600 South	130	-92.3 ± 8.6	-10.8 ± 1.6
<i>Terminus</i>			
Great Salt Lake	409	-63.7 ± 11.1	-4.5 ± 2.1

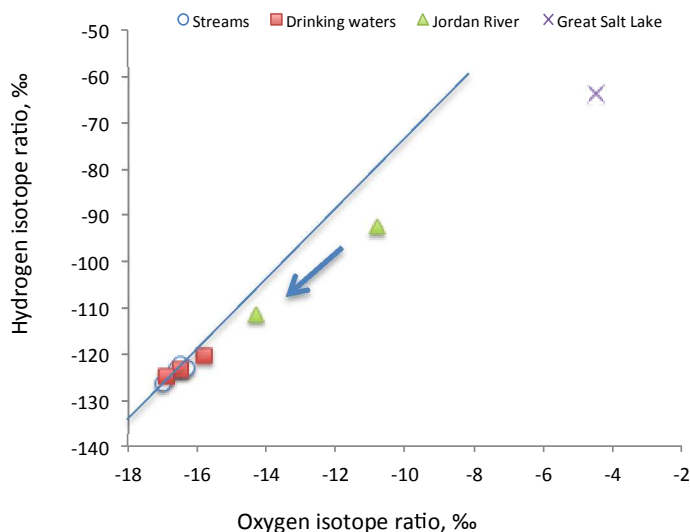


Figure 3. Long-term average hydrogen and oxygen isotope ratios of drinking water sources (montane streams), tap waters, Jordan River, and the Great Salt Lake (basin terminus). Data are from Table 1. Only stream waters and tap waters fall along the local meteoric water line (line in graphic from Figure 2). Note that δ values along the Jordan River increase from the south-to-north direction as indicated by the arrow.

4. CONCLUSIONS

Long-term stable isotope observations of water sources inputs, surface water hydrology, and drinking waters in a couple natural-human urban landscape provide insights on the dynamics of potential human impacts on the hydrological cycle as water moves through an urban system. Our long-term and continuous monitoring of water isotopes within the Salt Lake Valley form the basis of interpreting long-term trends in human impacts on this regional water cycle.

REFERENCES

- [1] COLEMAN, M.C., SHEPHERD, T.J., DURHAM, J.J., ROUSE, J.D., MOORE, G.R., Reduction of water with zinc for hydrogen isotope analysis, *Analytical Chemistry* 54 (1982) 993.
- [2] GEHRE, M., STRAUCH, G., High-temperature elemental analysis and pyrolysis techniques for stable isotope analysis, *Rapid Communications in Mass Spectrometry* 17 (2003) 1497.
- [3] EPSTEIN, S., MAYEDA, T., Variation of O^{18} content of waters from natural sources, *Geochemica et Cosmochimica Acta* 4 (1953) 213.
- [4] BRAND, W.A., GEILMANN, H., CROSSON, E.R., RELLE, C.W., Cavity ring-down versus high-temperature conversion isotope ratio mass spectrometry; a case study on δ^2H and $\delta^{18}O$ of pure water samples and alcohol/water mixtures, *Rapid Communications in Mass Spectrometry* 23 (2009) 1879.
- [5] CIRRUS ECOLOGICAL SOLUTIONS LC, Stantec Inc., Jordan River TMDL: Work Element 2 – Pollutant Identification and Loading, Utah State Division of Water Quality (2009), 160 p.

ID: 337

APPLICATION OF THE RATIO OF TRITIUM CONCENTRATIONS IN PRECIPITATION/SURFACE WATER RATIOS TO ESTIMATE TIMESCALES FOR HISTORICAL SURFACE WATER TRITIUM DATA

R. L MICHEL,

US Geological Survey, 345 Middlefield Dr., Menlo Park, CA USA 94025

E-mail address: rlmichel@usgs.gov

P. AGGARWAL, L. ARAGUAS-ARAGUAS,

Isotope Hydrology Section, International Atomic Energy Agency, Vienna, Austria

B. NEWMAN

Earth & Environmental Sciences Division, Los Alamos National Laboratory, Los Alamos, NM USA 87545

Abstract: Tritium has shown itself to be a useful tracer of the timescale of physical processes in the hydrosphere. There are many small tritium data sets over limited timescales that have generally received limited attention because of the size of the data sets and short time over which measurements are made. Here, we use the ratio of tritium concentrations in precipitation versus the concentrations in surface water C_p/C_r to obtain age estimates for surface waters from several small data sets located in Central Colorado and collected from the early 1970s to the mid-1990s. This approach tends to normalize the data and make it possible to obtain useful timescale information. Using IAEA precipitation data for C_p , age estimates for these waters varied from 2 to more than 20 years, with the oldest ages obtained for some spring samples and the youngest ages obtained for small lakes in the Flattops Wilderness Area.

The value of bomb tritium as a tracer of hydrologic and oceanographic processes has long been recognized [1, 2]. In general it is known that the best data sets for estimating are sets where measurements are made over a long time period at the same location [3]. However, there are many historical measurements that are limited to a short period, frequently only a year or two. Recent work by Michel et al. [4] has shown the value of the use of the ratio of tritium concentrations in precipitation versus the concentrations in surface water C_p/C_r as an indicator of the age of waters that compose surface waters. This utility of this ratio is that it normalizes tritium concentrations so that data from different times and locations can be compared.

Frequently, a small number of measurements of tritium in surface waters are made in programs over a relatively short time frame for research purposes. These measurements are rarely interpreted in any meaningful way. However, the above approach can be applied to small tritium data sets collected during the bomb transient to give estimates of the ages of small sets of surface waters that have collected. An example of the use of this approach is given below. Between 1970 and 2000, a small number of measurements were made of surface waters in the Colorado Rocky Mountains, USA. Tritium concentrations were measured on streams and seeps in the Colorado Rocky Mountains in the mid-1970s, and small lakes and springs in the Flattops Wilderness area on the western side of the Rockies in the early 1990s, all of which ultimately drain into the Upper Colorado River basin. Streams

and tributaries on the eastern side of the Rocky Mountains in the Loch Vale watershed were sampled in the late 1990s. No long-term series are available for these systems, but it is still possible to obtain information about the residence times of the waters that make up these outflows. Using a lumped sum parameter model [5], an estimate of stream water tritium concentrations in these watersheds for various timescales during the tritium transient was obtained. Figure 1 is a plot of the ratio C_p/C_r calculated for timescales of 2, 5, 10 and 20 years in this region of the US. Superimposed on these lines are the C_p/C_r ratio for the small streams and lakes measured in this area during the bomb transient. The stream samples from the 1970s and 1990s were all collected as grab samples. Almost all stream samples have ages that are close to decadal in nature. While these samples come from small mountain streams that are generally thought to have a small sustaining aquifer system which would suggest young water, recently it has been seen in some cases water that composes mountain streams can be decadal in age [6]. A few samples with ratios well over 1 suggest that these streams have a component of very old water that may be pre-bomb in origin. The lake samples are from the Flattops region of Colorado were also grab samples collected from the shore. All these lakes are less than 1 ha in surface area with a maximum depth of 5.5 meters. It can be assumed that they are well mixed. All tritium results indicate that the waters of these lakes are very young, probably less than 2 years in age. These results are supported by ^{35}S studies [7] on these same lakes that indicate that the water in them is largely replaced on a yearly basis. These results show the utility of using the ratio approach to estimate timescales for small sets of historical data.

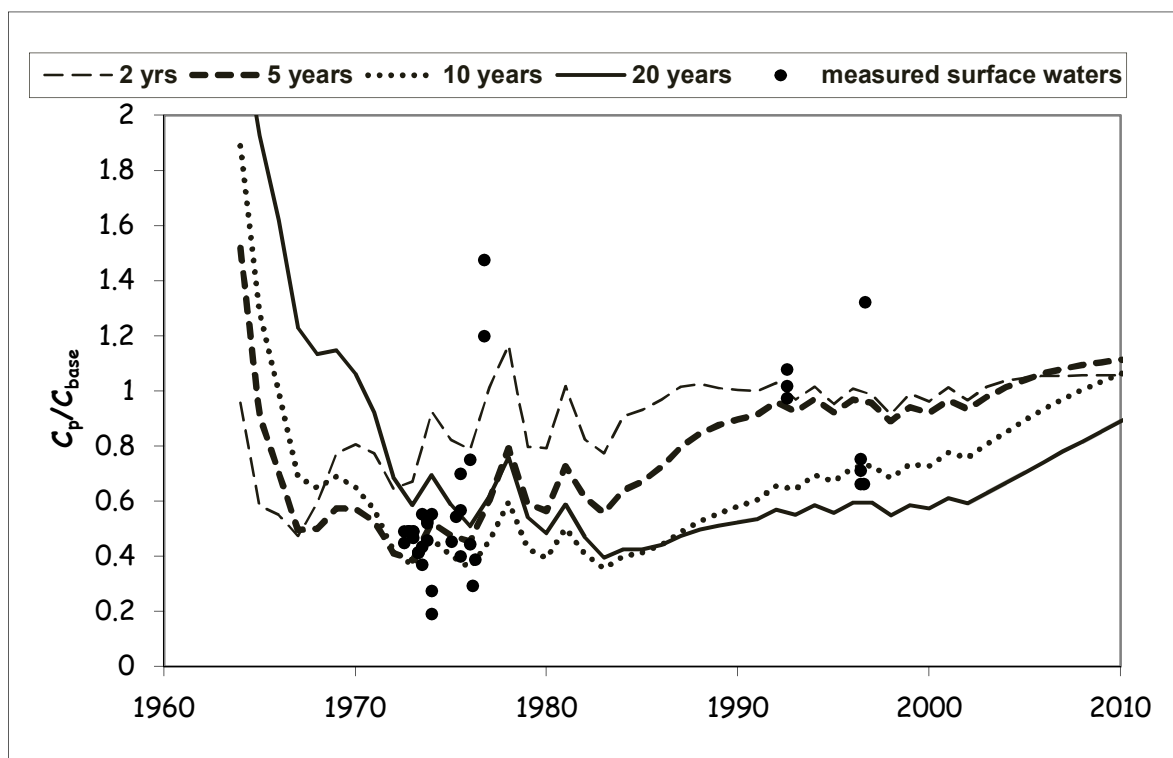


Figure 1. Response of the ratio C_p/C_r for the Central Colorado for residence times of 2-20 years during the tritium transient. Superimposed on the graph are the ratios for samples of springs and small lakes measured during the same period.

REFERENCES

- [1] BEGMMAN, F., LIBBY, W.F., Continental water balance, groundwater inventory and storage times, surface ocean mixing rates and world-wide water circulation patterns from cosmic-ray and bomb tritium, *Geochimica et Cosmochimica Acta* **12** (1957) 277.
- [2] SUESS, H. E., Tritium geophysics as an international research project, *Science* **163** (1969) 1405.
- [3] RANK, D., ALDER, L., ARAGUAS-ARAGUAS, L., FROEHLICH, K., ROZANSKI, K., STICHLER, W., Hydrological parameters and climatic signals derived from long-term tritium and stable isotopes time series of the River Danube. In: *Isotopic Techniques in the Study of Environmental Change*, International Atomic Energy Agency, (1998)191.
- [4] MICHEL, R. L., AGGARWAL, P., ARAGUAS-ARAGUAS, L., KURTTAS, T., NEWMAN, B., D., VITVAR, T., A simplified approach to analysing historical and recent tritium data in surface waters, *Hydrol. Process*, (2014) DOI: 10.1002/hyp.10174
- [5] MALOSZEWSKI, P. ZUBER, A. Determining the turnover time of groundwater systems with the aid of environmental tracers: 1. Models and their applicability, *J. Hydrol.*, **57** (1982) 207.
- [6] RADEMACHER, L.K., CLARK, J.F., CLOW, D.W., HUDSON, G.B., Old groundwater influence on stream hydrochemistry and catchment response times in a small Sierra Nevada catchment, Sagehen Creek, California. *Water Resour. Res.*, **41**, W02004, 10 pp. (2005) doi: 10.1029/2003WR002805.
- [7] MICHEL, R.L., TURK, J.T., CAMPBELL, D.H., MAST, A., Use of natural ³⁵S to trace sulphate cycling in small lakes, Flattops Wilderness Area, Colorado, USA, *Water, Air and Soil Pollution Focus*, **2**, (2002) 5.

ID: 338

ORIGINS OF WATERS IN THE AUSTRALIAN TROPICS USING $\delta^{18}\text{O}$ AND $\delta^2\text{H}$ VALUES

S. TWEED,

Institut de Recherche pour le Développement

E-mail address: sarah.leblanc@ird.fr

M. LEBLANC,

Université d'Avignon et des Pays de Vaucluse, Avignon, France

N. MUNKSGAARD,

James Cook University, Australia

Abstract: The temporal and spatial variations in weather systems recharging tropical Australian waters results in distinct $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values. In the humid tropics, these eastern Australia coastal environments receive annually a higher proportion of south-easterly versus north-westerly rainfall compared with the dry tropical inland systems. As a result, higher $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are observed in groundwater and surface water in the wet tropics compared with the dry tropics. The case study of a catchment that traverses the wet and dry tropics also highlights the seasonal variations in the provenance of waters feeding a large tropical river system. In the remote setting of northern Australia the use of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values to delineate sources of waters is significant in that it provides an additional approach to explore these systems that have been left relatively unexplored.

1. WET VERSUS DRY TROPICS

There remain large knowledge gaps on water dynamics in the tropical environments. In the Australian context this is largely due to the remoteness and challenging field conditions during the wet season. In this study we present observations of the stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) of surface water and groundwater across the Australian tropics, as well as a case study at one site where seasonal variations were analysed.

Across the Australian tropics, between 2011 and 2013 rain water, surface waters (lakes and rivers) and groundwater from wet and dry tropical areas were analysed for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values. From the wet tropics 9 groundwater and 84 surface samples were analysed, and from the dry tropics 41 groundwater and 11 surface water samples were analysed. Mean weighted rainfall samples are the results from 5948 $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values presented in Munksgaard et al. (2012). The collation of stable isotope data (Fig. 1) show that the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in tropical northern Australia are distinct between wet and dry tropical regions. For example, the $\delta^2\text{H}$ values in the wet tropics range from -41.7 to 7.7 ‰ (mean: -24.1 ‰) for surface water and -26.3 to -15.2 ‰ (mean: -22.4 ‰) for groundwater. In comparison, dry tropical values range from -47.9 to -20.0 ‰ (mean: -39.7 ‰) for surface water and -57.0 to -29.7 ‰ (mean: -44.9 ‰) for groundwater (Fig. 1).

$\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of rainfall, surface water and groundwater from the wet and dry tropical areas can potentially vary due to (1) rainout effects from the change in elevation between the elevated rainforest hill slopes in recharge areas of the wet tropics (e.g. 500-1500 mAHD) and the flat recharge area of the dry tropical savanna plains (e.g. 200-500 mAHD); or (2) these

two regions receiving different proportions of rainfall from different weather systems (northwesterly versus southeasterly). If the altitude effect controls variations in $\delta^{18}\text{O}$ values we would expect the savanna region to have waters with mean weighted annual isotope values that are higher compared with the rainforest highlands. For example, from a westerly rainfall system there can be a decrease in rainfall $\delta^2\text{H}$ values of up to -1.5 to -5.0 ‰ over the 1000 m rise in elevation between the savanna to rainforest areas (Clark and Fritz, 1997).

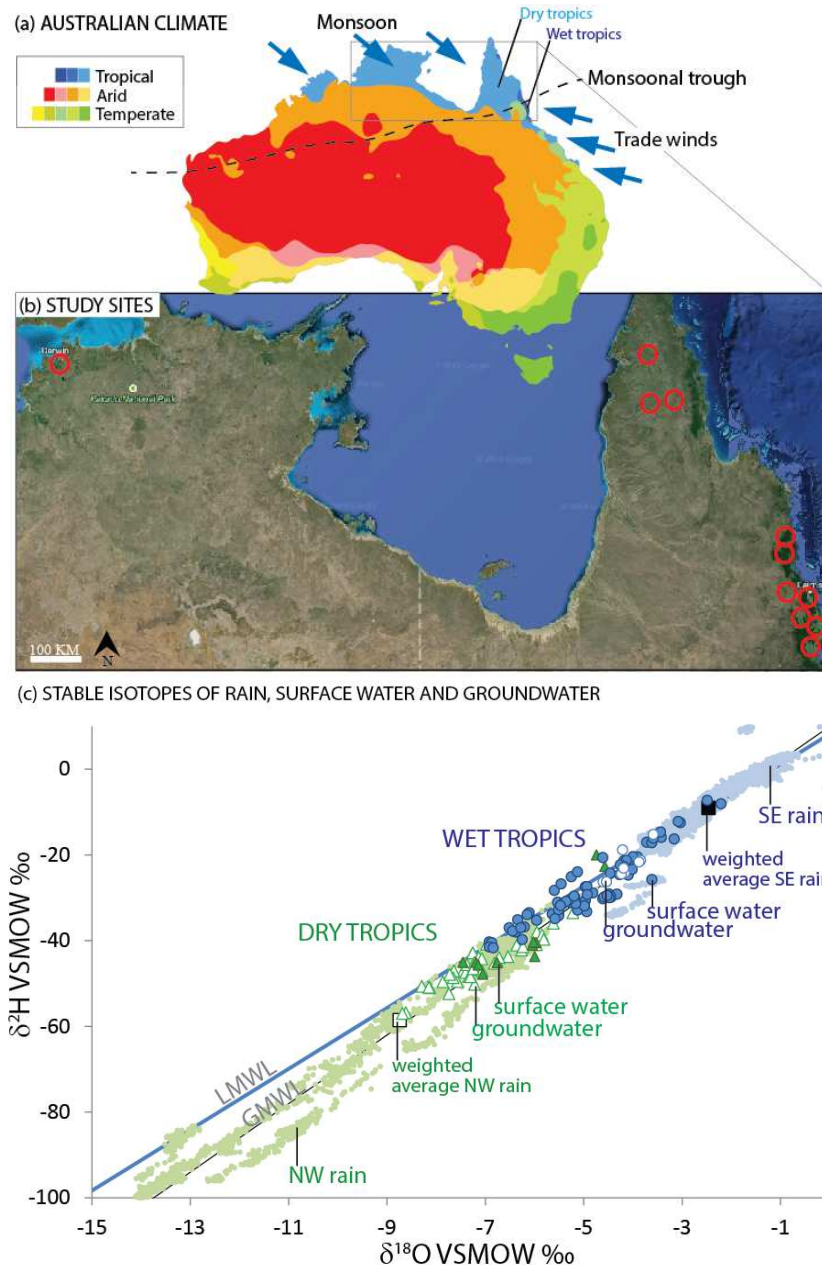


Figure 1. (a) Australian climate zones from the Köppen–Geiger climate map classifications (after Peel et al., 2007), and typical synoptic patterns in summer for northern Australia. (b) Location of sample sites in northern tropical Australia where water samples were collected. (c) Stable isotope results for rainfall (Munksgaard et al., 2012), groundwater and dry season surface water relative to the local (LMWL) and global (GMWL) meteoric water lines.

It is likely these isotope differences are due to differences in rainfall systems, where the savanna groundwater has lower $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values compared with rainforest groundwater because of the occurrence of the monsoonal trough during summer over northern Australia

(Fig. 1). The north westerly rainfall events associated with this trough have travelled great distances over land before arriving in the dry tropical study areas and are therefore subject to rainout effects. As a result, the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of north westerly rainfall events are generally more depleted compared with values of the south easterly rainfall systems. The wet tropics (along the NE Australian coast) receives rainfall from the north westerly monsoon systems, but proportionally more from the south easterly trade winds systems. Additional work is required to determine if the isotopic signatures in the waters are also affected by differences in the residence times of the atmospheric moisture between the monsoonal and southeasterly rainfall events (e.g. Aggarwal et al., 2012). The north westerly monsoon systems has much more convective activity (lower residence time) than the south easterly trade winds systems, which leads to a higher condensation height and therefore higher fractionation and lower rainfall deltas. Also, convection cells are often associated with widespread stratiform rain that can have even lower deltas (Kurita et al., 2011).

2. CASE STUDY: MITCHELL RIVER

In the Mitchell River, located in tropical north eastern Australia (Fig. 2), intense rainfall periods during the wet season and extensive flooding are followed by many months of dry conditions. These conditions result in significant seasonal variability in surface water fluxes and large groundwater elevation fluctuations. The Mitchell River traverses two distinct geographical provinces; wet tropical rainforest hill slopes and dry tropical savanna plains, and has strong seasonal variations in river discharge between the wet and dry seasons. The difference in wet and dry tropical water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures implies that these isotopes can be used to distinguish the provenance of waters in catchments that traverse the wet and dry tropics. In this case study the relative inflows to the Mitchell River from the rainforest versus savanna regions were analysed.

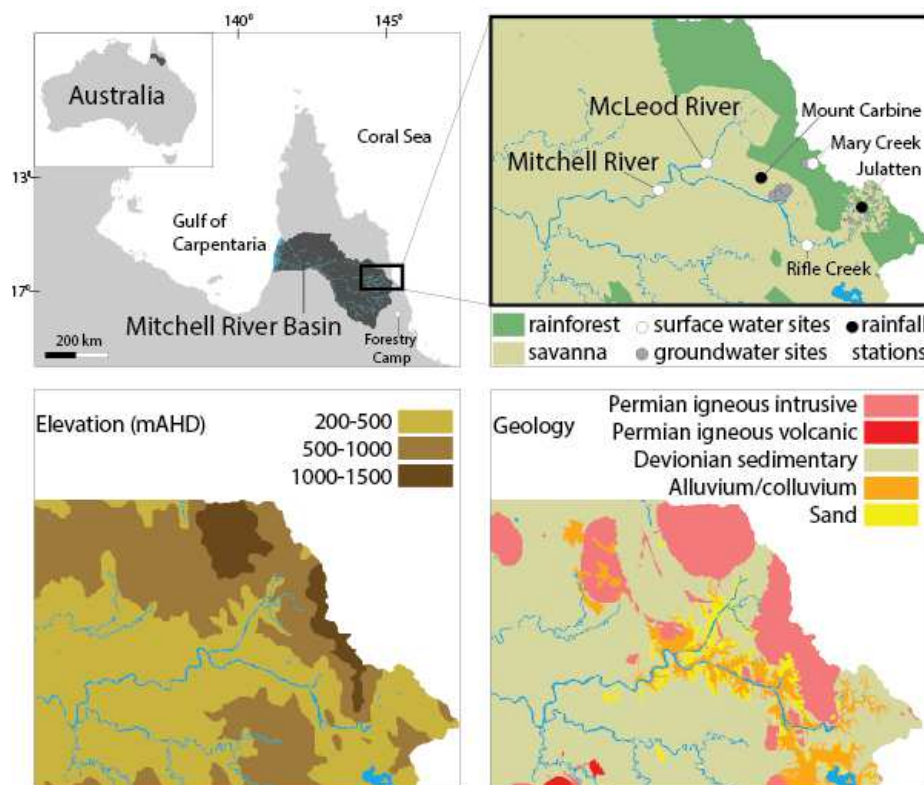


Figure 2. Location of Mitchell River Basin in northeastern Australia, locations of surface water and groundwater sampling sites, rainfall station locations, land use, elevation ranges in meters Australian Height Datum (mAHD) and geology of the study area.

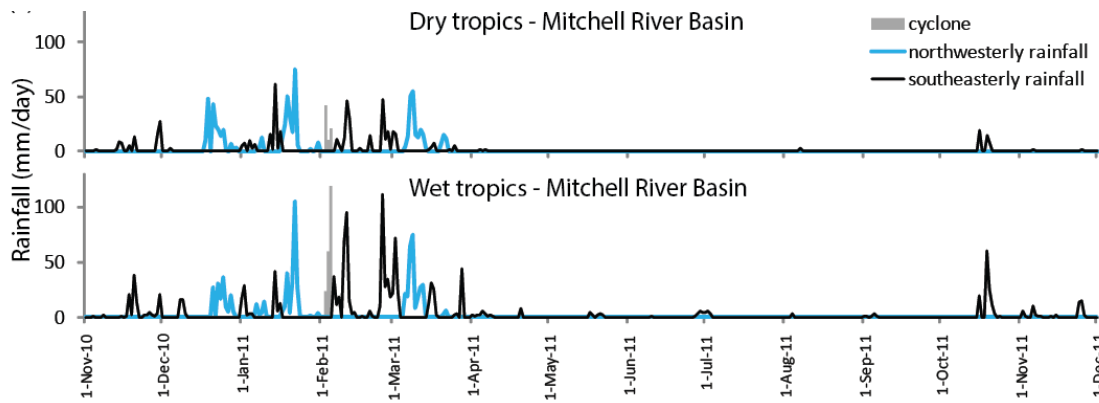


Figure 3. Rainfall (during 2010-2011) originating from the northwest or southeast in the wet and dry tropical areas of NE Australia.

During the wet season of 2010-2011, analysis of synoptic sea-level pressure maps shows that the wet tropics region received 55 and 31 % of the total rainfall from systems arriving from the southeast and northwest respectively. In comparison, the dry tropics region received 37 and 46 % of the total rainfall from the southeast and northwest respectively (Fig. 3).

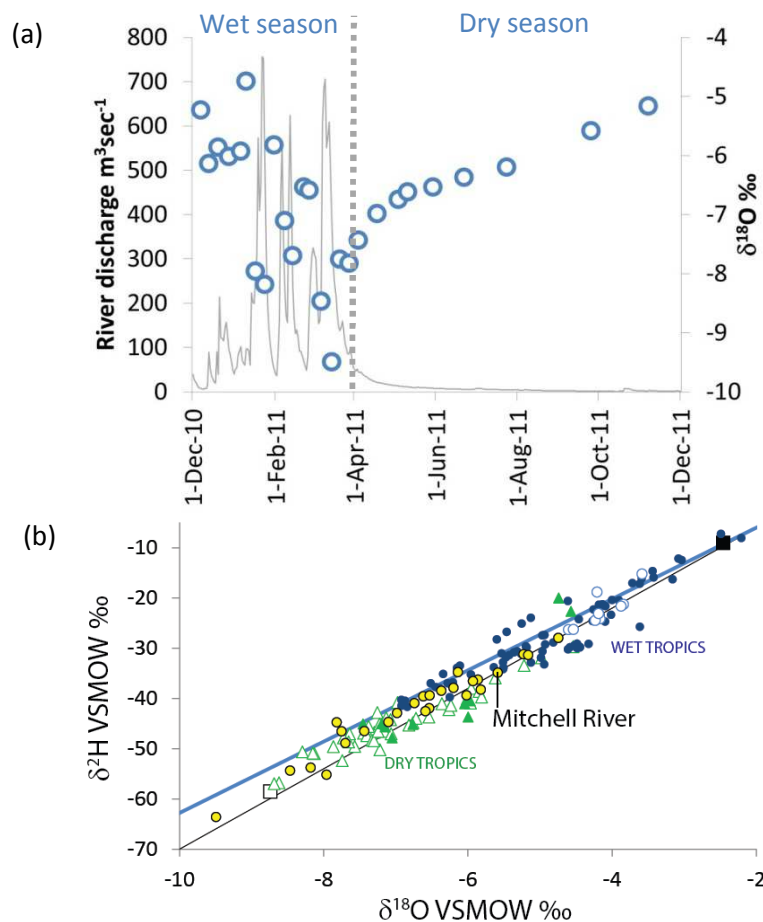


Figure 4. (a) River discharge data and results for $\delta^{18}\text{O}$ values of Mitchell River during the wet and dry seasons. (b) $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in the Mitchell River relative to all of the wet and dry tropical data collected in northern Australia (symbols as per figure 1c).

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values from the Mitchell River water are presented in figure 4. The Mitchell River showed decreasing $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values during the wet season ($\delta^{18}\text{O}$: -4.8 to -9.5 ‰ for the Mitchell River), and increasing $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values during the dry season ($\delta^{18}\text{O}$: -7.9 to -5.2 ‰ for the Mitchell River). The $\delta^2\text{H} / \delta^{18}\text{O}$ slope of 7.1 indicate there is no significant evaporation of river water as this slope is identical to the slope of local rainfall (Munksgaard et al., 2012). At this seasonal-scale the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values indicate that during the wet season the upper Mitchell River discharge is increasingly sustained by inflows from the dry tropical savanna plains; whereas during the dry season the river is increasingly sustained by inflows from the wet tropical rainforest region.

REFERENCES

- [1] AGGARWAL P.K., ALDUCHOV O.A., FROEHLICH K.O., ARAGUAS-ARAGUAS L.J., STURCHIO N.C. AND KURITA N. 2012. Stable isotopes in global precipitation: A unified interpretation based on atmospheric moisture residence time. *Geophysical Research Letters*, Vol. 39, L11705.
- [2] CLARK, I., FRITZ, P., 1997. *Environmental Isotopes in Hydrogeology*. Lewis, New York.
- [3] KURITA N., NOONE D., RISI C., SCHMIDT G.A., YAMADA H., YONEYAMA K., 2011. Intraseasonal isotopic variation associated with the Madden-Julian Oscillation. *Journal of Geophysical Research*, 116 D24101.
- [4] MUNKSGAARD N.C., WURSTER, C.M., BASS, A., BIRD, M.I., 2012. Extreme short-term stable isotope variability revealed by continuous rainwater analysis. *Hydrological Processes*. Vol. 26 (23), pp 3630–3634.
- [5] PEEL, M. C., FINLAYSON, B. L., MCMAHON, T. A., 2007 Updated world map of the Köppen-Geiger climate classification, *Hydrol. Earth Syst. Sci.*, 11, 1633-1644, doi:10.5194/hess-11-1633-2007.

ID: 358

CONTROLS ON SEASONAL $\delta^2\text{H}$ - $\delta^{18}\text{O}$ PATTERNS IN LARGE RIVERS FROM EASTERN CANADA

E. ROSA,

GEOTOP-UQAM, Montreal, QC, Canada

Groundwater Research Group - UQAT, Amos, QC, Canada

E-mail address: eric.rosa@uqat.ca

J.F. HÉLIE, A. MYRE, C. HILLAIRES-MARCEL

GEOTOP-UQAM, Montreal, QC, Canada

Abstract: This study documents processes controlling the seasonal $\delta^2\text{H}$ - $\delta^{18}\text{O}$ fluctuations observed in the Laurentian Great Lakes - St. Lawrence River system and in two rivers flowing towards the Hudson and James bays (Figure 1). Three stations of the St. Lawrence River basin were monitored from 1997 to 2008. They include the Ottawa River (Carillon sampling station), the St. Lawrence River southern channel (Montreal sampling station) and the St. Lawrence River fluvial estuary (Lévis sampling station). In addition, the La Grande and Great Whale rivers, located on the eastern shores of the James and Hudson bays, respectively, were monitored between 2007 and 2009. With the exception of the La Grande River, some seasonal isotopic cycles are observed at all monitoring stations, with heavy isotopes depletions peaking during the snowmelt period and gradual enrichments throughout the ice-off season (Figure 2). The data collected at the monitoring stations are also reported in $\delta^2\text{H}$ - $\delta^{18}\text{O}$ diagrams where the Eastern Canadian Interior Meteoric Water Line (ECIMWL) [1] is shown (Figure 3). With the exception the La Grande River, the data define $\delta^2\text{H}$ - $\delta^{18}\text{O}$ regression lines falling below the ECIMWL (Figure 3). The observed $\delta^2\text{H}$ - $\delta^{18}\text{O}$ fluctuations are dampened and out of phase with respect to precipitations, even in the relatively pristine Great Whale River basin. This is attributed to transient storage and mixing processes occurring within lakes, wetlands and aquifers prior to river drainage. The observed $\delta^2\text{H}$ - $\delta^{18}\text{O}$ regression lines also suggest evaporative enrichments. For example, isotopic mass balance calculations suggest that approximately 10% of the total inflow to the Ottawa River basin is lost through evaporation before reaching the river outlet, consistent with previously published estimates [2]. Yet, tributary mixing processes may also be important, as illustrated by the data from the St. Lawrence River fluvial estuary (Lévis sampling station). The observed $\delta^2\text{H}$ - $\delta^{18}\text{O}$ regression line (Figure 3) suggests a three component mixing system (between the Ottawa River, the St. Lawrence River south channel originating from Lake Ontario, and tributaries merging into the St. Lawrence). At last, in the La Grande River, hydrological buffering within hydroelectric reservoirs is interpreted as the main process smoothing out temporal isotopic fluctuations, suggesting an overall water residence time (within reservoirs) exceeding season durations.

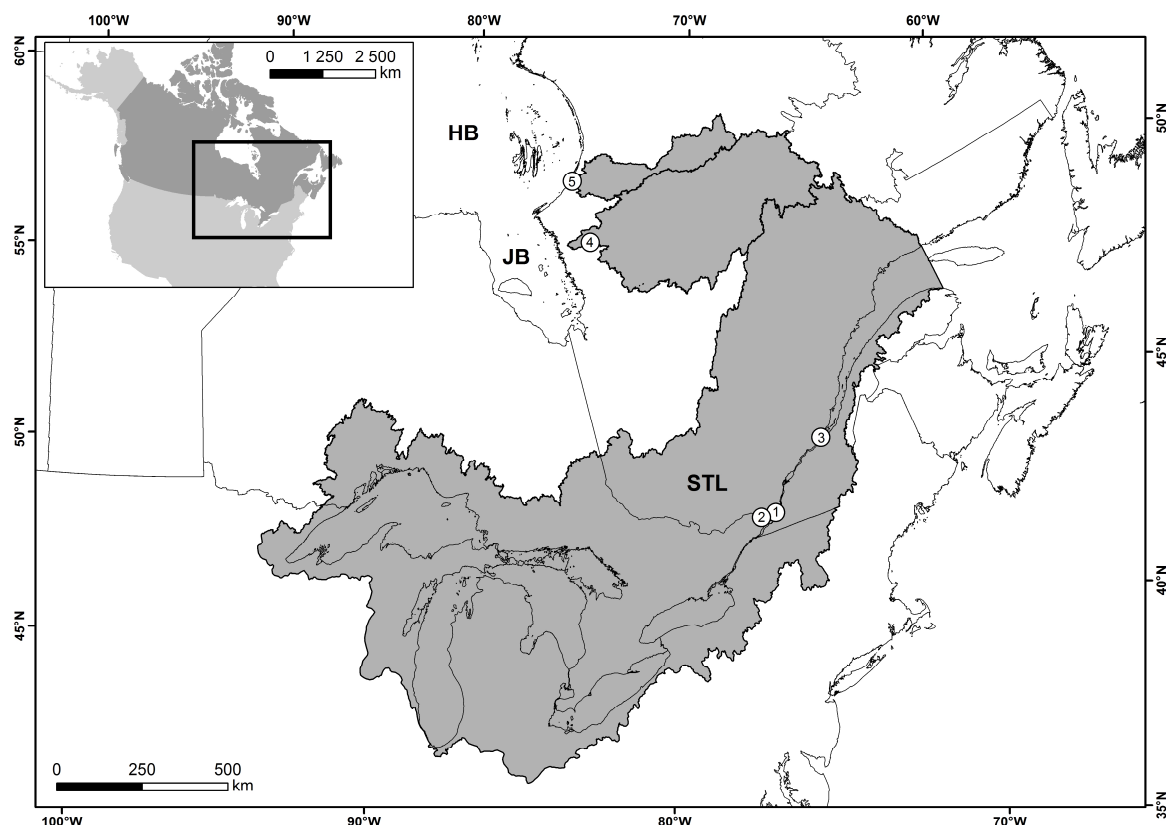


Figure 1. Study area STL: St. Lawrence River basin (sampling stations 1 (Montreal); 2 (Carillon); 3 (Lévis)). JB: James Bay (sampling station 4 (La Grande River)). HB: Hudson Bay (sampling station 5 (Great Whale River)). Contains information licensed under the Open Government Licence – Canada.

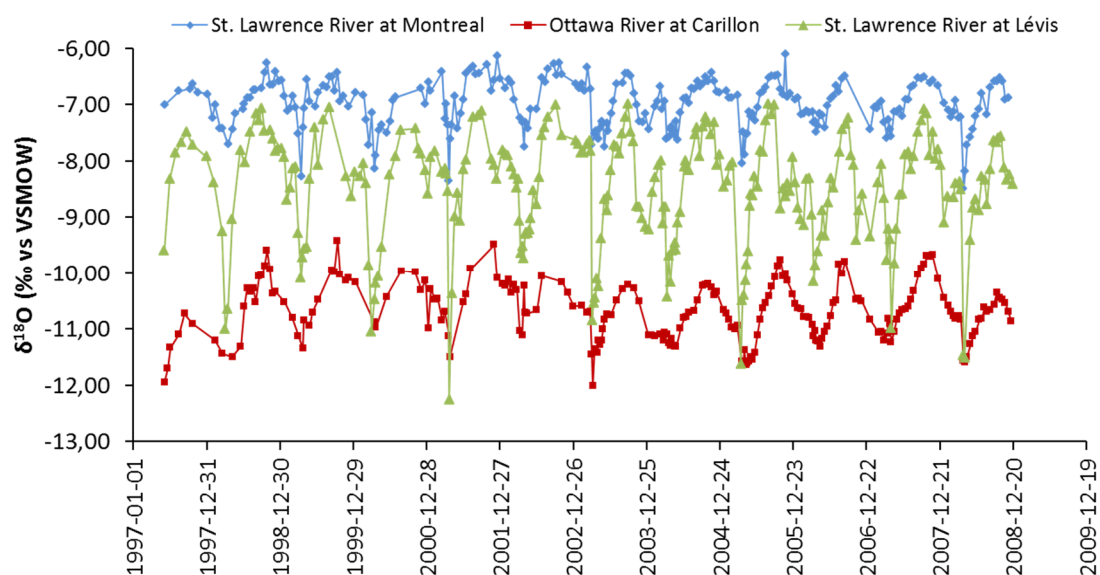


Figure 2. Seasonal $\delta^{18}\text{O}$ fluctuations in the Ottawa and St. Lawrence rivers

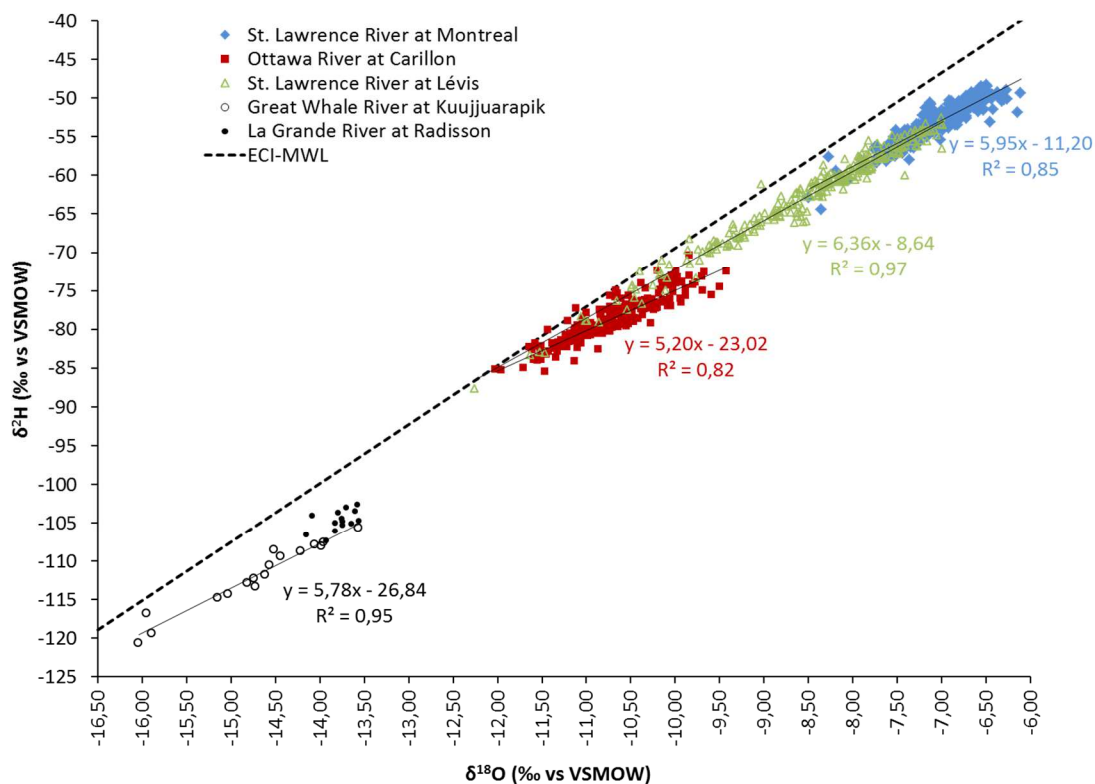


Figure 3. δ^2H - $\delta^{18}O$ data collected at the monitoring stations

REFERENCES

- [1] FRITZ P., DRIMMIE R.J., FRAPE S.K., O'SHEA O. (1987). The isotopic composition of precipitation and groundwater in Canada. In: Isotope Techniques in Water Resources Development, IAEA Symposium 299, March 1987, Vienna; 539 – 550.
- [2] TELMER K., VEIZER J. (2000). Isotopic constraints on the transpiration, evaporation, energy, and gross primary production budgets of a large Boreal watershed: Ottawa River basin, Canada. *Global Biogeochemical Cycles* 14: 149 – 165.



International Atomic Energy Agency
IAEA-CN-225

Vienna International Centre
PO Box 100
1400 Vienna, Austria

Telephone No.: +43 1 2600 (0) plus extension
Telefax No.: +43 1 26007
Email: official.mail@iaea.org

Conference web page:
<http://www.iaea.org/meetings>