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# Use of Stable Isotopes in Sydney Catchment Process and Water Quality Studies

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**EXECUTIVE SUMMARY**

The use of stable and radioactive isotopes as environmental tracers is becoming more widespread as isotopic analysis techniques become more accessible. ANSTO's Isotopes for Water Project aims to increase awareness of the potential uses of isotopes in the management of catchments, rivers, reservoirs, aquifers, estuaries and biota. This paper outlines a range of potential applications using a wide range of isotopes ($\delta^{18}$O, $\delta^{2}$H, $^{14}$C, $\delta^{13}$C, $\delta^{15}$N, $^{3}$H, $^{7}$Be, $^{210}$Pb, $^{35}$S, $\delta^{34}$S, $\delta^{18}$O and $\Delta^{17}$O) in hydrology, hydrogeology, ecology and contaminant geochemistry with examples from the Sydney basin. The studies being undertaken by ANSTO include:

- application of stable water isotopes to catchment and reservoir water balance;
- age dating of groundwater to underpin sustainability assessment;
- tracing the source of contaminants and nutrients such as nitrogen, organic matter and sulfate in catchments and waterways;
- quantifying contaminated sediment dynamics and contaminant uptake into biota using shorted-lived radioisotopes;
- tracing trophic linkages in aquatic food webs.

## INTRODUCTION

In recent decades there has been a rapid expansion in the use of stable and radioactive isotopes in many areas of environmental research. These have emerged as a suite of powerful tools for addressing pattern and process related issues in hydrology, geochemistry, meteorology, physiology, palaeontology, conservation and ecology based studies in freshwater catchments and the coastal marine environment. It is important, however, to appreciate that stable isotope applications are most effective when used in combination with other techniques that enable the quantification of process rates in hydrological and biogeochemical systems. This is the strength of radioactive tracers, which are often also naturally occurring in these systems. When combined with analyses of contaminants in water, sediments and biota, isotopic studies become powerful tools for tracing the flow of contaminants through catchments and food webs, and for understanding the relationships between trophic (food web) levels and bioaccumulation.

Isotope tracers have demonstrated capability to label water sources, identify flow pathways, and provide information on origin and evolution of natural water-cycling processes. As a complementary tool in hydrological and hydrogeological investigations, both radioactive and stable isotope tracers have contributed to the solution of water quality and quantity problems. Importantly, isotopes provide a method for studying groundwater/surface water interaction, and may contribute to a better understanding of the complex behaviour of solutes, nutrients and organic matter. Isotope hydrology also offers a methodology to partition hydrological parameters and determine tracer contaminant and water pathways using measurements that can integrate hydrological processes on a variety of scales including whole of catchment scales.

The ANSTO Isotopes for Water Project is studying freshwater catchment and coastal processes at a variety of locations in the Sydney region and beyond using naturally occurring stable and radioactive isotopes ($\delta^{18}O$, $\delta^{2}H$, $^{14}C$, $\delta^{13}C$, $\delta^{15}N$, $^{3}H$, $^{7}Be$, $^{210}Pb$, $^{35}S$, $\delta^{34}S$, $\delta^{18}O$ and $\Delta^{17}O$) in rainfall, rivers, reservoirs, groundwater, estuaries and biota. Applications of these isotopes focussing on hydrology (water quantity) or bio/hydrogeochemistry (water quality) are outlined below with examples from the Sydney region.

## WATER QUANTITY OR ISOTOPE HYDROLOGY APPLICATIONS

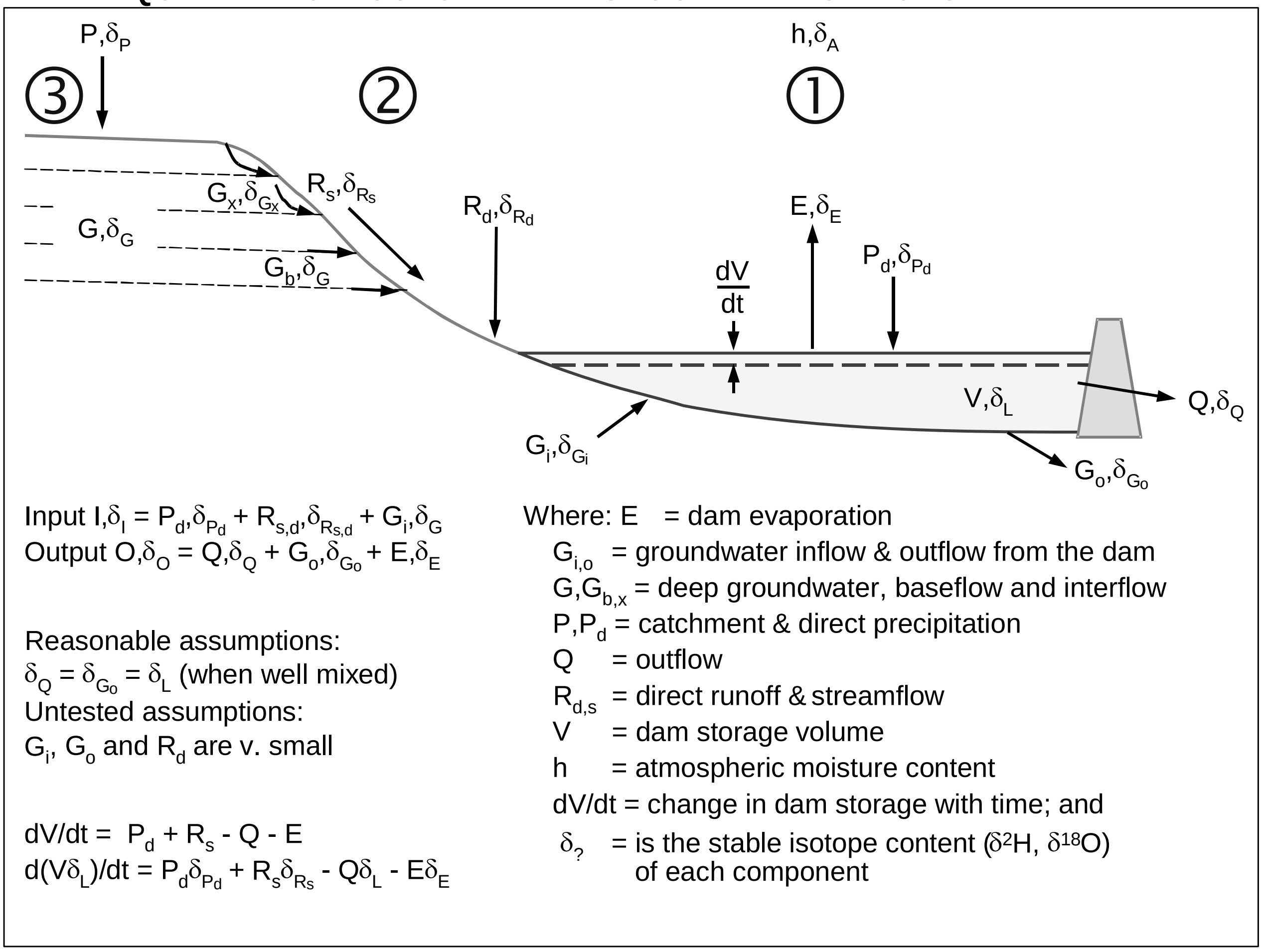


**Figure 1. Conceptual model of catchment and reservoir processes.**

Isotope balance using $^{2}H$ and $^{18}O$ is being applied to understand the water cycle processes affecting water supply and water quality in Sydney's water supply catchments in collaboration with the Sydney Catchment Authority. The major areas of research (Figure 1) include: (1) reservoir water balance, with studies addressing estimation of throughput, water residency, catchment yield and groundwater exchange, utilising the systematic heavy isotope enrichment signals acquired during exposure to evaporation, and (2) runoff generation processes, with studies utilising temporal variations in precipitation and runoff to investigate the partitioning of shallow versus deep groundwater pathways, and importance of contributions from various stratigraphic units. Related studies are also aimed at age dating of groundwater (Figure 1, see (3)), to assess the sustainability of potential emergency extraction of supplementary groundwater supplies.

**Applying stable water isotopes to catchment and reservoir water balance**

Ratios of oxygen ($^{18}O/^{16}O$) and hydrogen ($^{2}H/H$) in water are affected by climate variability, rainfall, recharge and evaporation. These naturally occurring isotope tracers can be used to improve catchment and reservoir water balances by estimating cumulative evaporation losses, groundwater-surface water interactions, catchment runoff ratio and reservoir residence time. Even in well gauged catchments there may be significant errors in conventional estimates of these parameters; these can be independently verified using isotope techniques. In ungauged catchments isotopes can economically provide a snapshot of the hydrological state of the catchment.

A preliminary isotope balance assessment of the Lake Burragorang reservoir using $^{18}O/^{16}O$ and $^{2}H/H$ was conducted during 2004 and 2005, a historically low period in terms of storage capacity. The analysis suggests that about 14% of water loss from the reservoir occurred via evaporation loss, the remainder being extracted for use in the Sydney water supply or released to sustain downstream environmental flows. Further partitioning of water exchange between surface and groundwater will help to better understand the water quality and sustainability controls. The first estimates of water residence time of the reservoir (~1.1 years), runoff ratio (8%), and throughflow confirm that it is a dynamic system with a low capacity for buffering extended drought.

**Age dating of groundwater to underpin sustainability assessment**

Rainfall and recharging groundwaters contain traces of the naturally occurring radioisotopes $^{35}S$, tritium ($^{3}H$), $^{14}C$ and $^{36}Cl$. These radioactive isotopes are formed in the earth's atmosphere by cosmic ray interactions. They possess quite distinct half-lives: 87 days for $^{35}S$, 12.3 years for $^{3}H$, 5730 years for $^{14}C$, and 301000 years for $^{36}Cl$. They may be used to determine the ages or mean residence times of stored water in 'at risk' aquifers, infer flow paths, as well as assisting in determining the degree of mixing between older and recently recharged groundwater sources. Such data is a valuable addition to conventional hydrogeological tools used by groundwater managers when assessing sustainable use.

The dating of water is highly dependent upon the estimated initial activity of the radioisotope in rain. Radioactive decay in streamflow or groundwater samples is measured to enable calculation of an apparent residence time. The first assumption is that there is a constant generation flux of the radioisotope in the atmosphere due to near constant cosmic ray flux, which is more valid for shorter lived than longer lived radioisotopes. Once formed the cosmogenic radioisotope undergoes varying rates of dilution as it mixes with the abundant stable S, H, C, and Cl atoms in the environment. This elemental dilution effect can be quantified using long term weighted averages or other geochemical indicators. The final assumption is that the dissolved radioisotope is chemically conservative i.e. does not interact chemically with stream sediment, biota or host rock minerals.

To assess groundwater sustainable use involves balancing recharge against short term deficits due to groundwater extraction without long term steady decline occurring. Quantifying the residence time may independently constrain estimates of recharge rate and flow velocities in conceptual or numerical flow models. Like many other isotope techniques, using radiodating to estimate residence time has the advantage of homogenising the variable flow paths and small scale heterogeneities inherent in difficult recharge and hydraulic conductivity measurement, as well as integrating varying climatic conditions.

**WATER QUALITY AND CONTAMINANT TRANSFER APPLICATIONS**

Applications of stable isotope analysis to contaminant transfer rely on the distinct isotope ratio fingerprint that certain sources of contaminants and nutrient such as carbon, nitrogen and sulphur exhibit. These ratios transferred into biota through uptake or consumption. Fractionation, or changes in the isotope ratios, may then result from metabolic or geochemical processes. So we can trace the source of contaminants and infer the physical and biological pathways they have followed.

**Tracing the source of sulfur and oxidation-reduction processes in catchments**

Different major-sulfate reservoirs in nature are well constrained. Stable isotopes of sulfate ($\delta^{34}S$ and $\delta^{18}O$) can differentiate anthropogenic (fossil fuel combustion, mineral smelting) and natural (sea spray, biogenic emissions) proportions in rainwater as well as in surface and groundwaters. Once the main end-members of a given catchment are known, sulfate isotopic signatures can contribute to reveal mixing paths and disturbances within the catchment (Robinson et al. 1997). Preliminary data on $\delta^{34}S$ and $\delta^{18}O$ of sulfate in the upper Nattai river (NSW) support this. The incorporation of $\Delta^{17}O$ (enrichment in the normally fixed $^{17}O/^{18}O$ ratio) is expected to help further to identify sulfate originated from reduced sulphur gases in the atmosphere and its contribution to rainwater.

**Tracing the source of nitrogen and organic matter in aquatic ecosystems**

Stable isotopes of nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) in biota and organic matter (e.g. POM and DOM) can be used to investigate the source, transport, behaviour and fate of nutrients in aquatic ecosystems. Difficulties in identifying nutrient and organic matter sources (e.g. sewage, agricultural, industrial) and sinks in aquatic systems can lead to management problems associated with identification of the various/specific contributors. By measuring the stable isotope ratios of carbon and nitrogen ($\delta^{15}N$ and $\delta^{13}C$) in biota and organic matter in the aquatic system, the relative contribution of nutrients in the aquatic system can be determined and used as an environmental source tracer.

For example, the high $\delta^{15}N$ associated with many anthropogenic nutrient sources, means that stable isotope ratios of N in aquatic biota (plants and animals) are potentially invaluable tools for gauging the impacts of man on coastal water bodies (McClelland et al. 1997). Stable isotopic techniques are of primary importance because of the magnitude of the effect of urban development on coastal water bodies through anthropogenically increased N loading. Analysis of $\delta^{15}N$ in biota collected from the Homebush Bay and Botany Bay found higher $\delta^{15}N$ values in fish captured from Homebush Bay than fish from Botany Bay (Figure 2). The higher $\delta^{15}N$ in Homebush Bay biota would be due to anthropogenic inputs, which need to be examined.

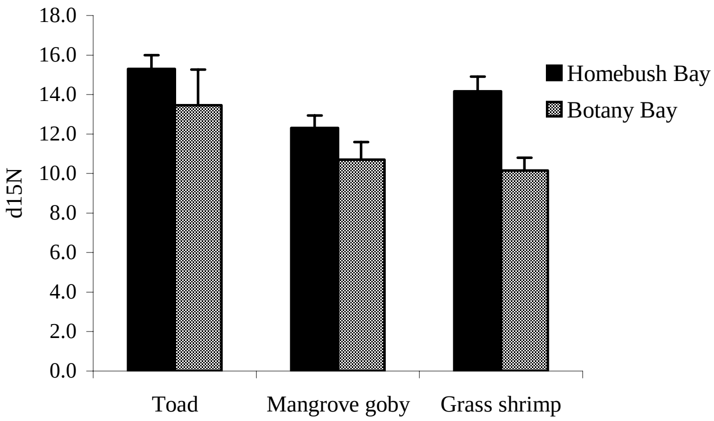


**Figure 2.** $\delta^{15}$**N values of fishes in Homebush Bay and Botany Bay 2005-2006 (Mazumder *et al*., in prep.))**

## Quantifying contaminated sediment dynamics using shorted-lived radioisotopes

The complex cycle of processes that occurs in sediments (deposition, diagenetic, resuspension, transport, burial, etc) plays an important role in the water quality of an aquatic ecosystem. An understanding of these processes is essential for determining biogeochemical cycles. In aqueous environments such as estuaries, hydrophobic contaminants rapidly become associated with suspended particles and colloids. While many of the contaminants are strongly bound to the particles, they can be released into the water column through changes in geochemistry on resuspension.

The distinction in time scales between temporary and permanent storage of sediments/particulates in estuaries is important in determining the ultimate fate of pollutants. Naturally occurring radioisotopes can be used to quantify these differences in time scales, by establishing the geochronology of the bottom sediments. They can also be used to determine rates of sedimentary processes and fluxes of sediments. The most commonly used sediment particle tracers are naturally occurring radioisotopes such as $^{7}$Be, $^{234}$Th and $^{210}$Pb.

Deposition is the temporary emplacement of sediment on the estuary bed and can be measured using $^{7}$Be and $^{234}$Th because of their short half-lives (53.3 days and 24.1 days respectively). On the longer time scale of years to decades, sediment accumulation can be determined by using $^{210}$Pb (half-life of 22.3 years) or $^{137}$Cs (half-life of 30.2 years). By comparing deposition to accumulation rates, it is possible to determine the net export of sediment from an area or the short-term resuspension rates. This approach is currently being applied in Homebush Bay, Sydney in a study to determine the fate of sediments, heavy metals and other pollutants.

## Tracing the trophic linkages in aquatic food webs

Ecological applications of stable isotope analysis rely on producer distinct isotope ratios of carbon and nitrogen. These ratios are transferred to consumer tissues upon consumption. Metabolic fractionation results in enrichment of the isotopic ratios (i.e. they become higher) in both carbon and nitrogen compared to the diet. In this way, we are able to determine at what trophic level an animal is feeding in relation to its ecosystem.

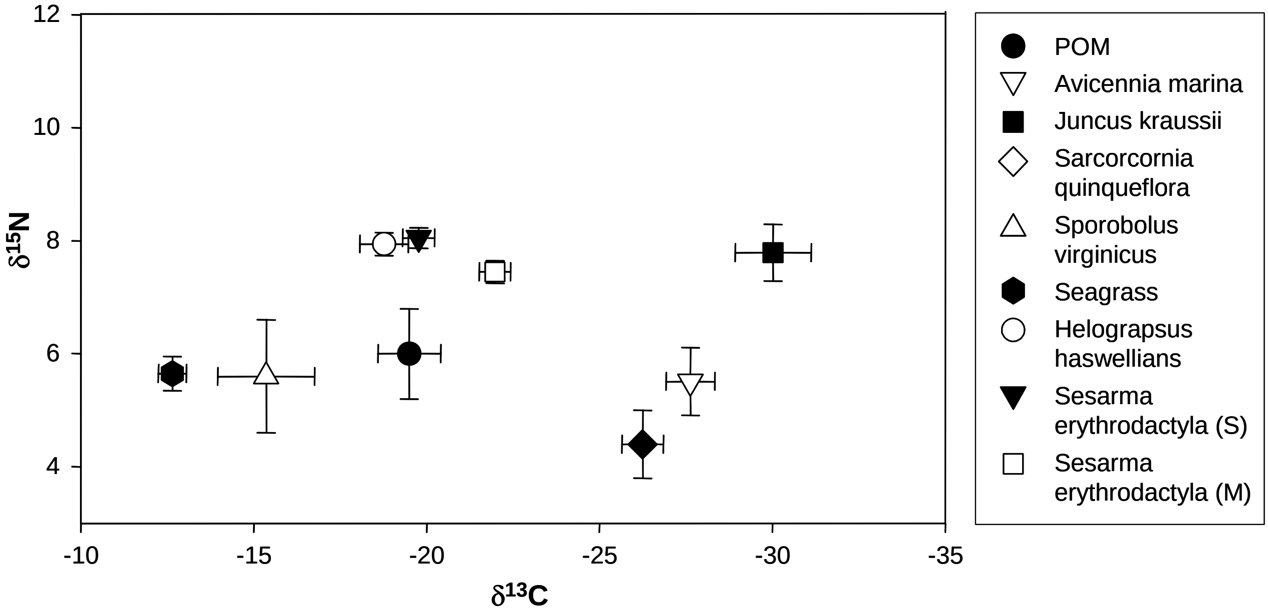


**Figure 3. Carbon and nitrogen isotope ratios of primary producers and consumers (crabs) at Towra Point, NSW, modified from Mazumder *et al*. (in prep.)**

As an example, Mazumder *et al*. (in prep.) applied stable C and N isotopes as tracers to investigate the trophic linkages between burrowing crabs and primary producers in saltmarsh. It appears from the stable carbon and nitrogen isotope study that diet of *S. erythrodactyla and H. haswellianus* in the saltmarsh is identical and that this differs slightly to the diet of *S. erythrodactyla* in the mangrove (Mazumder 2004). The result suggested species of crabs living in the saltmarsh are reliant on the same source of food for their nutrition and depend on particulate organic matter (POM, published by Melville and Connolly 2003) instead of saltmarsh and mangrove plants (Figure 3).

## ACKNOWLEDGEMENTS

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