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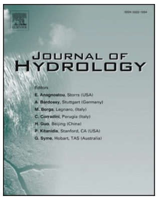

Research papers

Intensive agriculture, a pesticide pathway to >100 m deep groundwater below dryland agriculture, Cordoba Pampas, Argentina

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ABSTRACT

Groundwater pesticide pollution in shallow groundwater is a well-established global phenomenon. However, deep aquifers are widely thought to be naturally protected from such modern contaminants, by confining geological barriers and upwards hydraulic gradients. Here we document pervasive pesticide pollution in >100 m deep artesian wells in a sedimentary aquifer below dryland agriculture. The vertical distribution of key groundwater markers, including numbers and concentrations of pesticides, stable ($\delta^{18}O$ & $\delta^{2}H$) and radioactive (^{3}H & ^{14}C) isotopes and ion concentrations were used to develop a conceptual model of pollutant transport to deep groundwater. Tritium, stable isotope and pesticide distributions in unconfined groundwater indicate that water table rise to <1 m below the surface (due to anthropogenic landscape modification and periodic flooding), has created a rapid pollutant ‘doorway’ to groundwater. Despite a lack of deep borehole pumping for irrigation, these rising water tables have permanently inverted previously upward hydraulic gradients towards the underlying semi-confined aquifer in some areas. Physical heterogeneities and/or leaky domestic boreholes then act as preferential transport avenues for surface pollutants to both unconfined and semi-confined groundwater. These pathways allow small aliquots of highly contaminated surface water and modern unconfined groundwater to mix with the pre-existing pre-modern deep groundwater, resulting in mixed isotopic signatures in deep wells (e.g., radiocarbon <5 pMC but detectable tritium) and detections of multiple synthetic pesticides in the deep aquifer, including AMPA at concentrations up to 4.93 μg/L and Metolachlor up to 0.015 μg/L. Our results demonstrate how semi-confined deep groundwaters may be contaminated by current agricultural techniques even where deep groundwater exploitation is limited. We urge measures to eliminate these pollutant pathways.

1. Introduction

The use of herbicide and pesticide chemicals in global agriculture threatens to impair the quality of groundwater, through movement of potentially harmful compounds and their degradates into drinking water supplies (Leistra and Boesten 1989; Bexfield et al., 2021). While studies from the US and Europe have characterised broad patterns of pesticide occurrence in groundwater and key controls on their fate and transport in soil and aquifer media (such as sorption and degradation), there remains a lack of data and information on the potential risk of these pollutants (including degradates) migrating through various pathways into water supply aquifers in many parts of the world (Lutri et al., 2020).

Deep aquifers are commonly thought to be naturally protected from modern contaminants (such as pesticides and their degradates) by vertical distances to the surface, lithology and (in many cases) upwards artesian hydraulic gradients (e.g., GebreEgziabher et al., 2022). However, recent detections of the environmental isotope tritium (Jasechko et al., 2017; Thaw et al., 2022), significant concentrations of nitrate (e.g., Currell et al., 2010; Han et al., 2016) and presence of pharmaceuticals (Lapworth et al., 2018) in wells from deep pre-Holocene confined groundwater, have called this into question, and highlight the vulnerability of the world’s largest freshwater reserves to surface contamination.

Anthropogenic contamination of confined aquifers requires downwards hydraulic gradients, to allow surface polluted water to pass through overlying aquifers and soils, and secondly, pathways of

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sufficient permeability for this to occur on timescales of years to decades to transport modern pollutants into aquifers that primarily comprise water recharged thousands to tens of thousands of years ago (Currell et al., 2010; Khan et al., 2016; Lapworth et al., 2018; Jurgens et al., 2022). If such conditions are present, a significant contamination threat to vital, large freshwater resources exists, from the widespread usage of fertilizers and pesticides – many of which have poorly understood health and environmental effects (e.g., Aiassa et al., 2019; Battaglin et al., 2014) – in the world's croplands. Pesticides in groundwater are commonly documented in wells <40 m below surface (e.g., Hakoun et al., 2017; Li et al., 2023; Spalding et al., 2003), and in some cases have been identified at ~70–100 m depth (Bexfield et al., 2021; Cabeza et al., 2012; Leistra and Boesten, 1989), yet their vertical distribution beyond these depths is poorly characterized in most aquifer systems (e.g., Battaglin et al., 2014; Mas et al., 2020a; Schipper et al., 2008).

It is also currently unclear how tritium and nitrate (two key markers of recent surface input into an aquifer) bypass the unsaturated zone and overcome upwards vertical forces to reach confined aquifers, containing water recharged in pre-Holocene times, as has been observed in multiple global aquifer systems (Currell et al., 2010; Han et al., 2016; Jasechko et al., 2017; Khan et al., 2016; Lapworth et al., 2018). Many regions of the world converted to intensively produced croplands (e.g., Arancibia et al., 2020; Scanlon et al., 2007) have experienced inversions of hydraulic gradients towards confined aquifers where these are extensively exploited for irrigation water (GebreEgziabher et al., 2022; Thaw et al., 2022). Coupled with natural and man-made permeable pathways (such as poorly constructed or long-screen boreholes or pre-existing geological structures) this appears to have resulted in deep groundwater contamination in regions such as northern China, India, central Europe and the Middle East (Ascott et al., 2017; Currell et al., 2010; Han et al., 2016; Jiráková et al., 2010; Lapworth et al., 2018; Stadler et al., 2012; Thaw et al., 2022). However, the full scale of this problem is yet to be documented, and it is unclear whether areas without extensive deep groundwater exploitation, but similarly intensive surface agriculture (e.g., rainfed croplands), may also be vulnerable to pollutant transport into deep groundwater.

The purpose of this study was to identify the distribution of pesticides and their degradates in groundwater from a region of intensive cropland in South America (where such data are relatively scarce in the literature) and then, to develop a conceptual model to explain the occurrence of these chemicals in groundwater within a semi-confined artesian aquifer. To achieve this, we sampled a suite of agrochemicals in groundwater, to characterise their vertical distribution in a layered aquifer system, together with isotopic (stable and radioactive) and hydrochemical tracers. These tracers were analysed to inform an understanding of the potential pathways and timescales of pollutant movement into the groundwater. The study was conducted in one of the most agriculturally productive areas of the planet – the Central Argentinean Pampas in South America (Birgit Meade et al., 2016). Through better characterising the extent and mechanism(s) of pollutant migration into deep groundwater, the findings have significant implications for the vulnerability of global freshwater reserves in similar regions with intensive agriculture and valuable freshwater reserves in (semi-) confined aquifers.

2. Field area, samples and methods

The Cordoba Pampas (Fig. 1) comprise a layered unconfined/ confined aquifer system from an upper Holocene-Paleogene fluvio-aeolian sedimentary sequence (Kröhling, 1999). This region is characterized by dryland agriculture and intensive transgenic and chemical-dependant crop production – being one of the most productive global areas for soy, wheat and corn (Birgit Meade et al., 2016; Gobierno de la Provincia de Cordoba, 2019). Four main rivers, named from 1st to 4th (i.e., from Rio Primero to Rio Cuarto), drain water from the westwards Hills of Cordoba to the eastern Pampas (Rosello, 2018). These rivers, along with an extensive network of artificial surface channels are associated with agriculture – e.g., used in flow irrigation (Brandolin et al., 2013; Plencovich, 2018; Riera and Barrionuevo, 2015). There are numerous wells throughout both the shallow unconfined, and deeper (semi-)confined artesian aquifers; however, exploitation of groundwater for irrigation is limited in comparison to the central and southern Cordoba Pampas (Plencovich, 2018). Both surface water bodies (Bundschuh et al., 2012; Lerda and Prosperi, 1996) and unconfined

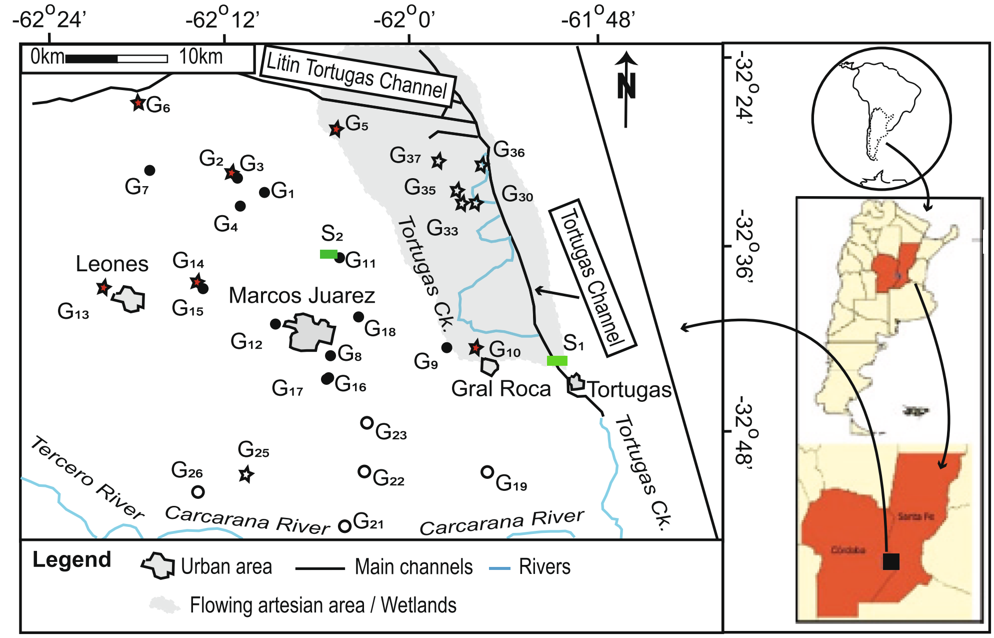

Fig. 1. Study area with sample sites and main surface waterways. Circles and stars mark monitored sites, black circles and red stars are unconfined and artesian sample sites, respectively. Green rectangles are surface water channel sampling sites. Top right regional map highlighting, from left to right, Cordoba and Santa Fe Provinces respectively, black square represents the study area. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

groundwater, are polluted by nitrate and pesticides (Corcoran et al., 2020; Giuliano Albo et al., 2015), while shallow and deep groundwater are affected by geogenic pollutants including arsenic and fluoride (Blarasin et al., 2014; Blarasin et al., 2016; Nicolli et al., 2012). The pollution of deep freshwater aquifers is of great significance, as these wells are often utilized as sources of drinking water, for example, in Rio Cuarto city (184561 inhabitants) ~270 km west of our sampling sites.

The area of study is located at the eastern margin of Cordoba Pampas surrounding Marcos Juarez town (Fig. 1), dominated by rain-fed agriculture (e.g., Giacobone et al., 2022; Gobierno de la Provincia de Cordoba, 2019). Fieldwork was undertaken during May 2019, where groundwater levels were measured on 17 unconfined and 12 confined wells. A total of 20 sites were sampled, including two surface channels, one permanent (Arroyo Tortugas) and one ephemeral; 12 boreholes from the unconfined aquifer, (depths included Fig. A1, supplementary material); and 6 wells in the confined aquifer (Fig. 1 and Fig. A1). Sample wells extract water from a range of depths, including the first 50 m of the unconfined aquifer, and between 116 and 140 m within the underlying deeper artesian aquifer (Figs. 1 and A1). We collected 9 distinct sample bottles from each site for isotopic, ionic, and molecular analyses, according to laboratory requirements. No aquifer exploitation for irrigation was reported by landowners, instead groundwater use is primarily for animal (e.g., cattle and pig) farming (Giacobone et al., 2022), and domestic activities.

Data have previously been reported to define the main lithological and geomorphological units and explore the groundwater flow systems and pollution vulnerability (Giacobone et al., 2022). The first 140 m b. s. in the area are formed by two layered sedimentary aquifers; unconfined (0–100 m) and semi-confined artesian (100–140 m), (Giacobone et al., 2022, Blarasin et al., 2014). The upper unconfined aquifer consists of a mixture of Quaternary fluvial (alluvial fan)-aeolian sediments (e.g., silts, sands and clays). The lower section of this unit contains approximately 25 m −thick red clays or silty-clay sands (Fig. A1). This is followed by well-graded very fine-medium sands interpreted as SAC B (Pliocene-Pleistocene), a semi-confined aquifer from approximately 100 to 140 m depth (from which our deep semi-confined groundwater samples are taken). This overlies ~300 m of continental/marine green clay-silt sediments (Fig. A1), interpreted as the SAC C (Palaeogene – Pleistocene) confined aquifer system (Giacobone et al., 2022). The two aquifers contain water with contrasting stable (δ^2H and $\delta^{18}O$) and radioactive (^{14}C) isotopic values, indicative of recent and pre-Holocene recharge, respectively (Giacobone et al., 2022).

2.1. Analytical methods for water samples

The methodology and data for stable isotopes of water (δ^2H and $\delta^{18}O$) and radiocarbon are reported in (Giacobone et al., 2022). Here we report data for the radioactive isotope tritium (^3H), major ions and trace elements, as well as pesticides. Tritium samples (Table A1 at repository) were collected in 1 L HDPE bottles, filtered using 0.45 μm in-field kits while major and minor element samples (Table A2) were collected in 250 ml plastic bottles and filtered, with samples for cations/metals acidified using concentrated nitric acid in-field. Analysis was conducted at the Australian Nuclear Science & Technology Organisation and Monash University, School of Earth, Atmosphere and Environment (Australia), respectively, as per the methods described in (Cendón et al., 2020) and (Currell et al., 2017). Water samples for molecular analysis (a range of 43 compounds, including herbicides and insecticides, (Table A3) were collected in 100 ml amber glass and plastic (for Glyphosate) bottles. Analysis was performed by UHPLC-MS/MS at INTA, Balcarce, Argentina. These samples were split into two aliquots, the first to determine the herbicide glyphosate and its biodegradation metabolite AMPA, following the methodology reported by Aparicio et al., (2013), and the second to perform the analysis of multiple pesticide/herbicide residues following the procedure reported by De Gerónimo et al., (2015) and Mas et al., (2020b). The limit of detection (LOD) and limit of quantification (LOQ) for each molecule is reported in supplementary material, table A3, and throughout the figures and table below. Quantification limits and/or standard uncertainties for all radioactive and stable and isotopic values from our sampling sites are presented in Tables A1, A4 and A5, respectively (supplementary material).

3. Results

3.1. Agrochemical and chemical water types

Our results show a) pervasive groundwater agrochemical contamination with detections at all measured depths, decreasing in concentrations, and diversity of molecules from the unconfined to semi-confined aquifer (Figs. 2 and 3); and b) distinctive isotopic and chemical water types, which appear to fall into groups based on the level of groundwater confinement (Figs. 4 and 5) and (particularly in the upper unconfined aquifer) the water table depth below the land surface (Fig. 4).

This study detected 22 synthetic molecules in ground and surface water, with the highest abundance and concentrations within the top 20 m of the unconfined aquifer (highest variety at 12 m depth, $n = 17$, Fig. 2; Fig. A1 and Table A3). Atrazine was detected at nearly all sample sites (16 out of 20) and depths, as previously reported by (Giacobone et al., 2022).

Water samples from man-made surface channels (Fig. 1), both perennial (S_1) and ephemeral (S_2), were also polluted with many agrochemicals ($n = 15$, see Figs. 3 and 4 below and Fig. A1, Table A3) and high concentrations of Atrazine (up to 0.102 μL). Atrazine derivatives – Hydroxyatrazine (HA), Desethylatrazine (DEA), and Desisopropylatrazine (DIA), the herbicide Ametryn, and the fungicide Tebuconazole, were detected in higher concentrations in surface water than groundwater, but occur in both (Fig. A1).

Conversely, some agrochemicals were only detected in groundwater (e.g., Chlorimuron-Ethyl and Piperonyl-Butoxide). Despite the generally low agrochemical concentrations detected in the deep (semi-)confined groundwater, pesticide presence was identified in 100% of sampled artesian wells. The relative abundance of compounds (8 molecule types Fig. 2; Fig. A1 and Table A3) is somewhat counter-intuitive, due to the well depths, generally upward hydraulic gradients (towards the overlying aquifer), and limited exploitation of artesian groundwater. Some analysed molecule types showed relatively high concentrations at great depth, for instance, the Glyphosate metabolite AMPA concentration in artesian bore G_5 was more than twice that detected in surface water (4.93 vs. 1.24 to 1.88 μg/l; Fig. 2, and Table A3).

Groundwater chemical-isotopic signatures discriminate distinct sets of contrasting water types, with multiple parameters, including electrical conductivity (EC), tritium (^3H), redox-sensitive trace metals (e.g., Fe and Mn), pesticides and degradates, and stable isotopes of water defining clear trends of being relatively enriched or depleted within the different sample groups (Fig. 4). The first distinction in water type relates to level of groundwater confinement. *Type A* groundwater and surface water (Fig. 4) is enriched in stable and radiogenic isotopes, major and minor elements and synthetic pollutants compared to *Type B* groundwater, from the (semi-)confined aquifer.

The second grouping was identified within the unconfined aquifer (Type A), based on depth to the water table. Where the unconfined aquifer has a thin unsaturated zone (<1 m), groundwater has enriched signatures for stable and radiogenic isotopes and redox sensitive elements, and is depleted in other markers (e.g., major ions, EC and non-redox sensitive elements). This group is denoted type A_1 in Fig. 4. These indicators exhibited opposite trends in the unconfined groundwater occurring beneath a thicker (<1 m) vadose zone, which we denote Type A_2.

Further detail on the results for the major environmental tracers sampled and their distribution in the aquifer system are provided in the following sections:

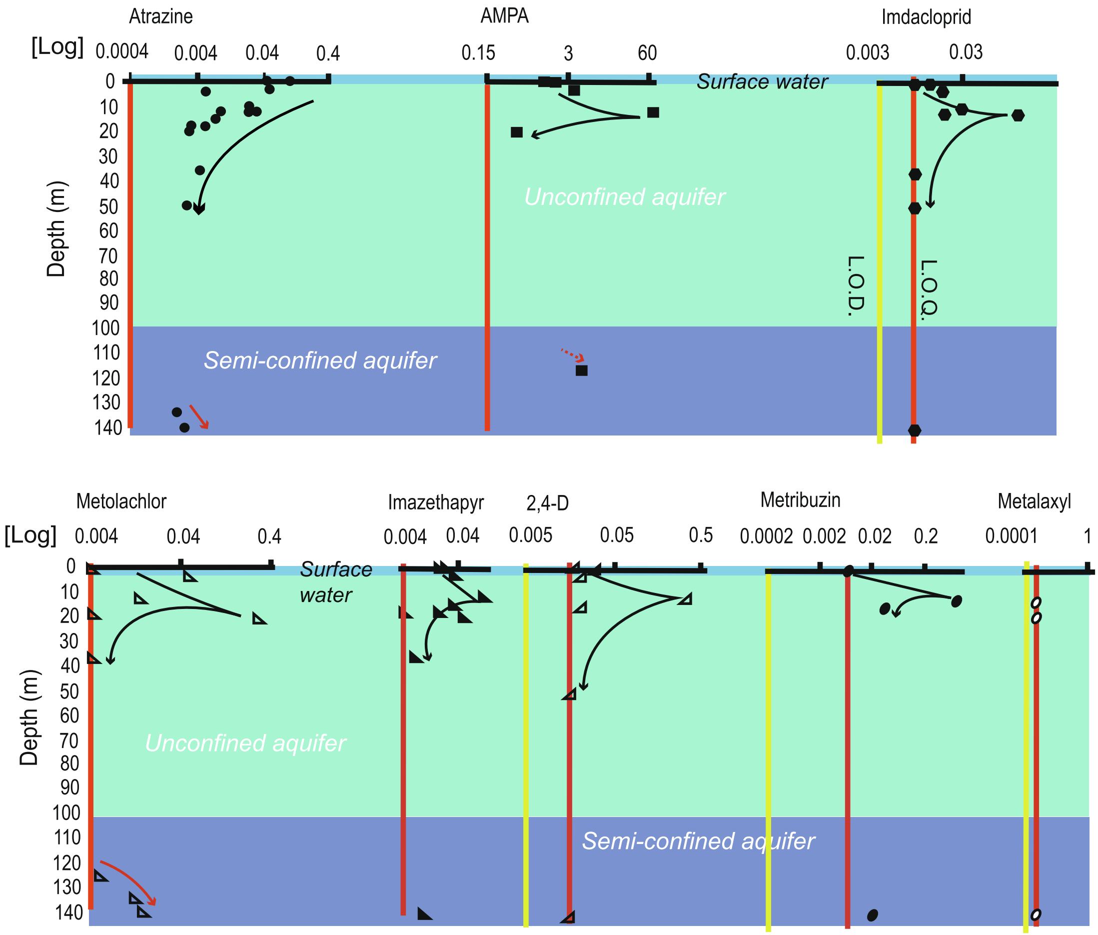

Fig. 2. Agrochemical detections vs depth, including in the deep artesian aquifer. Concentration profiles in logarithmic scale vs sampling depths in metres. Light blue, green and dark blue colours represent surface water, unconfined and semi-confined aquifers, respectively. Vertical red and yellow lines are limit of quantification (LOQ) and limit of detection (LOD), respectively. Arrows indicate relative decrease/increase concentration profiles with depth. Dotted red arrow for AMPA metabolite indicate a significant increase with depth from surface. The full data analysis and a more detailed distribution of molecular samples is included in supplementary material Fig. A1 and Tables A3, A7. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.1.1. *Radioactive isotopes*

Tritium – a natural component of the water molecule – reflects recent (surface) input from precipitation and the modern nuclear cycle; measurements of approximately 9–13 TU occur in rainfall from the Cordoba Pampas (Cabrera et al., 2011). Its rapid decay ($t_{1/2} = 12.3$ years) means that groundwater without relatively recent recharge (since the ~1950 s) is tritium-free. Group A (unconfined) waters range from 0.26 to 9.11 TU, with higher values (median 1.69) in group A_1 (shallow water table) vs. group A_2 (deep water table – median 0.73, Fig. 4 and Table A6). Group B (confined aquifer) has low tritium activities (range 0.02 to 0.06 TU) near the limit of detection (0.02; Figs. 4, 5, Tables A1, A6). However, detection of tritium nonetheless indicates a (minor) component of shallow groundwater/surface water input, within recent decades (Thaw et al., 2022). Groundwater tested from many different confined artesian aquifers in Cordoba Pampas shows measurable tritium activities, notably from >0.5 to <2.5 TU (Cabrera et al., 2011), strongly suggestive of some bypass flow of modern water to deep levels within the aquifer system, despite largely pre-Holocene water residence times indicated by radiocarbon data (pMC values < 10), and other lines of evidence – e.g. long-term hydrochemical evolution from bicarbonate to sulfate to chloride-type waters from the recharge to discharge areas (Blarasin et al., 2014; Cabrera et al., 2014).

Radiocarbon (^{14}C) data are here discussed in terms of semi-quantitative age estimates, to constrain modern vs. palaeo-recharge (not for precise residence time quantification). Values of pMC (2.4–5.72) in (semi-)confined groundwater (Type B) indicate recharge tens of thousands of years ago. This group is distinct from much higher values for unconfined groundwater (65.9–100.3 pMC), indicating sub-modern recharge (Fig. 5). These radiocarbon distribution characteristics in groundwater are similar to regional layered unconfined/confined aquifer systems elsewhere in the Pampas region – Cabrera et al., 2014, and analogous sedimentary basins globally – Currell et al., 2010). Within unconfined groundwater, radiocarbon activities are higher in group A_1 (shallow water table) than A_2 (Fig. 3 and Tables A4, A6) indicating shorter residence times and/or more recent recharge.

While it is hypothesised in some similar settings that endogenic CO_2 from deep geological sources may significantly affect groundwater ^{14}C values (making them appear older – see Wang et al., 2020), there is no evidence to support this hypothesis in the present study (e.g. from ^{13}C isotopes or groundwater hydrochemistry).

3.1.2. *Stable isotopes*

Stable isotopes of water reflect recharge source and evaporative processes (Giacobone et al., 2022). A clear difference between deep confined artesian groundwater signatures (Group B median: −6.05 ‰ and −36.9 ‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively) vs. shallower unconfined waters (Group A median: −5.1 ‰ and −28.8 ‰, Fig. 4 and Tables A5, A6) probably reflects a climatic shift, from recharge before the last glacial maximum to the semi-confined aquifer, and more recent Holocene recharge in the unconfined groundwater. Geochemical and isotopic

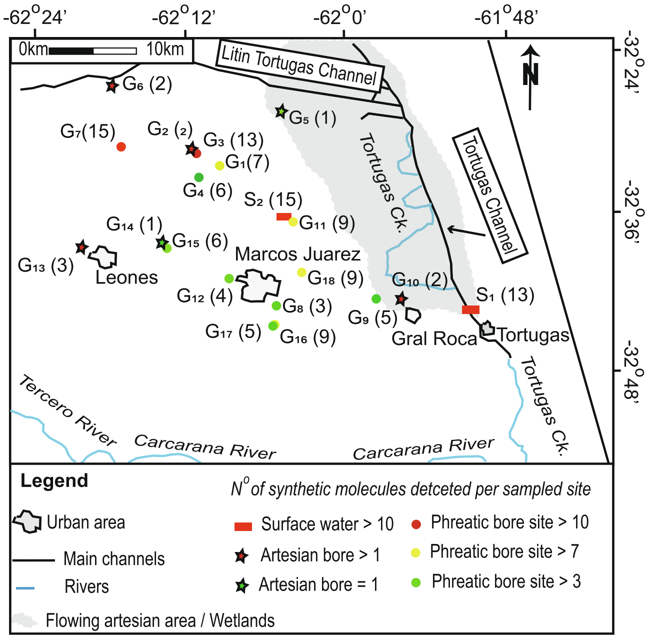

Fig. 3. Plan view map showing synthetic molecule distributions per sampled site in the study area.

studies conducted to the west of the study area validate these recharge timings (Cabrera et al., 2014; Cabrera et al., 2017; Giacobone et al., 2022; Maldonado et al., 2016). Additionally, depletion of hydrogen and oxygen isotopic values in the confined groundwater may also reflect some influence from recharge at higher elevations (e.g., long flow path from the mountainous region to the west).

3.1.3. *Major and minor elements*

Major and minor elements (Fig. 4, Table A2) are typically more concentrated in unconfined groundwater (Type A) compared to confined groundwater (Type B), possibly from evapotranspiration (ET) during diffuse recharge to the water table below intensive agriculture and/or lithological differences among the different groundwater flowpaths (Giacobone et al., 2022). The exception are redox sensitive markers – e.g., Fe and Mn. Mobilization of these elements in the dissolved phase is linked to reducing conditions that are typical of deep confined aquifers; Type B samples showed more negative ORP values than group A as well as enriched Fe and Mn concentrations (Fig. 4). There is also differentiation in the redox-sensitive elements depending on water table depth, with higher concentrations in group A_1 – which more closely resembles (polluted) surface water, compared to A_2.

Deep confined groundwater samples show a relatively clear hydrogeochemical profile for major elements – more saline groundwater is enriched in Na, Cl and SO_4; similar samples in unconfined groundwater (particularly the shallowest wells) show enrichment in practically all major elements (Table A2), denoting a likely anthropogenic influence, such as leakage of water impacted by evapotranspiration below the root zone of intensive cropland (Currell et al., 2010).

The difference in elemental and isotopic characteristics between the shallow (0 to 50 m) and deep (116–140 m) samples likely reflects a combination of different geochemical processes, and flow regimes (e.g., rate of recharge, extent of evaporative enrichment) between the unconfined and confined aquifers (e.g., Cabrera et al., 2011; Nicolli et al., 2012).

3.1.4. *Agrochemicals in groundwater*

Agrochemical diversity and concentration patterns mirror the distinctive chemical-isotopic markers identified in groundwater groups A_1 and A_2 (Table 1; Fig. A1 and Table A7), defining two major types. The group 'Agrochemicals I (surface-like)' have presence in both, surface water channels and groundwater, however these reach maximum concentrations in unconfined groundwater where there is a thin vadose zone <1 m (water type A_1). 'Agrochemicals group II' are mostly in all measured water types, but maximum concentrations and median values are in unconfined groundwater below areas of thicker vadose zone >1 m (water type A_2). Some molecules within this group are found only in groundwater (not surface water).

The grouping is consistent with different behaviour/persistence of various pesticides associated with the periodic connection/disconnection between groundwater and surface water. The group Agrochemicals I (e.g., triazine group, glyphosate and its degradation product AMPA) broadly correlates with literature data highlighting strong presence of these compounds in solution under atmospheric (Alonso et al., 2018; Mas et al., 2020b; Peluso et al., 2022) and/or near surface aerobic/anaerobic conditions; with degradation half-lives between weeks, months or years (Accinelli et al., 2001; Larsen and Aamand, 2001; Lutri et al., 2022; Mas et al., 2020a). Similar findings point to the predominance of Glyphosate (Lutri et al., 2020) and Atrazine (Lutri et al., 2022) in recently recharged groundwater from areas with shallow water tables (Giacobone et al., 2022), see Table 1, Figs. 2 and 4. In contrast, Agrochemicals II (more prevalent in thick vadose zone samples, (Table 1), have little or no presence at atmospheric or near surface conditions, are relatively unstable under sunlight (Choudhury and Dureja, 1996; Pirisi et al., 1996; Sukul and Spiteller, 2000; Wang and Zhao, 2013). These compounds generally have shorter degradation half-lives at surface conditions; between hours and weeks (Choudhury and Dureja, 1996; Daiss and Edwards, 2006; Pirisi et al., 1996; Schleier III et al., 2008; Sukul and Spiteller, 2001). Hence, these agrochemicals are only detected where they are able to rapidly penetrate to deeper levels in the unconfined aquifer.

Both agrochemical types (I and II, Table 1) show similar vertical distributions in concentrations vs. depth (Fig. 2, top row is made by agrochemicals type I). Agrochemical concentration profiles in groundwater generally decreasing from surface to depth but continuing into confined groundwater (Figs. 2 and 6), indicate downwards migration in solution of certain compounds from the surface to confined depths. Pesticide concentration profiles increasing from surface water to groundwater here (Fig. 2) and in other settings (e.g., Lutri et al., 2020) indicate pesticide storage in sediments that may subsequently become mobile, even where vadose zone thickness reaches 25 m (Lutri et al., 2022). We find this pattern, with increasing concentration vs depth, also in semi-confined groundwater between 125–140 m for both agrochemical types I and II (Figs. 2, and 6 e.g., Atrazine and Metolachlor, respectively).

Fig. 5 (and the Fig. 2 vertical profiles) shows how pesticide types and distribution in deep groundwater typically show a similar assemblage to the overlying shallow aquifer, with generally decreasing concentrations (consistent with a vertical transport pathway). It is highly unlikely pesticides applied in the recharge area (located over 200 km away to the west) would result in such similarity in the detected suite of compounds, i.e., if the contaminant sources represented flow to both units from two highly geographically distinct source areas.

4. Discussion

The presence of pesticides up to >100 m depth in groundwater (Figs. 2 and 6) is an alarming finding, contrasting with the common beliefs that:

a) the relatively short degradation times for pesticides (compared to groundwater flow rates to these depths) should protect deep aquifers from contamination.
b) limited agrochemical detections in shallow groundwater should indicate a lack of pollution pathway to deeper levels in an aquifer system.

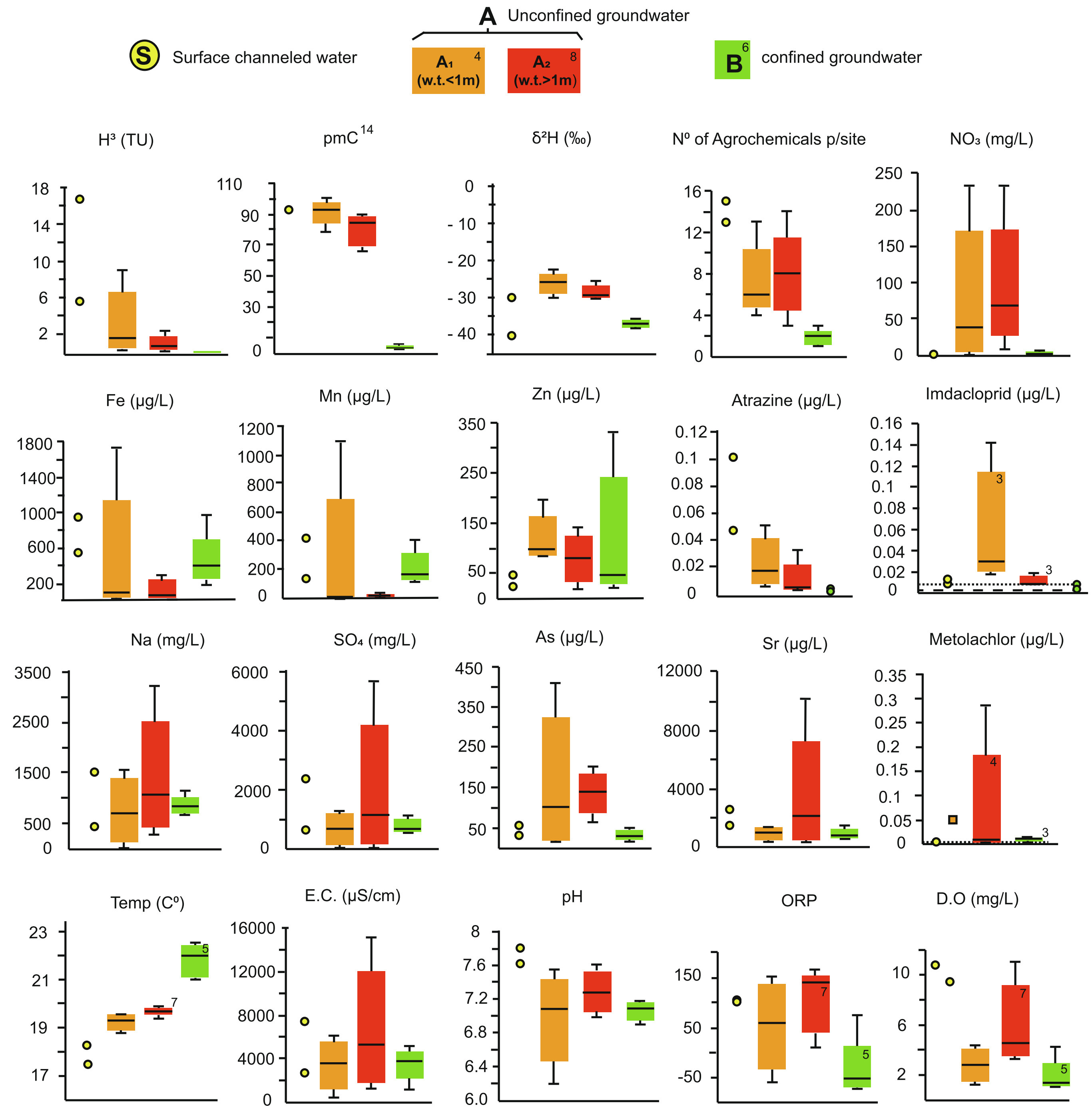

Fig. 4. Water isotopic and chemical signatures for major groups of samples (Methods and Tables A3, A6). Water types A and B reflect level of confinement (i.e., unconfined and confined artesian groundwater respectively), while A_1 and A_2 correspond to groundwater with different water table depths within the unconfined aquifer; groundwater samples with water table <1 m are denoted A_1 and those with water table >1 m, A_2. Circles indicate singular data, box and whisker plots show min/max, median, 1st and 3rd quartiles and numbers at the top right of boxes show number of samples. Dot and dashed lines in agrochemicals charts mark LOQ and LOD (µg/L) values respectively. First row: all groundwater indicators in type A are higher than type B. Second row: Most values (e.g., median, third quartile and max.) in unconfined groundwater A_1 higher than in A_2. Third and fourth rows show data values in unconfined groundwater where group $A_2 > A_1$.

Here, we observed agrochemicals deep in the aquifer system, at some sites even with limited detection of the same compounds in nearby shallower groundwater. For example, boreholes G_{15}/ G_{14} located ~100 m apart (Figs. 1 and 3) and with sampling depths of 10 and 125 m b. s. respectively, show no metolachlor in shallow groundwater but 0.005 µg/l at depth (Fig. 2, Table A3).

The distinct differences in radiocarbon activities (Fig. 5), stable isotopes and hydrochemistry indicate not only very different groundwater residence times (Cabrera et al., 2011; Giacobone et al., 2022) but also a general lack of long-term mixing between the shallow unconfined and deep confined aquifers, which would tend to cause homogenization of these hydrochemical and isotopic characteristics. Based on these and other data from regional studies of hydrochemistry, and groundwater flow patterns in the Pampas (e.g., Cabrera et al., 2014; Maldonado et al., 2016), these two aquifer systems have been identified as distinct layers with limited connectivity – unconfined (~0–100 m)

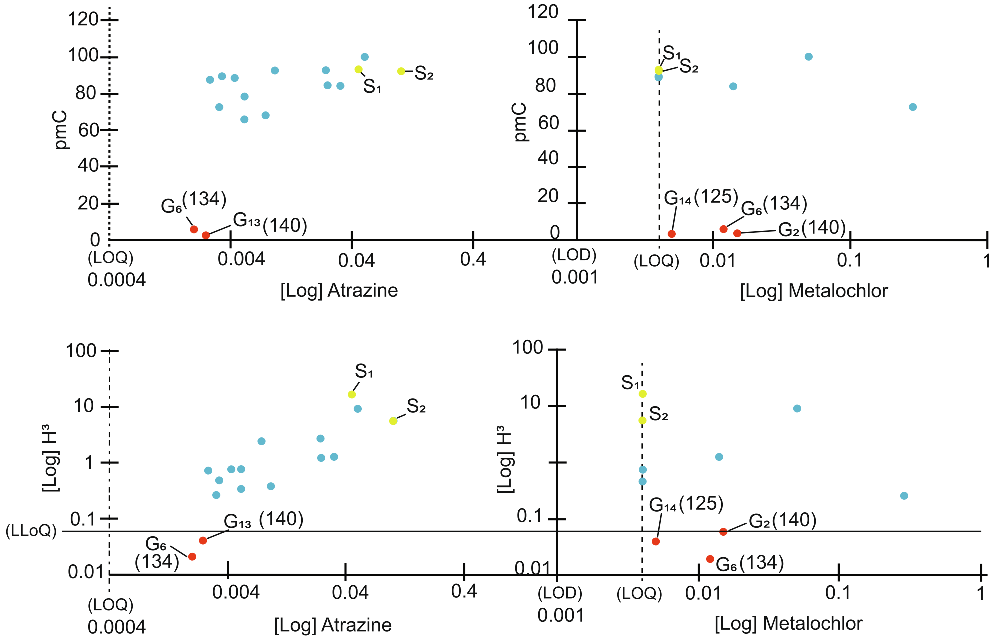

Fig. 5. Bivariant plots for radioactive isotopes and pesticides. Yellow, blue and red circles are sampled surface water, unconfined and confined groundwater bore sites, respectively. LOQ for pesticides and LLoQ for tritium activities are shown in vertical and horizontal dot lines respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Agrochemical detections and median values in μg/L within analyzed water types (as per Fig. 4). Bold numbers show maximum median values, numbers in brackets = number of analyzed samples (for detection range and full data see Table A7). Sampling number in water type S is 2 unless indicated. LOQ and LOD values in μg/L. All data above LOD values. Detections below LOQ have been discarded for median calculations unless number of samples = 1 where the value is taken as the maximum (e.g., <0.008 = 0.008). AMPA = Aminomethylphosphonic acid, * = degradation product of herbicide Glyphosate, ** = degradation products of herbicide Atrazine.

Agro type	Compound		Water type				
		S	A1	A2	B	LOQ	LOD
	Gliphosate	0.23	**3.01 (1)**	0.48 (1)		0.1	0.05
	AMPA*	1.56	**36.72 (2)**	0.44 (1)	4.93 (1)	0.15	0.08
I	**Imidacloprid**	0.012	**0.0293 (3)**	0.0183 (3)	<0.008 (1)	0.008	0.003
	Imazaquin		**0.002 (1)**	<0.001 (3)		0.001	0.0003
	Ametryn	**0.003 (1)**				0.0003	0.0001
	Tebuconazole	**0.008**	<0.005 (1)			0.005	0.002
	Atrazine	**0.074**	0.0169 (4)	0.00475 (8)	0.00225 (2)	0.0004	0.0001
	Atz-(HA)**	**0.045**	0.0361 (3)	0.0283 (3)		0.009	0.003
	Atz-(DIA**	**0.023**	0.0067 (2)	0.0045 (5)		0.006	0.002
	Atz-(DEA)**	0.0320	<0.002 (3)	**0.0365 (4)**		0.002	0.0004
	Imazethapyr	0.0095	0.017 (2)	**0.041 (5)**	0.002 (1)	0.0004	0.0001
	Metsulfuron- Methyl	<0.006	0.011 (2)	**0.033 (4)**		0.006	0.002
	Metaloclhor	<0.004	0.05 (1)	**0.285 (4)**	0.012 (3)	0.004	0.001
	Diclosulam	0.006	0.027 (1)	**0.1095 (4)**		0.006	0.002
II	**Metribuzin**	0.007 (1)		**0.4595 (2)**	0.021 (1)	0.0007	0.0002
	2,4-D	0.023		**0.185 (3)**	<0.015 (2)	0.015	0.005
	Clhorimuron- Ethyl		0.011 (1)	**0.027 (4)**		0.007	0.003
	Picloram		0.009 (1)	**0.013 (2)**		0.008	0.003
	Pirimicarb			**<0.003 (2)**		0.003	0.001
	Acetoclhor			**<0.008 (1)**		0.008	0.003
	Piperonyl butoxide			**0.003 (1)**		0.0025	0.0007
	Metalaxyl			**<0.0004 (2)**	<0.0004 (1)	0.0004	0.0001

and semi-confined (~100–150 m) SAC B (Cabrera et al., 2011; Giacobone et al., 2022).

However, the presence of tritium and agrochemicals in 100% of deep samples from the semi-confined aquifer (at lower concentrations than the unconfined aquifer see Fig. 5) indicates input of recent, contaminated water from the surface (Cabrera et al., 2014; Cabrera et al., 2017; Cabrera et al., 2011; Maldonado et al., 2016). Similar patterns have been observed worldwide in other regions of intensive agricultural development (e.g., Currell et al., 2010; Currell and Han, 2017; Thaw et al., 2022) and urbanisation (Lapworth et al., 2018), but the cause is largely unresolved. Below, a conceptual model is put forward to explain this phenomenon.

4.1. Conceptual model: migration of pesticides to confined groundwater

Our results are difficult to reconcile with typical models of groundwater flow and solute transport, given the limited time of the detected chemicals' existence (most were only widely applied to land since the

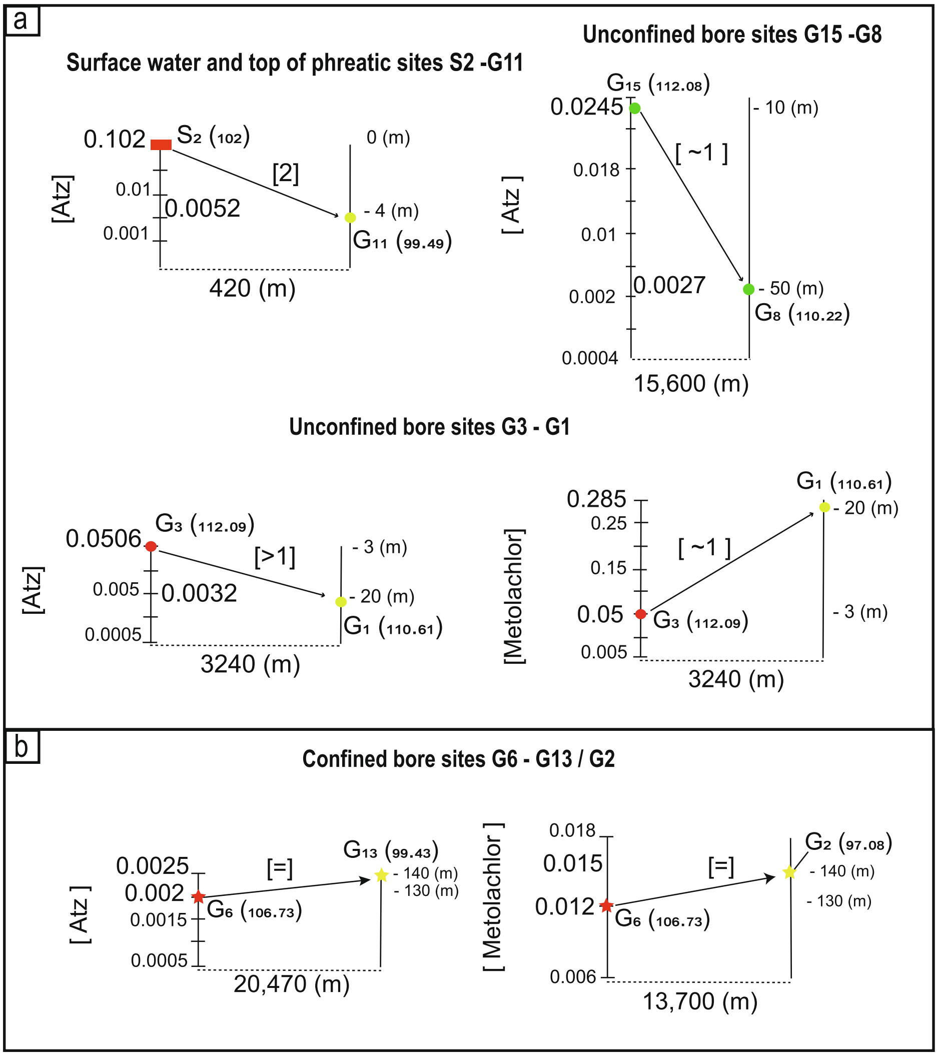

Fig. 6. Cross sections showing pesticide concentrations between sampled sites in the direction of the flow gradient. Horizontal dot line is LOQ for Atrazine and Metolachlor. Numbers between brackets, as in (112.08), are hydraulic potentials from Giacobone et al. (2022). Square brackets indicate order of magnitude in pesticide concentration variations between sampled sites. Symbols and colours for sampled sites are kept from Fig. 3. Numbers in metres (m) show horizontal and vertical distances between sampled sites (horizontal and vertical axes, respectively.

1960s), and the groundwater residence times of tens of millennia indicated by radiocarbon data in the deep aquifer (which are also supported through calculation of hydraulic ages and other lines of evidence – such as long-term hydrochemical evolution within the same regional aquifer system – Blarasin et al., 2014). While rapid lateral flow of groundwater (and pollutants) to the semi-confined aquifer from areas of recharge (e.g. through geological structures) could potentially explain modern pollutant occurrence in the semi-confined aquifer, this is considered highly unlikely. Water and solute transport flow rates through the aquifer media are expected to be orders of magnitude lower than would be required to move pollutants into the semi-confined aquifer SAC B on a timescale of decades (e.g., Jasechko et al., 2017). The deep confined aquifer is only exposed and readily recharged from the surface approximately 200 km to the west, and the radiocarbon data show that flow from this region to the study area occurs on 10,000-year timescales. As such, rapid bypass flow of some fraction of polluted shallow water into the semi-confined aquifer appears to be the only plausible explanation. This is illustrated in Fig. 6 where we contrast the same order of magnitude variation in pesticide concentration between measured bore sites with significant shorter vertical transport distances – ranging from a few meters up to ~140 m compared to horizontal transport over tens of kilometres.

Such vertical bypass flow, resulting in tritium (Fig. 5), nitrate and other pollutants in deep groundwater (Fig. 4) with radiocarbon ages of tens of thousands of years (Fig. 5), has been observed and explained in other settings as being due to intensive exploitation of deep groundwater, coupled with geological and/or man-made preferential conduits, such as fractures, poorly cemented or long-screened production wells (Currell et al., 2010; Currell and Han, 2017; Jasechko et al., 2017; Lapworth et al., 2018; Thaw et al., 2022). However, the lack of extensive deep aquifer pumping for irrigation in the current setting (Giacobone et al., 2022; Gobierno de la Provincia de Cordoba, 2019) makes these detections at depth even more difficult to explain, as artesian (upwards) flow gradients generally predominate (Fig. 7). Whether the pollutants identified in the deep artesian wells are localised (e.g., due to leakage around preferential points such as malfunctioning wells) or whether they are more widespread – e.g., if the pollutants are spreading from these points into wider areas – remains unclear without further data. This is a topic for urgent investigation.

The hydraulic gradient, and the distance required for pollutant transport from source (surface) to deep aquifer (receptor), are the two most fundamental controls that would be normally considered as providing protection for such confined aquifers from modern pollutants. The following sections outline our hypothesis for how both of these

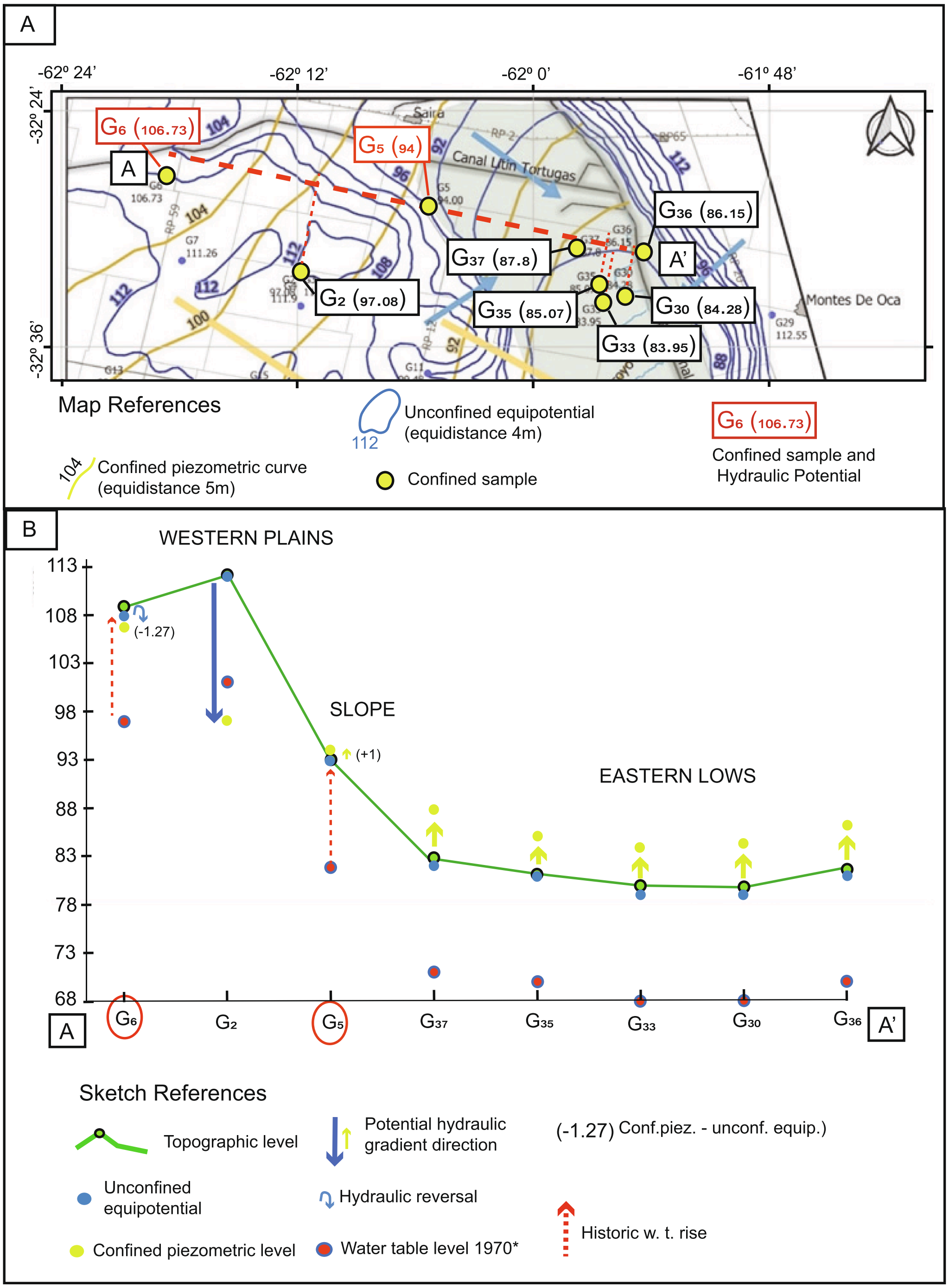

Fig. 7. Modified from (Giacobone et al., 2022). Hydraulic potential map from measurements taken in May 2019 for the studied area. Blue lines and numbers are equipotential for the unconfined aquifer and yellow line and numbers potentiometric surface for the confined aquifer. Blue and Yellow dots (Part B) are Hydraulic heads for the unconfined and confined aquifers respectively, while the red arrow shows rise in unconfined aquifer water table since 1970. Letters and Numbers (G3) are water table and potentiometric measurement and water sampling stations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

factors have been overcome, resulting in groundwater pollution to depths >100 m.

4.1.1. *Hydraulic gradient inversion*

Historically, hydraulic heads in the study area for the unconfined and semi-confined aquifers accorded with typical topography-driven groundwater flow systems in sedimentary basins (e.g., Tóth, 1963). The downward gradient in the recharge zone in the western plains (Fig. 1), potentially allows continuous infiltration of water (and any pollutants) into the unconfined aquifer (Figs. 2–6) (Giacobone et al., 2022). Any flow to deeper levels in the system (e.g., to the semi-confined aquifer) would be slow, allowing time for contaminant breakdown, and resulting in chemical homogenisation between groundwater at the different depths (which is generally not observed in the data). In contrast, the semi-confined aquifer in the eastern lowlands (shaded area in Figs. 1 and 3) is hydraulically protected from direct leakage from the unconfined aquifer (and thus downward infiltration of pollutants) by upward hydraulic gradients.

A hydraulic gradient provides a *potential* for flow along particular pathways; however, this may be dynamic over time (e.g., Currell et al., 2010; Scanlon et al., 2005; Thaw et al., 2022). This is demonstrated in the study area as depicted in Fig. 7, projecting current hydraulic heads from artesian boreholes at the central and northern section of our studied area and historic water level records from a long-term monitoring network of groundwater level in Marcos Juarez (from 1970 to 2018 in Brunori et al., 2017; Ovando, 2019). Here we assume the measured confined piezometric levels have remained ~ stable over time (e.g., 50 years), consistent with the regional flow path >200 km west from the mountain region (Blarasin et al., 2014), and long residence times reported in the literature and the radiocarbon data reported here (Blarasin et al., 2014; Cabrera et al., 2014; Cabrera et al., 2017; Giacobone et al., 2022; Maldonado et al., 2016).

Sub-artesian borehole G_6, sampling water at 130 m depth with a piezometric level of 2.24 m below surface (Tables A2, A8) is located in the northwest plains (Figs. 1 and 3). Plotting the measured potentiometric surface with the calculated current and historic unconfined water levels at this site (Fig. 7) shows how the rise in water table over five decades has overcome the confined piezometric level and inverted the confining vertical hydraulic gradient (formerly positive, now negative), providing the pre-condition for downwards movement of shallow water and pollutants. G_5 is a flowing artesian borehole, sampled at 116 m depth with a piezometric level 1 m above the land surface (Tables A2 and A8). Water table rise in the overlying unconfined aquifer over ~50 years (red dot and arrow in Fig. 7) has reduced the upwards vertical hydraulic gradient considerably, such that it is now only the ~1 m difference in hydraulic head between the two aquifers.

Phreatic water level rise during surface flooding occurs both in artificial (e.g., Yu et al., 2015) and natural settings (Pandey et al., 2014; Sanchez-Pérez and Trémolières, 2003), including the Pampas (Brandolin et al., 2013; Brunori et al., 2017; Plencovich, 2018). Flooding in the surroundings of Marcos Juarez occurs annually during the wet season (Brandolin et al., 2013). During such events, the water table rises and connects with overland flow (e.g., areas with thin vadose <1 m). This provides a temporary potential for downwards infiltration of surface pollution from surface water to first the unconfined, and then the confined artesian groundwater, even for bores where the gradient is normally upwards (e.g., G_5).

The confined aquifer's vulnerability to pollution is thus linked to the effects of recurrent surface loads of water above the aquifer system during the wet season, which also carry pollutants from the intensive agriculture (e.g., see data from surface water samples S_1/S_2 showing a variety of pollutants – Figs. 2, 3 and 4). Flooding is a problem in the area only since widespread monoculture soy plantations substantially modified soil, vegetation and drainage patterns (Arancibia et al., 2020). This land modification caused a dramatic increase in the groundwater table height and flood-prone areas, despite the many constructed surface channels (e.g., Litin and Tortugas channels) intending to mitigate this problem (Brandolin et al., 2013) Recurrent flooding affects low-lying areas permanently during the wet season (Fig. 1 shaded area), but also periodically for large areas of the plains, including within and surrounding Marcos Juarez town (Figs. 1 and 3), with flood levels observed >1 m above the surface (e.g., during April 2021). These events are anticipated to increase with global climate change (Mallakpour and Villarini, 2015), heightening the risk of ongoing pollutant migration via this mechanism.

Chemical markers identified in groundwater are consistent with a (temporary) link to surface water from flooded areas. Artesian boreholes G_6 and G_5 are the closest wells to surface water channels (i.e., within 2.5 km to Litin Channel in Figs. 1 and 3) and are the artesian wells with the strongest surface signatures for surface water – pesticide concentrations, NO_3, ^{14}C, and ^{3}H values are all higher than the median for confined and/or surface water samples (Fig. 4, Tables A2 and A6).

In the lowlands, artesian boreholes G_5 and G_{10} (with head levels 1 and 1.8 m above the surface, respectively, Table A2) are located within the permanent wet areas of the Tortuga's channel (Fig. 1), and as such are vulnerable to major flooding. Both flowing artesian bores recorded detections of a small number of agrochemicals yet at relatively high concentrations. For example, G_5 has detections of 4.93 µg/l of AMPA (i.e., > double values sampled in surface channels) and 6.66 mg/L of NO_3 (vs. median value from semi-confined aquifer of 2.39 and values in surface water of 2.9 and 1.10 in S_1 and S_2 sampled sites, respectively, Tables A3 and A6). Artesian borehole G_6 recorded detections of Metolachlor and Atrazine, with relatively high values for confined samples of 0.012 and 0.002 µg/l, respectively (Table A3), together with ^{14}C of 5.72 pmC, and NO_3 detections of 4.78 mg/L (Table A2); higher than the semi-confined aquifer median (Fig. 3, Table A6). Stable isotopes (δ^2H and $\delta1^8O$) from G_5 and G_6 respectively, were also the most enriched within the confined groundwater group, and both wells recorded tritium (near the detection limit of 0.02 TU, Table A2). This is consistent with the presence of a component of surface affected water mixing with the pre-existing groundwater.

The only slightly enriched tritium and stable isotopic values (Figs. 4, 5 and Table A2) in water from deep wells (see Fig. 5), implies limited volumes of polluted surface water entering the aquifer to mix with the pre-existing, unpolluted groundwater. To arrive at the observed pesticide concentrations (Figs. 2 and 5, Fig. A1 and Table A3), these shallow waters must be carrying high concentrations of certain pollutants (Figs. 3–5). This would result in a two-component mixture that retains much of the hydrochemical and isotopic signature of the un-polluted confined groundwater (i.e., low radiocarbon activities), but with detection of pollutants (nitrate and agrochemicals) and slightly elevated tritium and stable isotopic signatures, characteristic of recent surface water (Fig. 5).

While surface flooding and phreatic rise can create the necessary pre-condition (e.g., when hydraulic gradient reversal occurs) for periodic downward flux of pollutants from unconfined to confined groundwaters, an explanation is still required for how pollutants reach the semi-confined aquifer system so rapidly, given the lack of evidence of hydrochemical homogenization that persists between the unconfined/semi-confined aquifers (Fig. 4 and Table A2).

4.1.2. *Pollutant pathways during dynamic reversal of hydraulic gradients*

Our results show the phreatic aquifer behaving as a pollutant 'reservoir' above confining layer(s), marked by agrochemicals with relative high concentrations sitting within the first 50 m of unconfined groundwater (Fig. 2, Fig. A1). However, the question remains as to how biodegradable herbicide/pesticides can reach such vertical distances (e.g., 20, 36 and 50 m) rapidly enough to be transported further into semi-confined groundwaters (Figs. 2 and 6, e.g., >116 m) during temporary hydraulic gradient reversals described above (Fig. 7).

The first barrier between surface pollutants (e. g., agrochemicals applied to land and carried in surface water channels) and groundwater, is the unsaturated zone thickness (Dahan, 2020). Water table rise in the area since the intensification of agriculture has greatly decreased this thickness (Brunori et al., 2017; Ovando, 2019), to almost zero in places e.g., borehole $G_3 < 0.1$ m (Fig. 1, Table A2), putting surface water and contaminants in close contact with the phreatic surface (Fig. 7). While all analysed unconfined groundwater (including depths from 3 to 50 m b. s.) broadly shows hydrochemical similarity with surface water (Fig. 4 and Table A2), only groundwater in group A_1 (samples beneath thin vadose zone areas), show isotopic signatures indicative of high degree of atmospheric connection, with stable isotopes ($\delta^{18}O$ and δ^2H) values (−4.50 ‰ and −25.7) tritium (9 TU) and radiocarbon (100.3 pMC), within the range of regional precipitation records (Cabrera et al., 2011). Other key markers indicating a high degree of surface connectivity, include fresher EC compared to groundwater below thick vadose zones, (Fig. 5). Thin vadose zone groundwater samples also exhibit enrichment in certain redox sensitive elements (Fe, Mn), and metals as Zn (Fig. 4 and Table A2) consistent with polluted surface water. These characteristics imply a strong degree of surface-connection, which we interpret as reflecting ‘pulses’ of recharge propagating to significant depth in the unconfined aquifer.

Despite a lack of widespread, high volume deep groundwater pumping in the eastern Cordoba Pampas (Plencovich, 2018), deep wells have been drilled throughout the plains to provide local water supplies from the confined aquifers (Giacobone et al., 2022). Such wells often lack full integrity (i.e., cementing of the annular space from surface to the depth of the water intake) and/or have long screens, providing a localized pathway (Fig. 6) for rapid pollutant transport (Currell and Han, 2017; Jiráková et al., 2010). Physical heterogeneities in the geological profile may provide an alternative or additional pathway to such wells (Khan et al., 2016). Under a temporary hydraulic load that is in continuity with the surface (e.g., during flooding) water and highly soluble pollutants will seek a path of least resistance and propagate to deep groundwater (through confining layers) via zones of contrasting permeability – e.g., fractures and faults, zones of coarse sediment within aquitard layers and seepage along the borehole wall. Such transport pathways, provide the only means for rapid propagation of young water into deep wells, carrying pollutants, and result in vertical profiles of pollutants which decrease with depth, but in many cases, show limited degradation of the chemicals (which would be expected during more gradual vertical propagation).

Recent reviews of tritium data in public supply wells indicate widespread propagation of small fractions of ‘modern’ water into deep (semi-)confined aquifers under the influence of intensive groundwater extraction (Thaw et al., 2022; Jurgens et al., 2022). However, in this case, similar propagation of modern water (which contains substantial pollutant loads) to deep wells appears to be un-related to high volume groundwater extraction, occurring as a transient phenomenon during seasonal periods of high water tables, where the unsaturated zone’s pollutant attenuation capacity is markedly reduced due to full saturation.

4.2. *Risk from agrochemicals persisting deep artesian groundwater*

The great diversity and concentration of agrochemicals detected in this study, in deep artesian groundwater >116 m. s. (Fig. 2), and similar findings in India (i.e., Lapworth et al., 2018) are a new and alarming finding with respect to deep aquifer pollutant risk. Pesticide detections in groundwater tens to hundreds of meters deep (Figs. 2, 3 and 6, Fig. A1) are rarely (but nonetheless sometimes) found in the literature (Carretta et al., 2022; Grandcoin et al., 2017; Lapworth et al., 2018) as monitoring programs are rare, or it is simply deemed unlikely, due to the lack of a well-accepted conceptual model for their transport (e.g., Battaglin et al., 2014; Grandcoin et al., 2017). Here we show detections of the glyphosate metabolite AMPA in groundwater from an artesian borehole with 4.91 μg/L – higher than compiled borehole data from the USA including more than 1600 boreholes (i.e., 4.88 μg/L in Battaglin et al., 2014; Scribner et al., 2007).

In areas of dryland farming, as in the eastern Cordoba Pampas of Argentina, five decades of modification of the land surface and hydrology to establish intensive, chemical-dependent crop production (e.g., Arancibia et al., 2020; Baldi and Paruelo, 2008) is associated with a dramatic increase in surface flooding, and a continual rise of the water table (e.g., Brandolin et al., 2013; Brunori et al., 2017). We demonstrate that such landscape modification is associated with significant risk of pollutant transport including into deep levels within a sedimentary aquifer system, particularly where a high density of boreholes provides both important domestic water supplies, but also a pathway for rapid pollution transport to deep groundwater. Recent studies in Cordoba Pampas also suggest a likelihood of the appearance of agrochemicals in groundwater associated with shallow water tables (Lutri et al., 2022; Lutri et al., 2020). Like dryland farming, irrigated agriculture is also commonly associated with significant rises and fluctuations in water table, as well as reduction in groundwater levels in underlying deeper aquifers (e.g., Siebert et al., 2010). Pollutants associated with chemical fertilizers have been detected in such settings within deep confined aquifers, where groundwater residence times are naturally tens of thousands of years (Besser et al., 2022; Currell et al., 2010; Han et al., 2016); though few studies have sampled pesticides to determine their presence in such waters. Areas of intensive chemical agriculture may have thus become large pollutant ‘reservoirs’ that threaten groundwater quality in aquifers otherwise thought to be protected by confining layers.

5. Conclusions and implications for global groundwater quality

Our results, indicate rapid downwards vertical migration of water and pollutants – including synthetic pesticides from the surface to deep wells (Figs. 2 and 6). The lack of homogenization in chemistry between the unconfined and confined aquifers (Figs. 4 and 5) indicates that this must occur via bypass flow (Fig. 5), as opposed to widespread mixing, which would result in gradual chemical homogenization with depth. Surface flooding and groundwater recharge through irrigation return flow have both artificially raised the water table in recent decades, creating conditions for periodic (or long-term) inversion of previously upwards hydraulic gradients (Fig. 7). Our data indicate that this has created opportunities for pollutants to bypass the significant thickness of low-permeability sediments and reach deep groundwater, through preferential conduits (such as unsealed or damaged wells). This appears to allow synthetic organic molecules to reach wells with depths >100 m, without being degraded (Figs. 2 and 6).

To our knowledge, this is the first documented case where synthetic pollutants have been observed in a semi-confined artesian aquifer, where there is limited exploitation of the deep groundwater for irrigation. In such areas, the continual surface land modification and application of surface pollutants below intensive chemical agriculture lands can be considered a threat to ‘fossil’ groundwater reserves, which are relied upon as sources of fresh drinking water by hundreds of millions of people worldwide and are widely considered to have low vulnerability to surface pollution. We urge further investigation addressing both the vertical and horizontal distribution of hydraulic heads and surface pollutants in deep groundwater.

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CRediT authorship contribution statement

Agustín Cabrera: Investigation, Writing – original draft, Writing – review & editing, Conceptualization, Visualization. **Dioni I. Cendón:** Writing – review & editing, Methodology, Conceptualization. **Virginia Aparicio:** Writing – review & editing, Methodology. **Matthew J. Currell:** Writing – review & editing, Visualization, Supervision, Resources, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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