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Pollutant sources in an arsenic-affected multilayer aquifer in the Po Plain of Italy: Implications for drinking-water supply

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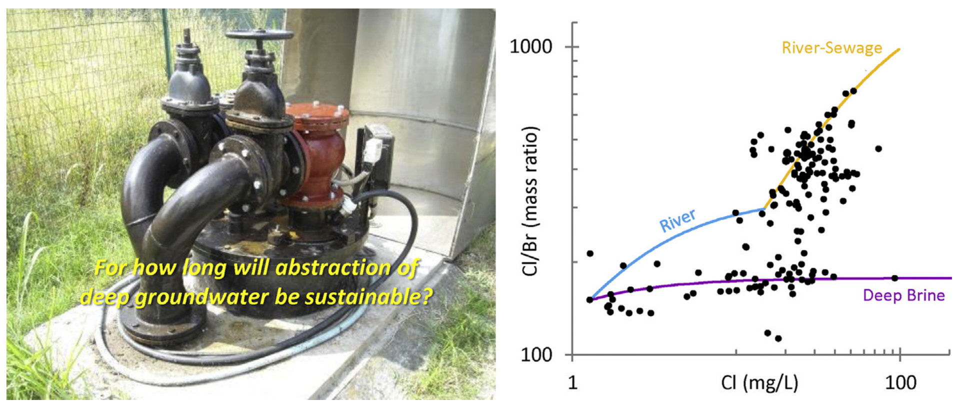
HIGHLIGHTS

- Deep aquifers of Lombardy, Po Plain, contain mostly <50 μg/L As.
- Deep aquifers are being flushed of historical salinity by fresher recharge.
- Arsenic concentrations in the deep aquifer may be increasing with time.
- Shallow aquifers are pervasively contaminated by sewage effluent in channel water.

GRAPHICAL ABSTRACT



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ABSTRACT

In aquifers 160 to 260 m deep that used for public water-supply in an area ~150 km^2 around the town of Cremona, in the Po Plain of Northern Italy, concentrations of arsenic (As) are increasing with time in some wells. The increase is due to drawdown of As-polluted groundwater (As ≤144 μg/L) from overlying aquifers at depths 65 to 150 m deep in response to large-scale abstraction for public supply. The increase in As threatens drinking-water quality locally, and by inference does so across the entire Po Plain, where natural As-pollution of groundwater (As >10 μg/L) is a basin-wide problem.

Using new and legacy data for Cl/Br, $\delta^{18}O/\delta^{2}H$ and other hydrochemical parameters with groundwater from 32 wells, 9 surface waters, a sewage outfall and rainwater, we show that the deep aquifer (160–260 m below ground level), which is tapped widely for public water-supply, is partly recharged by seepage from overlying aquifers (65–150 m below ground level).

Groundwater quality in deep aquifers appears free of anthropogenic influences and typically <10 μg/L of As. In contrast, shallow groundwater and surface water in some, not all, areas are affected by anthropogenic contamination and natural As-pollution (As >10 μg/L). Outfalls from sewage-treatment plants and black water from septic tanks firstly affect surface waters, which then locally infiltrate shallow aquifers under high channel-stages. Wastewater permeating shallow aquifers carries with it NO_3 and SO_4 which suppress reduction of iron oxyhydroxides in the aquifer sediments and so suppress the natural release of As to groundwater.

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1. Introduction

Contamination is the presence of a substance in the environment at a concentration that is unusually high. Pollution is contamination that causes environmental harm. Human settlements on alluvial plains commonly use underlying groundwater for domestic consumption, industry, and irrigation, both contaminating and polluting it in the process. Such aquifers may also be adversely affected by natural contamination (*e.g.* from Fe) and natural pollution (*e.g.* from As). These adverse influences lower groundwater quality and threaten aquifer sustainability, and the aquifers of the Po Plain of Northern Italy are not exempt (Onorati et al., 2006).

The Po Plain covers an area of 46,000 km^2 and is Italy's largest alluvial basin; it is also one of the larger in Europe. The plain is crossed by the Po River, which flows 650 km from W to E collecting water from 141 tributaries and hundreds of irrigation channels. The Po Plain is home to around 20 million inhabitants, is the most important economic area of Italy, and is subject to human influence across both the 75% of its area that is agricultural land and the 10% that is urban development (Falcucci et al., 2007).

Groundwater abstracted from the Po Basin is used for irrigation, domestic supply, and by industry (AdBPo, 2006). In order to avoid human influences, groundwater for public supply was initially taken from depths > 150 m. In some areas, such deep abstraction encounters natural pollution by As, *i.e.* concentrations > 10 μg/L (WHO, 2011; Carraro et al., 2015; Molinari et al., 2012; Rotiroti et al., 2014b). To avoid such As-pollution, abstractions were deepened to be some 200–300 m below ground level (m bgl) where As concentrations were < 10 μg/L. Groundwater from depths > 200 m is up to ~54,000 years old and its exploitation may constitute mining of a resource that is replenished only slowly (Martinelli et al., 2014) by leakage from overlying aquifers that are As-polluted (Rotiroti et al., 2014b) and/or by upconing from underlying aquifers that are saline (Conti et al., 2000; Martinelli et al., 2014).

Given the long-term threat to the sustainability of deep-groundwater posed by migration of As and salinity, we here (a) asses the source of recharge to deep aquifers tapped for domestic supply and (b) assess sources of salinity in deep groundwater and whether the deep aquifers are freshening or becoming more saline in groundwaters used for public supply; (c) assess whether As concentrations in the deep aquifer are changing with time; (d) discuss the impact of our findings on extant models of the mechanism of As-pollution in the aquifer system of the Po Plain; (e) evaluate the sources of recharge to, and human influences on, the shallow aquifer.

2. Geology and hydrogeology

2.1. The aquifers of the Po Plain

The alluvial aquifers of the Po Plain are underlain by Pliocene marine deposits. The aquifers comprise Pleistocene sediments that prograded from W to E and were then overlain by Holocene fluvial sediments (Garzanti et al., 2011; Marchetti, 2002). Alpine glaciation and deglaciation significantly increased the rate of glacio-fluvial aggradation and yielded gravel and sand units intercalated with units of silt/clay. The thickness of the silt/clay units increases from north (the Alpine foothills) to south (the Po River), reflecting the waning transport energy of glacial and post-glacial rivers (Ori, 1993). This geological setting is particularly evident in Lombardy Region (Fig. 1), where a monolithic aquifer of gravel and sand in the northern, higher, part of the plain passes southwards into a multilayer system around the Po River in the lower plain (Bonomi, 2009; Perego et al., 2014).

In the multilayer system of lower plain, the deeper aquifers have a sluggish circulation and so longer residence times for groundwater under natural conditions of flow (Martinelli et al., 2014). The long residence times and confinement of the deeper aquifers promote reducing conditions and the mobilization of As, Fe, Mn and NH_4 driven by degradation of organic matter buried in peaty sediments (Carraro et al., 2013; Francani et al., 1994; Rotiroti et al., 2014b; Zavatti et al., 1995).

2.2. The aquifers of the study area in the Po Plain

This work refers to a 150 km^2 area around the town of Cremona (lower Po Plain, N Italy; ~70,000 inhabitants). The details of aquifer architecture and aspects of groundwater quality, including As-pollution have been presented in Rotiroti et al. (2015a, 2015b, 2014a, 2014b) so only a summary is given here.

This multilayer aquifer comprises 5 aquifer units. These are designated *U*, *S*, *C1*, *C2* and *C3* (Fig. 2), where *U* means unconfined, *S* means semi-confined, and *C* means confined. Depth ranges are 0–25 m for *U*; 30–50 for *S*; 65–85 m for *C1*; 100–150 m for *C2*, and 160–260 m for *C3*. Aquifers underlying *C3*, classified as Aquifer Group B (Carcano and Piccin, 2002), are not exploited in this area since they are saline (Conti et al., 2000). Flow in aquifers *U* and *S* is from north to south owing to a strong topographic control. Flow direction in the deeper confined aquifers (*C1*, *C2*, *C3*) is from NW to SE, which is also the direction of regional groundwater flow (Vassena et al., 2012). The minimum hydraulic head is seen in *C2* (Rotiroti et al., 2014b), resulting in convergent flow into aquifer *C2* from both above and below. However, the presence of well-fields tapping aquifer *C3* for public water-supply locally induces a fall of hydraulic heads of up to 6 m (Cambi et al., 2005) that induce a reversal of flow to *C3*.

In aquifer *U*, redox condition range from reducing to oxidising in response to local factors. In other aquifers, groundwater is anoxic and contains As, Fe, Mn and NH_4 in concentrations that commonly exceed regulatory limits (10, 200, 50 and 500 μg/L, respectively).

The public water-supply to Cremona comprises groundwater from two well-fields, one of 9 wells that lies close to the western outskirts of Cremona (Fig. 1, box A) and another of 10 wells that lies close to the eastern outskirts (Fig. 1, box B). Both tap aquifer *C3*, which is the deepest aquifer. Before addition to the public supply, the groundwater is treated to reduce concentrations of As, Fe, Mn, and NH_4 (Sorlini and Gialdini, 2014).

The Adda and Po Rivers flow across the area (Fig. 1). In addition, multiple shallow irrigation channels both direct river water to fields for irrigation and act as drains at times of excess outflow when water tables are high *i.e.* from May to August. Two main collector channels, the Morbasco and Cerca channels (Fig. 1) were sampled for this work. The Morbasco is ~32 km long and flows into the Po River. It receives treated sewage from the municipal sewage-treatment plant of Cremona as well as untreated discharges from unsewered sanitation. The Cerca Channel (~6 km long) flows into the Morbasco Channel and is the tail of the Naviglio Civico di Cremona Channel, a ~57 km long canal fed by Adda and Oglio Rivers.

The study area comprises mostly agricultural land that is mostly engaged in livestock farming, especially pig rearing, and in the cultivation of maize (Bartoli et al., 2012). Animal manure is spread widely on land as a fertilizer to avoid use of more expensive synthetic fertilizers such as ammonium sulphate. The area is thus classified as nitrate-vulnerable zone (91/676/EEC). From May to August, maize is irrigated through an extensive network of irrigation channels.

Irrigation started in the 12th Century with the construction of the first irrigation channels (Marchetti, 2002), and it has been practised on its present scale since the 1950s. Today, irrigation water in Lombardy derives 96.8% from rivers, 0.7% from groundwater, and 2.5% from springs and lakes. The total volume of irrigation water is ~8×10^9 m^3/y (Zucaro and Corapi, 2009). Infiltration of irrigation water constitutes a major source of recharge for shallow aquifers and causes groundwater levels to increase during the growing season (April to September; Facchi et al., 2004). Rainfall provides a secondary source of recharge with total precipitation typically of 750 mm per year (Bonomi et al., 2008) falling

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