



Fate of arsenic, phosphate and ammonium plumes in a coastal aquifer affected by saltwater intrusion



N. Colombani^a, M. Mastrocicco^{b,*}, H. Prommer^{c,d,e}, C. Sbarbati^a, M. Petitta^a

^a Department of Earth Sciences, "Sapienza" University, Rome, Italy

^b Department of Physics and Earth Sciences, University of Ferrara, Ferrara, Italy

^c CSIRO Land and Water, Private Bag No. 5, Wembley, WA 6913, Australia

^d School of Earth and Environment, University of Western Australia, 35 Stirling Hwy, Nedlands, WA 6009, Australia

^e National Centre for Groundwater Research and Training (NCGRT), Flinders University, GPO Box 2100, Adelaide, SA 5001, Australia

ARTICLE INFO

Article history:

Received 19 January 2015

Received in revised form 27 May 2015

Accepted 2 June 2015

Available online 10 June 2015

Keywords:

Coastal aquifer

Groundwater pollution

Arsenic

Reactive transport modelling

ABSTRACT

A severe groundwater contamination with extensive plumes of arsenic, phosphate and ammonium was found in a coastal aquifer beneath a former fertilizer production plant. The implementation of an active groundwater remediation strategy, based on a comprehensive pump and treat scheme, now prevents the migration of the dissolved contaminants into the marine environment. However, due to the site's proximity to the coastline, a seawater wedge was induced by the pumping scheme. Additionally the groundwater flow and salinity patterns were also strongly affected by leakage from the site's sewer system and from a seawater-fed cooling canal. The objective of this study was to elucidate the fate of arsenic and its co-contaminants over the site's history under the complex, coupled hydrodynamic and geochemical conditions that prevail at the site. A detailed geochemical characterisation of samples from sediment cores and hydrochemical data provided valuable high-resolution information. The obtained data were used to develop various conceptual models and to constrain the development and calibration of a reactive transport model. The reactive transport simulations were performed for a sub-domain (two-dimensional transect) of an earlier developed three-dimensional flow and variable density solute transport model. The results suggest that in the upper sub-oxic zone the influx of oxygenated water promoted As attenuation via co-precipitation with Al and Fe oxides and copper hydroxides. In contrast, in the deeper aquifer zone, iron reduction, associated with the release of adsorbed As and the dissolution of As bearing phases, provided and still provides to date a persistent source for groundwater pollution. The presented monitoring and modelling approach could be broadly applied to coastal polluted sites by complex contaminant mixture containing As.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Arsenic (As) is a widely occurring geogenic and anthropogenic contaminant in groundwater and a common threat to drinking water resources throughout the world, particularly in the big river deltas of South East Asia (Amini et al., 2008; Berg et al., 2007; Fendorf et al., 2010; Mandal and Suzuki, 2002; Sharma et al., 2014; Smedley and Kinniburgh, 2002). In

groundwater, As is generally found in its inorganic form, either as arsenate (As^{V}) or as arsenite (As^{III}), while organic complexes, such as monomethyl arsonic acid and dimethyl arsenic acid, are less commonly reported (Moldovan et al., 2003). As prevails as As^{III} under geochemically reducing conditions, whereas As^{V} is dominating in oxic environments (Cullen and Reimer, 1989; Smedley and Kinniburgh, 2002). The predominating redox status is affecting both its mobility and bioavailability (Ahmed et al., 2004; Shaw, 2006). Due to the ubiquitous nature of geogenic As pollution and its past and current health impacts (Kapaj et al., 2006; Schwarzenbach et al., 2010) most research

* Corresponding author.

E-mail address: mtm@unife.it (M. Mastrocicco).

over the last two decades has focused on understanding the underlying mechanisms and patterns of As mobilisation, its mobility in the aqueous phase and on geochemical cycling in general (Charlet and Polya, 2006; Hering and Kneebone, 2002; Lin and Puls, 2003; McArthur et al., 2004). However, inorganic As has also been widely used in the production cycle of fertilizers and pesticides. Therefore anthropogenic contamination, e.g., through leakages into sub-soils and pollution of shallow groundwater has also occurred in many instances (Cancés et al., 2005; Davis et al., 1994; Root et al., 2009), whereby potential As pollution pathways may also include indirect diffusive sources such as phosphate fertilizer spreading (Campos, 2002). For both geogenic and anthropogenic pollution cases elucidating the past, present and future fate of As is generally non-trivial due to the many physical and chemical factors that can affect the mobility and migration rates between sources and potential receptors. For example, As is often mobilised where reductive dissolution of Fe-hydroxides occurs. In those cases As desorption can proceed either (i) because sorption sites are successively depleted or (ii) as a result of HCO_3^- production during organic matter mineralisation, which increases competition for the remaining sorption sites associated with Fe-hydroxides (McArthur et al., 2004; Wang et al., 2013). The As fate and transport is further exacerbated in polluted coastal aquifers, where complex flow patterns can arise from variable water densities, which overlap with steep geochemical gradients and is usually enhanced. The latter include strong variations in ionic strength, pH, and the redox environment, which are often the most important geochemical factors controlling As migration. Arsenic pollution of coastal groundwater has been reported in several studies, generally with a strong focus on the geochemical characterisation of the affected sites. Elevated As concentrations were detected in a coastal aquifer-aquitard system in the Pearl River delta in China (Wang et al., 2012), where aquatic As was derived from reductive dissolution of iron hydroxide and authigenic pyrite was recognised to control As groundwater concentrations (Wang et al., 2013). Foley and Ayuso (2008) showed that a variety of mineral phases containing As could be the responsible of the elevated groundwater concentrations found in the coastal aquifer of the Maine (USA). The south-western coastal aquifer of Taiwan was studied using sulphur isotopes to elucidate reductive dissolution of As-bearing iron hydroxides (Kao et al., 2011). A specific geomorphic model developed for the Stuarts Point aquifer (Australia) showed that As was derived from erosion of arsenic-rich stibnite (O'Shea et al., 2007). One of the few examples that provided a quantitative description of arsenic fate is the study of Jung et al. (2009) in which a two-dimensional reactive transport model was used to better understand the observed spatial patterns of iron and arsenic in sediments and groundwater at Waquoit Bay. However, more studies are still needed to further improve our capabilities in quantifying and predicting the behaviour, i.e., the spatio-temporal distribution of arsenic concentrations and mass fluxes in coastal groundwater environments as a basis for assessing the risks to sediments and marine waterbodies. On a local scale an important feature affecting coastal transport and reaction patterns is tidally induced mixing (Mao et al., 2006; Robinson et al., 2009). However, the impact may be negligible where the magnitude of the tidal fluctuations remains small (e.g., <0.2 m of amplitude, Sammari et al., 2006).

In the present study, we developed and applied a reactive transport model to analyse and quantify As behaviour in a highly polluted coastal aquifer system. A step-wise approach was employed to elucidate the fate and transport of As and its dependence on a multitude of geochemical factors, as well as on the fate of the two major co-contaminants ammonium (NH_4^+) and phosphate (PO_4^{3-}). Previously collected hydrogeological and geochemical characterisation data in conjunction with new detailed concentration profiles from a coastal field site, affected by saltwater intrusion, were employed to constrain a fully coupled model for reactive transport under variable density conditions.

2. Material and methods

2.1. Site description

The study site is a coastal aquifer that is comprised of recent alluvial deposits (Pleistocene–Holocene) that is hydrologically connected to the Mediterranean Sea. The main aquifer consists of sandy and sandy-loam deposits, interbedded by silt and silty-clay lenses and an aquifer thickness varying slightly between 25 and 30 m (Mastrocicco et al., 2011). The underlying aquitard consists of a thick clay layer that has an average thickness of 25 m, extending to a depth of –50 m above sea level (a.s.l.). The aquifer hosts over 70 pumping wells, which are part of an active “pump and treat” remediation strategy. That strategy also includes two slurry walls that were constructed to locally intercept groundwater flow towards the marine environment.

The piezometric surface in the unconfined aquifer shows seasonal changes that mostly respond to the variations in groundwater recharge and pumping rates. Groundwater flow occurs perpendicular to the coastline with an average hydraulic gradient of 0.6% and a maximum of 1% in proximity of the pumping wells. Inland, groundwater flow is largely driven by artificial recharge from a seawater-containing canal (Fig. 1). Mastrocicco et al. (2013) estimated that seawater discharges at a rate of approximately 20 L/s into the aquifer. Towards the sea, groundwater flow is captured by the pumping wells and therefore piezometric heads in this zone are below sea level (Fig. 1). This suggests that the pumping wells that form the remediation systems reverse the natural hydraulic gradient and therefore prevent that contaminated groundwater is discharged into the sea (Mastrocicco et al., 2013). Hydraulic tests at the site determined an average transmissivity in the sandy aquifer of about 320 m^2/day , corresponding to an average hydraulic conductivity of about 18 m/day (Mastrocicco et al., 2011, 2013).

The facility that was formerly hosted at the study site (Fig. 1) produced various agricultural fertilizers since the early 1970s until 1990 whereby As trioxide (As_2O_3) served as one of the raw materials for the fertilizer production. As_2O_3 was shipped to the manufacturing facility by trucks and then stocked above ground in large tanks, in front of the NH_3 plant. The end products were manufactured at the NH_3 plant and then stocked in large storage buildings located immediately south of the NH_3 plant. The above ground tanks area and the storage buildings area have been identified as past sources (Fig. 1). Arsenic that had accidentally escaped the facilities was dispersed by surface water runoff, movement of groundwater, and wind-blown. A detailed site characterisation has identified an area of over 4 ha underlain by

Download English Version:

<https://daneshyari.com/en/article/6386459>

Download Persian Version:

<https://daneshyari.com/article/6386459>

[Daneshyari.com](https://daneshyari.com)