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The transport behaviour of elemental mercury DNAPL in saturated porous media: Analysis of field observations and two-phase flow modelling

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ABSTRACT

Mercury is a contaminant of global concern. The use of elemental mercury in various (former) industrial processes, such as chlorine production at chlor-alkali plants, is known to have resulted in soil and groundwater contaminations worldwide. However, the subsurface transport behaviour of elemental mercury as an immiscible dense non-aqueous phase liquid (DNAPL) in porous media has received minimal attention to date. Even though, such insight would aid in the remediation effort of mercury contaminated sites. Therefore, in this study a detailed field characterization of elemental mercury DNAPL distribution with depth was performed together with two-phase flow modelling, using STOMP. This is to evaluate the dynamics of mercury DNAPL migration and the controls on its distribution in saturated porous media. Using a CPT-probe mounted with a digital camera, in-situ mercury DNAPL depth distribution was obtained at a former chlor-alkali-plant, down to 9 m below ground surface. Images revealing the presence of silvery mercury DNAPL droplets were used to quantify its distribution, characteristics and saturation, using an image analysis method. These field-observations with depth were compared with results from a one-dimensional two-phase flow model simulation for the same transect. Considering the limitations of this approach, simulations reasonably reflected the variability and range of the mercury DNAPL distribution. To further explore the impact of mercury's physical properties in comparison with more common DNAPLs, the migration of mercury and PCE DNAPL in several typical hydrological scenarios was simulated. Comparison of the simulations suggest that mercury's higher density is the overall controlling factor in controlling its penetration in saturated porous media, despite its higher resistance to flow due to its higher viscosity. Based on these results the hazard of spilled mercury DNAPL to cause deep contamination of groundwater systems seems larger than for any other DNAPL.

1. Introduction

The historical use of elemental and ionic forms of mercury in various industrial proce'sses has caused mercury to become a contaminant of global concern. This is due to its long-range transport in the atmosphere, its persistence in the environment, its ability to bioaccumulate in ecosystems and its substantial negative effect on human health and the environment (Horvat et al., 2003; Ullrich et al., 2001; Walvoord et al., 2008; World Chlorine Council, 2011). Contaminated industrial sites include former wood-preservation and mining sites as well as (former) chlor-alkali plants (e.g. Arbestain et al., 2009; Bernaus et al.,

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2006; Biester et al., 2002a, 2002b; Brooks and Southworth, 2011; Miller et al., 2013).

To date, the scientific research on mercury contamination in wastewater, soil, and groundwater systems has focussed largely on the behaviour and ecotoxicological effects of ionic and methylated Hg forms (Gabriel and Williamson, 2004; Horvat et al., 2003; Jackson, 1998; Johannesson and Neumann, 2012; Lopes et al., 2013; Schuster, 1991). Mercury species have contaminated groundwater due to their use in industrial processes. For example through the use of $HgCl_2$ in wood-preservation (Bollen et al., 2008). Other mercury species may result from the redox transformation of elemental mercury to mercury(II) compounds by oxidation or to methylmercury by subsequent methylation under reducing conditions. The extent to which mercury undergoes these redox transformations strongly depends on the soil and groundwater redox chemistry (Hu et al., 2013; Schuster, 1991). Under sufficiently reducing groundwater conditions, reduction of ionic mercury species may result in the formation of elemental mercury phase (Bollen et al., 2008).

Nowadays, chlor-alkali plants are still responsible for the largest industrial use of elemental mercury, although its global use is rapidly decreasing (World Chlorine Council, 2011) and the European chlorine producers are phasing out its usage by 2020 (EuroChlor, 2010). At numerous (former) industrial sites, liquid elemental mercury in the subsurface has been observed, particularly at (former) chlor-alkali plants. For example, liquid mercury was found at a former chlor-alkali plant near Onodaga Lake, New York, at depths down to 17 m below surface (Deeb et al., 2011; ITRC, 2012). Also, liquid mercury was observed in soil samples, and wells in Lavaca Bay (Texas), surrounding a former chlor-alkali plant (Scanlon et al., 2005). Moreover, at the Oak Ridge Y-12 National Security Complex, 11 million kg mercury was used during 1950 to 1963 from which an estimated 193,000 kg was lost to the soil (Brooks and Southworth, 2011). At such sites exposure to mercury DNAPL during handling is a key difficulty (Deeb et al., 2011).

Being the heaviest known liquid, with a density of 13.5 kg L^{-1} at standard conditions and immiscible with water, liquid elemental mercury can be considered as a dense non-aqueous phase liquid (DNAPL). Analogue to better known DNAPLs, sites contaminated with mercury DNAPL are likely to act as long-lasting sources for more mobile and toxic mercury compounds, either as mercury vapour or ionic mercury species in groundwater. However, in contrast with more common DNAPL types (e.g. creosote, carbon tetrachloride, trichloroethylene (TCE) and perchloroethylene: PCE), scientific studies on the infiltration behaviour of mercury DNAPL into soils and aquifers are still very limited (Devasena and Nambi, 2010). Contrasting behaviour for mercury DNAPL is however expected as liquid mercury is not only an order of magnitude denser than more commonly studied DNAPLs, but also its viscosity and particularly its surface tension deviate (Table 1). To date however, it is unknown how these different properties affect the transport and distribution behaviour of elemental mercury infiltrating the subsurface. Improved insight in the infiltration behaviour of mercury DNAPL, and how it differs from more common DNAPLs, will aid the characterisation, risk-assessments and evaluation of remediation options of mercury DNAPL contaminated sites.

Only recently, the saturation behaviour of mercury DNAPL in water-saturated sands has been studied by using short column experiments (Devasena and Nambi, 2010). As known for other DNAPLs, their results indicated that mercury DNAPL flow is governed by gravitational and capillary forces, hence its high density and surface tension, respectively. Moreover, they showed that for the water–sand system, mercury DNAPL can be considered as a non-wetting liquid because an entry-pressure was required for mercury to infiltrate the water-saturated sands. Following Cohen and Mercer (1990), this implies that water or air preferentially wets the surface of sand grains rather than mercury. In this respect, mercury acts as a non-wetting DNAPL similar to PCE (e.g. Schwille, 1988). However as shown in the study of Devasena and Nambi (2010), the distinctively different fluid properties may result in much lower residual saturations for mercury (0.04) than for TCE (0.14) and PCE (0.17).

The recent pioneering study by Devasena and Nambi (2010) provides valuable insight in the characteristics of the two-phase mercury DNAPL–water system. However the dynamic aspects of mercury infiltration and distribution remain unclear, particularly at the field scale. Therefore, in this study we combined field characterisation data of mercury DNAPL contaminated soil at a former chlor-alkali site in The Netherlands with a multi-phase flow model. Goals of this study were 1) to assess the field scale characteristics of mercury DNAPL infiltration and distribution, 2) to assess the ability of the multi-phase flow model for mercury to reproduce field observations using literature-derived input values and 3) to assess the differences and similarities in the behaviour of liquid elemental mercury and a common DNAPL (PCE).

2. Materials and methods

2.1. Field-site

The field study was performed at a former chlor-alkali plant in the Netherlands. During a previous study at this site, detailed geochemical analysis of shallow (<30 cm depth) soil samples confirmed contamination by various mercury species in the unsaturated zone (Bernaus et al., 2006). The site is located close to a river in an alluvial plain. Consequently the aquifer consists of river sediments, such as sandy and clayey materials. The groundwater level at the site is approximately 1 m below ground level. In this study, a cone penetration test (CPT) was performed at the site.

2.1.1. CPT-probe characterisation

Cone penetration tests are frequently used for describing the lithology of the subsurface. Measured parameters include the cone-pressure, which is the pressure at the tip of the cone, and the resistance of pushing the probe into the soil. The latter parameter was normalized to the cone-pressure, to obtain the friction number. The CPT-cone used was equipped (in-house) with a camera to acquire in-situ images to investigate the depth distribution of the mercury DNAPL contamination. The CPT-cone had a diameter of 36 mm, the overlying tube had a diameter of 56 mm and the length of the CPT-cone with camera was 1.2 m. In the CPT-cone a sapphire glass window (12 × 18 mm) was present, located 76 cm above the CPT-cone tip. Behind the glass window a mirror construction enabled a 2MP camera (1200 × 1600 pixels) equipped with LED-lights to visualize the subsurface, using a resolution of 10 μm by 11 μm per pixel. The camera visualized the soil profile including