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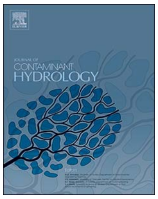

Elucidating the fate of a mixed toluene, DHM, methanol, and i-propanol plume during in situ bioremediation

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ABSTRACT

Organic pollutants such as solvents or petroleum products are widespread contaminants in soil and groundwater systems. In-situ bioremediation is a commonly used remediation technology to clean up the subsurface to eliminate the risks of toxic substances to reach potential receptors in surface waters or drinking water wells. This study discusses the development of a subsurface model to analyse the performance of an actively operating field-scale enhanced bioremediation scheme. The study site was affected by a mixed toluene, dihydromyrcenol (DHM), methanol, and i-propanol plume. A high-resolution, time-series of data was used to constrain the model development and calibration. The analysis shows that the observed failure of the treatment system is linked to an inefficient oxygen injection pattern. Moreover, the model simulations also suggest that additional contaminant spillages have occurred in 2012. Those additional spillages and their associated additional oxygen demand resulted in a significant increase in contaminant fluxes that remained untreated. The study emphasises the important role that reactive transport modelling can play in data analyses and for enhancing remediation efficiency.

1. Introduction

Organic pollutants such as solvents or petroleum products are widespread contaminants in soil and groundwater systems (Barker et al., 1987; Chapelle, 1999; Davis et al., 1999; Kao et al., 2006; Megharaj et al., 2011). Therefore a wide range of methods have been developed over the last three decades that attempt, with variable success, to completely remove those pollutants or to decrease residual concentrations and/or mass fluxes below regulatory levels. The methods include physical techniques such as air sparging, filtration, carbon adsorption (Bass et al., 2000; Benner et al., 2002; Fan et al., 2013; Hu et al., 2014; Keely, 1996; Leeson et al., 2002; Yang et al., 2005), chemical techniques such as chemical oxidation (Kang and Hua, 2005; Liang et al., 2008; Tsitonaki et al., 2010) and biological processes such as in situ bioremediation, biodegradation in reactors, phyto-remediation, and constructed wetlands (Chapelle, 1999; Compernolle et al., 2012; Declercq et al., 2012; Megharaj et al., 2011; Rivett and Thornton, 2008; Vogt et al., 2004). Among these various remediation technologies in situ bioremediation has often shown to be one of the most economic and environmentally friendly (Farhadian et al., 2008; Hyman and Dupont, 2001; Megharaj et al., 2011; Zou et al., 2009).

However, depending on site-specific hydrogeological and biogeochemical conditions many different factors can affect the efficiency of in situ bioremediation measures (Boopathy, 2000; El-Naas et al., 2014; Farhadian et al., 2008; Megharaj et al., 2011; Tyagi et al., 2010). In cases where oxidants such as hydrogen peroxide or oxygen are used to facilitate and accelerate biodegradation a clear understanding of the presence and reactivity of competing reductants, such as organic matter or reduced-form minerals such as iron sulfides can be important (Borden et al., 1997; Herold et al., 2011; Vencelides et al., 2007). The presence of theses reductants might consume a substantial part of the added oxidant, leaving little oxidation capacity for the targeted contaminant degradation processes (Prommer and Barry, 2005). Moreover, the lack of a detailed understanding of the pollution source zone (s) can severely affect the duration and efficiency of the treatment. Ideally the characterisation of sources includes both the knowledge of the spatio-temporal distribution as well as the temporally varying source composition throughout an in situ remediation effort (Datta et al., 2011). The success of any active remediation measure, especially those involving in situ biodegradation, is highly dependent on a thorough understanding of the physical and hydrogeochemical processes that control the efficiency of the biodegradation process (Herold

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et al., 2011). In such cases, the application of a numerical modelling framework with advanced geochemical capabilities is the only option to quantify the complex, spatially and temporally varying interactions. Modelling studies that simulate in situ biodegradation measures to analyse or predict remediation efficiency have previously been applied to a wide variety of pollution problems. For example, Thullner and Schäfer (1999) evaluate the efficiency of a bioremediation treatment on a pilot scale. Prommer et al. (2000) investigated a hypothetical BTEX contamination problem and used modelling to evaluate a remediation scheme in which nitrate was injected to enhance biodegradation and where pyrite acted as a competing reductant to the aromatic hydrocarbons. Around the same time Goltz et al. (2001) demonstrated the usefulness of modelling for gaining insight into the coupled physical, chemical and biological processes that control aerobic co-metabolism of chlorinated solvents, and used the findings to underpin the design of the remediation scheme on the base of predicted system performances. Subsequently, Wood et al. (2006) used a model to illustrate how physical mixing and dispersion impacts the remediation of a chlorinated solvents with hydrogen release compounds and how remediation design could profit from these insights. Also, Henderson et al. (2009) modelled the bioremediation of chlorinated compounds. In their case enhanced remediation was achieved through the addition of potassium permanganate. Huang et al. (2004) used modelling to study the design of a bioremediation system in which a dual-well groundwater circulation system was used to mix electron donors efficiently into perchlorate-contaminated groundwater. Huang et al. (2006) also developed a numerical modelling framework to simulate enhanced in situ bioremediation processes and used the framework to investigate the effects of parameter uncertainties on treatment efficiency. More recently, Yabusaki et al. (2011) studied an in situ uranium bioremediation field experiment via modelling to better understand the interplay of the transport processes and biogeochemical reactions that control the fate of uranium under pulsed acetate amendment and seasonal water table variation. Finally, Compernolle et al. (2013) used a model to evaluate the efficiency of a hypothetical but realistic case of a bioremediation project in comparison with a simple pump-and-treat scheme.

However, most of the previously investigated cases either involved hypothetical case studies, short-term remediation trials or otherwise relatively simplistic scenarios that are in stark contrast to ‘real-world’ bioremediation cases that often involve (i) complex contaminant mixtures, uncertain secondary contamination sources with compound mixtures that differ from the main contamination and (ii) complex temporal trends that may be caused by the variability of often uncertain source releases but may also be induced by the operational variations of the active (bio)remediation scheme.

In this study we present a detailed investigation of an actively operating field-scale enhanced bioremediation scheme, which has been in operation since 2009. We use this case to illustrate the significant value that a model-based analysis can provide for understanding the physical and biogeochemical factors controlling the efficiency of a bioremediation scheme. The investigations at our study site were originally triggered by rapidly increasing contaminant concentrations at the downstream site boundary, raising the need for a more detailed process understanding, including potential new sources of contamination. Reactive transport modelling was used to integrate and interpret the field data that were collected under the highly transient hydrological and hydrogeochemical conditions.

2. Materials and methods

2.1. Study site

The site investigated in this study is a chemical plant in the south of France. The plant is still operational and currently comprises three units of active chemical production. At the site, numerous contamination sources were identified, including some open channels that might be leaky. The unconfined aquifer is severely contaminated by various organic compounds and since March 2009 the contamination is being treated by an in situ biodegradation scheme.

2.1.1. Hydrogeology

The aquifer below the chemical plant is approximately 14 m thick and consists of homogeneous fine sand. It is underlain by a lignite layer of low permeability. The groundwater table is located approximately 7 to 8 m below the surface and the aquifer is unconfined. Groundwater level data collected between 2009 and 2013 indicate that the groundwater flow direction is predominantly from east to west along a hydraulic gradient of 0.004 at an estimated mean pore velocity of $0.4\ \mathrm{m{\cdot}day^{-1}}$. The groundwater levels at the site fluctuate seasonally over > 1.2 m. Based on pumping tests performed at the site, hydraulic conductivity values were estimated to lie between 1.6×10^{-4} and $6.5 \times 10^{-4}\ \mathrm{m{\cdot}s^{-1}}$. The estimated effective porosity is assumed to be approximately 26% (Corbier et al., 2010).

2.1.2. Contamination history and distribution

In September 2005, a leakage of light non-aqueous phase liquid (LNAPL) from one of the production units, mostly composed of monoaromatic hydrocarbons, alcohol and terpenes was discovered. One month later, sixteen cores were drilled near the main source area to identify the exact location of the spill and to estimate the mass of the leaked LNAPL. The results suggested that the main source area was located near wells P119, P120 and P121 (Fig. 1). In response to the problem, a pump-and-treat operation scheme was operated from September 2005 until August 2008 to remove the LNAPL source and to confine the dissolved plume. The quantity of spilled product was estimated at 5156 kg in October 2005. However, this estimate seems to have largely underestimated the spilled mass because the quantity of products that was recovered by February 2008 by the pump and treat scheme was > 7900 kg. Therefore, the residual amount of LNAPL in the soils is not quantifiable. The LNAPL consisted of a complex mixture of a large number of organic compounds with many of the minor compounds remaining uncharacterised. A partial characterisation of the chemical composition of the original oil phase was obtained February 2006 by analysing a sample from a well that was used for LNAPL abstraction. A total of 9 compounds, including toluene, alkanes and terpenic alcohols were identified in this sample. The identified compounds represent 53% of the total LNAPL mass. The most prominent compounds were toluene (C_7H_8), dimethadione ($C_5H_7NO_3$), dihydromyrcenol (DHM) ($C_{10}H_{20}O$) and dipentene ($C_{10}H_{16}$).

After 2005, no known further major leakages occurred. However, due to the high corrosivity of the chemicals used in the industrial process, several minor leakages are likely to have occurred from the numerous channels that were used to transport chemicals at the site. The possibility of such secondary leakages was concluded from more recent discoveries of methanol and i-propanol, which were never identified previously. Likewise, a local increase in toluene concentrations downstream of the main source area also suggested that minor leakages could have occurred. Besides the main source zone, elevated contaminant concentrations at specific monitoring locations suggested the existence of up to seven contaminant release events between 2008 and mid-2013 (Table 1 and Fig. 2). Through the detailed analysis of the peak concentrations it was shown that these peaks were not related to the historical (main) source.

2.1.3. Remediation scheme

After the initial pump-and-treat operation phase, a remediation scheme for the remaining contaminants in both the vadose and the saturated zone was implemented in March 2009. The groundwater remediation measure consists of two H_2O_2 injection lines that were implemented to enhance aerobic biodegradation. The first injection line was installed upstream of the source zone and consisted of fifteen injection needles (Fig. 1). The second injection line was installed