Effect of natural particles on the transport of lindane in saturated porous media: Laboratory experiments and model-based analysis

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ABSTRACT

Colloidal particles can act as carriers for adsorbing pollutants, such as hydrophobic organic pollutants, and enhance their mobility in the subsurface. In this study, we investigate the influence of colloidal particles on the transport of pesticides through saturated porous media by column experiments. We also investigate the effect of particle size on this transport. The model pesticide is lindane (gamma-hexachlorocyclohexane), a representative hydrophobic insecticide which has been banned in 2009 but is still used in many developing countries. The breakthrough curves are analyzed with the help of numerical modeling, in which we examine the minimum model complexity needed to simulate such transport. The transport of lindane without particles can be described by advective–dispersive transport coupled to linear three-site sorption, one site being in local equilibrium and the others undergoing first-order kinetic sorption. In the presence of mobile particles, the total concentration of mobile lindane is increased, that is, lindane is transported not only in aqueous solution but also sorbed onto the smallest, mobile particles. The models developed to simulate separate and associated transport of lindane and the particles reproduced the measurements very well and showed that the adsorption/desorption of lindane to the particles could be expressed by a common first-order rate law, regardless whether the particles are mobile, attached, or strained.

1. Introduction

Groundwater is the most important water resource for drinking-water production throughout the world (WHO/UNICEF, 2011). A particular reason for this lies in its low vulnerability to pollution by pathogens and chemical compounds, since the infiltrating water is filtered during the passage through soils and aquifers.

Pathogens (bacteria and viruses) can be considered as particles in the size range of colloids. Transport of such particles differs from that of dissolved compounds because of attachment, detachment, size exclusion and other filtration effects (DeNovio et al., 2004; Enfield et al., 1989; Liu et al., 2010; Pelley and Tufenkji, 2008). Change in the chemical environment (e.g., pH and ionic strength) also changes the mobility of

particles (Ben-Moshe et al., 2010; Saleh et al., 2008). This holds not only for biological particles (such as pathogens) but also for natural abiotic particles and engineered nanoparticles.

Colloids are ubiquitous in subsurface environments, they are defined as particles with diameters of up to 10 μm (DeNovio et al., 2004; Lapworth et al., 2005; Stumm, 1977). Transport of colloids is mostly described by colloid-filtration theory (CFT), involving effects of size exclusion, straining, as well as particle- and matrix-surface charge (Harvey and Garabedian, 1991; Martin et al., 1992; Rajagopalan and Tien, 1976). The colloid-filtration theory describes the deposition of suspended colloidal particles onto the grains of porous media by the following two major steps (Nelson and Ginn, 2005): the transport of particles to the grain surface (collector) and their attachment to this grain surface.

Particles can act as carriers for sorbing compounds (Fang et al., 2011; Grolimund and Borkovec, 2005; Kanti Sen and Khilar, 2006; Sun et al., 2010; Yin et al., 2010). Particle-facilitated

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transport has been studied in natural porous media (soils and aquifers) when considering the transport of viruses and bacteria (e.g., Harvey and Garabedian, 1991; Martin et al., 1992; Maxwell et al., 2007), the transport of heavy metals, metalloids, radionuclides, and persistent organic pollutants sorbed onto natural colloids (e.g., Bold et al., 2003; Delos et al., 2008; Hu et al., 2008; Malkovsky and Pek, 2009; Mills et al., 1991; Roy and Dzombak, 1997), the delivery of nano-sized reacting agents such as zero-valent iron for in-situ remediation (Hydutsky et al., 2007; Saleh et al., 2008; Tiraferri and Sethi, 2009), the enhanced transport of organic pollutants due to particle-facilitated transport and preferential flow (Bold et al., 2005), and most recently the risk assessment of engineered nanomaterials such as fullerenes and TiO_2-nanoparticles in subsurface environments (e.g., Choy et al., 2008; Lecoanet et al., 2004; Wang et al., 2008; Xie et al., 2008).

Pesticides are classical pollutants of high relevance for groundwater quality. Many persistent, strongly sorbing, hydrophobic pesticides, such as DDT (dichlorodiphenyltrichloroethane), have been banned in western industrialized countries, but are still frequently applied mainly in African developing countries. Because of their high tendency towards sorption, such compounds are strongly retained in the soil and could not cause groundwater contamination if there was no transport of particles carrying them. For more hydrophilic, modern pesticides, particle-facilitated transport may be of smaller relevance, but could still significantly contribute to the overall mass flux.

Lindane (gamma-hexachlorocyclohexane - $C_6H_6Cl_6$) and its isomers were produced worldwide since the 1940s and their production left behind huge amounts of wastes that were dumped in various anarchic ways (Vijgen, 2006). Lindane is the only hexachlorocyclohexane isomer used as an insecticide.

Like DDT and the other obsolete pesticides, stockpiles of lindane from old manufacturing industries and farming stores also contributed to soil and groundwater pollution by leakage through the soil (Elfvendahl et al., 2004; Lahav and Kahanovitch, 1974; Prakash et al., 2004; Vankar, 2011). Moreover, agricultural application of this pesticide can lead to groundwater contamination through leaching from crops by rain water and particle-facilitated transport through the soil. This contamination is controlled by many factors such as crop management practices, the load of the pesticide to the crops and the soil, and the properties of the soil.

Lindane usage was regulated due to its toxicity to human health and the environment, and its guideline value according to the World Health Organization (WHO) is 2 μg/l (WHO, 2004). According to the Environmental Protection Agency (EPA) and the United Nations Environment Programme (UNEP), lindane is carcinogenic and can bioaccumulate within tissues (EPA, 1999; UNEP, 2006). It is also considered to be very persistent in the environment as its degradation half-life has been estimated as up to 1146 days (WHO, 2004).

Although several countries have restricted the use of lindane in agriculture (Caicedo et al., 2011; UNEP, 2009), this ban has not yet been effective in all developing countries where it is still in use in agriculture and where stockpiles continue to be found (Brown, 2008; Glover-Amengor and Tetteh, 2008). Moreover, wastes of lindane isomers can still be found at former production sites or landfills in developed countries. Therefore groundwater contamination by this pesticide remains a current issue and needs to be solved.

Many studies have concentrated on the adsorption and degradation of lindane (e.g., Buser and Mueller, 1995; Elliott et al., 2009; Kouras et al., 1998; Liu et al., 2003; Sotelo et al., 2002), some on its transport through soil and aquifer systems under specific conditions (e.g., Chen and Zhu, 2005; Ehlers et al., 1969a, 1969b), and some on its leachability in soil (e.g., Ali and Jain, 2000; Caicedo et al., 2011). Many investigations on the transport of lindane through saturated porous media failed to understand its removal from groundwater because the evidence that colloidal particles could very well enhance its transport was not considered. A single study focused on the impact of biocolloids, namely bacterial extracellular polymers, on the transport of lindane (Chen and Strevett, 2001). However, to the best of our knowledge, studies on transport of lindane facilitated by natural particles such as lignite particles are still missing, particularly those combining laboratory experiments and modeling.

The main objective of this study is to investigate the influence of natural particles on the subsurface transport of lindane through saturated porous media. A quantitative understanding of separate and associated transports of lindane and particles is assessed by changing the size of the particles. Laboratory experiments are analyzed by numerical modeling in order to understand the transport processes involved and derive simple predictive models.

2. Governing equations

2.1. Transport of sorbing pollutants

The one-dimensional (1-D) transport through saturated porous media of sorbing pollutants undergoing reversible sorption to both slow and fast sorption sites of the matrix can be described by the well-known advection–dispersion equation (e.g., Selim et al., 1990):

$$R_{eq} \frac{\partial C}{\partial t} - D \frac{\partial^2 C}{\partial x^2} + v \frac{\partial C}{\partial x} = -\frac{\rho_b}{n}(r_1 + r_2) \tag{1}$$

in which the seepage velocity v, the hydrodynamic dispersion coefficient D as defined in Eq. (3) (Boving and Grathwohl, 2001; Scheidegger, 1961), the retardation factor due to equilibrium sorption R_{eq}, and the mass transfer rates r_1 and r_2 of dissolved lindane onto or from two kinetic sites (site 1 and site 2) of the matrix may be mathematically expressed as follows:

$$v = \frac{q}{n} \tag{2}$$

$$D = n D_{aq} + \alpha v \tag{3}$$

$$R_{eq} = 1 + \frac{\rho_b}{n} K_{d,eq} \tag{4}$$

$$r_1 = \frac{\partial S_1}{\partial t} = k_1 \frac{n}{\rho_b} C - k_2 S_1 \tag{5}$$

$$r_2 = \frac{\partial S_2}{\partial t} = k_3 \frac{n}{\rho_b} C - k_4 S_2 \tag{6}$$

All variables with their units are summarized in the list of abbreviations in Appendix A.