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# Altered transport of lindane caused by the retention of natural particles in saturated porous media

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ABSTRACT

Attachment and straining of colloidal particles in porous media result in their reversible and irreversible retention. The retained particles may either increase the retention of hydrophobic pollutants by sorption onto the particles, or enhance pollutant transport when particles, loaded with the pollutants, are remobilized. The present study examines the effects of retained particles on the transport of the hydrophobic pesticide lindane (gamma-hexachlorocyclohexane) in saturated porous media. The lignite particles used have median diameters of about 3 μm, 1 μm, 0.8 μm, and 0.2 μm, respectively. Laboratory column experiments were analyzed by numerical modeling in order to identify and understand the processes involved in the transport of the particles and of lindane. Four scenarios were considered in which the solution containing lindane is injected either during or after the elution of the particles. The results show that lignite particles retained in a sandy porous medium alter the transport of the invading lindane. Particle retention was high in all scenarios and increased with increasing particle size. Remobilization of particles occurred due to a change in solution chemistry, and continuous particle detachment was observed over time. Numerical modeling of particle transport suggests that both reversible attachment and irreversible straining affected the transport of the particles. Lindane was retarded in all scenarios due to the strong particle retention in conjunction with the sorption of lindane onto the sand and onto retained particles, and the limited number of mobile particles carrying lindane. Moreover, it was found that intra-particle diffusion limited adsorption/desorption of lindane onto/from both limestone fragments of the sand and lignite particles. We assume that retention of lindane is reversible even though lindane recovery was incomplete over the duration of the experiments. The analysis of the effluent concentration suggests that retained particles loaded with lindane may become a secondary source of lindane. Models describing the transport of lindane fitted the experimental data very well and indicated the specific contribution of retained particles to the retardation of lindane. Since the properties of lignite also known as brown coal are similar to those of biochar, the results of the present study could be extended to the potential effects of biochar on lindane and other contaminants in soils, which would include both their retention and their enhanced transport. However, while the transport mechanisms of lindane are similar in water-unsaturated soils and saturated porous media considered here, the behavior of particles is more complex, requiring additional studies.



## 1. Introduction

Natural colloidal particles are ubiquitous in subsurface environments. Their concentration in groundwater can range from $10^8$ to $10^{17}$ particles per liter of water (Kim, 1989, 1991). The evidence that colloidal particles can facilitate the

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transport of pollutants in porous media has been shown by many studies (e.g., Fang et al., 2011; Kersting et al., 1999; McCarthy and Zachara, 1989; McDowell-Boyer et al., 1986; Ngueleu et al., 2013; Yin et al., 2010). A potential consequence of colloidal transport on pollutant behavior is that the mobility of the pollutant may be enhanced leading to shorter travel times, larger transport distances, or higher concentrations of the pollutant in the effluent, as compared to the case where no particles are involved. Trapped colloids, however, may cause the opposite – retardation – because of their high sorption capacities.

Transport of colloid-sized particles through porous media has been studied mainly using the colloid filtration theory (CFT) (e.g., Friedlander, 1958; Hunt et al., 1987; O'Melia, 1980), which describes the processes of colloid deposition onto the grains of porous media such as attachment, filtration, and size exclusion (Happel, 1958; Nicholson and Petropoulos, 1968, 1971, 1973, 1975; Payatakes et al., 1974; Rajagopalan and Tien, 1976). Specific models may include trapping of particles at water–air interfaces in unsaturated soils (Simunek et al., 2006) or ionic-strength effects on particle coagulation, disintegration, attachment and detachment (Tosco and Sethi, 2009; Tosco et al., 2009).

Many studies have shown the necessity to understand the deposition and transport of colloids in underground systems for the assessment and prediction of colloid-facilitated transport of pollutants (e.g., DeNovio et al., 2004; Grolimund et al., 1996, 2007; Kretzschmar et al., 1999; McCarthy and McKay, 2004; Saiers and Hornberger, 1996; Zhuang et al., 2003, 2009). They contributed in giving the fundamental information on the transport of colloidal particles and their role in pollutant spreading through the subsurface.

Transport and deposition of engineered nanoparticles could be well predicted from their zeta-potential, whereas this was not the case for natural particles (Hydutsky et al., 2007; Wang and Keller, 2009). Size exclusion, restricted sampling of the velocity profile within the pores, or transport along water–air interfaces can lead to particle transport faster than the mean velocity of water (e.g., Panfilov et al., 2008). Several studies have highlighted the effects of ionic strength, pH, and colloid size on colloid transport (Bradford et al., 2006; Pelley and Tufenkji, 2008; Roy and Dzombak, 1997; Saleh et al., 2008; Zvikelsky and Weisbrod, 2006).

Controlled laboratory experiments on the transport of colloidal particles and associated chemical agents were done with latex particles (Pelley and Tufenkji, 2008; Wan and Wilson, 1994b; Zvikelsky and Weisbrod, 2006; Zvikelsky et al., 2008), C60 fullerenes (Lecoanet et al., 2004; Wang et al., 2008; Xie et al., 2008), (surface-modified) zero-valent iron nanoparticles (Saleh et al., 2008; Tiraferri and Sethi, 2009), as well as natural particles (Bold et al., 2003; Ngueleu et al., 2013). Optical detection was achieved by using fluorescent particle surfaces (Burkhardt et al., 2008; Zvikelsky and Weisbrod, 2006), or by matching the optical refraction index of the porous-matrix material and the fluid (Lachhab et al., 2008; Moroni et al., 2007).

The effect of dissolved particles on the transport of organic pollutants was illustrated by Magee et al. (1991) who showed that dissolved organic matter derived from soil enhanced the transport of phenanthrene in sandy porous media. Enhanced transport of phenanthrene by colloids released from natural sand was also shown by Roy and Dzombak (1998). The effect of groundwater flow velocity on the transport of natural lignite and activated carbon particles and trichloroethylene was studied by Bold et al. (2003) who showed simultaneous decrease of particles and trichloroethylene concentrations with the velocity. The latter results were in agreement with filtration theory which states that the decrease of flow velocity increases particle interception and sedimentation to the immobile matrix (McDowell-Boyer et al., 1986). Cheng et al. (2005) showed that nano-$C_{60}$ particles contained in soil affected naphthalene transport by contributing to its retention. The contribution of colloid-facilitated transport to the transport of glyphosate in undisturbed topsoil columns was shown by De Jonge et al. (2000) for particles with diameter > 0.24 μm.

The following conditions are necessary for colloid-facilitated transport of pollutants to be relevant: 1) colloid retention in the porous medium is weak or reversible; 2) the mobility of colloids is larger than that of the pollutant; and 3) the adsorption of the pollutant onto the colloids is stronger than adsorption onto the matrix of the porous medium (Magee et al., 1991; McCarthy and Zachara, 1989; Mills et al., 1991; Roy and Dzombak, 1998). The latter highly depends on the size of the particles as it has been shown that particle retention increases with particle size (Hahn et al., 2004; Pelley and Tufenkji, 2008).

Previous studies have shown that in water-saturated porous media, particles retained in the pore space can be remobilized as a result of change in solution chemistry, an example being the reduction of ionic strength which causes an increase of inter-particle repulsion (Lenhart and Saiers, 2003; McDowell-Boyer, 1992; Roy and Dzombak, 1996, 1997; Ryan and Gschwend, 1994a,b; Tosco et al., 2009). In polluted porous aquifers, this remobilization of particles can contribute to pollutant removal and was suggested as groundwater remediation technique, especially for pollutants that would be difficult to remove by conventional pump-and-treat (McCarthy, 1993). However, Bradford et al. (2002) showed that so-called straining, that is, the irreversible trapping of particles in pore throats, can limit this type of remobilization. Large particles are more susceptible to straining than small ones. The second mechanism of particle retention in porous media is the reversible attachment of the particles onto the surfaces of the matrix. Understanding the retention processes of the particles is a prerequisite to study particle-facilitated transport.

Particle-facilitated transport has been studied for various organic and inorganic pollutants. In the present study, the specific case of lindane is investigated. Lindane (gamma-hexachlorocyclohexane) is a representative hydrophobic insecticide which has been banned in 2009 but still occurs as diffuse pollution globally and is still in use in many developing countries, such as Bangladesh, Nepal, Sri Lanka, and India, among others (Bashir et al., 2013; IPEN, 2006; Pozo et al., 2011). Chen and Strevett (2001) investigated the impact of biocolloids (bacterial extracellular polymers) on the transport of lindane. Ngueleu et al. (2013) focused on the transport of lindane in the presence of organic colloidal particles. A major result of the latter study was that lignite particles with a size > 0.45 μm were strongly retained in the sandy porous media used, thus limiting the accelerated transport of lindane. The present study extends the work of Ngueleu et al. (2013) to improve our understanding on how the transport of lindane is