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A zero-valent iron and organic matter mixture enhances herbicide and herbicide degradation product removal in subsurface waters

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ABSTRACT

The pesticide atrazine, its degradation products, and 2,6-dichlorobenzamide (BAM) are persistent in groundwater environment. We studied whether their dissipation can be enhanced with a mixture of a complex carbon source and zero-valent iron (ZVI) called EHC®. The application rates were 1.0% and 2.0% (by weight) in subsurface sediments slurries (atrazine 30 mg/L), and 2.0% in 1.5 m pilot-scale sediment columns with groundwater flowing through (atrazine 0.08, desethylatrazine DEA 0.03, BAM 0.02 µg/L). In the slurries under aerobic conditions, atrazine of 0.88 ± 0.14 mg/g of EHC® was dissipated chemically, as concentrations did not differ significantly between the slurries and their sterilized controls. No degradation occurred in the slurries under anaerobic conditions. In the pilot-scale columns under water-saturated conditions, atrazine, DEA and BAM were not detected in effluents during 33, 64 and 64 days from the beginning of the water flow through EHC® columns, respectively, but thereafter traces of compounds could be detected. No atrazine or degradation products (BAM, DEA, deisopropylatrazine, desethyldeisopropylatrazine) could be extracted from the column sediments at the end of the experiment. As a result, the sum of dissipated pesticides was about 7.6 µg/g of EHC® in columns under water-saturated conditions, and 0.88 mg/g of EHC® in slurries under aerobic conditions. EHC® can be used to enhance the dissipation of studied pesticides in small quantities, preferentially under aerobic conditions.

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Introduction

The triazine herbicide atrazine [6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine] and dichlobenil [2,6-dichlorobenzonitrile] have been used worldwide for the weed control (Tomlin, 2000). The triazine ring of atrazine contains chlorine and two amino groups attached to the carbons at positions 2, 4 and 6. The amino groups are dealkylated to desethylatrazine (DEA), deisopropylatrazine (DIA), and desethyldeisopropylatrazine (DEDIA), which may also be

harmful (Tomlin, 2000; Ralston-Hooper et al., 2009; van Zelm et al., 2010). The benzonitrile herbicide dichlobenil has a nitrile group and chlorine in two *ortho*-positions attached to the benzene ring. The nitrile group is easily converted to an amide 2,6-dichlorobenzamide (BAM) (Holtze et al., 2008). After the application, atrazine and dichlobenil are usually degraded relatively fast in surface soil or surface water (Krutz et al., 2010; Solomon et al., 1996; Holtze et al., 2008). The primary mechanism of pesticide degradation has generally been related to microorganisms, while the chemical degradation has been regarded as less important (van der Meer, 2006; Wackett et al., 2002; Holtze et al., 2008). When these pesticides or their degradation products are able to leach into the

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groundwater, they are persistent and natural attenuation is extremely slow. Atrazine solubility in water is 33 mg/L, and that of dichlobenil is 18 mg/L (Tomlin, 2000; Holtze et al., 2008). Atrazine, dichlobenil and their degradation products are among common contaminants in aquifers (Arias-Estévez et al., 2008; Talja et al., 2008; Pukkila and Kontro, 2014).

The process of enhanced reductive dechlorination has been used successfully in the remediation of chlorinated persistent organic pollutants in soil and groundwater (Weber et al., 2008). ZVI has improved atrazine dissipation in a laboratory scale in liquids and soils under aerobic conditions, often in short-term experiments in the presence of ZVI in excess (Zhang et al., 2011; Allred, 2011; Ghauch and Suptil, 2000; Satapanajaru et al., 2008; Waria et al., 2009; Monson et al., 1998; Singh et al., 1998). ZVI also enhanced atrazine dissipation in soil on-site, and in river basin sediments in laboratory, both under aerobic conditions (Kim et al., 2007; Shea et al., 2004). EHC® is a mixture of a complex carbon source and micro-scale zero-valent iron (ZVI) particles (<5 to 45 µm in size), which provides an organic carbon electron donor and a reactive surface area to stimulate the direct chemical dechlorination of persistent compounds. EHC® has been used for the dechlorination of recalcitrant compounds such as organo-chlorine pesticides; chlorinated methanes, ethanes, and ethenes; and pentachlorophenol (Peale et al., 2010; Seech et al., 2008; Shetty et al., 2009; Molin et al., 2010), but its suitability for the remediation of pesticide atrazine and its degradation products, and groundwater contaminant BAM has not been studied in subsurface sediments. The hypothesis for this work was that the dissipation of atrazine, DEA and BAM can be enhanced using EHC®, while the null hypothesis was that EHC® has no effects on their dissipation. Experiments were conducted to determine whether 1.0% and 2.0% of EHC® (by weight) enhance the dissipation of the high atrazine concentration of 30 mg/L in vadose zone sediment-water slurries. In addition, the dissipation of low concentration of atrazine, DEA and BAM in groundwater (0.01–0.10 µg/L) was studied in pilot-scale sediment columns amended with 2.0% EHC®. The sand sediments were collected in drillings in Finland located within the boreal region.

1. Materials and methods

1.1. Sediments

Two drillings were done in Lahti (Finland) next to the railway station (60°97'62" N / 25°65'51" E; drilling depth 55 m) and in the city garden (60°97'18" N / 25°64'36" E; drilling depth 33 m) (Mattsson et al., 2015). The sediments were transferred at the drilling site directly to plastic bags, which were stored as closed at 4°C. The sandy sediments for slurries were collected from the depth of 11.3–14.6 m in drilling next to the railway station, where the groundwater level was about 15 m. For sediment columns, the sand sediments collected next to railway station (depths 6.1–55.0 m) and below garden (18.6–31.0 m) were pooled together prior to the use. The dry weights of sediments (4.5–5.0 g) and EHC® (2.5 g) (PeroxyChem, Philadelphia, PA, USA) were measured in triplicate after drying at 105°C for 16 hr, and the organic matter content was determined after heating at 550°C for 4 hr (SFS-EN 13040, 2000). The sediments were collected from a groundwater area having atrazine and BAM in groundwater and sediments (Mattsson et al., 2015).

1.2. The 1.0% and 2.0% EHC® application rates in the sediment slurries

The first degradation experiment was done using the same methods as presented by Talja et al. (2008). 15 g of sediment (dry weight) was supplemented with 50 mL of sterilized distilled water in 100 mL flasks with hole caps (diameter 5 mm), which were covered with aluminium foils. The flasks were shaken (120 r/min; Laboshake, Gerhardt, Königswinter, Germany) at 21 ± 2°C in the dark. The flasks were weighed at the beginning of the experiment and before samplings, and the evaporated water was replaced with sterile distilled water. The sterile control sediments and EHC® were autoclaved (Instru, Santasalo-Sohlberg, Helsinki, Finland) for 1 hr (121°C, 101 kPa) on three successive days. In the incubation jars filled with the experimental flasks, the anaerobic conditions were established using the reagent Anaerocult A (Merck, Darmstadt, Germany), and confirmed using a colorimetric anaerobic indicator Anaerostest (Merck, Darmstadt, Germany), checked weekly throughout the entire experiment.

In the sediment slurries, the EHC® application rates of 1.0% and 2.0% by weight of sediment were used according to the recommendation of the manufacturer (PeroxyChem, Philadelphia, PA, USA). The atrazine concentrations of 30 mg/L (110 mg/kg dry weight) were used in three parallel flasks. The 200 µL samples were taken at time points 0, 42, 78, 147 and 182 days from treatments under aerobic conditions. The anaerobic flasks without EHC® were sampled on days 0, 34, 103 and 181, and the anaerobic flasks with EHC® were sampled on days 0, 22, 58, 127 and 181. The treatments under aerobic and anaerobic conditions were ($n = 3$): (i) sediment slurries; (ii) sterile sediment slurries; (iii) sediment and 1.0% EHC® slurries; (iv) sterile sediment and sterile 1.0% EHC® slurries; (v) sediment and 2.0% EHC® slurries; (vi) sterile sediment and sterile 2.0% EHC® slurries. At the end of the experiment, the pH values of slurries were determined using WTW inoLab pH 720 meter (Weilheim, Germany).

1.3. The 2.0% EHC® application rate in the sediment columns

The second degradation experiment consisted of six pilot-scale columns, which were 2.0 m in height and 5.0 cm in diameter. The pilot-scale experiment enabled the reliable analysis of low pesticide concentrations, which are present in groundwater. Three control columns were filled with 4.45 ± 0.06 kg of sediments, and three more columns were filled with 4.14 ± 0.09 kg of sediments amended with 2% EHC® on the dry weight basis. After filling the columns, they were allowed to stabilize for 32 days, and the sediment height was adjusted to 1.5 m. Then the top 0.5 m was periodically filled first with sterile distilled water for 15 days (controls, 1.26 ± 0.02 L; EHC® columns, 1.05 ± 0.37 L), followed by pesticide-contaminated groundwater until day 205 (controls, 32.85 ± 0.35 L; EHC® columns, 20.91 ± 6.66 L). During the experiment, the outflow rate of groundwater was adjusted at the bottom of the column using multichannel pump (ISM 404B, Ismatec, Germany); such that it was modelling the flow rate of groundwater. EHC® caused a back pressure, which slowed the water flow even though the suction pressure was the same in all the columns. The outflow rate was 4.06 ± 1.82 mL/hr in columns filled with sediments and EHC®, and

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