Title: 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^{-1}), 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^{-1}). In the slurries under aerobic conditions, atrazine of 0.88±0.14 mg g^{-1} 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^{-1} of EHC® in columns under water-saturated conditions, and about 0.88 mg g^{-1} 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.

Keywords: Herbicides, subsurface sediments, dissipation, EHC®, organic matter, zero-valent iron

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 groundwater, they are persistent and natural attenuation is extremely slow. Atrazine solubility in water is 33 mg l^{-1}, and that of dichlobenil is 18 mg l^{-1} (Tomlin 2000; Holze 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^{-1} 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^{-1}) 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® (about 2.5 g) (PeroxyChem, Philadelphia, PA, USA) were measured in triplicate after drying at 105 ˚C for 16 h, and the organic matter content was determined after heating at 550 ˚C for 4 h (SFS-EN 13040). 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). Approximately 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 rpm; Laboshake, Gerhardt, Konigswinter, 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 h (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 Anaerotest (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^{-1} (110 mg kg^{-1} 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 h^{-1} in columns filled with sediments and EHC®, and 6.31±0.07 ml h^{-1} in control columns. The water samples of about 1.0 l were collected 33, 47, 64, 107, 140, and 180 days after the beginning of the experiment for pesticide and total organic carbon (TOC) analyses. The eluate pH was measured after 75 days using pH indicator paper (Merck, Kenilworth, NJ, U.S.A.). The concentration of TOC in water was measured using the Apollo 9000 HS Combustion TOC Analyser (Teledyne Instruments, Mason, OH, USA) according to the method

SFS-EN 1484. The effluent pH was measured using pH-indicator strips (Merck KGaA, Darmstadt, Germany).

1.4. Pesticide analyses

In the sediment slurries, six atrazine standards in methanol : water (3:1 v/v) ranged from 2.3 to 139.1 µM. Standards and 200 µl samples were amended with 24.8 µM internal standard simazine, and brought to 600 µl with methanol : water (3:1 v/v) (Talja et al. 2008). After filtration, 20 µl was analysed using HPLC as presented (Pukkila and Kontro 2014). The flow rate was 0.4 ml min^{-1}, UV detector wavelength was 225 nm, and the chromatographic profile was as follows: acetonitrile in filtered water was held at 30 % for 3.5 min, then stepwise increase to 65 % for 5 min, and decrease back to 30 % for 5.1 min, the overall runtime being 14 min.

In the sediment columns, 500 ml water sample and 2.2 mM internal standard propazine were filtered through folded qualitative filter paper 303 (particle retention 5-13 µm, VWR, Radnor, PA, USA); 1.6 µm GF/A and 0.7 µm GF/F filters (Whatman, GE Healthcare, Buckinghamshire, U.K.) using a Diaphragm vacuum pump (Vacuubrand, Wertheim, Germany); and through the solid phase extraction (SPE) column using SPF vacuum manifold (Strata-X 33u, 200 mg 6 ml^{-1}, 8B-S100-FCL Phenomenex, Torrance, CA, USA). Initially the column was washed with 5.0 ml of methanol, and 10.0 ml of water (Elga, Purelab Ultra, Partille, Sweden), and after the sample with 4 x 5 ml of water. After drying for 10 min, pesticides were eluted in 2 x 4 ml of methanol. Methanol was evaporated under a nitrogen flow, and the precipitate was extracted twice with 300 µl of acetone using sonication (15 min, 43 kHz / 320 W, Branson 8510 Ultrasonic Cleaner, W.A. Brown Industrial Sales Inc, Richmond, VA, USA), followed by centrifugation (13000 x g). The pooled acetone fractions were filtered, and pesticides were analysed by Shimadzu GCMS-QP-2010Ultra gas chromatograph mass spectrometer; autosampler AOC-20i+s; ZB-5MS capillary column (29 m, 0.25 mm, 0.25 µm); carrier gas helium (1.29 ml min^{-1}); injector temperature 250 °C; and 2 µl splitless injection. The oven temperature was 120 °C for 2 min, and then it increased 20 °C/min to 180 °C, held for 5 min, and then 20 °C/min to 280 °C, held for 8 min. In the mass spectrometer, electron energy was 70 eV; ion source temperature 230 °C; and interface 250 °C. Five atrazine, simazine, DEA, DIA, DEDIA, and BAM standards in acetone were between 0.116-3.435 µM. Ions followed were: atrazine, m/z 202 and 215 (q, quantification); simazine, m/z 173, 186 and 201 (q); DEA, m/z 174 (q) and 187; DIA, m/z 158 (q), 173 and 175; DEDIA, m/z 110, 145 (q) and 147; BAM, m/z 173 (q), 175 and 189; propazine, m/z 172, 187, 214 and 229 (q). DIA and DEDIA peaks were not detected.

The pesticides of the sediments, and pesticides adsorbed to sediments at the end of column experiments were extracted as has been presented by Mattsson et al. (2015). The pesticides of the sediments were analysed by HPLC (Mattsson et al. 2015), and those adsorbed to the sediments at the end of the column experiment were analysed by GC-MS as presented above.

1.5. Calculations

The results are presented as an average ± standard deviation (S.D., n=3). The parametric analysis of variance (ANOVA) or non-parametric Kruskal-Wallis test (K-W) (Kruskal et al. 1952) were used for the analysis of variance, depending on the significance of $p<0.05$ in the Levene's test of equality of error variances and in Kolmogorov-Smirnov test. The statistical analyses between the treatments were determined separately in each time point. When the ANOVA or K-W test result was significant ($p<0.05$), then the pairwise differences between the treatments were determined using the Tukey HSD or Mann-Whitney test (M-W) (Mann and Whitney 1947), respectively. The statistical analyses were performed with SPSS statistical package for Windows (SPSS Inc., Chicago, IL).

2. Results and discussion

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

The ability of the 1.0 and 2.0 % EHC® application rates (by weight of sediment) to enhance the dissipation of high atrazine concentrations of 30 mg l^{-1} was studied in the subsurface sediment slurries. The sterilized counterparts of the sediment slurries were included, to obtain insight whether the dissipation is due to the microbial activity or chemical. Besides aerobic treatments (Fig. 1a,c), the experiments were conducted under anaerobic conditions (Fig. 1b,d), which often prevail in groundwater. The percentage of organic matter in EHC® was 50 %. The experiments were followed for 182 days until atrazine concentration in the aerobic sediments differed statistically significantly in two sampling points according to the analysis of variance ($p<0.012$).

Under aerobic conditions, atrazine concentrations in the sediment slurries with 2.0 % EHC® were lower than in the unamend sediment slurries on days 147 (Tukey HSD, $p\leq0.012$) and 182 (Tukey HSD $p<0.009$; Fig 1a), independent of sterilization. The percentage of remaining atrazine was 75.0±4.3 % on day 182 in the aerobic sediment slurries with 2.0 % EHC®, indicating slow

dissipation when compared to the atrazine concentration of 91.6±9.0 % in the slurries without EHC® application. Compared to the control without EHC®, atrazine dissipation was 0.88±0.14 mg g^{-1} of EHC®. In the aerobic sterilized sediment slurries, the percentage of remaining atrazine on day 182 was 83.8±6.3 % without EHC® application, and 77.8±2.1 % with 2.0 % EHC® application, indicating slow dissipation. The dissipation was mainly chemical, as it was observed both in the sediment slurries and their sterilized counterparts. In the EHC® amended sediments slurries, atrazine dissipation was related to aerobic conditions, as no statistically significant decrease in the atrazine concentrations was observed under anaerobic conditions (Fig. 1b,d). Similarly, atrazine half-lives in surface and subsurface soils (0.8-1.0 m) under aerobic conditions were shorter than under anaerobic conditions, independent of sterilization (Accinelli et al. 2001).

ZVI increased pH in unbuffered solutions, which stopped atrazine dechlorination above pH 9, while below pH 8 atrazine was degraded (Kim et al. 2008). At low pH values below 6, atrazine dissipation has increased both in the presence and absence of ZVI (Satapanajaru et al. 2008; Krutz et al. 2010). At the end of this experiment, the pH values were 7.2±0.5, 6.6±0.6 and 6.4±0.6 in unamended slurries, and in slurries amended with 1.0 and 2.0 % EHC®, respectively, regardless of sterilization and oxygen. It is possible that the sediments and EHC® organic matter served as a buffer (Kim et al. 2007), or the ZVI dose was not high enough to increase pH. The pH in anaerobic slurries (6.2±0.7) was lower than in aerobic slurries (7.3±0.5) (Anova, $p<0.001$), which could result from anaerobic microbial fermentation and related acid production. Atrazine, however, did not dissipate in anaerobic slurries amended with ZVI, i.e. lower pH did not lead to enhanced atrazine dissipation. The pH difference might be too small, or the enhanced degradation by ZVI in low pH could be oxygen dependent.

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

The ability of the 2.0 % EHC® application rate to enhance the dissipation of atrazine, DEA and BAM was further studied in groundwater flowing through the pilot-scale subsurface sediment columns. The percentage of organic matter in EHC® was 52 %. The concentrations of atrazine, simazine and BAM in the sediments were about 12, 31 and 8 µg kg^{-1}, respectively. In groundwater, the concentrations of atrazine, DEA and BAM were 0.077±0.021 µg l^{-1}, 0.032±0.0075 µg l^{-1} and 0.016±0.0036 µg l^{-1}, respectively. Thus, the pesticide and metabolite concentrations in groundwater were just below the European Union limits for drinking water of 0.10 µg l^{-1} for one pesticide, and of 0.50 µg l^{-1} for several pesticides (European Union 1998), while the limit for one pesticide in the United States is 3 µg l^{-1} (U.S. EPA 2000). In the control columns, the concentrations of DEA and

BAM in the effluents decreased until 64-107 days and, thereafter, the quantities were almost between the minimum and maximum quantities in the influent groundwater (Fig. 2). DEA and BAM concentrations were elevated in the effluents of control columns at the early stages of the experiment due to elution of residues from the sediments with flowing water.

Atrazine, DEA and BAM were not detected in effluents of the EHC® amended columns during 33, 64 and 64 days from the beginning of the water flow in columns, respectively (Fig. 2a,b,c). Simazine residues of the sediments did not elute from the EHC® amended columns. Thus, the concentrations of atrazine, DEA and BAM in the EHC® amended columns differed significantly from controls (M-W, $p=0.037$) for 33, 64 and 64 days, respectively, but thereafter the differences from the controls were minor. At the end of the experiment, atrazine, simazine, DEA and BAM could not be extracted from the EHC® amended sediments. This indicates that the compounds became unextractable, or EHC® catalyzed chemical transformations of these molecules to other forms than atrazine, simazine, DEA, DIA, DEDIA, and BAM. Atrazine and BAM quantities dissipated from the sediments and groundwater in 33 and 64 days were about 216 and 116 µg, respectively; the DEA quantity dissipated from groundwater in 64 days was about 166 µg, and the sediments contained about 128 µg of simazine, altogether 627 µg. Thus, in the water-saturated columns, probably under low oxygen conditions, the quantity of dissipated pesticides and metabolites was about 7.6 µg g^{-1} of EHC®. This low concentration explains the absence of significant atrazine degradation in the anaerobic sediment slurries initially amended with 30 mg l^{-1} of atrazine, as presented above.

The capacity of EHC® to catalyze the dissipation of pesticides and metabolites weakened with time. However, due to the low concentration occurring in groundwater, the effluent was maintained clean for about one month, and since 64, 107 and 140 days the sum of pesticides and degradation products in the effluent still was as low as 0.07, 0.06, and 0.09 µg l^{-1}, respectively. After 180 days, the quantity of pesticides and metabolites in the effluent of the EHC® amended columns was 0.14 µg l^{-1}, while the concentration in the influent was 0.125 µg l^{-1} and in the effluent of the control columns 0.18 µg l^{-1}, that is EHC® had lost its ability to enhance the dissipation of the studied compounds.

Part of EHC® eluted out of the columns, as can be seen from decreasing TOC concentrations in the effluent during the experiment (Fig. 2d), which may have reduced the EHC® capacity to enhance pesticide and metabolite dissipation. The effluent pH was about 6 in control columns and 6-7 in EHC® amended columns, that is changes in pH cannot be related to pesticide and metabolite dissipation.

2.4. Remediation of atrazine, simazine, DEA and BAM contamination by EHC®

The results of this study showed that EHC® enhances atrazine dissipation in the subsurface sediment slurries and columns. The 2.0 % EHC® application rate improved atrazine dissipation 0.88±0.14 mg g^{-1} of EHC® under aerobic conditions. EHC® did not enhance atrazine dissipation in anaerobic slurries amended with 30 mg l^{-1} of atrazine. In the sediment columns under the water-saturated conditions, the 2.0 % EHC® application rate enhanced pesticide and degradation product dissipation about 7.6 µg g^{-1} of EHC®. Thus, the EHC® application improved pesticide and degradation product dissipation best under aerobic conditions. In the presence of ZVI, oxygen becomes reduced to hydroxyl ions, hydrogen peroxide and further to hydroxyl radicals, while iron is oxidized (Guan et al. 2015; Sun et al., 2016). This enhanced iron corrosion seemed to improve the ZVI performance and atrazine dissipation better than the reported iron oxidation under anaerobic conditions, which involves reduction of protons with the simultaneous liberation of hydrogen gas. It seems, that aerobic conditions or aeration would be beneficial for atrazine remediation by EHC® in deep sediments below the groundwater table, where conditions are often anaerobic. This can be achieved by direct air sparging, or by using slow-release oxygen compounds, like calcium or magnesium peroxide (Borden et al. 1997).

The differences in atrazine dissipation between the slurries and their sterilized counterparts were minor, which indicate that chemical pathways were more important than microbial for atrazine dissipation by the EHC® application. Indeed, the ZVI supplementation has been used in the remediation to chemically reduce and dechlorinate a broad range of contaminants (Karn et al. 2009; Tosco et al. 2014). In contrast to this result, atrazine degradation in soil has mainly been regarded to result from the microbial activity (Krutz et al. 2010; Mudhoo and Garg 2011). Organic matter has affected the adsorption, movement and biodegradation of pesticides (Briceño et al. 2007; Mudhoo and Garg 2011), and it has both enhanced and prevented contaminant removal by the ZVI treatment (Sun et al. 2016). The adjustment of EHC® organic matter content could affect the atrazine dissipation rate, which was slow over a long period of time.

The atrazine concentration typically found in groundwater is in maximum a few micrograms per litre (Spliid et al. 1998; Talja et al. 2008; Zhang et al. 1997), while the EU limit for a pesticide in drinking water is 0.10 µg l^{-1}. Under aerobic conditions, 1.0 g of EHC® enhanced dissipation of 0.88 mg of atrazine, which means that 1.0 g of EHC® can be used to clean 8800 l of water contaminated with pesticide within the EU limit value of 0.10 µg l^{-1}. However, the ability of EHC® with about 50 % of ZVI to improve atrazine dissipation may be too low for the reported use of EHC® injection into saturated zone to enhance the *in situ* dehalogenation (Caliman et al. 2011;

Molin et al. 2010; Quinn et al. 2005), due to possible adverse effects of high EHC® load in groundwater. However, in some other applications the observed enhancement in atrazine, its degradation products, and BAM dissipation could be useful; like in remediation of contaminated sites with a mixture of compounds including small quantity of atrazine and degradation products, and BAM.

3. Conclusions

In the aerobic subsurface sediment slurries, the 2.0 % EHC® application rate by weight enhanced atrazine dissipation 0.88±0.14 mg g^{-1} of EHC®. The atrazine concentration was reduced in 182 days to 75.0±4.3 % of the initial 30 mg l^{-1}. Atrazine dissipation under aerobic conditions was mainly chemical, due to the absence of a significant difference between the slurries and sterilized controls. In the 1.5 m pilot-scale columns filled with the subsurface sediments, water flowing through the column was maintained clean of atrazine, DEA and BAM for 33, 64 and 64 days, respectively. The sum of dissipated pesticides in the water-saturated sediments and groundwater was 7.6 µg g^{-1} or EHC®. In conclusion, EHC® can be used to enhance dissipation of small quantities of studied pesticides, preferentially under aerobic conditions.

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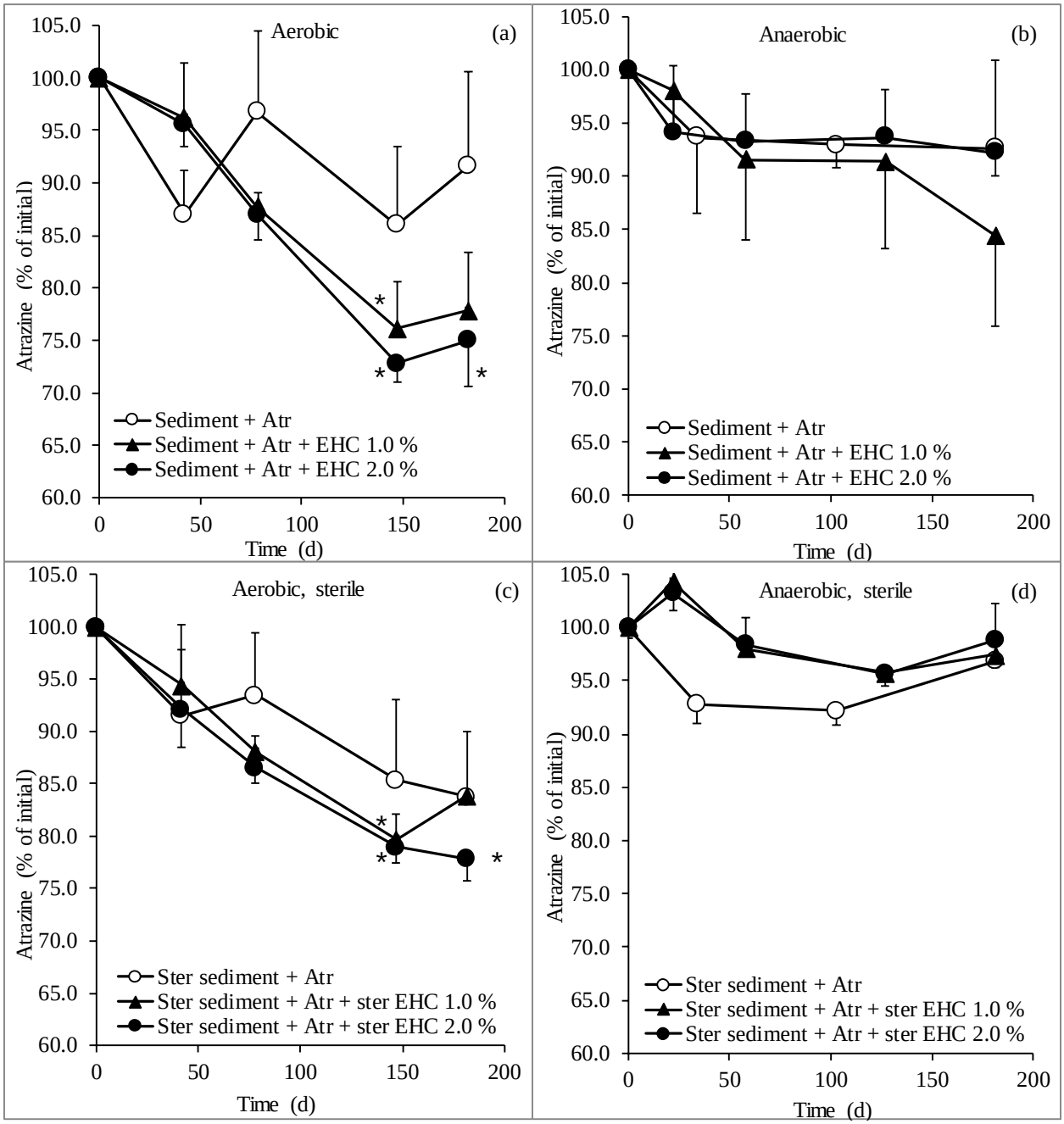
Figure legends.

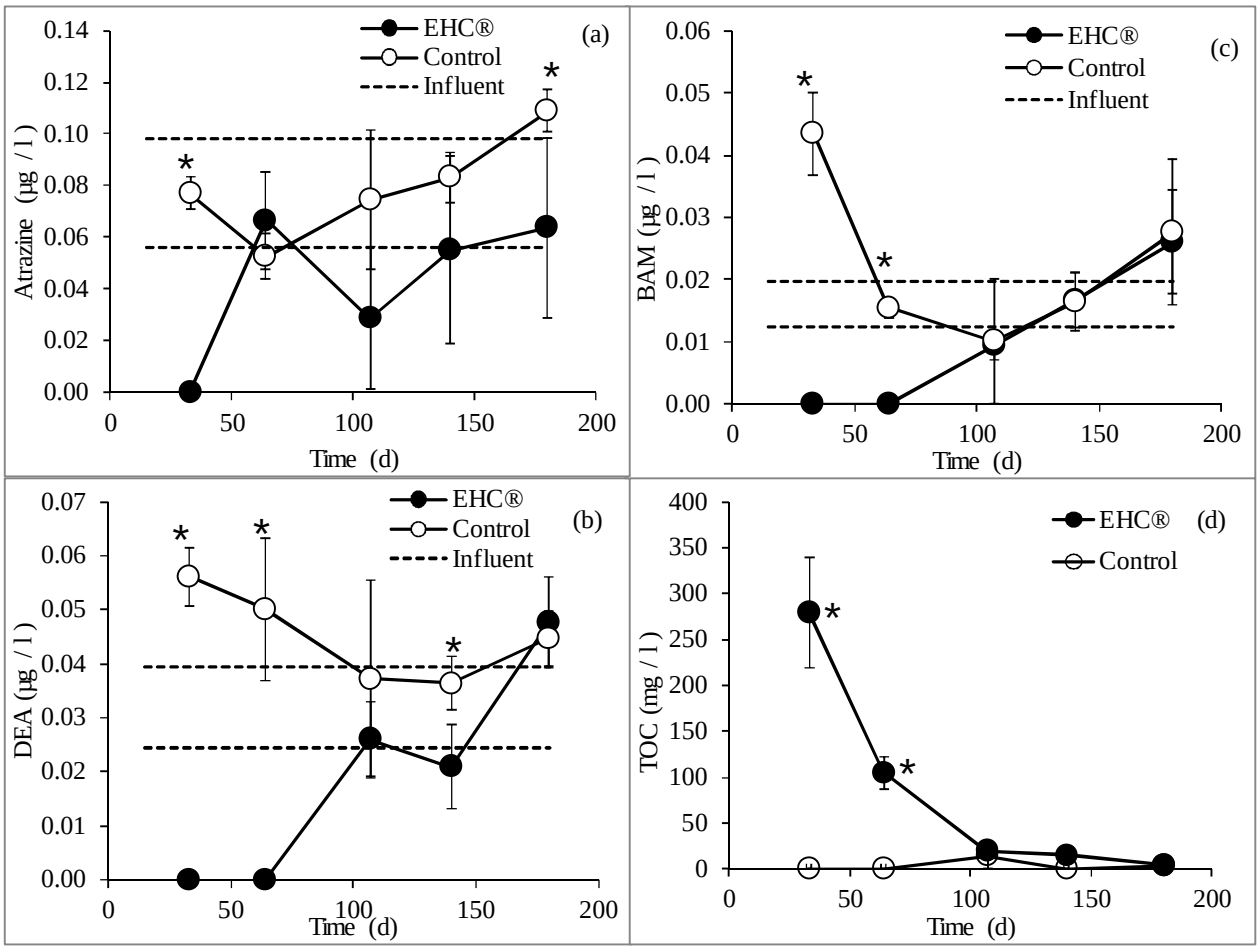
Fig. 1. The percentage of remaining atrazine in the water phase of the sediment (a,b) or sterile sediment (c,d) slurries supplemented with atrazine (Atr), or atrazine with 1.0 or 2.0 % EHC®, under aerobic (a,c) and anaerobic (b,d) conditions. The asterisks indicate statistically significant differences (Anova, $p \leq 0.05$; Tukey HSD test, $p \leq 0.05$) between sediment slurries without and with 1.0 and 2.0 EHC®. Bars indicate S.D. (n=3).

Fig. 2. Atrazine, DEA, BAM and TOC concentrations (mean±S.D., n=3) in the effluent water of sediment columns filled with 2.0 % EHC®, and in the control sediment columns. Asterisks indicate statistically significant differences (Mann-Whitney's test, $p \leq 0.05$) between the EHC® amended sediment columns and control columns, and bars indicate S.D. (n=3). The contamination level of groundwater used as an influent from day 15 forward is shown with two dotted lines representing upper and lower standard deviations from the mean.

Fig. 1.


Aerobic
(a)
Atrazine (% of initial)
Time (d)
Sediment + Atr
Sediment + Atr + EHC 1.0 %
Sediment + Atr + EHC 2.0 %
Anaerobic
(b)
Aerobic, sterile
(c)
Ster sediment + Atr
Ster sediment + Atr + ster EHC 1.0 %
Ster sediment + Atr + ster EHC 2.0 %
Anaerobic, sterile
(d)

1 Fig. 2.


(a)
EHC®
Control
Influent
Atrazine (µg / l)
Time (d)
(b)
DEA (µg / l)
(c)
BAM (µg / l)
(d)
TOC (mg / l)
*

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