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Influence of organic matter, nutrients, and cyclodextrin on microbial and chemical herbicide and degradate dissipation in subsurface sediment slurries

Authors (given name, surname): Kaisa Kerminen*, Romain Le Moël, Vilhelmiina Harju, Merja H. Kontro

Affiliation:

University of Helsinki, Department of Environmental Sciences, Niemenkatu 73, 15140 Lahti, Finland.

*Corresponding author: Kaisa Kerminen

E-mail: kaisa.kerminen@helsinki.fi

Phone: +358-40-8238446

Abbreviations: BAM = 2,6-dichlorobenzamide, CPS = compost-peat-sand mixture, cyclodextrin = methyl-β-cyclodextrin, Na-citrate = sodium citrate

Abstract

Pesticides leaching from soil to surface and groundwater are a global threat for drinking water safety, as no cleaning methods occur for groundwater environment. We examined whether peat, compost-peat-sand (CPS) mixture, NH_4NO_3, NH_4NO_3 with sodium citrate (Na-citrate), and the surfactant methyl-β-cyclodextrin additions enhance atrazine, simazine, hexazinone, dichlobenil, and the degradate 2,6-dichlorobenzamide (BAM) dissipations in sediment slurries under aerobic and anaerobic conditions, with sterilized controls. The vadose zone sediment cores were drilled from a depth of 11.3—14.6 m in an herbicide-contaminated groundwater area. The peat and CPS enhanced chemical atrazine and simazine dissipation, and the peat enhanced chemical hexazinone dissipation, all oxygen-independently. Dichlobenil dissipated under all conditions, while BAM dissipation was fairly slow and half-lives could not be calculated. The chemical dissipation rates could be associated with the chemical structures and properties of the herbicides, and additive compositions, not with pH. Microbial atrazine degradation was only observed in the *Pseudomonas* sp. ADP amended slurries, although the sediment slurries were known to contain atrazine-degrading microorganisms. The bioavailability of atrazine in the water phase seemed to be limited, which could be due to complex formation with organic and inorganic colloids. Atrazine degradation by indigenous microbes could not be stimulated by the surfactant methyl-β-cyclodextrin, or by the additives NH_4NO_3 and NH_4NO_3 with Na-citrate, although the nitrogen additives increased microbial growth.

Keywords: Sediment slurries, herbicides, dissipation, organic amendments, nutrients, methyl-β-cyclodextrin

1. Introduction

Herbicides are widely used throughout the world, and this has led to their occurrence in the environment. The herbicides atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine), simazine (2,4-bis(ethylamino)-6-chloro-1,3,5-triazine), hexazinone (3-cyclohexyl-6-dimethylamino-1-methyl-1,3,5-triazine-2,4-dione), and dichlobenil (2,6-dichlorobenzonitrile), and their degradation products desethylatrazine (2-amino-4-chloro-6-isopropylamino-1,3,5-triazine, DEA), deisopropylatrazine (6-chloro-2-N-ethyl-1,3,5-triazine-2,4-diamine, DIA), desethyldeisopropylatrazine (2-chloro-4,6-amino-1,3,5-triazine, DEDIA), and 2,6-dichlorobenzamide (BAM) have been found in groundwater, some commonly (Li et al., 2001; Hildebrandt et al., 2007; Vuorimaa et al., 2007; Holtze et al., 2008; Talja et al., 2008; Pukkila et al., 2009). For instance, atrazine, dichlobenil, and BAM dissipation in groundwater deposits has mostly been slow or nonexistent (Johnson et al., 2003; Talja et al., 2008; Pukkila and Kontro, 2014). Among the factors associated with slow herbicide dissipation in deep groundwater are the microbial community composition and activity, and the low organic matter, nutrient and oxygen concentrations (Kruger et al., 1993; Issa and Wood, 1999; Pukkila and Kontro, 2014; Mattsson et al., 2015).

The microbial degradation of xenobiotics can be enhanced by biostimulation and bioaugmentation. Biostimulation aims to improve the degradation rate of indigenous microbes by altering conditions, e.g. by adding nutrients favorable for microbes and herbicide degradation. Organic amendments, such as straw, manure, plant residues, and compost have lowered herbicide concentrations in subsurface soils (Hance, 1973; Kanissery and Sims, 2011), as well as an inorganic nutrient solution containing nitrogen in the form of NH_4 and/or NO_3 (Hance, 1973). Surfactants, such as hydroxypropyl-β-cyclodextrin have enhanced herbicide mineralization by increasing bioavailability to microorganisms (Villaverde et al., 2012). In bioaugmentation, microbes capable of degrading contaminants are added, because their presence is vital for bioremediation.

Pseudomonas sp. ADP is known for its ability to efficiently mineralize atrazine (Mandelbaum et al., 1995; Shapir et al., 1998; Silva et al., 2004). Remediation, however, is not limited to biological processes; abiotic processes are also important, such as low pH-induced chemical dissipation of triazines, oxidation-based destruction of organic pollutants, and reductive dehalogenation (Krutz et al., 2010; Laine and Cheng, 2007; Kerminen et al., 2017).

We examined whether atrazine dissipation could be enhanced in vadose zone sediment slurries by adding organic matter [peat; compost-peat-sand mixture (CPS)], nutrients (NH_4NO_3; NH_4NO_3 and Na-citrate), the surfactant methyl-β-cyclodextrin (hereafter, cyclodextrin), or the atrazine degrader *Pseudomonas* sp. ADP. The applicability of peat and CPS in the remediation of a wider group of groundwater contaminants was further studied with the herbicides atrazine, simazine, hexazinone, and dichlobenil, and with the degradation product BAM, which are the most common contaminants in groundwater in Finland (Vuorimaa et al., 2007; Pukkila and Kontro, 2014; Mattsson et al., 2015). Sterilized controls were included to separate microbial degradation from the abiotic effects of the additives. The importance of oxygen was studied by conducting the experiments under aerobic and anaerobic conditions. The vadose zone sediments were from a groundwater area contaminated with atrazine, simazine, and BAM, and they appeared to contain at least atrazine-degrading microorganisms (Kerminen and Kontro, 2017). The hypothesis of the study was that the additives, microbes, and oxygen could enhance atrazine dissipation, while the null hypothesis was that none of these would affect atrazine concentrations.

2. Materials and methods

2.1. Chemicals

The commercial compost-peat-sand (CPS) mixture (Musta Multa; Biolan, Kauttua, Finland) consisted of a composted soil mixture (wood-fiber extrudate, chicken manure, shredded bark, light horticultural peat), dark horticultural peat, sand, and magnesium-rich limestone. The unfertilized peat used in the experiments was from Kekkilä (Vantaa, Finland). The surfactant was cyclodextrin in an aqueous stock solution (50% wt vol^{-1}, Cawasol W7 M TL; Wacker Chemie AG, Munich, Germany). The NH_4NO_3, sodium citrate (Na-citrate), and culture media components were from Sigma-Aldrich (St. Louis, MO, USA), Merck KGaA (Darmstadt, Germany), Scharlab S.L. (Barcelona, Spain), OneMed Ltd (Vantaa, Finland), Acros Organics (Geel, Belgium), Mallinckrodt Baker B.V. (Deventer, Holland), Laboratorios Conda S.A. (Madrid, Spain), and Hispanlab S.A. (Madrid, Spain). The pesticides were from LGC (Teddington, UK). The solvents used in the experiments were high-performance liquid chromatogaphic (HPLC) grade (Merck, Darmstadt, Germany).

2.2. Sediments and chemical analyses

The sediments were collected by drilling next to the railway in the town of Lahti, Finland and transferred to sealed, sterilized plastic bags at the drilling site. The drill diameter was 75 mm from the soil surface down to a depth of 10 m, and 48 mm below that. The drilling site was located in a groundwater area contaminated with atrazine, simazine, and BAM of 13, 38, and 5 μg kg^{-1} (dry weight), respectively (Talja et al., 2008; Mattsson et al., 2015). The sediments used in the experiments were from 11.3 m to 14.6 m below the soil surface, while the groundwater table was at 15 m.

The dry weights were weighed after drying 3—5 g of the sediments, peat, or CPS in triplicate at 105 °C for 16 h, followed by heating at 550 °C for 4 h to determine the organic matter content (SFS-EN 13040). Total carbon (total-C) and total nitrogen (total-N) were determined, using a LECO Model 2000 carbon-nitrogen-sulfur (CNS) analyzer (LECO Corp., St. Joseph, MI, USA) according to the instructions as presented in Talja et al. (2008). The pH values of the sediment slurries were measured, using a WTW inoLab series pH 720 meter (Weilheim, Germany; atrazine experiments) or pH indicator paper (Merck, Kenilworth, NJ, USA; herbicide and BAM experiments).

2.3. Microbes and cultivations

Pseudomonas sp. *ADP* (German Collection of Microorganisms and Cell Cultures DSMZ 11735), was cultivated at 28 °C on selective plates containing per liter: 30 mg atrazine, 15 g agar, 1.0 g Na-citrate, 1.6 g K_2HPO_4, 460.0 mg $NaH_2PO_4 \cdot H_2O$, 2.0 mg $CoSO_4 \cdot 7\ H_2O$, 2.0 mg $ZnSO_4 \cdot 7\ H_2O$, 0.3 mg $CuSO_4 \cdot 5\ H_2O$, 0.2 mg $Na_2WO_4 \cdot 2\ H_2O$, 0.2 mg Na_2SeO_3, 0.1 mg $Na_2MoO_4 \cdot 2\ H_2O$, 0.2 mg $NiCl_2 \cdot 6\ H_2O$, 0.05 mg H_3BO_3, 0.1 mg $NaVO_3$, 24.6 mg $MgSO_4 \cdot 7\ H_2O$, 10.0 mg $MnSO_4 \cdot H_2O$, 11.4 mg $CaSO_4 \cdot 2\ H_2O$, 5.5 mg $FeSO_4 \cdot 7\ H_2O$, 1.0 mg thiamine, and 0.4 mg biotin. The bacterial biomass was collected from six plates in 4 mL of 0.9% NaCl, and 1.0 mL was inoculated per experimental flask. The microbial counts in the sediment slurries (dilution series) and the occurrence of microbial growth in the sterilized sediment slurries after 182 d (atrazine experiments) were determined by plating 100 µL on Luria-Bertani agar, which contained per liter: 10.0 g tryptone, 5.0 g yeast extract, 5.0 g NaCl, and 15.0 g agar.

2.4. Degradation experiments

The experiments were conducted in 100-mL glass flasks sealed with hole (diameter 5 mm) screw caps that were covered with aluminum foil. All flasks contained slurries consisting of 15.0 g of sediment (dry weight) and 50 mL of sterile distilled water. The sterilized sediments and additives were autoclaved on three consecutive days for 1 h at 121 °C and 101 kPa (Instru, Santasalo-Sohlberg, Helsinki, Finland). The anaerobic conditions in the incubation jars were created by Anaerocult® A, and ascertained with Anaerotest® (Merck, Darmstadt, Germany). The flasks were incubated in the dark at 22 ± 2 °C, with shaking at 120 revolutions per minute (rpm) (Laboshake; Gerhardt, Königswinter, Germany; Edmund Bühler GmbH, Hechingen, Germany). The flasks were weighed, and the evaporated water was replaced with sterile distilled water before the samplings. All the experiments were performed in triplicate, except that with the additives NH_4NO_3 and NH_4NO_3 with Na-citrate four parallel flasks were included. On day 182, microbial growth in the sterilized slurries was determined by cultivation, as presented above.

In the first experiment with 20 mg L^{-1} (no additive, and the additives NH_4NO_3 or NH_4NO_3 with Na-citrate) or 30 mg L^{-1} (no additive; other additives) of supplemented atrazine, the treatments under aerobic and anaerobic conditions were (on a dry weight basis): (1) slurry, (2) sterilized slurry, (3) slurry, CPS 5.0% (0.75 g), (4) slurry, sterilized CPS 5.0%, (5) sterilized slurry, sterilized CPS 5.0%, (6) slurry, sterilized CPS 15.0% (2.25 g), (7) sterilized slurry, sterilized CPS 15.0%, (8) slurry, peat 5.0% (0.75 g), (9) slurry, sterilized peat 5.0%, (10) sterilized slurry, sterilized peat 5.0%, (11) slurry, cyclodextrin 0.5% (5 g L^{-1}), (12) sterilized slurry, cyclodextrin 0.5%, (13) slurry, cyclodextrin 0.5%, *Pseudomonas* sp. ADP, (14) slurry, *Pseudomonas* sp. ADP, (15) slurry, NH_4NO_3 23.0 mg L^{-1}, and (16) slurry, NH_4NO_3 23.0 mg L^{-1}, Na-citrate 374.0 mg L^{-1}. Treatments 15 and 16 were conducted only under aerobic conditions. The experiments were conducted in six batches at one additive level, due to the large experimental setup. However, for CPS the level was the same as for peat (5.0) and increased (15.0%), to evaluate the appropriate dose. The batches and

sampling days were as follows: Aerobic treatments 1—13, sampling days 0, 42, 78, 147, 182; anaerobic treatments 1—5, sampling days 0, 43, 79, 148, 225; anaerobic treatments 1, 2, 6—9, sampling days 0, 34, 103, 180; anaerobic treatments 10—13, sampling days 0, 22, 58, 127, 182; aerobic treatments 1, 2, 15, 16, sampling days 1, 2, 4, 7, 28, 63, 100, 125, 146, 190, 217; aerobic and anaerobic treatments 1, 2, 14, sampling days 1, 8, 49, 157.

In the second experiment, 15 mg L^{-1} of atrazine and simazine, 20 mg L^{-1} of dichlobenil and BAM, and 25 mg L^{-1} of hexazinone were supplemented in the slurries, and the following treatments under aerobic and anaerobic conditions were conducted (on a dry weight basis): (1) slurry, (2) sterilized slurry, (3) slurry, CPS 15.0%, (4) sterilized slurry, sterilized CPS 15.0%, (5) slurry, peat 5.0%, and (6) sterilized slurry, sterilized peat 5.0%. Samples were collected from treatments 1 and 2 on days 1, 37, 101, 214, 231, 304, and 343; and from treatments 3—6 on days 1, 7, 21, 35, 49, 56, 93, 157, 270, 287, and 399.

2.5. Pesticide analysis

In the first experiment with the additives NH_4NO_3 and NH_4NO_3 with Na-citrate, 500-µL samples were analyzed, using external standards. In the first experiment with other additives, methanol : water (3:1, vol vol^{-1}, 370 µL) and the internal standard simazine (30 µL of stock 0.1012 µg μL^{-1}) were added to 200-µL samples. In the second experiment, methanol : water (3:1 vol vol^{-1}, 300 µL) and the internal standard propazine (2,4-bis(isopropylamino)-6-chloro-1,3,5-triazine) (100 µL of stock 0.0996 µg μL^{-1}) were added to 200-µL samples. The standards had the same amount of internal standard as the samples and 0.5, 2.5, 5, 10, 20, and 35 mg L^{-1} of atrazine in the first experiment and 0.5, 5, 10, 15, and 30 mg L^{-1} of atrazine, simazine, hexazinone, dichlobenil, and BAM in the second experiment. The samples and standards were filtered (0.45-µm GHP membrane, Acrodisc®; Gelman, Pall Corporation Ltd., Port Washington, NY, USA), and 20 µL were injected into the HPLC, comprising a Shimadzu Prominence SIL-20A auto sampler, LC-20AT solvent

delivery module, DGU-20A5 on-line degasser, SPD-20A ultraviolet/visible light (UV/VIS) detector (225 nm; Shimadzu, Kyoto, Japan), SunFire C18 3.5-µm guard column (3.0*20 mm) and column (3.0 * 150 mm; Waters, Milford, MA, USA) and Shimadzu LC Solution software control system. The mobile phase consisted of acetonitrile and filtered distilled water, and its flow rate was 0.4 mL min^{-1}. For the chromatographic separation, the following gradient was used: 30% acetonitrile for 3.5 min, increase to 65% and held until 8.5 min, and decrease back to 30% and held until 14 min. The quantification accuracy [(average of measured concentrations/actual value) ×100 %] for atrazine, simazine hexazinone, dichlobenil, and BAM was 100.4, 100.6, 97.1, 113.0, and 97.9 % using internal standard, and 100.0, 100.8, 96.1, 102.3, and 97.9 % using external standard, respectively. The quantification precision [(coefficient of variation ×100%] for atrazine, simazine hexazinone, dichlobenil, and BAM was 1.5, 5.4, 6.6, 14.7, and 4.2 % using internal standard, and 1.4, 4.5, 7.1, 10.4, and 4.3 % using external standard, respectively. Standards 5, 15, and 30 mg L^{-1} were analyzed to determine the accuracy and precision (n=5). Generally, only one quantification method was used, but in the case of clear outliers, the results of the second method were checked, to ensure results from long experiments.

At the end of the first experiment, the above liquid samples from the peat-amended slurries on day 78 were evaporated to dryness under a nitrogen flow, the residue was solubilized in 0.5 mL acetone, and analyzed by gas chromatography-mass spectrometry (GC-MS), as presented below. At the end of the second experiment, the pesticides adsorbed to the sediments were extracted three times with methanol : water (3:1 vol vol^{-1}) as presented in Pukkila and Kontro (2014), except that 9.96 µg of propazine in 100 µL of methanol : water (3:1, vol vol^{-1}) were used as an internal standard. The pooled extracts were evaporated to dryness, the herbicides were solubilized in acetone, and analyzed, using a Shimadzu GCMS-QP-2010Ultra GC-MS equipped with an AOC-20i+s autosampler and a ZB-5MS capillary column (29 m, 0.25 mm, 0.25 µm), using selected ion monitoring, as described in Kerminen et al. (2017). The herbicide standard concentrations and the ions followed to detect atrazine, simazine, and their degradation products BAM, DEA, DIA, and

DEDIA were as presented in Kerminen et al. (2017). The ions followed to detect hexazinone showed mass-to-charge (m/z) ratios of 83, 128, 171, and 252 (quantification ion), while those followed to detect dichlobenil showed m/z ratios of 100, 171 (quantification ion), and 173. The extraction efficiency of the method was 98.9 ± 10.8%.

2.6. Calculations and statistical analyses

The results are presented as an average ± the standard deviation (S.D.). The half-life ($T_{1/2}$) values were calculated, using the equation $\ln C_{(t)} = -kt + \ln (C_0)$, where $C_{(t)}$ is the concentration at time t, C_0 the initial concentration, and k the rate constant (Beulke and Brown, 2001). In the second experiment, the atrazine, simazine, and dichlobenil $T_{1/2}$ values were based on the fast dissipation phase. The $T_{1/2}$ values, end concentrations, and pH values were analyzed by the three-factor (oxygen, sterilization, additives) Kruskal-Wallis (K-W) test, followed by pairwise comparisons using the Mann-Whitney (M-W) U test, since the data were not normally distributed (Shapiro Wilk, $p < 0.05$) or lacked the equality of variances (Levene's test, $p < 0.05$).

3. Results

3.1. Additives and atrazine dissipation

The effects of the additives CPS, peat, the surfactant cyclodextrin, *Pseudomonas* sp. ADP, NH_4NO_3, and NH_4NO_3 with Na-citrate on atrazine dissipation were studied in the vadose zone sediment slurries (Fig. 1—2). The organic matter, total-C, and total-N concentrations decreased in the sediment and additive slurries as follows: sediment, 15.0% CPS > sediment, 5.0% peat > sediment, 5.0% CPS > sediment, NH_4NO_3, Na-citrate ≥ sediment, NH_4NO_3 ≥ sediment (Table 1).

The vadose zone sediment slurries and sterilized slurries without amendments were included as controls in several experimental batches under aerobic and anaerobic conditions, and the result was always the same: no atrazine dissipation without the additives (Fig. 1, Table 2). The atrazine concentrations in the experiments without the additives were 16.1 ± 1.6 mg L^{-1} (initial 20 mg L^{-1}) or 31.3 ± 2.2 mg L^{-1} (initial 30 mg L^{-1}) after 180—190-d incubations. The microbial numbers were 4.6 ± 1.8×10^4 colony-forming units (cfu) mL^{-1} in the slurries without the additives, and increased to 1.1 ± 1.1×10^6 cfu mL^{-1} in the slurries amended with NH_4NO_3, and to 2.0 ± 1.6×10^6 cfu mL^{-1} in the slurries amended with NH_4NO_3 and Na-citrate. Although nitrogen addition increased the microbial growth (M-W, $p = 0.021$), the combined nitrogen and carbon addition did not further increase the growth (M-W, $p = 0.386$). The additives NH_4NO_3 and NH_4NO_3 with Na-citrate increased the C/N ratio to 11.6 and 22.9, respectively, but did not enhance atrazine dissipation (Fig. 1G; Table 2). Similarly, 0.5% cyclodextrin did not improve atrazine dissipation (Fig. 1E,F; Table 2).

Other additives significantly affected atrazine dissipation in the sediment slurries, according to the three factor (additive, oxygen, sterilization) K-W test ($p < 0.05$) of the $T_{1/2}$ values and concentrations after 180—190 d. Oxygen and the sterilization of sediment-indigenous microbes did not affect the atrazine concentrations. The atrazine dissipated rapidly, showing $T_{1/2}$ values of 38.8—72.4 d in the 5.0% CPS-amended slurries (C/N ratio 25.3), and the concentrations fell to 1.3—6.2 mg L^{-1} in 180—190 d (Fig. 1A,B; Table 2). The increase in the CPS quantity to 15.0% accelerated atrazine dissipation in the slurries (C/N ratio 25.1; $T_{1/2}$ 20.9—33.6 d), while the concentrations after 180—190 d were 0.15—1.1 mg L^{-1}. The atrazine dissipation rate further increased in the 5.0% peat-amended slurries (C/N ratio 42.5), where the $T_{1/2}$ values were 15.6—19.5 d and the concentrations after 180—190 d were as low as 0.03—0.08 mg L^{-1} (Fig. 1C,D; Table 2). No DEA, DIA, or DEDIA was detected in the atrazine- and peat-amended slurries on day 78. When *Pseudomonas* sp. ADP was added to the sediment slurries, the atrazine $T_{1/2}$ values of 3.0—24.4 d were within the same range as with the 5.0% peat addition, and the concentrations after 180—190 d were 0.04—0.5 mg L^{-1}, regardless of the presence of cyclodextrin (Fig. 1E,F; Table 2). In all, the atrazine

concentrations in the slurries with 5.0% and 15.0% CPS and 5.0% peat differed significantly from each other and from the sediment slurries (M-W, $p < 0.001$) (Fig. 1; Table 2). The effects of the treatments on atrazine dissipation were as follows, based on $T_{1/2}$ values: no additive = cyclodextrin > CPS 5.0% > CPS 15.0% > peat 5.0% = cyclodextrin and *Pseudomonas* sp. ADP = *Pseudomonas* sp. ADP.

The average pH values varied between 6.9 and 7.7 in the slurries without additives and between 6.4 and 6.8 in the slurries amended with cyclodextrin; thus, the pH values of 6.4—7.7 could not be associated with the enhanced atrazine dissipation (Tables 2—3). The average pH values in the CPS-amended slurries were 6.2—7.7, except the low pH values of 5.2—5.9 that were measured in the sterilized and anaerobic 5.0% CPS-amended slurries. The lowest pH values of 4.6—5.5 were found in the peat-amended slurries. After 182 d of incubation, 26.9% of the sterilized controls showed microbial growth. However, the concentrations in the slurries with microbial growth did not differ from those in the parallel sterilized slurries, indicating that microbial growth in a few flasks did not affect the results.

3.2. Organic additives and herbicide and BAM dissipation

The ability of peat and CPS to enhance the dissipation of the herbicide and degradation product mixture containing atrazine, simazine, hexazinone, dichlobenil, and BAM was further studied (Fig. 2; Table 3). The three-factor (additive, oxygen, sterilization) K-W test ($p < 0.001$) showed that the additives only affected atrazine, simazine, and hexazinone dissipation. In accordance with the first experiment, no atrazine, simazine, or hexazinone dissipation occurred in the sediment slurries without the additives. Peat enhanced atrazine ($T_{1/2}$, 17.3—21.1 d), simazine ($T_{1/2}$, 14.0—17.2 d), and hexazinone ($T_{1/2}$, 221.9—729.9 d) dissipation, while CPS enhanced atrazine ($T_{1/2}$, 27.3—74.1 d) and simazine ($T_{1/2}$, 17.2—31.6 d) dissipation less than peat (Fig. 2A—F; Table 3). Similar trends were observed in the atrazine, simazine, and hexazinone concentrations

after 343—360 d, i.e. they were lowest in the peat-amended slurries, second lowest in the CPS-amended slurries, and highest in the sediment slurries. However, hexazinone did not dissipate after the initial reduction in the CPS-amended slurries, based on the $T_{1/2}$ calculations. Extraction of the wet sediments after discarding the liquid phase at the end of the experiment showed that the quantities of atrazine, simazine, and hexazinone remaining in the sediments were 4.7 ± 1.9, 10.7 ± 3.5, and 54.6 ± 25.6 μg L^{-1} of slurry, while the quantities in the peat-amended sediments were 0.02 ± 0.01, 0.04 ± 0.02, and 156.1 ± 72.7 μg L^{-1} of slurry, respectively, regardless of sterilization. DEA, DIA, and DEDIA were not detected.

Dichlobenil dissipation in the sediment slurries was quite rapid, regardless of oxygen, sterilization, and the additives, the $T_{1/2}$ values varying between 19.7 d and 38.2 d (Fig. 2G,H; Table 3). The dichlobenil concentrations after 343—360 d were, under aerobic conditions (0.01—2.7 mg L^{-1}), lower than under anaerobic conditions (0.14—3.1 mg L^{-1}), although the differences were small. In contrast, BAM was not dissipated in the sediment slurries, regardless of the additives, oxygen, or sterilization (Fig. 2I,J; Table 3), although the BAM concentrations in the anaerobic sediment slurries were slightly lower than in the aerobic sediment slurries. In the sterilized slurries, the BAM concentrations after 360 d decreased in the following order: slurry, 15.0% CPS < slurry < slurry, 5.0% peat. No dichlobenil or BAM could be extracted from the sediments at the end of the experiment.

The pH values in the slurries, peat-amended slurries, and CPS-amended slurries varied between 6.3 and 7.7, regardless of the additives, oxygen, and sterilization, except the pH was as low as 5.2—5.6 in the sterilized peat-amended slurries and in the 15.0% CPS-amended anaerobic slurries (Table 3). The pH was lower under anaerobic conditions than under aerobic conditions ($p < 0.01$) and in the peat-amended slurries than in the nonamended or CPS-amended slurries ($p < 0.05$), regardless of sterilization.

4. Discussion

4.1. Organic matter and herbicide and BAM dissipation

Peat or CPS addition decreased the atrazine and simazine concentrations in the subsurface sediment slurries, while peat addition decreased the hexazinone concentrations (Fig. 1A—D, and 2A—F; Tables 2—3). The quantities of triazines and degradation products DEA, DIA, and DEDIA extracted from the peat-amended sediments were low, and the degradation products were not detected in the slurries. The results suggest that the herbicides were transformed into other, non-phytotoxic (Ralebitso et al., 2002; Krutz et al., 2010) derivatives and/or they formed non-extractable bound residues. Since the herbicide concentrations in the peat or CPS-amended slurries were not affected by microbes, the dissipation was chemical. Currently, organic amendments are thought to increase microbial herbicide degradation by biostimulation (Briceño et al., 2007), but chemical atrazine hydrolysis was previously regarded as more important (Krutz et al., 2010). Bound residue formation has also been an important route in abiotic herbicide dissipation (Kruger et al., 1997; Miller et al., 1997). Although chemical triazine dissipation has been fastest in soils with pH below 6.0 (Krutz et al., 2010), in this study the dissipation rates were associated with the additives, not with the pH (Tables 2—3).

The chemical dissipation of atrazine, simazine and hexazinone in the peat-amended sediment slurries was oxygen-independent (Fig. 1C—D and 2A—F; Tables 2—3), suggesting the reductive dehalogenation type of dissipation (Laine and Cheng, 2007). The reaction was faster than atrazine dissipation in the zero valent iron-amended slurries under aerobic conditions (Kerminen et al., 2017). The chemical dissipation rates of the triazines in the peat- and CPS-amended sediment slurries appeared to be specific to the compounds (Fig. 2 A—F, Table 3). The triazine herbicides atrazine and simazine, with rather similar chemical structures, dissipated faster than hexazinone with the cyclohexyl ring. Thus, atrazine and simazine with the water solubility of 6.2-33 mg L^{-1},

organic carbon partition coefficients of 39-277 mL g^{-1}, sorption distribution coefficients of 0.2-18 L kg^{-1}, and Henry's constants of 5.6-15×10^{-5} Pa m^3 mol^{-1} chemically dissipated well in the peat-amended sediment slurries (Tables 2—4).

Dichlobenil dissipated rapidly under all conditions in this study and according to Pukkila and Kontro (2014), while BAM was the least reactive (Fig. 2G—J; Table 3). However, the degradation product BAM concentration did not increase, due to dichlobenil dissipation. No dichlobenil could be extracted from the sediments at the end of the experiment, even though dichlobenil showed higher affinity for soil than BAM, based on the K_d values (Table 4). Therefore, dichlobenil with the high Henry's constant evaporated, and/or chemically dissipated (Fig. 2G—H). Compared to atrazine and simazine, the slow hexazinone and BAM dissipations in the peat-amended sediment slurries could result from the better water solubility (2.7-33.0 g L^{-1}), and weaker binding to organic matter (K_{oc}, 10-54 mL g^{-1}) without evaporation (Henry's constant, 0.122-23×10^{-8} Pa m^3 mol^{-1}) (Fig. 2; Tables 3—4). As a result, hexazinone and BAM were less bound to the reactive sites of the peat, and remained in the slurries without reacting and evaporating.

Peat (5.0%) enhanced the atrazine, simazine, and hexazinone dissipations better than 5.0 or 15.0% CPS, even though the organic matter, total-C, and total-N contents in the 15.0% CPS slurries were higher than in the 5.0% peat slurries (Fig. 1A—D and 2A—F; Tables 1—3). Thus, the organic matter composition and the quantity of its reactive sites may be important factors to consider. The binding affinity of humic materials with different structures and sources varies widely (Kulikova and Perminova, 2002), and organic matter may adsorb herbicides (Briceño et al., 2007; Mudhoo and Garg, 2011). The reactive sites may differ between the herbicides and degradation products, or they may compete for the same sites. For example, BAM dissipation in the sediment slurries of this study ceased at higher concentrations (19.7 ± 2.9 mg L^{-1}) than in groundwater deposit slurries (3.0-11.3 mg L^{-1} after 56 d; Pukkila and Kontro, 2014), which could have been due to the presence of several herbicides binding the same reactive sites (Fig. 2I—J; Table 3). The interference between

pesticides cannot be excluded in the peat and CPS amended slurries, but the herbicides and BAM did not interfere in the sediment slurries without the additives, as dichlobenil only dissipated.

4.2. Microbial degradation of herbicides and BAM

The sediments of this study were contaminated with atrazine, simazine, and BAM (Mattsson et al., 2015), and they seemingly contained atrazine-degrading microorganisms (Kerminen and Kontro, 2017). Atrazine degradation genes have been found in boreal subsoils that lacked atrazine mineralization (Nousiainen et al., 2014). Similarly, dichlobenil- and BAM-degrading microbes occurred in all contaminated deposits examined (Pukkila et al., 2009; Pukkila and Kontro, 2014). Nevertheless, the indigenous microbes of the sediments slurries did not degrade atrazine below 56 ± 10.9 mg L^{-1} (Kerminen and Kontro, 2017), which is above the initial concentration in this study of 20-30 mg L^{-1}, and no atrazine dissipation was observed (Fig. 1—2; Tables 2—3). Similarly, the aquifer sediments with 10 mg kg^{-1} of atrazine lacked intrinsic atrazine mineralization (Shapir et al., 1998). The formation of complexes with organic and inorganic colloids (Meng and Carper, 2000; de Jonge et al., 2004) in the liquid phase of the sediment slurries may limit the atrazine bioavailability for microbial degradation at concentrations below 56 ± 10.9 mg L^{-1} (Kerminen and Kontro, 2017).

Pseudomonas sp. ADP degraded atrazine below the detection limit in the sediment slurries, oxygen-independently (Fig. 1E—F; Table 2). It could be used for atrazine bioremediation in contaminated aquifers, although bioaugmentation problems, such as poor survival, decreasing activity, competition, and overgrowth by indigenous microbes may limit its usability (Shapir et al. 1998; Newcombe and Crowley, 1999; Liu et al., 2015; Cycon and Piotrowska-Seget, 2016). Na-citrate and Na-succinate amendments have stimulated atrazine biodegradation in soil by *Pseudomonas* sp. ADP (Mandelbaum et al., 1995; Silva et al., 2004), but in the sediment slurries of this study Na-citrate had no effects (Fig. 1G; Table 2). Similarly, CPS, peat or NH_4NO_3 did not activate microbial atrazine degradation in the nitrogen-exhausted sediment slurries of this study

(Fig. 1—2), although earlier organic amendments, NH_4NO_3, KNO_3, and $(NH_4)_2HPO_4$ additions have improved microbial atrazine degradation (Hance, 1973; Briceño et al., 2007). Since atrazine acts as a nitrogen source, excess nitrogen may slow down atrazine biodegradation, though opposite reports also exist (García-González et al., 2003; Kannika et al., 2010; Alvey and Crowley, 1985). As a result of the NH_4NO_3, Na-citrate, CPS and peat additions, the C/N ratio was adjusted to 11.6-42.2 (Table 1), while the optimal C/N ratio is between 23-47 for terrestrial decomposers (Zechmeister-Boltenstern et al., 2015), and above 40 for atrazine mineralization by *Pseudomonas* sp. (Silva et al., 2004). None of the additives affected atrazine biodegradation in the sediment slurries by indigenous sediment microbes (Fig. 1—2).

Atrazine (30 mg L^{-1}) bioavailability for microbial degradation could not be enhanced by 0.5% surfactant cyclodextrin (Fig. 1E; Table 2). Free cyclodextrin has increased atrazine solubility 1.5-fold, and silica-anchored cyclodextrin 3.4-fold (de Carvalho and de Matos Alves Pinto, 2012), while silica- and polymer-bound β-cyclodextrin has also been used as an absorbent to remove pesticides from water (Sawicki and Mercier, 2006; Liu et al., 2011). The surfactants rhamnolipids and triton X-100 in a growth medium did not affect, or reduced microbial atrazine degradation, while the same surfactants slowed, accelerated or did not affect atrazine dissipation in different soils (Mata-Sandoval et al., 2001; Singh and Cameotra, 2014).

4.3. Remediation of herbicide-contaminated groundwater

Peat, and to a lesser extent CPS, enhanced chemical triazine dissipation (Fig. 1—2), contrary to the general view that organic amendments activate microbial herbicide degradation (Briceño et al., 2007). Peat has been used for instance in constructed wetlands and biobeds to prevent groundwater contamination (Del Pilar Castillo and Torstensson, 2007; Reichenberger et al., 2007). Based on our results, it is unclear to what extent the herbicide dissipation in the constructed wetlands/biobeds is microbiological and chemical degradation, or due to adsorption. The ability of

peat to improve the chemical dissipation of hazardous compounds brings many new opportunities for remediation independent of biological organisms, for example in filters, reactors and permeable reactive barriers (Foo and Hameed, 2010; Reichenberger et al., 2007). Peat can also be used in *in situ* herbicide remediation in groundwater using reactive walls or injection technology (Thiruvenkatachari et al., 2008; Cundy et al., 2008; Obiri-Nyarko et al., 2014). However, prior to applying peat or CPS in remediation, their effects on the water quality must be evaluated. Groundwater organic matter may be transformed to organohalogen contaminants in drinking water chlorination (Deborde and von Gunten, 2008). The compost with chicken manure in CPS may be microbially contaminated. In addition, peat does not enhance the chemical dissipation of all hazardous contaminants, for instance, BAM dissipation was not improved by the peat amendment in concentrations used in this study.

The results of this study showed that herbicide and metabolite degradation in the sediment slurries by indigenous microbes could not be enhanced by nutrients NH_4NO_3, peat, and CPS, opposite to surface soil studies (Mandelbaum et al., 1995; Silva et al., 2004; Hance, 1973; Fig. 1—2; Tables 2—3). *Pseudomonas* sp. ADP could degrade atrazine (Fig. 1E—F; Table 2), but it may not be stable in groundwater sediment slurries, as the distribution of *Pseudomonas* species between surface and subsurface environments differ significantly (Liu et al., 2015; Newcombe and Crowley, 1999). Nonetheless, *Pseudomonas* sp. ADP could degrade atrazine to lower concentrations than the indigenous subsurface/groundwater microbes.

5. Conclusions

In the subsurface sediment slurries, peat (5.0%) and CPS (15.0%) enhanced chemical atrazine and simazine dissipation, while peat (5.0%) slightly accelerated hexazinone dissipation, all regardless of microorganisms, oxygen, or slurry pH. The atrazine degradation products DEA, DIA, and DEDIA were not detected in the peat-amended slurries, and the herbicide and degradation product quantities

in the sediment extracts were low. The chemical dissipation appeared to be specific to contaminants, as herbicides and BAM had different dissipation rates. Dichlobenil dissipated under all conditions, while its degradation product BAM did not show clear dissipation. The microbial atrazine degradation could not be enhanced by the surfactant cyclodextrin or by the additives CPS, peat, NH_4NO_3 and NH_4NO_3 with Na-citrate. Since the sediment slurries were known to contain at least atrazine-degrading microorganisms, the herbicides and BAM in the water phase seemed not to be bioavailable, most likely due to complex formation with organic and inorganic colloids. However, *Pseudomonas* sp. ADP could degrade atrazine in the sediment slurries.

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Table 1. Organic matter, total carbon (total-C), total nitrogen (total-N), and C/N ratio in the sediments and in the sediments amended with compost-peat-sand (CPS), peat, NH_4NO_3, and NH_4NO_3 with Na-citrate.

	Organic matter	Total-C	Total-N	C/N ratio
	mg g^{-1}	mg g^{-1}	mg g^{-1}	
Sediment	4.3 ± 0.2	0.3 ± 0.2	< LOD[1]	-
Sediment, 5.0% CPS	68.6 ± 2.6	197.1 ± 5.1	7.8 ± 0.1	25.3
Sediment, 15.0% CPS	119.4 ± 3.7	590.6 ± 15.2	23.5 ± 0.4	25.1
Sediment, 5.0% peat	92.0 ± 2.1	395.5 ± 0.3	9.3 ± 0.1	42.5
Sediment, NH_4NO_3	4.3 ± 0.2	0.3	0.03	11.6
Sediment, NH_4NO_3, Na-citrate	4.6	0.6	0.03	22.9

[1]LOD, The limit of detection

Table 2. Atrazine half-lives, concentrations after 180—190 d, and pH values in the slurries and sterilized slurries under aerobic and anaerobic conditions (n = 3 or 4). The additives were compost-peat-sand (CPS) mixture, peat, the surfactant methyl-β-cyclodextrin, *Pseudomonas* sp. ADP, NH_4NO_3, and NH_4NO_3 with Na-citrate. According to the three-factor (additive, oxygen, sterilization) Kruskal-Wallis test, only the additives ($p < 0.05$) affected the atrazine half-lives and concentrations on days 180—190.

Additives	Mann-Whitney's test ($p<0.05$)	Aerobic (A)		Anaerobic (AA)	
		Slurry	Sterilized slurry	Slurry	Sterilized slurry
Half-lives (days)					
a) No additive	b-c, d, e-f, h	ND*	ND*	ND*	ND*
b) CPS 5.0 %	a, d, e-f, g, h	61.0±6.1		38.8±3.9	
c) Sterilized CPS 5.0 %		72.4±4.9	45.2±6.2	44.9±1.1	55.4±12.9
d) Sterilized CPS 15.0 %	a, b-c, e-f, g, h	27.4±1.2	32.4±4.6	20.9±3.0	33.6±2.0
e) Peat 5.0 %	a, b-c, d, g	17.9±1.8		15.6±0.2	
f) Sterilized peat 5.0 %		19.2±0.1	19.5±0.8	17.8±0.3	18.8±0.9
g) Cyclodextrin 0.5 %	b-c, d, e-f, h	ND*	ND*	ND*	ND*
h) Cyclodextrin 0.5 %, *Pseudomonas* sp. ADP	a, b-c, d, g	14.1±6.0		24.4±2.3	
i) *Pseudomonas* sp. ADP		3.1±0.1		3.0±0.1	
j) NH_4NO_3		ND*,1			
k) NH_4NO_3 and sodium citrate		ND*,1			
End concentrations on days 180-190 (mg L^{-1})					
a) No additive	b-c, d, e-f, h	30.4±0.3	28.8±0.4	32.8±0.6	32.8±2.7
b) CPS 5.0 %	a, d, e-f, g, h	4.4±0.8		1.3±0.4	
c) Sterilized CPS 5.0 %		6.2±0.4	1.9±0.6	1.9±0.1	3.1±1.7
d) Sterilized CPS 15.0 %	a, b-c, e-f, g, h	0.5±0.1	1.0±0.5	0.15±0.14[a]	1.1±0.3
e) Peat 5.0 %	a, b-c, d, g	0.04±0.01		0.03±0.01	
f) Sterilized peat 5.0 %		0.08±0.01	0.08±0.02	0.06±0.01	0.08±0.01
g) Cyclodextrin 0.5 %	b-c, d, e-f, h	30.4±0.1	29.6±0.4	32.6±0.6	32.6±1.6
h) Cyclodextrin 0.5 %, *Pseudomonas* sp. ADP	a, b-c, d, g	0.04±0.01		0.5±0.3	
i) *Pseudomonas* sp. ADP		0.28±0.02[2]		0.24±0.03[2]	
j) NH_4NO_3		16.4±1.6[1]			
k) NH_4NO_3 and sodium citrate		17.3±1.2[1]			
pH values (after 180-225 days) (Kruskal-Wallis: A differ from AA)					
a) No additive	e-f, g	7.7±0.2	7.1±0.1	6.9±0.6	7.0±0.4
b) CPS 5.0 %	a, e-f	7.3±0.1		7.7±0.8	
c) Sterilized CPS 5.0 %		7.2±0.2	5.8±0.2	5.9±0.9	5.2±0.5
d) Sterilized CPS 15.0 %	e-f	7.3±0.1	7.4±0.3	6.2±1.0	6.5±0.5
e) Peat 5.0 %	a, b-c, d, g	5.5±0.2		4.7±0.1	
f) Sterilized peat 5.0 %		5.1±0.1	4.6±0.2	4.7	4.7±0.1
g) Cyclodextrin 0.5 %	a, e-f	6.8±0.1	6.6±0.3	6.4±0.5	6.6±0.2

*ND, no degradation

[1]Initial concentration 20 mg L^{-1}

[2]Day 56

Table 3. Atrazine, simazine, hexazinone, dichlobenil, and 2,6-dichlorobenzamide (BAM) half-lives, concentrations after 343—360 d, and pH values in the slurries and sterilized slurries incubated under aerobic and anaerobic conditions (n = 3). The additives were compost-peat-sand (CPS) mixture and peat. According to the three-factor (additive, oxygen, sterilization) Kruskal-Wallis (K-W) test, the additives ($p < 0.001$) affected the atrazine, simazine, and hexazinone half-lives and concentrations on days 343–360, while oxygen ($p < 0.05$) affected the dichlobenil end concentrations and pH. Oxygen and sterility interacted with the BAM end concentrations (K-W, $p < 0.05$). The statistically significant differences are denoted with superscripts.

	Aerobic (A)		Anaerobic (AA)	
Additives	Slurry	Sterilized slurry	Slurry	Sterilized slurry
Half-lives (days)				
a) Atrazine, no additive	ND*	ND*	ND*	ND*
b) Atrazine, peat 5.0 %	17.3 ± 0.1 ^{a,c}	19.3 ± 1.3 ^{a,c}	19.6 ± 0.5 ^{a,c}	21.1 ± 1.3 ^{a,c}
c) Atrazine, CPS 15.0 %	42.6 ± 0.2 ^{a,b}	52.4 ± 1.8 ^{a,b}	27.3 ± 0.9 ^{a,b}	74.1 ± 3.6 ^{a,b}
a) Simazine, no additive	ND*	ND*	ND*	ND*
b) Simazine, peat 5.0 %	14.0 ± 1.3 ^{a,c}	16.6 ± 2.7 ^{a,c}	17.2 ± 1.6 ^{a,c}	15.2 ± 1.9 ^{a,c}
c) Simazine, CPS 15.0 %	17.2 ± 0.1 ^{a,b}	31.1 ± 1.5 ^{a,b}	22.0 ± 3.4 ^{a,b}	31.6 ± 3.2 ^{a,b}
a) Hexazinone, no additive	ND*	ND*	ND*	ND*
b) Hexazinone, peat 5.0 %	472.9 ± 91.6 ^{a,c}	221.9 ± 15.2 ^{a,c}	729.9 ± 122.4 ^{a,c}	437.8 ± 55.2 ^{a,c}
c) Hexazinone, CPS 15.0 %	ND*	ND*	ND*	ND*
a) Dichlobenil, no additive	33.2 ± 19.9	22.7 ± 0.6	19.7 ± 6.1	26.4 ± 8.3
b) Dichlobenil, peat 5.0 %	23.7 ± 3.3	38.2 ± 11.2	29.1 ± 1.2	28.6 ± 1.5
c) Dichlobenil, CPS 15.0 %	37.5 ± 4.2	28.7 ± 0.8	30.1 ± 1.3	29.6 ± 1.1
a) BAM, no additive	ND*	ND*	ND*	ND*
b) BAM, peat 5.0 %	ND*	ND*	ND*	ND*
c) BAM, CPS 15.0 %	ND*	ND*	ND*	ND*
End concentrations on days 343-360 (mg L^{-1})				
a) Atrazine, no additive (343 days)	15.3 ± 1.4 ^{b,c}	14.8 ± 0.4 ^{b,c}	15.7 ± 0.4 ^{b,c}	15.7 ± 0.4 ^{b,c}
b) Atrazine, peat 5.0 % (360 days)	0.25 ± 0.09 ^{a,c}	0.19 ± 0.16 ^{a,c}	0.26 ± 0.10 ^{a,c}	0.36 ± 0.25 ^{a,c}
c) Atrazine, CPS 15.0 % (360 days)	0.35 ± 0.05 ^{a,b}	0.81 ± 0.14 ^{a,b}	0.33 ± 0.14 ^{a,b}	0.66 ± 0.11 ^{a,b}
a) Simazine, no additive (343 days)	7.6 ± 6.7 ^{b,c}	10.1 ± 0.5 ^{b,c}	10.1 ± 0.4 ^{b,c}	10.1 ± 0.2 ^{b,c}
b) Simazine, peat 5.0 % (360 days)	1.0 ± 1.0 ^{a,c}	1.0 ± 0.9 ^{a,c}	2.1 ± 0.3 ^{a,c}	1.1 ± 0.2 ^{a,c}
c) Simazine, CPS 15.0 % (360 days)	1.9 ± 0.7 ^{a,b}	1.2 ± 0.1 ^{a,b}	3.6 ± 0.2 ^{a,b}	1.3 ± 0.1 ^{a,b}
a) Hexazinone, no additive (343 days)	24.6 ± 2.0 ^{b,c}	24.3 ± 0.4 ^{b,c}	23.9 ± 1.1 ^{b,c}	24.0 ± 0.5 ^{b,c}
b) Hexazinone, peat 5.0 % (360 days)	11.8 ± 0.6 ^{a,c}	10.5 ± 6.1 ^{a,c}	13.8 ± 1.5 ^{a,c}	12.7 ± 2.1 ^{a,c}
c) Hexaninone, CPS 15.0 % (360 days)	14.8 ± 0.3 ^{a,b}	16.4 ± 1.4 ^{a,b}	15.9 ± 0.8 ^{a,b}	17.8 ± 1.5 ^{a,b}
a) Dichlobenil, no additive (343 days)	2.7 ± 2.4 ^{AA}	1.3 ± 1.2 ^{AA}	3.1 ± 1.6 ^{A}	2.3 ± 0.2 ^{A}
b) Dichlobenil, peat 5.0 % (360 days)	0.01 ± 0.02 ^{AA}	0.35 ± 0.27 ^{AA}	0.19 ± 0.04 ^{A}	0.69 ± 0.12 ^{A}
c) Dichlobenil, CPS 15.0 % (360 days)	0.01 ± 0.01 ^{AA}	0.09 ± 0.04 ^{AA}	0.14 ± 0.03 ^{A}	0.49 ± 0.04 ^{A}
a) BAM (343 days)	29.4 ± 4.2 ^{AA}	26.6 ± 0.2 ^{b,c}	26.1 ± 0.5 ^{A}	26.1 ± 0.3 ^{b,c}
b) BAM, peat 5.0 % (360 days)	31.0 ± 1.6 ^{AA}	32.0 ± 11.7 ^{a,c}	24.4 ± 1.4 ^{A}	30.6 ± 9.9 ^{a,c}
c) BAM, CPS 15.0 % (360 days)	35.2 ± 3.5 ^{AA}	21.4 ± 2.5 ^{a,b}	20.7 ± 0.4 ^{A}	23.1 ± 2.8 ^{a,b}
pH values (157-270 days) (Kruskal-Wallis: A differ from AA)				
a) No additive	7.7 ± 0.3 ^{AA,b}	7.7 ± 0.4 ^{AA,b}	6.9 ± 0.7 ^{A,b}	7.0 ± 0.5 ^{A,b}
b) Peat 5.0 %	6.7 ± 0.3 ^{AA,a,c}	5.4 ± 0.4 ^{AA,a,c}	6.3 ± 0.6 ^{A,a,c}	5.6 ± 0.4 ^{A,a,c}
c) CPS 15.0 %	7.5 ± 0.1 ^{AA,b}	7.3 ± 0.3 ^{AA,b}	5.2 ± 0.3 ^{A,b}	7.1 ± 0.4 ^{A,b}
*ND, no degradation				

Table 4. Solubility in water, Henry's constant, organic carbon partition coefficient (K_{oc}), and sorption distribution coefficient (K_d) of the herbidices and 2,6-dichlorobenzamied (BAM) (Tomlin, 2000, unless otherwise mentioned).

Compound	Solubility	Henry's constant	K_{oc}	K_d
	mg L^{-1}	Pa m^3 mol^{-1}	mL g^{-1}	L kg^{-1}
Atrazine	33	1.5×10^{-4}	39 - 173	0.2 - 18
Simazine	6.2	5.6×10^{-5}	103 - 277	0.37 - 4.66
Hexazinone	33 000	2.3×10^{-7} [a]	10 - 54 [b]	0.28 - 2.68 [c]
Dichlobenil	14.6	1.10	500 - 896 [d]	2.6 - 126.01
BAM	2 700 [e]	1.22×10^{-9} [d]	33 - 35 [d]	0.10 - 0.93

[a] Sander, 2015

[b] Sarmah et al., 2004; Poulier et al., 2015

[c] Sarmah et al., 2009

[d] Holtze et al., 2008

[e] Geyer et al., 1981

Figure legends

Fig. 1. Atrazine dissipation in the sediment slurries and in the slurries amended with compost-peat-sand (CPS), peat, cyclodextrin, *Pseudomonas* sp. ADP, NH_4NO_3, and NH_4NO_3 with Na-citrate (n = 3 or 4). The experiments were incubated under aerobic and anaerobic conditions, and the sterilized (ster.) counterparts were included. The average standard deviation was 0.9 mg L^{-1}. The legends are the same for figures A-B, C-D, and E-F.

Fig. 2. Atrazine, simazine, hexazinone, dichlobenil, and 2,6-dichlorobenzamide (BAM) dissipation in the sediment slurries and in the slurries amended with peat and compost-peat-sand (CPS). The experiments were incubated under aerobic and anaerobic conditions, and the sterilized (ster.) counterparts were included (n = 3). The average standard deviation was 0.7, 0.8, 0.9, 1.0, and 1.6 mg L^{-1} for atrazine, simazine, hexazinone, dichlobenil, and BAM, respectively.

Figure 1.

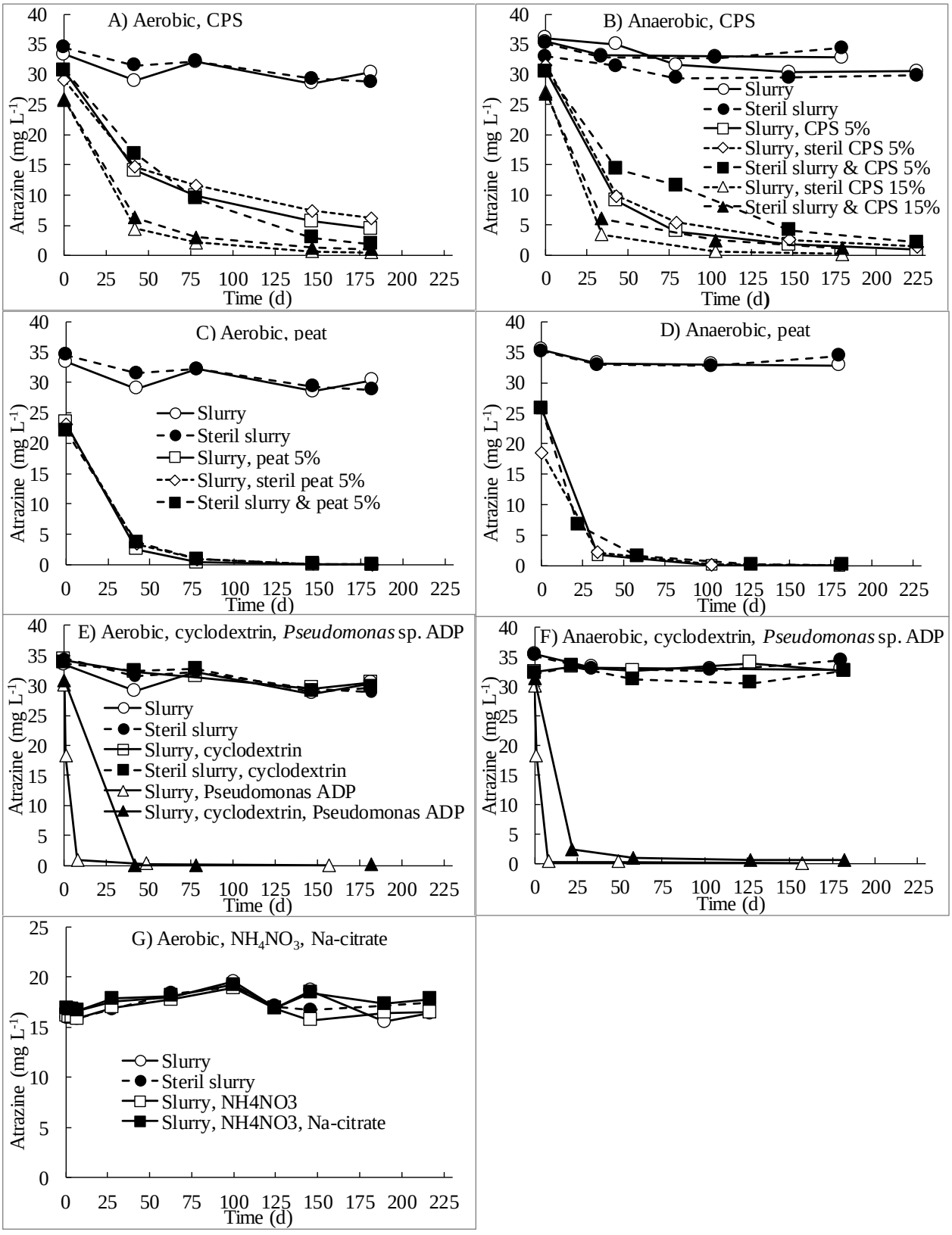
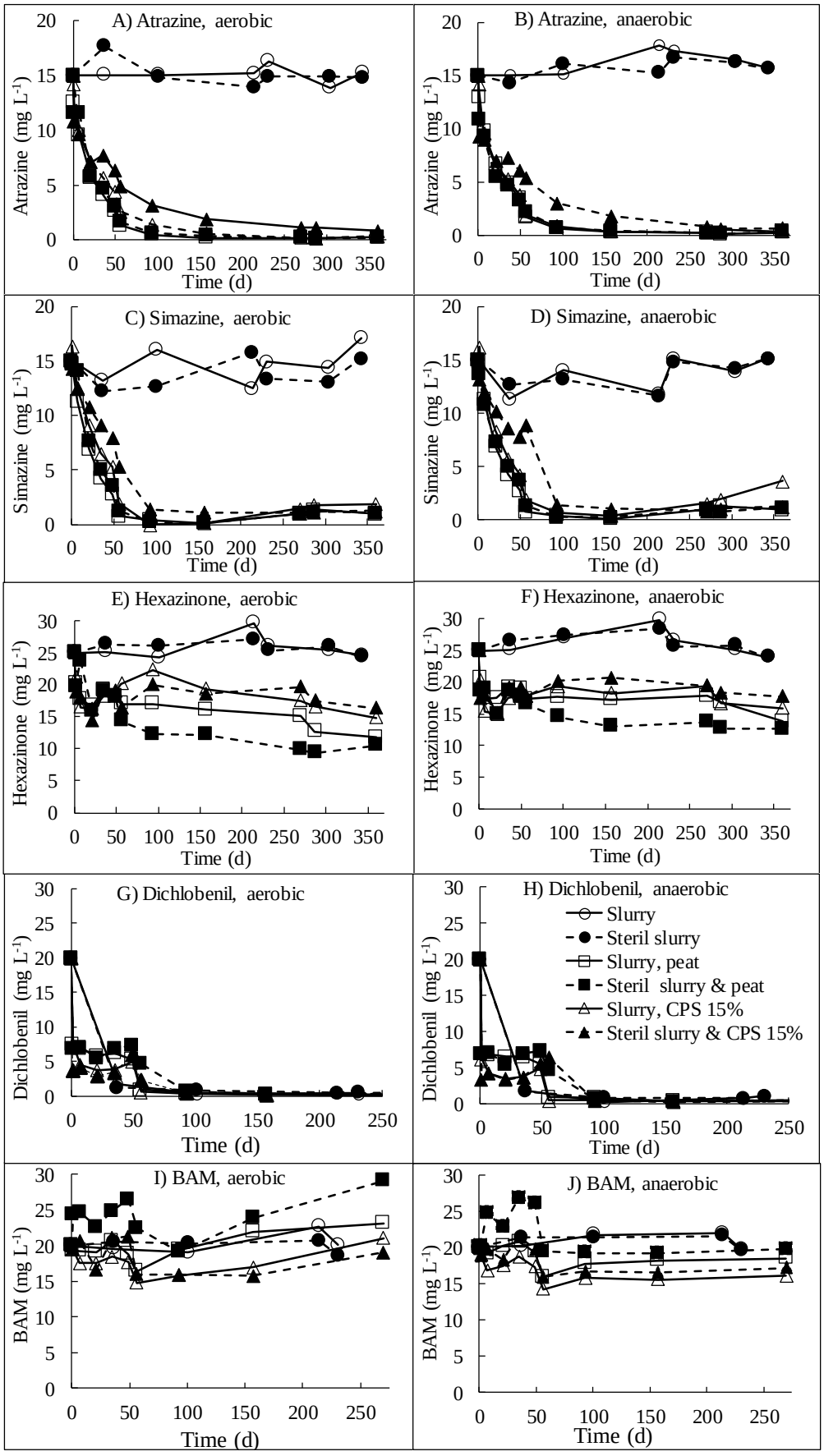

A) Aerobic, CPS
B) Anaerobic, CPS
C) Aerobic, peat
D) Anaerobic, peat
E) Aerobic, cyclodextrin, *Pseudomonas* sp. ADP
F) Anaerobic, cyclodextrin, *Pseudomonas* sp. ADP
G) Aerobic, NH_4NO_3, Na-citrate
Atrazine (mg L^{-1})
Time (d)
Slurry
Steril slurry
Slurry, CPS 5%
Slurry, steril CPS 5%
Steril slurry & CPS 5%
Slurry, steril CPS 15%
Steril slurry & CPS 15%
Slurry, peat 5%
Slurry, steril peat 5%
Steril slurry & peat 5%
Slurry, cyclodextrin
Steril slurry, cyclodextrin
Slurry, Pseudomonas ADP
Slurry, cyclodextrin, Pseudomonas ADP
Slurry, NH4NO3
Slurry, NH4NO3, Na-citrate

Figure 2.


A) Atrazine, aerobic
B) Atrazine, anaerobic
C) Simazine, aerobic
D) Simazine, anaerobic
E) Hexazinone, aerobic
F) Hexazinone, anaerobic
G) Dichlobenil, aerobic
H) Dichlobenil, anaerobic
I) BAM, aerobic
J) BAM, anaerobic
Atrazine (mg L-1)
Simazine (mg L-1)
Hexazinone (mg L-1)
Dichlobenil (mg L-1)
BAM (mg L-1)
Time (d)
Slurry
Steril slurry
Slurry, peat
Steril slurry & peat
Slurry, CPS 15%
Steril slurry & CPS 15%