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In-situ treatment of herbicide-contaminated groundwater - Feasibility study for the cases atrazine and bromacil using two novel nanoremediation-type materials

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In-situ treatment of herbicide-contaminated groundwater - Feasibility study for the cases atrazine and bromacil using two novel nanoremediation-type materials

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Graphical Abstract

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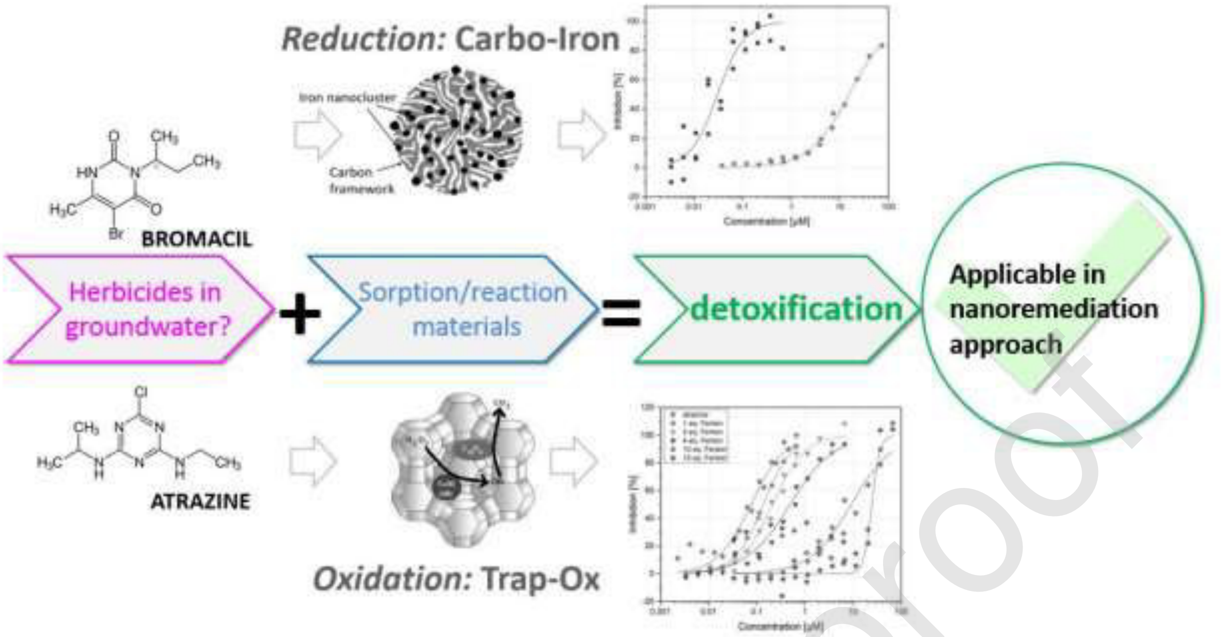

Highlights

- Carbo-Iron and Trap-Ox zeolites are recommended for nanoremediation of herbicides
- Carbo-Iron allows efficient reduction of bromacil, forming 3-sec-butyl-6-methyluracil
- Full transformation product analysis was achieved by time-resolved non-target screening
- Oxidation pathways of atrazine and bromacil with hydroxyl radicals were identified
- Both reduction and oxidation of atrazine and bromacil clearly reduce their phytotoxicity

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Abstract

Two injectable reactive and sorption-active particle types were evaluated for their applicability in permeable reaction zones for *in-situ* removal of herbicides ("nanoremediation"). As model substances, atrazine and bromacil were used, two herbicides frequently occurring in groundwater. In order to provide recommendations for best use, particle performance was assessed regarding herbicide degradation and detoxification. For chemical reduction, Carbo-Iron® was studied, a composite material consisting of zerovalent iron and colloidal activated carbon. Carbo-Iron reduced bromacil with increased activity compared to nanoscale zerovalent iron (nZVI). The sole reaction product, 3-sec-butyl-6-methyluracil, showed 500-fold increase in half-maximal-effect concentration (EC_{50}) towards the chlorophyte *Scendesmus vacuolatus* compared to the parent compound. The detoxification based on dehalogenation confirmed the dependency of the specific mode-of-action on the carbon-halide bond. For atrazine, neither nZVI nor Carbo-Iron showed significant degradation under the conditions applied. As novel subsurface treatment option, Trap-Ox® zeolite FeBEA35 was studied for generation of *in-situ* permeable oxidation barriers. Both adsorbed atrazine and bromacil underwent fast unselective oxidation. The transformation products of the Fenton-like reaction were identified, and oxidation pathways derived. For atrazine, a 300-fold increase in EC_{50} for *S. vacuolatus* was found over the duration of the reaction, and a loss of phytotoxicity to non-detectable levels for bromacil.

KEYWORDS: ISCR- and ISCO-based groundwater treatment, Carbo-Iron, Trap-Ox zeolites, reaction pathways, high-throughput screening diagnostic algae test (hts-DAT)

1. Introduction

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In order to protect and restore groundwater resources, it is essential to develop efficient techniques for the removal of micropollutants. Representative of emerging micropollutants are atrazine and bromacil, two halogenated herbicides of the triazine and uracile groups, respectively, both with the same specific mode-of-action: blocking the photosystem II (PSII) of plants [1]. Due to their mobility and persistence in the environment, they pose a high risk of leaching into surface waters and contaminating groundwater bodies. Atrazine is, in addition to the confirmed harmful effects on various species, suspected to act as an endocrine disruptor and regarded as possibly carcinogenic to humans [2–5]. In the USA, it is currently in use for broadleaf weed control, especially in corn fields [1]. Since atrazine is stable against hydrolysis in near-neutral solutions, half-lives in anaerobic aquatic environments are reported to range from 330 to 608 days [6]. Atrazine and its derivatives are, due to their persistence, high mobility and extensive use, among the most prevalent herbicides detected in surface- and groundwater in agricultural areas. In the EU, the use of atrazine is banned since 2004 due to the regulation to keep water contamination below a level of 0.1 µg L^{-1} in areas of use [7,8]. Although the detected levels of atrazine and derivatives in groundwater are decreasing, their abundance for example in Germany is still the highest among all pesticides [9]. Bromacil is used against a broad spectrum of weeds, e.g. in citrus and pineapple fields, and in the USA also in public terrains [10]. Since it was not included in 2002 into the EU list of approved pesticides, as for atrazine, its use is not permitted in any EU member state. In Germany, bromacil was already forbidden in 1993 due to its enormous subsurface persistence in combination with a high mobility, which is based on its stability against hydrolysis and photolysis [11]. Until its ban, bromacil was primarily used on railway tracks [12] and can still be found in Germany's groundwater, albeit with decreasing tendency [9,13]. Its toxicity to humans is even less well researched than that of atrazine and according to U.S. EPA, it is classified as a possible human carcinogen [14].

Current approaches for the destruction of atrazine and bromacil are mostly based on advanced oxidation processes, such as Fenton-like reactions, photocatalysis, ozonation or persulfate-based oxidation [15–21].

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Nevertheless, clean-up is mainly done by pump-and-treat of the contaminated groundwater. As a possible *in-situ* treatment option for atrazine, the reductive dehalogenation using metallic iron has been reported, with 2-ethylamino-3-isopropylamino-1,3,5-triazine (EIT) as sole reaction product [22,23]. However, the most commonly applied treatment method to remove both atrazine and bromacil from groundwater is adsorption to activated carbon (AC) [24]. Though the reported applications were designed for on-site treatment, adsorption to activated carbon is in principle also feasible for *in-situ* implementation.

Adsorption to AC-based *in-situ* permeable adsorption barriers can strongly extend the contaminant retention for years or even decades, and can therefore be sufficient as a remediation measure [25]. However, in cases where a fast breakthrough of contaminants passing a sorption barrier is expected, and where biodegradation and hydrolysis do not play a role, coupling of adsorption with contaminant destruction is desirable. Several types of injectable sorption-active particles with a targeted reactive function for contaminant transformation have been developed in recent years [26–30]. The idea behind these developments is the collection of contaminants in the treatment zone and simultaneously the regeneration of the adsorber particles by a built-in reaction function. The target contaminants are enriched at the reaction site; this not only increases the reaction rate, but also leads to less unwanted side-reactions with non-enriched competing groundwater constituents (e.g. nitrate) and thus less reagent consumption.

One example of a sorption/reaction composite for *in-situ* chemical reduction (ISCR) of halogenated organic contaminants are Carbo-Iron colloids (CIC), which consist of iron clusters embedded in about 1 µm-sized AC grains. The porous AC carrier not only leads to enrichment of the contaminants, it also provides improved particle subsurface transport compared to bare nZVI due to suppression of the agglomeration tendency, since AC acts as a spacer between the metallic iron clusters and thus shields against the magnetic attraction forces. CIC has already showed remarkable remediation performance in field applications with chlorinated solvents as target contamination. However, while Carbo-Iron is suitable for

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the treatment of reducible contaminants [31,32], heavy metals and highly hydrophobic substances, the material should not be applied in oxygen-rich aquifers and for oxidative treatment.

For *in-situ* chemical oxidation (ISCO) reactions, zeolites are suitable non-oxidizable adsorbents [33]. The choice of the zeolite type can be addressed to the needs of the target contaminants, as the group of zeolites offers a broad variety of framework types which differ in sorption properties due to well-defined, tiered pore sizes and Si : Al ratios. Together with the large inner surface, this leads to excellent sorption properties for small organic molecules. With Trap-Ox zeolites, injectable iron-exchanged heterogeneous Fenton-like catalysts were introduced which can form a stationary permeable oxidation barrier with contaminant retention [34]. After loading of the adsorbent, the barrier is flushed with diluted hydrogen peroxide in order to generate OH radicals which oxidize the adsorbed contaminants and at the same time regenerate the adsorbent [35]. In contrast to homogeneous Fenton systems, Trap-Ox zeolites can operate at neutral pH conditions and avoid the generation of iron oxide/hydroxide sludge.

For the *in-situ* application of any new remediation technique, the environmental compatibility of the process has to be carefully considered. Both CIC and Trap-Ox zeolites have previously been tested for their ecotoxicity and showed no adverse effects on the examined bacteria, algae, crustacean, earthworm, oligochaete and plant species up to concentrations as high as 100 mg L^{-1} [36]. Especially for oxidation processes, also transformation products (TPs) of the contaminants need to be examined carefully, since partially oxidized halogenated substances could have an even higher toxicity than their parent compounds [37]. In the present study, the TPs of the treatment processes were analysed and reaction pathways derived. In order to ensure the environmental benefit of the potential *in-situ* nanoremediation approaches for treatment of the herbicides atrazine and bromacil, the reaction products were subjected to toxicity assays with the chlorophyte *Scendesmus vacuolatus*. Next to growth inhibition as an integrated apical endpoint, effects on photosynthesis of the green algae were analysed as a specific observation parameter for the PSII – inhibiting parent substances.

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The goal of this work was to evaluate which of two nanoremediation-type materials for the generation of sorption-reaction barriers is best suited for treatment of groundwater contaminated with the herbicides atrazine or bromacil. In order to provide advice for users and authorities, the analysis of transformation products, deduction of reaction pathways and a phytotoxicity assessment using a high-throughput screening diagnostic algae test (hts-DAT) were carried out.

2. Materials and Methods

2.1 Chemicals

Atrazine (98.5 %) and its degradation products desethyl atrazine (DEA, 96 %), desisopropyl atrazine (DIA, 99 %) and hydroxyatrazine (HA, neat) were purchased from Dr. Ehrenstorfer GmbH and bromacil (neat) from Supelco. 3-*sec*-butyl-6-methyluracil (BMU) and 2-ethylamino-3-isopropylamino-1,3,5-triazine (EIT) were synthesized as sole products from bromacil and atrazine, respectively, by catalytic hydrodehalogenation with Pd/H_2. 10 mg of 5 wt% Pd on magnetite, prepared according to Hildebrand *et al.* [38], was added to the aqueous herbicide stock solutions and treated with hydrogen gas until no more educt was detectable via HPLC-MS. Methanol (GC grade), iron(II) sulphate heptahydrate (*p.a.*), hydrogen peroxide (30 %) and sodium bicarbonate (*p.a.*) were purchased from Merck. Acetonitrile (HPLC grade) was provided by Riedel-de Haën. Hydrochloric acid (35-38 %) was purchased from Chemsolute. All ingredients of the algal culture medium according to Grimme *et al.* [39] were *p.a.* grade and purchased from Merck, except for $Na_2EDTA \cdot 2H_2O$, which was ordered from Riedel-de Haën. Diuron was purchased from Sigma-Aldrich with analytical grade.

2.2 Nanoremediation-type particles

nZVI was purchased from Toda Kogyo Corp. Europe and stored under inert atmosphere. CIC were produced carbothermally according to Bleyl *et al.* [40]. Iron-exchanged Trap-Ox zeolite FeBEA35 was purchased from Clariant Produkte GmbH, Germany.

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Table 1: Characterisation of the nanoremediation-type particles under study.

Particle type	**Particle size [nm]**	**BET [$m^2\ g^{-1}$]**	**Composition**	**Mode of action**	**Intended use**
nZVI	d_{50} = 70*	30*	64 wt% Fe^0 36 wt% iron oxides	reduction (Fe^0)	ISCR
CIC [31]	d_{10} = 600 d_{50} = 1300 d_{90} = 3600	590	30.3 wt% total Fe 20.5 wt% Fe^0 55.5 wt% carbon	adsorption and reduction (Fe^0)	ISCR
Trap-Ox [33]	d_{10} = 400 d_{50} = 1000 d_{90} = 2100	600	1.3 wt% Fe Si : Al = 35*	adsorption and oxidation (Fenton-like)	ISCO

* manufacturer specifications

2.3 Adsorption experiments

Sorption experiments were conducted with the sorption/reaction materials and evaluated according to Freundlich and Langmuir (Supporting Information section SI-1). In order to avoid superposition of adsorption and reaction for CIC, the iron metal was deactivated by corrosion (aged CIC). For both adsorbers (Trap-Ox zeolite and CIC), various amounts from 0.2 to 2 g L^{-1} were suspended in water and a herbicide concentration of 30 mg L^{-1} adjusted with methanolic stock solutions of atrazine or bromacil. The samples were shaken at least 72 h for equilibration, filtered through 0.2 µm syringe filters and the remaining free substance concentrations measured via HPLC-MS (Shimadzu LC-MS 2020 system equipped with a Phenomenex Gemini 3 µm C_6-phenyl column).

2.4 Degradation experiments

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Reductive dehalogenation with nZVI and CIC

Reductive dehalogenation of the herbicides with nZVI and CIC was performed with Fe^0 concentrations of 1 g L^{-1} (corresponding to 4 g L^{-1} CIC and 1.5 g L^{-1} nZVI) and with the tenfold concentration of both reagents. The reactions were carried out in 0.1 M $NaHCO_3$ solution in order to slightly buffer the suspensions at a pH value of about 8.5. Concentrations of 30 mg L^{-1} atrazine, and 50 mg L^{-1} bromacil were adjusted by addition of methanolic stock solutions of the substances to the reaction vessel. Ion chromatography of the halide ions formed was used to monitor the reaction progress (Dionex IC system equipped with an IonPac AS11-HC column) while organic reaction products were identified with HPLC-MS. In order to show the general ability of nZVI and CIC to act as a reductant, dechlorination of PCE was likewise performed (SI2).

Herbicide oxidation with Trap-Ox

Oxidative treatment was carried out using aqueous stock solutions of the herbicides mixed with 1 g L^{-1} Trap-Ox zeolite. Before use, the aqueous stock solutions were equilibrated and continuously shaken to avoid the formation of microcrystals. The suspensions were agitated overnight and the reaction started by adding H_2O_2 ($c_{0,H2O2}$ = 3 wt%, in order to simulate the injected H_2O_2 flowing through the permeable barrier). Samples of the suspension were taken frequently for analysis. In order to stop the oxidation in these samples, methanol was added as radical quencher. Extraction of the reactants from the zeolite was performed by adding acetonitrile (water : methanol : acetonitrile = 1 : 0.5 : 0.5) and shaking for 72 h followed by HPLC-MS analysis of the extracts. In addition, freely dissolved reaction products in the original suspensions were identified via UPLC-TOF-MS without previous extraction.

2.5 Identification of oxidation pathways

The product solutions generated by homogeneous, stoichiometric Fenton reaction were used for the examination of the degradation pathways, because the oxidation using Trap-Ox is superimposed by

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adsorption processes to the material. Therefore, step-by-step progress of the homogeneous Fenton reaction was employed in order to simulate the progress of the oxidation reaction using Trap-Ox catalysts. For this, several stages of reaction progress (molar equivalents of Fenton's reagent referred to the herbicide [µmol/µmol]) were studied by adding multiples of 1.1 µmol iron(II) sulphate and 1.8 µmol hydrogen peroxide simultaneously to individual 15 mL batches of aqueous solutions of atrazine (17 mg L^{-1}; 1.2 µmol) or bromacil (25.5 mg L^{-1}; 1.5 µmol) until the educt conversion was >98 % in each batch. Oxidation in one complete step elapses too fast for time-resolved analysis under the examined conditions. Full analysis of TPs was performed via UPLC-TOF-MS using an ACQUITY UPLC system connected to a XEVO G2-XS TOF (Waters electrospray ionization source used in the MSE-mode). UPLC separation was achieved using an ACQUITY UPLC HSS T3 column (100 x 2.1, 1.7 µm). Data were evaluated by non-target-screening by MarkerLynx using multivariate statistics. The proposed structures are based on exact mass (elemental composition determined < 5 ppm). The corresponding fragments are given in tables SI-2 and 3.

2.6 Phytotoxicity assessment applying a high-throughput screening diagnostic algae test

Synchronized populations of the chlorophyte *Scenedesmus vacuolatus* (Shihira *et* Krauss strain 211-15, culture collection Pringsheim, SAG Göttingen, Germany) were cultured photoautotrophically in a sterile inorganic medium (Grimme-Boardman-culture medium [39], pH 6.4) at 28°C by using a 14 : 10 h light-to-dark cycle at about 400 µmol photons m^{-2} s^{-1} and subcultivated every 24 h in order to guarantee a full synchronized cell cycle of 24 h [41]. High-throughput screening algae tests were performed using atrazine, bromacil and their reduction and hydrolysis products EIT, HA, DEA, DIA and BMU. For the phytotoxicity assessment of the oxidation products, the mixtures of the step-by-step homogeneous Fenton reaction described in section 2.5 were used.

300 µL of each sample solution with a pre-adjusted carbonate concentration of 1.5 mM was given into the first column of a 96-well plate. A 10-step dilution series with 1.5 mM carbonate solution and a dilution

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factor of 1.8 were used, resulting in a sample amount of 135 µL per well. At the beginning of the cell cycle (t_0), 15 µL of a $7.5 \cdot 10^5$ cells mL^{-1} algal cell suspension, prepared in tenfold concentrated GB-culture medium with a carbonate concentration of 1.5 mM, were dosed to the sample solutions, resulting in an algal concentration of $7.5 \cdot 10^4$ cells mL^{-1} in the test. Additionally to two controls per sample, diuron was used as a positive control in order to guarantee the validity of the test. The test cultures were incubated at 28°C in an INFORS incubator with an illumination of 300 – 400 µE m^{-2} s^{-1} and under 300 rpm shaking. Autofluorescence was measured with a SpectraMax Gemini microplate reader and photosynthesis performance was quantified by measuring the maximum quantum yield (QY) of the photosystem II of the algae with the saturation pulse method [42] using a MAXI-Imaging PAM-fluorometer (Walz) after 2 h and at the end of the cell cycle after 24 h of incubation. Additionally, cell numbers were quantified after 24 h of incubation by a BD FACSCelesta flow cytometer, equipped with a 96-well autosampler option. Autofluorescence data and photosynthesis performance data after 2 h are given in table SI-4. Concentration-response relationships and half-maximal-effect concentrations were calculated from photosynthesis performance after 24 h ($EC_{50,\text{photo}}$) and cell numbers ($EC_{50,\text{CN}}$) after log-logistic modelling using Origin 2018. Model parameters are also given in table SI-4.

3. Results and discussion

3.1. Herbicide adsorption to CIC and Trap-Ox zeolites

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Adsorption tests were performed in order to verify the efficiency of herbicide retardation by the sorption/reaction materials in future permeable-barrier arrangements. In batch experiments, single-component adsorption isotherms of atrazine and bromacil on both aged CIC and Trap-Ox were determined and fitted by the Freundlich equation (Figure SI-1). Freundlich parameters for aged CIC were $\log(K_{\text{F,atrazine,CIC}}/[(\text{mg kg}^{-1})(\text{L mg}^{-1})^{1/n}]) = 5.1$ and $n^{-1} = 0.35$ for atrazine and $\log(K_{\text{F,bromacil,CIC}}/[(\text{mg kg}^{-1})(\text{L mg}^{-1})^{1/n}]) = 5.1$ and $n^{-1} = 0.15$ for bromacil. In the case of Trap-Ox zeolites, Freundlich parameters of $\log(K_{\mathrm{F,atrazine,TrapOx}}/(\mathrm{mg\ kg^{-1}})(\mathrm{L\ mg^{-1}})^{1/n}]) = 4.5$ and $n^{-1} = 0.27$ for atrazine and $\log(K_{\mathrm{F,bromacil,TrapOx}}/[(\mathrm{mg\ kg^{-1}})(\mathrm{L\ mg^{-1}})^{1/n}]) = 3.8$ and $n^{-1} = 0.60$ for bromacil were determined. These data show that both aged CIC and the Trap-Ox zeolite FeBEA35 show sufficiently high adsorption affinity for atrazine and bromacil, and are therefore suitable to achieve strong contaminant enrichment at the reactive particles and significant retardation in an *in-situ* permeable sorption barrier [25].

3.2 Reductive dehalogenation using CIC and nZVI

Dehalogenation experiments with CIC and nZVI revealed a poor reducibility of atrazine by Fe^0. No significant increase in the chloride concentration due to atrazine dechlorination was measured in the test systems with an atrazine concentration of 30 mg L^{-1}, neither with 1 g L^{-1} Fe^0 nor 10 g L^{-1} Fe^0, after 48 d reaction time at the applied conditions. Only traces of the expected reduction product EIT ($m/z_{E+} = 182$) were found. This observation is in accordance with the work of Dombek *et al.*, who did not observe atrazine dechlorination at near-neutral pH values after 2 h with 50 g L^{-1} Fe^0, but in contrast to the work of Satapanajaru *et al.*, who described marked atrazine degradation with 20 g L^{-1} Fe^0 within 1 h even in neutral milieu [22,23]. The latter work applied iron nano-particles produced by reduction with borohydride. One could speculate that, according to Liu *et al.*, the nZVI applied was catalytically active [43]. However, trace amounts of atrazine's hydrolysis product HA ($m/z_{E+} = 198$) were found in the samples, which we explain by the locally enhanced pH value in the close vicinity of the iron particles.

nZVI at both concentrations was also not able to reduce bromacil efficiently ($c_{0,\mathrm{bromacil}} = 50$ mg L^{-1}). The reduction product BMU was identified by HPLC-ESI-MS ($m/z_{E+} = 183$), but with a low yield of about 0.1 % after 48 d. In contrast, the application of CIC led to a more pronounced debromination of bromacil to BMU. The kinetics of bromide release did not vary significantly for Fe^0 concentrations of 1 g L^{-1} and 10 g L^{-1} (Figure 1). The reference dechlorination of PCE is shown in figure SI-2.

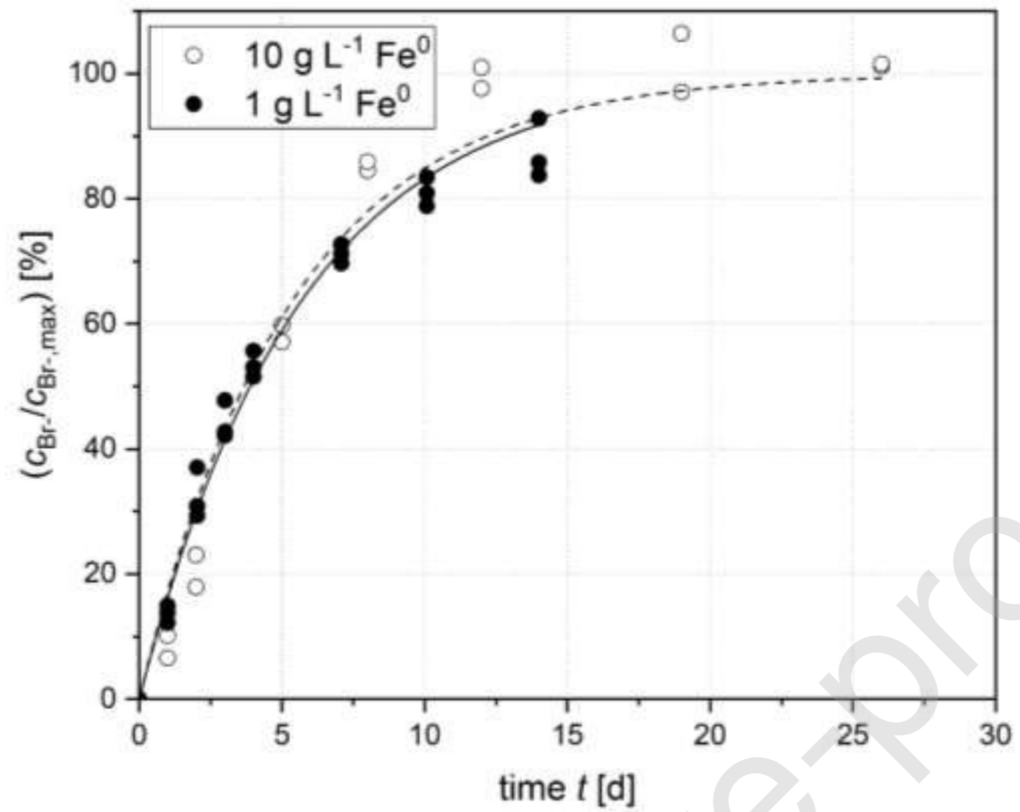

Figure 1: Bromide release during debromination of bromacil with 1 g L^{-1} and 10 g L^{-1} CIC ($c_{bromacil}$ = 50 mg L^{-1}, c_{NaHCO3} = 0.1 M) fitted to limited growth function ($y = S-(S-B_0)e^{(-k_{obs}\,t)}$) with initial condition B_0 = 0 % and limit S = 100 %.

The observable reaction rate constants were $k_{obs,10\ g\ L^{-1}}$ = (2.2 ± 0.2) 10^{-6} s^{-1} (R^2 = 0.96) and $k_{obs,1\ g\ L^{-1}}$ = (2.07 ± 0.07) 10^{-6} s^{-1} (R^2 = 0.98). This effect of similar values for k_{obs} in a broad range of iron concentrations in the system shows the full compartment transfer of the reaction scenario from the water phase to the composite phase. A “dilution” of the contaminant occurs in the adsorbed phase when adding more composite, but the Fe^0 concentration within the composite phase remains constant. Thus, the observed reaction rates for adsorbed herbicides are comparable. The same finding has already been reported for TCE, where k_{obs} for dechlorination was reported to be nearly constant for a wide Fe^0 concentration range [27]. In the case of TCE as contaminant treatment, promising results have already been reported for field application [27,31]. Since for bromacil, sorptive affinity towards CIC is given and the reaction rates are in the same range as for TCE, one can conclude that CIC can be considered as a suitable means for the *in-situ* remediation of bromacil-contaminated sites. However, in the case of atrazine, only adsorptive contaminant retention can be achieved with this material. Reduction barriers of nZVI are not suitable for either of the herbicides under study due to very low retention and extremely low reaction rates. The insignificant reduction rate of atrazine with the two kinds of ZVI is in conformity with the known limitation of (undoped) ZVI not to be able to reduce aromatic chlorinated compounds, as the chlorine substituent in atrazine is bound to an aromatic ring [44].

3.3 Oxidative herbicide degradation using Trap-Ox zeolites

Advanced oxidation processes such as the OH radical-based Fenton reaction are a common means for treatment of water containing non-easily removable organic compounds. The oxidation of both herbicides under study with the Fenton-like catalyst Trap-Ox showed promising results which are illustrated in Figure 2. The depletion in atrazine and bromacil concentrations shows that both substances are prone to fast oxidation with reaction rate constants of $k_{\mathrm{obs,atrazine}} = (0.97 \pm 0.09)\ \mathrm{h}^{-1}$ and $k_{\mathrm{obs,bromacil}} = (2.2 \pm 0.1)\ \mathrm{h}^{-1}$ for the different herbicide starting concentrations using 1 g L^{-1} zeolite and a H_2O_2 dose adjusted to $c_{0,\mathrm{H2O2}}$ = 3 wt%. For analysis of the reaction progress, the oxidation was stopped by addition of methanol for OH radical quenching. The herbicide concentrations were then measured after full extraction of the adsorber particles.

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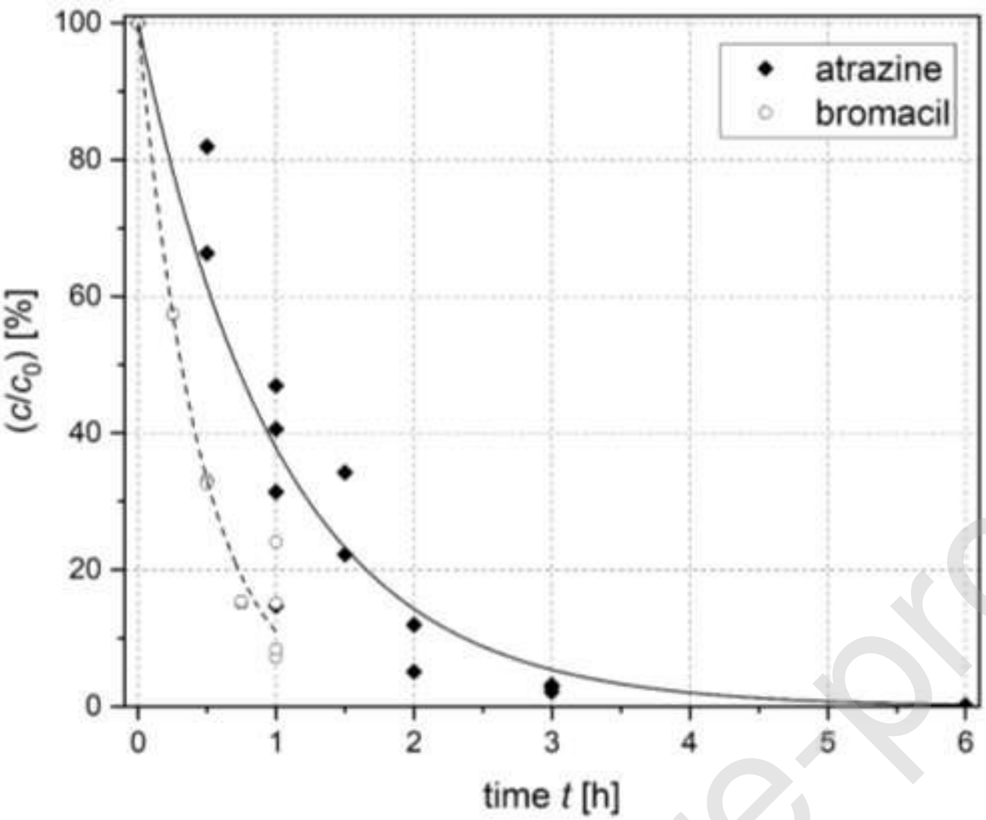

Figure 2: Decrease in atrazine and bromacil concentrations over time during reaction in the Trap-Ox system ($c_{zeolite}$ = 1 g L^{-1}, $c_{0,H2O2}$ = 3 wt%, $c_{0,atrazine}$ = 17 mg L^{-1}, $c_{0,bromacil}$ = 25.5 mg L^{-1}) fitted to exponential decay function ($y = B_0 + S\ e^{(-k_{obs}\ t)}$) with B_0 = 0 % and S = 100 % ($k_{obs,atrazine}$ = (2.7 ± 0.2) 10^{-4} s^{-1}, R^2 = 0.93; $k_{obs,bromacil}$ = (6.2 ± 0.3) 10^{-4} s^{-1}, R^2 = 0.99).

A slightly faster reaction of bromacil ($t_{0.5}$ = 0.3 h) compared to that of atrazine ($t_{0.5}$ = 0.7 h) can be seen. After more than six hours of reaction time, no bromacil or atrazine could be found in the extraction solution with a detection limit of 20 µg L^{-1} without any previous enrichment. This means that under the given conditions a contact time of several hours between zeolite, hydrogen peroxide and the adsorbed herbicides are sufficient to achieve depletion degrees of >99 %.

The transformation products and pathways of the oxidative transformation of atrazine and bromacil by OH radicals were studied in a homogeneous Fenton reaction (figure SI-3). Thereby, the assumption was made that the reaction pathways are similar for homogeneous and heterogeneous Fenton systems. Direct analysis of the Trap-Ox system was not possible, as full recovery of unknown TPs from the adsorbed state

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cannot be guaranteed. In order to deduce reaction pathways, the samples were analysed for TPs and their appearance and disappearance during the oxidation progress. Figure 3 andFigure 4 show the proposed degradation pathways of atrazine and bromacil in the Fenton reaction based on the concentration course of the transformation products. Molecular formulas of the TPs are given as detected by mass spectrometry as proton or sodium adduct. If there are isomers, only one possible structure is proposed.

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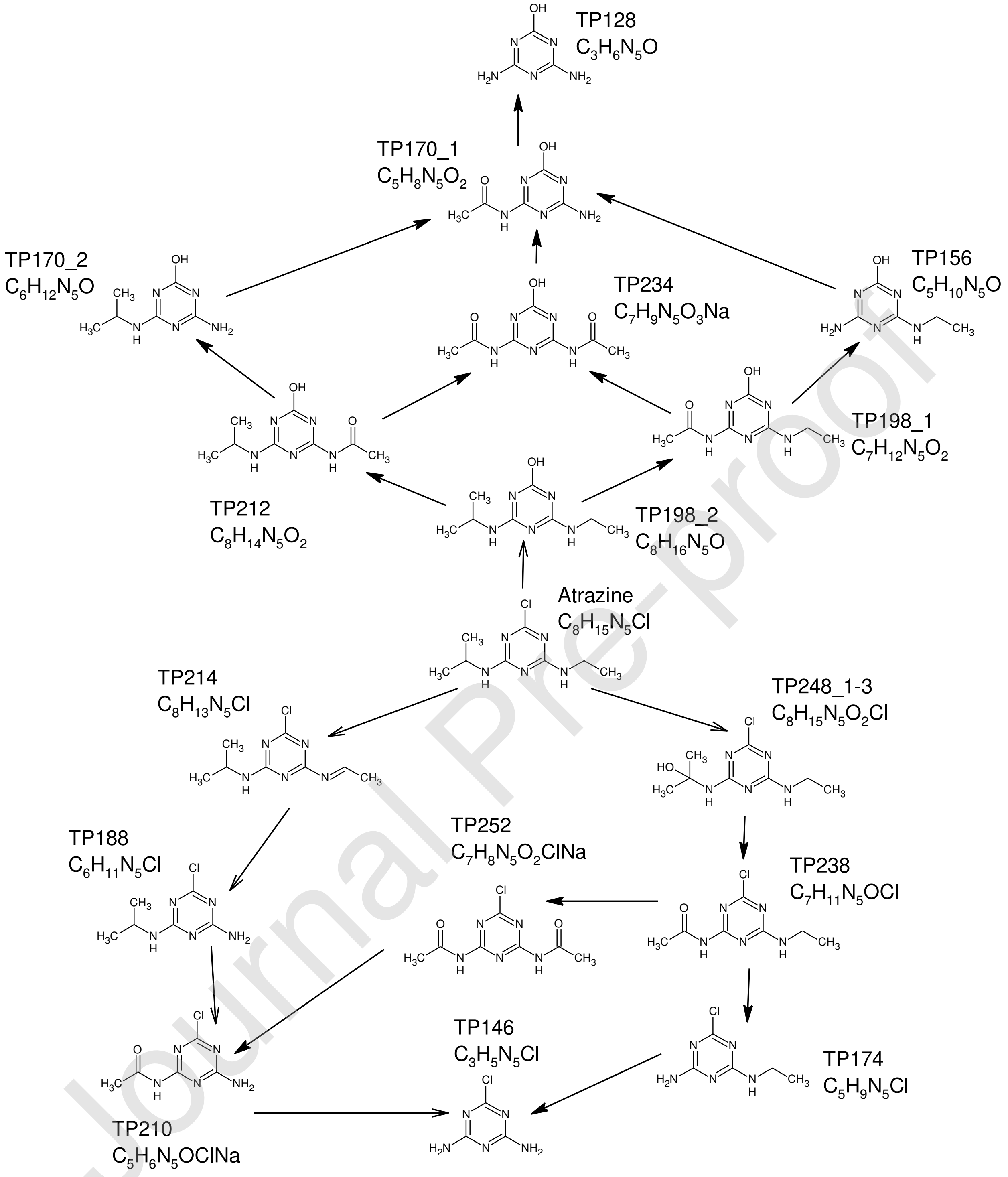

Figure 3: Proposed oxidation pathways of atrazine in the Fenton reaction. Molecular formula are given as detected by ESI-MS in the positive ion mode ($[M+H]^+$/$[M+Na]^+$ ions).

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For atrazine, mainly oxidation of the side chains is suspected, with subsequent cleavage of the amides formed. Side chains were attacked first, leading to hydrogen abstraction followed by the formation of an imine or by hydroxylation and further deprotonation. Conversion of atrazine to HA also took place, followed by the reaction channels described above. The detected TPs are in good agreement with previously reported products of OH radical-based degradation of atrazine [45].

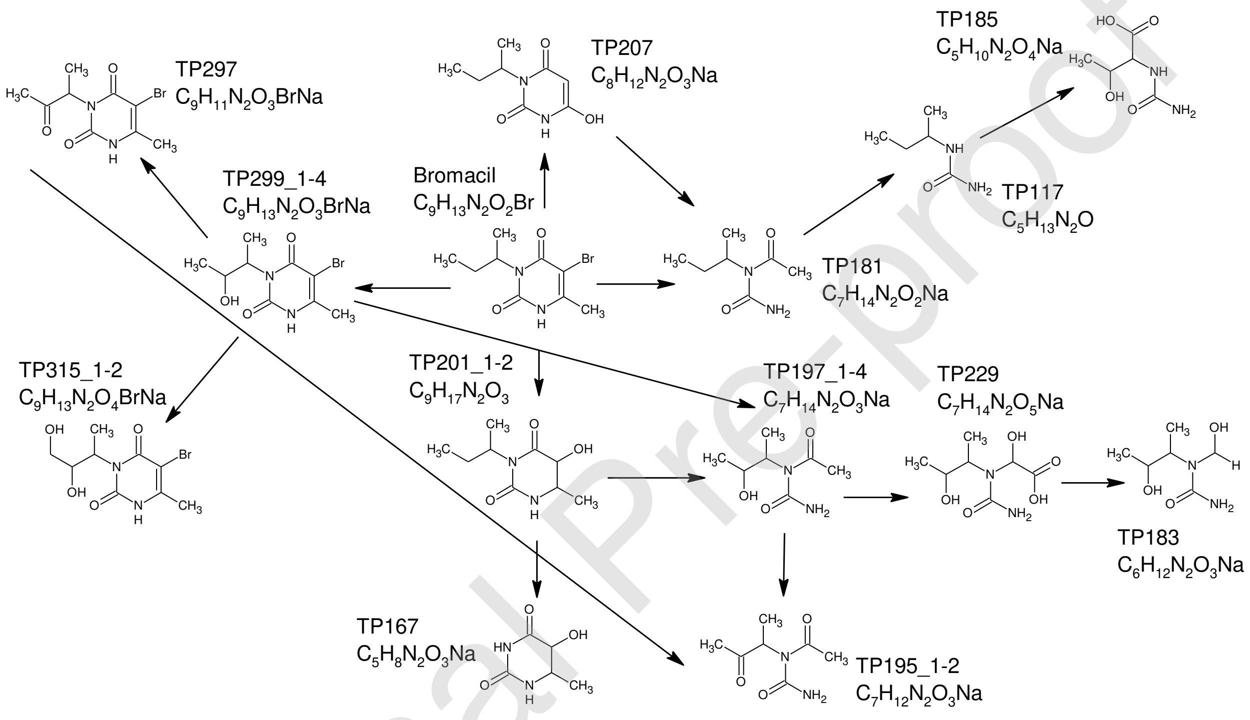

Figure 4: Proposed oxidation pathways of bromacil in the Fenton reaction. Molecular formula are given as detected by ESI-MS in the positive ion mode ($[M+H]^+$/$[M+Na]^+$ ions).

Bromacil was observed to react mainly via two different pathways. On the one hand, single and multiple oxidation of the side chain were observed. On the other hand, ring cleavage, caused by the addition of the OH radical to the double bond, took place.

The water bulk phase in the Trap-Ox suspension was also analysed for TPs. Only dechlorinated and at least partially dealkylated oxidation products of atrazine could be identified (e.g. TP128 and TP156 as seen in Figure 3). In the case of bromacil, mainly bromine-free ring-opening products were found outside the

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adsorber phase (TP185, TP183, TP229 and TP197 seen in Figure 4). That means that for both substances, the most hydrophilic TPs from the end of the transformation chains are released from the zeolite into the suspension bulk phase, and could therefore be detected. The same final products of both reaction variants speak for similar reaction pathways of heterogeneous and homogeneous Fenton systems.

3.3 Phytotoxicity assessment of parent compounds and reaction mixtures

In order to assess the suitability of the described herbicide transformations for any field application, the ecotoxicological impact of the remediation measure needs to be studied. Therefore, the shift of toxicity of the reaction medium was analysed. Since the herbicides' specific mode-of-action is well described by their effect towards green algae (inhibiting the D1-protein of the photosystem II, resulting in a decrease of reproduction and photosynthetic activity), this biological system was chosen for evaluation of the detoxification success.

The algae test was performed on the one hand with known and commercially available products of herbicide reduction and hydrolysis products, and on the other hand with mixtures from product solutions taken over the duration of the Fenton oxidation. Figure 5 shows the shift in concentration-response curves of atrazine and the oxidation product mixtures to higher effect concentrations with increasing reaction progress, achieved by the addition of growing amounts of Fenton's reagent.

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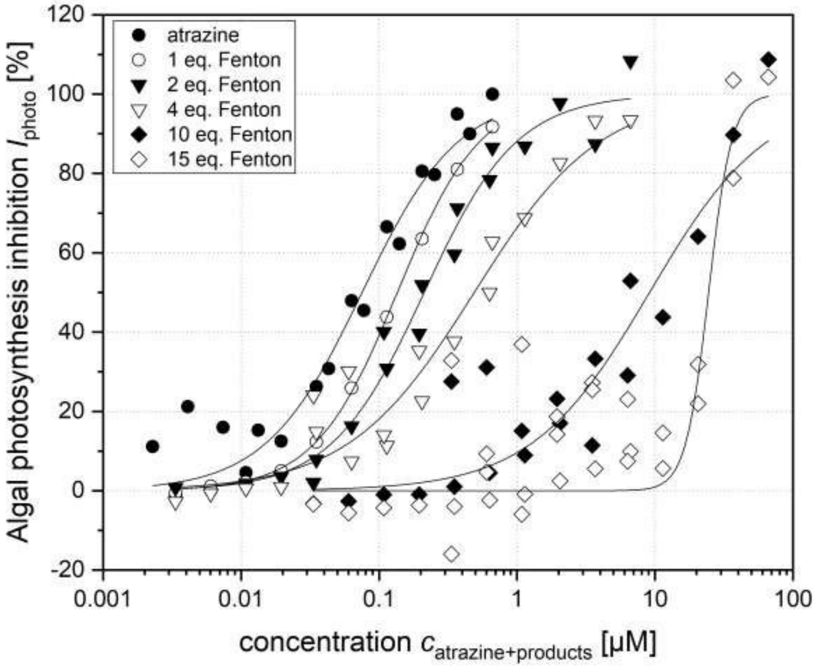

Figure 5: Concentration-response curves of inhibition of algal photosynthesis by atrazine and hydrolysis oxidation product mixtures after log-logistic modelling (model parameters given in table SI-4).

Bromacil and its oxidation product mixtures were examined similarly. Table 2 gives the EC_{50} values for atrazine and bromacil at each treatment step, derived from inhibition of photosynthesis activity ($EC_{50,photo}$), and reproduction (cell numbers, $EC_{50,CN}$). All values are given in µM, as the test was conducted with mixtures of TPs with undefined concentrations and different molar weights of the single products present.

Table 2: EC_{50} values, derived from inhibition of photosynthesis activity ($EC_{50,photo}$) and algal cell reproduction ($EC_{50,CN}$) after 24 h of exposure to atrazine, bromacil and their oxidation product mixtures formed by addition of increasing molar equivalents of Fenton's reagent.

	Atrazine		**Bromacil**	
Addition of Fenton's reagent [n_{H2O2} / $n_{herbicide}$]	**$EC_{50,photo}$ [µM]**	**$EC_{50,CN}$ [µM]**	**$EC_{50,photo}$ [µM]**	**$EC_{50,CN}$ [µM]**
0 eq.	0.08 ± 0.01	0.20 ± 0.02	0.03 ± 0.01	0.12 ± 0.01
1 eq.	0.14 ± 0.01	0.42 ± 0.07	0.05 ± 0.01	0.26 ± 0.03

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2 eq.	0.21 ± 0.01	0.57 ± 0.04	0.08 ± 0.02	0.60 ± 0.05
4 eq.	0.49 ± 0.06	1.4 ± 0.1	0.24 ± 0.05	2.0 ± 0.4
10 eq.	9 ± 2	12 ± 2	*46 ± 4*	*18 ± 3*
15 eq.	*24 ± 2*	*14 ± 2*	*No effect*	*35 ± 13*

The EC_{50} values for atrazine and bromacil derived for inhibition of cell reproduction were 0.20 ± 0.02 µM and 0.12 ± 0.01 µM, respectively. EC_{50} values determined from inhibition of photosynthetic activity (QY) of the green algae were significantly lower (0.08 ± 0.01 µM for atrazine and 0.03 ± 0.01 µM for bromacil) due to the specific mode-of-action of both contaminants. The values found in this study are within the range of previously documented effect concentrations for green algae [1,46].

For both atrazine and bromacil, a continuous detoxification during the progress of the reaction was found. The EC_{50} increased by two orders of magnitude after the addition of a ten- to fifteen-fold molar excess of Fenton's reagent to atrazine. Thereby, an $EC_{50,\text{photo}}$ higher than $EC_{50,\text{CN}}$ indicates the loss of the specific mode-of-action in atrazine's degradation products. Similar observations were made for bromacil; additionally, after spiking with the 15-fold molar excess of Fenton's reagent, $EC_{50,\text{photo}}$ could no longer be calculated due to an insignificant toxic effect. It is worth mentioning that for complete mineralization of atrazine a 71-fold, and for bromacil 54-fold, molar excess of Fenton's reagent would be necessary (equations SI-1 and SI-2). Thus, incomplete oxidation as achieved in the above experiments with 15-fold molar excess of Fenton's reagent already leads to significant detoxification.

Furthermore, the hydrolysis and reduction products of atrazine (DEA, DIA, HA and EIT), as well as the reduction product of bromacil (BMU), were examined in the assay for their individual effects. The EC_{50} values received from these assays are given in Table 3.

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Table 3: EC_{50} values, derived from inhibition of photosynthesis activity ($EC_{50,photo}$) and algal cell reproduction ($EC_{50,CN}$) after 24 h of exposure to atrazine and bromacil reduction/hydrolysis products.

Substance	**$EC_{50,photo}$ [µM]**	**$EC_{50,CN}$ [µM]**
HA (TP198.2)	No effect	No effect
DEA (TP188)	0.16 ± 0.01	0.36 ± 0.05
DIA (TP174)	5.1 ± 0.5	16 ± 3
EIT	No effect	No effect
BMU	15.4 ± 0.6	18 ± 4

The ecotoxicological assessment indicates a key role of the halide-carbon bond for the herbicide effect of both compounds, as the reductive debromination of bromacil alone, with scission of the C-Br bond as sole transformation step, achieved a detoxification with an order of magnitude similar to the last examined step of the oxidation after addition of 15 molar oxidation equivalents. For the effect of atrazine, the chlorine-carbon bond is also suspected to play a significant role, as HA is not considered to be phytotoxic [15,47]. DEA and DIA are still phytotoxic, whereby the isopropyl substituent contributes to the phytotoxicity to a higher extent than the ethyl substituent [48]. The results obtained in this study are in good agreement with the literature, as no significant phytotoxic effect for HA or for EIT was observed in the examined concentration range.

As they both significantly reduce the phytotoxicity of the herbicides, reductive and oxidative pathways are equally suitable for degradation of atrazine and bromacil in the environment.

4. Summary and Conclusion

In this study, two sorption-reaction composite materials designed for *in-situ* groundwater remediation were tested for their performance in treating water contaminated by the herbicides atrazine and bromacil. Herbicide adsorption, degradation kinetics and formation of transformation products were studied.

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Finally, the benefit of both remediation methods was evaluated based upon the influence on the phytotoxicity after treatment of the herbicide-contaminated water.

Carbo-Iron was able to degrade bromacil reductively to BMU almost completely with a half-life below 4 d using both 1 and 10 g L^{-1} Fe^0. On the other hand, only traces of the reduction product of atrazine, EIT, were found. Pure nZVI showed insignificant reductive dehalogenation of both atrazine and bromacil under the examined conditions. The Trap-Ox zeolite as catalyst for Fenton-like reactions showed suitable performance for both contaminants and both underlying processes – adsorption and degradation. Oxidation pathways for the Fenton reaction of both herbicides are proposed based on non-target screening of the product mixtures.

In order to ensure the ecotoxicological benefit of the degradation processes and to prevent risks from transformation products with higher toxicity, the target compounds as well as the reaction products and product mixtures were subjected to an hts-diagnostic algae test. All products showed lower toxicity than their parent compounds. Furthermore, it could be confirmed that the halide-carbon bond plays a key role in the specific phytotoxicity of both atrazine and bromacil. For evaluation of the ecotoxicological benefit of the treatment options, the hts-DAT proved its suitability. Nevertheless, studies concerning species endemic in groundwater could complement ecotoxicological assessment with regard to non-specific effects.

In conclusion, in the case of an aquifer contamination with bromacil, Carbo-Iron can be considered for remediation. For atrazine or mixed contaminations, Trap-Ox remediation is more suitable. However, prior to any *in-situ* application, both materials and methods should be subjected to column experiments with site sediment and groundwater in order to ensure the functionality and remediation success under field-simulating conditions. Besides contaminant removal, running and future pilot applications of the Trap-Ox

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approach should be further supported by studies concerning Fe leaching and re-loading of the zeolite in order to better control the lifetime of the barrier.

Credit author statement

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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