

Adsorption behaviors of glyphosate, glufosinate, aminomethylphosphonic acid, and 2-aminoethylphosphonic acid on three typical Baltic Sea sediments

Wael Skeff*, Constantin Recknagel, Yvonne Düwel, Detlef E. Schulz-Bull

Leibniz Institute for Baltic Sea Research Warnemuende, Department of Marine Chemistry, Seestrasse 15, 18119 Rostock, Germany

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ABSTRACT

A batch experiment was conducted to study the adsorption behaviors of glyphosate, glufosinate, aminomethylphosphonic acid (AMPA), and 2-aminoethylphosphonic acid (2-AEP) in marine sediments (mud, silt, and sand) from the Baltic Sea. The experiment took into account the influence of pH, salinity, and temperature on the adsorption behaviors of the studied compounds. In contrast to glufosinate, glyphosate exhibited an adsorption affinity for the three types of sediments. AMPA and 2-AEP showed similar adsorption behaviors on mud and silt, while their adsorption on sand was negligible. The equilibrium adsorption data for glyphosate, AMPA, and 2-AEP on mud and silt fit well with the linear partitioning and Freundlich isotherms, whereas the data for glyphosate on sand could only be fitted with the Freundlich isotherm. The Freundlich distribution coefficients (k_f) were in the range of 6.1–259.5 L/kg for glyphosate, 9.2–39.5 L/kg for AMPA, and 7.7–38.5 L/kg for 2-AEP under the experimental conditions of pH 8.1, temperature = 21 °C, and a salt concentration of 8 g/L. The adsorption kinetic was better described by the pseudo-second-order than the pseudo-first-order model, suggesting chemisorption as the adsorption mechanism. The order of adsorption of the compounds on the sediments was: glyphosate > AMPA \geq 2-AEP > glufosinate. The adsorption capacity of sediments followed the sequence: mud > silt > sand. Increasing the pH, salinity, or temperature of the solution significantly reduced the adsorption capacity of the compounds. The data obtained in this study provide valuable information on the fate and distribution of the investigated phosphonates in the Baltic Sea.

1. Introduction

Phosphonates are a group of organophosphorus compounds characterized by the presence of a carbon-phosphorus (C–P) bond, which makes them extremely resistant to thermal decomposition and chemical hydrolysis (Kononova and Nesmeyanova, 2002). They are also an important fraction of the dissolved and particulate phosphorus in aquatic ecosystems. For instance, in the marine environment they account for 5–25% of the dissolved organic phosphorus pool and 6–20% of the total amount of phosphorus in sediments (Baldwin, 2013). Their occurrence in the environment may be biogenic (e.g., phosphonolipids) or anthropogenic (e.g., pesticides) (Baldwin, 2013; Suzumura, 2005).

A common biogenic phosphonate is 2-aminoethylphosphonic acid (2-AEP), first isolated from rumen protozoa in 1959 (Horiguchi and Kandatsu, 1959) and subsequently identified in many marine invertebrates and plankton feeders (Cembella and Antia, 1986). In the last decade, the use of anthropogenic phosphonates has been rapidly grown mostly because of their intensive application in agriculture. Glyphosate (*N*-phosphonomethyl-glycine) is the world's most

commonly used commercial synthetic phosphonate and pesticide. As a non-selective, post-emergence, broad-spectrum organophosphorus herbicide, it is applied in agricultural and in urban regions under several commercial formulations, most prominently as Roundup® (Ibanez et al., 2005; Leaper and Holloway, 2000). Because of its strong adsorption on soils and lack of volatility glyphosate is considered to be immobile in the environment (Giesy et al., 2000). However, its detection in different aqueous environments, including surface water, has been reported (Botta et al., 2009; Skeff et al., 2015). The degradation of glyphosate in the environment is mainly microbial, yielding aminomethylphosphonic acid (AMPA) as the main degradation product (Battaglin et al., 2014). AMPA is also produced by the degradation of industrial aminophosphonates, which are used in cooling water, laundry agents, detergents and the textile industry. It therefore enters surface waters via wastewater treatment effluents (Jaworska et al., 2002; Kolpin et al., 2006). In the environment, AMPA is more mobile than its parent herbicide glyphosate and it is frequently found in surface water (Kolpin et al., 2006; Skeff et al., 2015). The engineering tolerance of the phosphonate herbicide glufosinate (ammonium DL-homoalanin-4-

* Corresponding author.

E-mail address: wael.skeff@io-warnemuende.de (W. Skeff).

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(methyl) phosphinate) in several varieties of crops suggests its widespread use as an alternative pesticide in glyphosate-resistant crops (Laugeray et al., 2014). Indeed, in Germany its agricultural application has increased rapidly in the last decade, reaching 100 t in 2014 (BVL, 2015).

Surface-water runoff is an important route for the transport of anthropogenic phosphonates into the coastal and marine environment. In previous work (Skeff et al., 2015) we reported the occurrence of glyphosate and AMPA in many German rivers and streams that empty into the Baltic Sea. Numerous studies have reported the negative effects of glyphosate exposure on marine phytoplankton, macroalgae, and sea grasses (Kittle and McDermid, 2016; Wang et al., 2016). Moreover, several microorganisms are able to use glyphosate, glufosinate, AMPA, and 2-AEP as a sole source of phosphorus (Cook et al., 1978; Quinn et al., 1993; Schowanek and Verstraete, 1990), thus potentially stimulating eutrophication. Studies on the fate of phosphonates in the marine environment will contribute to efforts aimed at its protection and are especially relevant to the semi-closed Baltic Sea, where high levels of pollution and eutrophication are serious problems (HELCOM, 2011).

Adsorption studies provide information on the behavior of organic compounds, including their mobility, transport, degradation and toxicological effects, in ecosystems (Yang et al., 2005). After entering the marine environment, organic compounds with a strong adsorption tendency can adsorb onto suspended particles in the water column before settling into the sediments (Doong et al., 2002). Adsorption at the liquid–solid interface is another important route by which organic compounds are transported from the water column into sediments (Tian et al., 2009). However, few studies have investigated the behavior of hydrophilic compounds (e.g., emerging pollutants and biogenic substances) in marine sediments, especially highly polar and amphoteric compounds as glyphosate (pka = 0.8–10.14), glufosinate (pka = 0.07–9.8), AMPA (pka = 1.8–10.0), 2-AEP (pka = 1.53–10.43) (Sidoli et al., 2016; Wang et al., 2008). Thus, the aim of this work was to examine the adsorption of the four phosphonates glyphosate, glufosinate, AMPA, and 2-AEP (Fig. 1) onto different types of Baltic Sea sediments and thereby assess the distribution and mobility of these compounds in the Baltic Sea. We specifically addressed: (i) the kinetics of the adsorption of the four phosphonates onto sediments, (ii) an isotherm-based description of the adsorption process, (iii) the influence of pH, salinity, and temperature on the adsorption behavior of the phosphonates onto sediments.

2. Material and methods

2.1. Chemicals and reagents

Standards of glyphosate, a glyphosate internal standard (1-^{2,13}C₂¹⁵N glyphosate), AMPA, an AMPA internal standard (¹³C ¹⁵N AMPA), and glufosinate were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). 2-AEP was supplied by Sigma-Aldrich

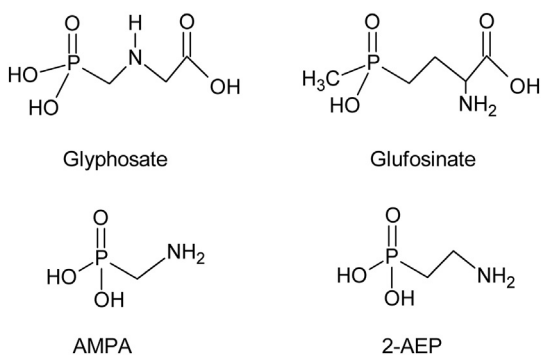


Fig. 1. Chemical structures of glyphosate, glufosinate, aminomethylphosphonic acid (AMPA), and 2-aminoethylphosphonic acid (2-AEP).

(Taufkirchen, Germany). Stock solutions of these compounds, except the internal standards, were prepared in polypropylene volumetric flasks at a concentration of 100 mg/L by dissolving 5 mg of each compound in 50 mL of LC-MS grade water (VWR International GmbH, Darmstadt, Germany). The stock solutions were stored at 5 °C in the dark. A stock solution (66.6 mM) of 9-fluorenylmethyl chloroformate (FMOC-Cl) (purity 99.0%, Sigma-Aldrich) was prepared by dissolving 1 g in 58 mL of acetonitrile (Walter-CMP GmbH, Kiel, Germany). Borate buffer at pH 9 was prepared by dissolving 1 g of sodium tetraborate decahydrate (Sigma-Aldrich) in 50 mL of Milli-Q water (Merck KGaA, Darmstadt, Germany). Artificial sea salt, contains all 70 trace elements found in natural seawater in the exact proportions found in nature, was purchased from Tropic Marin®, Germany. Chloroform was supplied by VWR AnalaR Normapure (Germany).

2.2. Sediment collection and characterization

Three types of sediment typical of the Baltic Sea were collected from the German Baltic Sea (Fig. 2) which are: S1 from Arkona basin (54° 50' N, 13° 30' E), S2 from Tromper Wiek (54° 39' N, 13° 35' E), and S3 from Oder Bank (54° 04' N, 14° 03' E). The sediments were collected using a multiple corer during research cruise EMB76, in June 2014. Samples of the uppermost sediment were sealed in glass jars, stored at –20 °C until dry. No sieving was done but large items such as stones, leaves, grass and animals were removed and the samples were manually homogenized. The bulk sediments were freeze-dried using a Chait ALPHA 1-4 LD freezer dryer and used as sorbents in this study. The grain sizes of the sediments were determined using a CILAS 1180 particle size analyzer. The TOC content of the sediments was analyzed with an elemental analyzer according to (Leipe et al., 2011). The major and trace elements in the sediments were measured using inductively coupled plasma optical emission spectrometry after acid total digested of the samples (Wegwerth et al., 2016). Data with respect to the grain sizes, total organic carbon (TOC), and major and trace elements of the sediments are listed in Table S1 of the Supplementary Material. Grain size distribution histograms obtained from the analysis of the sediments S1, S2 and S3 are shown in the Supplementary material Figs. S1, S2 and S3, respectively. The sediment grain sizes were distributed among the different classes: clay (< 2 μm), silt (2–63 μm), and sand (> 63 μm). The sediment S1 contained 6.6% clay, 92.3% silt, and 1.1% sand, with a median grain size 20.1 μm. The sediment S2 contained 3.6% clay, 69.9% silt, and 26.5% sand, with a median grain size 41.2 μm. The sediment S3 contained 1.7% clay, 10.7% silt, and 87.6% sand, with a median grain size 156.8 μm. The sediment S1, with organic-rich silt-size sediments, was classified as mud, while the sediment S2 as silt and the sediment S3 as fine sand (Leipe et al., 2017). The sediment TOC, total phosphorus, and major and trace elements followed the order: mud > silt > fine sand. Distribution map of major sediment types in the German sector of the Baltic Sea was published by Leipe et al. (2017). Chemical and sedimentological data of the three sediments can be found in (Ender et al., 2015; Gingele and Leipe, 1997).

2.3. Batch sorption experiment

To investigate the possible adsorption of the analytes onto the walls of the centrifuge tubes, the hydrolysis and degradation of the test compounds during the experiment, a control set of tubes was established in which sediment-free artificial seawater samples were spiked with 250 μg of the analytes/L for 48 h. An additional set of tubes containing sediments with unspiked artificial seawater controlled for possible desorption and the contamination of the sediments and media with the target compounds.

To initiate the experiment, artificial seawater was prepared at a salt concentration of 8 g/L. The pH of the solution was 8.1, measured using a conductivity meter (WTW Inolab cond® 720, Germany). Chloroform (0.1%) was added to the media to inhibit microbial activity (Huang and

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