



Glyphosate binding in soil as revealed by sorption experiments and quantum-chemical modeling



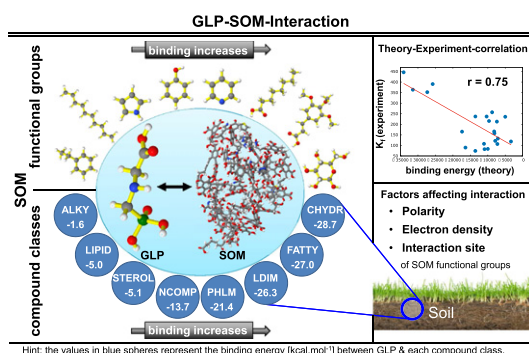
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GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 9 December 2016

Received in revised form 1 February 2017

Accepted 1 February 2017

Available online 21 February 2017

Editor: Dr. D. Barcelo

Keywords:

Glyphosate (GLP)

Soil organic matter (SOM)

Sorption isotherms

Molecular modeling

Quantum chemical calculations

ABSTRACT

The herbicide glyphosate (GLP) is supposed to be rapidly degraded or adsorbed strongly by soil solids but findings in soil years after application and concentrations in waters above legal limits question a harmless disappearance. Therefore, we conducted batch sorption experiments with 23 thoroughly characterized arable surface soils, correlated isotherm coefficients with numerous inorganic and organic soil parameters, and investigated GLP-SOM-complexes by quantum-chemical modeling. The Freundlich sorption model yielded the best fits, and coefficients K_f and n_f were correlated positively with the contents of clay/silt. The contents of organic C (C_{org}) and of the mass-spectrometrically determined SOM-compound classes carbohydrates, phenols/lignin monomers, lignin dimers, lipids, alkylaromatics, non-amide N and amides and sterols all were strongly positively correlated with the Freundlich coefficients. Quantum-chemical modeling showed that both GLP phosphonic and carboxylic functional groups interact similarly with the polar SOM functional groups via H-bond formation but the GLP phosphonic moiety is most important in the GLP-SOM-interaction. Moreover, the interaction mechanism between GLP and every modeled SOM-compound class was explored indicating the importance of the polarity, electron density, and site of attack of the SOM fragments in the GLP-SOM-interaction. Partial binding energies were combined to a total binding energy ($E_{B,tot}$) of GLP to the SOM, considering the mass spectrometrically quantified compound classes for each individual soil sample. The resulting strongly positive correlation between the $E_{B,tot}$ and the C_{org} provided compelling new experimental-theoretical evidence for the importance of SOM on the GLP binding and its behavior in the environment. In conclusion, the multitude of binding mechanisms to clay minerals and organic colloids make the occurrence of free GLP rather unlikely but a leaching of GLP complexes via preferential flow path through soil and transfer to waterways rather likely.

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1. Introduction

Glyphosate (GLP, N-(phosphonomethyl)-glycine) is the most used non-selective herbicide in the world. For 2017 a total application of 1.35 Mio t is forecasted (Global Analysis Industry Inc., 2011). GLP is highly soluble in water (12 g L^{-1}), has a low partitioning coefficient for the octanol-water system ($\log K_{ow} = -3.4$), and is charged according to the soil pH ($pK_{a1} = 0.8$, $pK_{a2} = 2.23$, $pK_{a3} = 5.46$, $pK_{a4} = 10.14$; Tomlin, 1997; Liu et al., 2016). Therefore, early work of Glass (1984) plausibly reported that GLP is strongly bound to mineral surfaces and assumed that it should be nearly immobile in mineral soils. Nevertheless, GLP and its primary metabolite aminomethylphosphonic acid (AMPA) have been detected in ground and surface water (e.g., Coupe et al., 2012; Van Stempvoort et al., 2014) and recently also in the Baltic Sea (Skeff et al., 2015). Since this contradicts the assumed immobility, the influence of soil parameters on GLP sorption mechanisms still is a scientific challenge.

It has been reported that sorption is influenced mainly by (1) soil texture (Sprinkle et al., 1975), (2) mineral composition (Dion et al., 2001; Piccolo et al., 1994), and (3) pH (Sidoli et al., 2016; Kumari et al., 2016). For soil organic matter (SOM) negative (e.g. Torstensson, 1985; Gerritse et al., 1996; Ololade et al., 2014; Arroyave et al., 2016) and positive (e.g., Roy et al., 1989; Piccolo et al., 1995; Okada et al., 2016) effects on GLP binding have been reported. Studies on SOM model systems concluded that (1) GLP binds to organic molecules via H-bonds leading to disaggregation of complex structures (Miano et al., 1992), (2) binding is positively influenced by aromatic substances (Albers et al., 2009) and (3) sorption capacity is similar or even higher compared with those of pure soil minerals or bulk soils (Piccolo et al., 1996). Despite these findings from model experiments, the effect of non-extracted, chemically unaltered SOM on GLP sorption in bulk soil samples is still unclear. Furthermore, the molecular structure of SOM also may have an impact on GLP sorption, but this has not yet been studied with bulk soil and SOM.

Pyrolysis field-ionization mass spectrometry (Py-FIMS) is a versatile analytical method for the determination of SOM building blocks (Leinweber et al., 2009), and it has been successfully applied to study the binding of xenobiotics to SOM (e.g. Thiele-Bruhn et al., 2004). Molecular modeling is a flexible tool for the investigation of elementary processes in soils (Ahmed et al., 2016; Schaumann and Thiele-Bruhn, 2011; Sündermann et al., 2015). It complements analytic and kinetic experiments in the development of a molecular level understanding of soil processes such as the interaction of xenobiotics with, for example, SOM or soil minerals. In general, modeling of SOM is not straightforward due to its high variability in chemical composition, spatial architecture, and multi-phase behavior (Senesi et al., 2009). Recently, Ahmed et al. (2014a, 2014b) have developed a new approach for SOM modeling based on SOM characterization by different analytical techniques (Ahmed et al., 2012), which is combined with quantum chemical and molecular dynamics calculations. The model is based on a large test set of separate representative molecules, covering the most relevant functional groups that exist in analytically quantified compound classes (Ahmed et al., 2012). The validity of this model has been demonstrated by comparison with experimental sorption of polar and non-polar xenobiotics on well-characterized soil samples (Ahmed et al., 2016). However, this promising combination of experimental and theoretical approaches has not yet been applied to explore the interaction of GLP with soil components, especially SOM.

The general objective of the present study was to disclose the binding nature between GLP and SOM at a molecular level. Specifically, we want to deduce which soil constituents are involved in GLP binding by correlating their contents with the sorption coefficients from batch experiments. Complementary, we performed quantum chemistry based molecular modeling of GLP-SOM binding by extending the recent SOM model by Ahmed et al. (2016). Linking the molecular modeling with the experimental sorption and correlation results will allow us to develop a molecular level understanding of GLP binding to soil.

2. Materials and methods

2.1. Soils samples and basic soil properties

Soil samples were selected from mineral A-horizons of agricultural sites in Germany and Sweden (Table 1). Agricultural uses involved arable (Ap-horizons, $n = 10$), grassland (Ah-horizons, $n = 6$) and short rotation coppice (SRC, Ah-horizons, $n = 7$). The soils represent most major soil units of agricultural soils in Pleistocene landscapes in Central and Northern Europe. Texture classes ranged from loamy sand to clay, and the pH values from strongly acidic (4.03) to slightly alkaline (7.19). The C_{org} contents range from 2.8 to 31.1 mg kg^{-1} and are typical for agricultural soils with sandy to clayey texture; they represent mineral soils ($C_{org} < 75 \text{ g kg}^{-1}$). These fields had not been treated with GLP so far.

Air dry samples were sieved $< 2 \text{ mm}$. Basic properties were analyzed: (1) particle size distribution by combined sieving (sand, 2 to 0.063 mm) and sedimentation (silt, 0.063 to 0.002 mm, and clay, $< 0.002 \text{ mm}$) analysis according to E DIN ISO 11277:06.1994–06 (Sedimat 4–12, Umwelt-Geräte-Technik GmbH, Müncheberg, Germany), (2) pH in 0.01 M CaCl_2 (pH-Meter 540 GLP WTW, Schott, Germany), (3) carbon and nitrogen content via CNS-analysis (VARIO EL analyser, Elementar Analysensysteme GmbH, Hanau, Germany), (4) detailed molecular-chemical composition of SOM.

For most samples ($n = 18$ archived soil samples) the SOM composition had been analyzed in previous projects by Py-FIMS (Leinweber et al., 1999: sample numbers 18, 19, 20; Jandl et al., 2015: sample numbers 1, 2, 21, 22; Acksel et al., 2016: sample numbers 4, 7, 8, 12, 13; Barth et al., submitted Applied Soil Ecology: sample numbers 3, 5, 6, 11, 16, 17). The methodology of Py-FIMS, also applied to the remaining $n = 5$ samples (sample numbers 9, 10, 14, 15 and 23) for the present study, has been described in detail by Leinweber et al. (2009). For Py-FIMS analysis about 5 mg of each sample was thermally degraded in the ion source mass spectrometer. The samples were heated under a high vacuum from 110 to 700 °C and 60 magnetic scans were recorded for the mass range of 55 to 500 a.u. Total ion intensity (TII) which is the sum of ion intensities of all recorded marker signals was calculated for each sample. Furthermore, the scans provide information about abundance and chemical structure of the chemical compounds. These chemical compounds are classified into 10 compound classes that are carbohydrates (CHYDR), phenols/lignin monomers (PHLM), lignin dimers (LDIM), lipids, alkenes, fatty acids, and n-alkyl esters (LIPID), alkylaromatics (ALKY), heterocyclic N and nitriles (NCOMP), sterols (STERO), amides (amino acids, peptides, amino sugars) (PEPTI), suberin (SUBER) and free fatty acids ($n\text{-C}_{16}$ to $n\text{-C}_{34}$), (FATTY). The particular ion intensity of each compound class was calculated according to well-established modes of spectra interpretation (Ahmed et al., 2012; Schulten et al., 1999). The contents of these compound classes based on soil weight [mg kg^{-1}] were calculated by multiplying the relative proportions of ion intensity (%TII) of these compound classes with the SOM content ($C_{org} \times 2, [\text{g kg}^{-1}]$). This calculation assumed that the total ion intensity is proportional to the SOM content. Detailed descriptions of the Py-FIMS methodology (Schulten, 1999) and statistical evaluations of sample weight and residue, volatilized matter, and total ion intensities were given by Sorge et al. (1993).

2.2. Sorption isotherms

Sorption experiments were carried out according to the method of Waiman et al. (2012) with slight modification. 2 g of soil were added to 10 mL of potassium chloride (KCl, purchased from Carl Roth, p.a.) solution (0.1 M) in 15 mL centrifuge tubes and spiked with GLP (purchased from Dr. Ehrenstorf, 99.0%) at 10 initial concentration levels (0, 10, 15, 20, 25, 30, 50, 75, 100, 150 mg L^{-1}) in five replicates. The concentration level of 0 mg L^{-1} was used for blank subtraction. Sorption was carried out over night for 16 h at room temperature with overhead shaking. Equilibrium soil solution was centrifuged (10 min, 1558 g) and 3 mL of the supernatant were used for determining the GLP

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