Behaviour of glyphosate in a reservoir and the surrounding agricultural soils

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Abstract

Glyphosate (GPS) is an herbicide currently used on olive crops in Spain, and can be transported to the nearby reservoirs currently used for human consumption. The purpose of this work was to study the behaviour and environmental fate of GPS in water and sediments of the Vibora Reservoir, its tributary river, and the surrounding agricultural soils to assess the risk of water pollution of this reservoir. The adsorption of GPS by different matrices was as follows: heading of the reservoir sediments (Cabecera) > tail sediment (Cola) > soils > Vibora sediment. The highest amount of oxides (especially Fe oxides) was observed in sediments from Cabecera and Cola whereas the lowest values were recorded on Vibora sediment. Results indicate that the highest GPS adsorption is due to the amorphous oxides and the edge sites of the clay minerals. Glyphosate adsorption increased with decreasing pH from 8 to 7. The desorption percentage of GPS from the four soils studied ranged only from 0.40 to 1.22%. Desorption was almost irreversible for Cabecera and Cola sediments, with values between 0 and 1.1%, respectively. Conversely, Vibora sediment presented about
20% desorption, probably due to its coarse texture and lower levels of amorphous oxides. Hockey-stick first-order kinetics was the best descriptor for water glyphosate dissipation at the Cabecera and Cola locations, and simple first-order kinetic for the water from the tributary Vibora River. The half-lives (DT50) were between 6.3-11.0 days. The rapid degradation of GPS in surface waters and its practically irreversible sorption on these soils and sediments implies that GPS use in similar agricultural areas is of very low environmental risk. This manuscript also outlines the importance of the presence of photo-sensitizers in waters in the degradation routes of GPS in reservoirs.

**Keywords:** Glyphosate, adsorption, dissipation, agricultural soils, reservoir sediments

**Highlights**
1. High GPS adsorption to surrounding soils due to amorphous oxides and clay minerals
2. Extremely high adsorption capacity of reservoir sediments for GPS
3. GPS desorption from soils and sediments almost irreversible.
4. High levels of amorphous oxides act as photosensitizers for GPS water dissipation
5. High GPS sorption on sediments and dissipation in water reduce its environmental impact
1. Introduction

Monitoring surveys carried out in United States and Europe have indicated that the use of pesticides in agricultural and non-agricultural areas have yielded contamination of surface and groundwater through runoff and soil leaching (Aparicio et al., 2013; Hildebrandt et al., 2008). Many researchers have found a strong correlation between water pollution due to pesticides and agricultural practices in the surrounding areas (Palma et al., 2009; Ricart et al. 2010). Water quality is an important issue in the European Union. The EU has prescribed the maximum concentration of 0.1 μg l⁻¹ for each pesticide and of 0.5 μg l⁻¹ for the whole in drinking water (Directive 2000/60/EC).

Most contaminants released into aquatic environments will be incorporated in sediments, and these sediments might later act as the major source of contaminants released to water and biota.

Glyphosate [N-(phosphonomethyl) glycine] (GPS), is a broad-spectrum, post-emergence, non-selective herbicide and very soluble in water (12 g l⁻¹). It is the world’s biggest-selling chemical used for weed control in agricultural, silvicultural and urban environments (Benbrook, 2016), and it is currently used on olive crops in Spain (Cañero et al., 2011). Some authors such as Giesy et al. (2000) and Howe et al. (2004) indicated that GPS is relatively safe environmentally, although nowadays some researchers indicated risks to humans and the environment stemming from applications of glyphosate (Myers et al., 2016). For this reason, the European Union, whose authorization procedure for pesticides is the strictest in the world, has approved a limited extension of the current approval of glyphosate only until the end of 2017, while studies about its carcinogenicity are carried out (European Commission, 2016). In relation to its behaviour in soil, some investigations showed possible leaching and
toxicity problems with its use (Veiga et al. 2001). Other authors have also shown that soil adsorption and degradation of glyphosate exhibit great variation depending on soil composition and properties (Gimsing et al. 2004a; Gimsing et al. 2004b; Mamy et al. 2005). Therefore, it is important to study the behaviour and fate of GPS in soils and sediments, including adsorption, dissipation and leaching. GPS is a polar, amphoteric compound that binds strongly to soil. GPS have a soil half-life that range between 2 to 215 days and in aquatic medium is of 2 to 91 days (Battaglin et al., 2014). Predicting the behaviour and transport of an herbicide in soil and sediments involves understanding its adsorption characteristics. Therefore, adsorption coefficients obtained from batch experiments are an important tool for understanding the processes and the prediction of the contaminant behaviour (Wauchope et al., 2002).

There are many papers that describe the factors that control the adsorption of glyphosate on soils and their components (Gimsing et al. 2004a; Morillo et al., 2000). However, there is no agreement between the different authors. Glyphosate is a polyprotic acid and forms, within the pH range of 4–8 found in most soils, mono- and divalent anions with high affinity for, in particular, trivalent cations such as Al$^{3+}$ and Fe$^{3+}$ (Barja and Dos Santos, 2005). GPS can mainly be adsorbed onto variable-charge surfaces and much less onto permanent-charge (negative) sites on layer silicates (Morillo et al., 1997).

Some authors have indicated that adsorption depended mainly on cation exchange capacity (CEC) and clay content (Glass, 1987; de Santana et al., 2006; da Cruz et al. 2007). However, others authors have postulated that iron and aluminium amorphous oxides or organic matter content had the major influence (Morillo et al., 2000; Maqueda et al., 2002, Prata et al., 2005). Some studies have shown that soil adsorption and degradation of GPS exhibit great variation depending on soil
composition and properties (Sorensen et al., 2006; Gimsing et al., 2007). In addition, the
effect of pH on adsorption of GPS in soils and clay minerals is crucial (Morillo et al.,
2000; Sheals et al., 2002; Gimsing et al., 2004a; Pessagno et al., 2008). Soil organic
matter (SOM) seems to play a controversial and dual role in soil adsorption of GPS.
Some authors indicated a negative correlation with GPS adsorption; however, Yu and
Zhou (2005) found a great influence of the OM on GPS adsorption. In addition,
Maqueda et al. (1998) showed a high GPS adsorption by a natural fulvic acid complex
and Piccolo et al. (1996) reported very high adsorption by 4 different purified humus
samples, explained by the formation of hydrogen bonding between humus and GPS.

Nevertheless, there is a general agreement in the literature that the adsorption of
GPS in soil is governed by the mineral rather than the organic phase (Sheals et al.,
2002; da Cruz et al., 2007; Gimsing et al., 2007; Rampazzo et al., 2013). The main soil
adsorption sites are found on surfaces of aluminium and iron oxides, especially
adsorption by goethite (α-FeOOH) (Maqueda et al., 2002; Dideriksen and Stipp, 2003),
poorly ordered aluminium silicates (allophane/imogolite) and edges of layer silicates.
Soils enriched with these variable-charge minerals have been demonstrated to be
effective GPS sorbents (Gimsing and Borggaard, 2007), whereas soils dominated by
permanent charge minerals such as illite, smectite and vermiculite adsorb less GPS (De
Jonge et al. 2001). The layer silicates can contribute with the OH groups on the
octahedral layer.

GPS has a limited risk of leaching to ground water because it is inactivated by
strong adsorption in soils and degrades relatively rapidly (Busse et al., 2001; Borgaard
and Gimsing, 2008). However, long-term use of GPS may cause surface, ground water
and sediments pollution (Kogan et al., 2003; Stewart, 2014). The presence of GPS in
natural waters is mainly due to off-site movement via surface waters (Landry et al.,
Once GPS has reached the reservoir, it can suffer degradation in water or can be adsorbed to sediments. Microbial degradation of GPS is an important dissipation pathway in surface waters, whereas photolytic decomposition and chemical degradation are comparatively minor (Degenhardt et al., 2012).

The purpose of this work was to study the behaviour and environmental fate of GPS to assess the risk of water pollution of a reservoir taking into account three environmental compartments: water and sediments of the Vibora Reservoir and its tributary river, and their surrounding agricultural soils. As far as we know, most of the previous studies carried out in reservoirs were restricted only to water. Vibora Reservoir is located in a semi-arid region where the main economic activity is the agriculture focused on the cultivation of olive trees. The herbicide GPS was selected because is one of the most used pesticides in olive tree orchards in Spain. The crop yields are strongly dependent on the use of pesticide because of climatic and soil conditions, with a potential risk of water contamination. The herbicides applied to olive crops can be transported to the nearby reservoir currently used for human consumption. Specific attention was given to the adsorption behaviour of GPS in the different media and its dissipation in the aquatic environment, for understanding the dynamic of herbicide contamination of surface waters.

2. Materials and methods

2.1 Pesticide

High purity glyphosate (98% purity) was used in adsorption and dissipation experiments. The herbicide was purchase from Dr. Ehrenstorfer GmbH (Augsburg,
Germany). GPS is a non-residual herbicide, with solubility in water of 12 g l⁻¹ at 25°C. GPS has a zwitterion structure depending on the pH.

2.2 Sampling site

Vibora Reservoir is located at the Vibora riverbed in the province of Jaen, in the south of Spain (37° 38'8" N 3° 59'36" W). It is a water reservoir for drinking water and fishing and has a capacity of 19 hm³. It has a tributary river with the same name, Vibora. In its surrounding environment there are olive trees planting. The province of Jaen is the region with higher olive production concentration in the world and made this zone a proper target to be studied based on the European Framework Water Directive 2000/60/EC (Robles-Molina et al., 2014).

2.3 Sampling soils, sediments and water

Four agricultural soils (olive trees) near the Vibora Reservoir were selected for this study. The soils were randomly sampled from the 0-15 cm layer, air dried, and crushed to pass through a 2 mm sieve before their use in the experiments. Three different sediments were also taken and named as such due to the different locations where they were sampled, Cabecera and Cola (belonging to the head-board and tail of the Viboratas Reservoir, respectively) and other one named Vibora, corresponding to the tributary river of the reservoir with the same name. The sediments were taken using a Van Veen grab sampler (0.5-L capacity), and were frozen and lyophilized before carrying out the different determinations. Soils and sediments were analysed for pH in a water:soil extract at the ratio 2.5:1, total carbonate content, particle size distribution and organic matter (OM) content. The amorphous and organically bound iron, manganese, and aluminium oxides were determined using ammonium oxalate-oxalic acid.
Water samples were collected at the head of the reservoir (Cabecera), the tail of
the reservoir (Cola), and the tributary river Vibora at a depth of 50 cm. Samples were
stored in amber bottles in the dark at 4°C during transport to the laboratory and then
frozen at -18°C until use. The sampling was performed in the beginning of April 2015
before GPS application on the olive orchards. The presence of GPS and AMPA were
determined in soils, sediments and waters before application of the herbicide, and no
residues were found.

2.4 Mineralogical determination

The mineralogical determination of the clay fractions (< 2μm) of the soils was
carried out as described in Maqueda et al. (2015). For soils and sediments, a
semiquantitative estimate of clay minerals was determined using the reflection powers
given by Schultz (1964).

2.5 Adsorption-desorption of glyphosate on soils and sediments

Before performing the batch adsorption experiments, preliminary kinetics
studies were carried out. It was found that 24 hours was longer enough to reach GPS
adsorption pseudo-equilibrium in soils and sediments. Triplicate adsorption experiments
were performed by mixing 5 g of the different soils with 10 mL solution containing
various concentrations (1-10 mg l⁻¹) of GPS, in 50 ml polypropylene centrifuge tubes.
The samples were shaken on a platform shaker for 24 h at 20 ± 1 °C. After shaking, the
dispersions were centrifuged and the concentration of GPS in the supernatant was
determined. All the experiments were carried out in triplicate. The differences between
initial and final herbicide concentrations were assumed to be due to adsorption. The
isotherms were obtained representing the amount adsorbed versus the amount remaining
in solution.
Desorption experiments were performed after adsorption equilibrium was achieved by removing half of the supernatant after centrifugation, then replacing it with distilled water and allowing equilibration for an additional 24-h period. The experiment then proceeded according to the protocol used for the adsorption experiment. This process was repeated twice more. The equilibrium pH was maintained both in adsorption and desorption isotherms at pH 8 due to the high carbonate content of soils and sediments samples that buffered the medium. Desorption isotherms were obtained representing the amount that remained adsorbed versus the concentration for each desorption process.

Adsorption isotherms were fitted to the Freundlich equation:

\[ \log C_s = \log K_f + n \log C_e \]

where \( C_s \) (\( \mu \text{mol kg}^{-1} \)) is the amount of herbicide adsorbed at the equilibrium concentration \( C_e \) (\( \mu \text{mol l}^{-1} \)), and \( K_f \) and \( n \) are constants that characterize the relative adsorption capacity and the adsorption intensity, respectively, of the herbicide.

The normalized distribution coefficient (\( K_{fOC} \)) of organic carbon (OC) was calculated from the \( K_f \) values (\( K_f/OC\times100 \)). The coefficient \( K_{fOC} \) is often used to characterize the adsorption of non-polar hydrophobic compounds. The concept is based on OC exhibiting the same affinity for a non-polar compound, independent of the source of OC (Morillo et al., 2014). The adsorption distribution coefficients were also determined (\( K_d \)) at selected \( C_e \) (0.01\( \mu \text{mol l}^{-1} \)). \( K_f \) and \( K_d \) values were used to compare the adsorption capacity of the different matrices.

For sediments, the adsorption experiments were carried out as in soils but using 1-g and 20-ml solutions containing various GPS concentrations (0.1 to 1.0 mg l\(^{-1} \)). GPS
adsorption experiments were performed at controlled pHs (7 and 8) by adding aliquots to the different initial solutions of sodium hydroxide or hydrochloric acid such that the final pH was maintained at that desired. These pHs were selected because are those usually found in the reservoir along the different seasons. Desorption experiments were carried out in the experiments only at pH 8 for comparison with the soils.

2.6 Glyphosate dissipation in water under aerobic conditions

Microbial degradation and photodegradation are routes of GPS dissipation in water. Laboratory experiments were carried out to elucidate the GPS dissipation kinetics in natural water collected from the reservoir and the Vibora tributary river under simulated light exposition. Experimental conditions were selected as closely possible to the natural aquatic environment. Various water samples were brought to our laboratory and premixed before dissipation experiments. Portions of 100 ml of this natural water were distributed in glass containers and GPS was added to obtain a concentration of 2.5 mg l\(^{-1}\). The water samples were placed in a climatic chamber at 25 ± 1°C with a 16 h light photoperiod at an intensity of 11 µE m\(^{-2}\) s\(^{-1}\). Over 20 days, samples were collected from the containers at different time intervals, the suspensions were filtered through a 0.22-µm Millipore glass fibre membrane and the concentration of GPS in the filtrate determined by HPLC-MS. All experiments were carried out in triplicate. A parallel experiment was performed to test potential sorption of GPS to glass surfaces. The operational conditions were identical but using distilled water instead and the containers covered by aluminium foil to prevent photodegradation. No GPS adsorption on the glass container was noticed.

The amount of dissipated GPS was plotted versus time. For the calculation of the kinetic parameters, dissipation curves were modelled according to the instructions of the
FOCUS guide (2011), using the least squares method with the SOLVER from the Microsoft Office Excel 2007 mathematical program. Dissipation kinetics were fitted to two models: a simple first-order (SFO) model and a first order sequential model (Hockey-Stick, HS), according to the following equations:

\[ C_t = C_0 \cdot e^{kt} \]

\[ C_t = C_0 \cdot e^{-k_{1t}} \cdot e^{-k_{2(t-tb)}} \]

Where \( C_t \) is the concentration of pesticide remaining in water (mg l\(^{-1}\)) at time \( t \) (days); \( C_0 \) is the initial concentration of pesticide (mg l\(^{-1}\)); \( K \) is the rate of dissipation (days\(^{-1}\)). In the HS model, \( k_1 \) and \( k_2 \) are the rate constants of dissipation for the fast and the slow fractions, respectively, and \( t_b \) is the time at which rate constant changes. The Chi-square \((\times 2)\) test with \( \alpha = 0.05 \) was used to estimate the appropriateness of the model and to assess the accuracy of each resulting fit. This test considers the deviations between observed and estimated values (numerator) for each model in relation to the uncertainty of the measurements (denominator). These models have been selected for consideration based on their relative simplicity and their potential to better fit the measured dissipation kinetics. The time required for 50% disappearance of GPS (DT50) was determined.

2.7 Herbicide analysis

8 ml of the soil supernatant were subjected to solid-phase-extraction (SPE) on an Oasis HLB 60 mg cartridge, previously conditioned with 2 mL of methanol and 2 mL of acidified water at pH 2.5, and the millilitres of the extract were collected on an
autosampler vial. Recoveries were between 90-97% for solutions of glyphosate and AMPA of 5 and 10 µg/l. The analysis of glyphosate was carried out by liquid chromatography-tandem mass spectrometry in an Agilent HPLC with a triple quadrupole mass detector (ABSciex) under the following conditions: Eluent A, 1% Acetic acid in Water + 5% MeOH; eluent B, 1% Acetic acid in MeOH; Column Hypercarb 2.1 x 100 mm 5 µm at 40°C; ionization mode, ESI negative; injection volume, 5µl; acquired mass transitions (m/z) for glyphosate, 168/63, 168/124, 168/150, 168/81; for AMPA, 110/63, 110/79, 110/81; retention times: Glyphosate, 3 min; AMPA, 1.86 min.

The percentage of the eluent A was changed linearly in the time-programmed gradient used as follows: 0 min, 100%; 10 min, 70%; and 12 min, 100%. The flow rate was constant at 0.2 ml min⁻¹. The limits of quantification (LOQ) of both glyphosate and AMPA were 10 µg l⁻¹, and their limits of detection (LOD) 3 µg l⁻¹.

3. Results and Discussion

3.1 Physico-chemical and mineralogical characteristics of the soils and sediments

The physico-chemical characteristics of the studied soils are shown in Table 1. The results indicated that the soils are calcareous with very high carbonate content, especially soils 1, 2 and 4. These soils had basic pH, showed a clay loam texture and typical values of organic matter in Mediterranean semiarid soils. In relation to levels of amorphous oxides, soils 3 and 4 presented the lowest and the greatest amounts, respectively, among the soils studied.

The semiquantitative determination of the clay minerals of the soils is shown in Table 2. The clay fraction of all soils contained mainly illite, but also kaolinite,
vermiculite, and chlorite are present, except in soil 4 that presented a small amount of smectite instead of chlorite. In general, the mineralogy of the soils is quite similar among them.

The sediments presented also high amount of calcium carbonate and in consequence basic pH, with medium values of OM similar to the surrounding soils (Table 1). Cola and Cabecera sediments showed similar physico-chemical characteristics. Conversely, the Vibora sediment showed higher values of carbonates. The values of amorphous oxides are slightly higher for Cabecera relative to Cola sediment, whereas the values for Vibora sediment are fairly lower than in the other sediments. The values of OM in sediments are very similar to the values showed by the soils under study. The calcium carbonate content in the sediments was lower for Cabecera and Cola, but was the highest in Vibora sediment. Conversely, the amount of amorphous oxides (especially Fe oxides) was much higher for Cabecera and Cola sediments, about three times higher than for the soils and Vibora sediment. The values of amorphous oxides of Vibora sediment were the lowest.

The semiquantitative determination of the clay minerals of the sediments confirmed that the mineralogy of the three sediments was similar, but with different proportions of minerals. They were constituted mainly by calcite, quartz and some feldspar (Table 2). Illite, kaolinite, and vermiculite were also present. Vibora sediment had the highest calcite content in comparison with the other sediments, which explains why this sediment exhibited decreased clay mineral content in relation to the other two sediments.

3.2 GPS adsorption-desorption on soils
The adsorption isotherms of GPS in the soils included in this study are shown in Fig. 1. The isotherms were of “L” type (concave initial curvature). The experimental data were well fitted to the Freundlich equation. The values of Freundlich parameters are listed in Table 3. The correlation coefficients were in all cases greater than 0.98. n is related to the surface heterogeneity and the diversity of the energies associates with the adsorption reaction. n values were close to 1, what could be indicative of low heterogeneity among the sites of the soils where GPS has been adsorbed. It was probably due to the low concentration of herbicide used in the adsorption isotherms experiments, implying that GPS was adsorbed on high affinity sites, which were not totally occupied in the range of concentrations used. Because n values were very similar among the samples, K_f values could be used to compare the adsorption capacity of the different soils. According to the K_f values the order of adsorption was the following:

soil 4 > soil 2 > soil 1 > soil 3

K_f values ranged from 81.4 to 133 (l kg^{-1}) for soils 3 and 4, respectively. These values are similar to the previously reported for GPS adsorption on soils with a wide variety of textures and properties (Vereecken, 2005; Bergstrom et al., 2011; Sidoli et al., 2016). The amount of GPS adsorbed in the soil 4 was higher than on the other soils. The physico-chemical characteristics of the four soils surrounding the reservoir are almost similar and the pHs obtained after equilibrating with the four soils were also similar with values about 8, indicating that pH was not responsible for the different adsorption behaviour. The four soils had high amount of clay fraction, with presence of phyllosilicates and medium content of organic matter. Morillo et al. (1997) indicated that GPS has low tendency to be adsorbed on phyllosilicates except on the broken bonds on the edges positions. However, Glass (1987) postulated that adsorption of GPS by soils is related to the clay content and the CEC of the soils. The mineralogical difference
between soil 4 and the others was the presence of smectite, amounting at about 10%, which also would increase the CEC.

The role of hydrophobic bonds in the adsorption of non-polar hydrophobic herbicides to soils can be compared by normalizing the Freundlich adsorption parameter to the percentage of organic carbon (K_{foc}) in each sample. A more hydrophobic molecule results in a greater probability of partitioning from the aqueous phase to the organic phase. For comparison among soils, the K_{foc} parameter can be used as a measure of this property in soils, and it is independent of other soil properties. For a specific pesticide, when hydrophobic bonds are the only factor responsible for its adsorption, the K_{foc} values should be relatively constant among the different soils. However, the values obtained in this study are quite different (Table 3), ranged from 7332 to 14263, indicating that the adsorption mechanism is related to some other soil properties in addition to the OC content (Morillo et al., 2002; Undabeytia et al., 2011; Rubio–Bellido et al., 2016). Morillo et al. (2000) observed that GPS adsorption to three soils of different characteristics was not related to their CEC and clay mineral content, but to levels of iron and aluminium amorphous oxides and organic matter. In this work soil 4 presented the greatest value of amorphous oxides of the four studied soils (Table 1), which could be a factor worthwhile considering the greatest adsorption of GPS in this soil. The fact that GPS adsorption follows the same pattern as total amorphous oxide content in these soils seems to indicate that the main soil adsorption sites are found on the variable-charge surfaces of such amorphous oxides.

GPS desorption from soils was very little. Table 4 shows the total percentages of GPS desorbed (after three cycles of desorption) from the soil samples treated with GPS 3, 5 and 10 mg l^{-1}. The adsorption was almost irreversible in the four soils, indicating a
strong hysteresis. Al-Rajab et al. (2008) indicate that adsorption and desorption were
depended on pH only but not to the initial quantity of glyphosate adsorbed to the soil.
However, other authors showed that in general the more the sorption of GPS the more
reversible it was, indicating that GPS was more strongly adsorbed when the surface
coverage was small (Okada et al., 2016). In this work the values of desorption were very
similar for the different points of adsorption although a little higher for the points with
higher adsorption. The percentage of GPS desorbed for the 4 studied soils ranged
between 0.40 to 1.22%.

Piccolo et al (1996) indicated that desorption of GPS was the inversely related to
its adsorption and a large part of the adsorbed herbicide can be easily returned to the soil
solution with desorption from around 15% to 80% of the adsorbed GPS, contrary to the
behaviour in our soils. The reason of such behaviour could be that the maximum GPS
used in in the present work was 20µg g⁻¹ and in Piccolo et al. (1996) was 7.5 mg g⁻¹. In
such case de desorption of GPS was carried out not only from high affinity sites, but
also in positions where the interactions were very weak and from which the herbicide
was easily desorbed. According with our results, Farenhorst et al. (2009) observed also
that GPS was relatively immobile in experiments carried out using 90 soils from
different depths in the soil profile, even under rainfall scenario (384 mm) when GPS
had been applied at recommended field rates. This behaviour was also confirmed by
Bergstrom et al. (2011) who observed in a lysimeter study that 59% of the initial
amount of GPS added to a clay soil was present after 748d after application; also Okada
et al. (2016) obtained less than 0.24% of the applied pesticide leached in the whole set
of soils studied.

The presence of AMPA was not detected in these adsorption-desorption studies.
The complete sorption-desorption experiments were performed in shorter time (4 days)
than the half-life times usually recorded (15-23.8 days, IUPAC Pesticide Properties Data Base).

3.4 GPS adsorption-desorption on sediments

The adsorption experiments of GPS in the three studied sediments were carried out at controlled pHs of 7 and 8 by addition of NaOH or HCl aliquots to the different initial concentrations in order to obtain equilibrium pHs similar to pH levels found in the reservoir throughout the year. The adsorption isotherms of Cabecera, Cola and Vibora sediments at pHs 7 and 8 are shown in Figure 2. The adsorption isotherms of the sediments are presented in separated figures due to the large difference in the amount of GPS adsorbed by Cabecera and Cola sediments in comparison with Vibora sediment. GPS adsorption in Cabecera and Cola sediments were not well described by the linearized Freundlich equation. In the case of Vibora, the $K_f$ values obtained were 212 (n, 0.9558; $R^2$ 0.9762) and 46.2 (n, 0.9376; $R^2$ 0.9098) for pHs 7 and 8, respectively. These values are similar to those obtained for the studied soils (Table 3).

As equilibrium concentrations reached in Cabecera and Cola sediments were very low, distribution coefficient (Kd) for the three sediments were calculated at an equilibrium concentration of 0.01 µmol l$^{-1}$ to compare the capacity of the different sediments to adsorb GPS (Table 5). The GPS adsorption by these sediments was almost complete at an equilibrium pH of 7. The Kd values for GPS adsorption to sediments ranged from 67.3 (Vibora pH 8) to 11800 (Cabecera pH 7). According with Kd values the order of GPS adsorption to sediments was as follows:

Cabecera pH 7 > Cola pH 7 > Cabecera pH 8 > Cola pH 8 >> Vibora pH 7 > Vibora pH 8
GPS adsorption to Cabecera and Cola sediments show extremely high Kd values (in the range 4810-11800) in comparison with Vibora sediment (67.3 and 404). This behaviour could be related with several physicochemical properties. First of all, the higher amorphous oxides values in these two sediments in comparison with Vibora (almost four times higher, Table 1) and also with the soils previously studied (about three times higher). According to Morillo et al. (2000), the possible adsorption mechanism of the GPS to the oxides and hydroxides of soils and sediments as well as to the surfaces of variable charge on the organic matter is through the formation of bonds adsorbent-metal-phosphonic group of GPS. Thus, amorphous Fe- and Al-oxides, in general, seem to be a key parameter for glyphosate adsorption in soils (Rampazzo et al., 2013; Ololade et al., 2014; Paradelo et al., 2015; Sidoli et al., 2016). Secondly, the clay minerals content is very low in Vibora in comparison to the other two sediments (Table 2) providing lower amount of charge variable sites located on the edge broken bonds. According to Farenhorst et al. (2009) GPS adsorption was lower in soils with lower clay content, even if those contained more OM. And finally, Vibora sediment presented a loamy sand texture, and Cabecera and Cola sediments present a silt loam texture, providing much higher surfaces for adsorption. To the best of the authors’ knowledge, this is the first study where GPS adsorption to sediments presented such high values, and this is due to the previous arguments. Therefore, a higher GPS adsorption is observed in Cabecera than in Cola sediment, due both to its higher amorphous oxides (Table 1) and clay minerals contents (Table 2).

Kd values were also calculated for GPS adsorption to the soils under study (carried out at pH 8) at an equilibrium concentration of 0.01 µmol l⁻¹, in order to compare their adsorption capacity with that of the sediments. Soil Kd values ranged from 197 to 213,
indicating that adsorption was more similar to that observed in Vibora sediment as compared to Cabecera and Cola sediments (Table 5).

Glyphosate adsorption increased with decreasing pH from 8 to 7. The effect of pH may be due to the influence on the charge of the GPS molecule and the surface charge of the adsorbent (Gimsing et al. 2007). A decrease in pH facilitates the adsorption of GPS in sediments which pose a high content of oxides, because when pH decreases the variable charge surface of the oxides is more protonated. Therefore, the adsorption of negatively charged species of GPS will be favoured. In addition, there is also a reduction in the amount of ionized acid functional groups over the surface of the organic matter, enhancing GPS sorption. Moreover, there is a slight difference in GPS species in solution at pH 7 and 8 attending to GPS pKa values that drives larger sorption at the lower pH. The concentration of negatively charged species is reduced about 2-3% at pH 7 relative to pH 8 (Saitúa et al., 2012).

In spite of the high amount of studies dealing with GPS adsorption to soils, its adsorption to sediments has been poorly studied and understood, especially in reservoir sediments, where it is very interesting to know the behaviour of this herbicide in relation to the quality of freshwater ecosystems. The scarce studies carried out are related to GPS content in wetland sediments (Xu et al., 2009; Degenhardt et al., 2012) but only some works deal with GPS adsorption to sediments. Dollinger et al. (2015), in a review about GPS adsorption in soils and sediments, presented GPS adsorption parameters on sediments from France, Canada and Germany with different physico-chemical properties (Bailly et al., 2015; Xu et al., 2009; Litz et al., 2011). In these studies, $K_f$ values ranged from 1.89 to 319. $K_f$ for Vibora sediment is included in this range: 46.2 and 212 for GPS adsorption at pH 8 and 7, respectively. However, none of the mentioned sediments showed so high adsorption as Cabecera and Cola sediments.
GPS desorption behaviour varied substantially among Vibora and the other two sediments (Table 6). It is almost irreversible for Cabecera and Cola sediments, with values from 0% to 1.1%, while in Vibora about 15-20% GPS was desorbed. It could be related with its coarse texture and the much lower amount of amorphous oxides in Vibora sediment. There is also difference between Vibora GPS desorption and that observed previously for soils (about 1%), due to their clay loam texture in comparison to the loamy sand texture of Vibora sediment, with lower surfaces and, therefore, less adsorption sites.

3.6 Dissipation of GPS in water under aerobic conditions

The kinetics of GPS degradation in water at the same places where the different studied sediments were taken is shown in Figure 3, and the corresponding kinetic parameters are presented in Table 7. In these studies, the degradation of glyphosate to its major metabolite AMPA was monitored but the remaining amount in water was below the LOQ of the analytical technique, and after 11 days under the LOD.

DT$_{50}$ values obtained for Cabecera and Cola water dissipation were 6.3 and 6.4 days, respectively, and 11.0 for Vibora water. These data are in agreement with those reported by other authors for natural water dissipation. Mallat and Barcelo (1998) indicated that the main factors affecting the degradation of glyphosate in water can be summarized as a combination of microbial activity, temperature and, to a lesser extent, photolysis. These authors indicated that the degradation of glyphosate is fast under natural conditions, for ground water and river water samples half-lives were 60 h and 100 h, respectively. The complexity of the water matrix is an important factor to take into account since it can change the degradation rate of glyphosate. Goldsborough and Brown (1993) reported that dissipation of glyphosate and aminomethylphosphonic acid
in water and sediments of boreal forest ponds is typically rapid with first-order DT$_{50}$ values ranging from 3.5 to 11.2 d.

The more rapid dissipation observed in the case of Cabecera and Cola water in relation to Vibora could be due to indirect photolysis through photosensitizers. Shifu et al. (2007) showed that GPS is easily degraded by assisted photocatalysis in aqueous dispersion under radiation by UV light. Assalin et al. (2010) observed half-lives for GPS degradation of 6.2 minutes for TiO$_2$/UV irradiation. Although GPS is difficult to dissipate via direct photodegradation by sunlight, many iron complexes have photoactivity and various iron species are abundant in natural water (Chen et al., 2007). Iron oxides were proposed as photocatalysts because of their semiconductor properties (Bandara et al., 2001). The suspended solids in these natural waters which are the finer fraction of the sediments will have a high content of iron oxides acting as a photosensitizer and explaining the rapid GPS dissipation.

**Conclusions**

The results of this study indicate high GPS adsorption capacity of the soils surrounding the Vibora Reservoir due to their high amorphous oxides and clay mineral content. GPS adsorption follows the same sequence as total amorphous oxide content. GPS adsorption to sediments has been poorly studied and understood, especially in reservoir sediments, which is very interesting to know the behaviour of this herbicide in relation to the quality of freshwater ecosystems. In the present study, those sediments taken from the heading and tile of the reservoir showed extremely high adsorption capacity, with Kd values in the range 4810-11800 in comparison to the adsorption to sediments from the tributary river (Vibora, Kd values 67.3 and 404), very similar to...
those values observed in the surrounding soils. The adsorption of GPS to the different matrices was as follows: heading of the reservoir sediments (Cabecera) > tile sediments (Cola) >>> soils > Vibora sediment. To the best of the authors’ knowledge, this is the first study where GPS adsorption to sediments presented such high values, and this is due especially to the amount of oxides (especially Fe oxides) present in such sediments, which was about three-fold higher for Cabecera and Cola sediments than for the soils and Vibora sediment. In addition, Cabecera and Cola sediments presented a fine texture (silt loam) providing much higher surfaces for adsorption. Glyphosate adsorption to sediments increased with decreasing pH from 8 to 7, due to an increasing positive charge on the sediment surfaces and to the formation of GPS species with lower negative charge, which are adsorbed more easily to the negatively charged surfaces of the sediments.

GPS desorption for the studied soils and sediments were almost irreversible, percentages ranging from 0 to 1.22%, except in Vibora sediment, which presented 15-20% desorption, probably due to its coarse texture (loamy sand) and much lower level of amorphous oxides.

The dissipation of glyphosate in the water from the same places where the different studied sediments were taken was also studied. The DT$_{50}$ values obtained for water from Cabecera and Cola were 6.3 and 6.4 days, respectively; for Vibora, this value was 11 days. The more rapid dissipation observed in the case of Cabecera and Cola water could be due to indirect photolysis through photosensitizers. The suspended solids in these natural waters coming from the finer fraction of the sediments are likely to have high levels of iron oxides acting as photosensitizers and explaining the rapid GPS dissipation.
The importance of the contribution of sediments from reservoirs to the behaviour of glyphosate is pointed out in this paper because there is limited information available in the literature. The rate of GPS degradation in the water from Vibora Reservoir was very rapid, decreasing the potential risk impact on the aquatic ecosystem. This behaviour together with the almost irreversible adsorption of GPS from its sediments and the surrounding soils indicate the low toxicity risk of GPS in this zone, where this herbicide is widely used for olive crops.

Acknowledgments

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REFERENCES


Assalin, M.R., de Moraes, S.G., Queiroz, S.C.N., Ferracini, V.L., Duran, N. 2010. Studies on degradation of glyphosate by several oxidative chemical processes:


Figure legends

Figure 1. Glyphosate adsorption isotherms on soils.

Figure 2. Glyphosate adsorption isotherms on sediments: a) Cabecera and Cola sediments; b) Vibora sediment.
Figure 3. GPS dissipation profiles in waters from the Vibora river and from the heading and tail of the reservoir (Cabecera and Cola, respectively).

**GRAPHICAL ABSTRACT**

![Graphical abstract with tables and figures](image)

Table 1. Physico-chemical characteristics of the soils and sediments.

<table>
<thead>
<tr>
<th></th>
<th>Soils</th>
<th>Sediments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>OM (%)</td>
<td>1.69</td>
<td>1.59</td>
</tr>
<tr>
<td>CaCO₃ (%)</td>
<td>34.5</td>
<td>37.6</td>
</tr>
<tr>
<td>pH</td>
<td>7.65</td>
<td>7.73</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>33.6</td>
<td>31.3</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>31.9</td>
<td>30.5</td>
</tr>
<tr>
<td>Fine sand (%)</td>
<td>6.0</td>
<td>11.1</td>
</tr>
<tr>
<td></td>
<td>Soils</td>
<td>Sediments</td>
</tr>
<tr>
<td>----------------------</td>
<td>---------------------------</td>
<td>----------------------------</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Coarse sand (%)</td>
<td>28.5</td>
<td>27.0</td>
</tr>
<tr>
<td>Amorphous Fe oxides (%)</td>
<td>1.79</td>
<td>1.71</td>
</tr>
<tr>
<td>Amorphous Al oxides (%)</td>
<td>1.16</td>
<td>1.33</td>
</tr>
<tr>
<td>Amorphous Mn oxides (%)</td>
<td>0.19</td>
<td>0.21</td>
</tr>
<tr>
<td>∑ amorphous oxides (%)</td>
<td>3.14</td>
<td>3.25</td>
</tr>
</tbody>
</table>

Table 2.
Semiquantitative estimation (%) of the clay minerals in soils and sediments.

<table>
<thead>
<tr>
<th></th>
<th>Soils</th>
<th>Sediments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Illite</td>
<td>70</td>
<td>60</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>Chlorite</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>Smectite</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Quartz</td>
<td>≪ 5</td>
<td>≪ 5</td>
</tr>
<tr>
<td>Calcite</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Feldspars</td>
<td>≪ 5</td>
<td>≪ 5</td>
</tr>
</tbody>
</table>

*Calcite was not detected in soils because it was previously removed.

Table 3.
Freundlich adsorption isotherm parameter (K, and n values), coefficients of determination (R²) and organic carbon normalized distribution coefficients (K_{oc}) of GPS sorption on the soils. Errors are < 2%.

<table>
<thead>
<tr>
<th>Soil</th>
<th>K (L kg⁻¹)</th>
<th>n</th>
<th>R²</th>
<th>K_{oc}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil 1</td>
<td>91.09</td>
<td>0.9654</td>
<td>0.987</td>
<td>9,295</td>
</tr>
<tr>
<td>Soil 2</td>
<td>98.06</td>
<td>0.8995</td>
<td>0.9876</td>
<td>10,659</td>
</tr>
<tr>
<td>Soil 3</td>
<td>81.39</td>
<td>0.9537</td>
<td>0.9966</td>
<td>7,332</td>
</tr>
<tr>
<td>Soil 4</td>
<td>132.6</td>
<td>0.8109</td>
<td>0.991</td>
<td>14,263</td>
</tr>
</tbody>
</table>

Table 4.
Percentages of GPS desorbed (%) from the studied soils. Errors are < 2%.

<table>
<thead>
<tr>
<th>GPS initial conc. (mg L⁻¹)</th>
<th>GPS adsorbed (μmol kg⁻¹)</th>
<th>GPS desorbed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>25.54</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>43.46</td>
<td>0.40</td>
</tr>
<tr>
<td>10</td>
<td>84.33</td>
<td>0.45</td>
</tr>
<tr>
<td>Soil 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>26.17</td>
<td>0.52</td>
</tr>
<tr>
<td>5</td>
<td>41.27</td>
<td>1.04</td>
</tr>
<tr>
<td>10</td>
<td>84.0</td>
<td>1.22</td>
</tr>
<tr>
<td>Soil 3</td>
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<td></td>
</tr>
<tr>
<td>3</td>
<td>25.1</td>
<td>0.62</td>
</tr>
<tr>
<td>5</td>
<td>42.56</td>
<td>1.07</td>
</tr>
<tr>
<td>10</td>
<td>83.59</td>
<td>1.18</td>
</tr>
<tr>
<td>Soil 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>26.49</td>
<td>0.32</td>
</tr>
<tr>
<td>5</td>
<td>44.57</td>
<td>0.40</td>
</tr>
<tr>
<td>10</td>
<td>94.16</td>
<td>0.49</td>
</tr>
</tbody>
</table>
Table 5.
Distribution coefficients (Kd, L kg⁻¹) of GPS sorption on the soils and sediments. Errors are < 2%.

<table>
<thead>
<tr>
<th></th>
<th>pH 7</th>
<th>pH 8</th>
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<tbody>
<tr>
<td>Soil 1</td>
<td>–</td>
<td>197</td>
</tr>
<tr>
<td>Soil 2</td>
<td>–</td>
<td>200</td>
</tr>
<tr>
<td>Soil 3</td>
<td>–</td>
<td>192</td>
</tr>
<tr>
<td>Soil 4</td>
<td>–</td>
<td>213</td>
</tr>
<tr>
<td>Vibora sediment</td>
<td>404</td>
<td>67.3</td>
</tr>
<tr>
<td>Cabecera sediment</td>
<td>11,800</td>
<td>6225</td>
</tr>
<tr>
<td>Cola sediment</td>
<td>7961</td>
<td>4810</td>
</tr>
</tbody>
</table>

Table 6.
Percentages of GPS desorbed (%) for the studied sediments at pH 8.

<table>
<thead>
<tr>
<th></th>
<th>GPS initial conc. (mg L⁻¹)</th>
<th>GPS adsorbed (μmol kg⁻¹)</th>
<th>GPS desorbed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cabecera</td>
<td>0.25</td>
<td>30.83</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>96.96</td>
<td>0.97</td>
</tr>
<tr>
<td>Cola</td>
<td>0.25</td>
<td>29.90</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>95.02</td>
<td>0.60</td>
</tr>
<tr>
<td>Vibora</td>
<td>0.25</td>
<td>19.54</td>
<td>14.71</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>57.16</td>
<td>19.53</td>
</tr>
</tbody>
</table>

Table 7.
Kinetic parameters (k1, k2, tb, and DT50) obtained from glyphosate dissipation in water.

<table>
<thead>
<tr>
<th>Water</th>
<th>Kinetic model</th>
<th>K1 (days⁻¹)</th>
<th>K2 (days⁻¹)</th>
<th>tb (days⁻¹)</th>
<th>DT50 (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vibora</td>
<td>SFO</td>
<td>0.06713</td>
<td>–</td>
<td>–</td>
<td>10.3</td>
</tr>
<tr>
<td>Cabecera</td>
<td>HS</td>
<td>0.11012</td>
<td>0.00131</td>
<td>7.01</td>
<td>6.3</td>
</tr>
<tr>
<td>Cola</td>
<td>HS</td>
<td>0.10932</td>
<td>0.00637</td>
<td>11.0</td>
<td>6.4</td>
</tr>
</tbody>
</table>