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Glyphosate and AMPA distribution in wind-eroded sediment derived from loess soil☆

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ABSTRACT

Glyphosate is one of the most used herbicides in agricultural lands worldwide. Wind-eroded sediment and dust, as an environmental transport pathway of glyphosate and of its main metabolite aminomethylphosphonic acid (AMPA), can result in environmental- and human exposure far beyond the agricultural areas where it has been applied. Therefore, special attention is required to the airborne transport of glyphosate and AMPA. In this study, we investigated the behavior of glyphosate and AMPA in wind-eroded sediment by measuring their content in different size fractions (median diameters between 715 and 8 μm) of a loess soil, during a period of 28 days after glyphosate application. Granulometrical extraction was done using a wind tunnel and a Soil Fine Particle Extractor. Extractions were conducted on days 0, 3, 7, 14, 21 and 28 after glyphosate application. Results indicated that glyphosate and AMPA contents were significantly higher in the finest particle fractions (median diameters between 8 and 18 μm), and lowered significantly with the increase in particle size. However, their content remained constant when aggregates were present in the sample. Glyphosate and AMPA contents correlated positively with clay, organic matter, and silt content. The dissipation of glyphosate over time was very low, which was most probably due to the low soil moisture content of the sediment. Consequently, the formation of AMPA was also very low. The low dissipation of glyphosate in our study indicates that the risk of glyphosate transport in dry sediment to off-target areas by wind can be very high. The highest glyphosate and AMPA contents were found in the smallest soil fractions (PM_{10} and less), which are easily inhaled and, therefore, contribute to human exposure.

1. Introduction

Glyphosate (N-phosphonomethylglycine, $C_3H_8NO_5P$) is the active ingredient of many commercial formulations of herbicides extensively used worldwide for weed control. Its annual global production has been estimated at approximately 720 000 tons in 2012 (IARC, 2015). It is intensively used in agriculture, particularly in combination with genetically modified crops (GMC) that are resistant to it.

Glyphosate is a broad-spectrum, systemic, post-emergent herbicide that decays in soil mostly by microbial activity (Bento et al., 2016; Giesy et al., 2000; Schnurer et al., 2006). Its persistence in soil varies widely, with a half-life ranging between 1 and 197 days, depending on temperature, soil moisture, soil type, soil binding extent, microbial breakdown and phosphate levels (Bento et al., 2016; EU, 2002; Giesy et al., 2000; Nomura and Hilton, 1977). The main metabolic pathway of glyphosate is its degradation to aminomethylphosphonic acid (AMPA), which is more persistent in soil than glyphosate itself (half-life ranging between 23 and 958 days) (Bento et al., 2016; U.S.EPA, 1993; Yang et al., 2015a).

Glyphosate and AMPA are considered non-volatile and, therefore, their loss to the atmosphere via volatilization is considered negligible (EU, 2002; Giesy et al., 2000; U.S.EPA, 1993). However, offsite movement can occur through spray drift (Marrs et al., 1993;

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Payne, 1992; Payne et al., 1990) or by airborne particulate transport. Glyphosate and AMPA strongly adsorb to soil particles (Beltran et al., 1998; Cheah et al., 1997). However, their adsorption coefficients can vary greatly, with reported Freundlich adsorption coefficients (K_f) ranging between 93 and 2754 $\mu g^{(1-1/n)} mL^{1/n} g^{-1}$ for glyphosate and 38 and 1517 $\mu g^{(1-1/n)} mL^{1/n} g^{-1}$ for AMPA (Báez et al., 2015). The degree to which glyphosate and AMPA adsorb to soil depends mostly on soil properties such as clay content, soil phosphate content, soil aluminum and iron oxides/hydroxides, pH, and organic matter (Borggaard and Gimsing, 2008; De Jonge and De Jonge, 1999; Gimsing et al., 2004; Sprankle et al., 1975). Glyphosate and AMPA transport to off-target areas by wind erosion is, therefore, very likely. In fact, the occurrence of glyphosate and/or AMPA in the atmosphere (air and/or rain) has already been reported in some studies (Humphries et al., 2005; Messing et al., 2011; Quaghebeur et al., 2004). Since glyphosate is non-volatile and AMPA is a degradation product of glyphosate, their occurrence in the atmosphere can only be associated to spray drift (glyphosate) or transport in wind-eroded sediment (glyphosate and AMPA). Nevertheless, work on their transport by wind erosion hasn't been published so far, even though glyphosate is the most widely used herbicide worldwide.

Loess soils represent ≈10% of the global land surface and are among the most agriculturally productive soils in the world. They are present in many parts of the world such as the USA, Argentina, China and Europe. A great part of them are intensively used for agriculture and to grow GMC (den Biggelaar et al., 2001). Consequently, huge amounts of pesticides, particularly glyphosate-based herbicides, are applied every year in these soils.

Agricultural soils account for a significant source of airborne particulate matter because of wind erosion and tillage activities (Gill et al., 2006). Therefore, off-site airborne transport of glyphosate and AMPA from farmland in loess soils is extremely likely. This off-site transport is mostly associated to the finest particles (dust), which can travel over large distances. Small particles can travel from ≈500 km (particle sizes between 10 and 20 μm) to thousands of kilometers (particle sizes <10 μm) during moderate wind storms (Pye, 1987). Moreover, in a sediment sample, the largest amounts of pesticides are normally adsorbed to the fine particles (Agassi et al., 1995; O'Hara et al., 2000). Their contents in these particles can also be much higher than those in the parent topsoil (Clymo et al., 2005). The inhalation of polluted particles is strongly linked to human diseases such as asthma, heart and lung diseases, and cancer (Besancenot et al., 1997; Ichinose et al., 2005; Järup, 2003; Moorthy et al., 2015; Prüss-Ustün et al., 2011). As for glyphosate, the International Agency for Research on Cancer (IARC) classified it, in 2015, as "probably carcinogenic to humans" (IARC, 2015). Although the European Food Safety Authority (EFSA) disagreed with this evaluation, it proposed for the first time for glyphosate an acute reference dose (ARfD) of 0.5 mg kg^{-1} of body weight (bw) (EFSA, 2015). EFSA has set this same dose as an acceptable daily intake (ADI) for consumers. An acceptable operator exposure level (AOEL) of 0.1 mg kg^{-1} of bw day^{-1} has also been proposed (EFSA, 2015). It is, therefore, very important to study the transport of glyphosate and AMPA in wind-eroded sediment, particularly for fine particles (dust), which may contribute to human exposure. Risk assessment studies on human health could also benefit and improve from such information.

This study investigates the occurrence of glyphosate and AMPA in wind-eroded sediment derived from loess soil produced during wind erosion in a wind tunnel. It aims to 1) investigate the distribution of glyphosate and AMPA in different size fractions of wind-eroded sediment; 2) study the effect of several physicochemical parameters (clay, silt, organic matter) on glyphosate and AMPA transport during wind erosion; and 3) estimate the potential of glyphosate and AMPA to become transported over large distances from the pollution source.

2. Materials and methods

2.1. Soil

We used the topsoil of a silty loam loess soil from Huldenberg, Belgium. The soil was air-dried and then sieved through a 1-mm sieve. It was tested for glyphosate and AMPA residues and found free of glyphosate and AMPA.

The main soil properties of the sieved soil are shown in Table 1. Fig. 1 shows the grain size distribution of the soil after disintegration of all aggregates.

2.2. Glyphosate preparation and application in the soil

2.2.1. Preparation of glyphosate solution

Glyphosate solution was prepared by diluting 980 μL of CLINIC®, a glyphosate-based herbicide that contains 360 g L^{-1} of glyphosate, in Millipore water to achieve a final stock solution of 0.42 g L^{-1}. A concentration of glyphosate in soil of 8.4 mg kg^{-1} was used in this study, which corresponds to an application rate of 1.26 kg a.i. ha^{-1} (typically applied in agricultural fields), assuming a soil depth of 1 cm and a bulk density of 1.5 g cm^{-3}.

2.2.2. Application in soil

A plastic sheet was put on the ground and an approximately 5-cm thin layer of the air-dried and sieved soil (42 kg) was spread on it. The soil was then sprayed with the prepared glyphosate solution (see Section 2.2.1). During the application, the soil was thoroughly mixed with a rake. The soil was then stored in a plastic bag at room temperature (22 °C) and dark conditions.

A small portion of the soil was collected after glyphosate application and oven-dried (105 °C) for 24 h to determine the initial soil moisture content, which was found to be 5.4% (w/w).

2.3. Facilities and instrumentation

The experiment was carried out in the facilities of the Geography and Tourism Research Group of the Katholieke Universiteit Leuven, Belgium. A closed-return wind tunnel was used. The tunnel has two test sections, both of which were used in this study. The dimensions of the large test section are 760 cm (length) x 120 cm (width) x 60 cm (height), and those of the small test section are 150 cm (length) x 35 cm (width) x 30 cm (height). A detailed description of the wind tunnel can be found in the technical report by Goossens and Offer (1988); a scheme of the tunnel is shown in Fig. 2a.

Table 1
Soil properties of the loess soil used in this study.

Parameters	Value
Particle size distribution:	
<2 μm (clay) (%)	10
2–50 μm (silt) (%)	79
>50 μm (sand) (%)	11
pH $CaCl_2$	5.8
Organic matter (OM) (%)	3.2
Particle density (g cm^{-3})	2.5
N total (g kg^{-1})	1.7
P available (mg kg^{-1})	0.4
K available (mg kg^{-1})	209
Mg available (mg kg^{-1})	121
Na available (mg kg^{-1})	10
C/N ratio	9