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Distribution of glyphosate and aminomethylphosphonic acid (AMPA) in agricultural topsoils of the European Union

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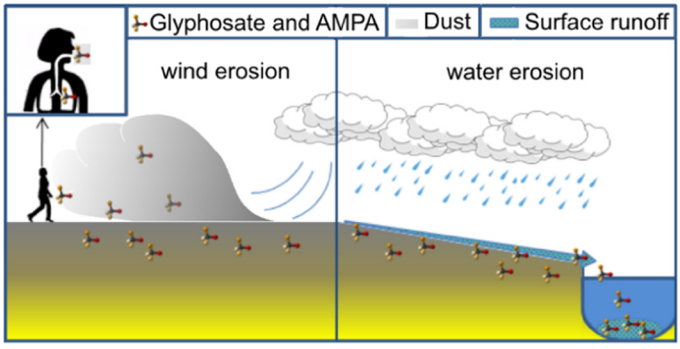
HIGHLIGHTS

- Data on occurrence and levels of glyphosate residues in EU soils is very limited.
- Glyphosate and its metabolite AMPA were tested in 317 EU agricultural topsoils.
- 21% of the tested EU topsoils contained glyphosate, and 42% contained AMPA.
- Both glyphosate and AMPA had a maximum concentration in soil of 2 mg kg^{-1}.
- Some contaminated soils are in areas highly susceptible to water and wind erosion.

GRAPHICAL ABSTRACT



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ABSTRACT

Approval for glyphosate-based herbicides in the European Union (EU) is under intense debate due to concern about their effects on the environment and human health. The occurrence of glyphosate residues in European water bodies is rather well documented whereas only few, fragmented and outdated information is available for European soils. We provide the first large-scale assessment of distribution (occurrence and concentrations) of glyphosate and its main metabolite aminomethylphosphonic acid (AMPA) in EU agricultural topsoils, and estimate their potential spreading by wind and water erosion. Glyphosate and/or AMPA were present in 45% of the topsoils collected, originating from eleven countries and six crop systems, with a maximum concentration of 2 mg kg^{-1}. Several glyphosate and AMPA hotspots were identified across the EU. Soil loss rates (obtained from recently derived European maps) were used to estimate the potential export of glyphosate and AMPA by wind and water erosion. The estimated exports, result of a conceptually simple model, clearly indicate that particulate transport can contribute to human and environmental exposure to herbicide residues. Residue threshold values in soils are urgently needed to define potential risks for soil health and off site effects related to export by wind and water erosion.

1. Introduction

Glyphosate (*N*-phosphonomethylglycine), the active substance in glyphosate-based herbicides (GlyBH), is up for renewal in the

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European Union (EU) as an ingredient in Plant Protection Products. All the active substances approved by the European Commission are re-evaluated after a certain period of time and the authorization for its use must be renewed for selling and application again. Within this context, an important prerequisite is that glyphosate should not adversely affect the environment and human and animal health (EC, 2009). Currently, there is strong debate about the potential harmfulness of glyphosate (e.g., EFSA, 2015; IARC, 2015; Myers et al., 2016), with some studies associating its use with cancer and endocrine disruption in humans and acute and chronic toxicity to aquatic species (Annett et al., 2014; Gasnier et al., 2009; Guyton et al., 2015; Mesnage et al., 2015; Thongprakaisang et al., 2013). The European Chemical Agency (ECHA) prepared a scientific opinion on the harmonized classification of glyphosate (ECHA, 2017), to be used as a decision base by the European Commission. According to ECHA (2017), glyphosate is not proven to be carcinogenic, mutagenic or to negatively affect reproduction (e.g., reduction of fertility or occurrence of malformations), but it can cause serious eye damage and exert toxicity on aquatic biota, with long-lasting effects. ECHA's opinion is based on evaluating only glyphosate's hazardous properties, not addressing its levels in the different environmental compartments (atmosphere, aquatic and terrestrial ecosystems) or the likelihood of exposure and associated risks for humans and wildlife. Hazardous properties, potential exposure and risks of glyphosate's main metabolite aminomethylphosphonic acid (AMPA) have not been considered in the ECHA study at all.

GlyBH are intensively applied to agricultural fields, before planting the crop, pre- or post-harvest, in both conventional and reduced/no-till farming, to control the growth of annual and perennial weeds. Minor non-agricultural applications (<10% of global GlyBH use) include weed control in railway lines, parks and home gardens. The large fields of genetically modified soybeans, maize, canola, cotton and corn tolerant to glyphosate in the USA, Argentina and Brazil strongly contribute to the high amounts of GlyBH applied every year worldwide (Benbrook, 2016). In Europe, where no genetically modified crops are used, GlyBH are mainly applied to cereals (wheat, rye, triticale, barley and oats), oilseeds (rapeseed, mustard seed and linseed) and orchards and vineyards. Here GlyBH are usually applied one (cereals and oilseeds) to three times a year (orchard crops and vines), at recommended rates between 0.72 and 2.88 kg glyphosate ha^{-1} per treatment, and at a maximum annual application rate of 4.32 kg glyphosate ha^{-1} (EFSA, 2013, 2015).

Numerous laboratory and field studies have been performed to investigate glyphosate and/or AMPA behavior in more detail, especially their transport to the aquatic environment (Al-Rajab and Hakami, 2014; Borggaard and Gimsing, 2008; Daouk et al., 2013; Laitinen et al., 2006, 2009) indicating some recognition and concern that these substances can move towards surface waters. At the same time, glyphosate and AMPA are only sporadically detected in deep groundwater systems and at low concentrations (Battaglin et al., 2014; Horth, 2012; Poiger et al., 2017) indicating that the leaching of these compounds is generally unlikely and probably negligible. Although GlyBH use is almost limited to terrestrial application, information regarding occurrence and cumulative and/or background levels of glyphosate residues in soils have received less attention, especially at the European scale. In fact, despite some recent studies on the distribution of glyphosate and AMPA in soils from Argentina (e.g., Aparicio et al., 2013; Lupi et al., 2015; Primost et al., 2017), U.S.A. (e.g., Battaglin et al., 2014; Scribner et al., 2007) or Australia (e.g., Todorovic et al., 2013), in Europe, where the approval for GlyBH use will be decided by the end of 2017, information on occurrence and levels of these substances in soil is still very limited and out of date (Grunewald et al., 2001; Laitinen et al., 2006, 2007, 2009). The European long term use of GlyBH, as the most sold herbicide in Europe, urgently require monitoring of residues in agricultural soils.

The lack of information on soil residues prevents proper evaluation of on-site soil pollution and proper risk estimation of potential particulate transport of these compounds by soil erosion processes to surrounding environments. Therefore, the main objective of this study is to evaluate the distribution (occurrence and concentrations) of glyphosate and its main metabolite AMPA in several agricultural topsoils across the EU, covering different locations and crop systems. Concentration data were also used for estimating potential export rates of these compounds by wind and water erosion, based on recently derived European soil loss maps (Borrelli et al., 2017; Panagos et al., 2015).

2. Materials and methods

2.1. The soil samples

Glyphosate and AMPA distributions were assessed in 317 topsoil samples: 300 samples from the LUCAS 2015 survey – Land Use/Cover Area Frame Survey, a harmonized assessment of topsoil characteristics across EU Member States (Toth et al., 2013), and 17 samples from three independent vineyards in north-central Portugal, where a parallel study on transport of pesticide residues by water erosion was conducted (Zuilhof, 2016).

The samples from the LUCAS 2015 survey were collected between April and October of 2015 as described in ESTAT (2015a), and represent the uppermost 15/20 cm of soil. The samples selected for this work followed two main criteria: they were collected in i) the countries of each EU region with the highest percentage of agricultural area and pesticide use per hectare of arable and permanent croplands (FAO, 2013, 2014) and ii) the crops with the highest pesticide use per hectare or highest extension of cultivated area in those countries (Muthmann, 2007). Pesticide use included, but was not restricted to, GlyBH use since other pesticide residues were also analyzed in the samples. These sample selection criteria provide a worst-case estimate of distribution of multiple pesticide residues in EU agricultural topsoils.

The countries selected by EU region were, from largest to smallest in order of pesticide use per hectare, in the northern region: United Kingdom (UK) and Denmark (DK); southern region: Italy (IT), Greece (EL) and Spain (ES); eastern region: Hungary (HU) and Poland (PL); western region: The Netherlands (NL), France (FR) and Germany (DE). The crops selected were: cereals (wheat, barley, rye, maize, triticale, oats), root crops (potatoes, sugar beet), non-permanent industrial crops (sunflower, rapeseed), dry pulses and fodder crops (floriculture, alfalfa, temporary grassland), permanent crops (citrus, vines, olives, other fruit trees and berries), vegetables (tomatoes, other fresh vegetables). Additionally, some bare soils which were croplands in the previous LUCAS 2009 and 2012 surveys were included in the category others. The exhaustive list of crops within each LUCAS category is available in (ESTAT, 2015b). Not all the crops of each category were covered by the samples selected for this study; the covered ones are listed between brackets. Preference was then given to samples having the same land cover in previous LUCAS surveys and from different regions. All EU Member States are subdivided into regions, according to the Nomenclature of Territorial Units for Statistics (NUTS) classification, to ensure comparable regional statistics. The NUTS classification includes three hierarchical levels: NUTS 1 - major socio-economic regions, NUTS 2 - basic regions for the application of regional policies, and NUTS 3 - small regions for specific diagnoses (EUROSTAT, 2015). In this study, results are presented for basic regions (NUTS 2), defined according the NUTS 2013 classification. The distribution of samples by country, NUTS 2 region and crop system is present in Table S1.

The samples from the LUCAS 2015 survey were air dried and stored in the Joint Research Centre (JRC) installations in Ispra, Italy. The 300 LUCAS samples selected for this study were homogenized (by stirring the soil with a spoon until obtain a visually homogeneous sample) and sub-samples (of approximately 50 g dry weight) were collected for pesticide analysis. The sub-samples were sieved with a 2-mm sieve and frozen until chemical analysis. The Portuguese (PT) soil samples were collected in September of 2015, also following method described

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in ESTAT (2015a), and treated as the LUCAS (sub-)samples, i.e. air dried, 2-mm sieved and frozen until chemical analysis.

2.2. Glyphosate and AMPA analysis

The day before the analytical determinations, the soil samples were thawed and homogenized as described above for the selected LUCAS samples. Two aliquots of 2 g were collected from each sample. Glyphosate and AMPA concentrations were determined in the aliquots through HPLC-MS/MS using the same extraction and derivatisation method (see the Supporting Information for full details), chemicals, mobile phases, column characteristics and instrumentation conditions as described in Bento et al. (2016) and Yang et al. (2015).

All the validation parameters and quality control criteria were in line with those described in the guidance document for pesticides residues analysis in food and feed (EC, 2015). Briefly, glyphosate and AMPA analytes were identified according to the retention time and peak shape of isotopically-labelled internal standards, glyphosate (1,2-^{13}C, ^{15}N) and AMPA (^{13}C, ^{15}N). Two transitions were measured by analyte [the quantification (Qn) and confirmation transitions (Ql)], and all positive results/samples presented an ion ratio of the two transitions within ±30% of the mean ion ratio of the solvent standards. The responses of the analytes were normalized according to the response of the isotopically-labelled internal standards. Glyphosate and AMPA concentrations were calculated based on one-point calibration, the solvent standard of 0.1 μg mL^{-1}, which analyzed every 10–15 injections/samples. A calibration curve (of the solvent standards 0, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5,1 and 2 μg mL^{-1}) was injected at the start, middle and end of the sample sequences. All calibration curves presented satisfactory linearity of response versus concentration, with correlation coefficients ≥0.99 and individual residuals within ±20%. Blank soil standards fortified with a mixture of glyphosate and AMPA standards (0.25 μg g^{-1}) presented a recovery of both analytes between 70 and 120%. Similar recovery values (75–120%) were observed in soil samples fortified with the same mixture of glyphosate and AMPA standards (a third aliquot was prepared from approximately 10% of the soil samples). The concentration of glyphosate and AMPA measured in each of the two aliquots (replicates) collected per sample was typically within ±30%, and always within ±35%, the mean concentration of both aliquots. The mean concentrations of glyphosate and AMPA of aliquots were adopted as the concentrations of the sample.

The limit of detection (LoD) of glyphosate and AMPA were 0.02 and 0.03 mg kg^{-1}, respectively, while the limit of quantification (LoQ) of both compounds was 0.05 mg kg^{-1}.

2.3. Data analysis

Only measurements/samples with glyphosate or AMPA (≥ the LoQ 0.05 mg kg^{-1}) were considered in data analysis.

Distribution of the concentrations of glyphosate and AMPA in the soils was presented in box-and-whisker plots per country and crop systems. Normality and homogeneity of variances of glyphosate and AMPA concentrations were tested with, respectively, Shapiro-Wilk W and Levine's tests. As the parametric assumptions were not met, even after log, ln, square root or arcsine transformation, differences among EU regions, countries and crop systems were tested with Kruskal-Wallis H tests. At the presence of significant differences ($p < 0.05$), Pairwise Mann-Witney *U* test with Bonferroni corrections were performed to test differences between each two EU regions, countries or crop systems. The box-and-whisker plots and the statistical analyses were performed using SPSS 22.0.

Wind erosion rates in European agricultural soils were estimated by Borrelli et al. (2017) using a GIS version of the Revised Wind Erosion Equation model (GIS-RWEQ) while Panagos et al. (2015) used a modified version of the Revised Universal Soil Loss Equation (RUSLE) model to estimate water erosion rates in Europe. The complete wind and water erosion datasets are available via the European Soil Data Centre (ESDAC, 2017). Glyphosate and AMPA concentration data is represented at the basic region NUTS2 level and not on exact locations due to privacy issues, and plotted together with erosion rates (although the different time scales; the erosion maps are annual maps and the soil samples were from a single time point) to indicate immediately if high concentrations in soil appear in areas vulnerable to wind and water erosion, to present a first idea of the dimension of the potential problem which was relevant to be further studied. Since the application pattern of GlyBH in croplands is similar each year, it is expected that concentration data is representative of a normal, recurrent soil situation. The maps of frequency of detection and maximum concentration of glyphosate and AMPA by NUTS 2 region were produced in ArcGIS 10.4.1.

To estimate the potential export of glyphosate and AMPA to other locations, glyphosate and AMPA concentrations in topsoils were multiplied by the potential annual soil loss rates from wind and water erosion at the sample collection points (extracted with ArcGIS from soil loss by wind and water erosion datasets). Export values were obtain for individual soil sampling points, if glyphosate or AMPA concentration in soil ≥0.05 mg kg^{-1} and there was a risk of wind or water erosion >-0 Mg ha^{-1} year^{-1}. Export rates of individual soil sampling points were then aggregated by (i) content of residues in soil, i.e. low to medium (defined in this study as 0.05–0.5 mg kg^{-1}) or high glyphosate or AMPA contents (>0.5 mg kg^{-1}), (ii) EU region, (iii) country, (iv) NUTS 2 region and (v) crop system. The threshold of 0.5 mg kg^{-1} used in this work corresponds to the 80th and 85th percentile of glyphosate and AMPA overall concentrations, respectively.

The proportion of AMPA to glyphosate in soil was determined for each sample containing glyphosate and/or AMPA (≥0.05 mg kg^{-1}), as the ratio of AMPA concentration in soil to the combined glyphosate and AMPA concentration in the soil, [AMPA / (Glyphosate + AMPA)] * 100.

3. Results and discussion

3.1. Overall distribution of glyphosate and AMPA in topsoils

Glyphosate and/or AMPA were present (≥0.05 mg kg^{-1}) in nearly half (45%) of the soil samples, with 18% of the tested soils containing both compounds. AMPA was the predominant form, being present in 42% of the soils while glyphosate was present in 21%. Both compounds were present at higher frequencies in northern soils, while eastern and southern regions generally had the most glyphosate- and AMPA-free soils (<0.05 mg kg^{-1}), respectively. At national levels, the frequency of soils with glyphosate ranged from 7% in Poland to 53% in Portugal, while the frequency of soils with AMPA ranged from 17% in Italy and Greece to 80% in Denmark (Fig. 1A and Table S2). Samples from permanent crops and root crops had the highest frequency of soils with glyphosate and AMPA (30 and 52%, respectively), and dry pulses and fodder crops the lowest for both compounds (5 and 29%, respectively, see Fig. 1B and Table S2).

The highest concentrations of glyphosate and AMPA in soil were observed in southern parts of the EU (Fig. 1C and Table S2), suggesting higher application rates of GlyBH in this region. Nevertheless, only concentrations of glyphosate were significantly higher in this region [glyphosate: Kruskal-Wallis (H) = 3.03, degrees of freedom (df) = 3, $p < 0.001$, $n = 67$; AMPA: $H = 20.50$, $df = 3$, $p = 0.387$, $n = 133$]. Soils from southern parts of the EU also presented the lowest proportion of AMPA (Table S2), suggesting more recent GlyBH applications and/or slower degradation of glyphosate into AMPA under drier conditions. Portuguese topsoils (all from vineyards) presented significantly higher amounts of glyphosate ($H = 31.97$, $df = 10$, $p < 0.001$, $n = 67$) and AMPA ($H = 27.73$, $df = 10$, $p = 0.02$, $n = 133$) than the other countries, with both compounds reaching concentrations as high as 2 mg kg^{-1} (Fig. 1 and Table S2). NUTS 2 regions such as FR71, EL51, NL23, ES24 or ITC4 seem to contain low herbicide residues or be residue free

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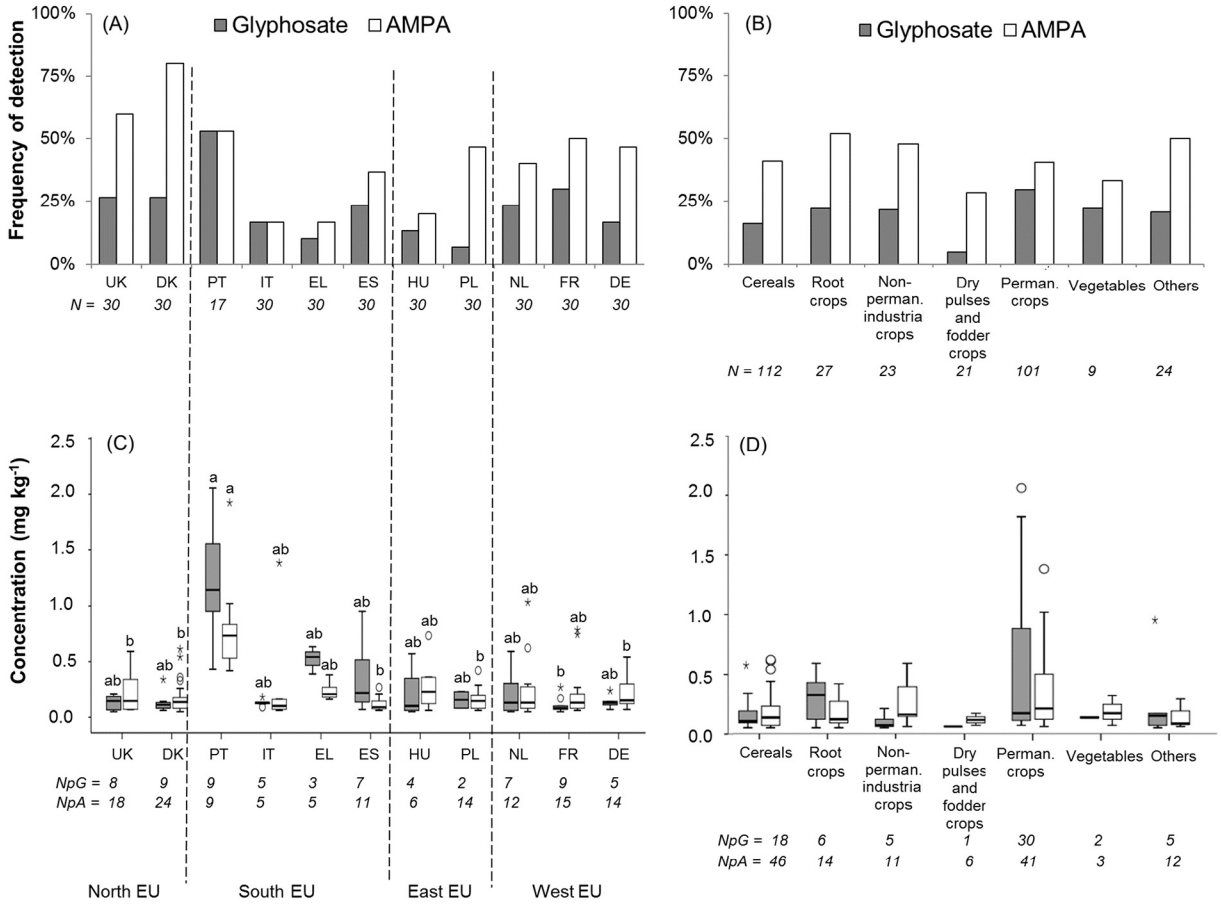

Fig. 1. Overall distribution of glyphosate and AMPA in EU topsoils (0–15/20 cm). Frequency of detection of glyphosate and AMPA (≥0.05 mg kg^{-1}) in soils from different (A) EU countries and (B) crop systems. Box-and-whisker plot representation of the distribution of glyphosate and AMPA contents in soils by the same factors: (C) country and (D) crop system. Only measurements ≥0.05 mg kg^{-1} were considered in the box-and-whisker plots. Each box represents the 25th percentile, median and 75th percentile. Whiskers represent 1.5 times the interquartile range or minimum and maximum concentrations of glyphosate or AMPA. Outliers (1.5–3 times the interquartile range) are marked with points and extreme outliers (>3 times the interquartile range) with asterisks. Different letters represent significant differences [($p < 0.05$): a > b] in glyphosate or AMPA concentrations between countries or crop systems. N – number of samples tested, Np = number of positive samples ≥0.05 mg kg^{-1}, G – glyphosate, A – AMPA.

(<0.05 mg kg^{-1}). Other NUTS 2 regions, including DK04, HU10, ES62, PT16 and ITH1, appear to have hotspots of glyphosate and/or AMPA contamination (>0.5 mg kg^{-1}; Fig. 2 and Table S3).

Glyphosate and AMPA contents in soil were highest under permanent crops and lowest with dry pulses and fodder crops (Fig. 1D and Table S2), yet no significant effect of the crop system was observed (glyphosate: $H = 10.29$, $df = 6$, $p = 0.113$, $n = 67$; AMPA: $H = 11.57$, $df = 6$, $p = 0.72$, $n = 133$). Vineyards presented the highest concentrations of glyphosate, yet at lower levels than those expected in soils of this crop, with maximum predicted environmental concentration (PEC) of 3.06–4.60 mg kg^{-1}. On the other hand, the measured glyphosate concentrations in cereals occasionally exceed the respective maximum PEC value of 0.30 mg kg^{-1} (EFSA, 2013). Maximum PEC values for AMPA, of 3.08–6.18 mg kg^{-1}, available only for the worst case scenario of a single application of 4.32 kg glyphosate ha^{-1}, were never been exceeded. Discrepancies between field measured concentrations and maximum PEC values probably result of an application regime by the farmers different from the recommended (in terms of number of treatments and on the amounts applied), of the growth stage (and interception) of the crop or of different edaphic, management or environmental conditions. In the calculation of PEC values, a worst case interception of 90 (cereals) and 0% (orchards and vineyards), a fixed bulk density of 1.5 g cm^{-3}, a tillage depth of 5 cm (permanent crops) or of 20 cm (annual crops) and a half-life time (DT_{50}) of 143.3 days for glyphosate and of 514.9 days AMPA are assumed (EFSA, 2013).

3.2. Off-site transport by wind and water erosion

In areas with low to medium glyphosate or AMPA contents in soil (0.05–0.5 mg kg^{-1}), estimated glyphosate and AMPA removal by wind erosion reaches 1941 mg ha^{-1} $year^{-1}$, while in areas with contents >0.50 mg kg^{-1} it could exceed 3000 mg ha^{-1} $year^{-1}$. Water erosion could lead to higher potential losses/exports of glyphosate and AMPA, with estimated maximum exports of 9753 mg ha^{-1} $year^{-1}$ in soils with low to medium herbicide contents, and of 47,667 mg ha^{-1} $year^{-1}$ in soils with higher contents (Fig. 3A and Tables S4 and S5). The highest export potentials are observed in Southern parts of the EU (Fig. 3B and Tables S4–S7), in areas highly vulnerable to water erosion. Different crop systems, with different soil covers, lead to different transport potentials of glyphosate and AMPA: non-permanent industrial crops and root crops show the highest potential exports through wind erosion, while permanent crops and cereals present the highest exports through water erosion (Fig. 3C and Tables S4 and S5).

A ratio between these potential exports and the typical GlyBH application rates (the exact application rates in the soil sampling points are not known) could provide an indication of the % of the initially applied products lost by erosion processes, potentially reaching water systems and atmosphere. The highest estimated potential export of glyphosate by water erosion (5715 mg ha^{-1} $year^{-1}$; Table S4), for example, would correspond to loss 0.13% of the recommended maximum application rate of 4.32 kg glyphosate ha^{-1} $year^{-1}$. As only glyphosate is

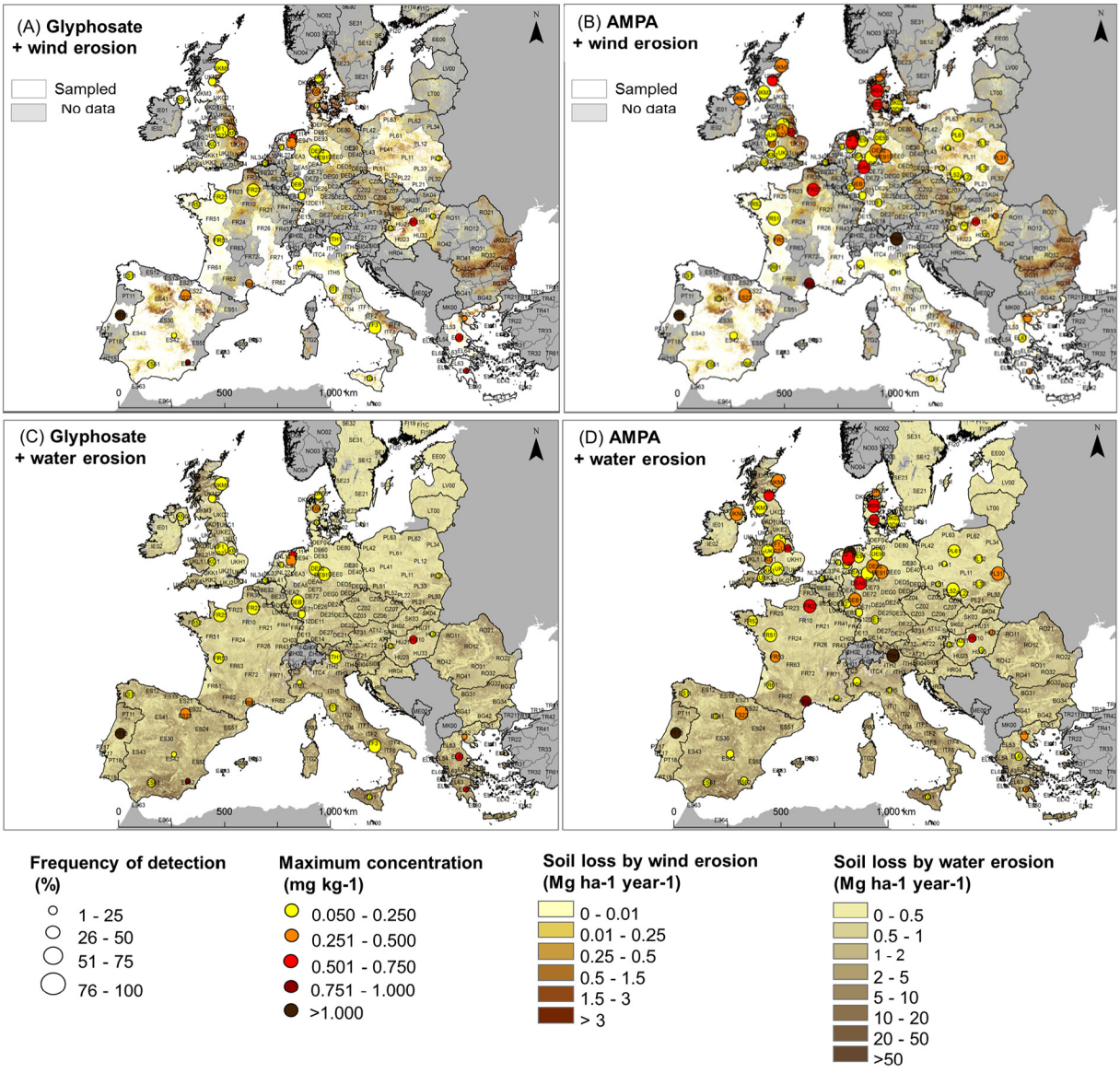

Fig. 2. Frequency of detection of glyphosate and AMPA (≥ 0.05 mg kg^{-1}) and respective maximum concentrations (mg kg^{-1}) in EU agricultural topsoils (0–15/20 cm) by NUTS 2 region, imposed on maps of soil loss by wind [Panel A (glyphosate)/Panel B (AMPA)] and water [Panel C (glyphosate)/Panel D (AMPA)] erosion (Mg ha^{-1} $year^{-1}$). Circles in a NUTS 2 region indicate at least one soil sample containing glyphosate or AMPA (≥ 0.05 mg kg^{-1}).

applied to fields, no ratio can be calculated for AMPA, the most common compound in soils. Furthermore, such ratio can led to misleading results because glyphosate and AMPA are persistent compounds in soil, and their concentrations in soil (the ones used to estimate the potential exports by wind and water erosion) often result of more than one year of treatments. Therefore, the ratio should consider not only the amount applied but also the amount accumulated from previous treatments.

Recent experimental and monitoring studies confirm wind-driven transport of glyphosate and AMPA (Bento et al., 2017; Farenhorst et al., 2015; Lamprea and Ruban, 2011; Quaghebeur et al., 2004). Bento et al. (2017) demonstrated in a wind tunnel experiment that contents of AMPA and especially of glyphosate were particularly high (respectively >0.6 and >15 μg g^{-1}) in the finest soil particle fractions (<10 μm), which can be inhaled by humans directly. In addition, both glyphosate and AMPA were often (>50%) detected in air samples collected from agricultural areas in the U.S.A, reaching concentrations of respectively 9.1 and 0.97 ng m^{-3} (Chang et al., 2011). The presence of glyphosate in atmosphere can result of spray drift during the application and/or wind erosion of contaminated soil particles. However, for AMPA, which is formed in soil, wind erosion is the only source. The contribution of wind erosion to the atmospheric concentration of glyphosate is still unknown. In a comprehensive environmental survey conducted in the U.S.A., Battaglin et al. (2014) observed the presence of glyphosate and AMPA in over 70% of the precipitation samples analyzed, at maximum concentrations of respectively 2.5 and 0.5 μg L^{-1}. In Europe, lower frequencies of detection are reported, with glyphosate and AMPA present in respectively 10 and 13% of the rainwater samples, but with higher maximum concentrations, 6.2 and 1.2 μg L^{-1}, respectively (Quaghebeur et al., 2004). Glyphosate is supposed to degrade rapidly in the atmosphere by photochemical oxidative degradation (EFSA, 2013), but the results from air and rain analyses indicate that glyphosate and AMPA can persist in the atmosphere and can be washed out and redistributed by rain (wet deposition).

Particulate transport via water erosion is an important pathway for glyphosate and AMPA towards surface water bodies (Todorovic et al., 2014; Yang et al., 2015). In fact, after a 60 min rain simulation at a rain intensity of 1 mm min^{-1}, Yang et al. (2015) observed that 4–5% of the initially applied glyphosate was lost/transported by runoff in the dissolved phase while 8–11% of the applied glyphosate was transported by the suspended load. Glyphosate and AMPA are

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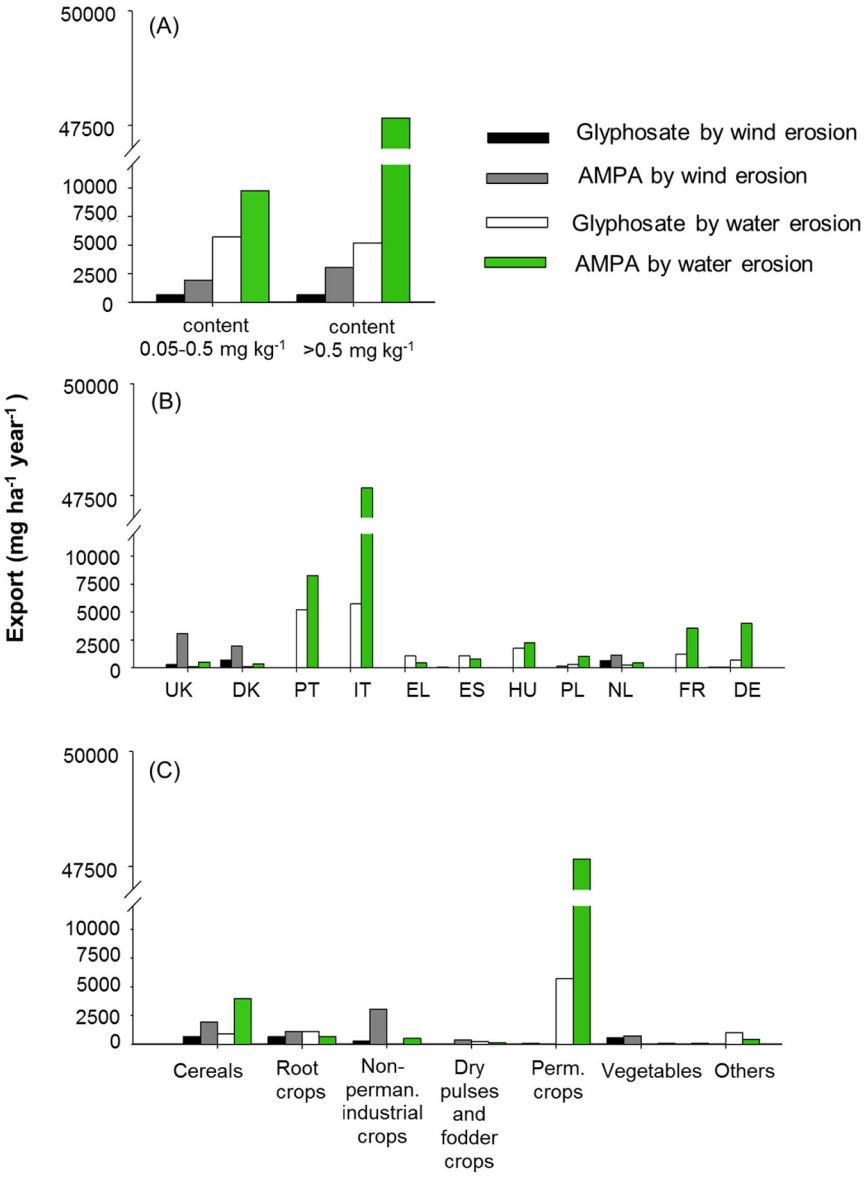

Fig. 3. Potential export of glyphosate and AMPA by wind and water erosion. Maximum export estimations according to (A) glyphosate or AMPA content in topsoil, (B) country and (C) crop system. Perm. – Permanent.

frequently detected in U.S. large rivers (53–89%, respectively), streams (53–72%, respectively), lakes, ponds and wetlands (34–30%, respectively) at maximum levels of respectively 300 and 48 μg L^{-1} (Battaglin et al., 2014). In Europe, glyphosate and AMPA have been analyzed in respectively 75,350 and 57,112 surface water samples, and detected in 33% and 54% of the samples at levels up to 370 μg L^{-1} and >200 μg L^{-1} (Horth, 2012). Correlations between these concentrations in waters and the concentrations measured in this study in soils would be too speculative given the different time collection and location between the information that is available for glyphosate in streams and the soil samples analyzed for this study. However, the spatial relationship between erosion rates and pesticide distribution in soils and water bodies should be further explored. Particulate transport processes are particularly important for the off-site transport of pesticides strongly adsorbed to soil particles, just like glyphosate and AMPA. Quantification of the extent of transport off the field to surface waters (or to the atmosphere) should be explored, too. It should be noted that current EU legislation presents environmental quality standards in the field of water policy for only some pesticides, not including glyphosate or AMPA (EC, 2013).

3.3. Implications for exposure and risk assessment

Within the context of this study, some considerations can be made. First, soil samples used in this study were collected during the spring and summer of 2015. No information is available regarding prior GlyBH application dates and rates per sample location, indicating that the 317 samples represent a mixture of real-field conditions, ranging from samples with no trace of glyphosate and/or AMPA to samples with very high levels. Despite the European Commission (EC) recommendations on the frequency of treatments and application rates, information on the actual use/sales of GlyBH in the EU, or of the active substance glyphosate, is not available and the amounts applied per crop system is confidential in almost all countries (Muthmann, 2007). The half-life times of glyphosate and AMPA, also of importance in the respect of the amounts found in soils, are highly variable, ranging from a few days up to one or two years, depending on edaphic and environmental conditions, namely temperature and soil moisture (Bento et al., 2016; EFSA, 2013). AMPA is more persistent than glyphosate, and the degradation of both compounds is slower at colder

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and dryer conditions (Bento et al., 2016). The drier soils in southern EU might then explain the lower AMPA propotion found there.

Second, it is well-known that glyphosate and AMPA strongly adsorb and accumulate in the top centimeter(s) of soils (Laitinen et al., 2006; Okada et al., 2016; Yang et al., 2015). As glyphosate and AMPA contents determined in this study are average values for entire topsoil layers up to 15/20 cm depth (a consequence of using topsoil samples from an already established survey), actual contents in the surface layer could be higher than the determined average, implying that the presented potential erosion-driven transport rates of glyphosate and AMPA could be underestimated. The distribution of glyphosate and AMPA at the surface layer (the region most prone to soil erosion) and within topsoil should be considered in future work and should cover different soil management practices, as tillage results in the incorporation/redistribution of contaminants accumulated in surface into deeper layers.

Third, pesticide residue transported by wind and water erosion do not necessarily end up in the atmosphere and surface water systems alone; other land and even ocean regions can be reached by such phenomena, with deposition of transported compounds as a result (DeSutter et al., 1998; Mercurio et al., 2014). This stresses the need for better monitoring of the occurrence and spatial distribution of glyphosate and AMPA across the interlinked environmental domains of soil, water and air.

Fourth, from a regulatory and legislation perspective, greater effort is needed to more thoroughly assess glyphosate and AMPA contents in soils, to define critical limits to protect soil quality and soil biodiversity, and to minimize the risk of further distribution of these compounds by wind and water erosion. Some EU countries have legislation and screening values for pesticide residues in soil but they are mainly limited to persistent organochloride pesticides (Carlon, 2007). Air quality monitoring programs should also target pesticide residues in transported soil dust, in particular glyphosate and AMPA, and the potential risk of inhalation by humans.

Finally, despite its limitations, the results of this study are concerning; high levels of glyphosate and of its main metabolite AMPA have been often detected in agricultural soils across the EU. The presence of glyphosate and AMPA in agricultural soils may not only form a risk for soil health but also a potential risk of further spreading of these compounds across land, water, and air domains. Indeed, besides potential effects on local edaphic communities and on humans, that can be exposed to these substances by inhalation of contaminated dust particles, dermal contact or ingestion of contaminated surface water, wind and water erosion have the potential to transport contaminants to all the environmental compartments: atmosphere, other soils and surface waters. This information should be fully accounted for in reconsidering approval and use of GlyBH. Additional efforts should be made to fully quantify the extent of soil contamination by glyphosate residues in agricultural soils worldwide, and to assess the related risk for humans and the environment.

Author information

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at https://doi.org/10.1016/j.scitotenv.2017.10.093.

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