



Glyphosate and Aminomethylphosphonic acid (AMPA) contents in the respirable dust emitted by an agricultural soil of the central semiarid region of Argentina



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1. Introduction

Wind erosion, tillage, and driving on agricultural soils generate airborne dust, which affects the environment in a variety of ways. One environmental issue in the semiarid Pampas of Argentina and elsewhere is the possible accumulation of glyphosate [N-(phosphonomethyl) glycine] in the dust emitted by agricultural soils. This is because this herbicide is, according to the International Agency for Research on Cancer (IARC), classified as “probably carcinogenic to humans” (IARC, 2015) and thousand tons of glyphosate-based herbicides are applied to produce genetically modified crops in Argentina (Kleffmann Group, 2014; Lupi et al., 2015). Glyphosate is a small molecule with three polar functional groups (carboxyl, amino and phosphonate groups), that can be strongly sorbed by soil colloids (Sheals et al., 2002; Gimsing et al., 2007). Studies have shown that the half-life times of glyphosate in the soil ranges from few days to 1000 (Borggaard and Gimsing, 2008, Bento et al., 2016). The main metabolic pathway of glyphosate is its microbial degradation to aminomethylphosphonic acid (AMPA), which is more persistent in soils than glyphosate (Bento et al., 2016).

Glyphosate is accumulated in the soil when it is sorbed by soil compounds like clays, phosphates, organic matter (OM), aluminum- and iron oxides, which reduces its microbial degradation (Gimsing et al., 2004; Vereecken, 2005; Borggaard and Gimsing, 2008). However, the role of some soil compounds like the OM and clay on sorption is ambiguous. Whereas some studies have shown that it is not related to OM contents (Gimsing et al., 2004; Borggaard and Gimsing, 2008) a recent research showed that glyphosate can easily react with OM, promoting its accumulation in the soil (Gros et al., 2017). According to Gimsing et al. (2004) sorption of glyphosate is not related to soil clay contents, but Okada et al. (2016) demonstrated that it is influenced by clay contents in silty clay-loam- and silty-loam soils of different regions of Argentina. The high variability and uncertainty regarding glyphosate sorption and degradation in the soil make difficult to draw clear and

unambiguous decisions about glyphosate behavior in the soil (Borggaard and Gimsing, 2008).

Glyphosate and AMPA were already detected in groundwater and water streams in Argentina (Aparicio et al., 2013), as well as in the dust emitted from wind eroded agricultural soils of Argentina and Belgium (Aparicio et al., 2014; Bento et al., 2017). To our knowledge, there are no glyphosate concentration measurements in the respirable dust emitted by the soils and its different aggregate-size fractions. This fact is critical because tillage operations destroy the whole soil, being possible the emission from all aggregate-size fractions; and in the wind erosion events aggregates finer than 0.84 mm are mobilized (Mendez et al., 2015). The aim of this study was to determine, for an agricultural soil of the central semiarid region of Argentina, the concentrations of glyphosate and AMPA in the respirable dust emitted by the bulk soil and its aggregate-size fractions. In addition, we explored if the content of glyphosate in the respirable dust was related to the OM and clay.

2. Material and methods

Three undisturbed topsoil samples (3 cm), each composed by five sub-samples, were randomly taken from a 25 ha field placed in the Faculty of Agronomy of the University of La Pampa (S36° 46'; W64° 16'; 210 m.a.s.l.) (Fig. 1). Each subsample was collected in 0.5 m wide-, 1 m long- and 3 cm depth trails, weighing approximately 13 kg. The sampled soil was a fine sandy-loam Entic Haplustoll with an A-AC-C-Ck horizon sequence, with 8.1% clay, 13.3% silt, 78.6% sand and 1.7% organic matter (OM). Soil sampling was done on November 15, 2015, 1 year after the last glyphosate application in the experimental plot (Table 1). No glyphosate was applied to the fields surrounding the experimental plot, which ensures that glyphosate drift from such sources did not happen. Weed control and seedbed preparation were made by plowing with a disker on October 10, 2015. This produced a flat soil surface at the sampling time (Fig. 1).

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Fig. 1. a) Experimental plot and surrounding plots b) photo of the experimental plot at the sampling time.

Table 1
Glyphosate spray record in the experimental plot two years before sampling date (November 15, 2015).

Plot	Date	Glyphosate dose kg a.i. ha ⁻¹
Experimental plot	26-Nov-2013	1.39
	27-Aug-2014	0.42
	11-Nov-2014	1.08
	23-Nov-2014	0.79

The way that samples were obtained and analyzed is schematized in Fig. 2. The undisturbed soil samples were carefully transported from the plot to the lab, avoiding the destruction of the aggregates. Soil samples were air dried and split in two parts, one of them was sieved by 2 mm (bulk soil) and the other one sieved with a rotary sieve (Chepil, 1942) in order to separate the following aggregate-size fractions: < 0.42 mm, 0.42 to 0.84 mm, 0.84 to 2 mm, 2 to 6.4 mm, 6.4 to 19.2 mm, and >

19.2 mm. Disaggregation occurred during sieving was low and only well-preserved aggregates were used for generating dust with the Easy Dust Generator. From now on, the samples corresponding to the bulk soil and each aggregate-size fraction will be denominated “Source”.

An electrostatic precipitator (C & L model number GH-939) coupled to the Easy Dust Generator (EDG, Mendez et al., 2013) was used to generate and collect the dust emitted by the Source samples. This procedure consisted of the following steps: 40 g of Source sample was introduced into the EDG during 30 min (Fig. 3). The EDG was connected to a chamber where an electrostatic precipitator was installed (Fig. 3). The emitted dust was mobilized by a fan towards the electrostatic precipitator that collected it on an aluminium plate. The accumulated dust was removed from the aluminium plate with a brush and weighted with an analytical scale. This procedure was repeated until obtaining the 2 g of dust needed to make all planned chemical analysis. Approximately, 4 kg of Source sample and 5 h of separation using the EDG were needed in order to obtain that amount of dust sample.

The following determinations were carried out on each Source- and

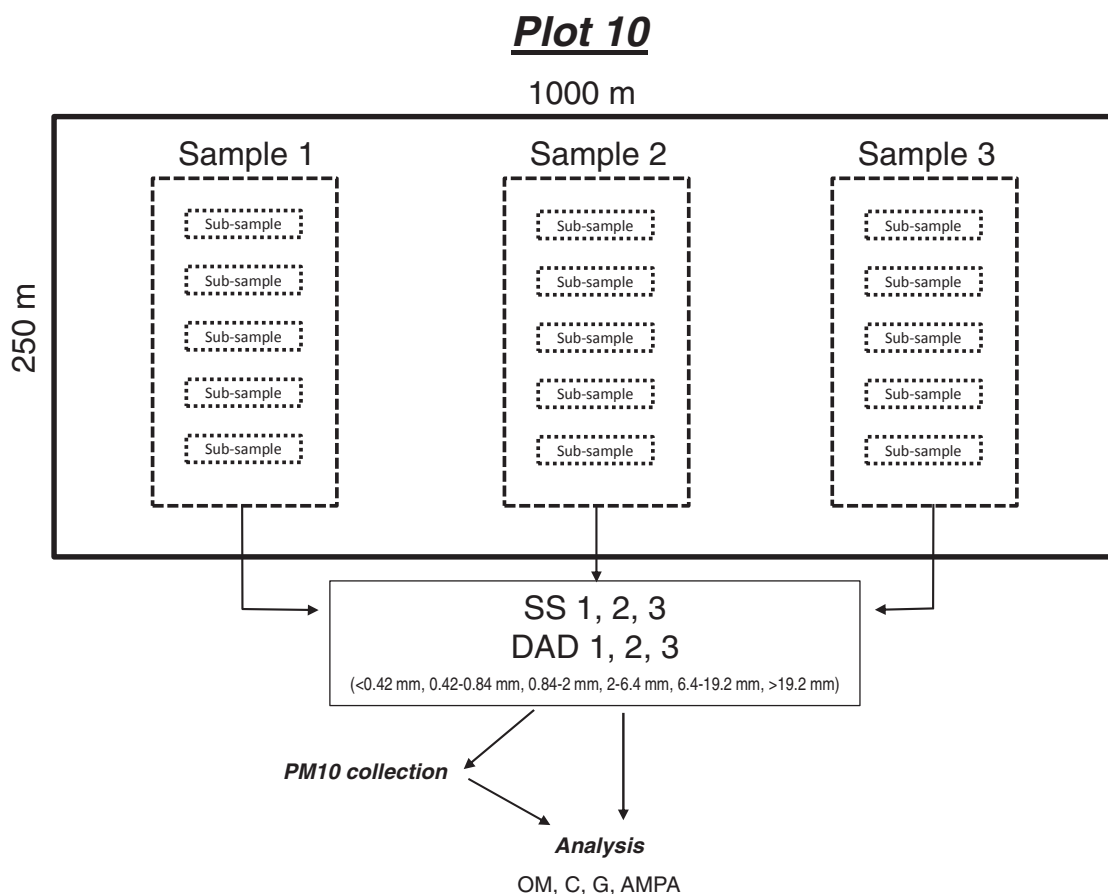


Fig. 2. Scheme of the procedure followed to obtain soil samples and analysis. Where, SS soil sieved by 2 mm, DAD dry aggregate distribution, OM organic matter, C clay, G glyphosate and AMPA (Aminomethylphosphonic acid; CH₆NO₃P).



Fig. 3. Easy dust generator (EDG) coupled to the electrostatic precipitator (C & L model number GH-939).

dust sample: organic matter contents (OM) by means of the wet digestion method (Walkley and Black, 1934), particle size distribution with a laser counter using the wet mode (Hydro Malvern Mastersizer 2000) and glyphosate and Aminomethylphosphonic acid (AMPA) contents following the procedure described by Aparicio et al., (2013). A representative sub-samples of each Source (2 g) and the respirable dust (0.5 g), were uniformly overloaded with 15 μ L of isotope-labeled glyphosate (1,2-¹³C, ¹⁵N) stock solution (10 mg L⁻¹). After 30 min

stabilization, the samples were treated with 5 ml of KH₂PO₄/Na₂B₄O₇ buffer solution (0.1 M, pH=9) in an ultrasonic bath for 30 min (Aparicio et al., 2013). Then, they were centrifuged at 3500 rpm for 10 min, and an aliquot of the supernatant (2 mL) was derivatized with 2 mL of fluorenylmethyloxycarbonyl chloride (FMOC-Cl) reagent in acetonitrile (1 mg mL⁻¹). The tube was shaken vigorously and left overnight at room temperature (between 12 and 15 h). After that, a liquid-liquid extraction with 5 ml of CH₂Cl₂ and a centrifugation at 3000 rpm for 10 min was performed in order to eliminate the excess of FMOC. Finally, the aqueous phase was filtered through a 0.22 μ m nylon filter and 20 μ L of the final extract was injected into the ultra-performance liquid chromatography-electrospray ionization/ mass spectrometry (UPLC-ESI-MS/MS) system.

The linearity of the method was confirmed by performing a calibration curve standard solutions at concentrations of 1, 5, 10, 50 and 100 μ g L⁻¹, each point by triplicate. Satisfactory linearity using weighed (1/X) least squares regression was assumed when the correlation coefficient (r^2) was higher than 0.99, based on analyte peak areas measurement, and the residuals lower than 30%. An equivalent amount to that expected in the analyzed samples of isotope-labeled glyphosate was added to standard solutions in order to evaluate the matrix effect. The limit of detection (LD), defined as the lowest concentration that the analytical process can reliably differentiate from background levels, were 0.36 μ g kg⁻¹ for glyphosate and 0.41 μ g kg⁻¹ for AMPA. The limit of quantification (LQ), defined as the smallest value of analyte that can be determined quantitatively, were 1.19 μ g kg⁻¹ and 1.6 μ g kg⁻¹ for glyphosate and AMPA, respectively.

2.1. Instrumental analysis

For the chromatographic separation, an Acquity UPLC BEH C18 column (1.7 μm , 50×2.1 mm) (Waters) fitted with an Acquity VanGuard BEH C18 pre-column (1.7 μm , 5×2.1 mm) (Waters) was used. The flow rate for the mobile phase was 0.4 mL min^{-1} . Mobile phase was a time-programmed gradient using organic-free water modified with ammonium acetate 5 mM (phase A) and methanol modified with ammonium acetate 5 mM (phase B). The percentage of organic modifier (B) was changed linearly as follows: 0 min, 0%; 0.2 min, 0%; 2.5 min, 70%; 3.5 min, 100%; 4.5 min, 100%; 5.0 min, 0%; and 6 min, 0%. The column was kept at 60°C and the sample manager was maintained at 8°C . Drying as well as nebulizing gas was nitrogen, obtained from a nitrogen generator. The cone gas and desolvation gas flows were optimized at 2 L h^{-1} flow and 600 L h^{-1} , respectively. For operation in MS/MS mode, collision gas was Argon 99.995% with a pressure of 4.04×10^{-3} mbar in the T-Wave cell. Positive ionization mode was performed using capillary voltage of 3.0 kV. The desolvation gas temperature was set to 400°C and the source temperature to 120°C . Dwell times of 0.10 s/scan were chosen. Masslynx NT v 4.1 (Waters) software was used to process quantitative data obtained from calibration standards and from samples.

2.2. Enrichment ratio calculation

The enrichment ratios for OM, clay, glyphosate and AMPA were calculated with the following equation:

$$ER_x = \frac{DC}{SC} \quad (1)$$

where, ER is the enrichment ratio of x ($x = \text{OM, clay, glyphosate or AMPA}$), DC is the concentration of x in the dust emitted by each Source and SC the concentration of x in each Source.

All results were compared by means of ANOVA and LSD multiple comparison tests using the Infostat program (Di Rienzo et al., 2002), considering a 0.05 probability level. Relationships between variables were analyzed by means of simple regression analysis.

3. Results and discussion

The particle size distribution analysis of the Sources (aggregate size fractions and the bulk soil) showed that the geometric mean diameter (GMD) varied between 70 and 110 μm and the concentration of particles finer than 10 μm (PM10) varied between 18% and 23% (Fig. 4). The material emitted by the different Sources showed GMD values ranging from 4.6 to 5.2 μm and PM10 concentrations higher than 70% in all cases. From now on the dust emitted by all Sources will be denominated RD (respirable dust) (Fig. 4).

OM contents in the Sources ranged from 1.4% (> 19.2 mm aggregate-size) to 2.9%, showing higher concentrations in the intermediate aggregate-size fractions (Fig. 5), in agreement with results of other authors (Noellemeyer et al., 2008; Fernandez et al., 2010; Mendez et al., 2015). Clay contents in the sources ranged from 6.5% to 8.5%, being higher in the coarsest aggregate-size fractions (Fig. 6). This agrees with results of Fernandez-Ugalde et al. (2013) who also found higher clay contents in the coarsest aggregate-size fractions of a silt loam Luvisol of France. OM- and clay contents were similar in the RD emitted by all Sources, ranging from 3.5% to 3.7% and 17.5% to 19.0%, respectively. Probably this happened because microaggregates were bound together into macroaggregates in the sandy soil used in this study (Oades and Waters, 1991; Six et al., 2000; Zhao et al., 2017). Thus, different aggregate-size fractions and the bulk soil are probably composed by the same type of microaggregates which contain similar amounts of OM- and clay. Our results suggest that OM- and clay contents will be similar in the RD emitted from different aggregate sizes. However, this result should be confirmed for other kind of soils.

Glyphosate contents varied between 1 ppb and 3 ppb in the Sources (Fig. 7). These results show that measurable concentrations of glyphosate were present in all aggregate-size fractions and the bulk soil, even 12 months after glyphosate application. Long persistence of glyphosate was found in Danish soils in which less than 5% was mineralized after 3 months and glyphosate half-life time (DT50) was estimated in 1000 days (Borggaard and Gimsing, 2008). Finnish arable soils also showed DT50 values of 8 months (Laitinen et al., 2006).

The long persistence of glyphosate found in our study may be due to the sorption of glyphosate in the topsoil layer, under low soil moisture conditions. It is known that glyphosate dissipation decreases when soil moisture decreases (Bento et al., 2016; Borggaard and Gimsing, 2008) and its sorption by the soil increases (Borggaard and Gimsing, 2008; Gimsing et al., 2004). More than 50% of the initially applied glyphosate is accumulated in the topsoil (Laitinen et al., 2006; Okada et al., 2016) where soil moisture is low, excepting for short periods of time, after rain (Chanzy et al., 2008). Other factors that contribute to explain the long persistence of glyphosate in the soil are the contents of iron- and aluminium oxides, both related to the sorption of glyphosate in the soil (Sørensen et al., 2006; Borggaard and Gimsing, 2008). Although iron- and aluminium oxides were not measured in this study, it is known that they are highly accumulated in the soils studied here (Hepper et al., 2006; Aimar, 2016).

Contents of glyphosate in the RD varied between 11.0 ppb and 19.5 ppb (Fig. 7), in agreement with the results of Aparicio et al. (2014) and Bento et al. (2017) who found glyphosate in wind-eroded sediments. Our results show that measurable concentrations of glyphosate were present in the RD emitted by different aggregate-size fractions, even 12 months after glyphosate application. Glyphosate contents in RD were not explained either by OM or clay in the Sources or RD. No evidences were found in the literature about the relationship between glyphosate and OM or clay in different aggregate-size fractions of the same soil. Previous studies explored this relationship on the bulk soil obtaining ambiguous results, but it was not explored on aggregate-size fractions. Gimsing et al. (2004), found that glyphosate sorption in the soil is not correlated with OM and clay. However, Gros et al. (2017) showed that glyphosate can easily react with the OM promoting the glyphosate accumulation in the soil. Okada et al. (2016) showed that sorption of glyphosate was influenced by soil clay contents in silty clay-loam soils and silty-loam soils of different regions of Argentina. Possible reasons explaining the behavior of glyphosate in the respirable dust may be related to the differences in the iron and aluminium oxides content and the chemical composition of OM in the dust emitted by different sources. Sorption of glyphosate is affected by the chemical composition of OM (Gros et al., 2017) as well as by iron- and aluminum oxides content (Borggaard and Gimsing, 2008). Aggregate-size fractions content OM of different chemical composition (Riestra, 2012) and variable contents of iron- and aluminum oxides (Fernandez-Ugalde et al., 2013; Aimar, 2016). However, it is not known the chemical composition of OM and the content of iron- and aluminium oxides in the dust emitted by different sources. Other studies with specific methodologies should be run to confirm these hypotheses.

Glyphosate contents in RD were not explained by glyphosate contents in the Sources. In this sense, glyphosate contents in the > 19.2 mm size fraction were very low (not detected in two of the three replicates), but high in all RD samples emitted by this fraction (Fig. 7). This suggests that glyphosate accumulates in RD, even when it is not detected in the Source.

Aminomethylphosphonic acid (AMPA) contents varied between 80 ppb and 150 ppb in the Sources and between 520 ppb and 750 ppb in RD (Fig. 8). These results indicate that AMPA remains in all aggregate-size fractions, the bulk soil and the RD emitted by them, even 12 months after glyphosate application. AMPA behaved similarly to glyphosate, though its contents were higher than glyphosate in both, the Sources and RD. Aparicio et al. (2013) and Aparicio et al. (2014) also found that AMPA contents were higher than those of glyphosate in

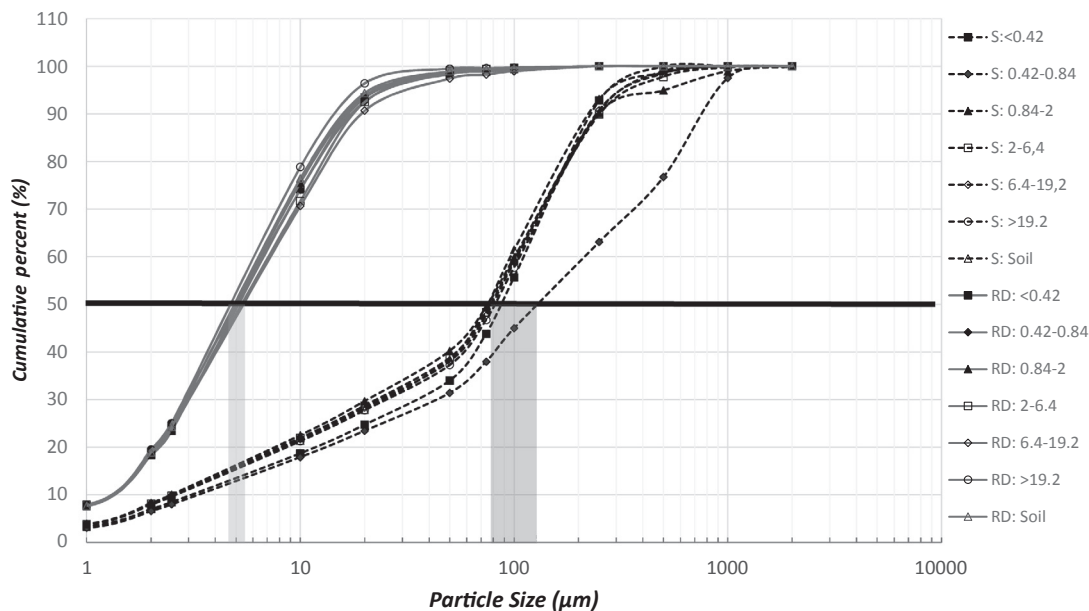


Fig. 4. Cumulative particle size distribution for the bulk soil and its aggregate-size fractions, and the respirable dust emitted by them. Where S is source (soil or aggregate fractions), RD respirable dust. Numbers following S indicate the size of soil aggregate-size fraction (mm). Numbers following RD indicate the size of the soil aggregate-size fraction that emitted the respirable dust. The word “Soil” after S or RD indicates that the source was the bulk soil in both cases. The light shaded area indicates the range of the geometric mean diameter values (GMD) of RD. The dark shaded area indicates the range of GMD values of all Sources.

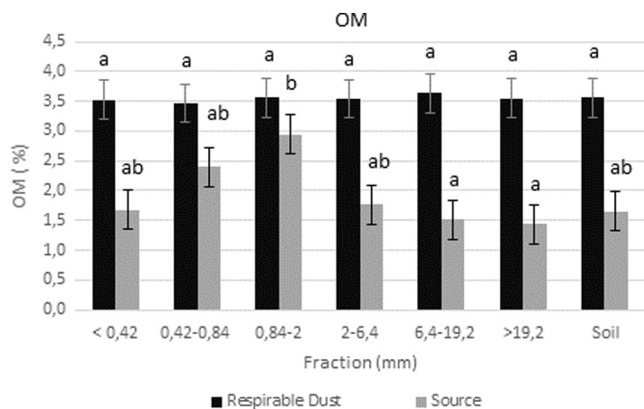


Fig. 5. Organic Matter (OM) contents in the sources (aggregate-size fractions and bulk soil) and respirable dust (RD) emitted by them. Different lowercase letters mean significant differences between fractions ($p < 0.05$), error bars show the Least Significant Difference of the mean of sources and respirable dust.

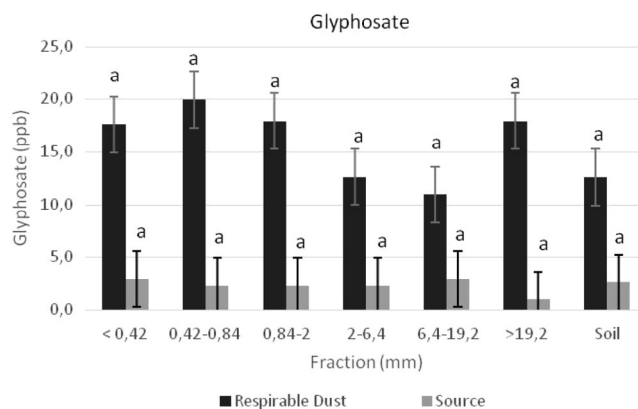


Fig. 7. Glyphosate content in the sources (aggregate-size fractions and bulk soil) and respirable dust (RD) emitted by them. Different lowercase letters mean significant differences between fractions ($p < 0.05$), error bars show the Least Significant Difference of the mean of sources and respirable dust.

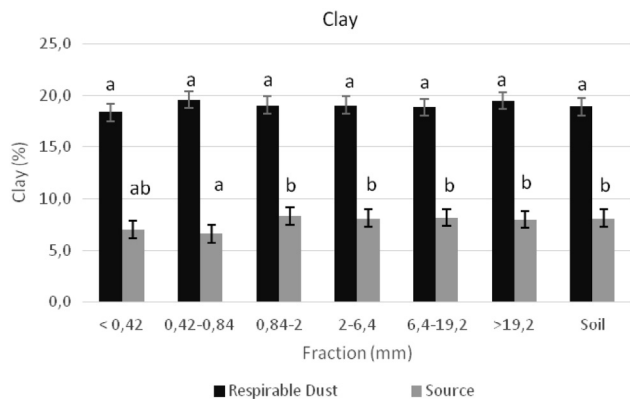


Fig. 6. Clay contents in the sources (aggregate-size fractions and bulk soil) and respirable dust (RD) emitted by them. Different lowercase letters mean significant differences between fractions ($p < 0.05$), error bars show the Least Significant Difference of the mean of sources and respirable dust.

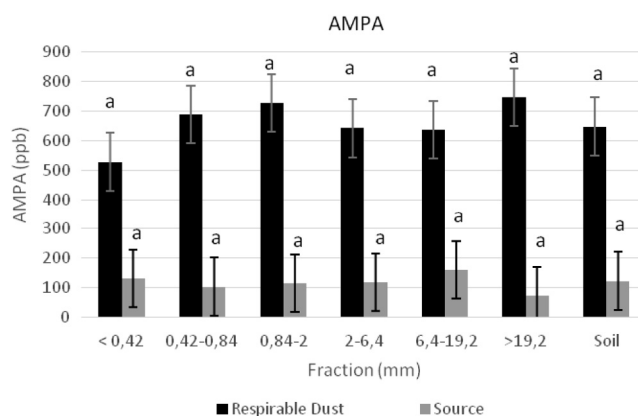


Fig. 8. AMPA content in the sources (aggregate-size fraction and bulk soil) and respirable dust (RD) emitted by them. Different lowercase letters mean significant differences between fractions ($p < 0.05$), error bars show the Least Significant Difference of the mean of sources and respirable dust.

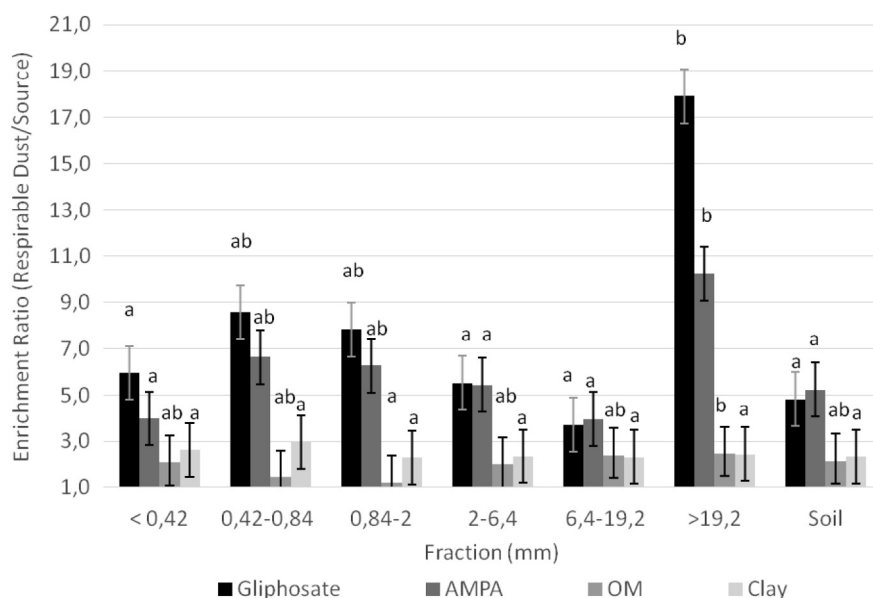


Fig. 9. Enrichment ratio for organic matter (OM), clay, glyphosate and AMPA in different aggregate-size fractions and bulk soil. Different lowercase letters mean significant differences between fractions ($p < 0.05$), error bars show the Least Significant Difference of the mean of glyphosate, AMPA, OM and clay.

soils and sediments transported by the wind of different regions of Argentina. Such tendencies can be explained on the basis of the longer AMPA persistence in the soil compared to that of glyphosate (Bento et al., 2016).

Enrichment ratios (ER) for OM, clay, glyphosate and AMPA were higher than 1, indicating that all these compounds were accumulated in the RD (Fig. 9). The ER_{OM} and ER_{clay} varied between 1.2 and 3, being different between Sources only for OM ($p < 0.05$). Field wind erosion studies showed that clay- and OM contents increased with decreasing size of the sediments (Zobeck and Fryrear, 1986; Li et al., 2009). In our study, the geometric mean diameter was 90 μ m in the Source and 5 μ m in RD. The $ER_{glyphosate}$ varied between 3.8 and 17 (< 19.2 mm aggregate-size) being different between Sources ($p < 0.05$) (Fig. 9). The ER for glyphosate was higher than those for OM and clay indicating that glyphosate is more accumulated than MO and clay in RD. The highest $ER_{glyphosate}$ was found in the > 19.2 mm size aggregate fraction, contrasting with very low glyphosate concentrations in the Source (it was not detected in two of the three replicates). ER_{AMPA} ranged between 4 and 9 (> 19.2 mm aggregate-size) and it was different among Sources ($p < 0.05$, Fig. 9). Our results are in agreement with those of Bento et al. (2017) who found higher glyphosate and AMPA contents in the sediments with the finest textures.

4. Conclusions

Measurable concentrations of glyphosate and AMPA were detected in different aggregate-size fractions, the bulk soil and the respirable dust emitted by them, of an agricultural soil of the central semi-arid region of Argentina, 12 months after glyphosate application. The respirable dust had 4 to 17 times more glyphosate and 4 to 9 times more aminomethylphosphonic acid (AMPA) than the sources of emission (bulk soil and aggregate-size fractions). This indicates that glyphosate and AMPA are accumulated in the respirable dust and it can potentially be a source of air contamination in the studied region. Further studies are needed in order to evaluate probable effects of these concentrations on human health and in the environment.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.aeolia.2017.09.004>.

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