Geoderma 322 (2018) 140–148

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Glyphosate sorption to soils of Argentina. Estimation of affinity coefficient by pedotransfer function

Eduardo De Gerónimo*, Virginia C. Aparicio, José L. Costa

Instituto Nacional de Tecnología Agropecuaria (INTA), Estación Experimental Agropecuaria Balcarce, Route 226 Km 73.5 (PC7620), Balcarce, Buenos Aires, Argentina

ARTICLE INFO

Handling Editor: A.B. McBratney

Keywords:
Glyphosate
Soil
Sorption coefficient
Multiple linear regression
Pedotransfer function

ABSTRACT

Argentine agricultural production is fundamentally based on a technological package that combines direct seeding and glyphosate with transgenic crops (soybean, maize and cotton), which makes glyphosate the most widely employed herbicide in the country. Glyphosate is strongly sorbed to soil in a reversible process that regulates the half-life and mobility of the herbicide, with the resulting risk of contaminating surface and groundwater courses. However, this behavior may vary depending on the characteristics of the soil on which it is applied. Sorption coefficients are thus the most sensitive parameters in models used for environmental risk assessment. The aim of this work was to study the affinity of glyphosate to 12 different soils of Argentina and create a model to estimate the glyphosate Freundlich sorption coefficient (K_f) from easily measurable soil properties. Batch equilibration adsorption data are shown by Freundlich adsorption isotherms. Principal component analysis and multiple linear regressions were used to correlate the effects of soil properties on glyphosate adsorption coefficients. Results indicate that pH and clay contents were the major soil parameters governing glyphosate adsorption in soils. The Freundlich (K_f) pedotransfer function obtained by stepwise regression analysis has 97.9% of the variation in glyphosate sorption coefficients that could be attributed to the variation of the soil clay contents, pH, P_{Bray} and Al_{in}.

1. Introduction

Glysophate (*N*-[phosphonomethyl] glycine) is a broad-spectrum herbicide, used non-selectively in agriculture to control weeds and herbaceous plants. It is absorbed by the foliage, with rapid translocation throughout the plant. Glyphosate interferes in the biosynthesis of aromatic amino acids phenylalanine, tyrosine and tryptophan by inhibiting the enzyme 3-enol-pyruvylshikimate-5-phosphate synthase (EPSP Synthase), located in the chloroplast, which forms part of metabolic pathway of the shikimic acid (Roberts et al., 1998). Biosynthesis pathway inhibition only occurs in plants, bacteria and fungi and does not exist in animals; due to this fact acute toxicity in animals is low. Nevertheless, some studies have reported adverse effects on aquatic and terrestrial species (Contardo-Jara et al., 2009; Paganelli et al., 2010) and concern about potential environmental impacts has risen due to its widespread use and the large amounts annually applied (Schuette, 1998). Glyphosate is the most commonly used herbicide in Argentina, both in frequency of use and intensity, associated with transgenic crops (soybean, maize and cotton) and direct seeding (Aapresid, 2012), where weed control is only performed chemically during cultivation and fallow periods.

After its application, glyphosate is strongly sorbed to soil through a reversible process that regulates the half-life and mobility of the herbicide, with the resulting risk of contaminating surface and groundwater courses. Despite the low mobility that glyphosate presents in soil and its microbiological degradation, it has been found in natural water courses (Peruzzo et al., 2008; Battaglin et al., 2009), where it is principally bound to the suspended particulate matter and deposited in the sediment (Aparicio et al., 2013). Transport of the glyphosate molecule strongly bound to soil colloids to other environmental compartments is the result of runoff or leaching (Kjær et al., 2005; Scribner et al., 2007) or air pollution (Neary et al., 1993).

Sorption to soil depends on the physicochemical properties of the pesticide and soil (Gevao et al., 2000; Aparicio et al., 2013). The glyphosate molecule is a zwitterion with three polar functional groups (amine, carboxylate, and phosphonate) that can bind to metal polyvalent cations (Morillo et al., 1997; de Jonge and de Jonge, 1999; Borggaard and Gimsing, 2008). It is known that glyphosate is adsorbed to soil mineral fractions such as clay and amorphous iron and aluminum oxides (Vereecken, 2005; Borggaard and Gimsing, 2008) and that it is released from these sites by competition with inorganic phosphates (Schuette, 1998; Prata et al., 2003). Although the role played by

---

* Corresponding author.
E-mail address: degeronimo.eduardo@inta.gob.ar (E. De Gerónimo).

https://doi.org/10.1016/j.geoderma.2018.02.037
Received 26 September 2017; Received in revised form 14 January 2018; Accepted 22 February 2018
0016-7061/ © 2018 Elsevier B.V. All rights reserved.

organic matter in glyphosate adsorption mechanisms is as yet unclear, glyphosate seems to be adsorbed on humic substances in soil (Albers et al., 2009). Soil pH is the major factor governing glyphosate adsorption because its net charge is pH-dependent (McConnell and Hossner, 1985). With increasing pH, the net charge of the glyphosate molecule becomes more negative; simultaneously the negative charge of clay minerals, iron and aluminum oxide can be increased as well. Therefore, the adsorption of glyphosate decreases by electrostatic repulsion with the negative charge surfaces (Morillo et al., 1997, 2000; Wauchope et al., 2002; Damonte et al., 2007).

The affinity of the molecule to soil is the most sensitive input parameter in pesticide fate models (Farenhorst et al., 2008). This parameter depends on the nature of the pesticide molecule and selected soil properties such as organic carbon, pH, clay, CEC and texture (Wauchope et al., 2002; Weber et al., 2004). Because of such complex and interactive processes, it is essential to identify a set of soil properties that can predict location-specific pesticide sorption and thereby mobility. Several mechanisms have been proposed to explain the sorption of glyphosate to soils. The formation of strong adsorbent–cation–P(glyphosate) bonds by ligand exchange between the glyphosate phosphonate group and singly coordinated Al–OH and Fe–OH groups on the surfaces of variably charged soil minerals has been proposed as a possible sorption mechanism (Nicholls and Evans, 1991; Piccolo et al., 1994; Morillo et al., 1997; de Jonge et al., 2001; Dideriksen and Stipp, 2003; Mamy and Barriuso, 2005; Wang et al., 2006; Borggaard and Gimsing, 2008).

The identification of the soil properties that govern sorption makes it possible to establish a pedotransfer function (Weber et al., 2004; Vinther et al., 2008), which is very important for understanding pesticide leaching, modeling their fate, and implementing best management to limit groundwater contamination. Pedotransfer functions have been commonly developed to estimate soil hydraulic properties (Medina et al., 2002) and have potential in agronomy to study management practices, especially irrigation and chemical application. Pedotransfer functions were developed for different soil properties such as prediction of the oxygen-diffusion coefficient in soils (Bakker et al., 1987), the cation exchange capacity (CEC) of different soil horizons (Breeuwsma et al., 1986), the yearly pyrite oxidation rate (POR) (Bronswijk et al., 1995) and to predict the potential supply of soil nitrogen (SN), phosphorus (SP), and potassium (SK) for maize (Janssen et al., 1990). For adsorption studies, an early pedotransfer function was presented for heavy metal sorption to soil (Chardon, 1984; van der Zee and van Riemsdijk, 1987) that was later adapted by other authors (Anderson and Christensen, 1988; Reinds et al., 1995; Streck and Richter, 1997; Wilkens et al., 1998; Elzinga et al., 1999; Ingwersen et al., 2000). In a similar way, pedotransfer function it has been developed for estimating sorption soil capacity of phosphate (Breeuwsma et al., 1986; Borggaard et al., 2004), sodium (Rashidi and Seilsepour, 2008) and ammonium (Li et al., 2006; Vogeler et al., 2011).

There is not much information on the current literature about pedotransfer functions applied to sorption parameters of pesticides to soil.

Mathematical equations that correlate the pesticide soil/solution distribution coefficients (Kd) reported in the literature with the respective soil properties were developed for 57 pesticides in order to estimate Kd values based on some soil parameters (Weber et al., 2004). In another study, dinoseb pesticide sorption was studied exploring the relationship between adsorption parameters and soil factors using a pedotransfer function regression (Guan et al., 2013). Regarding glyphosate, a pedotransfer function that allows the prediction of sorption parameters (Kd, Kf and n) was built for a wide range of soils and sediments (Dollinger et al., 2015). Additionally, adsorption of the herbicide glyphosate and its main metabolite AMPA was investigated on 17 different agricultural soils, in this case, using a nonlinear multiple regression equation (Sidoli et al., 2016). Accordingly, the objectives of the present work were (i) to identify the soil properties responsible for the glyphosate adsorption in various Argentinean agricultural soils; (ii) to use PCA and stepwise regression analysis to relate the glyphosate sorption coefficient with the soil physical and chemical properties; and (iii) to build pedotransfer functions for the estimation of sorption parameters (K_f, n) from the currently available soil properties. This function allowed us to identify the most significant explanatory variables of adsorption and, through a sensitivity study of these variables, to evaluate to what extent the pedotransfer rules can be used when certain soil property data are missing.

2. Materials and methods

2.1. Chemicals

Glyphosate reference standard was purchased from Seasinglab (Tandil, Argentina).Isotope-labeled glyphosate (1, 2-^{13}C, ^{15}N), used as internal standard (IS), was purchased from Sigma (Bs. As., Argentina). Analytical reagent-grade disodium tetraboratedecahydrate, ammonium acetate (NH_4Ac, reagent grade), and 9-fluorenmethylcholoroformate (FMOC-Cl) were supplied by Seasinglab. HPLC-grade methanol, HPLC-grade acetonitrile and dichloromethane (CH_2Cl_2) were purchased from Seasinglab. HPLC-grade water was obtained by purifying demineralized water in ELGA purelab ultra (Illinois, USA).

2.2. Soil samples

Twelve representative soils were selected from different regions of Argentina, with no history of glyphosate application at least in the last 10 years, corresponding to different taxonomic orders (Fig. 1): Marcos Juárez (Córdoba province), Santiago del Estero (Santiago del Estero province), Famaillá (Tucumán province), Pergamino (Buenos Aires province), Cerro Azul (Misiones province), Balcarce (Buenos Aires province), Alto Valle (Río Negro province), Corrientes (Corrientes province), Chaco (Chaco province), Reconquista (Santa Fe province), Cerro Amigo (Buenos Aires province), and Barrow (Buenos Aires province).

The sampling depth was 0–5 cm. The samples were dried at 30 °C, ground and sieved to 2 mm. The physicochemical and granulometric characteristics of the studied soils are shown in Table 1.

2.3. Glyphosate adsorption isotherms

Glyphosate sorption isotherms were performed by shaking 1 g of soil sample with 10 mL of 0.01 M $CaCl_2$ solution (to minimize changes in ionic strength and avoid dispersion) containing different concentrations of glyphosate (0, 1, 2, 5, 10, 20, 30 and 50 $mg\,L^{-1}$). The samples were incubated with agitation at 25 °C during 24 h to reach equilibrium. They were then centrifuged at 3000 rpm for 10 min and the supernatants were filtered through a 0.22 μm nylon membrane to determine equilibrium glyphosate concentration in the solution (Aparicio et al., 2013).

The amount of glyphosate adsorbed on the soil was calculated as the difference between the amount initially present in solution and the amount remaining at the end of the experiment. Blanks of each sample did not reveal the presence of glyphosate in the soils before the experiments.

The experimental data were fitted to the Freundlich model

$$C_s = K_f \cdot C_{aq}{}^{n}$$

where C_s is the concentration of glyphosate in the soil ($mg\,kg^{-1}$), C_{aq} is the concentration of glyphosate in the aqueous phase ($mg\,L^{-1}$), K_f is the Freundlich sorption coefficient, and n is the nonlinearity parameter.

2.4. Instrumental analysis

The glyphosate concentration in the centrifuged solution was

Download English Version:

https://daneshyari.com/en/article/8894077

Download Persian Version:

https://daneshyari.com/article/8894077

Daneshyari.com