

Glyphosate adsorption in soils compared to herbicides replaced with the introduction of glyphosate resistant crops

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Abstract

Use of glyphosate resistant crops was helpful in addressing observed increases in environmental contamination by herbicides. Glyphosate is a broad-spectrum herbicide, and its behaviour—as well as that of other herbicides—in soils is an important consideration for the overall environmental evaluation of genetically resistant crop introduction. However, few data have been published comparing glyphosate behaviour in soil to that of the herbicides that would be replaced by introduction of glyphosate resistant crops. This work compares glyphosate adsorption in soil with that of other herbicides frequently used in rape (trifluralin and metazachlor), sugarbeet (metamitron) and corn (sulcotrione). Herbicide adsorption was characterised in surface soils and in the complete soils profiles through kinetics and isotherms using batch equilibration methods. Pedological and molecular structure factors controlling the adsorption of all five herbicides were investigated. Glyphosate was the most strongly adsorbed herbicide, thus having the weakest potential for mobility in soils. Glyphosate adsorption was dependent on its ionisable structure in relation to soil pH, and on soil copper, amorphous iron and phosphate content. Trifluralin adsorption was almost equivalent to glyphosate adsorption, whereas metazachlor, metamitron and sulcotrione adsorption were lower. Trifluralin, metazachlor and metamitron adsorption increased with soil organic carbon content. Sulcotrione was the least adsorbed herbicide in alkaline soils, but its adsorption increased when pH decreased. Ranking the adsorption properties among the five herbicides, glyphosate and trifluralin have the lowest availability and mobility in soils, but the former has the broadest spectrum for weed control.

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1. Introduction

Introduction of genetically modified (GM) plants resistant to glyphosate (a broad-spectrum herbicide), provides a technical approach to weed control con-

straints in various crops. In theory, this approach allows a reduction in the total amount of herbicide needed, from 20% to 85% according to various scenarios (Mes-séan, 2000), with a related decrease in number of active ingredients applied. This can contribute positively when overall benefits/impacts balance of GM crops will be considered. Furthermore, glyphosate is believed to have a lesser ecotoxicological impact than other herbicides, especially in aquatic ecosystems (Giesy et al., 2000). Therefore, introduction of GM plants can be part of a

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strategy to protect water quality and to decrease water contamination by those herbicides often found in water monitoring. However, a concomitant increase of treated area may increase glyphosate content in vulnerable waters, aggravated by the development of non-agricultural uses for glyphosate. Furthermore, in a long run, glyphosate widespread use may result in weed resistance or alter biological functions of soils.

Soil plays a key role in the environmental fate of herbicides. A large proportion of applied herbicides reaches the soil, because of direct application and/or after foliage wash off (Torstensson, 1985). Dispersion of herbicides towards other media (water, plants and atmosphere) will strongly depend on their behaviour in soil, and particularly on their retention, which regulates their availability in soils.

The introduction of GM glyphosate resistant plants will replace the use of other herbicides depending on the crop. GM rape, sugarbeet and corn are candidates for introduction in France, and the most frequently used herbicides on these crops are trifluralin and metazachlor, metamitron and sulcotrione, respectively. Previous researchers have shown that metazachlor, metamitron, and sulcotrione adsorption in soils is low (Baer and Calvet, 1999; Madsen et al., 2000; Beulke and Malkomes, 2001): consequently, dispersion risk seems high, especially towards water because of the close relationship between herbicide leaching potential and its adsorption coefficient (Calvet, 1989). On the contrary, trifluralin adsorption in soils is very high (Peter and Weber, 1985; Tavares and Rezende, 1998; Coquet and Barriuso, 2002); similarly, glyphosate adsorption in soils is typically high, therefore leaching risks are limited (Hance, 1976; Piccolo et al., 1994; de Jonge et al., 2001). However, these results are obtained in different experimental conditions and on different soils, and rigorous evaluation of environmental risks associated with the substitution of the weed control strategy with glyphosate resistant crop introduction is difficult.

The aim of this work was to compare, on the same soils and with the same experimental conditions, glyphosate adsorption to that of trifluralin, metazachlor, metamitron and sulcotrione. Herbicides were chosen due to their general use on the three crops (rape, sugarbeet and corn) and their contrasting physico-chemical characteristics. Soils used were obtained from various experimental French inter-institutes platforms where GM crops have been cultivated since 1995. The contrasted physico-chemical properties of these soils and their distribution in various climatic regions are representative of typical situations in which these crops are cultivated. Herbicide adsorption in surface soils and in soil profiles was characterized with kinetics and equilibrium data. Results will allow evaluation of glyphosate leaching risks compared with that of other herbicides when introducing GM crops. They will also allow a better understanding of soil pedological fac-

tors and molecular structure factors controlling adsorption of the five herbicides.

2. Materials and methods

2.1. Herbicides

Herbicides used were the following (agronomically homologated doses in g a.i. ha⁻¹): glyphosate (1440–3060) used for GM crops, trifluralin (1200) and metazachlor (1250) used for rape, metamitron (2800) used for sugarbeet, and sulcotrione (450) used for corn (Table 1). [Methyl-¹⁴C]glyphosate was purchased from Sigma Chemicals (St Louis, USA; 122 MBq mmol⁻¹, 97.7% radiopurity), [U-ring-¹⁴C]trifluralin from Amersham (Buckinghamshire, UK; 2960 MBq mmol⁻¹, 98.6% radiopurity), [U-phenyl-¹⁴C]metazachlor from BASF (Limburgerhof, Germany, 1761 MBq mmol⁻¹, 95.5% radiopurity), [U-phenyl-¹⁴C]metamitron from International Isotope (Munich, Germany; 477 MBq mmol⁻¹, 98.0% radiopurity) and [U-phenyl-¹⁴C]sulcotrione from Izotop (Budapest, Hungary; 720 MBq mmol⁻¹, 91% radiopurity). Solutions of ¹⁴C-labelled herbicides were prepared in 0.01 M CaCl₂ by isotopic dilution with non-labelled herbicides (analytical standards, >99% purity) at six different concentrations: 10, 5, 2, 1, 0.5, 0.2 mg l⁻¹ for glyphosate, metazachlor, metamitron and sulcotrione, and 0.16, 0.12, 0.08, 0.05, 0.03, 0.02 mg l⁻¹ for trifluralin because of its low solubility in water. Glyphosate solutions were also prepared in deionised water. Each solution contained 0.166 MBq l⁻¹.

The first-order connectivity index (¹χ) of each herbicide was calculated as described by Baum (1998) and Sabljic (2001):

$${}^1\chi = \sum (\delta_i \delta_j)^{-0.5}$$

where δ_i is connectivity atom i value and is equal to the number of adjacent atoms other than hydrogen. For each pair of atoms i and j that are linked by chemical bonds, a product $\delta_i \delta_j$ is calculated.

Herbicide parachor (P) was calculated using McGowan's method as the sum of atomic parachors (Baum, 1998):

$$P = \sum n_i A_i - 19 N_{\text{bonds}} \text{ (cm}^3 \text{ g}^{1/4} \text{ s}^{-1/2} \text{ mol)}$$

where n_i is number of atoms of type i in the molecule, A_i is the contribution of atom i and N_{bonds} is the number of chemical bonds in molecule.

CHEM-3D molecular modelling software (CambridgeSoft) was used to build three-dimensional chemical structures to calculate herbicides dipole moment (μ). Like Reddy and Locke (1994), structures were energy-minimized in MOPAC using Austin Model parameterisation and ground electronic states were obtained as

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