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Occurrence and Downslope Mobilization of Quaternary Herbicide Residues in Vineyard-Devoted Soils

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Abstract The aim of this study was to examine the fate of quaternary herbicides in soil deposits derived from erosion of vineyard-devoted soils. Herbicide occurrence in the crop soils was due to the farmer application inputs. Special attention should be paid to the presence of paraquat (PQ) in the studied vineyard-devoted soils. The major factor governing the sorption of PQ was the solid state organic fraction with the clay mineral content also making a significant contribution. The mobilization and transport of quats-enriched soil particles may generate downslope and downstream environmental problems that mainly affect detritivore ecology.

Keywords Quaternary herbicides · Downslope mobilization · Vineyard-devoted soils · Erosion

Quaternary nitrogen herbicides were developed from the observation that quaternary ammonium germicides, like cetyl trimethylammonium bromide, desiccate young plants (De Liñán y Vicente 1997a, b). Table 1 shows the chemical structure, chemical and common names, together with the physico-chemical properties of these ammonium quaternary herbicides. Paraquat (PQ) was first synthesized in 1882 and has been used as a redox indicator (under the name methyl viologen) in chemical laboratories since 1933. Its herbicidal properties were discovered in 1957, and since 1962 PQ has been marketed in over 130 countries as a highly effective contact herbicide. The bipirydinium herbicides diquat (DQ) and PQ were introduced by Imperial Chemical Industries in 1958. They are very quick-acting herbicides that are absorbed by plants and translocated, thus causing desiccation of the foliage. These herbicides are strongly adsorbed by colloidal constituent soil, and are effectively deactivated as soon as they come into contact with soil (Weber et al. 1993). DQ and PQ are included in a priority list of herbicides of potential concern established for the Mediterranean countries by the European Union (EU), due to their widespread usage in this area (Barceló 1993). Consequently, they may be present as residues in environmental, food and biological samples (Galcerán et al. 1994; Zen et al. 1996). DQ and PQ are extremely toxic and are often encountered in cases of poisoning (Tsakis et al. 1996; Pond et al. 1998). The pyrazolium monocation difenzoquat (DFQ) is also used throughout the world as a selective herbicide for post emergence control of wild oats in barley and fall-seeded wheat. It is the active ingredient in registered trademarks of American Cyanamide Co.

A large part (45%) of the total area of land in the world dedicated to vine growing (3.4 million ha) is concentrated in Europe where this activity annually generates 4,500 million € (European Commission 2006). Since ancient times, vines have been grown in shallow soils located on steep slopes where the exposure to sun light improves grape ripening. The location of vineyards in these topographic and pedologic conditions produce favorably growing conditions for vines in Mediterranean countries such as Italy, France, Greece and Spain, but also in other European countries

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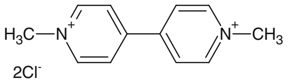
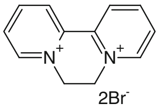
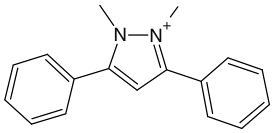
Table 1 Characteristics of the quaternary herbicides studied

Common name	PQ	DQ	DFQ
Chemical structure name	 1,1′-dimethyl-4,4′-bipyridinium	 1,1′-ethylene-2′2′-dipyridylium	 1,2-dimethyl-3,5-diphenyl-4,5-dihydro-1*H*-pyrazol-2-ium methyl sulphate
CAS no.	1910-42-5	85-00-7	43222-48-6
MW[a]	257.2	344	362.4
S[b] (g/L)	620	677	740
Log Pow[c]	−4.5	−4.6	0.3
Koc[d]	15–51	164–134	23–36
Soil half-life[e]	644	3,450	6,810

Data were obtained from Kenaga (1980), Haag and Yao (1992), and US-EPA (1994)

[a] Molecular weight

[b] Solubility in water 20°C

[c] Octanol/water partition coefficient at 20°C

[d] Partition coefficient normalized to organic carbon content (mL g_{oc}^{-1} or L kg_{oc}^{-1})

[e] Aerobic soil half-life (Average, days)

(Germany and Bulgaria) and South America (e.g., Chile and Argentina). During the last few decades, vineyards growing in steep soils in Europe have been progressively abandoned due to social and economical change. As a consequence of abandonment, soil loss through erosion has raised serious environmental concerns (Dunjó et al. 2003; Martínez-Casasnovas and Ramos 2006; Koulouri and Giourga 2007). Erosion has the ability to transport a variety of sorbed contaminants. The aim of this study is to examine the fate of quats in soil deposits derived from vineyard soil erosion. This work was part of an ongoing research project intended to increase available knowledge about the current levels of pesticides in crop soils.

Materials and Methods

Samples of soil were obtained from the 0–5 cm deep layer of vineyard-devoted soils developed on granite and schist materials in Galicia (NW Spain). The soils differed in the length of time they had been used for vine growing. Five replicates of each soil were collected within 0.5 m of each other and pooled. Once in the laboratory, the soils were dried at room temperature, passed through a 2 mm mesh sieve, homogenized and stored until analysis.

The pH of 1:2.5 suspensions of soil in water or 0.1 M KCl was measured with a combined glass electrode. The organic carbon content was determined by elemental analysis on a ThermoFinnigan 1112 Series NC instrument. The proportions of sand (2–0.05 mm), silt (0.05–0.002 mm) and clay (<0.002 mm) were determined by using the wet sieving and pipette methods. Exchangeable cations were extracted with 0.2 M NH_4Cl and determined by atomic absorption spectroscopy (Ca_e and Mg_e) or flame emission spectrometry (Na_e and K_e). Exchangeable aluminum was quantified by displacement with 1 M KCl, followed by atomic absorption spectrophotometry. Finally, the cation exchange capacity, CEC, was determined as the combination of bases (Na_e, K_e, Ca_e and Mg_e) and exchangeable Al. The characteristics of the soils are summarized in Table 2.

PQ, DQ and DFQ in the soils were extracted by a method developed by us with analyte recoveries of about 100% (Pateiro-Moure et al. 2007). Mean recovery rates for the herbicides in soils ranged from 98% to 102%, whereas relative standard deviations were lower than 15%. Quantification limits in soils ranged from 10 µg/kg for DFQ to 20 µg/kg for DQ and PQ. A sample of 5 g of soil was extracted for 3 h with 30 mL of a 70:30 mixture of MeOH/5% EDTA, which was previously acidified with the addition of 2% (v/v) formic acid. The resulting extract was concentrated to 4 mL following pH adjustment to 9–10 with 3 N NaOH and cleaned up by passage through silica cartridges and elution with 10 mL of 70:30 MeOH/6.5 M HCl (Chichila and Walters 1991). Finally, the extract was evaporated to dryness and filled up to a volume of 1 mL with a mixture of 100 mM ammonium formate and formic acid pH 3 and 15 mM heptafluorobutyric acid (HFBA) before analysis by liquid chromatography.

Liquid chromatography system was a Thermo Fisons including a P200 binary pump, an AS 1000 autosampler, a TSP SCM 1000 vacuum membrane degasser and a UV 2000 detector. Separations were done on a Luna C18

Table 2 General properties of the studied soils and soil deposits, together with the levels of quaternary herbicides found

Sample	Location	Sand (%)	Silt (%)	Clay (%)	$pH_{(H2O)}$	$pH_{(KCl)}$	C (%)	CEC ($cmol_{(c)}\ kg^{-1}$)	PQ ($\mu g\ kg^{-1}$)	DQ ($\mu g\ kg^{-1}$)	DFQ ($\mu g\ kg^{-1}$)
1soil	Leiro	70	17	13	5.30	3.65	0.8	3.07	53		
1dep1		35	45	20	5.37	3.71	2.4	5.35	75		
1dep2		43	38	19	5.72	4.13	2.4	6.85	183		
2soil	O Inquial	65	21	14	5.28	4.00	1.9	3.96			
2dep1		42	34	24	6.24	5.15	7.0	10.2			
2dep2		52	28	20	6.17	5.04	5.3	8.19		77	
3soil	Toén	40	38	22	6.23	4.89	1.1	4.31			
3dep		27	55	18	7.49	6.57	2.1	7.27		38	26
4soil	Toén	43	41	16	5.82	4.55	2.0	4.81			
4dep		26	56	18	5.96	4.74	3.2	3.93		20	66
5soil	Toén	44	42	14	6.51	5.63	1.9	5.08	157		
5dep		23	60	17	6.81	5.75	4.4	6.87	404	260	
6soil	Amandi	57	30	13	4.38	4.02	4.3	4.71	126		
6dep		51	36	13	3.88	4.09	3.3	4.65	214		
7soil	Vilamartín	45	35	20	5.29	5.37	1.5	4.91		20	40
7dep		30	53	17	5.96	5.64	3.0	5.63		38	56

column (150 mm long × 4.60 mm i.d., 5 μm particle size) obtained from Phenomenex (Madrid, Spain) and a guard column (4 mm long × 2 mm i.d., 5 μm particle size) packed with the same material. The mobile phases used were water containing 100 mM ammonium formate/formic pH 3/15 mM HFBA (A) and methanol (B). The gradient was: 90% A for 3 min, change to 90% B 10% A in 3 min, hold 5 min, change to 90% A and 10% B in 0.1 min and hold 9 min. The total analysis time was 20 min. The injected volume was 50 μL and the LC flow-rate 0.7 mL/min. The wavelengths used for detection were 258 nm for PQ and DFQ, and 310 nm for DQ.

Basic and descriptive statistics, and linear correlation analyses were performed using SPSS v. 14.0 for Windows.

Results and Discussion

The occurrence and distribution of quaternary herbicides in sloping vineyards of Ourense (NW Spain) was the main aim of this work. The reason for investigations in this area is the persistence and the transport associated to particulate matter of these herbicides. Their residues in the soil surface could potentially pose some environmental risk through soil erosion that may enter the aquatic environment. Therefore, studying the factors controlling their mobility seems to be a substantial contemporary issue to guarantee environmental quality.

The presence of the investigated herbicides in 20 soils and 25 soil deposits from Ourense vineyards decreased in the following order (Table 2), according to measured levels (minimum–maximum): PQ (53–404 μg/kg) > DQ (20–260 μg/kg) > DFQ (26–66 μg/kg). Overall, a 20% (5/20) of the soils analyzed were contaminated by quats, but a 32% (8/25) of soil deposits were contaminated in a higher degree (by a factor of 2–3, in general). It was also clear that patterns of quats use are vinegrower dependent: the predominant use is for the divalent cations PQ and DQ; the lowest presence of the monovalent DFQ is associated to their synergistic effects together with DQ (Rytwo and Tropp 2001; Rytwo and Tavasi 2003). Comparing the relative presence of quats in different vineyards (Fig. 1), vineyards at Toén versus those at other locations had a larger proportion of DQ residues in soils and soil deposits. The largest increase in soil deposits *vs.* soils has taken place for DQ in sample 5 (<10–260), increase associated

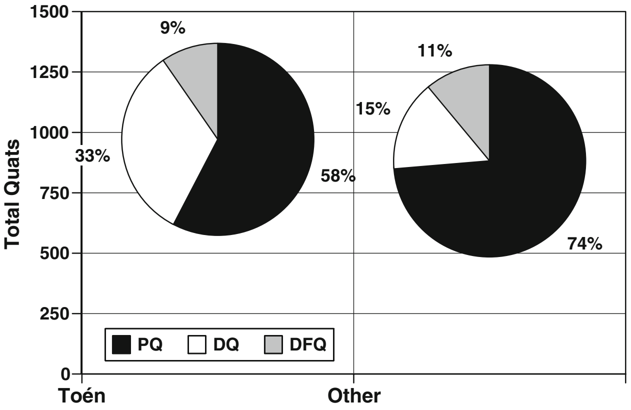


Fig. 1 Total quats (y-axis) and quats % in soils and soil deposits of different vineyard locations (x-axis)

with the increase in silt%, C% and CEC in the soil deposit. When working with the ratios of the variables measured between soil deposits and soils, it was found a significant correlation between the increase of PQ in soil deposits and their increase in CEC ($r = 0.826$, $p = 0.43$, n = 6). Considering all three quats together, the only significant correlation between quat level and the properties of soils and soil deposits is that for C% ($r = 0.585$, $p = 0.003$, n = 23). This is in good agreement with the finding that the major factor governing the sorption of PQ is the solid state organic fraction with the clay mineral content also making a significant contribution (Spark and Swift 2002). A significant correlation coefficient ($p < 0.1$) was also found (Rodríguez-Cruz et al. 2007) between the PQ adsorption constant (K_f) and wood CEC ($r = 0.71$).

The herbicides concentrations found in the samples show the need for a monitoring program for the residues of quats in vineyard-devoted soils, especially in the more sloping areas, and especially for PQ and DQ. Weeds in the field are regularly covered with dust to some extent. The applied herbicide binds to dust particles, thus becoming inactivated. Because of such an inactivation, growers have to increase the rates used to obtain efficient weed control. This increases considerably the levels of herbicides applied. However, herbicides residues found in this study were much below the levels required in cause phytotoxicity in the Strong Adsorption Capacity-Wheat Bioassay (SAC-WB) test (Riley et al. 1976; Roberts et al. 2002). The SAC-WB is assessed as the PQ concentration (mg PQ/kg soil) that reduces root growth by 50%: 25–250, 50–150, 150–1,500 and 500–5,000 mg/kg for, respectively, sandy, peaty, loamy and clay soils. Using the McCall scale (McCall et al. 1980) for assessing mobility of chemicals in soil, PQ was classified as “immobile” in all the soils studied and had no potential to be leached. This strong binding to soil greatly limits any leaching or surface run-off of these herbicides (Pateiro-Moure et al. 2007) but also reduces their availability for microbial breakdown in the soil water, so that these compounds are persistent in soil though not active therein. Anyway, since vineyard soils have been identified as the most erodible agricultural soils (Kosmas et al. 1997), the mobilization and transport of quats-enriched soil particles may generate downslope and downstream environmental problems that mainly affect detritivore ecology. Detritivores are animals and plants that consume organic material, and in doing so contribute to decomposition and the recycling of nutrients (Wetzel 2001). Most detritivores live in mature woodland, though the term can be applied to certain bottom-feeders in wet environments, which play a crucial role in benthic ecosystems, forming essential food chains and participating in the nitrogen cycle.

To sum up, this work helps to cover some of the most important research needs in the area of herbicide residues in soils of vineyard crops to asses the state of their environmental fate due to erosion. Herbicide pollution in crop soils was produced by their application inputs, being the producer the responsible for such an action. The results revealed that special attention should be paid to the presence of PQ. The downslope transport by erosion of quats-enriched soil particles has received little attention because the mobilization of quats-enriched particles can occur slowly and it is less apparent than the soil mass movements promoted by erosion.

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