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Influence of Soil Physicochemical and Biological Properties on the Degradation and Adsorption of the Nematicide Fosthiazate

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The degradation and adsorption of the organophosphorus nematicide fosthiazate were investigated in nine soils with various physicochemical and biological characteristics. Fosthiazate was more persistent in acidic soils (pH <6), with half-life ($t_{1/2}$) values ranging from 53.3 to 57.7 days, compared to soils with higher pH (pH >7), with $t_{1/2}$ ranging from 14.1 to 20.7 days. Application of antibacterial and antifungal antibiotics to soil samples resulted in a significant inhibition of fosthiazate degradation only in two of the three acidic soils. In contrast, soil autoclaving resulted in doubling the $t_{1/2}$ of fosthiazate in all studied soils, suggesting that both microbial and abiotic processes contribute to fosthiazate degradation. Statistical analysis indicated a significant negative correlation ($P < 0.01$) between soil pH and $t_{1/2}$. Fosthiazate was generally weakly adsorbed with Freundlich adsorption coefficient (K_f) values ranging from 1.23 to 2.74 mL/g. Fosthiazate concentration was strongly correlated with soil organic matter content with higher K_f values in soils with higher organic matter content ($P < 0.01$). The mean $t_{1/2}$ and K_f values derived from the laboratory studies were used to parametrize the FOCUS groundwater (GW) models PRZM, PELMO, PEARL, and MACRO for nematicide application in potato and tomato crops. Predicted environmental concentrations produced by the models PEARL and MACRO suggested a potential risk for GW in several scenarios, unlike PELMO and PRZM, which predicted low risk for GW. These findings suggest that the environmental fate of fosthiazate is strongly influenced by soil characteristics and that this nematicide should be used with care in acidic, light soils with low organic matter content.

KEYWORDS: Fosthiazate; nematicide; degradation; adsorption; leaching; FOCUS groundwater models

INTRODUCTION

Fosthiazate [(*RS*)-*S*-*sec*-butyl-*O*-ethyl 2-oxo-1,3-thiazolidin-3-ylphophonothioate] is a relatively novel nonfumigant organophosphorus nematicide that is registered in Greece for the control of root-knot nematodes (*Meloidogyne* spp.) in protected crops and in other European countries including the United Kingdom for the control of potato cyst nematodes (*Globodera rostochiensis* and *Globodera pallida*) in potato fields. Previous field studies have documented the efficacy of fosthiazate against different groups of phytoparasitic nematodes in various crops (*1*−*4*). Recent comparative field tests with other nonfumigant nematicides showed that fosthiazate and oxamyl were the most efficient nematicides in controlling root-knot nematodes in a cucumber plantation (*5*).

Although a lot of information is available regarding the efficacy of fosthiazate, only a few studies so far have examined the degradation and adsorption of fosthiazate in soil. Qin et al. first presented laboratory degradation and adsorption studies of fosthiazate in three contrasting soils with half-life ($t_{1/2}$) values ranging from 17.7 to 46.8 days and Freundlich adsorption coefficients (K_f) ranging from 0.1 to 1.2 mL/g (*6*). The only other study related to the degradation and adsorption of fosthiazate could be obtained from registration data which report a similar range of values for soil degradation and sorption, indicating low sorption and relatively high leaching potential (*7*). Although the former study provided preliminary evidence for a negative effect of soil pH on nematicide persistence, the low number of soils tested did not allow further conclusions (*6*). Therefore, more detailed studies are needed to further investigate the influence of soil physicochemical but also biological properties on the degradation and adsorption of

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Table 1. Physicochemical and Biological Properties of the Soils Studied

soil	sand (%)	clay (%)	loam (%)	pH	$CaCO_3$ (%)	organic matter[a] (%)	organic carbon (%)	biomass (μg of C/g of soil)	N (μg/g)	P (μg/g)	K (μg/g)	Ca (μg/g)	Fe (μg/g)
1	39.8	5.0	55.2	7.46	22.88	1.88	1.02	316.3	10.93	13.08	261.2	1800	7.91
2	54.3	21.7	24.0	5.26	0.66	1.24	0.67	77.1	14.13	17.28	157.0	300	65.60
3	51.3	5.9	42.8	7.41	56.32	1.62	0.87	155.1	23.42	11.88	188.7	1650	5.35
4	49.3	32.8	17.9	4.66	0.44	1.88	1.02	88.1	21.98	10.20	160.7	250	84.52
5	49.5	31.5	19.0	7.66	0.66	1.52	0.82	135.3	6.18	11.04	143.5	350	14.72
6	44.0	35.8	20.2	6.07	0.66	1.65	0.89	322.8	18.34	16.44	259.1	450	47.44
7	64.0	12.9	23.1	8.3	3.96	1.04	0.56	329.6	6.30	16.08	146.6	1050	12.94
8	45.9	32.5	21.6	7.15	20.68	2.13	1.08	308.6	7.58	15.36	613.5	1650	11.02
9	32.0	40.6	27.4	7.45	18.92	1.12	0.60	228.8	29.03	34.56	585.5	1800	77.54

[a] Calculated by the equation organic matter = organic carbon/0.54.

fosthiazate in soil. Knowledge of these factors is important in predicting the levels of pesticides likely to remain in soils and allows assessment of the potential risk associated with exposure.

Degradation and adsorption are the most important processes controlling the pesticide persistence (*8*), and their parameters derived from standard laboratory tests can be used for the parametrization of mathematical models to assess pesticide leaching potential. In recent years, mathematical modeling has become an integral part of the pesticide regulatory scheme. Separate FOCUS (FOrum for the Co-ordination of pesticide environmental fate models and their USe) groups, established within Europe, produced guidelines for proper model use and recommended specific models to be used in standard agricultural scenarios for estimating the risk for groundwater (GW) contamination (*9*, *10*). It is now well documented that all mathematical models are particularly sensitive to the degradation and adsorption parameters, and their results are strongly influenced by the parametrization of these variables (*11*−*14*). Given the strong influence these parameters have on model predictions, this will transpose into uncertainty in model predictions. Therefore, the selection of such parameters should be done with due care using high-quality datasets to minimize as much as possible model uncertainty.

The aim of the current paper is to (1) examine the effect of soil physicochemical and biological properties on the persistence of fosthiazate in soil and (2) to investigate the leaching potential of fosthiazate using the FOCUS GW models.

MATERIALS AND METHODS

Soils and Pesticides. Soil samples (5 kg) were collected in April 2005 from nine orchards from the area of Veria, northern Greece. After collection, samples were immediately transported to the laboratory, where they were partially dried overnight and passed through a 3 mm mesh sieve. Subsamples were removed for the determination of soil moisture and maximum water-holding capacity (MWHC). Moisture content was determined by oven-drying subsamples at 110 °C for 24 h. MWHC was measured gravimetrically following saturation of the soil (30 g) with distilled water in a funnel with Whatman no. 1 filter paper and allowing it to drain for 24 h.

The soil samples included in the study were selected among soils from 120 field sites with known physicochemical properties. Soil selection was based on differences in soil pH, organic matter content, and soil texture to obtain, as much as possible, a wide range of values for the main soil characteristics known to influence the degradation and adsorption of pesticides. Measurement of organic matter content was performed by using the Walkley and Black oxidation method (*15*). Soil pH was measured in mixtures of air-dried soil/deionized water (1:2 w/v). Soil texture was determined using the pipet method (*16*). $N\text{-}NO_3$ was measured using the KCl method (*17*). Soil P was measured using the method described by Olsen et al. (*18*). Soil K and Ca were measured using the ammonium acetate method (*19*). Finally, soil Fe was determined using the DTPA method (*20*). Soil C microbial biomass was also determined using the chloroform fumigation−incubation method as described by Mele and Carter (*21*). The physicochemical and biological properties of the studied soils are summarized in **Table 1**.

A commercial formulation of fosthiazate (Nemathorin EW 15% ai) was utilized for the preparation of aqueous solutions used in the degradation and adsorption studies. An analytical standard of fosthiazate (Ishihara Sangyo Kaisha, Belgium-RCC, Itingen, Switzerland, 99.3%) was used for analytical purposes.

Analysis of Fosthiazate Residues in Soil. Residues of fosthiazate in soil samples (10 g) were extracted after two successive shaking periods on an orbital shaker for 45 and 30 min with methanol/water 70:30 v/v. The supernatant from the two shakings and the soil slurry were gathered and centrifuged for 10 min at 3500 rpm. After centrifugation, the clear supernatant was collected and mixed with distilled water up to a volume of 100 mL. The extract (100 mL) was subsequently passed through a C18-BondElut cartridge. Fosthiazate residues were subsequently eluted with ethyl acetate (2 mL), which was used for chromatographic analysis. Fosthiazate residues in the aqueous phase (0.01 M $CaCl_2$) were determined in a similar way. A Hewlett-Packard 6890 (Palo Alto, CA) gas chromatograph equipped with a nitrogen−phosphorus detector (GC-NPD) and fitted with an HP-5 capillary column (30 m × 0.32 mm and 0.25 μm film thickness) connected to a 50 cm deactivated precolumn was used. Two microliters of extract was injected on the splitless mode. Injector and detector temperatures were 250 and 325 °C, respectively The carrier gas was helium at a constant flow rate of 3.2 mL/min, the detector gases were air and hydrogen at flow rates of 60 and 3.2 mL/min respectively, and the makeup gas was helium at a flow rate of 6.7 mL/min. The column temperature was initially set to 80 °C and then increased to 230 °C at a rate of 30 °C/min, at which it was held constant for up to 14 min. At these operating conditions the retention time for fosthiazate was 6.3 min. The detection limit (LOD) for fosthiazate was 0.05 μg/g with recoveries always exceeding 90%.

Degradation of Fosthiazate in Soils. Triplicate samples (600 g) from each of the nine soils were separated, and the first two were sterilized via two different means to examine the microbial involvement in the degradation of fosthiazate. The first sample received a dose of 50 μg/g (30 mL; 1000 mg/L) of each of the antibiotics chloramphenicol (broad-spectrum bactericide) and cycloheximide (fungicide). Samples were subsequently mixed by hand to ensure uniform distribution of the antibiotics and incubated for 48 h at 25 °C. The second sample was autoclaved for 20 min at 120 °C, and the third sample received no treatment. Subsequently, all samples received a dose of 3 μg/g fosthiazate (9 mL; 200 mg/L), which corresponds to the maximum recommended dose for the control of phytoparasitic nematodes. Additional water was added to adjust the water content to 45% of the MWHC, and samples were briefly mixed by hand. Sterilized distilled water was added in the antibiotic-treated and autoclaved soil samples. Subsequently, bulk samples were divided into 21 subsamples (25 g), which were placed in aerated plastic bags (100 mL) and incubated in the dark at 20 °C. It should be stressed that the antibiotic-treated and the autoclaved samples were handled in different parts of the laboratory compared to the nonsterilized samples to minimize the risk of cross-contamination. Immediately before incubation and 7, 14, 28, 42, 70,

and 100 days later, triplicate samples from each treatment and soil were removed from the incubator and analyzed for residues as described before. The moisture content of the soils was maintained constant with regular additions of water when needed. Sterilized distilled water was used for moisture adjustment in sterilized soils.

Adsorption of Fosthiazate in Soils. The adsorption of fosthiazate in soils was determined using the standard batch equilibrium method (*22*, *23*). Preliminary studies were conducted to determine the time required for equilibrium of pesticide concentration in the two phases (soil and water) to be reached. Therefore, 15 subsamples (10 g air-dried) for each soil were placed in conical flasks (100 mL) and mixed with 20 mL of a fosthiazate solution (8.5 μg/mL) in 0.01 M $CaCl_2$. Soil samples were shaken on a platform shaker, and at different intervals (2, 4, 8, 10, and 24 h) triplicates from each soil were removed and centrifuged at 10000 rpm for 15 min. The supernatant was then collected and used to determine the concentration of fosthiazate remaining in the water phase.

Fifteen air-dried soil subsamples (10 g) for each of the studied soils were weighed into conical flasks (100 mL) and were subsequently mixed with 20 mL of 0.01 M $CaCl_2$ solution containing fosthiazate at concentrations of 2, 4, 6, 8, and 10 μg/mL. Triplicate samples were prepared for each concentration level. Soil samples were agitated for 24 h at room temperature (20 $\pm$ 3 °C) and centrifuged as described above, and the aqueous supernatant was collected and used to determine the concentration of fosthiazate in the aqueous phase (C_w, μg/mL). The amount of fosthiazate remaining adsorbed on the soil phase (C_s, μg/g) was calculated from the difference between the amount of pesticide in the initial solution and the amount of pesticide recovered in the solution after the 24 h shaking period, assuming that no other processes including degradation, volatilization, or photolysis are significant during this short time period. This is a valid assumption considering the low vapor pressure and the stability of fosthiazate to photolysis and hydrolysis at the conditions of the experiment (*7*). In addition, the results derived from the degradation experiment showed negligible degradation of fosthiazate during the 24 h period.

Prediction of the Leaching Potential of Fosthiazate. The leaching of fosthiazate was estimated using the FOCUS versions of the GW models Pesticide Root Zone Model (PRZM) 2.4.1 v, Pesticide Emission Assessment at Regional and Local scales model (PEARL) 2.2.2 v, Pesticide Leaching Model (PELMO) 3.2.2 v, and MACRO 4.3 b.v for applications into potato and tomato crops, which are the two registered uses of fosthiazate in the European Union (EU). Potato crop simulations are included in all nine scenarios, unlike tomato crop, which is included in only five scenarios (Chateaudun, Piacenza, Porto, Sevilla, Thiva). The mean of the $t_{1/2}$, K_f, and N values calculated for the studied soils were used as input parameters for all four GW models. Different adsorption parameters are required from each model; thus, the mean K_{fom} value was used as input for the PEARL model, the K_{foc} was calculated and used as input for the PRZM and MACRO models, and the K_{oc} was calculated and used as input for the PELMO model. All other pesticide physicochemical parameters including molecular weight, vapor pressure, and water solubility were obtained from the literature (*7*). No correction of $t_{1/2}$ for temperature was required because the degradation studies were conducted at 20 °C, which is the reference temperature. In contrast, $t_{1/2}$ values were corrected manually for soil moisture following the guidelines of the FOCUS GW group (*9*); thus, model corrections for moisture were disabled. The recommended application rate of fosthiazate for the control of phytoparasitic nematodes was used (3 kg of ai/ha), but the mode of pesticide application was varied among crops according to the GAP document (*7*). Thus, application of fosthiazate in potato crops was done with incorporation at the top 15 cm of the soil, unlike application to tomato crop, which was considered as surface application without incorporation. The application time of the nematicide to potato and tomato crops was assumed to occur at the time of seeding and 1 day prior to emergence, respectively.

Statistical Analysis. The data obtained from the degradation and adsorption experiment were subjected to one-way analysis of variance (ANOVA). Correlation coefficients between the different physicochemical and biological soil properties and adsorption−degradation parameters were obtained using Pearson's correlation coefficient. In all cases statistical analysis was performed using SPSS Win 11.01.1 v.

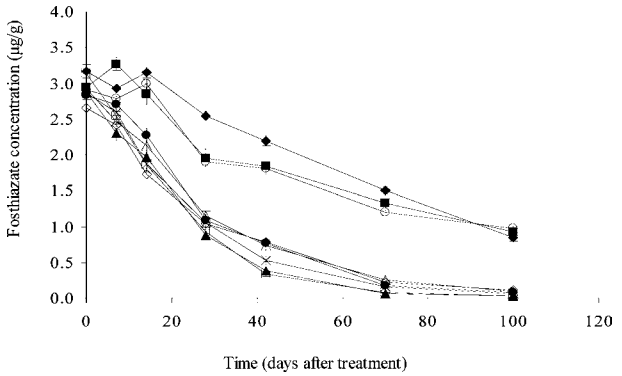

Figure 1. Degradation of fosthiazate in soils 1 (◇), 2 (■), 3 (∗), 4 (○), 5 (□), 6 (◆), 7 (▲), 8 (△), and 9 (●). Each value is the mean of three replicates with error bars representing the standard deviation of the mean at each sampling point.

RESULTS

Fosthiazate Degradation in Soils. Degradation of fosthiazate in autoclaved, treated with antibiotics, and nonsterilized soils followed first-order kinetics (**Figure 1**), and their $t_{1/2}$ values were calculated using the formula

$$t_{1/2} = \ln 2/K_{deg} \quad (1)$$

where $t_{1/2}$ (days) is the pesticide half-life and K_{deg} is the pesticide first-order degradation rate (1/day). The $t_{1/2}$ and K_{deg} of fosthiazate in all soil samples tested are summarized in **Table 2**. Significantly shorter $t_{1/2}$ values for fosthiazate ($P < 0.05$) were observed in soil samples with pH values exceeding 7.0, and their values ranged from 14 days in soil 7 to 20.7 days in soil 1. In contrast, significantly longer $t_{1/2}$ values for fosthiazate ($P < 0.05$) were obtained in the acidic soils (pH <6.1), where values ranged from 53.3 days in soil 6 to 57.7 days in soil 4 (**Table 2**).

There was no significant inhibition ($P > 0.05$) in the degradation of fosthiazate between soil samples treated with antibiotics and the corresponding nonsterilized samples in six soils that were all characterized by high soil pH. In contrast, antibiotic treatment resulted in a significant increase ($P < 0.05$) in the $t_{1/2}$ of fosthiazate in soils 2 and 4, which were characterized by low soil pH. Sterilization of soil 6 decreased the persistence of fosthiazate compared to the persistence of the nematicide in the corresponding nonsterilized samples. Autoclaving the soils resulted in a significant ($P < 0.01$) increase in the $t_{1/2}$ values of fosthiazate in all soils compared to the $t_{1/2}$ values recorded in the corresponding non-autoclaved soil samples (**Table 2**). For example, the $t_{1/2}$ values of fosthiazate in the nonsterilized samples of soils 4 and 5 were 57.7 and 14.1 days, respectively, compared to 92.3 and 26 days recorded in the corresponding autoclaved soil samples (**Table 2**).

Fosthiazate Adsorption in Soils. The results of the preliminary investigation regarding the time required for pesticide equilibration in the nine soils are shown in **Figure 2**. Equilibrium in all soils was reached within 10 h, and further decreases in fosthiazate concentration in the aqueous phase were negligible. Therefore, 24 h was taken as the equilibrium period to facilitate sample processing and analysis.

The adsorption isotherms obtained for each of the soils tested are shown in **Figure 3**. In general, isotherms deviated from linearity and were better described ($r^2 > 0.96$) (**Table 3**) by

Table 2. $t_{1/2}$ Values of Fosthiazate in Nonsterilized, Treated with Antibiotics, or Autoclaved Samples of the Soils Studied

	nonsterilized			antibiotic-treated			autoclaved		
soil	$t_{1/2}$ (days)	K_{deg} (1/day)	r^2	$t_{1/2}$ (days)	K_{deg} (1/day)	r^2	$t_{1/2}$ (days)	K_{deg} (1/day)	r^2
1	20.7	0.0334	0.993	20.1	0.0344	0.997	44.4	0.0156	0.919
2	55.4	0.0125	0.967	82.4	0.0084	0.927	86.5	0.008	0.895
3	17.3	0.0401	0.994	16.9	0.0409	0.998	36.1	0.0192	0.922
4	57.7	0.0120	0.954	65.9	0.0105	0.945	92.3	0.0075	0.986
5	14.1	0.0491	0.987	13.9	0.0500	0.980	26.0	0.0266	0.985
6	53.3	0.0130	0.943	47.0	0.0148	0.970	62.4	0.0111	0.869
7	14.0	0.0496	0.989	14.0	0.0506	0.985	40.7	0.0170	0.944
8	19.4	0.0357	0.998	19.4	0.0357	0.992	43.5	0.0159	0.931
9	18.3	0.0359	0.985	18.1	0.0384	0.994	48.1	0.0144	0.956

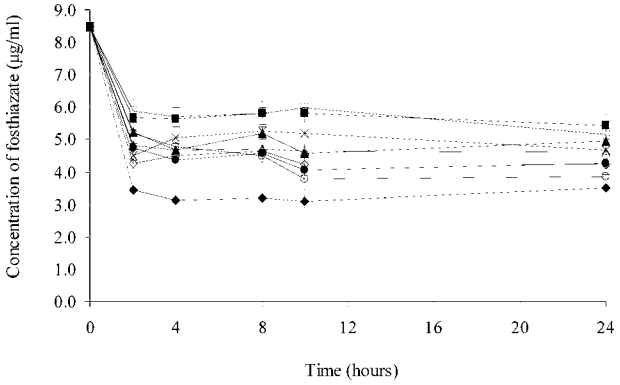

Figure 2. Equilibration of fosthiazate concentrations in solution in soils 1 (◇), 2 (■), 3 (∗), 4 (○), 5 (□), 6 (◆), 7 (▲), 8 (△), and 9 (●). Each value is the mean of three replicates with error bars representing the standard deviation of the mean at each sampling point.

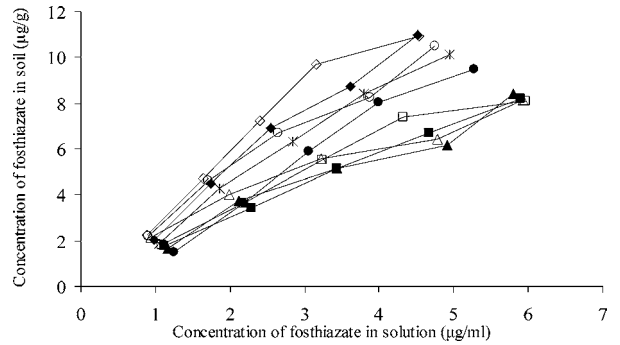

Figure 3. Adsorption isotherms of fosthiazate in soils 1 (◇), 2 (■), 3 (∗), 4 (○), 5 (□), 6 (◆), 7 (▲), 8 (△), and 9 (●).

Table 3. Adsorption of Fosthiazate in the Soils Studied

soil	K_d (mL/g)	K_f (mL/g)	N	r^2	K_{foc} (mL/g)	K_{fom} (mL/g)
1	2.77	2.74	1.02	0.971	268.6	145.7
2	1.48	1.60	0.93	0.999	238.8	129.0
3	2.12	1.98	1.07	0.983	227.6	122.2
4	2.39	2.58	0.91	0.983	252.9	137.2
5	1.62	1.77	0.92	0.982	215.9	116.4
6	2.44	2.27	1.08	0.983	255.1	137.6
7	1.48	1.60	0.93	0.963	285.7	153.8
8	1.75	2.34	0.70	0.986	216.7	117.0
9	1.72	1.23	1.31	0.980	205.0	109.8

the Freundlich equation

$$C_s = K_f C_w^{\ N} \quad (2)$$

where K_f is the Freundlich adsorption coefficient and N is the Freundlich exponent. The adsorption coefficients K_d, K_f, and their corresponding coefficients normalized for organic carbon K_{foc} and organic matter K_{fom} and N calculated for each soil are shown in **Table 3**. K_d was calculated by using the equation $K_d = C_s/C_w$, assuming that adsorption of fosthiazate can be described by linear isotherms. The K_f values of fosthiazate ranged from 1.23 mL/g in soil 9 to 2.74 mL/g in soil 1. Generally, higher K_f values were associated with soils with higher organic matter content (**Table 1**). N values ranged from 0.7 in soil 8 to 1.3 in soil 9, although for all other soils the exponent values ranged from 0.91 to 1.01. Normalization of the K_f values for organic carbon content resulted in a smaller variation in K_{foc} values between soils, which ranged from 205 to 285 mL/g (**Table 3**).

Correlations between Soil Properties and Degradation and Adsorption of Fosthiazate. Correlations between fosthiazate $t_{1/2}$ and adsorption coefficient K_f with soil physicochemical and biological parameters are shown in **Table 4**. A significant negative correlation (-0.953, $P < 0.01$) between fosthiazate $t_{1/2}$ and soil pH was evident, suggesting higher persistence of fosthiazate in acidic soils. Soil Ca showed a significant negative correlation (-0.687, $P < 0.05$) with fosthiazate $t_{1/2}$, unlike soil Fe, which was positively correlated (0.701, $P < 0.05$) with fosthiazate $t_{1/2}$. A strong positive correlation between soil organic matter content and K_f was observed (0.814, $P < 0.01$), suggesting a higher adsorption of fosthiazate in soils with increasing organic matter content. No other significant correlation between fosthiazate degradation and sorption and soil properties was obtained.

Prediction of the Leaching Potential of Fosthiazate. The mean $t_{1/2}$, K_{foc}, K_{fom}, and N values for the nine soils studied in the experiments described above were 31 days, 240.7 mL/g, 129.9 mL/g, and 0.99, respectively. These mean values were used for the parametrization of the FOCUS GW models. The 80th percentile value of the annual average concentration of fosthiazate at the 1 m depth for a 20 year simulation period was considered to be the relevant predicted environmental concentration (PECs) for pesticide risk assessment (*9*). Generally, lower PECs were predicted when pesticide leaching was simulated under tomato crop compared to the corresponding PECs predicted when potato crop simulations were performed (**Table 5**). Different results were obtained from the different models used. Generally, PRZM predicted low risk for GW contamination for fosthiazate with GW PECs not exceeding 0.1 μg/l in any of the FOCUS scenarios for both tomato and potato crops. Similar results were obtained with PELMO, with fosthiazate PECs exceeding 0.1 μg/L in only the Piacenza scenario cropped with potatoes. In contrast to the previous two models, PEARL suggested a relatively high leaching potential for fosthiazate, with PECs well above 0.1 μg/L in seven of the nine scenarios with potato crop and in four of the five scenarios with tomato crop. Finally, the MACRO model produced GW PECs

Table 4. Pearson's Correlation Coefficients of $t_{1/2}$ and K_f of Fosthiazate with Soil Physicochemical and Biological Properties[a]

	K_f	sand	clay	loam	pH	$CaCO_3$	OM	biomass	N	P	K	Ca	Fe
$t_{1/2}$	0.271	0.048	0.311	–0.363	–0.953**	–0.490	0.271	–0.395	0.292	–0.152	–0.291	–0.687*	0.701*
K_f	1.000	–0.112	–0.216	0.309	–0.311	0.069	0.814**	0.188	–0.171	–0.651	–0.099	0.002	–0.207

[a] *, correlation is significant at the 0.05 level; **, correlation is significant at the 0.01 level.

Table 5. PECS (Micrograms per Liter) GW Predicted by the FOCUS GW Models PRZM, PELMO, PEARL, and MACRO, Which Were Parametrized with Degradation and Adsorption Parameters Derived from the Laboratory Studies

	PRZM		PELMO		PEARL		MACRO
scenario	tomato	potato	tomato	potato	tomato	potato	potato
Chateaudun	<0.001	<0.001	<0.001	<0.001	2.645	3.282	0.303
Hamburg	–[a]	<0.001	–	0.002	–	2.373	–
Jokioinen	–	<0.001	–	<0.001	–	5.319	–
Kremsmunster	–	<0.001	–	<0.001	–	5.003	–
Okehampton	–	<0.001	–	0.001	–	2.610	–
Piacenza	0.025	0.074	0.046	1.168	7.836	7.760	–
Porto	<0.001	<0.001	<0.001	<0.001	0.002	0.003	–
Sevilla	<0.001	<0.001	<0.001	<0.001	0.160	0.060	–
Thiva	<0.001	<0.001	<0.001	<0.001	0.370	0.606	–

[a] No such crop—region scenario is available.

exceeding 0.1 μg/L for the potato Chateaudun scenario, suggesting a potential risk for GW contamination in soils where the dominant transport mechanism is preferential flow.

DISCUSSION

Degradation and adsorption of fosthiazate varied between soils, with certain soil properties significantly influencing the rate of these processes. The $t_{1/2}$ in the soils tested varied between 14.1 and 57.7 days, which are within the range reported in the literature (*5*−*7*). Soil pH was identified as the dominant soil property affecting the degradation of fosthiazate, and a strong negative correlation between soil pH and $t_{1/2}$ of fosthiazate was established. Therefore, a rapid degradation of fosthiazate was evident in all six soils with pH values of 7.2−8.3, unlike the remaining three soils which were characterized by pH values of 4.7−6.1. A similar effect of soil pH on the degradation of other organophosphorus soil insecticides/nematicides has been observed before for isazofos (*24*), cadusafos (*25*), and fenamiphos (*26*). Qin et al. reported a similar relationship between soil pH and fosthiazate degradation, although the limited number of soils studied did not allow the establishment of further correlations (*6*). This positive effect of soil pH on the degradation of organophosphorus pesticides has been attributed to a concurrent increase of both microbial and abiotic degradation. Generally, soil bacteria, which are more active in the degradation of xenobiotics, flourish in alkaline soil pH (*27*). In addition, several previous studies have documented the rapid degradation of organophosphorus pesticides in soils with high pH due to their vulnerability to chemical hydrolysis (*28*−*30*). Previous registration studies have shown that fosthiazate is rapidly hydrolyzed in an alkaline environment (pH 9), with $t_{1/2} = 3.2$ days compared to its $t_{1/2} = 191$ days in an acidic environment (pH 5) (*7*). The significant negative correlation observed between $t_{1/2}$ and soil Ca could be explained by the well-established positive relationship between soil Ca and soil pH.

Application of antibiotics to soils did not significantly inhibit degradation of fosthiazate with the exception of two acidic soils (pH <5.6), where a significant increase in $t_{1/2}$ values was evident. In contrast, autoclaving resulted in an approximate doubling of $t_{1/2}$ of fosthiazate in almost all soils studied. The inability of the antibiotics chloramphenicol and cycloheximide to significantly inhibit the degradation of fosthiazate in the studied soils could be attributed to the presence of microbes that were resistant to the specific antibiotics. Application of a more drastic sterilization method such as autoclaving resulted in a significant inhibition of the degradation of fosthiazate. Antibiotics application is considered to be a mild sterilization method that does not alter soil physical and chemical properties and consequently does not modify quantitatively and qualitatively soil−xenobiotic−microbe interactions. In contrast, soil autoclaving is a more efficient sterilization method that has been found to significantly alter the physicochemical status of the soil (*31*, *32*). Our results suggest that both abiotic and biotic processes are involved in the degradation of fosthiazate in soils.

Adsorption of fosthiazate in soils was generally weak, with K_f values ranging between 1.23 and 2.74 mL/g. The adsorption coefficients observed in our study are somewhat higher but close to the range of K_f values reported in previous studies. Qin et al. measured fosthiazate adsorption in three contrasting soils and reported K_f values ranging from 0.1 to 1.2 mL/g (*6*). In registration studies, fosthiazate adsorption was measured in six contrasting soils with K_f values ranging from 0.74 to 1.7 mL/g (*7*). Our findings suggested a strong positive correlation between K_f values and the organic matter content of the soils studied. A similar increase in the adsorption of fosthiazate in soils with higher organic matter content was also reported before (*6*). Previous studies with nonionized pesticides such as organophosphates have shown that organic matter content is the major factor controlling their adsorption onto soil particles (*26*, *33*). No other soil physicochemical or biological properties were found to significantly influence adsorption of fosthiazate in soil.

The leaching potential of fosthiazate was also determined by simulating its fate using the four FOCUS GW models for potato and tomato crop scenarios. Predictions varied among different models with the capacity models PRZM and PELMO producing similar results in accordance with their common root in development, suggesting low risk for GW contamination in both crop situations. In contrast, PEARL predictions indicated a potential risk for GW contamination in both tomato and potato cultivations with PECs exceeding the 0.1 μg/L trigger value for GW risk assessment in the majority of the scenarios. Similarly, MACRO suggested also a potential risk for GW contamination in soils vulnerable to preferential flow mechanisms. Several studies so far have illustrated that the estimation of the leaching potential of a compound is significantly influenced by the model used (*34*, *35*). Model selection is therefore likely to present a significant source of uncertainty in pesticide fate modeling. The most appropriate way to account for this uncertainty is to predict pesticide leaching using a range of models (*14*). According to current practice for pesticide registration in the EU, the results from a single FOCUS GW model are considered to be adequate for the assessment of the risk for GW contamination (*9*). In our case application of PRZM or PELMO for simulating leaching of fosthiazate would have indicated that there can be confidence that the substance is safe in the great majority of situations in the EU. The parallel

simulation of fosthiazate leaching with the other chromatographic flow model PEARL suggested a potential risk for GW, although safe uses for the compound were identified in both potato and tomato crop scenarios, which are significant in terms of agriculture in the EU. Our modeling results are in agreement with the inclusion of fosthiazate in Annex I of the 91/4141/EEC under the specific provision that "member-states should pay particular attention to the protection of GW, when fosthiazate is applied in regions with vulnerable soil and/or climate conditions" (*36*). Our finding are consistent with results reported by Qin et al. (*6*), who concluded that fosthiazate may leach easily through soils under conducive conditions and particularly in soils with relatively low pH. However, in this study the authors estimated the leaching potential of fosthiazate using an empirical model, the groundwater ubiquity score (GUS) index (*37*), and not sophisticated mathematical modeling.

Overall, laboratory studies indicated longer pesticide persistence in acidic soils with high organic matter content due to increased hydrolytic stability and soil adsorption. This is particularly important for the potato monoculture areas in Greece, where fosthiazate might be used, which are characterized by light acidic soils with low organic matter content. In such soils, the persistence of fosthiazate would be prolonged, offering longer protection from potato-cyst nematodes. On the other hand, in such soils, the slower degradation of fosthiazate due to low soil pH and its weak adsorption due to low organic matter content would favor fosthiazate leaching, entailing a risk for GW contamination. Spatial analysis with the use of geographical information systems could identify such vulnerable areas, and higher tier studies such as lysimeter studies, field leaching studies, and monitoring could facilitate the identification of safe uses or the requirement for mitigation measures.

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