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# Degradation and sorption of the herbicide pelargonic acid in subsoils below railway tracks compared to a range of topsoils

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## Abstract

**Background** Pelargonic acid is a non-selective herbicide derived from natural sources with a range of potential applications in areas where synthetic herbicides may be less acceptable. One such use area is weed control on railway tracks. To assess the potential leaching of pelargonic acid to groundwater for this specific use, we conducted degradation and sorption studies with soils from railway tracks and, for comparison, with a range of topsoils.

**Results** Degradation of pelargonic acid was very rapid in subsoils from railway tracks with half-lives ( $DT_{50}$ ) of < 1 day (geom. mean  $DT_{50}$ , 5.8 h), and even faster in the selected agricultural topsoils (1.5 h). The starting concentration had a strong influence with much slower degradation at higher spike levels. Adsorption to the railway soils (alkaline soils with low organic matter content) was expectedly weak (Freundlich adsorption coefficients  $K_F$  of 0.06–0.31 mL/g) and clearly stronger in the topsoils (0.2–40 mL/g). Organic carbon normalized adsorption coefficients ( $K_{Foc}$ ) ranged from 11 to 371 mL/g (all soils) and were pH dependent, consistent with the behaviour of weak acids. Computer modelling using the software PELMO and a set of scenarios for herbicide use on railway tracks developed for the authorisation in Germany yielded predicted environmental concentrations in groundwater of < 0.001  $\mu\text{g/L}$  when parameterised with the adsorption and degradation endpoints from subsoils.

**Conclusions** The leaching potential of pelargonic acid may be considered low even in application scenarios with sandy soils with low organic matter content such as those found below railway tracks.

**Keywords** Pelargonic acid, Soil degradation, pH-dependent adsorption, Subsoil, Groundwater exposure

## Background

Herbicides based on pelargonic acid are becoming increasingly important in organic farming but also for weed control in areas where the use of synthetic organic chemicals may be less acceptable (i.e., parks, schools, gardens and indoor sites) [1]. In recent years, pelargonic acid also gained interest for weed control on railway tracks, preferably in combination with the herbicidally active

substance flazasulfuron [2, 3]. Currently, herbicides used for weed control on railway tracks are mainly based on glyphosate [4–7] because of its good activity against most weeds that are commonly present on railway tracks and its low groundwater contamination potential [8–10]. However, alternative substances and substances complementing the activity spectrum of glyphosate are strongly desired.

Pelargonic acid (nonanoic acid) is a naturally occurring, linear, saturated fatty acid which is commercially produced from rapeseed oil by ester cleavage and ozonation [1, 11]. The compound is used as a non-selective herbicide to control annual broadleaf and grass weeds as well as mosses, with application rates of typically 10–30 kg/ha. The compound solely acts by contact

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(insignificant translocation in the plant and no root uptake). Its herbicidal activity is due to damage to plant cell membranes, leading to desiccation and bleaching of the treated plants [12, 13].

Pelargonic acid, like other fatty acids, is expected to be rapidly degraded in biologically active soils via  $\beta$ -oxidation [14, 15]. In laboratory degradation studies required in the context of the authorization, the compound was degraded with half-lives ( $DT_{50}$ , time required for dissipation to 50%) of 0.7 to 1.6 days [14, 16]. Sorption of pelargonic acid to soils was found to be pH-dependent, as expected for weak acids ( $pK_a$ , 4.94–5.0), with stronger sorption at low soil pHs (range of  $K_{Foc}$  values, organic carbon normalized sorption coefficients, of 8.1–570 mL/g) [14, 16].

Based on these data, the leaching potential of pelargonic acid was assessed for a number of agricultural and non-agricultural uses. While the majority of agricultural uses with application rates up to 60 kg active substance/ha (for example,  $3 \times 20$  kg/ha in vines) were found to pose no risk of groundwater contamination, a number of uses with higher application rates and, particularly, non-agricultural uses on paths lead to soil leachate concentrations above the legal parametric limit of 0.1  $\mu\text{g/L}$  [16].

Soils below the railway ballast usually have low organic carbon contents, which results in weak sorption of most organic compounds. Further, subsoils may also exhibit lower biological activity and, consequently, degradation of substances may be slower. Herbicides applied on railway tracks thus are more likely to leach to groundwater than in typical agricultural application scenarios [17]. The aim of the present study was, therefore, to assess the leaching potential of pelargonic acid when applied to railway tracks at typical application rates used for weed control in this area. We determined adsorption and degradation rate coefficients in a number of railway subsoils, selected to represent a realistic worst-case regarding both properties. For comparison, we also determined degradation rate coefficients in 4 and sorption coefficients in 12 topsoils. Based on these data, the leaching of pelargonic acid was modelled in a number of railway scenarios.

## Materials and methods

### Chemicals

Fully deuterated pelargonic acid (nonanoic acid- $D_{17}$ , purity, 98%) was used as test substance while partially deuterated pelargonic acid (nonanoic acid-9,9,9- $D_3$ , 98%) was used as internal standard. Both compounds were obtained from Cambridge Isotope Laboratories (Tewksbury, MA). Stock solutions were prepared in methanol or acetonitrile.

### Soils

For degradation and adsorption experiments, we used subsoil samples collected at 3 locations with 25–33-year-old railway tracks in Switzerland. The railway sites were selected to cover situations with high pH and low organic carbon contents (and thus comparatively low adsorption of organic acids). Subsoil samples were collected in July and August, 2019. At location Lanzenhäusern and Notwil, material was taken from the layer below the ballast at 30–60 cm depth. At location Wabern (W), subgrade material was taken at the lateral cess from the layer just below the gravel at a depth of 8–30 cm.

For comparison, we selected topsoils with a wide range of soil properties (pH 3.9–7.3, organic carbon content 1.2–10.7%). Samples of topsoil were collected at various locations in Switzerland in April 2013, October 2016, February 2017, and July, August and December 2019 from eighteen locations in Switzerland (soils collected before 2019 were only used for adsorption experiments). Standard equipment was used to sample soil from the top 10 cm layer. The field-moist soils were sieved (2 mm) and stored in plastic bags at 4 °C. Data on the characterization of the soils are provided in Table 1.

The soils were stored longer than recommended in the OECD 307 guideline (max. 3 months, as storage may adversely affect microbial activity [18]), prior to using them for soil degradation experiments. In the case of the topsoils used for degradation experiments, storage ranged from 10–12 months while subsoils were stored longer, up to 18 months. From the very rapid degradation of pelargonic acid in the experiments and the minimal difference in degradation rates between replicate incubations in soils Möhlin and Brislach, which were up to 6 weeks apart (Additional file 1: Table S1), it seems that soil storage did not adversely affect pelargonic acid degrading microorganisms.

### Soil incubation

Incubation experiments were conducted at spike levels of 5 and 15 mg/kg, corresponding to application rates of 3.75 and 11.25 kg/ha, respectively, assuming a mixing depth of 5 cm and a soil bulk density of 1.5 g/cm<sup>3</sup> and thus at the lower end of typical application rates in agriculture (10–40 kg/ha, ref. [14]). Experiments were set up 10–12 (5 mg/kg) and 12–17 months (15 mg/kg) after collection of the soils. Portions of 100 g field-moist soil were spread in a crystallizing dish (width, 23 cm) and the test substance was applied evenly to the soil surface with a polyethylene spray bottle. For experiments at 5 mg/kg, 50  $\mu\text{L}$  of a solution of the test substance (10 mg/mL nonanoic acid- $D_{17}$  in acetonitrile) were diluted into 5 mL water. For experiments at 15 mg/kg, 9 mg test substance

**Table 1** Selected properties of the soils used for degradation and sorption experiments (fraction < 2 mm)

	Sampling date [dd.mm.yy]	Coordinates	Altitude [m]	Type	Texture <sup>a</sup>	Sand [%]	Silt [%]	Clay [%]	C <sub>org</sub> [%]	pH <sup>b</sup> (CaCl <sub>2</sub> )	WHC <sup>c</sup>
<i>Subsoils from railway tracks</i>											
Lanzenhäusern	08.07.19	46°50'45"N/7°20'53"E	730	Railway subsoil	Sandy loam	66	24	10	0.54	7.5	39
Nottwil	09.07.19	47°07'37"N/8°09'33"E	510	Railway subsoil	Sandy loam	58	31	10	0.78	7.6	42
Wabern	13.08.19	46°55'33"N/7°27'16"E	560	Railway subsoil	Sandy loam	69	22	9	0.21	7.6	39
<i>Topsoils</i>											
Brislach	06.12.19	47°25'40"N/7°32'36"E	405	Seeded pasture	Silt loam	13	68	19	1.6	6.4	61
Burgdorf	19.10.16	47°02'54"N/7°37'54"E	545	Forest	Sandy loam	61	22	17	2.4	6.5	75
Dulliken	07.02.17	47°20'37"N/7°57'29"E	415	Forest	Loam	38	41	21	2.1	4.0	75
Entlebuch	02.04.13	47°01'36"N/8°06'29"E	955	Fertilized pasture	Sandy loam	70	11	19	3.7	5.3	94
Etziken	07.02.17	47°11'53"N/7°38'28"E	465	Forest	Loam	47	35	17	2.3	3.9	71
Ins	02.04.13	46°59'31"N/7°07'29"E	432	Arable land	Clay loam	40	24	36	7.5	7.1	89
Kestenholz	19.10.16	47°16'46"N/7°44'26"E	452	Arable land	Clay loam	39	32	29	2.8	6.5	71
Möhlin	06.12.19	47°34'18"N/7°52'07"E	340	Arable land	Silt loam	23	63	14	1.2	5.1	55
Sargans	05.12.19	47°03'20"N/9°27'45"E	481	Arable land	Silt loam	19	62	19	3.2	7.3	83
Schafisheim	07.02.17	47°22'11"N/8°08'51"E	422	Seeded pasture	Sandy loam	54	27	19	1.6	4.6	53
Steig	03.04.13	41°32'09"N/8°37'01"E	680	Forest	Sandy loam	62	21	17	10.7	4.5	174
Zuzwil	12.12.19	47°03'17"N/7°29'10"E	550	Arable land	Loam	41	41	18	1.5	6.8	53

<sup>a</sup> USDA classification<sup>b</sup> Suspension of soil in 0.01 M aqueous CaCl<sub>2</sub> solution, 1:5 (w/w)<sup>c</sup> Maximum water holding capacity in g water per 100 g dry soil

and 120  $\mu\text{L}$  0.5 M NaOH (to increase water solubility) were dissolved in 30 mL water (of which 5 mL were applied to each 100 g batch of soil). The addition of a small excess of NaOH (1.5  $\mu\text{mol}$  per batch of soil) was not expected to significantly change the soil pH. After spiking, the soils were thoroughly mixed and filled into 0.5-L Erlenmeyer flasks that were closed with air-permeable cellulose plugs. The soils were then incubated at 20 °C in the dark under aerobic conditions for 3–5 h. At appropriate time intervals, aliquots of 10 g soil were removed, filled into 20-mL glass vials, topped with 10 mL acetonitrile, vigorously shaken and immediately put in a freezer at  $-45$  °C until extraction.

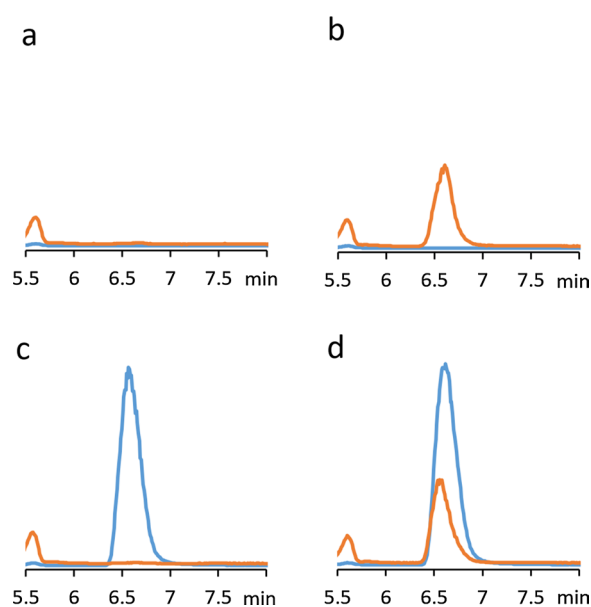
### Soil extraction

The acetonitrile soil suspensions were removed from the freezer, fortified with internal standard (100  $\mu\text{g}$  nonanoic acid-9,9,9- $\text{D}_3$  in 100  $\mu\text{L}$  methanol) and allowed to come to room temperature. After vigorous shaking ( $\approx 1$  min), the suspensions were centrifuged (RCF $\approx 1500$  g for 3 min; Eppendorf 5804 with rotor A-4–44, Hamburg, Germany) and the supernatants were transferred to 40-mL glass vials. A second extraction was performed with 10 mL acetonitrile, and a third extraction with 10 mL 0.01 M aqueous  $\text{CaCl}_2$ . The combined extracts were brought to roughly equal volume (30 mL) with 0.01 M aqueous  $\text{CaCl}_2$  and an aliquot was diluted 1:10 with methanol for analysis by LC–MS/MS.

### LC–MS/MS analysis

Pelargonic acid is a natural compound that occurs ubiquitously in the environment. During initial method development, substantial signals for pelargonic acid were obtained when analyzing blank samples. These signals were high enough to interfere with analyses of trace amounts of pelargonic acid, for example, the lowest concentrations of the adsorption isotherm measurements. It was not possible to eliminate the blank signals by switching to different batches of organic solvents (acetonitrile and methanol) or water (used as eluent). Therefore, we decided to instead use fully deuterated pelargonic acid- $\text{D}_{17}$  as test substance, and pelargonic acid-9,9,9- $\text{D}_3$  as internal standard. Both compounds were not affected by significant interferences even though the lack of any useable fragmentation prevented a selectivity gain as usually observed in LC tandem mass spectrometry (Fig. 1). The chromatograms also show that pelargonic acid  $\text{D}_3$  did not cause any interferences in the mass trace of  $\text{D}_{17}$  and vice versa.

Pelargonic acid- $\text{D}_{17}$  and the corresponding internal standard pelargonic acid-9,9,9- $\text{D}_3$  were analyzed with liquid chromatography-tandem mass spectrometry. The instrument was configured with an autosampler (PAL



**Fig. 1** LC–MS/MS mass traces of pelargonic acid- $\text{D}_{17}$  (test substance, orange trace,  $m/z$  174  $\rightarrow$  174) and pelargonic acid-9,9,9- $\text{D}_3$  (internal standard, blue trace,  $m/z$  160  $\rightarrow$  160) of blank soil extract (a) and extract spiked with the equivalent of 0.3  $\mu\text{g/g}$   $\text{D}_{17}$  (b), 6  $\mu\text{g/g}$   $\text{D}_3$  (c) or both substances (d). Note that the signal for  $\text{D}_3$  was scaled down by a factor of 10 for better comparability

RSI, CTC Analytics, Zwingen, Switzerland), a binary HPLC pump for gradient elution, an additional HPLC pump used for sample transfer, a column oven (set to 25 °C), a 6-port valve used for column switching, a solvent degasser (Exion LC, Sciex, Framingham, MA), and a triple quadrupole mass spectrometer (API 6500+, with turbo ion spray source, Sciex). LC conditions were as follows: The sample was injected into a 3  $\mu\text{L}$  PEEK loop and then transferred from the injection loop to a cartridge precolumn used for sample cleanup (Gemini NX C18, two stacked  $4 \times 3$  mm pre-columns, 5  $\mu\text{m}$  particle size, Phenomenex, Torrance, CA) with 1 mM ammonium acetate at a flow rate of 1 mL/min (for 1.5 min). Then, the enriched analytes were eluted backwards directly on to a Gemini NX C18 column (150  $\times$  2.0 mm i.d., 5  $\mu\text{m}$ ) protected by a  $4 \times 2$  mm pre-column with the same stationary phase. Gradient elution with the solvents ammonium acetate (1 mM in water) and acetonitrile (initial conditions, 0% acetonitrile for the first 1.5 min, linear increase to 50% during 1 min, linear increase to 100% during 4 min, 3.5 min isocratic hold, initial conditions re-established within 0.1 min, followed by an equilibration time of 1.9 min) was done at a flow of 0.2 mL/min.

The MS was operated in negative mode (ion spray voltage,  $-3.8$  kV, 400 °C). Since nonanoic acid did not produce any fragment ions ( $> m/z$  50) at significant yield, the test substance and internal standard were analyzed using

pseudo single ion monitoring of the respective molecular ions using ion transitions of  $m/z$  174  $\rightarrow$  174 (M-H of nonanoic acid- $D_{17}$ ) and  $m/z$  160  $\rightarrow$  160 (nonanoic acid- $D_3$ ) with a collision energy of 90 eV. Quantification was based on peak area ratios relative to the internal standard and in reference to matrix-matched standard solutions. For that, untreated soil was extracted as described above and test substance and internal standard were added to the extracts directly before transfer to the autosampler vial and dilution with water.

#### Recoveries, precision, and limits of quantification

Recovery experiments were performed with one agricultural soil (Brislach) and one railway soil (Lanzenhäusern), respectively, at fortification levels of 1 and 10 mg/kg. Recoveries were in the range of 85–91%. The precision was expressed as relative standard deviation (RSD) of 4 replicate extractions of soil samples fortified with 1 and 10 mg/kg. The analytical procedure was well reproducible with RSD values of 1.5–2.6%. The limit of quantification (LOQ) in the diluted soil extracts was determined at a signal-to-noise ratio of  $\approx 10$  and corresponded to concentrations of  $\leq 0.03$   $\mu\text{g/g}$  moist soil. The analytical method was thus sensitive enough to quantify  $\leq 0.6\%$  of the initial concentration in the incubation experiments. The LOQ in diluted aqueous 0.01 M  $\text{CaCl}_2$  solution (adsorption experiments, see below) was  $\leq 0.002$   $\mu\text{g/mL}$  and thus at least  $5\times$  below the lowest concentrations measured in the aqueous phase of the soil suspensions after equilibration.

#### Kinetic analysis

Kinetic parameters for the degradation of pelargonic acid were determined using the software CAKE (version 3, available at <https://cake-kinetics.org/>). We applied the single first-order (SFO) and the hockey-stick model (HS, this bi-phasic model assumes two sequential first-order curves with a breakpoint at a certain time) [19]. Initial concentrations were adjustable. For fitting, the iteratively reweighted least squares optimizer was selected. Fits were only accepted when statistically significant parameters (based on the 95% confidence interval) could be determined, with a  $\chi^2$  error  $< 15\%$  [19]. Visual assessment and residuals were further acceptance criteria. The two other kinetic models usually tested in the context of pesticide authorization, the double first-order in parallel model (DFOP, [19] this bi-phasic model assumes two compartments in which the compound is degraded according to first-order kinetics, but with different rate constants), and the first-order multi-compartment model (FOMC, [20] this bi-phasic model assumes a continuum of micro-compartments in which the compound is degraded according to first-order kinetics) initially were considered, but quickly dropped as both these models

are suited for situations where degradation slows down over time while, in our experiments, we observed the opposite.

#### Soil adsorption experiments

Batch adsorption experiments were performed in accordance with OECD guidance 106 at 20 °C in the dark [21]. In all tests, the indirect method was used, where only the remaining concentration in the aqueous phase was measured after achievement of adsorption equilibrium.

The sieved, field-moist soils were dried at 105 °C prior to use. Typically, 10 g dry soil was weighed into 40 mL clear glass vials with Teflon-lined screw caps. To these soils, 10 mL of a 0.01 M  $\text{CaCl}_2$  solution was added (resulting soil:solution ratio, 1:1). Suspensions for soil:solution ratios of 1:5 and 1:10 were prepared using 25 mL  $\text{CaCl}_2$  solution, and 5 and 2.5 g dry soil, respectively. Due to the rapid degradation of the test substance, the microbial activity in soils had to be suppressed for the duration of the experiment. Therefore, vials were capped, autoclaved (121 °C, 20 min), and allowed to cool to room temperature. Then, each vial was weighed and any losses that occasionally occurred during autoclaving were corrected by addition of autoclaved 0.01 M  $\text{CaCl}_2$  solution. The suspensions were then spiked with test substance dissolved in 10  $\mu\text{L}$  methanol. The vials were mounted on a reciprocal shaker (90 oscillations  $\text{min}^{-1}$ ) and agitated for several hours. The soil slurries were then centrifuged at  $\approx 1500g$  for 10 min and an aliquot of the supernatant (100  $\mu\text{L}$ ) was transferred to an autosampler vial where internal standard (100  $\mu\text{L}$  of nonanoic acid- $D_3$  in methanol, 2  $\text{ng}/\mu\text{L}$ ) and 800  $\mu\text{L}$  methanol were added. These solutions were analysed by LC-MS/MS in reference to standards prepared in 0.01 M  $\text{CaCl}_2$  solution diluted with methanol in the same way. The centrifugation conditions led to clear supernatants with no visible suspended particles. However, conditions may not have been sufficient to sediment all particles  $> 0.2$   $\mu\text{m}$  as recommended in the OECD guideline. Any particles potentially still present in the supernatant would have led to an overestimation of the test substance in solution and thus to an underestimation of the calculated  $K_F$  values. However, in the case of weakly adsorbing compounds, this effect is expected to be very small.

Preliminary tests were performed with topsoils to determine adequate soil:solution ratios. These tests were performed at a single concentration level (0.5  $\mu\text{g}/\text{mL}$ ). Based on these tests, soil:solution ratios of 1:1, 1:5, and 1:10 were used for isotherm measurements (Table 3). Adsorption in the railway soils was expected to be weak due to the low organic carbon content in these soils. Therefore, a soil:solution ratio of 1:1 was used for

isotherm measurements in these soils without preliminary testing.

The time required to reach the adsorption equilibrium was tested by agitation of soil suspensions for various time periods up to 24 h. From the declining concentration in the aqueous phase, the necessary equilibration time was determined by visual assessment. The equilibration was rapid in all soils with minimal changes in the aqueous phase concentrations after 4 h. Based on these results, an equilibration time of 12–16 h (shaking overnight) was considered appropriate.

To account for possible degradation, concentrations in the total system (soil and water) were determined over varying time periods. For analysis in the total system, the aqueous phase was decanted and the residual soil was extracted twice with 10 mL acetonitrile. Extracts and aqueous phase were combined and then analysed in the same way as soil extracts. Only minimal decline was observed ( $\leq 7\%$  after 24 h), indicating that pelargonic acid was stable in the autoclaved soil suspensions (a mass balance  $\geq 90\%$  is required in the OECD guideline [21]). Isotherms were not corrected for possible degradation.

For adsorption isotherms, to achieve measurements at 5 concentration levels, spanning two orders of magnitude, dilution series were prepared from a stock solution in methanol (concentration 10 mg/mL). A total of 10 concentration levels were prepared by sequentially diluting 1.5 g of the next higher concentration level with 1.2 g of methanol. These methanolic solutions were

then diluted 1:1000 in 0.01 M CaCl<sub>2</sub>. All 10 concentration levels (10, 5.56, 3.09, 1.72, 0.953, 0.529, 0.294, 0.163, 0.091, and 0.050  $\mu\text{g/mL}$ ) were used for the preparation of calibration standards and every other level was used for adsorption measurements.

The parameters of the Freundlich equation were determined from linear regressions of  $\log_{10} c_w$  vs  $\log_{10} c_s$ , with  $\log_{10}(K_F)$  as the intercept and  $1/n$  as the slope, using the *lm* function of the stats package in R [22].

## Results and discussion

### Degradation of pelargonic acid

Initially, degradation of pelargonic acid was investigated at a fairly low starting concentration of 5 mg/kg. The rationale behind the low spike levels was that on railway tracks the herbicides would be used for spot treatment, with substantial interception by weeds, rather than broadcast application. At this low starting concentration, degradation in the four topsoils was very rapid with  $DT_{50}$  values of  $<< 1$  h (9–12 min, Table 2). In the railway subsoils, degradation was considerably slower, but still very rapid with  $DT_{50}$  values of 1.0–2.3 h. The degradation could be fitted reasonably well assuming SFO decline in all 7 soils (blue lines, Fig. 2). In two subsoils, a pronounced lag phase was observed with slower decline in the initial 1–2 h and more rapid decline thereafter. The hockey stick model fitted the data clearly better than SFO (dashed lines, Fig. 2).

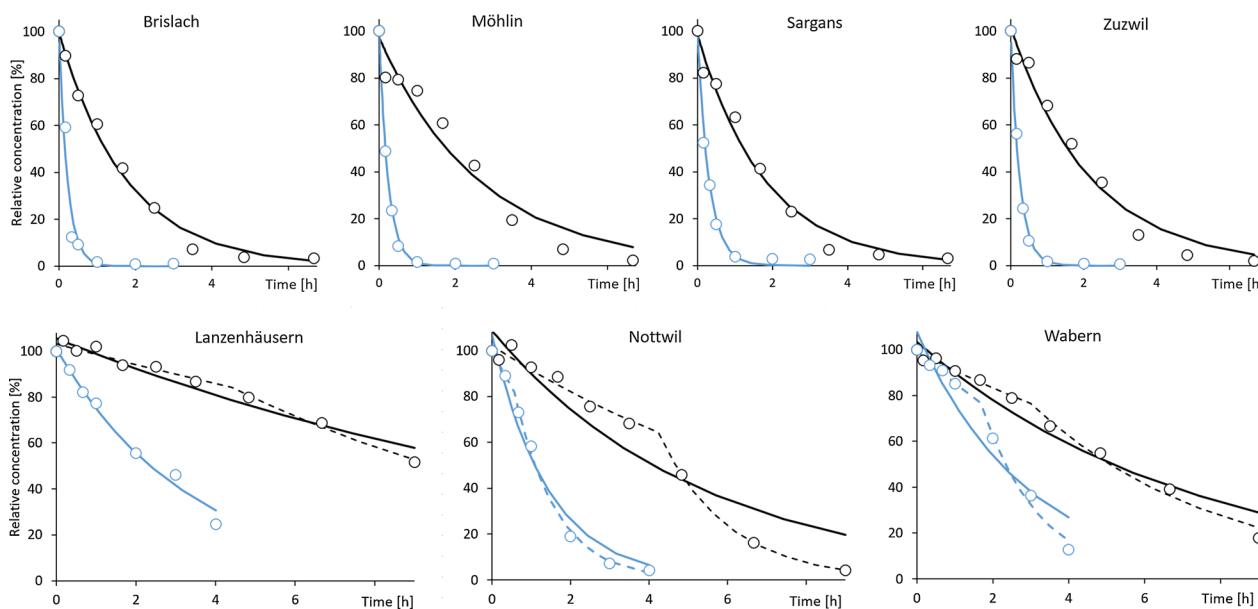
**Table 2** Half-lives<sup>a</sup> ( $DT_{50}$ ) of pelargonic acid in subsoils from railway tracks and agricultural topsoils

Starting concentration	5 mg/kg			15 mg/kg		
	water content [% WHC]	$DT_{50}$ [h]	95% CI <sup>b</sup>	water content [% WHC]	$DT_{50}$ [h]	95% CI <sup>b</sup>
<i>Subsoils from railway tracks</i>						
Lanzenhäusern	62	2.3	(2.0–2.8)	54	10.5	(8.7–13.2)
Nottwil	48	0.99	(0.76–1.41)	44	3.7	(2.7–5.7)
Wabern	67	2.0	(1.4–3.4)	51	4.9	(4.1–6.2)
<i>Geom. mean for railway soils</i>		1.7			5.8 (0.24 d)	
<i>Agricultural topsoils</i>						
Brislach	60	0.15	(0.11–0.24)	38	1.2	(1.1–1.4)
Möhlin	72	0.16	(0.15–0.17)	49	1.8	(1.4–2.7)
Sargans	58	0.20	(0.18–0.23)	49	1.3	(1.0–1.6)
Zuzwil	58	0.17	(0.15–0.20)	37	1.5	(1.2–1.9)
<i>Geom. mean for agricultural soils</i>		0.17			1.4	
<i><math>DT_{50}</math> value used for exposure modelling in the EU: range 0.70–1.58 days (n = 4)</i> <sup>c</sup>					29.3 (1.22 d)	

<sup>a</sup> All determined assuming exponential decline (SFO fit); additional data, also for “hockey-stick” fits, see additional file (chapter 1)

<sup>b</sup> 95% confidence interval

<sup>c</sup> Ref. [14]

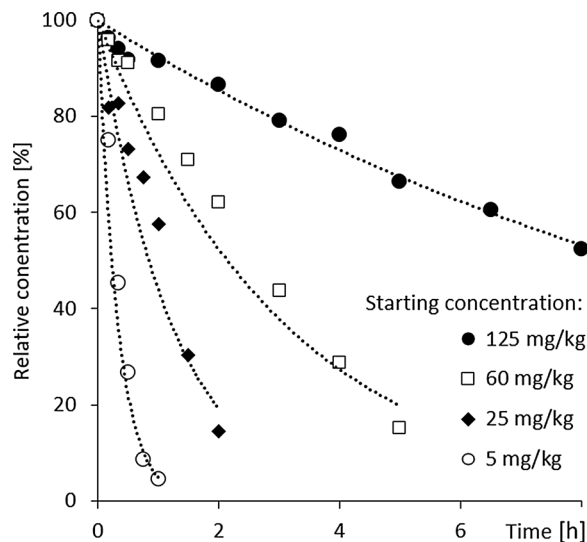


**Fig. 2** Degradation of pelargonic acid-D<sub>17</sub> in 4 agricultural topsoils (top row) and 3 soils from railway tracks (bottom row). Fitted single first order (SFO) decline curves are plotted as solid lines, bi-phasic decline (hockey stick) as dashed lines. Data from experiments with starting concentration 15 mg/kg are shown in black, those with 5 mg/kg in blue

Data on the degradation of pelargonic acid in soils from studies submitted for renewal of the authorization of the substance in Europe [16] became available shortly after we had conducted our experiments. Dissipation of pelargonic acid in those soils was also rapid, with DT<sub>50</sub> values in the range of 17–38 h (0.7–1.6 d values normalized to reference conditions) but considerably slower than in our soils.

In view of the significant differences between our results and those in the registration dossier, we conducted various additional experiments with two of the soils (Brislach and Möhlin) in which the potential influence of soil handling (pre-incubation of the soils at room temperature before spiking), different spiking procedures, and different extraction methods were investigated. While none of the aforementioned factors had any significant influence on the dissipation rate of the test substance, we found a quite remarkable impact of the starting concentration with substantially slower degradation at higher concentrations. In soil Brislach, DT<sub>50</sub> values increased from 0.15 h at a spike level of 5 mg/kg to 7.9 h at 125 mg/kg (Fig. 3, Table 2, and Additional file 1: Table S2). Even at the highest dose level, degradation in this soil was thus faster than in the studies in the EU registration dossier (DT<sub>50</sub>, 17–38 h) which were conducted at dose levels of 20 mg/kg [16].

To describe the degradation of pelargonic acid over a range of dose levels, we applied two kinetic models which are based on different mechanistic considerations. The



**Fig. 3** Degradation of pelargonic acid-D<sub>17</sub> in soil Brislach at 4 different starting concentrations. Dashed lines (SFO) shown for illustration purposes only

first was a logistic degradation model which was suggested by the FOCUS kinetics working group [23] to be applied to data showing pronounced lag phases and is based on the assumption that the substance initially inhibits the microorganisms. The second assumes conventional Michaelis–Menten (enzyme) kinetics which can describe the transition of reaction kinetics from

zero order (reaction independent of substrate concentration but limited by the concentration and turnover rate of the enzyme present) to first order [24]. Both of these models are able to describe the observed behaviour. However, without further information on, for example, microbial biomass, both model approaches do not provide the definitive explanation for the observed concentration-dependent decline, except that they both hint at inhibition of decline at higher dose levels. More details on the fitting procedure and results can be found in the additional file (chapter 2, Additional file 1: Tables S2, S3, Figures S1–S4).

To obtain  $DT_{50}$  values representative of application rates potentially used on railway tracks, we conducted an additional round of experiments with the same set of soils, but at a threefold higher starting concentration of 15 mg/kg. These experiments expectedly yielded higher  $DT_{50}$  values for all soils than the respective experiments at 5 mg/kg (black lines, Fig. 2; Table 2). To some extent, this slower degradation may be due to the fact that the soil moisture was lower than in the experiments at the starting concentration of 5 mg/kg. However, only 2 experiments were slightly below the recommended range of 40–60% of the maximum water holding capacity (soils Brislach and Zuzwil, with 38 and 37%, respectively). A pronounced bi-phasic behaviour was observed in all 3 railway soils and the corresponding HS kinetic model fitted the data clearly better than the SFO model (Fig. 2). However, models used for groundwater exposure assessment in the context of pesticide authorisation require SFO- $DT_{50}$  values which ranged from 3.8 to 10.5 h in railway soils. These  $DT_{50}$ -values overestimate the degradation directly after application, but underestimate the degradation on the long term. For groundwater exposure calculation these values would thus represent a worst-case.

### Adsorption to soils

Since pelargonic acid clearly was not stable in soils, adsorption experiments were carried out in autoclaved soil. Initial experiments confirmed that pelargonic acid was stable in soil suspensions after a single autoclaving cycle, at least for the duration of the equilibration (12–16 h). This pretreatment of the soils was chosen based on availability at our laboratory. This and other pretreatments, such as addition of chemical disinfectants ( $HgCl_2$ ,  $NaN_3$ ) and gamma-irradiation were all found to alter the properties of the soils and the aqueous medium and thus potentially affect adsorption of chemicals [25–29]. Some of these changes may increase (e.g., increased surface area), some decrease adsorption (e.g., change in pH, or quantity and quality of organic matter), depending on substance properties. This should be considered when

interpreting the determined adsorption endpoints. As soil pH is an important factor for adsorption of pelargonic acid (see below), actual pH of the soil suspensions was measured at the end of the equilibration phase.

Adsorption experiments were analyzed with the Freundlich model [30],

$$c_s = K_F c_w^{\frac{1}{n}} \quad (1)$$

where  $c_w$  is the concentration in the aqueous phase (in  $\mu\text{g/mL}$ ) and  $c_s$  is the concentration in soil ( $\mu\text{g/g}$ ). The Freundlich adsorption coefficient ( $K_F$ ; unit,  $\mu\text{g}^{1-1/n} \text{mL}^{1/n} \text{g}^{-1}$ ) and the Freundlich exponent ( $1/n$ ) were determined from linear regressions of  $\log c_w$  vs  $\log c_s$  at a reference concentration  $c_{\text{ref}} = 1 \mu\text{g mL}^{-1}$ . Freundlich isotherms in the 12 topsoils and 3 railway soils are shown in Fig. 4. The corresponding  $K_F$  values (Table 3) varied considerably between soils, indicating very weak adsorption in the subsoils ( $K_F$  0.060–0.31 mL/g) and stronger adsorption in most topsoils ( $K_F$  up to 39.7 mL/g).

Adsorption appears to correlate to some extent with the organic carbon content of the soils ( $R^2 = 0.63$ ). The  $K_{\text{Foc}}$  (organic carbon normalized adsorption coefficients) values thus lie within a narrower range (11–371 mL/g; coefficient of variation, CV, 110%) than the corresponding  $K_F$  values (0.06–39 mL/g; CV, 210%). When these  $K_{\text{Foc}}$  values are plotted against the pH of the soil suspensions, it is evident that adsorption of pelargonic acid is pH dependent with stronger adsorption at low soil pHs, as expected for weak acids (Fig. 5).

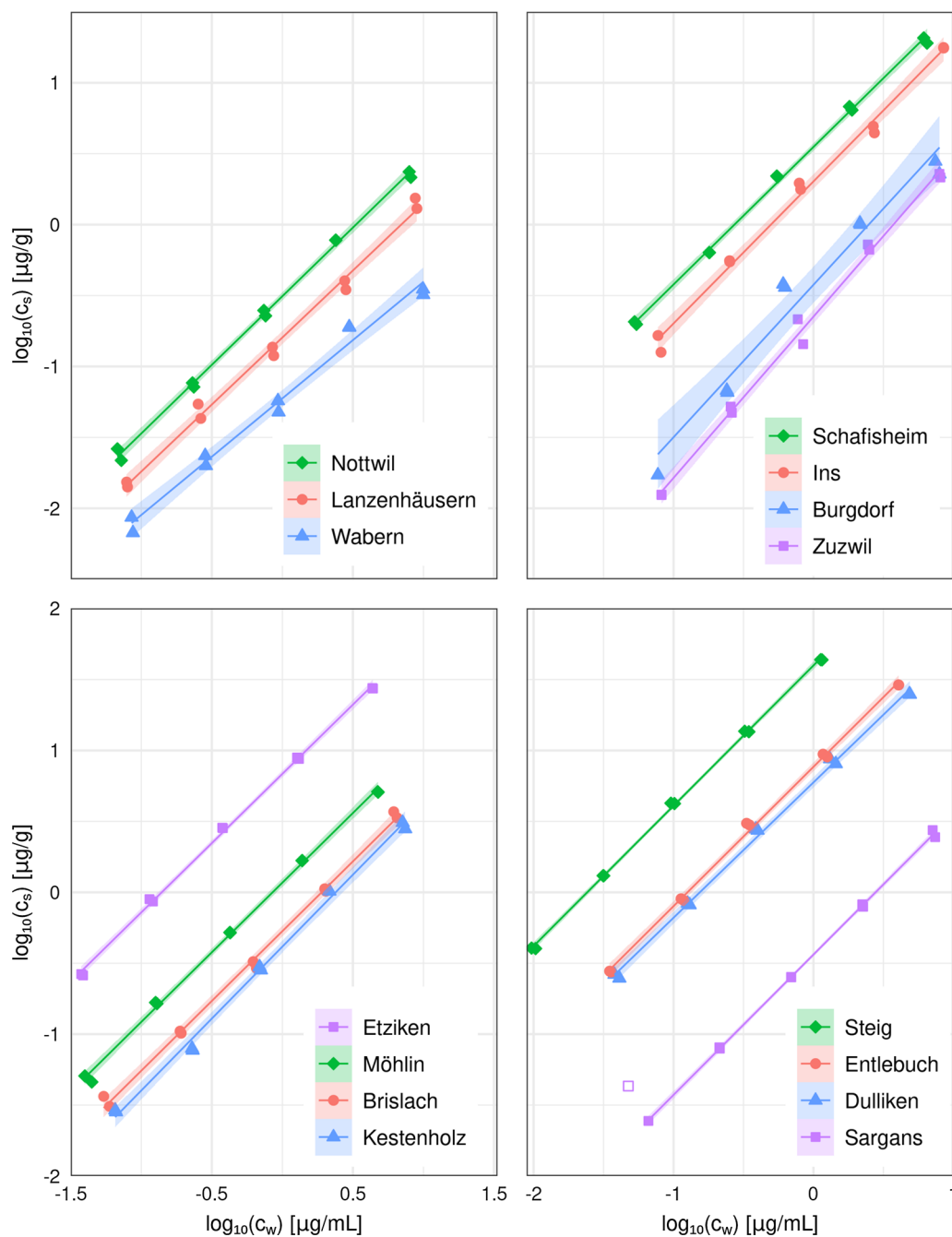
The  $K_{\text{Foc}}$  values observed in the different soils were fitted assuming a pH dependent equilibrium between the neutral (protonated) form of pelargonic acid and the anionic (deprotonated) form which is determined by the dissociation constant, using the following equations (adapted from [31]):

$$K_{\text{Foc}}^{\text{obs}} = \alpha^{\text{HA}} \cdot K_{\text{Foc}}^{\text{HA}} + (1 - \alpha^{\text{HA}}) \cdot K_{\text{Foc}}^{\text{A}} \quad (2)$$

$$\alpha^{\text{HA}} = \frac{1}{1 + 10^{(\text{pH} - \text{p}K_a)}} \quad (3)$$

where the fit parameters  $K_{\text{Foc}}^{\text{HA}}$  and  $K_{\text{Foc}}^{\text{A}}$  are the  $K_{\text{Foc}}$  values of the neutral and anionic form, respectively, and the  $\text{p}K_a$  is the negative logarithm of the apparent dissociation constant in the soil–water suspension. To account for the fact that pH at the adsorption complex might differ from pH in bulk solution,  $\text{p}K_a$  was included as a fit parameter. This is equivalent to an approach proposed by van der Linden et al., where the term  $(\text{p}K_a + \Delta\text{pH})$  was optimized, with  $\text{p}K_a$  being the literature value and  $\Delta\text{pH}$  (correction accounting for possible surface acidity effects) the fitting parameter [32]. Fitting this equation to all 15 data points





**Fig. 4** Adsorption isotherms of pelargonic acid-D<sub>17</sub> in 3 soils from railway tracks (top left panel) and 12 topsoils (all others).  $c_s$ : amount adsorbed to soil,  $c_w$ : concentration in solution. Note the different scales. The shaded areas are the 95% confidence intervals for the fitted curves. The open symbol (soil Sargans) is considered an outlier

yielded the curve shown in Fig. 5 and corresponding  $K_{FOC}^{HA}$  and  $K_{FOC}^A$  values of 338 and 20.0 mL/g, respectively. The fitted  $pK_a$  value of 4.86 is very close to  $pK_a$  values reported in the literature (4.94–5.0) [14]. Details of the fitting procedure and confidence intervals for the fitted parameters are provided in the additional file (chapter 3).

Consistent with our results, pH-dependent adsorption with  $K_{FOC}$  values of 8.1 to 570 mL/g was observed in a study submitted with the EU registration dossier [16].

Freundlich exponents in batch adsorption studies usually are  $<1$ , indicating that adsorption gets weaker at higher concentrations as higher affinity sorption sites

**Table 3** Freundlich adsorption coefficients ( $K_F$ ) and exponents ( $1/n$ ) in soils from railway tracks and various topsoils

	pH in experiment <sup>a</sup>	C <sub>org</sub> [%]	Soil:solution ratio	Fraction adsorbed [%]	$K_F$ <sup>b</sup> [mL/g]	95% CI <sup>c</sup>	$K_{Foc}$ [mL/g]	95% CI <sup>c</sup>	1/n	R <sup>2</sup>
<i>Subsoils from railway tracks</i>										
Wabern	6.85	0.21	1:1	2–13	0.060	(0.052–0.068)	28.4	(0.74–0.90)	0.82	0.986
Lanzenhäusern	7.32	0.54	1:1	10–24	0.160	(0.144–0.178)	29.6	(0.88–0.99)	0.95	0.993
Nottwil	7.44	0.78	1:1	18–33	0.313	(0.293–0.334)	40.1	(0.93–1.01)	0.97	0.998
<i>Mean values<sup>d</sup></i>							32.3		0.91	
<i>topsoils (sorted by pH)</i>										
Etziken	3.73	2.3	1:5	55–61	6.84	(6.46–7.24)	297	(0.95–1.01)	0.98	0.999
Dulliken	3.83	2.1	1:5	49–59	5.95	(5.48–6.47)	284	(0.91–1.00)	0.95	0.997
Steig	3.98	10.7	1:5	88–90	39.7	(37.4–42.2)	371	(0.97–1.01)	0.99	0.999
Schafisheim	4.38	1.6	1:5	36–45	3.53	(3.32–3.76)	221	(0.94–1.00)	0.97	0.998
Entlebuch	4.87	3.7	1:5	59–65	7.67	(7.13–8.24)	207	(0.95–1.02)	0.98	0.998
Möhlin	5.22	1.2	1:1	49–57	1.17	(1.09–1.25)	97.5	(0.95–1.02)	0.98	0.998
Brislach	6.29	1.56	1:1	31–41	0.532	(0.488–0.580)	34.1	(0.93–1.03)	0.98	0.996
Zuzwil	6.60	1.49	1:1	12–26	0.224	(0.201–0.251)	15.1	(1.07–1.20)	1.14	0.995
Ins	7.02	7.5	1:10	11–21	2.02	(1.80–2.26)	26.9	(0.93–1.07)	1.00	0.993
Burgdorf	7.06	2.4	1:1	18–39	0.378	(0.281–0.505)	15.7	(0.88–1.27)	1.07	0.961
Sargans	7.21	3.18	1:1	24–48	0.364	(0.351–0.377)	11.4	(0.97–1.01)	0.99	0.999
Kestenholz	7.24	2.8	1:1	24–34	0.414	(0.376–0.456)	14.8	(0.96–1.07)	1.01	0.995
<i>Mean values (our data, topsoils)<sup>d</sup></i>					<i>acidic soils (pH ≤ 6.2, n = 6)</i>		228		0.976	
					<i>alkaline soils (pH &gt; 6.2, n = 6)</i>		18.2		1.03	
<i>Values used for exposure modelling in the EU<sup>e</sup></i>					<i>acidic soils (pH ≤ 6.2, n = 2)</i>		95		1	
					<i>alkaline soils (pH &gt; 6.2, n = 2)</i>		8.4		0.987	

<sup>a</sup> Measured in soil suspensions after sampling for isotherm measurements (i.e. after autoclaving and agitation for 16 h)

<sup>b</sup> The unit of the distribution coefficient  $K_F$  ( $\mu\text{g}^{-1/n} \text{mL}^{1/n} \text{g}^{-1}$ ) was evaluated at a reference concentration  $c_{\text{ref}} = 1 \mu\text{g mL}^{-1}$

<sup>c</sup> 95% confidence interval <sup>d</sup>geom. mean  $K_{Foc}$  and arithm. mean  $1/n$  <sup>e</sup> ref [14]

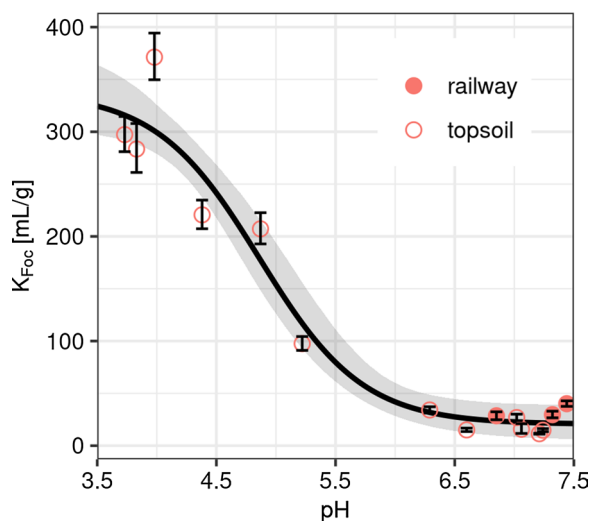
are gradually depleted. This was also the case for pelargonic acid in most soils studied with the exception of 2 soils for which Freundlich exponents  $> 1$  were observed (soils Burgdorf and Zuzwil, Table 3), whereby only for soil Zuzwil the 95% confidence interval does not include 1 (linear sorption). From the soil properties listed in Table 1, these two soils cannot be set apart from the other soils studied. It is thus unclear what caused this rather unusual behaviour which was also observed in 2 out of 5 soils used for batch adsorption experiments in the EU registration dossier [16]. The lowest  $1/n$  value of 0.82 was observed in soil Wabern which has the lowest organic carbon content. This is consistent with data for the herbicides 2,4-D and quizalofop and their metabolites for which low  $1/n$  values were observed in a range of subsoils with low organic carbon content [17].

#### Assessment of the leaching behaviour of pelargonic acid when applied to railway tracks

Leaching of herbicides applied to railway tracks is expected to be more likely than from application in agricultural fields. Various factors contribute to that, particularly the

coarse texture and low content of organic matter in the soil below railway tracks leading to efficient drainage and minimal retention of organic substances in the soil column. In addition, subsoils often show lower biological activity and thus slower degradation of organic substances applied [17, 33, 34]. For the assessment of the leaching behaviour in this situation, the tools otherwise used in the context of pesticide authorization are thus of limited use. However, for German national authorization of herbicides intended for use on railway tracks, a set of 3 scenarios was developed [35]. The scenarios provide “crop”, soil, and climate data for the software PELMO [36].

The aforementioned railway scenarios were used to assess the potential leaching of pelargonic acid after application to railway tracks (for details, see additional file, chapter 4). Two sets of substance parameters were used, the EU-wide harmonised endpoints for  $DT_{50}$ ,  $K_{Foc}$  and  $1/n$  for use in exposure modelling published by the European Food Safety Authority (EFSA [14];  $K_{Foc}$  and  $1/n$  values for alkaline soils, Table 3) as well as the values obtained in the present study (geom. mean  $DT_{50}$ -value for railway soils at 15 mg/kg, Table 2, as well as the



**Fig. 5** Adsorption  $K_{Foc}$ -values of pelargonic acid- $D_{17}$  versus pH of the soil suspensions. The line represents the relationship of  $K_{Foc}$  on pH in Eq. (2), fitted to the data points for topsoils and soils from railway tracks. Bars indicate the 95% confidence intervals for  $K_{Foc}$  and the grey shaded area is the 95% confidence interval for the fitted curve

corresponding geom. mean  $K_{Foc}$  and arithm. mean  $1/n$  values, Table 3).

Calculations with the EU endpoints yielded annual mean concentrations in soil leachate at 1 m depth (“predicted environmental concentrations in groundwater”,  $PEC_{GW}$ ), which is the regulatory value against which the parametric drinking water limit for pesticides  $0.1 \mu\text{g/L}$  is evaluated) in the range of  $<0.001$ – $1.2 \mu\text{g/L}$  (depending on the date of application for a single application between 1 May and 30 September, see Additional file 1: Figure S5) in one of the scenarios (Lindau) whereas  $PEC_{GW}$  in the other two scenarios were always  $<0.001 \mu\text{g/L}$ . In contrast to the calculations with the EU endpoints, none of the scenarios indicated any leaching potential ( $PEC_{GW} < 0.001 \mu\text{g/L}$ ) when parameterised with our data for railway subsoils. This is likely due to both faster degradation and somewhat stronger adsorption. In any event, given the rapid degradation in soil, leaching to some depth below railway tracks might occur under extreme circumstances [37], but it seems highly unlikely that the compound would lead to groundwater contamination as further degradation between the lower boundary of the model at 1 m below the railway track and actual groundwater would be expected.

## Conclusions

Our results from laboratory incubation experiments demonstrate that pelargonic acid is rapidly degraded not only in agricultural topsoils but also in subsoils

from railway tracks at concentrations in soil resulting from typical applications in the field, with  $DT_{50}$  values well below 1 day. The observed, pronounced concentration dependence with slower degradation at higher concentrations could not be fully explained without further experimental work. However, more elaborate kinetic fitting than is typically applied to soil degradation experiments points to the capacity of the microbial population in the soil for degradation of the substance as the limiting factor, probably in combination with an inhibitory effect at higher dose levels.

Adsorption of pelargonic acid was found to be pH dependent, with stronger adsorption at lower pH. With  $K_{Foc}$  values of  $20$ – $40 \text{ mL/g}$  in the alkaline subsoils, pelargonic acid can be considered a very mobile substance. However, model calculations with scenarios specifically developed for application on railway tracks yielded  $PEC_{GW} < 0.001 \mu\text{g/L}$  when parametrised with the endpoints obtained in this study. From the point of view of groundwater protection, pelargonic acid thus appears to be suitable for application as a herbicide on railway tracks, even in situations that are vulnerable to leaching.

## Abbreviations

1/n	Freundlich exponent
95% CI	95% Confidence interval
$C_{org}$	Organic carbon
CV	Coefficient of variation
$DT_{50}$	Dissipation time to 50%
DFOP	Double first-order in parallel (kinetic model)
EFSA	European Food Safety Authority
EU	European Union
HS	Hockey-stick (kinetic model)
$K_f$	Freundlich adsorption coefficient
$K_{Foc}$	Organic carbon-normalised Freundlich adsorption coefficient
FOCUS	FORum for the Co-ordination of pesticide fate models and their Use
FOMC	First-order multi-compartment (kinetic model)
HPLC	High performance liquid chromatography
LC-MS/MS	Liquid chromatography-tandem mass spectrometry
LOQ	Limit of quantification
OECD	Organisation for Economic Co-operation and Development
$PEC_{GW}$	Predicted environmental concentrations in groundwater
RCF	Relative centrifugal force
RSD	Relative standard deviation
SFO	Single first-order (kinetic model)
USDA	U.S. Department of Agriculture
WHC	Maximum water holding capacity

## Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s12302-023-00825-1>.

**Additional file 1. Chapter 1.** Kinetic fitting of degradation experiments at 5 and 15 mg/kg. **Chapter 2.** Simultaneous kinetic fitting of degradation experiments at various starting concentrations. **Table S1.** Experimental conditions of the incubation experiments in the Brislach and Möhlin topsoils. **Figure S1.** Degradation of pelargonic acid- $D_{17}$  in the Brislach and Möhlin topsoils with different starting concentrations between 5 and 125

mg/kg. The decline curves are fitted with the logistic degradation model. **Table S2.** Best estimates and confidence intervals in parentheses for the parameters in the logistic degradation model for treatments with different starting concentrations in the Brislach and Möhlin topsoils. **Figure S2.** Effect of the starting concentration on the initial degradation rate coefficient for the Brislach and Möhlin topsoils. **Figure S3.** Degradation of pelargonic acid-D<sub>17</sub> in the Brislach and Möhlin topsoils with different starting concentrations between 5 and 125 mg/kg. The decline curves are fitted with the Michaelis-Menten kinetic model without and with substrate inhibition. **Table S3.** Best estimates and confidence intervals in parentheses for the parameters in the Michaelis-Menten kinetic model without and with substrate inhibition for treatments with different starting concentrations in the Brislach and Möhlin topsoils. **Figure S4.** The reaction rate of an enzyme catalysed reaction as a function of the initial substrate concentration for the Brislach (with substrate inhibition) and Möhlin (without substrate inhibition) topsoils. **Chapter 3.** Fitting of pH-dependent adsorption of pelargonic acid. **Table S4.** Fitted pH-dependent adsorption parameters for pelargonic acid using adsorption K<sub>foc</sub> values from all 15 soils tested. **Chapter 4.** Modelling of leachate concentrations. **Table S5.** Substance and application parameters used for the simulation of the leaching potential of pelargonic acid for use on railway tracks using PELMO 4.01. **Table S6.** Selected climate properties of the railway scenarios. **Table S7.** Selected soil properties of the railway scenarios. **Figure S5.** Annual mean concentration of pelargonic acid in soil leachate at 1 m depth after a single application of 5 kg of the substance/ha on a railway track as a function of application date.

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#### Author contributions

TP, IB, and RK were involved in the study design, data analysis, and drafting of the manuscript. JM was mainly concerned with the experimental work.

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#### Availability of data and materials

The datasets used and analyzed during the current study are mostly available in the supporting information and otherwise from the corresponding author on reasonable request.

#### Declarations

##### Ethics approval and consent to participate

Not applicable.

##### Consent for publication

Not applicable.

##### Competing interests

The authors declare that they have no competing interests.

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