Leaching of herbicides and their metabolites in lysimeters filled with soils from railway tracks

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HIGHLIGHTS

- 2,4-D, flazasulfuron, and metabolites found in leachate at concentrations >1 µg/L.
- Quizalofop-P, pelargonic-acid, and glyphosate show a low potential for leaching.
- From a perspective of groundwater protection, glyphosate is the best option for uses on railways.

GRAPHICAL ABSTRACT
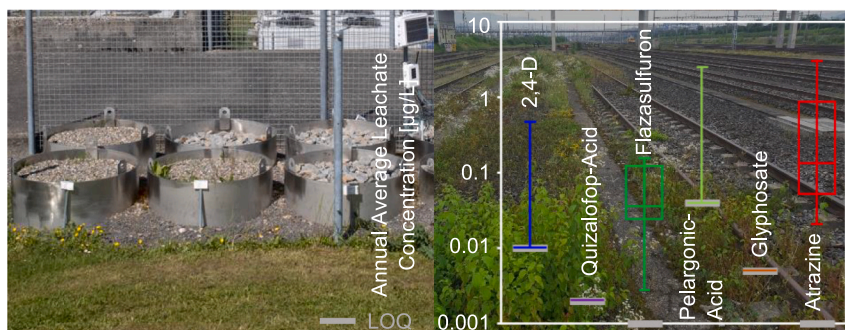
ABSTRACT

Glyphosate currently is the most-widely used herbicide for weed control on railway tracks. However, railway companies look for non-chemical and chemical alternatives. Glyphosate has a low potential for leaching to groundwater and alternative herbicides should ideally share this behavior. We investigated the leaching of glyphosate and five potential alternatives in lysimeters filled with three different soils from railway tracks. Herbicides were applied in three consecutive years to 4–7 lysimeters. Leachate was collected and analysed for herbicides and major metabolites. Highest annual average concentrations of 23 µg/L were found for atrazine, which was selected as mobile reference compound. 2,4-D, flazasulfuron, and its major metabolite DTPU reached annual average concentrations of 0.60, 0.43, and 0.50 µg/L, respectively. Pelargonic-acid was detected in single samples shortly after application and heavy rainfall. Quizalofop-P, glyphosate, and metabolites were only sporadically found in leachate at annual average concentrations ≪0.1 µg/L. Highest leachate concentrations were generally observed in lysimeters with a high proportion of sandy fine material and little organic carbon, except for the quickly-degradable pelargonic-acid and 2,4-D that reached highest concentrations in lysimeters with high gravel content and thus small effective transport volume. After three years, up to 30, 6.5, and 0.56 % of the applied mass of flazasulfuron, atrazine, and 2,4-D, respectively, was recovered in leachate in form of the active substances and/or their metabolites (expressed in parent equivalents). Although recoveries of flazasulfuron exceeded those of atrazine, concentrations were lower due to the 100-fold lower application rate. From the perspective of groundwater protection, the currently used glyphosate still is by far the best (chemical) option while all tested possible glyphosate alternatives did show some potential for leaching which may, however, be

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manageable with certain restrictions (e.g., spot spraying). These findings are likely applicable to other uses in non-agricultural settings with gravel or paving stone surfaces.

1. Introduction

Weed control on railway tracks is mostly accomplished with herbicides (Cederlund, 2022; Ramwell et al., 2004; Schweinsberg et al., 1999; Torstensson, 2001). However, several railway companies currently seek for strategies to reduce the herbicide use and thus environmental impact of chemical weed control. A number of non-chemical alternatives (Nolte et al., 2018) are tested such as hot water or steam treatment, weed control by flaming or application of high-voltage ("electro-herb"), autonomous weeding or mowing robots, prevention of plant growth by installation of geotextiles, or targeted greening ("green carpet"). Nonetheless, while a complete substitution of herbicides seems challenging, the amounts used on railway tracks may be reduced, e.g., by weed wiping or spot spraying technology (Gerhards et al., 2022).

An important property of herbicides suited for use on railway tracks is that leaching to groundwater is minimal (Schweinsberg et al., 1999; Torstensson et al., 2002). Compounds with (i) strong sorption (to railway ballast, subgrade, and subsoil), (ii) fast degradation (also in soils with low microbial activity), and/or (iii) low application rates are thus generally advantageous.

Glyphosate is currently the most widely-used herbicide for railway tracks with broad-spectrum activity (Duke, 2018) and low potential for leaching to groundwater (Albers et al., 2020; Borggaard and Gimsing, 2008; Vereecken, 2005), although it should be noted that the compound may reach shallow groundwater after (particle-bound) transport through preferential flow paths (Börjesson and Torstensson, 2000; Carretta et al., 2022; Cederlund, 2022; Vereecken, 2005). Due to uncertain, future authorization in Europe (European Union, 2017), railway companies look for alternatives. Two potential alternative herbicides, quizalofop-P-ethyl and 2,4-D, were therefore investigated in a previous study in terms of their leaching potential in soils below railway tracks (Buerge et al., 2020). Quizalofop-P-ethyl has a rather narrow spectrum of activity against grasses (European Food Safety Authority, 2009), but would complement the herbicide 2,4-D that acts primarily against broad-leaved weeds (European Food Safety Authority, 2014). Based on laboratory sorption and degradation experiments with these herbicides in different soils from railway tracks, the potential for leaching was concluded to be low for quizalofop-P-ethyl and moderate for 2,4-D (Buerge et al., 2020). In a second study, similar experiments were performed with pelargonic-acid (Poiger et al., in prep), a saturated C9-fatty acid, manufactured from rapeseed oil. Due to its extremely fast degradation in railway soils, the potential for leaching was also concluded to be low. Pelargonic-acid is a contact herbicide and not systemic, i.e., only aerial parts of the plants are burnt down (European Food Safety Authority, 2021). Several applications per year are therefore required for sufficient weed control. However, pelargonic-acid was found to notably improve the activity of flazasulfuron (Kilian and Marienhagen, 2019), a promising herbicidal compound already used by railway companies in certain countries. Flazasulfuron has quite a broad spectrum of activity and is effective at low application rates. Unfavorable are its weak sorption in soils and moderate degradability (European Food Safety Authority, 2016), similar to atrazine which, however, requires two orders of magnitude higher application rates. A few decades ago, atrazine was widely used for weed control on railway tracks, and contamination of groundwater was, in several cases, linked to uses on railways (Schweinsberg et al., 1999).

In the present study, leaching of glyphosate, the four potential alternative herbicides quizalofop-P-ethyl, 2,4-D, pelargonic-acid, and flazasulfuron, as well as atrazine was investigated in parallel in several lysimeters that were filled with three different soils from railway tracks. The herbicides were applied in three consecutive years to 4–7 of the 10

lysimeters. Leachate samples were collected during three years and were analysed for the active substances as well as for eleven metabolites. This study allows a direct comparison of the leaching behavior of six herbicides and their metabolites in lysimeters specifically constructed to assess a possible use on railway tracks.
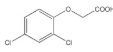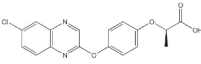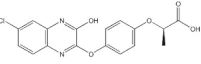
2. Materials and methods
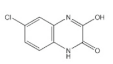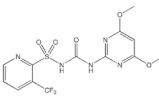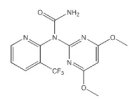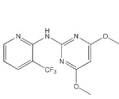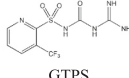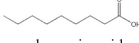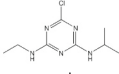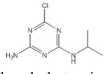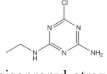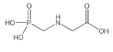
2.1. Chemicals and herbicides

Details on chemicals used in this study are given in Tables 1 and A1. Stock solutions were prepared in methanol, except for 3-OH-CQO (methanol/0.03 M NaOH 1/1 (*v/v*)), GTPS (acetonitrile/water 1/1), *N,N*-dimethyl-D$_6$-nicosulfuron, desethyl-atrazine-D$_6$, and desisopropyl-atrazine-D$_5$ (acetone), and glyphosate and AMPA (acetonitrile/0.02 M NaOH 7/3). Commercial herbicides were purchased from local distributors in Switzerland (Table A2).

2.2. Soils

Ballast (coarse material which forms the track bed upon which railroad ties are laid), subgrade (technical material between ballast and subsoil), and subsoil samples were collected in July and August 2019 from railway tracks at three locations in Switzerland (coordinates, see Table A3). Ballast and subgrade had last been replaced 25–33 years before. At location Lanzenhäusern (L, Fig. A1), material was taken from 6 layers, relatively clean ballast from the top 10 cm (layer L1), "dirty"

Table 1
Chemical structures of the analysed herbicides and soil metabolites included in the analytical protocol.

[a] Abbreviations for metabolites as defined in the respective conclusions of the European Food Safety Authority (2009, 2014, 2016).

ballast with fine material at 10–30 cm depth (L2), and subsoil down to 140 cm (L3–L6). At location Nottwil (N), clean ballast was taken at 0–15 cm depth (N1), dirty ballast at 15–40 cm (N2), subgrade at 40–60 cm (N3), and subsoil at 60–80 cm (N4). At location Wabern (W), subgrade material was taken at the lateral cess (maintenance path) from 7 layers down to 170 cm (W2–W8). Data on the grain size distribution of the different soil layers and on selected properties of the fine fraction (<2 mm) are given in Table A3.

2.3. Installation and filling of the lysimeters

Ten cylindrical lysimeters were installed at the research institute of Agroscope in Wädenswil, Switzerland (47°13′22″N/08°40′33″E/470 m. a.s.l., Fig. A3). The lysimeters, made of stainless steel, had a diameter of 80 cm, equivalent to a surface area of 0.5 m^2, and a height of 145 cm. They were positioned in two rows of five lysimeters at a distance of ≈6 cm between each other on a concrete foundation (Fig. A2). Between the lysimeters, gravel was filled up to a height of 120 cm for insulation against variations in air temperature.

The bottom of the lysimeters was flat with a 3 cm borehole in the middle, covered with a 20 × 20 cm sieve, made of stainless steel (mesh size, 2.0 mm; wire size, 1.0 mm). From there, leachate was drained into 20-L stainless steel collection vessels via 2.5–5 m long pipes with 1–2 % inclination (also made of stainless steel). All connections were tightly sealed. The collection vessels were placed in a cooling container at 4 °C (KC1420, Pircher Partner, Schachen, Switzerland) in an underground room (Fig. A4). One vessel was placed on a scale to follow the collection of leachate on-line every 30 min (type PBD769 with terminal ICS689 from Mettler-Toledo, Greifensee, Switzerland).

For optimal drainage conditions, three layers of calcined quartz sand (Siligran, from Euroquarz, Dorsten/Laussnitz, Germany) were filled into the lysimeters, starting with a 7-cm layer of 3–6 mm fine gravel, followed by a 7-cm layer of 0.7–1.2 mm coarse sand, and a 3-cm layer of 0.1–0.5 mm fine sand. A few days later, in August 2019, the lysimeters were filled with the different layers of material collected at the three railway locations (L1-L6, N1-N4, and W2-W8, Table A3). Layer W2 was covered with an additional 5-cm layer of new, medium gravel (W1, obtained from Südostbahn railways), which is typically used on lateral maintenance paths along railway tracks. Note that filling depths in the lysimeters slightly differed from the sampling depths. At location Nottwil, it was technically not possible to collect material from deeper soil layers (Section 2.2).

Four lysimeters were filled up with material from location Lanzenhäusern (L_a, L_b, L_c, L_d), three each with material from Nottwil (N_a, N_b, N_c) and Wabern (W_a, W_b, W_c). In lysimeter L_d, four temperature probes were installed at depths of 55, 85, 105, and 119 cm, respectively, below the gravel surface (Vantage Connect station from OS Technology, Gümligen, Switzerland, Fig. A3). They were buried around the center of the lysimeters. The cables were installed along the wall of the lysimeter in a PVC pipe (diameter, 1 cm).

Excavation and repacking certainly resulted in a changed soil structure, for example with regard to possible occurrence of preferential flow paths. While existing preferential flow paths were eliminated in the process, others (e.g. along the lysimeter walls) may have been created. The impact of this repacking on leaching processes is difficult to assess. As railway tracks are technical systems and the underground materials are always disturbed during construction works, we believe that our packing procedure reflects a normal case. To minimize the impact of possible artefacts of the filling procedure, the material in the lysimeters was allowed to settle for >8 months prior to the first application.

2.4. Application of bromide

Bromide was applied as a conservative tracer on lysimeter L_d on April 20, 2020, on lysimeters L_b, L_d, N_b, and W_b on March 12, 2021, and on lysimeters L_d, N_a, N_b, and N_c on March 10, 2022 (Table A4). For that, a

solution containing 1 g $CaBr_2$ (anhydrous, 99.98 %, Sigma-Aldrich; corresponding to 0.8 g bromide) dissolved in 13.3 mL water was evenly applied with a polyethylene spray bottle to a concentric area with ≈65 cm diameter (corresponding to 0.33 m^2, two-thirds of the lysimeter surface). Afterwards, for quantitative transfer of bromide, the spray bottle was rinsed with a few mL of water which was also sprayed onto the lysimeter. One hour after application of bromide on April 20, 2020, all lysimeters were irrigated with 10 L of deionised water/tap water (95/ 5), i.e., the equivalent of 20 mm precipitation. Irrigation was accomplished slowly, in several portions within 7 h. Lysimeters were irrigated because the weather forecast predicted no precipitation in the following days. However, this was the only time during the three-year study that irrigation was applied.

2.5. Application of herbicides

Herbicides were applied in 3 consecutive years (2020–2022) around the beginning of May. Additional applications of pelargonic-acid were performed once in 2020 (August), and twice in 2021 and 2022 (June and August). The herbicides were applied separately to the designated lysimeters (Table A4), 2,4-D and quizalofop-P-ethyl on the "a"-series, flazasulfuron and pelargonic-acid on the "c"-series, and all six herbicides on the "b"- and "d"-series. Commercial herbicides (amounts of 0.5–7.2 g) were appropriately diluted with tap water to achieve the targeted application rates and spray volumes corresponding to 400 L/ha. For each application, 13.3 mL spray broth was filled into a polyethylene spray bottle and evenly applied to a concentric area with ≈65 cm diameter of the respective lysimeter (0.33 m^2, two-thirds of the lysimeter surface). Afterwards, for quantitative transfer of the herbicides, the spray bottle was rinsed with a few mL of water which was also sprayed onto the lysimeter. The spray broth of pelargonic-acid was applied dropwise with a Pasteur pipette since the spray bottle did not work properly with the respective formulation. The target application rates were similar as for agricultural uses, for glyphosate as currently used on railway tracks in Switzerland, and for atrazine as formerly used: 1250 g 2,4-D/ha, 125 g quizalofop-P-ethyl/ha, 50 g flazasulfuron/ha, 5440 g pelargonic-acid-D_{17}/ha (together with 5440 g unlabeled pelargonic-acid/ha), 4500 g atrazine/ha, and 2900 g glyphosate/ha (application rates in relation to the treated area). Concentrations of the active substances in the respective spray broths were verified with LC-MS/MS (see below), and were within 88–117 % of the targeted levels. Since pelargonic-acid was consistently detected in lysimeter leachate also prior to application (naturally present and/or from laboratory contamination), we conducted the lysimeter study with pelargonic-acid-D_{17}, which was added to a spray broth of the products Natrel or Finalsan Unkrautfrei. Pelargonic-acid-D_{17} is not naturally occurring and was not detected in leachate prior to application. Herbicides and bromide were applied to only two-thirds of the lysimeter surface and not to the peripheral area to avoid artefacts due to possible transport along the lysimeter walls.

2.6. Leachate samples

Leachate was typically sampled when the containers were filled with 10–20 L (corresponding to 20–40 mm), before a weekend with expected precipitation, or at the latest 14 d after the last sampling. Aliquots of 50 mL each were filled into 150 mL clear glass bottles (for analysis of all analytes except glyphosate and AMPA) and 60 mL HDPE bottles (for glyphosate and AMPA). The remaining leachate was discarded. The leachate in the HDPE bottles was fortified with 100 μL of internal standard (a solution of $^{13}C_2^{15}N$-glyphosate and $^{13}C^{15}ND_2$-AMPA in acetonitrile/water 7/3 with concentrations of 5 and 20 ng/mL, respectively), whereof 5 mL were filled into 10-mL autosampler vials and stored at −20 °C until analysis, typically within 2 months. The clear glass bottles and the remaining leachate in the HDPE bottles (retain samples) were also stored at −20 °C until analysis within 2 months.

Leachate for bromide analysis was filled into 50 mL polyethylene bottles and stored at −20 °C.

2.7. LC-MS/MS analysis of the herbicides and metabolites

Five herbicides and eleven metabolites were analysed in the lysimeter leachate samples. Quizalofop-ethyl was not included in the analysis protocol since it was not expected to be detectable in the leachate. In railway soils, the compound showed high sorption and underwent fast hydrolysis to quizalofop-acid (Buerge et al., 2020), which is the herbicidally active substance. Analysis was based on on-line enrichment and liquid chromatography-tandem mass spectrometry (for details, see supplementary material and (Buerge et al., 2020)). Glyphosate and AMPA were analysed after derivatization with FMOC-Cl by online solid-phase extraction LC-MS/MS as described previously (Poiger et al., 2017).

The stability of the compounds in frozen leachate from Lanzenhäusern, Nottwil, and Wabern was investigated by comparative analysis of freshly spiked leachate and spiked leachate stored in the freezer for 2 months (spike levels, 0.1 μg/L). These experiments confirmed that the test substances were stable in the frozen leachate samples with recoveries of 81–125 % (in comparison to freshly spiked leachate). Analogous experiments also showed that the test substances were stable in leachate stored at 4 °C for 4 weeks with recoveries of 81–127 %. Lower recoveries at 4 °C were only found for GTPS (67–76 %) and pelargonic-acid-D_{17} (39–58 %). However, leachate was stored for a maximum of 2 weeks at 4 °C in the collection vessels, i.e., possible degradation of GTPS and pelargonic-acid-D_{17} was expected to be <20 % and <40 %, respectively (assuming first-order degradation), which was considered acceptable.

Limits of quantification in leachate were determined at a signal-to-noise (S/N) ratio of ≈10 using the primary ion transitions. LOQs were 0.001 μg/L for atrazine, desethyl-atrazine, flazasulfuron, and its metabolites (note that the LOQ for DTPU was set higher than the value corresponding to S/N ≈ 10 to account for possible cross-contamination from previously injected samples with high concentrations), 0.002 μg/L for desisopropyl-atrazine and quizalofop-acid, 0.003 μg/L for 3-OH-quizalofop-acid, 0.005 μg/L for 3-OH-CQO, glyphosate and AMPA, 0.01 μg/L for 2,4-D (note that also this LOQ was set higher than the value corresponding to S/N ≈ 10 since 2,4-D-D_3 also showed a small signal at the ion transition of the unlabeled compound), 0.03 μg/L for 2,4-DCP, and 0.04 μg/L for pelargonic-acid-D_{17}. Typical chromatograms of a leachate sample are depicted in Fig. A5.

3. Results and discussion

3.1. Soil temperatures, precipitation, and leachate – substantial net infiltration

Soil temperatures were recorded at 55–119 cm depth in lysimeter L_d and varied between 0 °C and 27 °C during the study, with somewhat higher amplitudes at 55 cm depth than further down in the soil profile (Fig. A6, left). The top of the lysimeters may have been frozen sporadically. At the weather station Wädenswil (MeteoSchweiz), located in 240 m distance from the lysimeters, the soil temperature temporarily dropped below 0 °C at 5 cm depth, but only on two days (recorded minimum in January 2021, −0.1 °C). The mean soil temperatures at the different depths of lysimeter L_d were 11.8–12.2 °C in study year 1, 11.2–11.6 °C in year 2, and 12.7–13.1 °C in year 3 (we define study years as approximate 1-year periods following the herbicide applications around the beginning of May, Table 2).

At the weather station Wädenswil precipitations of 1386, 1403, and 1261 mm were measured in the three study years (Table 2; for comparison, the mean annual precipitation was 1338 mm for the period 2001–2020). The cumulative amounts of rainfall differed notably in the 4 months following application in May, with 636, 925, and 414 mm in years 1, 2, and 3, respectively (Fig. A6, middle).

Total leachate amounts of 1144–1218, 1191–1241, and 984–1078 mm were collected in years 1, 2, and 3, respectively, which corresponds to 78–88 % of the annual precipitation (Table 2). Fig. A6 (right) shows the progression of the cumulative leachate in the ten lysimeters during the three years of the study in comparison with the cumulative precipitation. The amounts of leachate were comparable in the different lysimeters. Evapotranspiration, calculated as the difference between cumulative precipitation and cumulative leachate, amounted to 12–22 % of the cumulative precipitation. This is clearly lower than in agricultural soils. The ballast in lysimeters Lanzenhäusern and Nottwil and the gravel layer in lysimeters Wabern served as evaporation barriers. Furthermore, transpiration was minimal, since almost no weeds grew on the lysimeters (note that weeds, primarily horsetail, were removed mechanically twice a year).

3.2. Fast breakthrough of the conservative tracer bromide in N lysimeters – "chromatographic" behavior in the other lysimeters

Before application of the herbicides in April/May, bromide was applied as a conservative tracer to selected lysimeters. The corresponding breakthrough curves are depicted in Fig. 1. Leaching of bromide through the three soil materials differed substantially, with a clearly faster breakthrough in N lysimeters (first detection in leachate after 3–25 d and 39–40 mm of cumulative precipitation) than in L and W lysimeters (first detection after 22–60 d and 122–166 mm). Material from Nottwil contained a higher proportion of gravel, and consequently less fine material than Lanzenhäusern and Wabern (Table A3). The effective transport volume was thus smaller in the N lysimeters. Differences were also observed in the three replicate N lysimeters with elevated concentrations found earlier in lysimeter N_b than in N_a and N_c (Fig. 1, bottom). This is consistent with the observation that, after a precipitation event, the leachate level in the collection vessel of lysimeter N_b normally started to increase earlier than in all other lysimeters.

Peak concentrations, however, tended to be lower in N lysimeters (2.6–4.6 mg/L) than in L and W lysimeters (4.6–12 mg/L, Fig. 1), hinting

Table 2

Mean soil temperatures in different depths of lysimeter L_d, precipitation, and cumulative amount of leachate in the different lysimeters. With a lysimeter surface of 0.5 m², precipitation of 2 mm corresponds to 1 L. The volume of the lysimeters is ≈700 L.

Period[a]	Mean soil temperature at 55/85/105/119 cm depth [°C]	Precipitation [mm][b]	L_a	L_b	L_c	L_d	N_a	N_b	N_c	W_a	W_b	W_c
			Leachate [mm] (in % of precipitation)									
May 04, 2020–May 05, 2021	11.8/12.0/12.0/12.2	1386	1170 (84)	1182 (85)	1190 (86)	1177 (85)	1151 (83)	1144 (83)	1155 (83)	1152 (83)	1218 (88)	1190 (86)
May 06, 2021–April 29, 2022	11.2/11.5/11.4/11.6	1403	1218 (87)	1241 (88)	1217 (87)	1231 (88)	1191 (85)	1204 (86)	1219 (87)	1197 (85)	1231 (88)	1234 (88)
April 30, 2022–May 04, 2023	12.7/13.0/12.9/13.1	1261	1021 (81)	1039 (82)	1015 (80)	1027 (81)	999 (79)	1016 (81)	1025 (81)	984 (78)	1062 (84)	1078 (86)

[a] In years 2021 and 2022, no leachate samples were taken on the day of herbicide application, but 2 d later. Therefore, the periods in this table slightly deviate from those defined by the days of application (Table A4).

[b] Data from MeteoSchweiz weather station Wädenswil, located in 240 m distance from the lysimeters.
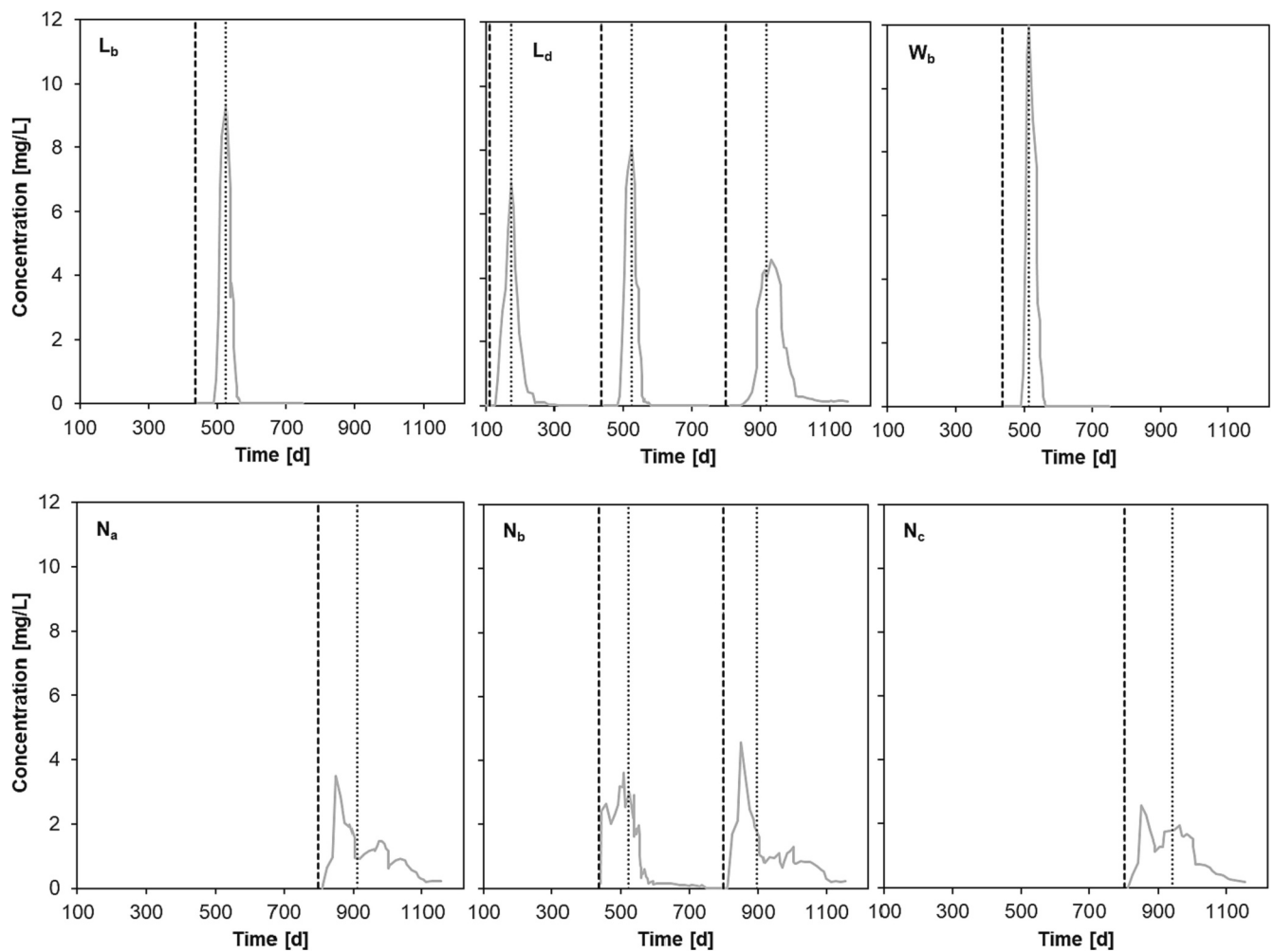
Fig. 1. Breakthrough curves for the conservative tracer bromide in leachate of selected lysimeters. Dashed lines indicate application days, dotted lines days after last application when 50 % of bromide was detected in leachate ($t = 0$ d on January 01, 2020).

at a larger variability in local water flow velocities, i.e., a higher dispersivity, in lysimeter N. On the other hand, elevated leachate concentrations were recorded during a longer period in N lysimeters as compared to L and W lysimeters, in which bromide showed sharp and almost symmetric elution profiles.

Half of the amount of bromide eventually detected in the leachate samples, passed through the lysimeters within 63–142 d (Fig. 1 and Table 3, note that mass flows were calculated as product of measured concentrations and respective leachate volumes). Within these times,

249–406 mm precipitation were recorded and 200–306 mm leachate were collected. Recoveries (expressed as % of the applied amount) were determined ≈1 year after application. Recoveries ranged from 55 to 63 % in year 3, to 73 % in year 1 (only one lysimeter treated), and 75–105 % in year 2 (Table 3). At the end of year 3, bromide was still detectable (Fig. 1), i.e., the tracer was not completely washed out of the lysimeters, which partly explains the low recoveries in year 3.

Recoveries thus tended to be highest in the wet year 2 and lowest in the dry year 3. In lysimeter L_d, to which bromide was applied every year,

Table 3
Recoveries [in % of the applied amount] of the conservative tracer bromide in leachate of selected lysimeters, and approximate elapsed time, precipitation, and leachate amounts required for the elution of 50 % of the total recovered bromide.

Lysimeter	Year 1				Year 2				Year 3			
	Recovery [%]	Elution of 50 %			Recovery [%]	Elution of 50 %			Recovery [%]	Elution of 50 %		
		DALA[a]	[mm][b]	[mm][c]		DALA	[mm][b]	[mm][c]		DALA	[mm][b]	[mm][c]
L_b	n.a.[d]				89	87	307	244	n.a.			
L_d	73	63	260	206	94	88	318	240	63	116	353	268
N_a	n.a.				n.a.				55	111	310	264
N_b	n.a.				75	86	298	238	61	97	249	200
N_c	n.a.				n.a.				57	142	406	306
W_b	n.a.				105	76	278	226	n.a.			

[a] DALA = days after last application.
[b] Cumulative precipitation.
[c] Cumulative leachate.
[d] n.a. = not applied.

recoveries were 73, 94, and 63 % in years 1–3 and 319, 420, and 238 mm of precipitation was recorded during a two-month interval around the peak maxima, respectively. A possible explanation for bromide recoveries <100 % is that during dry periods, bromide may diffuse into soil regions that do not participate to water flow, e.g., under larger stones. Bromide that resides in these immobile regions may no longer be amenable for percolating water on the short term (Van Genuchten and Wierenga, 1976). Also the peak maxima differed a lot with 7.0, 8.1, and 4.6 mg/L in L_d in years 1–3.

3.3. Sharp peak concentrations of flazasulfuron in lysimeter leachate – delayed occurrence of metabolites

In the following, we first discuss concentrations observed in leachate of the "b"-series, since all herbicides were applied to the respective lysimeters, which allows a direct comparison of their breakthrough behavior. Results in the replicate lysimeters are then presented in Section 3.6.

Flazasulfuron was detectable in leachate of lysimeter N_b already 3 d after the first application (and 32 mm of cumulative precipitation) and reached a peak concentration of 0.41 µg/L within only 8 d (70 mm, Fig. 2, top, middle, Table A6). Thereafter, the concentration dropped quickly to values <0.02 µg/L. First detections of flazasulfuron in

leachate of lysimeters L_b and W_b were clearly later, 56 and 32 d after application (264 and 121 mm), with peak concentrations of 0.074 and 1.2 µg/L, respectively (Fig. 2, top, Table A6). The faster breakthrough in N_b is consistent with that of bromide (Fig. 1).

In the second year, again sharp peak concentrations were observed with maxima of 0.32, 0.92, and 2.9 µg/L in L_b, N_b, and W_b, respectively (Fig. 2, top, Table A7). These values were higher than in the first year, possibly as a result of high precipitation in the weeks following application in year 2 (Fig. A6, right). In year 3, however, concentration maxima were clearly lower (0.083, 0.22, and 0.51 µg/L, respectively, Table A8), likely the consequence of only low rainfall after application. Low rainfall and thus less leachate means that there is more time for degradation of flazasulfuron.

All four metabolites of flazasulfuron included in the analysis protocol were detectable in lysimeter leachate. DTPU and TPSA were the major metabolites. In lysimeter N_b, also GTPS reached similar concentrations (Fig. 2, top, Tables A6–A8). DTPU, TPSA, and DTPP are hydrolysis metabolites that can also be formed abiotically, whereas GTPS was not observed in hydrolysis studies (European Food Safety Authority, 2016). Peak concentrations of the metabolites were delayed compared to those of flazasulfuron and reached maxima of 1.3 µg/L DTPU and 0.26 µg/L TPSA in W_b and 0.11 µg/L GTPS in N_b. Also, the decline of the concentrations was delayed and breakthrough curves showed a distinct
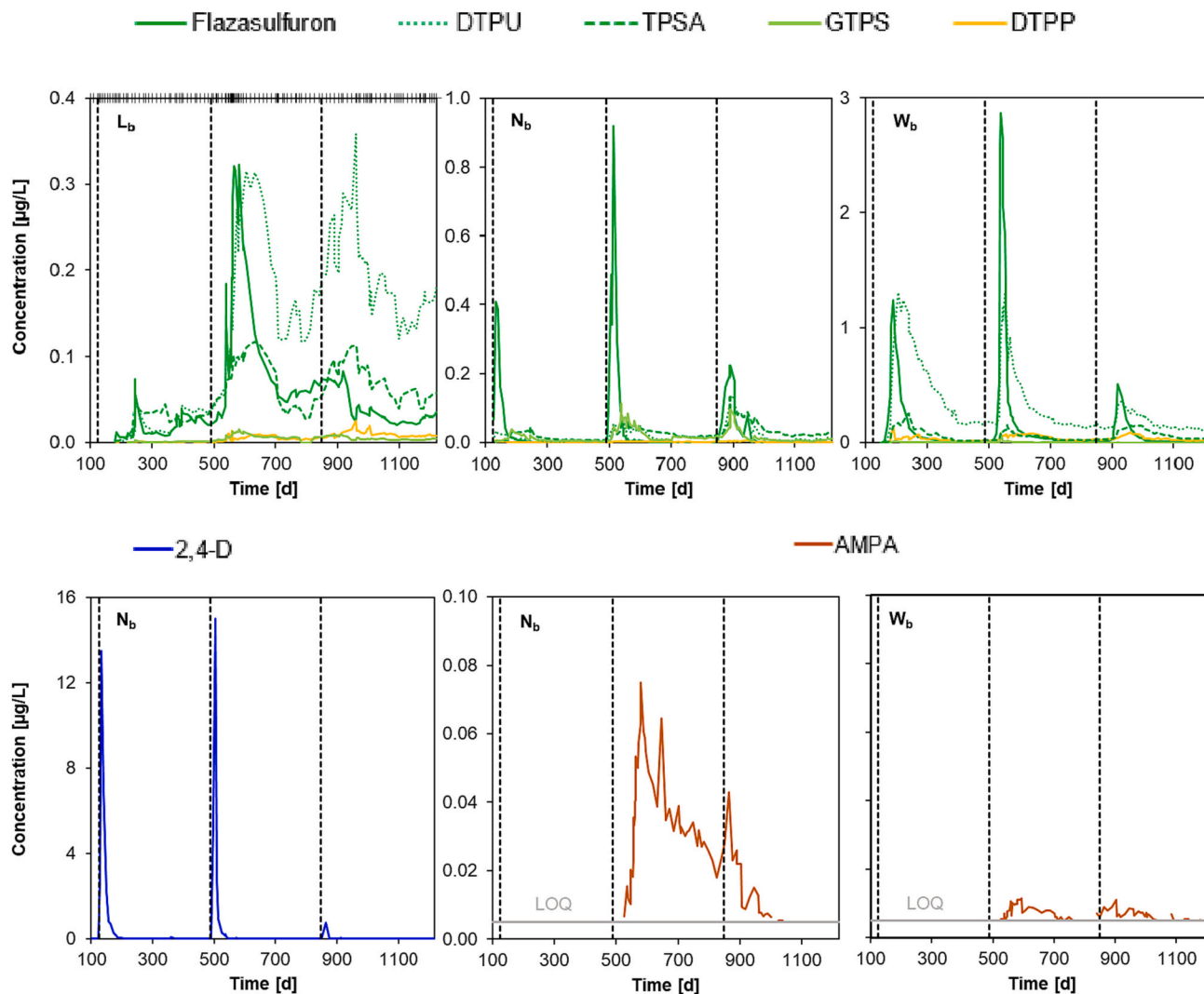
Fig. 2. Concentrations of flazasulfuron and metabolites (top), 2,4-D, and AMPA (bottom) in leachate of lysimeters after treatment with 50 g flazasulfuron/ha, 1250 g 2,4-D/ha, and 2900 g glyphosate/ha (treated area, 2/3 of the lysimeter surface). Dashed lines indicate application days (t = 0 d on January 01, 2020). Note the different concentration scales. Sampling times, depicted for lysimeter L_b (upper scale), are identical for all other lysimeters and analytes.

tailing (in particular DTPU in W_b, Fig. 2, top).

3.4. Breakthrough of 2,4-D in leachate of lysimeter N – only sporadic detection in L and W lysimeters

First detection of 2,4-D in leachate of lysimeter N_b as well as the concentration maximum in year 1 were observed on the same sampling days as for flazasulfuron, also with rapid concentration decline (Fig. 2, bottom, left). In the following two years, breakthrough of 2,4-D was even earlier than that of flazasulfuron. 2,4-D reached peak concentrations of 13, 15, and 0.73 µg/L in the three years (Tables A6–A8). As for flazasulfuron, highest peak concentrations were found in year 2 (wet) and lowest peak concentrations in year 3 (dry). The primary metabolite 2,4-dichlorophenol was quantifiable in only two leachate samples at concentrations of 0.053 and 0.039 µg/L in year 1, when 2,4-D reached the highest concentrations.

In leachate of lysimeters L_b and W_b, 2,4-D was only sporadically detected with maximum concentrations of ≈0.007 and 0.015 µg/L, respectively, and 2,4-dichlorophenol was not detected at all. 2,4-D thus showed a different behavior than flazasulfuron that was consistently found in all lysimeters of the "b"-series. Both compounds are highly mobile in soil with somewhat lower sorption coefficients for 2,4-D (for agricultural soils (European Food Safety Authority, 2014; European Food Safety Authority, 2016)). Probably more important, flazasulfuron is expected to be degraded slower than 2,4-D (based on half-lives

observed in agricultural soils (European Food Safety Authority, 2014; European Food Safety Authority, 2016)) and may thus be stable enough to reach the bottom of all lysimeters in quantifiable amounts. High leachate concentrations of 2,4-D in lysimeter N_b as opposed to very low concentrations in L_b and W_b can be explained by the fast breakthrough in N_b (as seen for bromide), so that the time for degradation was clearly shorter.

3.5. Detection of atrazine and metabolites in leachate of untreated lysimeters – high concentrations in treated lysimeters

Atrazine, desethyl-atrazine, and desisopropyl-atrazine were detected in leachate of all lysimeters, i.e., also in those that had not been treated with atrazine (Fig. 3, top). In Switzerland, the herbicide had been used for weed control on railway tracks until the early 1990s. Apparently, a fraction of the atrazine applied at the time was still leaching from the material. Concentrations showed clear seasonal fluctuations with maxima in summer and minima in winter. Possibly, higher temperatures in summer may have an effect on sorption and/or diffusion of the compounds in favor of the water phase (Costa Paraiba and Pulino, 2003; Shariff and Shareef, 2011; ten Hulscher and Cornelissen, 1996), which may explain the higher concentrations in leachate.

In leachate of lysimeter N_b, which had been treated with atrazine, concentrations were clearly higher than in the corresponding untreated lysimeter N_a (Fig. 3, middle). Atrazine followed a similar trend as 2,4-D
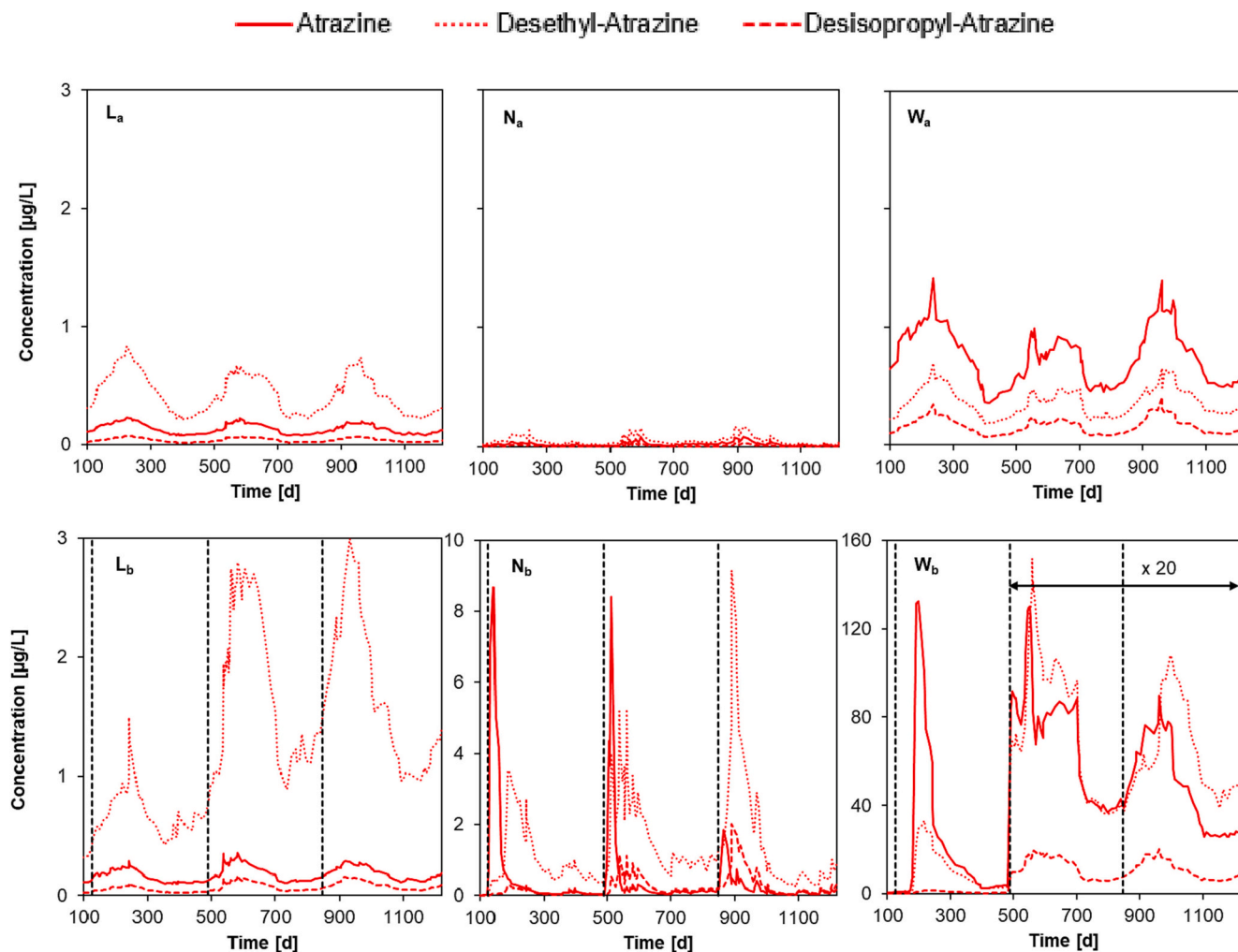

Fig. 3. Concentrations of atrazine and metabolites in leachate of lysimeters that had not been treated (top) and after treatment with 4500 g/ha (treated area, 2/3 of the lysimeter surface, bottom). Dashed lines indicate application days (t = 0 d on January 01, 2020). Note the different concentration scales. Concentrations for lysimeter W_b in years 2 and 3 were magnified by a factor of 20 for better visualisation.

and flazasulfuron with sharp peak concentrations of 8.7, 8.4, and 1.8 μg/L in the three years (Tables A6–A8). Again, lowest peak concentrations were observed in year 3, but concentrations in year 2 were comparable to year 1 (and not higher).

Both atrazine metabolites were also found at elevated concentrations in leachate of lysimeter N_b (Fig. 3, bottom, middle). As for flazasulfuron metabolites, the breakthrough curves showed maxima later than that of the active substance with a distinct tailing. Peak concentrations were increasing from year to year, with values of 3.5, 5.3, and 9.2 μg/L for desethyl-atrazine and 0.29, 1.1, and 2.0 μg/L for desisopropyl-atrazine (Tables A6–A8).

In lysimeter L_b, likewise treated with atrazine, concentrations of atrazine and desisopropyl-atrazine were only marginally higher than in the corresponding untreated lysimeter L_a (Fig. 3, left). Only desethyl-atrazine showed increased concentrations, primarily in years 2 and 3. The concentrations followed a similar trend as the flazasulfuron metabolite DTPU in lysimeter L_b (Fig. 2, top, left).

In lysimeter W_b, however, concentrations of atrazine, desethyl-atrazine (and desisoproyl-atrazine) were considerably higher than in the corresponding untreated lysimeter W_a (Fig. 3, right). In year 1, the compounds reached high peak concentrations of 132, 33, and 1.6 μg/L, respectively (Table A6). Interestingly, concentrations were clearly lower after applications in year 2 and 3 and reached maximum values of only 6.5, 7.6, and 1.0 μg/L, respectively. The concentration pattern observed for atrazine and metabolites in lysimeter W_b, with clearly lower concentrations in year 2 and 3, was thus completely different from that of flazasulfuron (Fig. 2, top, right) and may have been the result of enhanced microbial degradation (Cheyns et al., 2012; Krutz et al., 2010; Vanderheyden et al., 1997). Microbial communities may have readapted after the first application of atrazine after a pause of >25 years, leading to enhanced degradation of the compound and its metabolites.

3.6. Similar leachate concentrations in replicates of L and W lysimeters – more differing concentrations in replicates of N lysimeters

Until now, we discussed leachate concentrations found in lysimeters of the "b"-series (L_b, N_b, and W_b), but the herbicides were also applied to replicate lysimeters filled with soil from the same location (Table A4). In general, similar concentrations of flazasulfuron, atrazine, and metabolites were observed in leachate from the L and W lysimeters, more precisely, for flazasulfuron and metabolites in $L_b/L_c/L_d$ and W_b/W_c (Fig. A7, top), atrazine and metabolites in treated lysimeters L_b/L_d (middle, right), and untreated lysimeters L_a/L_c, N_a/N_c, and W_a/W_c (bottom).

However, pronounced differences were recorded in N lysimeters. Flazasulfuron showed distinct peak concentrations of 0.41, 0.92, and 0.22 μg/L in leachate from lysimeter N_b, whereas peak concentrations were only 0.007, 0.020, and 0.007 μg/L in the replicate lysimeter N_c (in years 1, 2, and 3, respectively, Fig. A7, middle, left; note that concentrations of flazasulfuron metabolites were nevertheless comparable). This observation is consistent with the faster breakthrough of bromide in N_b as compared to N_c (see Section 3.2), i.e., the time available for degradation of flazasulfuron was clearly shorter in N_b than in N_c.

Notable differences were also found for 2,4-D with peak concentrations of 8.8, 1.1, and 0.011 μg/L in N_a vs. 13, 15, and 0.73 μg/L in N_b (Fig. A7, middle). This can likewise be explained by the faster breakthrough of bromide in N_b as compared to N_a (see Section 3.2). Apparently, filling of replicate lysimeters with material from Nottwil was less reproducible than with material from the other two locations. Note that Nottwil soil contained high proportions of gravel (Table A3) and it was thus more difficult to repack them in exactly the same way.

3.7. Low leachate concentrations of glyphosate, AMPA, and (3-OH-) quizalofop-acid

Glyphosate was detected only in leachate of lysimeter N_b with a

maximum concentration of 0.022 μg/L. The metabolite AMPA, however, was more frequently found in leachate of lysimeters N_b and W_b and reached peak concentrations of 0.075 and 0.011 μg/L, respectively (Fig. 2, bottom, middle and right). The most pronounced peak concentration in lysimeter N_b was recorded in year 2. Due to the strong sorption of AMPA and the associated, long travel time in the soil column, it cannot be excluded that this peak results from application of glyphosate in the first (rather than the second) year.

Quizalofop-acid and 3-OH-quizalofop-acid were only sporadically detected in leachate of lysimeters N_a and N_b with maximum concentrations of 0.033 and 0.021 μg/L in year 2, respectively. The tertiary metabolite 3-OH-CQO was not found in quantifiable amounts (<0.005 μg/L).

3.8. High concentrations of pelargonic-acid after heavy rainfall

Pelargonic-acid-D_{17} was detected in leachate of lysimeters L and N only on a single sampling day, but the concentrations were higher than those of all other analytes in any sample (7.6–561 μg/L, Table A8). These singular high detections followed application #7 of pelargonic-acid-D_{17} (June 22, 2022 at ≈4 p.m.; note that no other herbicides were applied at this time). Two hours later, an unexpected, heavy rainfall was recorded (29 mm within only 20 min). The next day (June 23 at ≈2 p.m.), the leachate samples were taken and immediately frozen until analysis. We assume that the compound must have leached through the soil profiles via preferential flow paths. In the leachate samples, we recovered 0.04–4.2 % of the amount applied on the day before (maximum in lysimeter N_b). No pelargonic-acid-D_{17} was found in leachate of lysimeters W_b and W_c, which always reacted more slowly to heavy rain events (greater hydraulic resistance compared to L and N lysimeters).

Pelargonic-acid-D_{17} was found to be quickly degraded in railway materials with DT_{50} values of 4–11 h and DT_{90} values of 12–35 h (Poiger et al., in prep). The time between application and leachate sampling (≈22 h) was thus not sufficient for complete degradation. However, already in the next leachate samples that were taken ≈190 h later, pelargonic-acid-D_{17} was no longer detectable (<0.04 μg/L), i.e., the compound must have been degraded in the meantime in the soil (or in the collection vessels before samples were frozen, see Section 2.7).

3.9. Highest annual average leachate concentrations for atrazine, lowest for glyphosate and quizalofop-acid

Annual average concentrations of all analytes in leachate of the different lysimeters are listed in Tables A9–A11 for years 1–3. They were calculated from the sum of the mass flows in the leachate (concentration × volume) divided by the cumulative leachate volume.

The highest annual average concentrations were observed for atrazine (23 μg/L in lysimeter W_b in year 1), pelargonic-acid-D_{17} (15 μg/L in N_b, year 3 from detection in a single leachate sample, see Section 3.8), and desethyl-atrazine (9.0 μg/L in W_b, year 1). Further analytes with annual average concentrations >0.1 μg/L were 2,4-D (0.60 μg/L in N_b, year 1), desisopropyl-atrazine (0.51 μg/L in W_b, year 2), flazasulfuron (0.43 μg/L in W_b, year 2), and DTPU (0.50 μg/L in W_b, year 2). Analytes with annual average concentrations above LOQ, but <0.1 μg/L were DTPP (0.045 μg/L in W_b, year 2), GTPS (0.038 μg/L in N_b, year 2), TPSA (0.079 μg/L in W_c, year 3), and AMPA (0.032 μg/L in N_b, year 2), and below LOQ were 2,4-DCP (<0.03 μg/L), quizalofop-acid (<0.002 μg/L), 3-OH-quizalofop-acid (<0.003 μg/L), 3-OH-CQO, and glyphosate (<0.005 μg/L).

The extensive data in Tables A9–A11 are also depicted in a summarized form as box plots in Fig. 4. The box plots show lower and upper quartiles, median, and 10 % and 90 % quantiles of all annual average concentrations (12–21 values per substance, depending on the number of lysimeters to which the corresponding herbicide was applied).

For many compounds, median and maximum annual average concentrations differed considerably, since high concentrations were
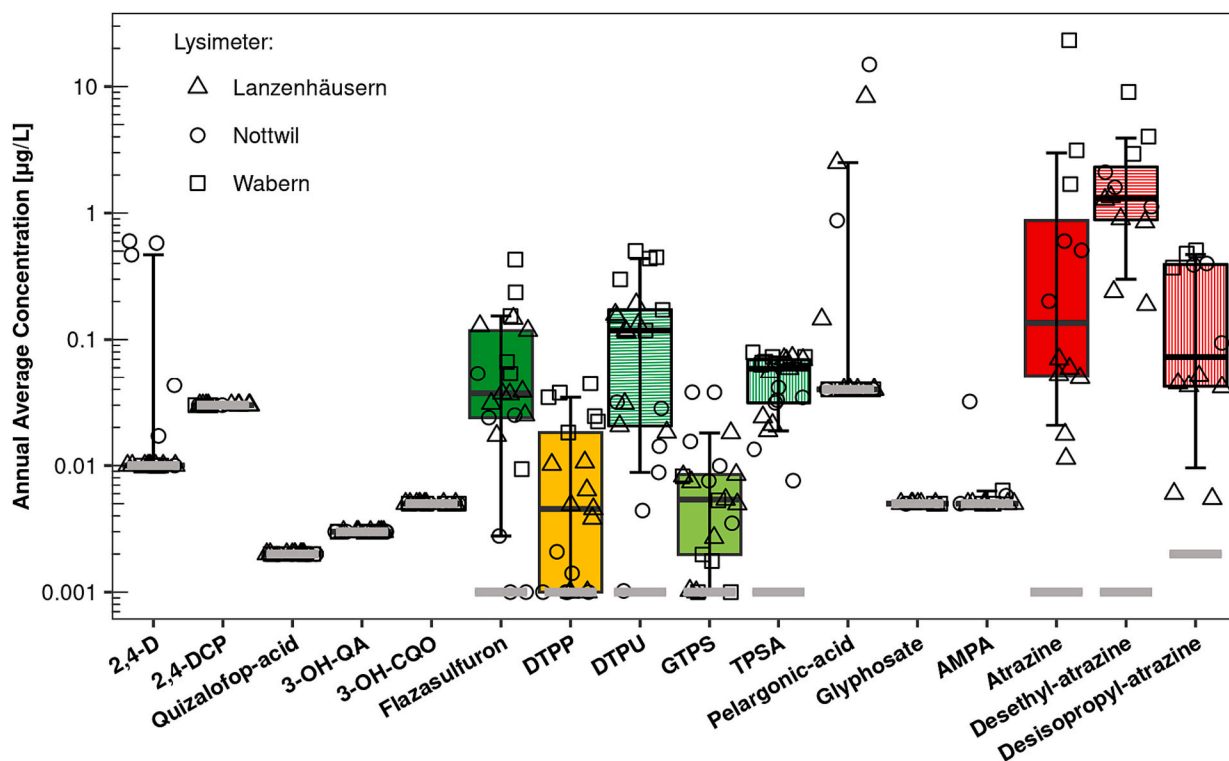
Fig. 4. Annual average concentrations of the six investigated active substances and different metabolites in leachate of herbicide treated lysimeters (4 in the case of atrazine and glyphosate, 7 for all others), collected during 3 years. Box plots show lower and upper quartiles, median, and 10 % and 90 % quantiles (whiskers). Background concentrations of atrazine and its metabolites found in untreated lysimeters were subtracted from those in treated lysimeters. Grey lines represent LOQs.

primarily found in one lysimeter type. For example, annual average concentrations of 2,4-D were above LOQ only in the N lysimeters (up to 0.60 μg/L), whereas the median was below LOQ (<0.01 μg/L). In case of atrazine, annual average concentrations were highest in W lysimeters (up to 23 μg/L) and thus clearly higher than the median (0.14 μg/L). Widely differing annual average concentrations were also observed for pelargonic-acid-D_{17}. Its detection in single leachate samples of the L and N lysimeters (annual average, up to 15 μg/L) contrast with the low median (<0.04 μg/L, LOQ). Annual average concentrations of flazasulfuron and its metabolites, however, differed less between lysimeters and years (Fig. 4).

3.10. High recoveries in leachate of W lysimeters

Recoveries as a measure of the total mass of applied herbicides (including their metabolites, expressed in parent equivalents) leaching through the soil columns within the 3 year duration of the lysimeter study were calculated from the measured leachate concentrations and respective leachate volumes in relation to the applied amounts (in %). Recoveries for lysimeters L_b, N_b, and W_b are depicted in Fig. 5. The highest recoveries were found for flazasulfuron (including its metabolites: 11 %, 4.9 %, and 30 % in L_b, N_b, and W_b, respectively). The parent compound accounted for 20–26 % of the residues in leachate, and DTPU (19–53 %) and TPSA (14–36 %) were the major metabolites (in N_b also GTPS: 19 %).
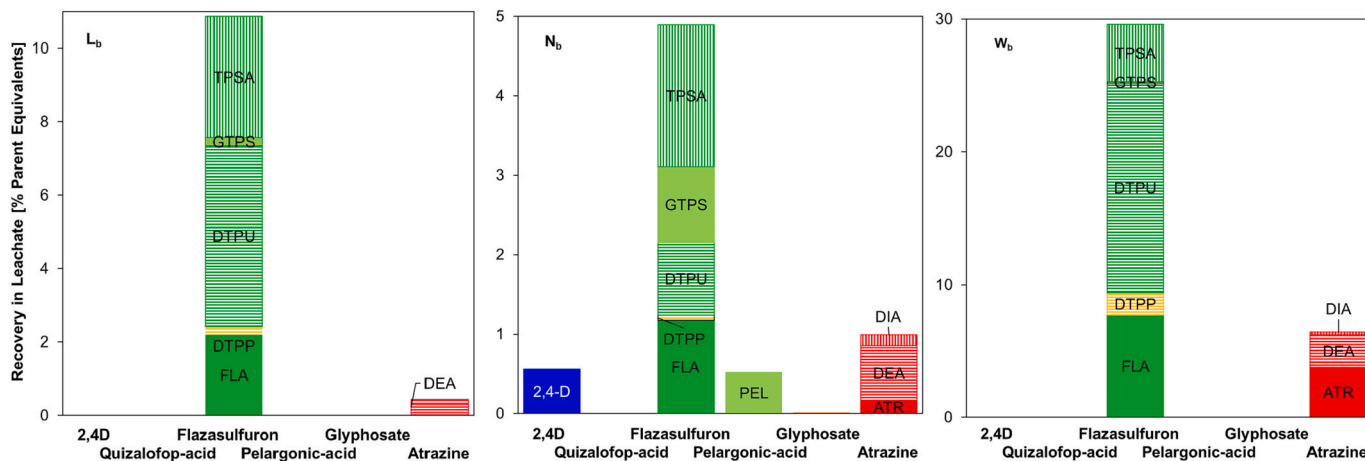

Fig. 5. Recoveries [in % of the applied amount] of the six investigated active substances and different metabolites in leachate of lysimeters L_b, N_b, and W_b for the whole study period (metabolites in parent equivalents). Note the different scales.

High recoveries were also observed for atrazine and metabolites (0.45 %, 0.96 %, and 6.5 % in L_b, N_b, and W_b, respectively, Fig. 5). Desethyl-atrazine was the major component and accounted for 38–92 % parent equivalents of the residues in leachate. It has to be mentioned that only the most mobile metabolites of flazasulfuron and atrazine were analysed and that further metabolites such as HMTU (European Food Safety Authority, 2016), hydroxy-atrazine, or desethyl-desisopropyl-atrazine (Guillon et al., 2019) may contribute to some extent to the overall recoveries.

2,4-D was detected primarily in leachate of N lysimeters with a recovery of 0.56 % in N_b at the end of the study. A similar recovery was found for pelargonic-acid-D_{17} in leachate of lysimeter N_b with 0.52 % after 8 applications during the three years, but from the single detection at high concentration of 561 μg/L. Recoveries of 2,4-D and pelargonic-acid-D_{17} in leachate of L_b and W_b were, however, <0.01 %. Recoveries of quizalofop-acid, glyphosate, and their metabolites were <0.01 % in all lysimeters, except for AMPA, which reached 0.012 % in lysimeter N_b.

The recoveries found in this lysimeter study are comparable to those observed for some of the substances in other lysimeter studies. Previously reported recoveries from lysimeters that were at least 1 m deep were up to 1.8–9.6 % for atrazine (Hall et al., 1989; Tindall and Vencill, 1995; Torrentó et al., 2017), 3 % for 2,4-D (Tindall and Vencill, 1995), and <0.02–0.06 % for glyphosate (Bergström et al., 2011; Fomsgaard et al., 2003).

3.11. Comparison of the leaching behavior of the six herbicides

For this lysimeter study specifically designed to represent subsoil beneath railway lines, we selected soil materials with high sand contents (in the fine fraction, 47–84 %, Table A3). In addition, high gravel and stone contents in material from Nottwil (>68 %) gave rise to low transport volumes and thus fast transport of water (and substances) through these lysimeters. The organic carbon content, an important parameter for sorption of most organic compounds, was low in material from Wabern (in the fine fraction, 0.08–0.39 %, Table A3), somewhat higher in Lanzenhäusern (0.32–1.3 %), and highest in Nottwil (0.78–2.5 %). The soil pH values were high (7.4–7.8, measured in 0.01 M $CaCl_2$) to represent a worst-case for ionizable compounds as they will be present in their deprotonated, more mobile form at alkaline conditions. The measured precipitation of 1261–1403 mm in the three study years at location Wädenswil is quite typical of many regions of the Swiss Midland, but probably higher than in many regions of Central Europe. Overall, this lysimeter study thus represents typical conditions with regard to precipitation, texture, pH, and C_{org}.

Atrazine was selected in this study as a reference compound for which substantial leaching was expected. The measured concentrations of atrazine and desethyl-atrazine (annual average, up to 23 and 9.0 μg/L, respectively) clearly confirm that atrazine would pose a risk of groundwater contamination when used on railway tracks (Schweinsberg et al., 1999). The functionality of the lysimeters in terms of leaching is thus demonstrated. In addition, the detection of elevated levels of atrazine-metabolites after the application of atrazine shows that the soil materials were biologically active. After three study years, up to 6.5 % of the applied mass of atrazine were recovered in lysimeter leachate, as the parent compound and in form of the metabolites desethyl- and desisopropyl-atrazine.

Recoveries of flazasulfuron in lysimeter leachate were even higher (up to 30 %) with DTPU and TPSA as major metabolites. Nonetheless, annual average concentrations were clearly lower (up to 0.43 μg/L flazasulfuron, 0.50 μg/L DTPU) than those of atrazine and metabolites, since application rates differed by two orders of magnitude.

Flazasulfuron may potentially be applied in mixture with pelargonic-acid, which was detected in lysimeter leachate only on a single sampling day after a heavy rain event (see Section 3.8). This resulted in annual average concentrations up to 15 μg/L in year 3 as compared to <0.04 μg/L in years 1 and 2. The compound may thus sporadically and locally

reach shallow groundwater. However, the compound is degraded quickly, even in subsoil (Poiger et al., in prep), and further degradation may also be expected in groundwater. Therefore, it is safe to assume that a larger groundwater aquifer would not be affected from uses on railway tracks.

2,4-D reached similar annual average concentrations (up to 0.60 μg/L) as flazasulfuron, but only in N lysimeters, in years 1 and 2. A potential mixing partner of 2,4-D is quizalofop-P-ethyl. The herbicidally active substance quizalofop-P-acid was only sporadically found in lysimeter leachate (annual average < 0.002 μg/L). This also applies to glyphosate, currently used for weed control on railway tracks in many countries. Annual average concentrations were <0.005 μg/L and ≤0.032 μg/L for its metabolite AMPA.

4. Conclusions

From the perspective of groundwater protection, glyphosate still is by far the best chemical option for weed control on railway tracks. For three of the four tested possible glyphosate alternatives, flazasulfuron (and its metabolite DTPU), pelargonic-acid, and 2,4-D, annual average concentrations were found to exceed 0.1 μg/L in lysimeter leachate. Concentrations in groundwater, however, would be lower depending on the dilution from soil leachate to groundwater (Aller et al., 1986), on the treated area in a groundwater catchment, and on the frequency of use. In this study, 67 % of the lysimeter surface areas were treated with herbicides. Railway tracks normally represent only a small percentage of a groundwater catchment, except for larger train stations or marshalling yards. Furthermore, when only single weeds are treated (e.g., application with knapsack sprayers, by weed wiping or spot spraying technology), expected concentrations in groundwater will decrease accordingly. For flazasulfuron (and quizalofop-P-ethyl), management strategies would be required to avoid development of resistance (Moss, 2017), for example, application only every second or third year. That would also lead to lower concentrations in groundwater. The risk of groundwater contamination by use of flazasulfuron, pelargonic-acid, or 2,4-D on railway tracks thus depends on the local conditions and actual use and management practices.

Our findings on the leaching behavior of herbicides in railway lysimeters may also be applicable to other uses in non-agricultural settings with gravel or paving stone surfaces such as industrial sites, roads, footpaths, parking areas, etc. In these areas, topsoils are normally removed, i.e., soils have a low organic carbon content. Sorption of most organic compounds will thus be low, and degradation slow.

CRediT authorship contribution statement

Declaration of competing interest

Data availability

Data will be made available on request.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.168396.

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