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Environmental fate of glyphosate used on Swedish railways — Results from environmental monitoring conducted between 2007–2010 and 2015–2019

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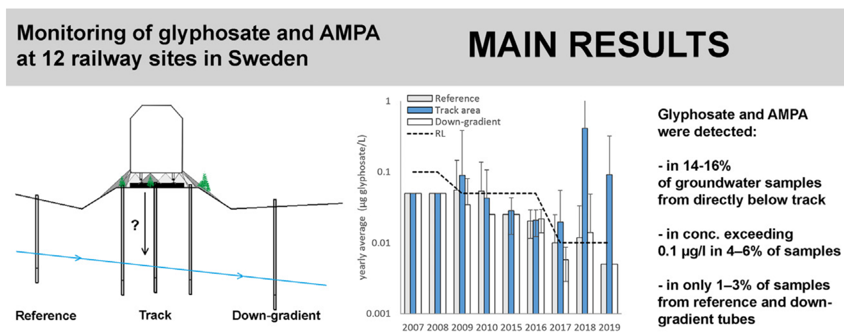
HIGHLIGHTS

- Concentrations of glyphosate and AMPA were monitored in groundwater close to railways.
- Glyphosate and AMPA were found in 14–16% of samples from directly below the railway.
- Lateral transport of glyphosate and AMPA in the groundwater zone was limited.
- Glyphosate did not accumulate over time in the ballast/subgrade.

GRAPHICAL ABSTRACT



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ABSTRACT

Glyphosate herbicides are widely relied upon by European railway operators for controlling vegetation growing on railway tracks. In Sweden, concentrations of glyphosate and its main degradation product AMPA have been monitored in the groundwater close to railways during two monitoring periods: between 2007–2010 and 2015–2019. In total, 603 groundwater samples from 12 different monitoring sites and 645 soil samples from 5 of these sites were analyzed. Glyphosate and AMPA were detected in 16% and 14%, respectively, of groundwater samples taken from directly beneath the track, with concentrations exceeding the EU groundwater quality standard of 0.1 μg/L in 6 and 4% of the cases, respectively. The highest concentrations detected in single samples were 7 μg glyphosate/L and 1.1 μg AMPA/L. However, further horizontal spread in the groundwater zone appeared to be limited as glyphosate and AMPA were only detected in 1–3% of the groundwater samples taken from outside the track area itself, and since no difference was seen between water from reference and down-gradient wells. In the autumn of 2018, higher concentrations were detected in the groundwater from beneath 3 out of the 5 then active monitoring sites and a possible explanation is that the unusually hot and dry summer of 2018 limited degradation, thus leading to an increased susceptibility of leaching. The contents of glyphosate and AMPA in soil samples from three of the sites were very low (average < 0.05 mg/kg in soil from 0 to 30 cm), indicating that they were only sprayed to a limited degree, whereas the contents from two of the test sites were in line with what would be expected based on the used dose and a predicted half-life of about 4 ± 2 months (average 0.22–0.84 mg/kg). No signs of accumulation of glyphosate in the railway ballast over time were observed.

1. Introduction

Vegetation in the railway track area may cause a variety of problems, including reduced visibility of railway signals, increased fire hazard and reduced traction for railway vehicles. In addition, plants that colonize the track contribute to the buildup of organic matter in the railway ballast, which impacts its elasticity and impairs drainage. In the long-term, the altered ballast properties may lead to speed reductions, increase the needed

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frequency of costly maintenance measures such as ballast cleaning and ultimately shorten the life-span of the railway (Nolte et al., 2018). Vegetation growing in the track itself is most commonly controlled using herbicides, and glyphosate continues to be the herbicide that European railway operators rely on the most for this purpose, although efforts have been launched in many countries to replace glyphosate with other herbicides, non-chemical methods, and generally switching to a more integrated approach for vegetation management (Pietras-Couffignal et al., 2021). On Swedish railways, glyphosate has been the main herbicide since 1993 when the use of diuron was phased out due to concerns about its high persistence and mobility (Torstensson et al., 2002). Tests conducted between 1984 and 2003 established that an application rate of 5 L Roundup Ultra/ha (corresponding to 1800 g a.e./ha) gave excellent weed control but that the application rate preferably should not exceed 3 L/ha in order to avoid groundwater contamination (Torstensson et al., 2005). For a few years this reduced rate was used when glyphosate was applied in combination with the herbicide Arsenal 250 (containing imazapyr). But the approval of imazapyr in Sweden expired at the end of 2002, and since then, glyphosate-herbicides have been used at a rate of 1800 g a.e./ha, in most cases applied only once annually.

Studies show that the environmental fate of herbicides used on railways or in other non-agricultural settings may differ significantly from their fate in agricultural soils. The low microbial activity and functional diversity as well as the low moisture content of the ballast and subgrade (Cederlund et al., 2008) can contribute to longer half-lives (Buerge et al., 2020; Cederlund et al., 2007; Svendsen et al., 2020; Torstensson et al., 2002) and the lack of fine materials and organic matter can make railways sensitive to leaching, although there is not a lot of data published that directly demonstrate this (Cederlund et al., 2012; Ramwell et al., 2004). And while no-spray zones are in place to protect surface waters, groundwater and other areas that are deemed sensitive, concerns about the possibility of groundwater contamination from herbicide usage on railways have still lingered on in Sweden. In 2006 it was decided to institute a monitoring program that was meant to increase the knowledge about the environmental fate and impact of glyphosate used on Swedish railways. A second objective was to appease Swedish municipalities by demonstrating that the environmental impact of the application was in fact being monitored at several representative sites at the national level. The Swedish environmental regulation specifies that anyone that applies herbicides on railways needs to notify the local municipalities that the railway runs through. Thus, each year the Transport administration sends a letter to roughly 180 different municipalities with information about how and where herbicides will be applied to railways in their local area. The municipalities, in their turn, have the legal right to specify various conditions that need to be met for the spraying to occur, such as for instance demanding that the concentrations that reach the groundwater should be measured by the Transport administration and then reported back to them. At the time, pressure was coming from some Swedish municipalities to monitor leaching in their respective areas, something that would not have been feasible for 180 individual municipalities.

The monitoring program, as initially conceived, was meant to also include an indirect assessment of the impact of wind drift by studying the vegetation close to the railway in comparison to untreated reference surfaces. However, these assessments were deemed too difficult to perform in practice, and during the first monitoring period (2007–2010) the program came to focus solely on the assessment of leaching by monitoring concentrations of N-(phosphonomethyl)glycine (glyphosate) and its main metabolite aminomethylphosphonic acid (AMPA) in monitoring wells installed in or close to the railway. During the second monitoring period (2015–2019) soil/ballast concentrations were also measured to ensure that neither glyphosate nor AMPA were accumulating over time.

The aim of the current study was to evaluate the results from the two sampling periods, produce statistics on the likelihood of contaminating the groundwater close to the railway, and if possible, draw general conclusions about the mobility and persistence of glyphosate when applied to Swedish railways.

2. Methods

2.1. Monitoring program between 2007 and 2010

The first iteration of the environmental control program initially comprised 8 sampling locations (S1–S8). At each sampling location, 3 monitoring wells were typically installed in the center of the railway track, a few meters apart, two monitoring wells were installed at about 5 m and 100 m distance perpendicularly to the railway, in what was deemed to be the main flow direction of the groundwater, and one well was installed up-gradient of the railway as a reference well. The sampling locations were selected to cover several representative hydrogeological environments, types of tracks and climate zones (Fig. 1. Table 1). However, it was not considered if the sites were normally treated with herbicides (if they were weed covered) nor if there were other potential users of glyphosate nearby (e.g. agricultural fields).

One of the initial sampling locations (S8) was only ever used for evaluative tests of the mobility of new herbicides, and in 2009, a further two locations (S3 and S4) were used for leaching tests of a glyphosate and fluroxypyr combination that was considered for use at the time. The results from the latter tests have been published elsewhere (Cederlund et al., 2012) and are not included here.

2.2. Monitoring program between 2015 and 2019

A second iteration of the monitoring program started in 2015. Five new sampling locations (S9–S13) were established according to similar selection criteria as in the first period (Table 1. Fig. 1). Additional requirements were that the sampling locations should be situated on railway sections that would normally be treated with herbicides (i.e. be at least partially weed-covered) and not be situated in the immediate vicinity of any agricultural lands where glyphosate may be applied to avoid potential cross-contamination. At each sampling location, three groundwater monitoring wells were installed in the track area. The monitoring wells were typically installed in a transect across the track with one well in the center of the track and two wells placed a little bit offset to each side, but with all wells within the sprayed zone in order to sample the saturated zone directly beneath the treated area. One monitoring well was placed down-gradient from the track at a distance varying between 8 and 75 m depending on local conditions, and one was placed as a reference well at a distance of 20–35 m on the opposite side.

2.3. Installation of monitoring wells

Drilling was usually performed using a water rotary drill with a casing drive system. That is, a temporary drill casing is driven into the soil as drilling proceeds to prevent cave-ins where soil from top layers may contaminate deeper layers. The monitoring well is then inserted, and the temporary casing gradually removed as filling materials is poured into the borehole surrounding the well. Monitoring wells were constructed of high-density polyethylene (HDPE; ø 63 mm) with a 0.5–1 m screen situated below the groundwater level. A sand filter was placed at the bottom of the borehole, and up to a level about half a meter above the well screen, while the top part of the borehole was sealed with bentonite clay. When situated in the track area, the top of the wells were recessed below the soil surface and all wells were covered by caps that could be removed for sampling. Some deviations from the above protocol occurred. In two cases, it was deemed appropriate by the contractor to install the monitoring wells directly into preexisting boreholes (where soil samples had been retrieved for initial characterization of the sites), i.e. not using a temporary drill casing but otherwise an identical installation (S11 and S12). In one case (S10), the geology did not permit installation of HDPE-wells, so instead steel wells (ø 32 mm) were driven into the soil using a hydraulic hammer in 4 of the 5 sampling points at that site (only the reference well was installed normally). After installation, the wells were developed to ensure a stable flow of clean groundwater.

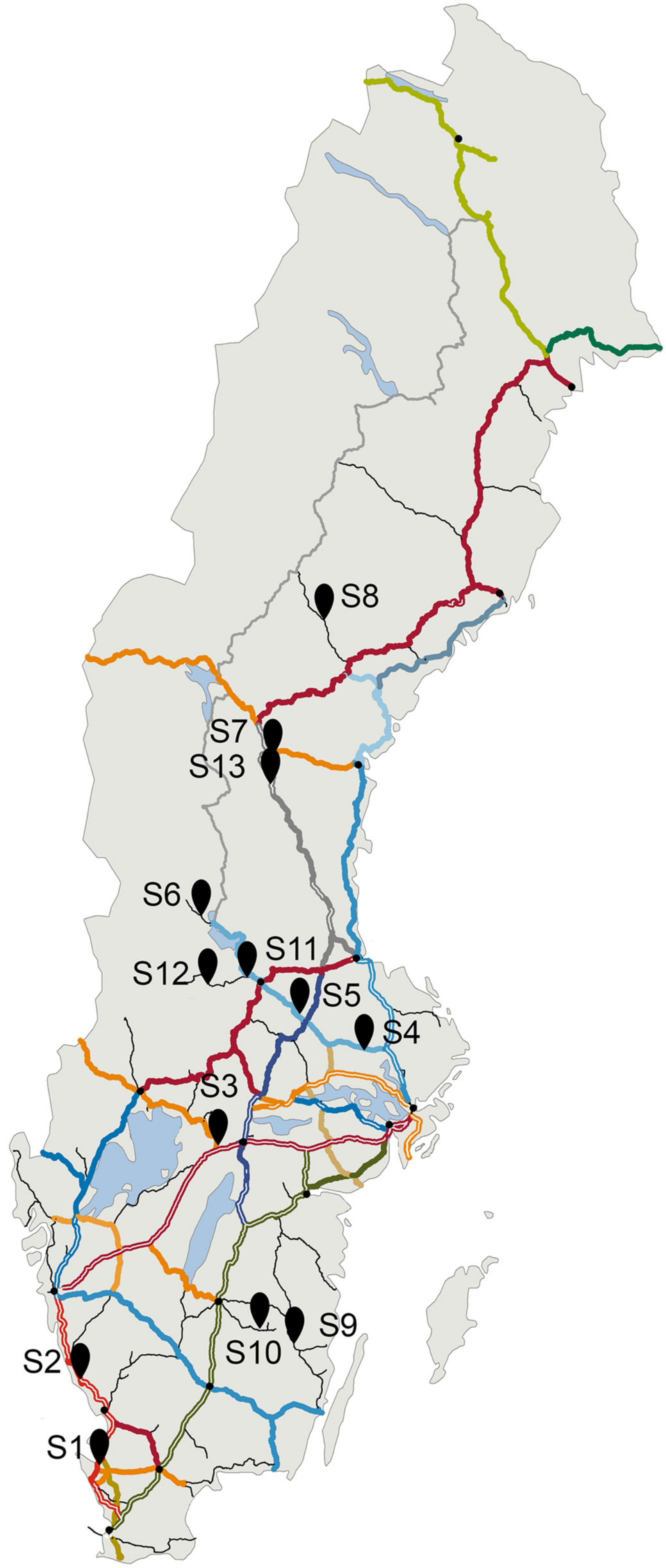

Fig. 1. Map showing the Swedish railway network and approximate locations of the sampling sites. S1–S4 were used from 2007 to 2010. S5–S7 were used only in 2007. S8 was used only for research and S9–S13 were used from 2015 to 2019.

2.4. Herbicide treatments on the test sites

During both monitoring periods, glyphosate was applied as the herbicide formulation Roundup Bio (Monsanto), which was renamed to Roundup Ultra in Sweden in 2016. According to the material safety data sheet the formulation(s) contains 486 g of glyphosate-isopropylamine salt/L (360 g a.e./L) together with 13% trimethylethoxypolyoxypropyl-ammonium chloride and 3% Tween 20. Information on application dates is given in the Supplementary dataset.

During the first monitoring period, all sampling locations, ± 50 m from the central monitoring well, were blanket sprayed once a year with an herbicide spraying train from the contractor *Banverket produktion* (renamed *Infranord* in 2010) irrespective of the degree of weed infestation. The application rate was 5 L/ha, equivalent to 1800 g a.e./ha, and the spray width was 4.5 m, resulting in an applied amount of 0.8 g glyphosate per track meter. An exception to this occurred in 2009 when two of the sites (S3 and S4) were sprayed with a mixture of Roundup Bio at an application rate of 3 L/ha and Tomahawk 180 EC (with the active ingredient fluroxypyr) at 2 L/ha, equivalent to 1080 g glyphosate/ha and an applied amount of 0.486 g glyphosate/m.

During the second monitoring period, the sampling locations were treated in the same way as the rest of the railway network, i.e. they were treated with herbicides according to need/degree of weed infestation. The contractors responsible for treating the railway network were *Bayer Crop Science* (2015) and *WeedFree on Track* (2016–2019), both of which employ herbicide spraying trains with weed detection systems that automatically control the activation of the spray nozzles, which helps reduce the overall amounts applied. Just as in the first period, the application rate was 1800 g a.e./ha, but the spray width was now 5.2 m. In both cases, the spray widths reflected what was used on the rest of the network. The weed detection system was activated, which resulted in variable amounts being applied across sites and years, and in a spotty application pattern, depending on the degree and pattern of weed infestation. Sites were normally treated once per year. However, in 2019 treatment of two of the sites (S11 and S12) was not carried out at all due to unfavorable weather conditions (no treatments are carried out during rain or if the wind speed is >5 m/s). One of the sites (S13), was not on the main line and was therefore treated by a different contractor using an ATV equipped with a spray boom or using backpack sprayers (also according to need but without a weed detection system). Due to the spotty application, pattern, specific information about how much was applied to a section of the track ±50 m from the location of the monitoring wells is needed to estimate the applied amounts with any certainty. However, this information was not collected during 2015–2017 and for S13, information about applied amounts was only available as a daily report, which only recorded the total amount applied to a larger area. Nevertheless, the available statistics for 2018–2019 indicated large variations in how the sampling sites were treated, with average amounts applied for the sections of track close to the monitoring sites varying between 0.07 and 0.8 g/m (Table 4).

2.5. Groundwater and soil sampling and analysis of samples

The monitoring focused on measuring concentrations of glyphosate and AMPA in groundwater and soil. An overview of the more relevant physicochemical properties of these compounds is presented in the Supplementary materials (Table S1). During the first monitoring period, all groundwater samples were collected using disposable bailers (one per monitoring well). Groundwater samples were taken twice in 2007 (summer and winter). However, as neither glyphosate nor AMPA were detected at any of the sites during the first year, sampling was concentrated to 4 of the sites (S1–S4) from 2008 onwards. At the same time, the sampling frequency was increased to 3 times per year, where 2 of the samplings were adjusted to occur within two weeks after glyphosate application. This was done because preliminary findings from field experiments had indicated that the chances of finding glyphosate in the groundwater were higher shortly after application. The monitoring wells were emptied at least once, and groundwater was allowed to reenter the wells prior to taking the groundwater samples that were used for analysis (to avoid sampling stagnant water). Samples were collected in containers provided by the commercial analytical labs used, stored cold and in the dark. The samples were analyzed by GC–MS at ALS Scandinavia and the reporting limit was initially 0.1 μg/L

Table 1
Overview of sampling locations.

	Location	Description of geology	Surroundings	Groundwater depth (m)	pH-value (groundwater)	pH-value (track bed)	Sampling years
S1	Skörpinge	Silty-clayey moraine	Agricultural fields	1.5 m	7.9 ± 0.2	–	2007–2010
S2	Stafsinge	Gravelly sandy moraine	Agricultural fields	2.9 m	7.6 ± 0.3	–	2007–2010
S3	Hasselfors	Silty-clayey moraine	Forest	1 m	6.7 ± 0.6	–	2007–2010
S4	Lunda	Silty-clayey moraine	Forest, agricultural fields	2–4 m	7.0 ± 0.3	–	2007–2010
S5	Broddbo	Moraine	Forest, garden, agricultural field	3.6 m	7.4 ± 0.2	–	2007
S6	Hökberget	Glacial sediment, sand	Forest	6–7 m	6.9 ± 0.1	–	2007
S7	Ånge bangård	Silty-clayey moraine	Other railway tracks	1.5 m	7.3 ± 0.4	–	2007
S8	Tågsjöberg	River sediments, sand, peat	Forest, mire	2.9 m	6.5 ± 0.8	–	2007–2008
S9	Ryningsnäs	Sandy silty moraine	Forest, roadside, garden	1.5 m	6.7 ± 1.4	6.0 ± 0.2	2015–2019
S10	Alseda	Gravelly sand	Forest	4.5–5.5 m	7.1 ± 1.2	6.3 ± 0.5	2015–2019
S11	Lennheden	Sandy silty moraine	Forest	4–5 m	6.8 ± 0.8	8.1 ± 0.8	2015–2019
S12	Strömsheden	Coarse silt, fine sand	Forest	2.8 m	7.0 ± 0.6	6.7 ± 0.7	2015–2019
S13	Mellansjö	Gravelly sand/fine sand (moraine)	Forest	0.7–2 m	6.8 ± 0.6	6.6 ± 0.6	2015–2019

for both glyphosate and AMPA in 2007–2008, which was lowered to 0.05 μg/L in 2009–2010. The author has not managed to retrieve further details on the analytical procedures.

During the second monitoring period, groundwater samples were taken primarily using a peristaltic pump and disposable polyethylene or silicon tubes. Groundwater samples were taken in the spring before herbicide application, 10–15 days after herbicide application and about 3 months after herbicide application. Also, in addition to the groundwater samples, three soil samples from the surface (0–0.3 m) and three "deep samples" from a depth that varied quite a lot between sites and years (0.33–1.25 m) were taken using an auger (Active Auger TDU155 or a Stihl BT130 Ø 120 mm). Three soil samples were taken from the track area each time and analyzed separately. Care was taken not to sample the exact same spot more than once. At S13 soil sampling was challenging due to a lack of fine materials in the surface layer so a soil sample could not always be retrieved. Groundwater and soil samples were analyzed by accredited commercial laboratories, ALcontrol laboratories/SYNLAB Analytics & Services Sweden AB, using an LC-MS-MS-method. Soil samples were extracted with a basic solution and derivatised with 9-fluorenylmethyl chloroformate (FMOC). This was followed by liquid chromatography with on-line solid phase extraction (Agilent PLRP-S) and reverse-phase liquid chromatography (column: Zorbax Eclipse Plus C18, 3.5 μm 2.1 × 150 mm, Agilent) with a mobile phase consisting of an ammonium acetate/acetonitrile gradient. Mass detection was done using and Agilent 6400 Triple Quadrupole system. Water samples were directly derivatised with FMOC and otherwise analyzed in the same way. The reporting limit for groundwater for glyphosate and AMPA was 0.05 μg/L in 2015–2016 but this was lowered to 0.01 μg/L from 2017 onwards. In a few individual samples the reporting limits were higher than in the rest due to a reduced sample volume leading to a higher limit of quantification. The soil samples were analyzed by the same lab and the reporting limit was 0.01 mg/kg for both glyphosate and AMPA throughout the period.

2.6. Data analysis

For the purposes of the data analysis, samples with concentrations below the reporting limit were treated as RL/2. The dataset was explored using basic descriptive statistics such as max, mean, median-values and percentiles (calculated by Microsoft Excel 2016), and boxplots in order to visualize the distribution of concentrations (produced in Sigmaplot 14.0). Calculation of expected topsoil concentrations following herbicide application was done using the methods described by the Soil Modelling Work group of FOCUS (FOCUS, 1997) assuming an annual application rate of 1800 g/ha (on June 1st each year) a mixing depth of 5 cm, a bulk density of 1.5 g/cm^3 and no plant interception. AMPA ratios were calculated using molar equivalents of glyphosate and AMPA:

$$AMPA\ ratio = \frac{C_{AMPA}/Mw_{AMPA}}{C_{AMPA}/Mw_{AMPA} + C_{glyphosate}/Mw_{glyphosate}} \times 100$$

3. Results and discussion

3.1. Concentrations of glyphosate and AMPA in groundwater samples

The distributions of glyphosate and AMPA concentrations in the groundwater samples were heavily skewed with most concentrations below the reporting limits and only a few higher concentrations being detected (Fig. 2). Nevertheless, glyphosate was detected in 16% of the groundwater samples from directly beneath the track but in only 3 and 2% of reference and down-gradient samples, respectively (Table 2). The same figures for AMPA were 14%, 3% and 1% of samples from beneath the track, reference well and down-gradient wells, respectively.

The highest concentration of glyphosate detected in any individual sample was 7 μg/L (mean value: 4.5 ± 3.3 μg/L for the three monitoring wells in the track area) and was detected in September 2018 at S12. This prompted an extra round of sampling for this site, which was carried out in October 2018, and this time, lower concentrations were detected: 0.61 μg/L in the well where the highest concentration had been found and a mean value of 0.2 ± 0.3 μg/L for the three monitoring wells in the track. Throughout both monitoring periods, concentrations of AMPA generally followed those of glyphosate albeit at a lower level. The highest concentration of AMPA detected in an individual sample was 1.1 μg/L in a sample from S3 in October 2009 (mean value: 0.6 ± 0.7 μg/L). Other

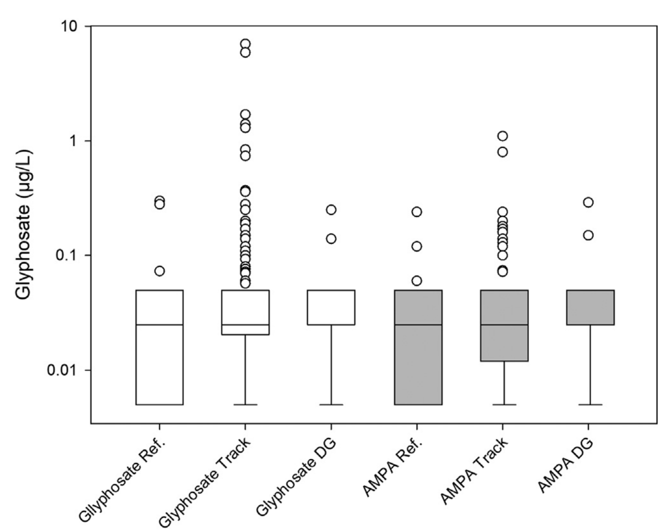

Fig. 2. Boxplots showing the distribution of glyphosate and AMPA concentrations in groundwater samples from reference wells, from directly beneath the railway track and from down-gradient wells. The boxes cover everything from the 25th to the 75th percentiles, the line in the boxes shows the median value, the whiskers show the 10th and 90th percentiles and any data points above the 90th percentile are shown as circles.

Table 2
Summary statistics of analyzed groundwater samples and concentrations of glyphosate and AMPA in groundwater[a].

	Glyphosate			AMPA		
	Reference	Below track	Down-gradient	Reference	Below track	Down-gradient
Number of samples 2007–2019	N = 94	N = 335	N = 174	N = 94	N = 335	N = 174
Max conc. (μg/L)	0.30	7.0	0.25	0.24	1.1	0.29
Mean conc. (μg/L)	0.03	0.09	0.03	0.03	0.03	0.03
Median conc. (μg/L)	<RL	<RL	<RL	<RL	<RL	<RL
95th percentile (μg/L)	<RL	0.15	<RL	<RL	<RL	<RL
90th percentile (μg/L)	<RL	0.057	<RL	<RL	<RL	<RL
Samples > reporting limit	3 (3%)	55 (16%)	3 (2%)	3 (3%)	46 (14%)	2 (1%)
Samples > GQS[b] for groundwater	2 (2%)	21 (6%)	2 (1%)	2 (2%)	12 (4%)	2 (1%)

[a] Excluding the results from an extra round of sampling conducted at S12 in 2018.
[b] GQS = groundwater quality standard.

monitoring studies have found both higher glyphosate and higher AMPA concentrations in groundwater (Carretta et al., 2021). The AMPA ratio, i.e. the molar ratio of AMPA in relation to the sum of glyphosate and AMPA, can be a useful tool to assess the transformation dynamics of glyphosate in contaminated groundwater. Recent glyphosate inputs are expected to lead to lower AMPA ratios, and conversely, higher AMPA ratios are expected to occur in deeper groundwater reservoirs or groundwater with longer residence times, due to the fact that glyphosate is transformed to AMPA over time (Battaglin et al., 2014; Carretta et al., 2021). In this study, AMPA ratios were rather low, with an overall median of 39%, which is consistent with the rather shallow groundwater investigated and which may also be indicative of an overall slow degradation rate. However, there was significant variation in AMPA ratios both across sites and over time (Figs. S1-S2) with e.g. high AMPA ratios consistently being detected at S13.

The general pattern was that the frequency of detections of both glyphosate and AMPA increased over time, while the mean and median concentrations decreased. This is probably largely because the reporting limit was lowered by a factor of 10 from 0.1 to 0.01 μg/L during the period. However, a break from this pattern was seen in 2018 with elevated concentrations detected in 3 out of 5 monitoring sites (Figs. 3B and 4A). As of the end of 2019, while the concentrations had declined again, they had not returned to the levels they were at before 2018. It is plausible that the extremely hot and dry conditions in Sweden during the summer of 2018 may have indirectly contributed to the increase in leaching seen later that year. It is well known that drought limits microbial activity in soil due to reduced bioavailability of organic molecules and because microorganisms need to spend more energy to maintain their osmotic pressure (Moyano et al., 2013; Yan et al., 2016). And while the mineralization of glyphosate may be controlled by other factors, such as exchangeable acidity (Nguyen et al., 2018), strong adsorption (Bergström et al., 2011; Ghafoor et al., 2011; Sørensen et al., 2006; Zhelezova et al., 2017) and the population size of degrading microorganisms (Gimsing et al., 2004), it would also often be limited by dry conditions in practice (Bento et al., 2016; Schroll et al., 2006). The half-life of glyphosate in Swedish railway embankments, previously determined from field experiments, is 4 ± 2 months (Cederlund, 2016; Torstensson et al., 2005) and it is likely that some of that variability is explained by differences in moisture conditions. Thus, it is plausible that the dry conditions during the summer of 2018 could have retarded the degradation of glyphosate, leading to a greater potential for leaching as the autumn rains set in. The temporal pattern of AMPA ratios (Fig. S2) does seem to support this hypothesis with AMPA ratios dipping to below 10% during the autumn of 2018 for sites S11 and S12, recovering slowly thereafter, indicating that a pulse of glyphosate reached the groundwater. However, no unusual accumulation of glyphosate was seen in the soil samples taken during 2018. In fact, no clear correlation whatsoever was seen between the concentrations measured in soil samples and in the groundwater when studying the whole dataset. Also, the highest leaching was seen at sites S11 and S12 where soil concentrations were determined to be low (Table 3), and where statistics of the applied amounts also indicated that spraying was limited (Table 4). Climate data from the Swedish meteorological and hydrological institute (SMHI) clearly shows that the summer of

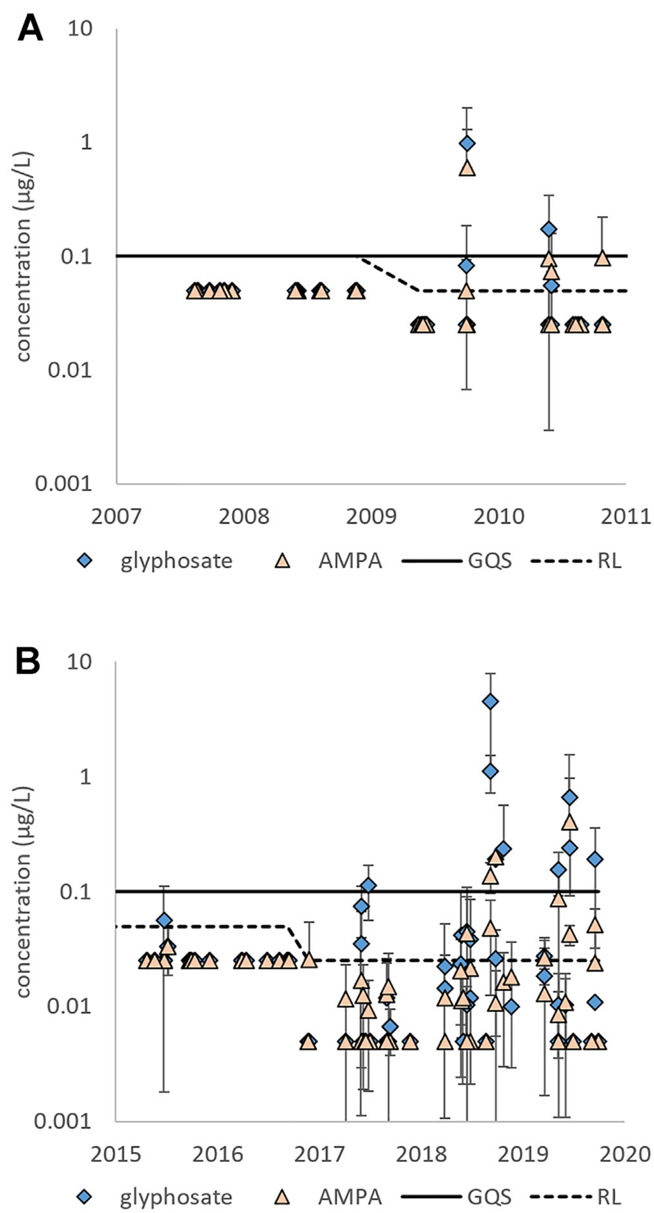

Fig. 3. Average concentrations of glyphosate and AMPA ± standard deviation in samples taken from directly beneath the railway track in monitoring sites S1–S7 (A) and monitoring sites S9–S13 (B). The solid line shows the EU groundwater quality standard of 0.1 μg/L and the dotted line shows the reporting limit (RL) of the commercial labs.

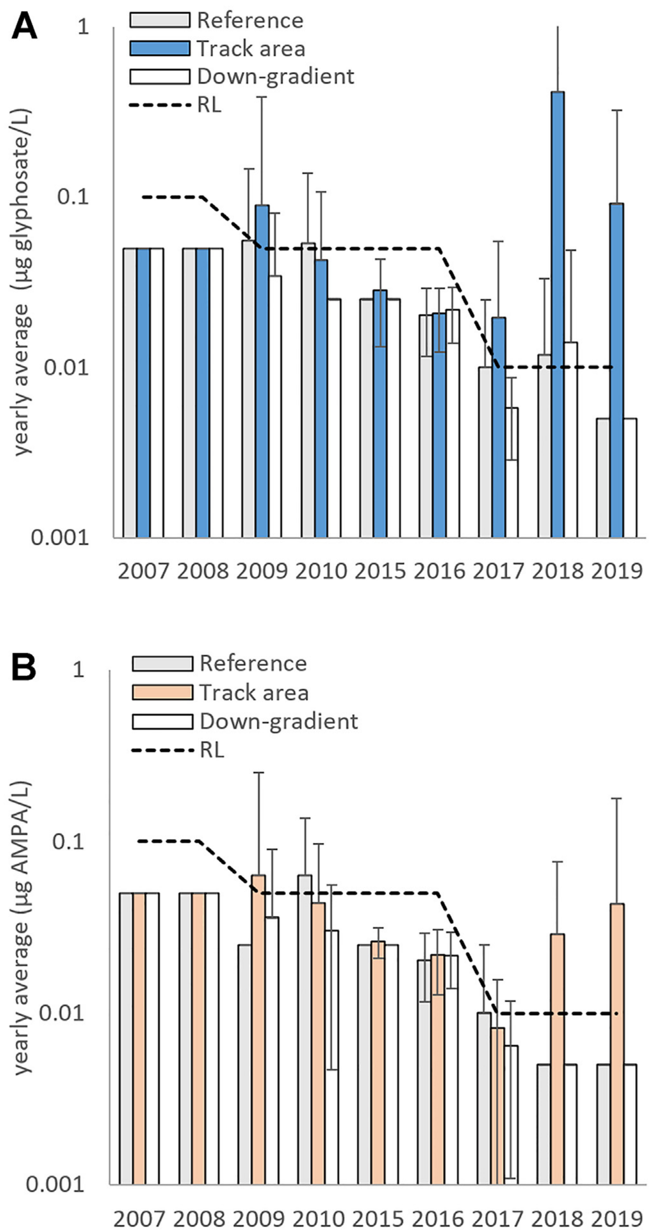

Fig. 4. Yearly average concentrations of glyphosate (A) and AMPA (B) in groundwater samples from directly beneath the track, reference wells and down-gradient wells. The dotted line shows the reporting limits (RL) of the commercial labs.

2018 was unusually hot and dry in Sweden (Fig. S3). More detailed data from the closest available climate monitoring stations is presented in Figs. S4–S7 and seem to indicate that in 2018 significant rainfall events (19 to 26 mm day^{-1}) occurred 17 days and 12 days after application at

Table 4
Spraying data for the sampling locations shown as an estimated % of the 5.2 m width treated with a full application of 1800 g/ha.

	S9	S10	S11	S12	S13[a]
2019	78%	8%	Untreated	Untreated	42%
2018	85%	51%	37%	28%[b]	30%

[a] Information comes from daily reports that cover a larger area than just the test site, making it difficult to judge to what extent the area directly surrounding the monitoring wells were treated.

[b] Information is actually for a 100 m section directly adjacent to the test site but it probably reflects the level of spray.

S11 and S12, respectively, followed by a dry and hot period of a little more than a month, and then some more rainfall that occurred from the end of July (Figs. S5 and S6). Due to the timing of the sampling, which occurred 9 days after application, before the first significant rainfall events, and then only after about 3 months, it is possible that glyphosate leached to deeper soil levels or even reached the groundwater before the dry period started, but that this was only detected in the autumn. Of course, since summer rainfall events can be very local in nature, and precipitation was measured at distances of 8.5 to up to 40 km from the monitoring sites, the true rainfall pattern at the sites is difficult to ascertain.

The adsorption of glyphosate in soil is also well known to be influenced by the pH-value and the mineralogical composition of the soil, particularly the content of variable charge iron- and aluminium oxides (Borggaard and Gimsing, 2008). However, the pH-values determined in the subgrade and groundwater samples (Table 1) did not correlate in any obvious way with the observed leaching and the mineralogy of the railway subgrade was never characterized. During both monitoring periods, samples were taken shortly after application of the herbicide, since preliminary data had indicated that the likelihood of leaching was higher then. However, although glyphosate was detected occasionally in these samples, it was more frequently detected, and in higher concentration, in the samples taken 3–-4 months after application. This is likely an indication that it generally takes longer than just a few days for glyphosate to reach the groundwater. It is also possible that more leaching 3–4 months after application may simply mean that conditions during the early autumn were more conducive to leaching, with higher precipitation and lower evapotranspiration. No time-of-flight analysis was performed to try and predict the time when the highest concentrations would be expected to reach the groundwater. However, because the distance to the groundwater varies so much between the different monitoring sites (Table 1) it is likely that the expected breakthrough-time would vary significantly between sites. However, there was no obvious relationship between groundwater depth and detected concentrations (Fig. S8) indicating that other site characteristics were more important. Another observation is that during both monitoring periods, significant concentrations were only detected after about 3 years of sampling (Fig. 3A and B), perhaps indicating that it takes even longer for glyphosate to move through the railway ballast and subgrade and reach the groundwater. This could have been a factor during the first monitoring period where it is conceivable that several of the sites only started receiving herbicide applications because of the monitoring program. However, for the second monitoring period one of the selection criteria for the

Table 3
Average concentrations of glyphosate and AMPA in soil samples from the track area ± standard deviation; 90th percentile shown within brackets.

	Surface samples (depth 0–0.3 m)		Deep samples (depth 0.33–1.25 m)	
	Glyphosate (mg/kg)	AMPA (mg/kg)	Glyphosate (mg/kg)	AMPA (mg/kg)
S9	0.84 ± 1.1; (2.7)	0.64 ± 0.8; (1.4)	0.43 ± 0.44; (1.0)	0.38 ± 0.44; (0.95)
S10	0.31 ± 0.43; (0.73)	0.22 ± 0.25; (0.50)	0.15 ± 0.28; (0.36)	0.11 ± 0.21; (0.26)
S11	0.013 ± 0.022; (0.028)	0.028 ± 0.069; (0.049)	<RL[a]	<RL[a]
S12	0.032 ± 0.064; (0.095)	0.041 ± 0.068; (0.061)	<RL[a]	<RL[a]
S13	0.029 ± 0.12; (0.026)	0.024 ± 0.069; (0.042)	<RL[a]	<RL[a]

[a] Both the mean values and the 90th percentiles were below the reporting limit in these cases.

test sites was that they were already regularly treated with herbicides. No changes were made to the normal treatment regime during the monitoring period and the initial glyphosate application would therefore have occurred many years prior to the start of the monitoring.

During the first monitoring period, some of the sampling locations were situated close to agricultural fields (Table 1), and in at least one case it was not possible to attribute detected concentrations specifically to the railway application, since concentrations of glyphosate and AMPA were similar in the reference well and beneath the railway track. However, during the second monitoring period no sampling sites were in the vicinity of other potential users of glyphosate. Still, the frequency of detections and the detected concentrations were not different in reference and down-gradient samples, indicating limited lateral transport. One reason for this may be that the leaching of pesticides from railways (Jarvis et al., 2006; Torstensson et al., 2005) and glyphosate in general (de Jonge et al., 2000) has been proposed to be controlled by particle-bound or particle associated transport and occur mainly through preferential flow paths, and such mechanisms are likely to be less important for lateral transport in the saturated zone. In general, glyphosate is expected to leach readily from the upper ballast of the railway, which consists of crushed rock, but be rather immobile in the sandy non-structured materials that make up the lower and sub-ballast and generally lack such preferential flow paths (de Jonge et al., 2000; Strange-Hansen et al., 2004). In fact, it is possible that the installation of monitoring wells directly into the track bed may introduce such preferential flow paths, allowing herbicides to reach groundwater more readily. This was observed by Schmidt et al. (1999), who demonstrated that a tracer solution could reach the groundwater within minutes in some instances when monitoring wells were installed directly next to the rails. The same authors also showed that while some findings of diuron were made in the groundwater directly below the track when using conventionally installed monitoring wells, diuron was not found when monitoring wells were installed at an oblique angle, with the screen situated directly below the treated area but the opening for sampling at 10 m distance from the track.

3.2. Concentrations of glyphosate and AMPA in the soil samples

The spotty application pattern that occurred because of the use of a weed detection system on the spraying train resulted in highly variable soil concentrations being recorded both within and between the different sampling sites. This makes it difficult to spot any trends or to directly estimate half-lives of glyphosate from the results, and probably have also contributed to the poor correlation between soil and groundwater concentrations. Nevertheless, concentrations were logical in the sense that sites that were sprayed more (S9 and S10; Table 4) also showed the highest concentrations of glyphosate and AMPA in the ballast. At these locations, glyphosate and AMPA were also regularly detected in the "deep samples". By contrast, the concentrations of glyphosate and AMPA at S12 and S13 were low in the surface soil, and they were only sporadically detected in the deep soil. At site S11, glyphosate and AMPA were only detected in 4 and 6, respectively, of the 32 samples from the surface soil, indicating very limited application of herbicides in the vicinity of the monitoring wells (Table 3).

No trend of accumulation of glyphosate over time was seen in the topsoil samples. For S9 and S10, the fluctuating levels were in general agreement with what may be expected in the surface soil based on the previously estimated half-life of 4 ± 2 months (Torstensson et al., 2005) and an annual application rate of 1800 g/ha (Fig. 5). For S11, S12 and S13 the levels were consistently lower than this, indicating lower application rates. Overall, the distribution of concentrations of glyphosate and AMPA in the upper subgrade were comparable to what has been reported for European agricultural soils (Geissen et al., 2021; Silva et al., 2018). At S9, the concentrations in the "deep" soil samples increased over time, which initially caused some alarm. However, upon closer examination of the sampling protocols it was discovered that the specified sampling depth for these deep samples became shallower over time from a depth of roughly 80 cm to only 40 cm, which probably caused the increase seen in concentrations

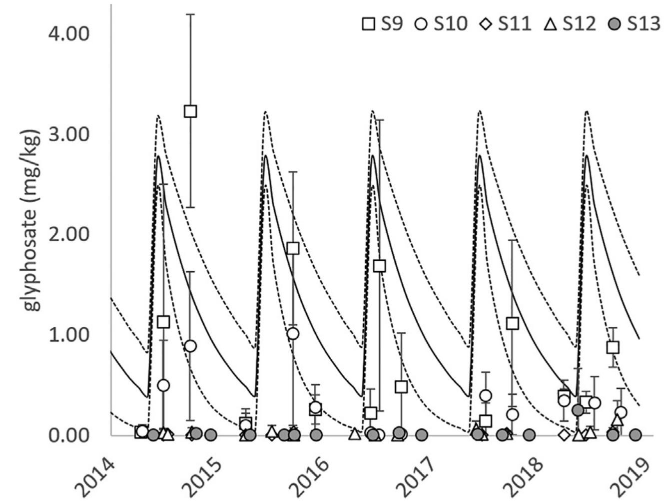

Fig. 5. Levels of glyphosate detected in the topsoil during the second iteration of the monitoring program. The solid, upper and lower dotted lines show the expected surface concentration of glyphosate assuming half-lives of 4, 6 and 2 months, respectively. Expected initial concentrations after application were estimated using the methods described by the Soil Modelling Work group of FOCUS (FOCUS, 1997) assuming an annual application rate of 1800 g/ha (on June 1st each year) a mixing depth of 5 cm, a bulk density of 1.5 g/cm^3 and no plant interception.

(Fig. S2). No similar indications of increasing glyphosate or AMPA levels in the deep samples over time were seen for the other sites.

3.3. Implications of the results

The results show that applications of glyphosate on railways can sometimes lead to glyphosate reaching shallow groundwater directly beneath or in the immediate vicinity of the track in concentrations that exceed the groundwater quality standard (GQS) of 0.1 μg/L that has been set for pesticides by the EU in its groundwater Directive 2006/118/EC. The purpose of the GQS is to function as a threshold value against which the chemical status of bodies of groundwater should be assessed by member states. However, the legislation specifies that the chemical status of a body of groundwater can still be considered good even though the GQS is exceeded in one or several monitoring points. In fact, in Annex III of the directive it is specified that it is "*the extent of a body of groundwater having an annual arithmetic mean concentration of a pollutant higher than a groundwater quality standard or a threshold value*" that should be considered when investigating if the conditions for good chemical quality are met (along with several other specified considerations).

It is also worth noting that not all groundwater is considered to be part of "bodies of groundwater", which is what the legislation is focused on protecting. However, this aspect was not considered when selecting the monitoring sites. In fact, during the second monitoring period, only one of the five sites (S12) was situated next to an identified "body of groundwater". Incidentally, this was the site at which the highest concentrations were detected; the annual arithmetic mean value for S12 based on solely our data was 0.15 μg/L in 2018 (weighing results from reference, track, and down-gradient samples), so still exceeding the GQS. However, at S12, the body of groundwater in question extends over 20 km southwards from the monitoring site and has an estimated outtake volume of 2000–10,000 m^3/day, so in this case, the extent of the body of groundwater in which the GQS is exceeded is likely to be very small.

A body of groundwater is defined in Directive, 2000/60/EC (somewhat vaguely) as "*a distinct volume of groundwater in an aquifer or aquifers*" and since aquifers by definition should "*allow either a significant flow of groundwater or the abstraction of significant quantities of groundwater*", bodies of groundwater are usually of a significant volume as well. However, it is likely that it is bodies of groundwater of limited volume (relative to other bodies of groundwater), and that have a large relative exposure to the railway, that would be most at risk from the railway herbicide applications. It should also be noted that, in Sweden, bodies of groundwater that are currently used for human consumption are generally protected and that Trafikverket has opted not to use herbicides in any groundwater protection zones, so these considerations are mostly valid for bodies of groundwater, not currently protected, but that could become important resources in the future. Thus, overall, the risk posed to valuable groundwater resources is probably not that large.

3.4. Implementation of the monitoring in the past and in the future

The initial focus of the monitoring program was that it should assess groundwater concentrations of glyphosate used along Swedish railways at a few representative sites, in order to increase the knowledge on its environmental fate when applied to railways. However, the original selection process did not consider whether there was any vegetation present at these sites or not. So, while the sites did cover different types of geological and hydrogeological conditions, they were not necessarily representative of the type of railways to which glyphosate is typically applied, and it was realized that without intervention many of the sites would not have been sprayed at all. Therefore, it was decided that glyphosate would be applied annually to all the sites with the full application rate, irrespective of the actual need for weed control. Thus, what was intended as a pure monitoring program was run more like a series of field leaching tests and doubts were cast as to the representativeness of some of these tests.

For the second monitoring period it was decided to try again to treat the monitoring sites in the same way as the rest of the network. Therefore, one of the preconditions for the selected sites was that they would be at least partially covered by weeds; and during the monitoring period the sites were all treated in the same way as the rest of the railway network (i.e. sprayed according to the need for vegetation control). Meanwhile, spraying trains with automatic weed detection systems had now been introduced. This shift has reduced the average amounts of herbicides applied to Swedish railways significantly and would have correspondingly reduced the amounts applied to each site. However, unfortunately the *actual* amounts applied to the monitoring sites were not recorded prior to 2018, and this in combination with the spotty application pattern has made interpretation of the results difficult.

Typically, a key factor when designing a groundwater monitoring study is to define the protection goals, i.e. what groundwater needs to be protected and what levels of contamination may or may not be allowed in it (Gimsing et al., 2019). However, for the railway monitoring programs described here, no such protection goals were formally identified and agreed upon. This has made it difficult to judge whether findings of glyphosate and AMPA detected in the groundwater immediately below the railway track, are acceptable or not. Looking forward, it may be wise to take the time to reflect and decide on such protection goals and let them inform how the monitoring should be developed in the future. For instance, as discussed above, one such protection goal could be that the chemical status of bodies of groundwater found along the railway should not be affected negatively and that the annual mean concentrations of such bodies of groundwater should not exceed the QGS. To assess this goal, it may be prudent to conduct the monitoring at sites near or directly above bodies of groundwater that could potentially be at risk (i.e. of smaller size/large relative exposure to railway). It may also be wise to install and sample monitoring wells in a way that could better assess this goal, focusing more on the potential for transport of contaminants away from the railway than on monitoring the groundwater directly beneath the railway.

3.5. Conclusions

The results show that when glyphosate herbicides are applied at a rate of 1800 g/ha to railways, both glyphosate and AMPA can reach the groundwater directly beneath the track and that concentrations occasionally exceed the EU groundwater quality standard for groundwater. However, as shown by the few detections of glyphosate and AMPA in the monitoring wells flanking the railway, horizontal mobility in the groundwater zone appears to be limited, and this in combination with the no-spray zones that surround bodies of groundwater presently used for human consumption indicate that valuable groundwater resources are unlikely to be impacted by leaching.

CRediT authorship contribution statement

Harald Cederlund: Conceptualization (in part), Formal analysis, Data curation (in part), Writing, Visualization, Project administration and Funding acquisition (for synthesis).

Declaration of competing interest

The writing of this paper and the monitoring itself have been funded by the Swedish Transport Administration. However, the synthesis and interpretation of the data set has been performed independently by the author.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.152361.

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