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New methods for determination of glyphosate and (aminomethyl)phosphonic acid in water and soil

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Abstract

New methods were developed to determine glyphosate, *N*-(phosphonomethyl)glycine, and its major metabolite, (aminomethyl)phosphonic acid in groundwater and soil. The methods involve ligand-exchange, anion-exchange and derivatisation and final identification and quantification by GC–MS. The limits of quantification in this experiment were 0.1 $\mu g\ l^{-1}$ for both compounds in water and 0.006 $\mu g\ g^{-1}$ for both compounds in soil. Decomposition in soil and occurrence in groundwater of the herbicide glyphosate was studied after its application for weed control on a Swedish railway embankment.

Keywords: Water analysis; Soil; Environmental analysis; Glyphosate; Aminomethylphosphonic acid; Phosphonic acids; Pesticides

1. Introduction

Glyphosate is the most frequently used herbicide in the world. In Sweden it has been used since 1975 for weed control in agriculture, forestry and gardens. Glyphosate is also used by the Swedish National Rail Administration for weed control on railway embankments. Since reports [1,2] have been made on possible contamination of glyphosate in groundwater, there is an increasing requirement for studies on this task in Sweden as well as elsewhere. Glyphosate is a non-selective systemic herbicide, absorbed by the foliage, with rapid translocation throughout the plant. Methods to determine glyphosate and its major metabolite, (aminomethyl)phosphonic acid, (AMPA), in different matrices have frequently been described over the years [3–16]. However, these methods were not sufficiently sensitive or not conformable to current equipment.

The aim of this study was to develop a sensitive and selective method for determination of glyphosate and AMPA in soil and groundwater. Using this method we aimed to study the environmental fate of the substances used around railway tracks.

The requirements for a sensitive analytical method for glyphosate in water were a limit of quantification of 0.1 $\mu g\ l^{-1}$ and acceptably low background noise for blanks. During our efforts to find a useful method to analyse glyphosate and AMPA in water and soil, we studied the literature. Derivatisation of glyphosate and AMPA by a mixture of trifluoroacetic anhydride (TFAA) and trifluoroethanol (TFE) was reported to give a product suitable for gas chroma-

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tography–mass spectrometry (GC–MS) analysis [6,8]. Using GC–MS in the selected-ion monitoring mode, it became obvious to us that this technique would give sufficient sensitivity and selectivity.

As the groundwater and soil samples we collected for analysis sometimes contained humic acids and other substances that influenced the analysis, we looked for an efficient clean-up procedure. We found the clean-up procedure according to ''Method No. 405'' [15] to be the most efficient and sensitive, although it is rather time-consuming.

After evaluation of the method, we studied decomposition and transport of glyphosate and AMPA in a railway embankment after application of the herbicide for weed control of the track environment.

2. Experimental

2.1. Reagents

Standards used for calibration were (trivial name in italics): *N*-(phosphonomethyl)glycine, *glyphosate* and (aminomethyl)phosphonic acid (*AMPA*), both pure certified (Dr. Ehrenstorfer, Augsburg, Germany). HCl, concentrated analytical-reagent grade, and HPLC-grade methanol and ethylacetate from Kebo Lab (Stockholm, Sweden) were used for extraction and solvation. Chelex 100, Na form and AG 1-X8, 200–400 mesh, Cl form, from Bio-Rad Labs. (Sundbyberg, Sweden) were used for ion-exchange and clean-up. Trifluoroacetic anhydride (TFAA) and trifluoroethanol (TFE) were used for the derivatisation, both analytical-reagent grade from Sigma–Aldrich (Stockholm, Sweden). Water used for analysis was deionised by reversed osmosis.

2.2. Calibration

For long-term storage, stock solutions of glyphosate and AMPA were diluted in water to concentrations of 100 μg ml^{-1}. A solution containing glyphosate and AMPA, 1 μg ml^{-1}, was prepared as a working standard.

2.3. Clean-up and derivatisation

2.3.1. Water samples

A 200-ml volume of a groundwater sample was adjusted to pH 2. An 8-ml volume of Chelex 100 was poured into a 15-ml disposable polypropylene tube fitted with 20 μm polyethylene frit and a stopcock. The sample was applied on the Chelex column at a rate of 7 ml min^{-1}. The bottle was rinsed with 5 ml of water which was added to the column. The column was washed with 20 ml of water, 40 ml of 0.2 *M* HCl and 1 ml of 6 *M* HCl. All preceding fractions were discarded. The isolates were eluted with 1×2.8 and 2×3.7 ml of 6 *M* HCl at a rate of 4 ml min^{-1}. The isolate-containing eluates were collected into a sample tube and 4 ml of 10 *M* HCl was added.

A 4-ml volume of AG 1-X8 was poured into a 15-ml disposable polypropylene tube fitted with a 20 μm polyethylene frit. After the gel had settled, the column was prepared with three portions of 2.5 ml 6 *M* HCl and 1 ml concentrated HCl. The pooled elutes from above were added and passed through the column by gravity. The sample was eluted from the column with 1×1 ml and 2×2 ml of 6 *M* HCl. All eluates from the sample were collected in pear-shaped glass bottles.

The sample was evaporated to dryness under vacuum, 5 ml of water was added and the evaporation was repeated. The sample was dissolved in 1 ml of water–methanol–HCl (160:40:2.7) and transported to a 2-ml GC vial. The sample was evaporated to dryness under nitrogen. Derivatisation was carried out by adding 800 μl of TFAA and 400 μl of TFE and the sample was held at 100°C for 1 h. After being acclimatised to room temperature the sample was evaporated under nitrogen and redissolved in 1 ml of ethyl acetate prior to analysis.

2.3.2. Soil samples

A 10-g amount of soil was extracted for 30 min with 25 ml of 1 *M* NaOH. The sample was centrifuged for 10 min at 5000 rpm. The supernatant was filtered through a F1 Whatman filter to a 250-ml glass bottle. The extraction was repeated once. A portion of 4.2 ml concentrated HCl was poured into the pooled extracts and the sample was diluted with water to a volume of 200 ml. The pH was adjusted to 2.0 and the sample was kept at room temperature for approx. 1 h (to let the particulates sink to the bottom). Then 50 ml of the clear upper part of the sample was treated identically to the water samples.

2.4. Instrumentation

GC–MS analyses were performed with a Hewlett-Packard 6890 GC system, equipped with a 30 m× 0.32 mm I.D. (0.25 μm film thickness) fused-silica capillary column (HP-5 for GC–MS), a mass spectrometer 5973, a split/splitless injector and software Chemstation, all from Hewlett-Packard (Kista, Sweden). Samples were injected (1 μl out of 1000 μl of sample) in the splitless mode at 270°C, oven temperature 70°C. After 2 min, the oven temperature was raised to 170°C at 30°C min^{-1} and then from 170 to 270°C at 120°C min^{-1}. Helium (N47 grade, 99.997%) was used as the carrier gas and the flow-rate was 0.7 ml min^{-1}. The mass spectrometer was operated in the electron impact (EI) mode; the transfer line and manifold temperatures were 260°C and 230°C, respectively. m/z 302 and 371 were used for identification of the AMPA derivative and m/z 411 and 511 were used for the glyphosate derivative. Peak areas were obtained from the chromatograms generated by the total ion chromatograms (TICs) of the selected ions. Verification of compound identification was based on comparison of the areas of the selected ions in the samples with those of the standards. The relative standard deviation (RSD) for replicate injections was 5%. The TIC response was found to be linear in the practical concentration range (10–1000 pg) of individual components injected.

2.5. Field experiment

The field experiment was conducted in the central area of Sweden, at the railway line between Borås and Varberg. The sampling areas were located about 10 km east of Varberg (application rate A) and about 30 km west of Borås (application rates B and C) where groundwater and soil were sampled. The herbicide was applied along the railway line using spraying equipment mounted on a train used only for this purpose. The overall width of the application area was 6 m. The herbicide was applied on 14 May 1998. The formulation used in this experiment was RoundupBio (360 g a.i. l^{-1}, Monsanto) and three rates were applied; 3 l ha^{-1} (A, normal rate), 6 l ha^{-1} (B) and 18 l ha^{-1} (C).

For groundwater sampling, six iron tubes, 1.5 m of length and 6 cm in diameter (Fig. 1), were installed beside the tracks down into the railway embankment. Two tubes were installed at the sample area with application rate A and three tubes at each of the areas receiving rates B and C. A layer of bentonite was put around the tubes to avoid mechanical transport of contaminated soil particles and surface water along the tube walls. A layer of gravel filling was put around the bottom of the tubes to facilitate groundwater percolation into the tubes. Soil samples were taken within the same area as the water samples.

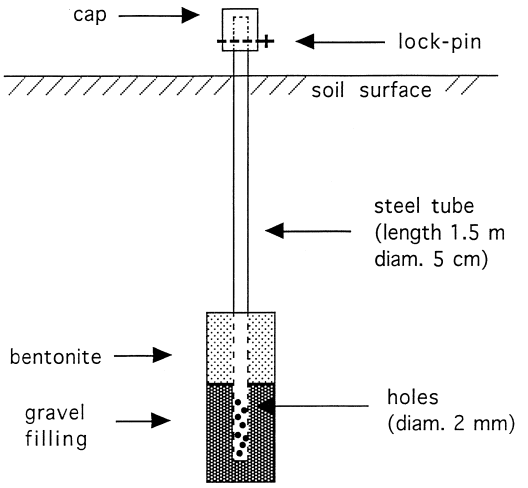

Fig. 1. Steel tube installed in the railway embankment for groundwater sampling.

2.6. Sampling

Field sampling was carried out on three occasions in 1998 (May, August and November) and on two occasions in 1999 (May and September), when the soil was unfrozen. The soil samples from the treated embankment were taken from a randomly chosen area of 25×40 cm from sites A, B and C. They were collected using two different spades, a small one (9×14 cm) and a bigger one (23×33 cm). The uppermost layer (0–10 cm) was sampled by cutting a cubic sample of an area of 9×9 cm and 10 cm depth with the small spade. After that the whole 10 cm layer within the sample area (25×40 cm) was removed. Then the procedure was repeated for each of the remaining layers to be sampled. The samples were stored in plastic bags at −20°C until analysis (within 3 months), when they were thawed.

The groundwater samples were collected from the sampling tubes by putting a PTFE tube fixed to a suction bottle and a hand-driven pump down into the bottom of the tubes. From 500 to 1000 ml were collected in a glass bottle for each sample and stored at +4°C before analysis. The samples were analysed within a week. Sampling frequency was the same as for soil sampling of the embankment. On some sampling occasions, no water was found in some of the tubes.

3. Results and discussion

3.1. GC–MS

Derivatisation products of glyphosate and AMPA are formed as shown in Fig. 2. Derivatisation product of glyphosate has a molecular mass of m/z 511. Its mass spectrum (Fig. 3) shows a molecular ion at 511 and an ion of strong intensity at m/z 411 (loss of TFE). Derivatisation product of AMPA (compound IV) shows a molecular ion at m/z 371 and a strong intensity ion at m/z 302 (loss of CF_3). Fragments with relatively high molecular masses and the molecular ions are used for identification due to their high selectivity and a minimum of interfering peaks are seen in the chromatograms. The sensitivity can easily be increased if required, by measuring an additional ion for both substances.

Representative chromatograms illustrating TIC profiles for soil and water samples with glyphosate and AMPA, analysed by the method described, are shown in Fig. 4. The TIC profiles show (a) a water sample containing glyphosate and AMPA concentrations around the quantification level (0.14 μg l^{-1} and 0.06 μg l^{-1}, respectively). Chromatogram (b) in Fig. 4 similarly shows a soil sample with 0.02 μg g^{-1} glyphosate and 0.013 μg g^{-1} AMPA; (c) is a chromatogram from a standard injection of 20 ng of both substances; (d) shows a soil sample without any measurable amounts (<0.003 μg g^{-1}) of the compounds. The very good signal-to-noise ratios at low concentrations shown here makes it possible to decrease the quantification levels if required.

3.2. Limit of detection, limit of quantification and linearity

The limit of detection was determined from repeated analyses of the compounds at low concentrations. The concentration at which the mean ex-

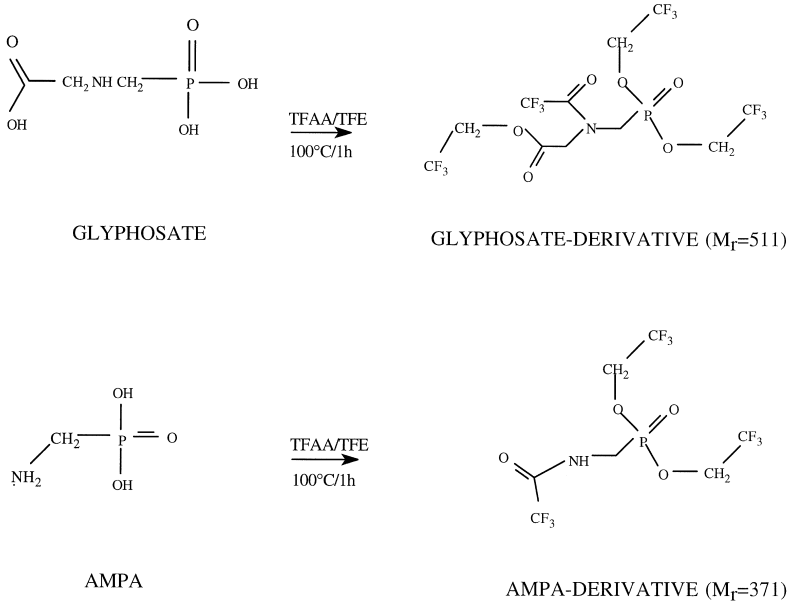

Fig. 2. Derivatisation of glyphosate and AMPA with trifluoroethanol (TFE) and trifluoroacetic anhydride (TFAA).

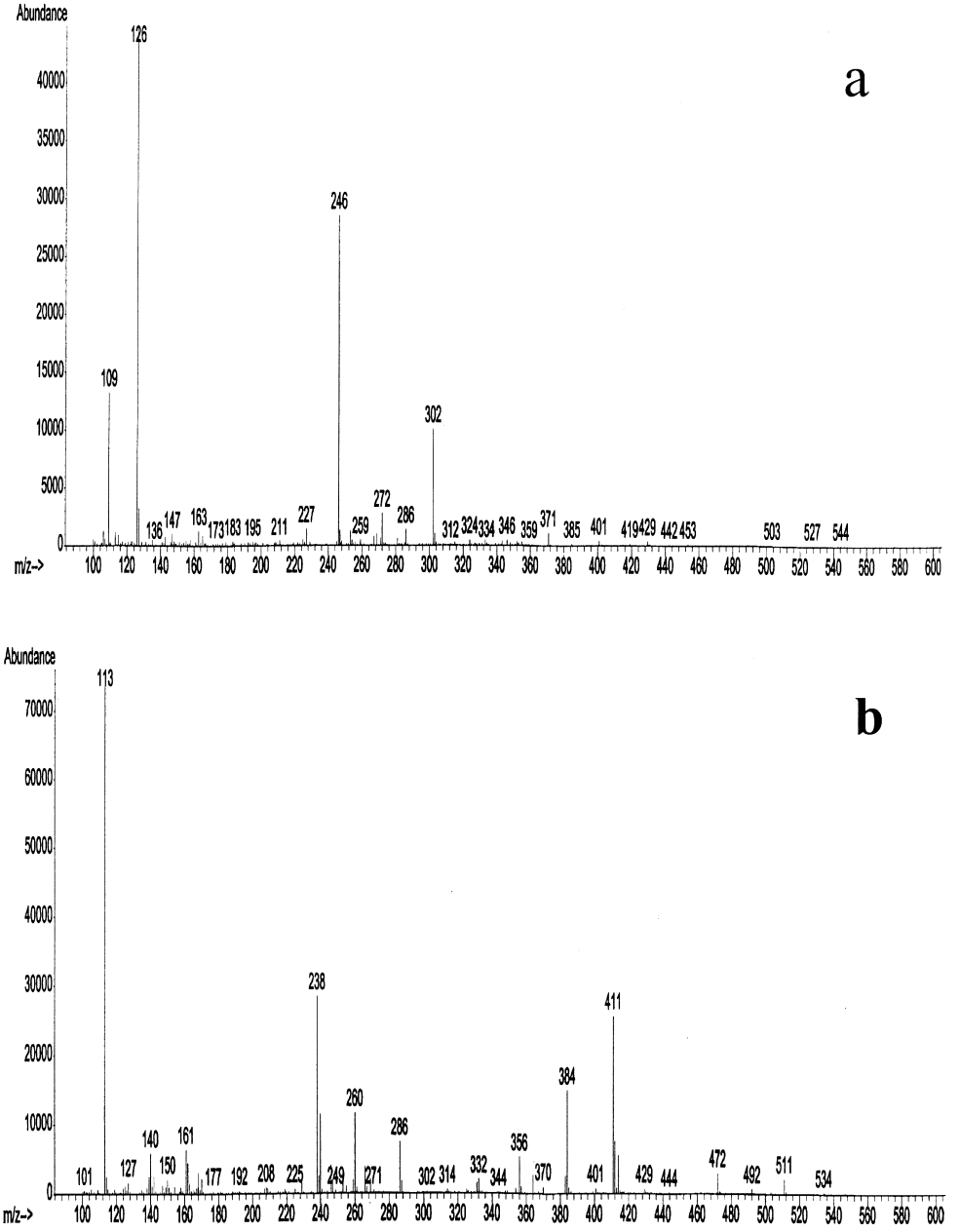

Fig. 3. Mass spectrogram from a derivatised standard sample, (a) AMPA and (b) glyphosate.

ceeded the baseline noise by more than 5 SD was taken as the limit of detection.

The limit of detection in this study was 0.05 μg l^{-1} in groundwater and 0.003 μg g^{-1} in soil for glyphosate and AMPA.

The limit of quantification in this study was 0.1 μg l^{-1} for groundwater and 0.006 μg g^{-1} for soil. It was approximately calculated as 10-times the standard deviation of the baseline noise for the blanks.

A linearity test was made using standard glypho-

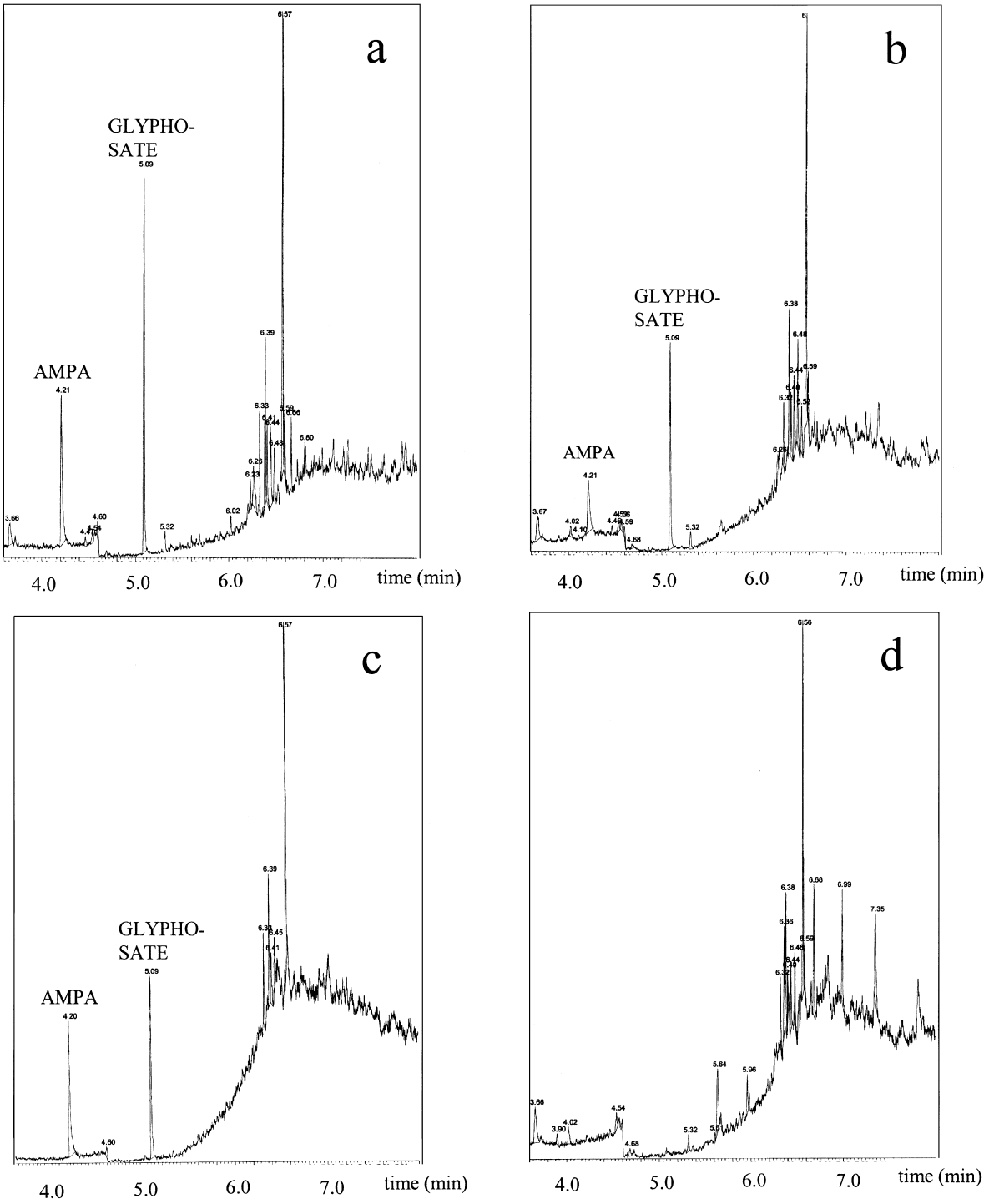

Fig. 4. Total ion chromatograms from samples just above the limit of quantification. (a) A groundwater sample, 0.06 μg l^{-1} AMPA and 0.14 μg l^{-1} glyphosate, (b) a soil sample, 0.013 μg g^{-1} AMPA and 0.02 μg g^{-1} glyphosate, (c) standard sample, 20 ng of AMPA and glyphosate derivatives injected, (d) a soil sample without any detectable amounts of the substances.

Table 1
Recovery of added[a,b] glyphosate and AMPA using the method described

Sample No.	Recovery (%)			
	AMPA in water	Glyphosate in water	AMPA in soil	Glyphosate in soil
1	94	104	66	58
2	102	104	81	86
3	99	109	79	91
4	102	111		
5	85	85		
Mean	96	103	75	78
RSD (%)	8	10	11	23

[a] 0.5 μg l^{-1} of glyphosate and AMPA added to water samples.
[b] 0.05 μg g^{-1} of glyphosate and AMPA added to soil samples.

sate and AMPA added to tap water. The linearity was excellent over the range 0.1 to 2.5 μg l^{-1} for glyphosate (r^2=0.9483, P=0.0001) and AMPA (r^2=0.9751, P=0.0001).

A similar test was made for soil samples in the concentration range 0.006 to 0.3 μg g^{-1}, by adding the substances to a sandy soil. The linearity was good for glyphosate (r^2=0.9201, P=0.0001) and AMPA (r^2=0.8757, P=0.0001).

Typical regression lines and correlations for glyphosate and AMPA coefficient of the standard curves were: glyphosate: $y=0.03219+9.6037\cdot10^{-5}$, r^2=0.9803; AMPA: $y=0.03404+1.0472\cdot10^{-5}$, r^2=0.9903 in the concentration range 10–1000 pg of injected standard.

3.3. Accuracy and precision

Recovery data for the glyphosate and AMPA are presented in Table 1. The pesticides were added to fresh tap water and clean sandy soil and extracted by the methods described in this paper. The mean recovery was found to be between 85 and 111% and the variation was 7.5% for glyphosate and 9.8% for AMPA in groundwater. Recovery for analysis of soil in this experiment varied from 58 to 91% and the variation was 23% for glyphosate and 11% for AMPA.

Recovery in sandy soils like those on the railway embankments requires a mention. Old embankment material most probably contains high levels of iron. As glyphosate binds strongly to iron [17], the recovery rates can be strongly affected, especially at low concentration rates.

In order to check the precision of the method, water samples, percolated through a standard soil spiked with glyphosate and AMPA at three different concentration rates, were analysed. The staff at the Fresenius Institute in Frankfurt, Germany carried out the percolation, spiking and analysing. Analysis of samples from the same batches were also made at the Department of Microbiology by the authors (Table 2). The samples were analysed as unknowns and the results were compared afterwards.

The data in Tables 1 and 2 indicate the good repeatability and reproducibility of the method outlined. Apart from the errors resulting from repeated injection, further inaccuracies might be caused by adsorption of glyphosate and AMPA onto glass or precipitated coextractives and by possible insufficiency of the derivatisation. The adsorbtion onto glass is avoided in this method by dissolving both standard solutions and evaporated sample elutes in a mixture of water, methanol and HCl before evaporation and derivatisation.

3.4. Derivatisation

The derivatisation is sometimes a critical step due

Table 2
Interlaboratory test[a]

Spiking level (μg l^{-1})	Glyphosate (μg l^{-1}) Fresenius	AMPA (μg l^{-1}) Fresenius	Glyphosate (μg l^{-1}) Univ. Agric. Sweden	AMPA (μg l^{-1}) Univ. Agric. Sweden
–	<0.05	<0.05	<0.05	<0.05
0.12	0.11	0.11	0.11	0.04
2.40	2.02	1.98	1.55	1.50

[a] Water samples spiked and analysed by Fresenius Institute, Frankfurt, Germany. Analysed as unknowns by the authors.

to leaking vial caps at high temperatures. Careful tightening of the caps is recommended. A stability test on frozen derivatized standards showed that after 5 weeks the standard areas had decreased to about 90% and after 4 months they were about 50% of the original levels. Measuring on the derivatised standards and samples are therefore recommended within a week after derivatisation.

The temperature during the derivatisation reaction is optimised [6] but the derivatisation yield can probably be higher with increased amounts of reagents [8].

The derivatisation of glyphosate and AMPA seems to be very sensitive to hydrolytic conditions. A leaking seal during derivatisation always results in low recovery.

Residues from the iron-loaded Chelex ion exchanger seems to compete with glyphosate during derivatisation. This can be avoided by carefully handling of the AG 1-X8 clean-up procedure.

3.5. Appearance of glyphosate in the railway embankment

The method developed for analysis of glyphosate and AMPA was used to identify the herbicide and its metabolite in the railway embankment after a normal application for removal of weeds from the tracks. At the time of the first sampling after application, most of the glyphosate was found in the uppermost 10 cm of the embankment. Thereafter, part of the herbicide started to degrade and the metabolite AMPA could be detected. Both glyphosate and AMPA also started to slowly move downward into the embankment. Table 3 shows the amounts of glyphosate and AMPA found at different levels below the surface of the embankment in the sampling 105 days after application. At the two higher application rates, both glyphosate and AMPA were found down to a depth of 60–70 cm below the surface. AMPA was found at greater depth, 70–80 cm, only at sampling 377 days after application of the highest rate.

Degradation of pesticides is often supposed to follow a reaction of first-order kinetics [17]. To get an idea about the rate of degradation of glyphosate in the embankment, the amounts of glyphosate found at different depths were added up at each sampling occasion after application and then visualised in Fig. 5. The half-life of glyphosate at each application rate from A–C was calculated to be 6.5, 7.5 and 12 months, respectively. The phosphonic acid moiety of glyphosate adsorbs to the soil, whereafter the mineralization process proceeds without any lag phase. This seems to be a co-metabolic process that occurs under both aerobic and anaerobic conditions [18]. The principle degradation product of glyphosate is AMPA, which is also biologically degradable. A slower degradation of AMPA than glyphosate has been reported [18].

Concentrations of glyphosate and AMPA found in the tubes at different intervals after application of RoundupBio to the track area are shown in Table 4. At the lowest application rate (A), which also is the normally applied rate, no glyphosate was found in the groundwater. At rate (B), two times the normal rate, mostly trace amounts of glyphosate and AMPA,

Table 3
Amounts of glyphosate and AMPA (mg kg^{-1} sample) in the railway embankment at different depths and at three sampling sites, A–C, at sampling 105 days after the application of RoundupBio (application rate at A 3 l ha^{-1}, at B 6 l ha^{-1} and at C 18 l ha^{-1})[a]

Sampling depth (cm)	A		B		C	
	Glyphosate	AMPA	Glyphosate	AMPA	Glyphosate	AMPA
0–10	0.207	0.180	0.813	0.151	2.700	0.382
10–20	0.006	0.010	0.012	0.024	0.156	0.024
20–30	<0.003	Traces	Traces	Traces	0.011	0.009
30–40	<0.003	0.007	<0.003	<0.003	Traces	<0.003
40–50	Traces	Traces	<0.003	<0.003	Traces	Traces
50–60			Traces	<0.003	0.007	0.006
60–70			Traces	Traces	Traces	Traces
70–80			<0.003	<0.003	<0.003	<0.003
80–90			<0.003	<0.003	<0.003	<0.003

[a] Limit of detection=0.003 mg kg^{-1}; limit of quantification=0.006 mg kg^{-1}; traces=0.003–0.006 mg kg^{-1}.

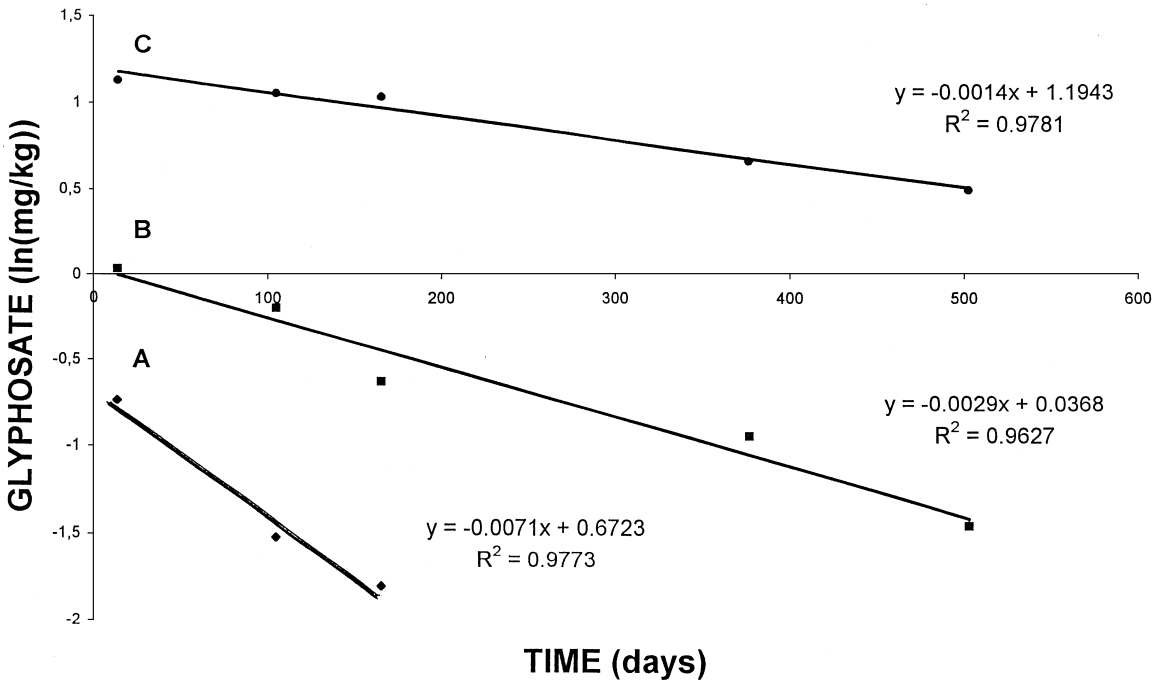

Fig. 5. Recovery of glyphosate in the railway embankment at three sites, A–C. The amounts of glyphosate at different depths have been added up for each sampling occasion after the application of RoundupBio [application rate at (A) 3 l ha^{-1}, at (B) 6 l ha^{-1} and at (C) 18 l $ha]^{-1}$.

Table 4
Amounts of glyphosate and AMPA (μl l^{-1} water) in samples from ground water tubes along the railway line at three different sampling places, A–C, at sampling occasions after the application of RoundupBio (application rate at A 3 l ha^{-1}, at B 6 l ha^{-1} and at C 18 l ha^{-1})[a]

Time (days)	A 1	A 2	B 3	B 4	B 5	C 6	C 7	C 8
Glyphosate								
14	NS	NS	Traces	0.31	0.12	0.38	0.53	0.93
105	<0.05	<0.05	<0.05	<0.05	<0.05	Traces	0.45	0.77
166	<0.05	<0.05	Traces	<0.05	<0.05	<0.05	0.52	1.42
377	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.20	0.11
503	<0.05	<0.05	<0.05	<0.05	<0.05	0.14	0.69	<0.05
AMPA								
14	NS	NS	<0.05	0.30	Traces	0.23	0.27	0.43
105	<0.05	<0.05	<0.05	<0.05	Traces	Traces	0.23	0.46
166	<0.05	<0.05	Traces	<0.05	<0.05	<0.05	0.15	0.81
377	<0.05	<0.05	<0.05	NS	NS	<0.05	NS	NS
503	<0.05	<0.05	Traces	Traces	<0.05	<0.05	0.23	Traces

[a] Limit of detection=0.05 μl l^{-1} water; limit of quantification=0.10 μl l^{-1} water; traces=0.05–0.10 μl l^{-1} water.
NS=No sample.

were found. Only at the sampling 2 weeks after application were higher concentrations found, probably as a result of ''preferential flow'' [17]. At the highest application rate (C), six times the normal rate, considerable concentrations of both glyphosate and AMPA were found on all sampling occasions. It is obvious there is a great variation between the findings in ground water tubes C 6–C 8. In tube C 8 sampled after 166 days after application, the highest amounts of glyphosate and AMPA was found. This is probably due to the heterogeneity of the railway embankment and the differences in downward transport caused by this.

A certain mobility of glyphosate in the railway embankment soil investigated is apparent in the data shown in Fig. 5. However, at all of the sampling sites only minor amounts were transported deeper than 20 cm at the normal and two times the normal dosages. This should be compared to what was found for the herbicide diflufenican in the same environment [19] and to findings of the herbicide diuron down to at least 150 cm depth in a comparable railway embankment [20]. Glyphosate has occasionally been found along railway tracks in Germany in surface and groundwater in the vicinity of the site of application [2]. However, the main conclusion of this study is that a substance with a good degradation and sorption behaviour such as glyphosate, used at normal dosages, will not lead to a significant environmental impact, in spite of the unfavourable conditions on railway embankments. We consider the methods described to be very useful for this kind of study due to their sensitivity and selectivity properties.

Acknowledgements

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