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A simple and rapid direct injection method for the determination of glyphosate and AMPA in environmental water samples

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Abstract

Glyphosate is currently the most widely used herbicide in the world, yet screening of environmental waters for this chemical is limited by the need for specialized derivatization and measurement methods that can be tedious and time-consuming. In this work, we present a novel method for the detection and quantification at trace levels of glyphosate and aminomethylphosphonic acid (AMPA) in environmental water samples. The detection and quantification of the analytes was performed by liquid chromatography (LC) coupled with tandem mass spectrometry (MS/MS). Chromatographic separation was achieved with an ion-exchange column and a pH-gradient elution of a solution of ammonium hydroxide and ammonium acetate. The limit of detection for glyphosate and AMPA was 0.25 μg L^{-1} and the limit of quantification was 0.5 μg L^{-1} with a 20-μL injection. The method was used to investigate the levels of glyphosate and AMPA in surface water samples from the Yarra River catchment area and urban constructed stormwater wetlands. The results indicate that at the time of sampling, no glyphosate or AMPA was present in the samples from the Yarra River catchment area ($n = 10$). However, glyphosate was detected above the limit of quantification in 33% of the wetland samples ($n = 12$), with concentrations ranging from 1.95 to 2.96 μg L^{-1}. Similarly, AMPA was quantified in 83% of the wetland samples, with concentrations ranging from 0.55 to 2.42 μg L^{-1}. To our knowledge, this is the first report of a pH-gradient LC–MS/MS method for glyphosate and AMPA analysis at ultratrace levels, with minimal sample processing, avoiding costly, time-consuming derivatization and preconcentration steps.

Keywords Direct injection · Ion-exchange column · pH gradient · Glyphosate

Introduction

Glyphosate (N-(phosphonomethyl)glycine) is a broad-spectrum, postemergence, foliar herbicide. It is currently the most used pesticide in agriculture worldwide, mainly because of its high efficacy and low residual activity in soil and the introduction of glyphosate-resistant field crops (e.g. soybean, maize, cotton, canola) [1]. Moreover, it is also widely used for urban and residential weed control. In that context, there are almost 600 glyphosate-containing products registered for use in Australia, of which almost 500 are registered for use in the state of Victoria [2].

The increase in the use of glyphosate-based herbicides has raised concerns about the occurrence of glyphosate and its main metabolite aminomethylphosphonic acid (AMPA) in the environment. Glyphosate is considered a pseudopersistent compound since it accumulates to a great extent in agricultural soils [3]. Moreover, glyphosate and AMPA have been detected in streams [4, 5] and sediments [6, 7], since they can be transported off-site by spray drift, by surface runoff or in wind-blown material reaching surface water bodies [8, 9]. Glyphosate and AMPA are polar compounds, non-volatile and highly water soluble (Fig. 1). Both molecules are zwitterions and are found negatively charged at pH > 6. These particular physicochemical characteristics make the detection of glyphosate and AMPA at trace levels difficult. Quantification methods that involve gas chromatography do not yield good results because of the low volatility of glyphosate and AMPA [10]. At present, liquid chromatography (LC) is considered the most suitable technique for the detection of phosphonic
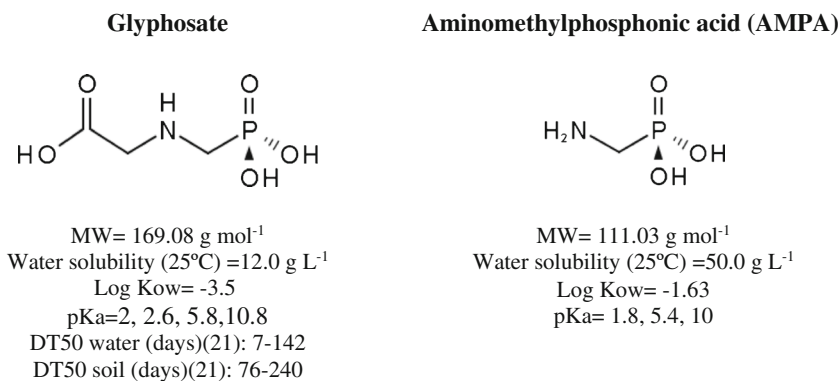
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Fig. 1 Chemical structures and selected general characteristics of glyphosate and aminomethylphosphonic acid (AMPA). DT50, time for 50% degradation, MW, molar mass

Glyphosate

Aminomethylphosphonic acid (AMPA)

MW= 169.08 g mol^{-1}
Water solubility (25ºC) =12.0 g L^{-1}
Log Kow= -3.5
pKa=2, 2.6, 5.8,10.8
DT50 water (days)(21): 7-142
DT50 soil (days)(21): 76-240

MW= 111.03 g mol^{-1}
Water solubility (25ºC) =50.0 g L^{-1}
Log Kow= -1.63
pKa= 1.8, 5.4, 10

and amino acid type herbicides at low concentrations. However, the lack of chromophore or fluorophore groups makes it difficult to use conventional detection methods such as detection by UV absorption or fluorimetry. Hence, most of the analytical methods for glyphosate and AMPA involve a precolumn or postcolumn derivatization to increase selectivity and method sensitivity [11]. Typically, this involves a derivatization step to reduce the polar character of glyphosate and AMPA, which in turn increases the retention and improves the chromatographic separation of the analytes and allows their detection by fluorimetry, UV absorption or mass spectrometry (MS) [11]. The most commonly used derivatization agent is chloroformic acid 9*H*-fluoren-9-ylmethyl ester (FMOC-Cl) [12]. Derivatization with FMOC-Cl involves a nucleophilic substitution in the secondary amino group undertaken in alkaline conditions. FMOC-Cl has low water solubility and stability; therefore, it has to be prepared in organic solvents that are miscible with water (e.g. acetonitrile). FMOC-Cl can be rapidly hydrolysed to FMOC-OH, and can also form other amino acid FMOC derivatives [13], which reduces the performance of the reaction with glyphosate and AMPA, and therefore it has to be added in excess [14]. Once the derivatization step is complete (time ranges from 3 to 24 h), it is necessary to add a clean-up step to extract the excess FMOC-Cl and any remaining organic impurities [15]. Such derivatization procedures are time-consuming, involve a great amount of sample manipulation, are costly and would ideally be avoided.

Given glyphosate's widespread use and its increasing detection in the environment, it is important to develop a simple, efficient method for routine analysis that involves minimal sample handling and no derivatization [12]. Direct analysis of glyphosate and AMPA can be performed with an ion-exchange column. The use of an ion-exchange column increases the chromatographic retention of non-derivatized glyphosate and AMPA, and therefore allows direct injection of the samples [16–18]. However, the elimination of sample preparation work can result in reduced sensitivity and a narrower linear dynamic range compared with use of enrichment and derivatization steps [16]. Previous direct injection methods involved the chromatographic separation of the

compounds using an isocratic elution and a mixed-mode reversed phase and a weak-anion-exchange column [16], an anion-exchange column [17], or a cation-exchange column [18]. In this work, we present a novel direct injection method for glyphosate and AMPA using a pH-gradient elution, an anion-exchange column and tandem MS (MS/MS). The method was validated with environmental surface water samples from wetlands and streams. To our knowledge, this is the first report of a pH-gradient high-performance LC–MS/MS method for the analysis of glyphosate and AMPA at ultratrace levels in environmental water samples.

Material and methods

Chemicals

Glyphosate (purity greater than 98%), AMPA (purity 99%), isotopically labelled glyphosate ([1,2-^{13}C,^{15}N]glyphosate; purity greater than 99%), ammonium acetate (purity 99.99%) and ammonium hydroxide (purity greater than 99%) were purchased from Sigma-Aldrich. Ultrapure water (resistivity 16.7 MΩ cm) was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Standard stock solution of 1000 mg L^{-1} were prepared for each standard. Standard working solutions for LC–MS/MS analysis and for sample fortification were prepared by dilution with ultrapure water.

Instrumental analysis

The MS compound optimization consisted of full-scan MS and product-ion MS/MS spectra of glyphosate, AMPA and isotopically labelled glyphosate performed under negative electrospray ionization with a 200 µg L^{-1} reference standard solution. After adequate separation had been achieved, MS/MS parameters were optimized for maximum sensitivity of glyphosate.

The chromatographic separation was performed with an Agilent Technologies 1290 Infinity II liquid chromatograph with a Metrosep A Supp 4 9 µm, 250 mm × 4.0 mm ion-
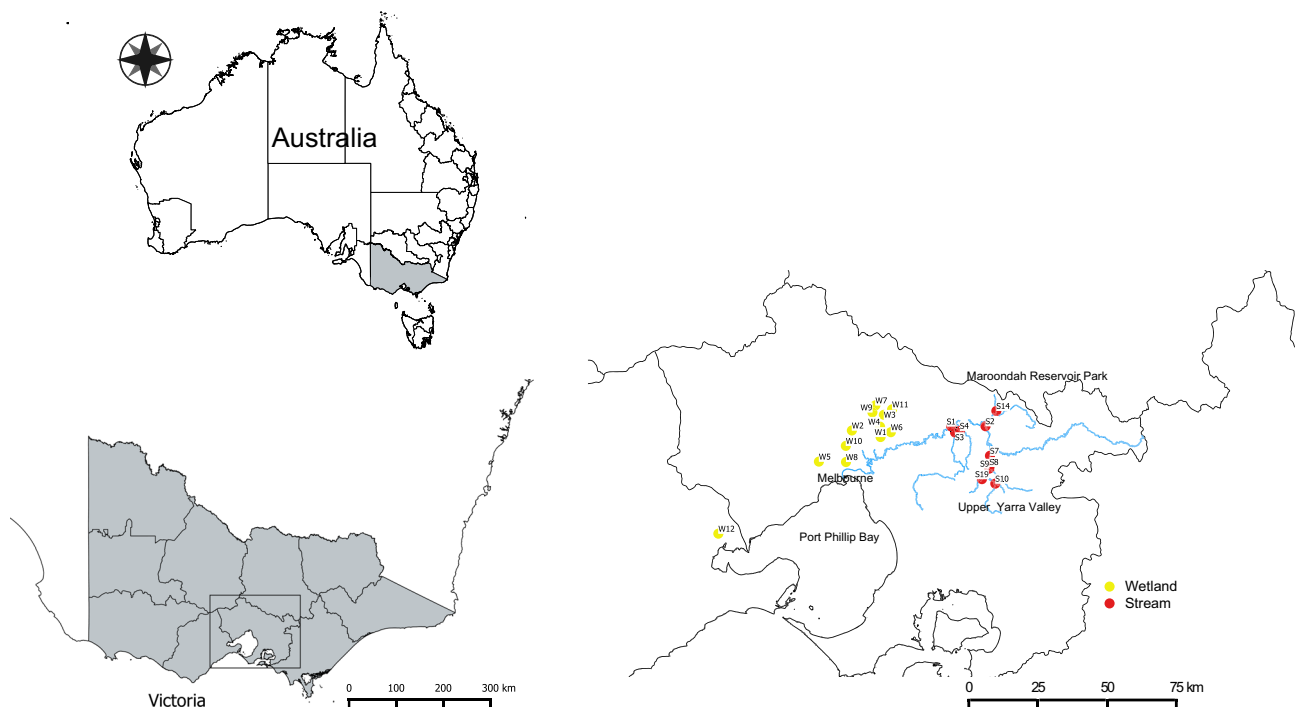
Fig. 2 Location of the surface water sampling sites of wetlands within Melbourne suburban areas and Geelong, and rural streams from the Upper Yarra Valley (Victoria, Australia). (Map from [31], Copyright the State of Victoria)

exchange column (Metrohm, Gladesville, NSW, Australia). The injection volume was 20 μL. The mobile phase flow rate was set at 0.8 mL min^{-1}. The mobile phase consisted of buffer A (22.5 mM NH$_4$Ac, 30 mM NH$_4$OH) and buffer B (45 mM NH$_4$Ac, 10 mM NH$_4$OH), with a gradient set as follows: 0% buffer B from 0 to 3 min, 100% buffer B from 3 to 11 min and 0% buffer B from 11 to 18 min.

The target molecules were detected with an Agilent 6495B triple-quadrupole mass spectrometer (MS/MS). The transitions of the analytes were monitored in multiple-reaction monitoring (MRM) scan mode. Target compounds were monitored according to the retention time and two ion transitions and were quantified with Agilent MassHunter Quantitative

Analysis (version B.08.00). The area of the most sensitive MRM transition for each analyte was used for target compound identification and quantification (q_1), and the second transition (q_2) was used for further confirmation.

Sample preparation

Two millilitres of water sample was spiked with 20 μL of 200 μg L^{-1} isotopically labelled glyphosate solution. Then 200 μL of buffer A was added. Samples were shaken vigorously and then filtered into a vial through 0.22-μm nylon membrane syringe filters.

Method validation

Limit of detection and limit of quantification

The limit of detection (LOD) was established as the lowest concentration that could be reliably differentiated from the background levels with a signal-to-noise ratio of 3 or greater. The method limit of quantification (LOQ) was determined as the lowest fortification level in the matrix sample that had a mean recovery between 70–120% of the spiking concentration, a relative standard deviation (RSD) of 15% or less and a signal-to-noise ratio of 10 or greater.

Linearity, accuracy and precision

The method linearity was assessed by a standard curve calibration of glyphosate and AMPA at six concentrations: 0.5, 1, 2.5, 5, 10 and 20 μg L^{-1} ($n = 3$). Accuracy was tested in

Table 1 Tandem mass spectrometry (MS) source and ion funnel parameters optimized for the detection of glyphosate and aminomethylphosphonic acid

MS conditions	Ion funnel parameters
Sheath gas heater temperature 300 C	Negative high pressure RF 110 V
Sheath gas flow rate 12 L min^{-1}	Negative low pressure RF 60 V
Gas temperature 160 °°C	
Desolvation gas flow rate 13 L min^{-1}	
Nebulizer pressure 25 psi	
Capillary voltage 3 kV	
Nozzle voltage 500 V	
Delta EMV 400 V	

EMV electron multiplier voltage

Fig. 3 Multiple-reaction monitoring (MRM) scan chromatograms of the primary transitions for glyphosate and aminomethylphosphonic acid (AMPA) in standard solution and a surface water sample spiked at 1 μg L^{-1}

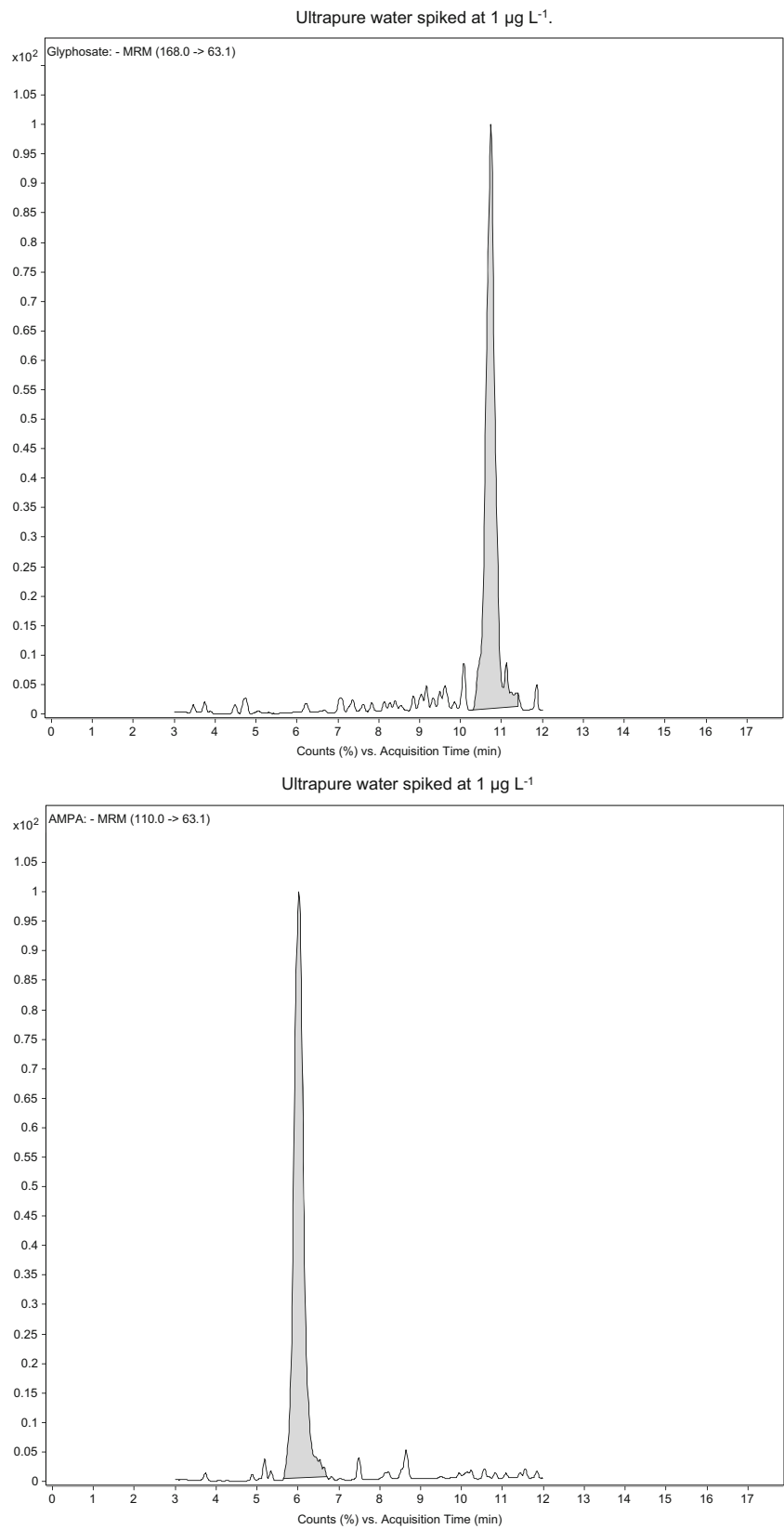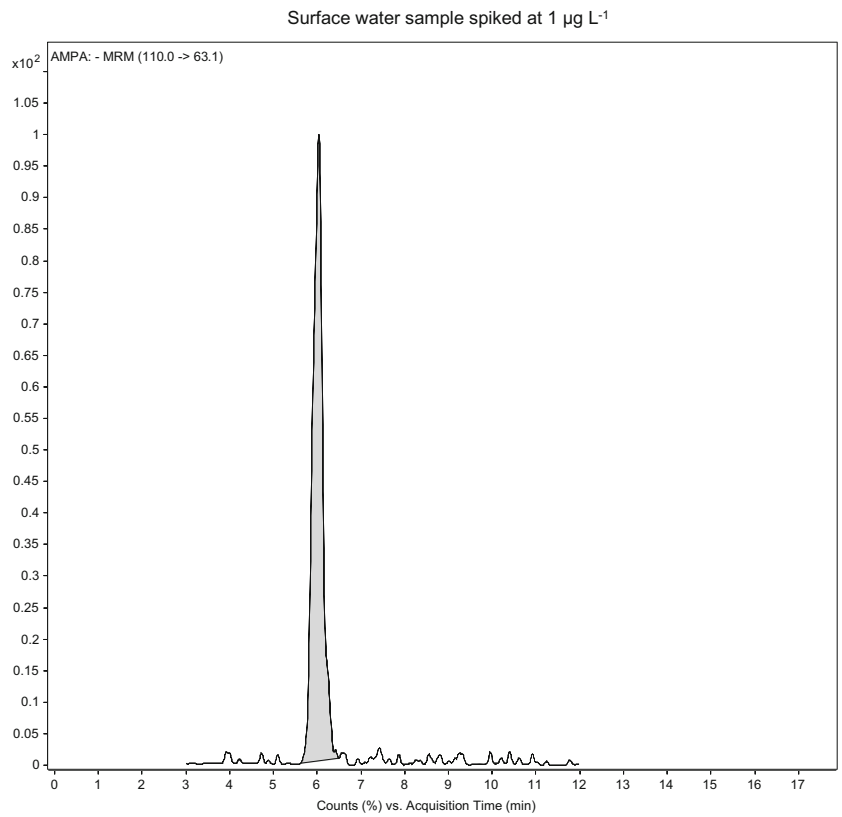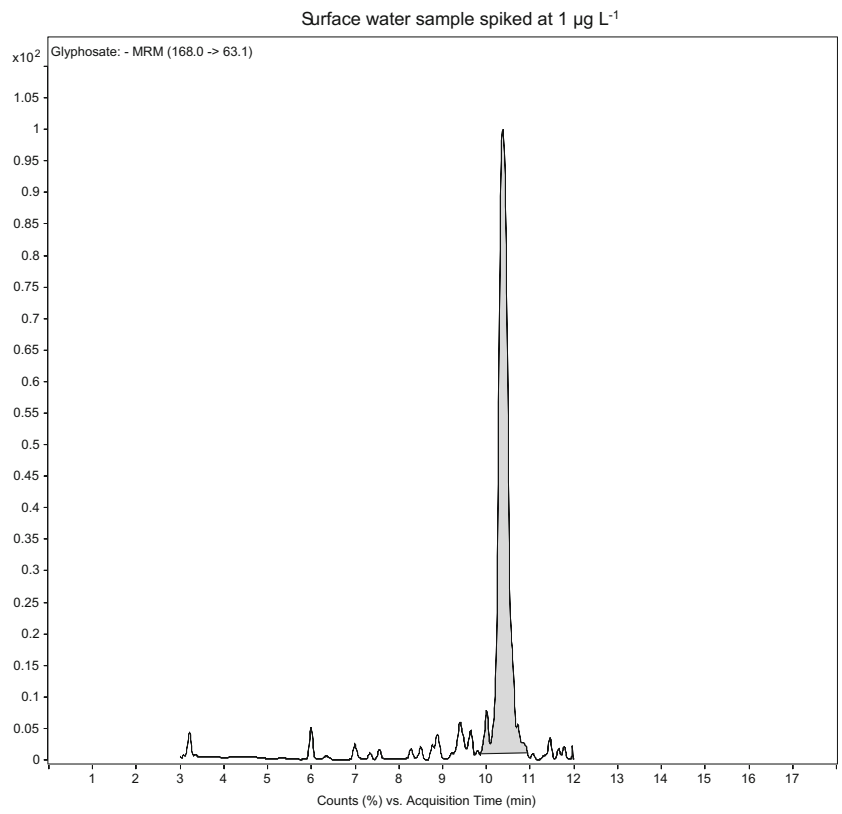**Fig. 3** (continued)

Surface water sample spiked at 1 μg L⁻¹

Surface water sample spiked at 1 μg L⁻¹

Table 2 Precursor ion and primary (q_1; quantifier ion) and secondary (q_2; qualifier ion) transitions of glyphosate, aminomethylphosphonic acid (AMPA) and [1,2-^{13}C,^{15}N]glyphosate and their respective optimized liquid chromatography–tandem mass spectrometry parameters obtained with an ion-exchange column

Compound	Retention time (min) ($n = 346$)[a]	Precursor ion (m/z)	q_1 (m/z)	Dwell time (ms)	Fragmentor voltage (V)	CE (V)	q_2 (m/z)	Dwell time (ms)	Fragmentor voltage (V)	CE (V)
Glyphosate	10.9 (3.10%)	168	63.1	100	380	22	149.9	100	10	380
AMPA	5.9 (3.16%)	110	63.1	100	380	26	78.9	100	30	380
[1,2-^{13}C,^{15}N]Glyphosate	10.9 (2.32%)	170	63.0	100	380	28	–	100	–	380

CE collision energy

[a] The relative standard deviation is given in parentheses

ultrapure water and in surface water spiked at 0.5, 1 and 10 µg L^{-1} ($n = 3$). Accuracy was calculated as the measured concentration divided by the theoretical concentration multiplied by 100, and it was considered satisfactory when the analyte percentage recovery was within the range from 70% to 120%. The precision acceptance criterion was set at an RSD of 15% or less for each spiking level. The method was also validated in a matrix (environmental surface water) determined to be free of glyphosate and AMPA (see "Analysis of environmental samples"). In addition, the method trueness was assessed

with glyphosate in drinking water certified reference material ($n = 4$) (QC1435, Sigma-Aldrich).

Quality control and quality assurance

Procedural blanks that consisted of ultrapure water spiked with internal standard were used to monitor any background concentration. In addition, to ensure the lack of carryover, blank injections of ultrapure water were run after the highest level of the calibration curve and every six samples. For quality assurance, spiked matrix samples were checked for recovery at the end of every run.

Analysis of environmental samples

Surface water samples were taken from creeks and rivers of the Yarra River catchment area ($n = 10$) and from stormwater wetlands ($n = 12$) located in suburban developments of Melbourne and Geelong, Victoria (southeast Australia) (Map from [19], Fig. 2). The Yarra River catchment area is characterized by horticultural and viticulture production and pastures used for cattle and sheep grazing. Two of the watercourse samples belong to the main branch of the Yarra River (S1 and S2), and the rest are from smaller tributary creeks. Sample S14 was taken in Donnelly's Creek (S14), which is located upstream of the agricultural area in the Maroondah Reservoir Park, a protected water supply catchment area; therefore, this sample was used in the matrix validation analysis after confirmation that it did not have any background concentration of glyphosate and AMPA. The sampled wetlands were in different urban areas of the city of Melbourne. These wetlands collect stormwater from urban settings and are used for urban stormwater flood mitigation and treatment, as a source of irrigation water and for amenity value.

Samples were collected between 2 and 4 October 2017 with use of 500-mL polypropylene bottles, rinsed three times with the sampled water. The water pH, electrical conductivity and dissolved oxygen content were measured in situ with a
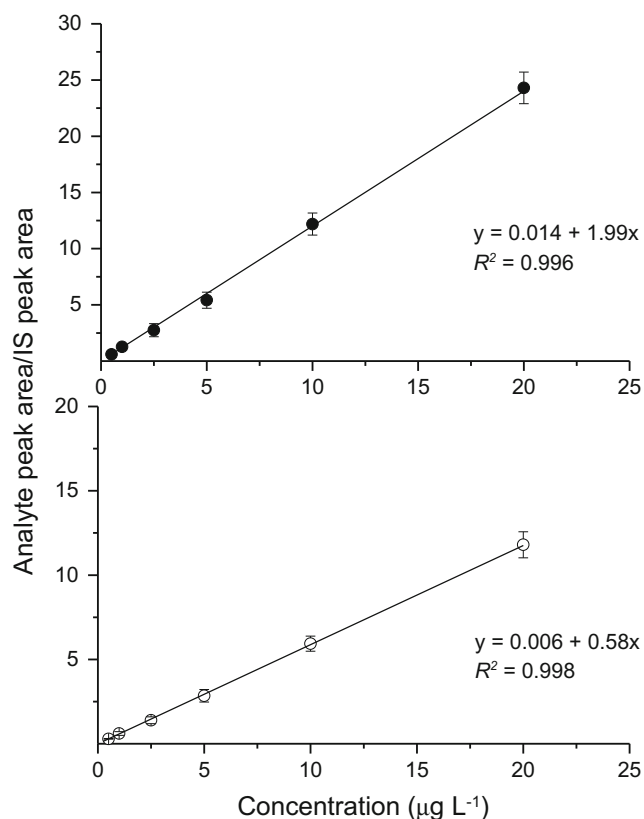
Fig. 4 Calibration curves ($n = 6$) for glyphosate (closed circles) and aminomethylphosphonic acid (open circles)

y = 0.014 + 1.99x
R^2 = 0.996

y = 0.006 + 0.58x
R^2 = 0.998

Table 3 Percentage recovery of the analytes and relative standard deviation (RSD) in different matrices

| | Glyphosate reference material[a] ($n = 4$) | Ultrapure water ($n = 3$) | | | | | | Surface water ($n = 3$) | | | | | |
		Glyphosate			AMPA			Glyphosate			AMPA		
Spiking level (µg L^{-1})	392	0.5	1	10	0.5	1	10	0.5	1	10	0.5	1	10
Recovery (%)	99.6	100.7	101.1	103.9	111.7	112.3	111.5	111.3	118.9	114.0	116.0	116.6	114.2
RSD (%)	2.8	0.9	6.5	7.3	14.6	11.5	7.8	11.5	11.7	11.9	14.7	13.1	11.9

AMPA aminomethylphosphonic acid

[a] Glyphosate in drinking water certified reference material (QC1435, Sigma-Aldrich)

field meter (556 MPS multiprobe system, YSI, Yellow Springs, OH, USA). On arrival at the laboratory, samples were stored at -18 °C until analysis.

Results and discussion

LC–MS/MS optimization

Full-scan MS and product-ion MS/MS for glyphosate and AMPA were performed under negative electrospray ionization. The optimized source parameters for MS/MS are shown in Table 1. The precursor ion for glyphosate had a mass-to-charge ratio (m/z) of 168, and that for AMPA had m/z 110. The most abundant peak of the isotopically labelled glyphosate had a m/z 170. On the basis of the MS/MS spectra, we selected the transition with the highest peak area as the primary transition (q_1) for the quantification of the analytes. The transition with the second highest peak area was selected as the secondary transition (q_2) and the corresponding ion was used as the qualifier ion. The selected primary transition was m/z 168→63.1 for glyphosate and m/z 110→63.1 for AMPA (Fig. 3).

The pH mobile phase gradient gave satisfactory chromatographic separations and peak resolution for glyphosate and AMPA. No peak deterioration or tailing was observed after each batch (80–100 samples), indicating good column stability and reproducibility. The optimized LC–MS/MS parameters for the precursor ions and the primary and secondary transitions of the analytes are shown in Table 2.

Method validation

Using dilute standard solutions, we determined that the LOD, defined as the lowest concentration that could be differentiated from the background solution with a signal-to-noise ratio of 3 or greater, was 0.25 µg L^{-1}. The LOQ, estimated as the lowest concentration that could be fully validated in matrix water and had peak areas with a signal-to-noise ratio of 10 or greater, was 0.5 µg L^{-1}. The calibration curves were linear over the entire calibration range ($R^2 > 0.997$) (Fig. 4).

The accuracy and precision of the method were evaluated by analysing ultrapure water and matrix water samples spiked with the analytes at a final concentration of 0.5, 1 and 10 µg L^{-1}. The accuracy and precision of the method were assessed as the percentage recovery of a known spiking level, and method tolerances were set at 70–120% for accuracy and less than 15% RSD for precision The recoveries of the reference material, ultrapure water and surface water were all within acceptable limits and were considered satisfactory (Table 3). The recovery of glyphosate displayed better accuracy and precision in ultrapure water, when compared with surface water, for all concentrations: 0.5 µg L^{-1}, $(100.7 \pm 0.9)\%$ vs $(111.3 \pm 11.5)\%$; 1 µg L^{-1}, $(101.1 \pm 6.5)\%$ vs $(118.9 \pm 11.7)\%$; 10 µg L^{-1}, $(103.9 \pm 7.3)\%$ vs $(114.0 \pm 11.9)\%$. This suggests slight matrix enhancement was occurring in surface water samples, but was consistent, indicating the method was still performing adequately at the lower limit of quantification (0.5 µg L^{-1}) in the sample matrix. Additionally, the method trueness was validated with a reference material of drinking water spiked with glyphosate. The measured concentration was within the acceptance interval of the manufacturer's specifications (216–586 µg L^{-1}), with an average recovery of 99.6% (Table 3).

When compared with other direct injection methods that do not involve a derivatization step, the main advantage of the present method is its simplicity and high sensitivity. From a process standpoint, a simple pH adjustment and filtration is much simpler than, for instance, the direct injection method of Nagatomi et al. [17] for beer samples, which also uses an anion-exchange column but involves several solid-phase extraction steps and the resuspension of the sample before analysis. There were also no obvious instrumental and/or detection problems with our method when large batches of samples were screened compared, for example, with the peak broadening and excessive tailing observed by Hao et al. [16] after running several batches of samples.

From a sensitivity standpoint, the LOQ in our study was 0.5 µg L^{-1}. This is more than adequate for screening of drinking water and environmental samples in Australia and New Zealand, where the drinking water standard is 1000 µg L^{-1} [20], with the strictest level of protection (for 99% of freshwater species) in pristine ecosystems of 370 µg L^{-1} [21]. Our method's LOQ is also lower than that of Hao et al. [16], where the LOQ for glyphosate in water samples was 10 µg L^{-1} and

Table 4 General characteristics of the surface water samples from streams and wetlands and glyphosate and aminomethylphosphonic acid (AMPA) detection levels

Type of sample sites	Site	Electrical conductivity (μS cm^{-1})	pH	Dissolved oxygen (%)	Glyphosate (μg L^{-1})	AMPA (μg L^{-1})
Rural streams and creeks	S1: Yarra River	124	7.3	105	ND	ND
	S2: Yarra River	105	7.2	109	ND	ND
	S3: Olinda Creek	571	8.8	101	ND	ND
	S4: Stringybark Creek	709	9.5	109	ND	ND
	S7: Woori Yallock Creek	185	7.8	107	ND	ND
	S8: Woori Yallock Creek	172	9.1	106	ND	ND
	S9: McCrae Creek	165	7.8	109	ND	ND
	S10: Shepherd Creek	132	7.7	109	ND	ND
	S14: Donnelly's Creek	81	7.9	118	ND	ND
	S19: Woori Yallock Creek	148	9.4	80	ND	ND
Average		239.2	8.2	105	0.0	0.0
Standard deviation		215.9	0.9	10	0.0	0.0
Minimum value		81	7.2	80	–	–
Maximum value		709	9.5	118	–	–
FOD (%)		–	–	–	0	0
Suburban wetland	W1	224	9.6	35	<LOQ[c]	<LOQ[c]
	W2	113	8.63	111	ND	ND
	W3	1026	9.36	106	ND	0.56
	W4	1647	9.5	96	2.52	1.21
	W5	344	9.07	55	ND	0.84
	W6	1677	9.39	43	1.95	1.66
	W7	1263	9.34	104	ND	0.55
	W8	2069	8.2	80	ND	ND
	W9	220	9.92	71	ND	<LOQ[c]
	W10	335	9.25	101	ND	1.0
	W11	362	10	117	2.96	1.16
	W12	653	8.79	57	ND	2.42
Average[a]		827.8	9.3	81	0.64	0.82
Standard deviation[a]		683.0	0.5	28	1.13	0.71
Minimum value[b]		113.0	8.2	35	1.95	0.55
Maximum value		2069.0	10.0	117	2.96	2.42
FOD (%)		–	–	–	33	83

FOD frequency of detection, *LOQ* limit of quantification, *ND* not detected

[a] Values below the LOQ were considered as 0.25 μg L^{-1}

[b] Only considering those values above the LOQ

[c] Above the limit of detection but below the LOQ

that for AMPA in water samples was 20 μg L^{-1}. However, our method does have lower sensitivity when compared with methods that involve a derivatization step, which is a trade-off for the elimination of preinjection work. Moreover, although the LOQ does not comply with the European Union threshold of 0.1 μg L^{-1} for any pesticide in drinking water [22], our method can be used easily in other types of monitoring programmes or screening studies in other jurisdictions. For example, the LOQ achieved is more than adequate for drinking water studies in North America, where the maximum allowed glyphosate concentration in drinking water is 700 μg L^{-1} in the USA [23] and 280 μg L^{-1} in Canada [24]. Also, the LOQ is suitable for environmental screening in Australia and other regions (e.g. in the USA, where the chronic aquatic life benchmarks for glyphosate are 25,700 and 49,900 μg L^{-1} for fish and for aquatic invertebrates, respectively [25], and in Canada, where the water quality guideline for glyphosate for the protection of freshwater life is 45 μg L^{-1} [26]). The method's sensitivity is adequate for most ecotoxicology studies given that the glyphosate no-observed-effect

concentrations for extremely sensitive organisms such as algae and diatoms are 200 and 300 μg L^{-1}, respectively [27]. Overall, for the purposes of this study, which were to evaluate glyphosate and AMPA levels in slightly to severely disturbed aquatic ecosystems, the LOD and LOQ achieved are satisfactory, particularly if one takes into account the advantages of this safe and cost-effective technique, which has minimal sample processing steps, does not use toxic reagents and chemicals, does not require time-consuming extractions (e.g. solid-phase extraction) or derivatization and allows the running of a large number of samples without reduction of column stability or reproducibility.

Analysis of surface water environmental samples

The method was used to assess the levels of glyphosate and AMPA in surface water samples from streams of the Yarra River catchment area (Upper Yarra Valley) and urban wetlands located within Melbourne and Geelong (Victoria, Australia). This allowed us to validate the method using samples from diverse settings. The samples from the Yarra River catchment area were taken from permanent watercourses that are mainly influenced by agriculture and cattle, with minimum urban inputs. On the other hand, the sampled wetlands were mainly quiescent water bodies, which have a major water input only during storm events and therefore are a sink for any compounds that may be washed away from houses or industrial developments. In general, wetlands had higher electrical conductivity, slightly higher pH and lower dissolved oxygen content than stream samples (Table 4).

Glyphosate and AMPA can be found in streams and rivers that are influenced by agricultural land use usually at concentrations below 10 μg L^{-1} [5, 7, 15], but levels as high as 73 μg L^{-1} have been reported [4]. In this study, no glyphosate or AMPA was detected in any of the stream samples from the Upper Yarra Valley, which may be a function of land use and associated herbicide use timing and/or may be because glyphosate is strongly retained in the soil matrix, which limits its off-site transport [28]. However, we did observe detectable levels of glyphosate in 33% of the wetland samples (Table 4). Three of those samples had concentrations above the LOQ, ranging from 1.95 to 2.96 μg L^{-1}. Glyphosate's metabolite, AMPA, was detected in 83% of the wetland samples. Eight of the samples had quantifiable levels of AMPA, with concentrations ranging from 0.55 to 2.42 μg L^{-1}. The observed concentrations are consistent with previous reports of glyphosate and AMPA concentrations in surface water from urban areas [29]. Urban settings are usually more vulnerable to glyphosate contamination since glyphosate is one of the main herbicides used for weed control on impervious surfaces, business and residential properties, and golf courses. Also, because glyphosate is less absorbed by hard surfaces (e.g. asphalt, concrete) than by soil, it can be easily transported by stormwater into urban watersheds. In that context, glyphosate and AMPA have been detected in urban stormwater wetland inlets at concentrations between 0.2 and 15.0 μg L^{-1} and between 0.2 and 21.0 μg L^{-1}, respectively [30], and in storm sewer samples at maximum concentrations of 6.1 μg L^{-1} and 5.8 μg L^{-1}, respectively [31].

Conclusion

We have presented a simple, fast and cost-effective method for the detection and quantification of glyphosate and AMPA. The method was used to quantify the levels of glyphosate and AMPA in environmental samples from diverse surface water sources. We found that no glyphosate or AMPA was present in surface water samples taken from rural streams. However, glyphosate and AMPA were detected in 33% and 83% of the urban wetland samples, respectively, indicating that household use might be an important source of glyphosate contamination in urban stormwater wetlands.

Overall, the present method allows the routine analysis of water samples and can be easily applied since (1) it involves few sample preparation steps (reducing handling errors), (2) it requires low-cost laboratory material (no use of organic solvents, no derivatization agent, no preconcentration steps), (3) results are obtained on the same day of analysis and (4) it is highly sensitive and allows the analysis at ultratrace levels of both glyphosate and AMPA.

Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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