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Mixed-mode solid-phase extraction coupled with liquid chromatography tandem mass spectrometry to determine phenoxy acid, sulfonylurea, triazine and other selected herbicides at nanogram per litre levels in environmental waters

Pei Zhang[a,c,*], Anhduyen Bui[a,c], Gavin Rose[a,c], Graeme Allinson[b,c]

[a] *Department of Environment and Primary Industries, Farming Systems Research Division, TER 4 Ernest Jones Drive, Macleod 3085, Victoria, Australia*
[b] *Department of Environment and Primary Industries, Farming Systems Research Division, Queenscliff Centre, Queenscliff 3225, Victoria, Australia*
[c] *Centre for Aquatic Pollution Identification and Management (CAPIM), c/o School of Chemistry, The University of Melbourne, Parkville 3010, Victoria, Australia*

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ABSTRACT

The method presented uses a mixed-mode anion exchange SPE and liquid chromatography tandem mass spectrometry to analyze 5 sulfonylurea, 8 phenoxy acid, 12 triazine and 6 other herbicides in environmental waters. The mixed-mode SPE cartridge is able to retain a wide range of herbicides with acidic–neutral–basic characteristics, particularly the highly polar and acidic compounds clopyralid, dicamba and picloram. The neutral and basic herbicides can be effectively eluted with methanol, after which the acidic herbicides can be eluted using acidified methanol. The method has achieved an LOD of 0.7–3 ng/L for the sulfonylureas, 4–12 ng/L for the phenoxy acids and 0.4–30 ng/L for the triazine and additional herbicides, with recoveries in the range 76–107%, 73–126%, and 65–104%, respectively. The precision of the method, calculated as relative standard deviation (RSD), was below 10% for both sulfonylurea and phenoxy acid herbicides, and less than 20% for the remaining herbicides. The developed method was used to determine the concentration of target herbicides in a range of environmental waters, and many of the target herbicides were detected at ng/L level.

1. Introduction

Nationally, there are over 7280 agrochemical and veterinary medicine products registered for use in Australia [1]. The category of agrochemicals (pesticides) with the highest volume of sales, are the herbicides, principally because they are used extensively in agricultural production and in urban utilities management, such as renovation of sporting grounds, bowling greens and golf courses, railway easements and roadway nature strips. Based on 2011–2012 data, there are 2420 herbicide products with a combined sales value of A$1302 million, which is more than three times the sales value of insecticides (A$413 million; 1166 products), and nearly six times that of fungicides (A$218 million; 703 products) [1]. The most widely used herbicides after glyphosate in Australia are the triazines (e.g. simazine and atrazine), and phenoxy acids (e.g. 2,4-D, MCPA) [2]. In the last ten years, new classes of herbicides have been increasingly deployed, including the sulfonylureas, which are used for the control of weeds in broadleaf crops and tolerant cereal crops where weeds have become resistant to triazines and phenoxy acid herbicides. The 'National Strategy for Agricultural and Veterinary Chemicals' [3] and more recently the 'National Framework for Chemicals Management in Australia' [4] have identified the need to better understand the potential impacts of agricultural chemical use on the environment, an issue supported internationally such as through the OECD's pesticides programme [5]. To fulfil those needs ultimately requires robust analytical methodologies to monitor broad range of chemicals at relevant low levels [6].

The wide structural differences and physicochemical properties of herbicide groups have usually meant individual analytical methods are required to determine members of each group. Triazine herbicides are neutral or weakly basic compounds with medium polarity. Historically, liquid–liquid extraction (LLE) was used to concentrate triazine herbicides from water samples, followed by determination on gas chromatography (GC) with either a nitrogen–phosphorous detector (NPD) or MS detector [7–12]. Phenoxy acid herbicides, such as 2,4-D and MCPA, are non-volatile and highly water soluble acidic compounds that are not directly amenable to separate and determine on GC. The US

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* Corresponding author at: Department of Environment and Primary Industries, Farming Systems Research Division, TER 4 Ernest Jones Drive, Macleod 3085, Victoria, Australia. Tel.: +61 3 84582612; fax: +61 3 84582301.
E-mail address: pei.zhang@depi.vic.gov.au (P. Zhang).

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Environmental Protection Agency (EPA) method 515.3 involves derivatizing the acids to their methyl esters using diazomethane, subsequently determined on GC–ECD. While the sensitivity of GC techniques is adequate, the derivatization procedure is not only time consuming, but also presents serious occupational health and safety concerns due to the carcinogenic materials used and their labile properties [13]. Sulfonylurea herbicides are highly water soluble compounds, which results in high mobility and risk of transfer to surface water bodies. Compared to the early generation herbicides, sulfonylurea herbicides are used with much lower application rates, typically 2–10 g/ha compared with triazines at 20–100 times higher. Although very low ng/L concentrations of residues are expected in environmental waters, such concentrations are toxicologically important given the toxicity of the sulfonylureas to plants and algae.

In the past two decades, solid phase extraction (SPE) has become the method of choice instead of LLE for environmental water sample extraction, enrichment and simultaneous elimination of interferences. There are wide ranges of sorbents available; the selection of an appropriate SPE sorbent depends on understanding the mechanisms of interaction between the sorbent and the analyte of interest. The first sorbents available were silica coated reverse phase and modified with C_{18}, C_8, phenyl or CN. The major drawbacks of these sorbents are instability at extended pH and lack of retention for polar compounds [14,15]. Recently, graphitized carbon black (GCB) was developed to simultaneously extract neutral, basic and acidic compounds with no need to adjust pH for acidic compounds. The versatility of this sorbent is likely due to its behaviour as both a non-specific (i.e. van der Waals interactions) and an anion-exchange (electrostatic) sorbent. However, the disadvantage of GCB is its high retention of chemicals, which makes it difficult or even impossible to elute some compounds [16,17]. To overcome the problem of extraction of polar analytes from environmental water, highly cross-linked styrene–divinylbenzene (PS–DVB) co-polymers with high surface areas (in the range 500–1200 m_2/g) were introduced to allow more interactions between the analytes and sorbents [16,17]. One limitation of the traditional polymeric sorbents is that they must be conditioned with a wetting solvent and not allowed to dry before loading of an aqueous solvent. The new generation of polymers is typified by hydrophilic–lipophilic balanced sorbent (Oasis® HLB), a copolymer of divinylbenzene (lipophilic) and *N*-vinylpyrrolidone (hydrophilic), which is designed to extract lipophilic, hydrophobic, acidic, basic and neutral compounds with a single cartridge. Since its introduction, a large number of applications using Oasis® HLB have been reported in which this sorbent has been used to pre-concentrate organic pollutants from environment water [15,18–22]. However, Peruzzi et al. [15] reported poor recovery for dicamba (17%) without pH adjustment. Rodil et al. [18] described using pH 7.0 buffer solution in conjunction with ion-pairing agent in order to improve the retention of the most polar and acidic analytes. Biesaga et al. [21] and Tran et al. [22] reduced sample pH to 2.5 and 3, respectively, to ensure efficient extraction of the acidic compounds. To overcome the limitation of Oasis® HLB in retaining acid compounds, mixed-mode Oasis® MAX sorbent was introduced; this sorbent has the Oasis® HLB skeleton (*N*-vinylpyrrolidone–divinylbenzene) but has been chemically modified with quaternary amines. The mixed-mode sorbent is designed to interact with ionic species and also effectively retain non-charged species through hydrophobic and hydrophilic interactions.

As instrumental technology have advanced in the recent decades, liquid chromatography–tandem mass spectrometry has gained widespread interest, and become the technique of choice in multi-residue determination of medium to high polarity compounds. A number of analytical methodologies are already available in the literature for determination of the three specific groups of herbicides individually, namely for the triazine herbicides [23–26], phenoxy acid herbicides [18,27–29] and sulfonylurea herbicides [30–34], using solid phase extraction (SPE) followed by LC–MS/MS detection. However, the cost of using multiple tests can be prohibitive both for the end-users of the data (paying clients) and also for the laboratory. In order to encourage screening for a wider range of trace organic chemicals, several multi-residue methods have been recently published for determination of a large number of contaminants in environment water, including pharmaceuticals, personal care products, some herbicides and flame retardants [18,19,35,36].

A multi-residue method covering the three important herbicide classes (the phenoxy acids, sulfonyl ureas and triazine herbicides) has not been reported. Particularly, it is rare to encounter a multi-residue method including all of the problematic acidic herbicides, such as clopyralid, picloram and dicamba, as they are highly polar compounds and difficult to extract with standard extraction procedures. The aim of this study was to develop such a highly sensitive and selective analytical method to extract herbicides with neutral, basic and acidic characteristic using a signal mixed-mode SPE to achieve sample enhancement and purification at the same time, followed by determination on liquid chromatography tandem mass spectrometry. The methodology includes all the important triazine, phenoxy acid and sulfonylurea herbicides registered and used in Australia, most of which are also registered for use in America and Asia. The method was tested using stormwater samples collected in 2011–2012 by the Victorian Centre for Aquatic Pollution Identification and Management (CAPIM) and Department of Environment and Primary Industries Victoria.

2. Experimental

2.1. Reagents and materials

2.1.1. Chemicals

Methanol Lichrosolv® gradient grade for liquid chromatography were obtained from Merck (Darmstadt, Germany). Type 1 water, 18 MΩ cm^{-1} resistivity was prepared by passing reverse osmosis water through Milli-Q system (Millipore, USA). Trifluoroacetic acid Reagentplus® (99%) was purchased from Sigma–Aldrich (St. Louis, USA). Formic acid (98–100%), hydrochloric acid (32%, GR for analysis), acetic acid (Glacial, 100%) and sodium hydroxide (AnalaR® 99%) were obtained from Merck (Darmstadt, Germany). pH indicator strips (pH 1–14) were purchased from Merck (Darmstadt, Germany). Sodium acetate (≥99%) was obtained from Sigma–Aldrich (St. Louis, USA).

2.1.2. Standards

All herbicide standards were of analytical purity and supplied by Dr Ehrenstorfer GmbH (Augsburg, Germany). Triazine herbicides (Table 1) stock standards were individually prepared by accurately weighing 20 ± 1 mg of reference material and dissolving it in 100 mL of acetone/toluene (1:1). Phenoxy acid herbicides (Table 1) and sulfonylurea (Table 1) stock standards were individually prepared by accurately weighing 20 ± 1 mg of reference material and dissolving in 100 mL of acetonitrile. Three intermediate concentration mixture standards of each herbicide group were prepared at 5–10 μg/mL by dilution of the stock standards with acetonitrile.

2.1.3. SPE cartridges

Solid phase extraction was carried out with Oasis® MAX 6 cm^3 (500 mg) LP extraction cartridges (Waters, Milford, MA, USA). A similar phase SPE, Bond Elut® Plexa Pax 500 mg, 6 mL (Agilent Technologies, Santa Clara, CA, USA), was compared with the Oasis® MAX.