

A METHOD DEVELOPED FOR THE EXTRACTION, DETECTION AND QUANTIFICATION OF ORGANOPHOSPHORUS PESTICIDE IN AQUEOUS MEDIA

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ABSTRACT

Extraction of filtered river and canal water, fortified with five organophosphorus pesticides (OPs), was conducted using solid-phase extraction and eluted with a variety of solvent combinations. The best recoveries (70-110%) were obtained using 1:1 acetonitrile/dichloromethane. Liquid chromatography-mass spectrometric conditions were chosen that provided the optimum analyte resolution on a C₁₈ reverse-phase LC column, along with optimum selectivity and sensitivity for an ion-trap MS/MS detector. A mobile phase gradient consisting of water and methanol with the addition of 0.1% formic acid (to aid protonation) provided the optimum resolution and ionization of the OPs using electrospray ionization in the positive mode, respectively. The use of acetic acid, however, resulted in an interfering contaminant ion in all samples. The major OP ions and subsequent daughter ions used for both analyte confirmation and quantitative analysis were presented. Reproducibility of spiked water samples was <15% RSD for all compounds, with instrumental detections limits ranging over 0.20~10 µg/L, allowing this method to be applied for OP analysis in water samples collected in the vicinity of agricultural areas.

Keywords: SPE, Daughter Ions, Mobile Phase, Water Samples

INTRODUCTION

Many organophosphorus pesticides (OPs) are currently replacing their organochlorine counterparts because of their lower persistence and tendency not to bioaccumulate. Although increased pesticide use has resulted in many benefits including increased crop production, concerns about potential adverse effects of pesticides and pesticide transformation products on the environment, human health and non-target organisms have grown steadily with ongoing concerns about the widespread use of OP insecticides (Majewski *et al.*, 1998).

Organophosphorus insecticides are widely used in agriculture with approximately 37 compounds divided between phosphorothioates and phosphorodithioates with varying vapour pressures (1.3E-5 - 0.04 Pa, 298 K) and aqueous solubilities (0.0042 - 790 g/L; 293 - 298 K) (Mackay *et al.*, 1996; Barcelo and Hennion, 1997). Many of these compounds (e.g. chlorpyrifos, chlorfenvinphos, diazinon, dimethoate, malathion, fenitrothion, parathion ethyl, azinphos methyl, azinphos ethyl, fenthion) are now included in the Priority Pollutant Lists for legislation like the EU's Water Framework Directive which require environmental quality standards for water (EC,

2000; EC, 2001). Common methods developed for the determination of organophosphorus pesticides in environmental samples include GC - NPD (Karamfilov *et al.*, 1996; Szymczyk and Malczewska, 1998) and GC-EI-MS (Cairns *et al.*, 1993; Lacorte *et al.*, 2000; Stan, 2000; Peck and Hornbuckle, 2005). However, some of the more ubiquitous OPs are relatively water soluble (e.g. malathion, dimethoate) and/or are subject to transformation in aqueous systems through a number of abiotic and biotic processes (McConnell *et al.*, 1998; Castillo *et al.*, 2000; Weber *et al.*, 2009b) that give rise to polar by-products that are suitable for liquid chromatography.

There are now a number of studies that have utilised LC-MS methods for analysing OPs and their degradates (Bossi *et al.*, 2002; Liu *et al.*, 2006; Kuster *et al.*, 2007) and it is likely that the use of LC-MS methods will increase as concern over pesticide degradates continues to grow (Boxall *et al.*, 2004).

This study was designed to develop effective extraction and recovery experiments for the quantitative analysis of water samples using solid-phase extraction (SPE) cartridges. The matrix effects on chromatography and chemical

ionization were also investigated. The organophosphorus pesticides used for this study were chosen because of their widespread occurrence and potential impact on the environment, specifically in the aquatic environment. Many of these compounds while present in agricultural regions have now been detected in more remote environments such as the Arctic snowpack (Hermanson *et al.*, 2005) and, in some cases, are susceptible to (photo) degradation in aquatic systems resulting in water soluble transformation products which require LC-MS for analysis (Weber *et al.*, 2009b; Weber *et al.*, 2009a).

The motivation for this study was that in using acetonitrile as the mobile phase, and with similar instrumental conditions, parent ions for some of the OP analytes (fenitrothion, methyl parathion, chlorpyrifos) could not be obtained according to several previous studies (Sancho *et al.*, 2000; Hernandez *et al.*, 2001; Williamson *et al.*, 2006). Furthermore, some of the OPs, such as methyl parathion are thermolabile and chemically reactive, and can decompose during sample preparation/analysis using GC-MS (Betowski *et al.*, 1988), therefore an LC-MS method is required.

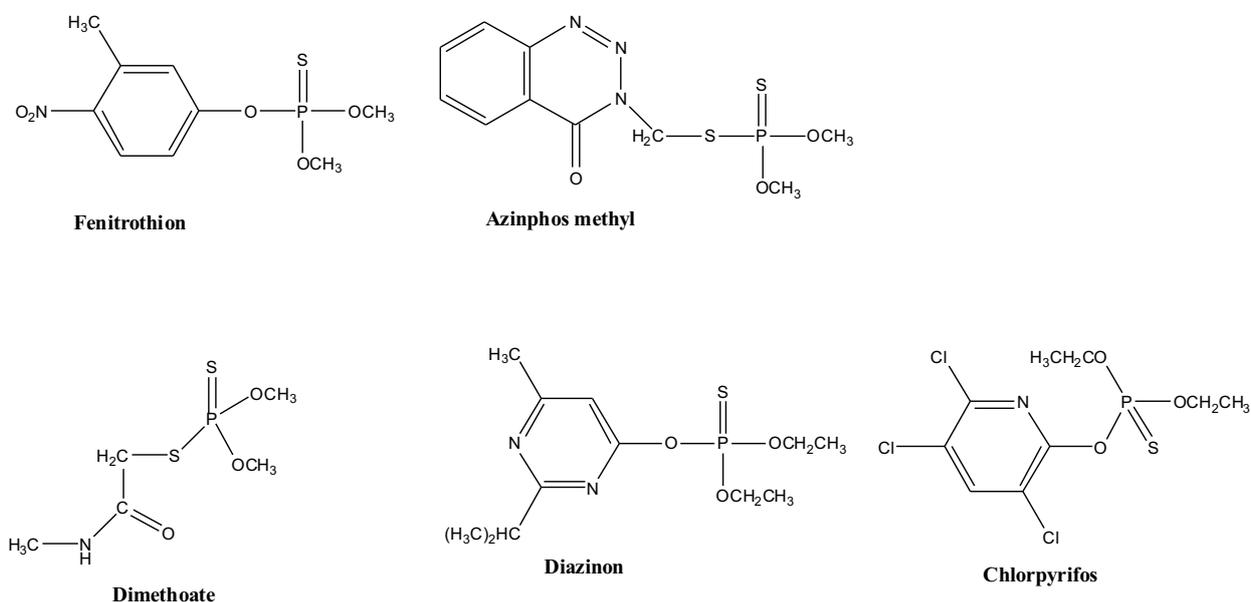


Figure 1: Chemical Structure of the Organophosphorus Pesticides Studied.

Table 1: Chemical Names and Selected Physical-Chemical Properties of The Five OP Insecticides Used in this Study

Name	Chemical name	CAS number	Molecular weight (g/mol)	log K_{ow}	Solubility in water (mg/L) ¹	Vapour pressure - ² 293 – 298K
Dimethoate	O,O - dimethyl - S - methylcarbamoyl methyl phosphorodithioate	60-51-5	229	0.70	23	1.1E-03
Fenitrothion	O,O-dimethyl-O-4-nitro-m-tolyl phosphorodithioate	122-14-5	277	3.43	14	1.8E-02
Diazinon	O,O-diethyl-O-2-isopropyl -6- methyl (pyrimidine - 4-yl) phosphorothioate	333-41-5	304	3.30	40	1.2E-02
Azinphos methyl	S-(3,4- dihydro -4-oxobenzo[d]-[1,2,3]- triazin-3-yl methyl O, O - dimethyl phosphorodithioate	86-50-0	317	2.96	29	1.84E-04
Chlorpyrifos	O,O-diethyl -O- 3,5,6- trichloro-2- pyridyl phosphorothioate	2921-88-2	349	4.70	1.4	2.7E-03

1, 2(Extoxnet, 1996; Mackay *et al.*, 1996; Barcelo and Hennion, 1997), 3(USEPA)

MATERIALS AND METHODS

Analytical grade pesticides including azinphos methyl, dimethoate, chlorpyrifos, diazinon, fenitrothion, (>97% purity) were purchased from Sigma Aldrich (UK). Analytical grade methanol, ethyl acetate, dichloromethane (DCM), acetone, hexane and acetonitrile (ACN) were purchased from Fisher Scientific (UK). Envi-chrom P, C₁₈ and C₁₈ EC were purchased from Supelco (UK). All experiments (unless otherwise stated) were carried out with water from a MilliQ water purification system (resistivity = 18 MΩcm) (Millipore, USA). Stock solutions of the pesticide (10 mg mL⁻¹) were prepared in acetonitrile and stored at < 4 °C. Working solutions were then prepared by diluting aliquots of stock solution to obtain a concentration range of 1 – 20 µg mL⁻¹. Fresh solutions were prepared as needed.

Instrumental Conditions

A liquid chromatograph (Model 55278) interfaced to a mass spectrometer (Model LDP00360) was used for this work. The mass spectrometer was utilised with an orthogonal electrospray interface (ThermoFinnigan, UK) where sheath and aux gas (nitrogen) obtained from a nitrogen generator (Peak Scientific, UK), while helium gas was used as the damping gas. Xcalibur software (Version 1.3, ThermoFinnigan, UK) allowed instrument control and chromatographic processing. Ionization was done in positive mode with a capillary voltage of 4.5 kV, cone temperature of 320 °C, sheath and aux gas of 35 and 5 respectively. Selection and tuning of target pesticides were done by direct infusion of a solution of each pesticide standard in methanol (5 mg/L) using a Hamilton 500 µL syringe. A dwell time of 200 ms per transition was used to maximise sensitivity for ion confirmation. The flow rate of the ESI source (300 µL/min) was kept identical to the LC.

The mass spectrometer was interfaced to a Thermo Scientific Surveyor™ LC System consisting of a ThermoFinnigan Surveyor autosampler equipped with a binary ThermoFinnigan Surveyor MS pump (ThermoFinnigan, UK), fitted with a 20 µL sample loop. In addition to an MS detector a photodiode array detector was utilized, which allowed for a rapid check on chromatographic performance. Organophosphorus pesticides were resolved on a

Synergi Fusion RP HPLC Column; 150 x 2.0 mm, 4 µm particle size (Phenomenex Cheshire, UK) preceded by a guard column (4 mm x 2 mm, 4µm) with a mobile phase consisting of 0.1% HCOOH in water (mobile phase A) and 0.01% HCOOH in methanol (mobile phase B). Formic acid was added as an organic modifier to decrease the pH of the solvent and aid protonation of the pesticides. The analytes were eluted with MeOH/H₂O as the mobile phase, maintained at a flow rate of 300 µL/min. The mobile phase gradient was set initially at 100% mobile phase A, then to 65% A in 5 mins and then to 45% A in 11 mins and held for 9 mins then to 20% A in 13 mins and finally to 0% A in two minutes. The mobile phase was then conditioned and reset back to the initial combination ready for the next injection.

Sample Preparation and Extraction

Recovery studies were carried out on spiked water samples extracted using reverse phase C₁₈ SPE cartridges (3 mL Envi Chrom-P C₁₈ cartridges, (Supelco UK)). A pesticide solution containing all the five OP chemicals (each 0.1 mg/L) was prepared in ACN and evaporated to dryness under a gentle stream of nitrogen and then reconstituted with 100 mL MilliQ water. Environmental samples comprising river and canal water were first filtered using a 0.4 µm filter (Sigma Aldrich, UK), and the filtered water used to reconstitute the reduced ACN solution (containing the five OP analytes) to examine the effects of dissolved constituents on the chromatography, chemical ionization and recoveries of the OP analytes.

The SPE cartridges were mounted on a Supelco vacuum manifold (Visiprep Supelco™) and sequentially conditioned with 10 mL methanol and 10 mL MilliQ water, before the sample was then loaded on the cartridge followed by 1 mL of MilliQ water. Each cartridge was then dried through a partial vacuum for about 20 minutes to remove residual water. The sample extracts were then eluted using a variety of solvent combinations to assess the best recoveries for the range of OPs selected in this study, with solvents varying from ACN, methanol, DCM, acetone and then binary combinations of ACN:methanol, and DCM:methanol etc. Elution volume for each solvent type was kept to 20 mL at a flow rate of ~1

mL/min. For each solvent the eluate was evaporated to dryness under a gentle stream of nitrogen on a heating block maintained at 30°C and reconstituted to 1 mL with methanol. The concentration of recovered analyte was determined by internal calibration method using seven concentrations (1-20 mg/L)

Limit of Detection (LOD)

The limit of detection is taken as the lowest concentration of an analyte in a sample that can be detected, but not necessarily quantified, under the stated conditions of the test. This was done by preparing a series of results on blank samples and a series of results on very low – level samples. The results for the blank samples are used to provide a threshold where higher values can be interpreted to indicate a positive sample. The detection limit for each pesticide is then determined using the equation below:

$$DL = \frac{3.3 \times SD}{b}$$

where

DL = detection limit

SD = standard deviation from replicate injections; and

b = slope of the regression line

RESULTS AND DISCUSSION

Instrumental Conditions and Performance

For the LC method, the C₁₈ column with the aforementioned solvent gradient provided baseline separation with good peak shapes, with most of the pesticides eluting before the mobile phase gradient had reached 100% methanol. Organophosphorus pesticide retention times and major ions are presented in Table 2. The observed advantage of methanol over acetonitrile was the complete resolution of all the target OP analytes including diazinon; which co-eluted with acetonitrile. Similar results obtained by Lacorte and Barceló (1996). However, the disadvantage of substituting acetonitrile with methanol was a longer run time and slightly broader peak shape. All the compounds gave good chromatographic peaks.

Table 2: Retention Time and Masses of the Major OP Ions for the LCMS

Pesticide	Retention time (min)	Quantification ion (m/z)	Instrumental limit of detection (µg/L)	RSD (%)
Dimethoate	11.49	230 , 199, 125	0.21	3.06
Azinphos methyl	24.20	318 , 160, 132	2.97	4.79
Fenitrothion	30.51	278 , 246, 152	9.99	12.35
Diazinon	37.51	305 , 169, 153	0.56	8.77
Chlorpyrifos	45.21	351 , 323, 296, 198	0.39	13.87

Numbers in bold are the parent ions

Mass spectral data were obtained in the positive ionization mode because of the higher sensitivity exhibited by organophosphorus pesticides in this mode (;). However, as electrospray ionization is a 'soft' ionization technique, then several compounds (e.g. chlorpyrifos and fenitrothion) did not readily ionize with use of a pure solvent phase (i.e. methanol, acetonitrile and MilliQ water). Instead, ionization was aided with the addition of an organic acid modifier capable of liberating hydrogen ions to aid protonation of the

analyte molecules. An initial trial with acetic acid resulted in a highly suppressive contaminant peak (m/z 294) which interfered with the qualifying ions of chlorpyrifos. The source of this ion was unclear, although another prominent interfering ion (m/z 391) was due to a plasticizer (diisooctyl phthalate - [M+H]⁺) possibly leaching from the solvent delivery tubes. Formic acid provided the highest sensitivity and did not yield the contaminant ion (m/z 294) observed with acetic

acid. For most of the analytes, the protonated ion, $[M+H]^+$, was found to be the most abundant. The sodium ion adduct of methanol was however not evident. MS/MS mode was used for qualitative and quantitative identifications and gave rise to daughter ions from the collision-induced spectra obtained by full scan of the parent ion for each OP analyte (see table 2).

MS/MS analysis using the ion trap provided good selectivity and improved the signal to noise ratio (S/N) of the target analytes (Fig. 1). This was done by isolating the parent ion and subsequently applying a voltage to induce fragmentation into daughter ions peculiar to each of the OP analytes. The fragmentation ions for the OPs obtained matched those of Banerjee *et al.* (2007) and Hernandez *et al.* (2001) who also used electrospray ionization (ESI). The fragment ions (m/z 169) obtained for some of the compounds, for example diazinon and fenitrothion (Table 2), were consistent with $[(C_2H_5O)_2POS]^+$, which has also been reported by Banoub *et al.* (1995) and Molina *et al.* (1996). The daughter peak (m/z 125) obtained

for dimethoate was from the fragment ion, $[(CH_3O)_2PS]^+$.

SPE Performance and Method Validation

Various solvents were used to obtain the most appropriate solvent for effective recovery of the OPs from the SPE cartridge. Solvents were chosen that ranged in polarity from methanol to the low polarity solvents like *n*-hexane and results are presented in Figure 2. Ethyl acetate gave the lowest recoveries for most of the OPs, especially chlorpyrifos. Acetonitrile generally gave good recoveries, but gave a lower recovery ~33.10 – 56.30% for the low polarity compounds (e.g. chlorpyrifos). A binary solvent system comprising 1:1 solution of dichloromethane and acetonitrile gave the best recoveries for both the polar and non-polar OPs (Table 3). Chlorpyrifos gave the highest recovery (103.40%) while fenitrothion the lowest (79.02%), although values obtained were within the 70 – 110% range for recovery as stipulated by the EU guidelines for evaluating the accuracy and precision of a method (EU, 1999).

Table 3: % Recoveries of Selected OPs from MilliQ Water and Environmental Samples (River and Canal Water)

Pesticide	MilliQ water	River water sample	Canal water sample
Dimethoate	91.66 ± 2.14	77.54 ± 1.44
Azinphos methyl	85.41 ± 0.90	92.54 ± 5.06	109.39 ± 7.27
Fenitrothion	79.02 ± 2.30	92.01 ± 3.35	73.90 ± 4.85
Diazinon	92.28 ± 3.11	72.30 ± 4.62	100.12 ± 1.41
Chlorpyrifos	103.4 ± 3.28	80.96 ± 2.26	95.36 ± 1.81

Spiked SPE cartridges were eluted with 20 mL of 1:1 DCM/ACN and the eluate divided into three

aliquots at a volume ratio of 2:1:1, with each aliquot analyzed separately using LC-MS.

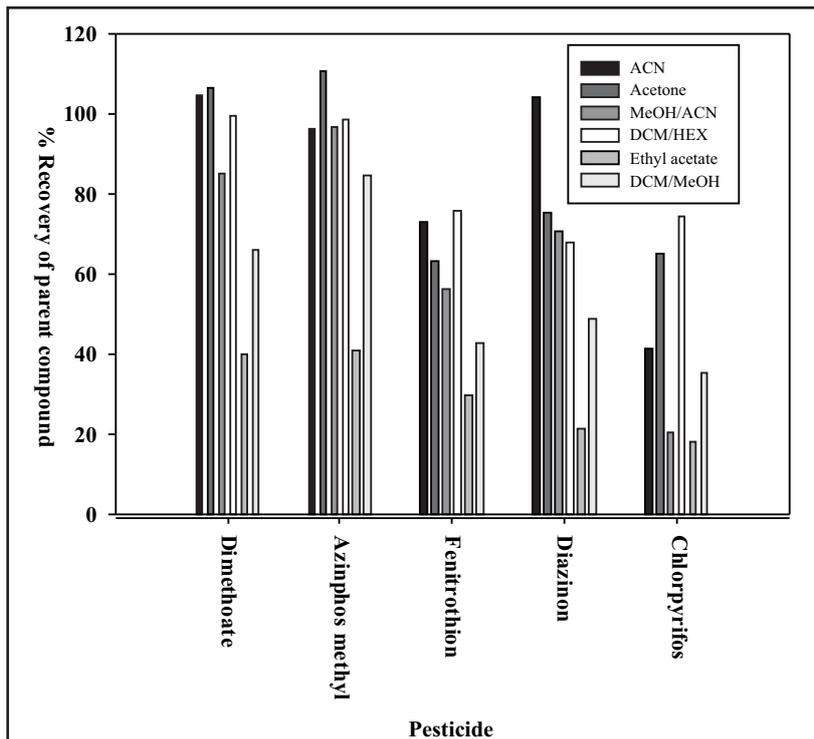
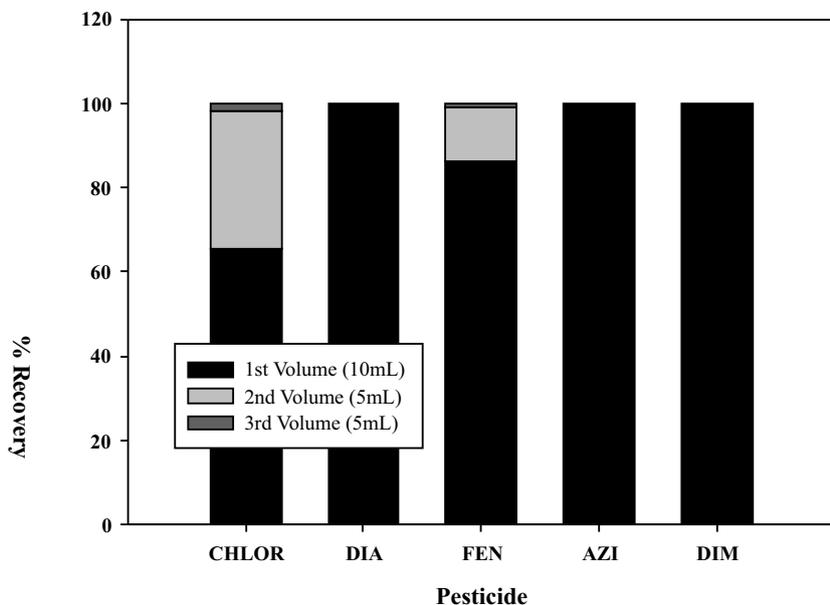


Figure 2: Recoveries Obtained for Different Solvents for a Selection of OP Pesticides, of Varying Polarity and Aqueous Solubility.

Results obtained are shown in Figure 3. The pesticides diazinon, azinphos methyl, dimethoate eluted in the first aliquot (i.e. 10 mL) while chlorpyrifos was present in the second aliquot (5

mL) and fenitrothion was present in the final 5 mL. Increasing the total volume of solvent (>20 mL) however did not yield a significant increase in analyte recovery.



NB: % recovery values were normalized to 100%.

Figure 3: Percentage of OPs Recovered from Envi – Chrom P SPE Cartridges for Different Elution Volumes of ACN/DCM.

To examine the effect of an environmental matrix on LC-MS performance, the collected river and canal water sample, previously fortified with the five OPs were analysed using LC-MS, following water filtration and SPE extraction as earlier itemized. The pH of the two water types was similar with values of 7.13 (river) and 7.77 (canal), but with marked differences in the concentrations

of total dissolved solids (TDS) and conductivity (e.g. TDS of 162 and 234 mg/L; conductivity of 331 and 478 μ S/cm, for river and canal respectively (Table 4). 'Native' OPs were not detected in these samples. For both water types, most of the pesticides exhibited good recoveries (75–109%).

Table 4: Physical Chemical Properties of Environmental Water Samples Spiked.

Sample	NO ₃ ⁻ (mg/L)	pH	Conductivity (μ S/cm)	TDS (mg/L)	Dissolved oxygen (mg/L)	Resistivity (M Ω .cm)
River	193.51	7.13	331	162	3.73	0.0300
Canal	1820	7.77	478	234	5.35	0.0021

Limits of Detection

The instrumental limits of detection (LOD) were determined for all compounds with values given in Table 3. For the LC-MS, LODs ranged from 0.20–9.99 μ g/L (20 μ L loop injection) with the highest sensitivity observed for dimethoate (0.21 μ g/L) and the lowest for fenitrothion (9.99 μ g/L). The relative standard deviation as a measure of the precision of the LC-MS method was obtained by repeat extraction and analysis of OP 'spiked' water samples at three different concentrations (n = 8), with values of RSD ranging from 3.06 to 13.87% and generally <10% for the majority of the compounds. For the ion-trap LC-MS method, the limits of detection were found to be relevant for monitoring environmental concentrations of OP contaminants in water samples. For example, Kuster *et al.* (2007) detected concentrations of diazinon and fenitrothion at 0.044 μ g/L and 0.681 μ g/L respectively in river water samples collected from the Ebro river delta in the agricultural area of Spain using LC-ESI-MS.

CONCLUSION

A sensitive and effective method for the separation and analysis of organophosphorus insecticides in aqueous solutions has been developed using SPE and LC-MS as the main analytical tool. The extraction method gave good recoveries of the OP analytes from aqueous solutions and should also be applicable for a wider range of OP insecticides. ESI in positive mode followed by the creation of daughter ions in

MS/MS was highly selective and provided ions suitable for both compound confirmation and quantification. River and canal water samples high in dissolved solids and presumably dissolved organic carbon did not provide interfering artefacts to analyte ionization using this method. The instrumental detection limits on the LC-MS were found to be suitable for detecting and quantifying OPs in environmental samples close to areas of pesticide use. Importantly, the use of LC-MS will allow the detection of water soluble, polar degradates of the pesticides considered.

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