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Sensitive determination of pendimethalin and dinoseb in environmental water by ultra performance liquid chromatography–tandem mass spectrometry

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Abstract Direct injection (DI) and solid phase extraction (SPE) methods for the simultaneous determination of pendimethalin (PDM) and dinoseb (DNS) in environmental water have been optimized using the ultra performance liquid chromatography–tandem mass spectrometry (UPLC–MS/MS) method. The limits of quantification (LOQs) of PDM and DNS were 0.01 µg/L using the DI method and 0.0001-0.0002 µg/L using the SPE method. The precision by SPE UPLC-MS/MS was less than 11 % for intra-day and inter–day analyses. When the proposed SPE method was used to analyze two analytes in environmental water, PDM was detected in a concentration range of 0.0002-0.011 µg/L in 31 samples of the 114 surface water samples, and DNS was detected in a concentration range of 0.0005-0.045 µg/L in 17 samples of the 114 surface water samples analyzed. When the DI method was used to analyze target compounds in the same samples, the detected concentrations of the two analytes were within 21% in samples with concentrations above 0.01 µg/L. The DI UPLC–MS/MS method can thus be used for the routine monitoring of PDM and DNS in environmental water, and the SPE LC–MS/MS method can be used for the determination of the ultra-trace PDM and DNS residues in environmental water.

Key words: pendimethalin, dinoseb, ultra performance liquid chromatography–tandem mass spectrometry, direct injection, environmental water

1. Introduction

Pendimethalin (PDM, N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidene) and dinoseb (DNS, 2-*sec*-butyl-4,6-dinitrophenol) (*Table* 1) are used as selective herbicides both before the sprouting of weed seeds and early postemergence to control most annual grasses and certain broadleaf weeds. Pendimethalin is slightly toxic if ingested, inhaled, or absorbed through the skin and is a mild skin irritant. DNS is a highly to extremely toxic compound, and is classified as a possible human carcinogen.[1]

PDM and DNS are expected to biodegrade slowly, adsorb into soil and have low volatility, low mobility,

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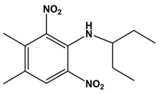
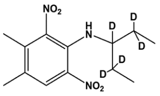
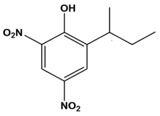
Table 1. Structure, molecular weight, precursor ion, product ions, fragment voltage, and collision energies of PDM, PDM-d5 and DNS

Full name	Structure	CAS No	Molecular formula	Molecular weight	Ion mode	Precursor ion (m/*z*)	Product ions (m/*z*)	Fragment voltage (V)	Collision energy (eV)
PDM		40487-42-1	$C_{13}H_{19}N_3O_4$	281.31	Positive	282 $[M+H]^+$	*212 $[M+H-C(C_2H_5)_2]^+$ 194 $[M+H- OHCH(C_2H_5)_2]^+$ 91$[C_6H_3\ NH_2]^+$	50	1 15 25
PDM-d5		1219803-39-0	$C_{13}H_{14}D_5N_3O_4$	286.34	Positive	287 $[M+H]^+$	*213$[M+H--CD(C_2D_2H_3)_2]^+$ 194$[M+H- OHCD(C_2D_2H_3)_2]^+$ 91$[C_6H_3\ NH_2]^+$	50	3 13 19
DNS		88-85-7	$C_{10}H_{12}N_2O_5$	240.21	Negative	239 $[M-H]^-$	* 193 $[M-H-C_3H_{10}]^-$ 163 $[M-H- C_4H_{12}O]^-$ 134 $[M-H - C_4H_9O_3]^-$	80	23 33 33

*Quantification ion

Table 2. Comparison of analytical methods for determining of PDM and DNS in environmental water

Ref	Analyte	Matrix	Sample preparation	Measurement	Detection limit (μg/L)	
					LOD	LOQ
8	PDM	Water	SPE (C 18)	GC-ECD	0.08	-
10	PDM	SW	SPE	GC-ECD	0.008	-
11	PDM	SW	SPE	GC-ECD	0.02	0.06
13	PDM	Environmental water samples	LLE	GC-NPD	20	-
18	PDM	Water	SPE	GC-MS/MS	-	0.013-0.022
19	PDM	DW	SPE(C18)	GC-MS	-	0.01
20	PDM	SW	SPE	GC-MS	0.02	-
21	PDM	Water	SPE	GC-MS	-	-
23	DNS	DW	Derivatization	GC-MS	0.005	-
26	PDM	SW	SPE (C18)	HPLC	0.5	-
29	DNS	DW	SPE	HPLC	-	-
31	DNS	WW	SPE	LC-MS/MS	5.0	-
This Study	PDM	SW and DW	Direct	LC-MS/MS	0.003	0.01
	DNS				0.003	0.01
	PDM	SW and DW	SPE (MCX)	LC-MS/MS	0.00003	0.0001
	DNS				0.00007	0.0002

SW=Surface water; DW=Drinking water; WW= Wastewater; SPE=solid-phase extraction; LLE=liquid-liquid extraction

and low water solubility, and thereby present a high persistence in soil and sediments.[1-3] Therefore, it is thought that these pesticides may exist in very trace amounts in surface water and drinking water.

PDM and DNS are considered potential surface and drinking water pollutants. The US EPA set a maximum drinking water contaminant level of 7.0 μg/L for DNS,[4] while the WHO proposed a guideline value of 20 μg/L for PDM in drinking water.[5] A European Union directive (98/83/EC) set a maximum admissible concentration at 0.1 μg/L for each individual pesticide and 0.5 μg/L for total pesticides in drinking water.[6] Germany set a quality target concentration of 0.27 μg/L for PDM in surface water for aquatic life,[7] and Canada and Netherlands, respectively, set quality target concentrations of 0.05 μg/L and 0.03 μg/L for DNS in surface water for aquatic life.[7] Monitoring, in this context, therefore requires sensitive analytical methods with substantially lower detection limits than required by the guideline values or target concentrations established by various nations.

A wide range of analytical methodologies has been developed to monitor for PDM or DNS in foods and environmental samples. Most of these procedures are based on determining PDM and DNS by gas chromatography techniques coupled to either an electron–capture detector,[8-11] a nitrogen phosphorous detector,[12,13] a flame ionization detector,[14] or a mass spectrometry detector (GC–MS),[15-23] or high performance liquid chromatography (HPLC).[24-30] Some of these methods were applied in environmental water,[8,10,11,13,18-21,23,26,29,31] as described in *Table* 2. The detection limits of these analytical methods [8,18-20] are 0.01–0.08 µg/L, which has been found to be sufficiently sensitive to measure the water quality target concentration (0.1 µg/L) for PDM in drinking water as established by the EU. Otherwise, these analytical methods have been limited for determining PDM in water and no method has met the detection limit for the water quality target concentration (0.03 µg/L) for DNS in surface water as established by the Netherlands. GC–MS has been widely used in various matrices due to its high sensitivity and selectivity, but requires more purification and concentration, and especially derivatization for DNS

Tandem mass spectrometry (MS/MS) has been developed to monitor DNS in foods and environmental samples.[30-32] The methodology[31] was to measure DNS concentrations in waste water in view of a photocatalytic degradation assay, and this method did not meet the quality target concentration for DNS in surface water as established by the Netherlands. In addition, no LC–MS/MS method has been published to quantify PDM until now.

The simultaneous monitoring of PDM and DNS in surface water may require a different analytical method than the methods published until now because of such different physical and chemical characteristics such as the former being basic and the latter acidic.

The objective of this study was to develop a rapid and simple direct injection (DI) UPLC–MS/MS method, and an ultra-sensitive UPLC–MS/MS method after SPE extraction of PDM and DNS from surface. This study focused on optimizing the parameters of UPLC–MS/MS, and the simultaneous extraction of PDM and DNS in water. Three types of SPE cartridges were tested and compared in terms of their extraction efficiencies and matrix effects. The developed methods were applied in the analysis of 114 surface water samples.

2. Experimental

2.1. Materials

PDM (99 %) and DNS (99 %) were purchased from Sigma-Aldrich (St. Louis, MO, USA). PDM–d5 (99 %) (internal standard) was purchased from Toronto Research Chemicals Inc. (North York, ON, Canada). Analytical grade KOH and HCl (Sigma and Aldrich, St. Louis, MO, USA) were used as reagents and methanol and acetone (E. Merck, Darmstadt, Germany) were used as solvents. The pure water used in this study was purified by a Milli–Q–Reagent–Grade water system (ZD 20) and had a resistivity of over 17 MW.

Several cartridges were purchased from Waters (Milford, MA, USA). A hydrophilic–lipophilic balance (HLB) cartridge (200 mg, 6.0 mL), mixed-mode cation exchange (MCX) cartridge (150 mg, 6.0 mL), and Sep–Pak C18 (360 mg, 6.0 mL) were evaluated to determine PDM and DNS. The cartridges were initially conditioned according to manufacturer instructions, in order to remove contaminants and to stabilize the solid phase. Conditioning was carried out with methanol and pure water.

2.2. Water sampling

Surface water samples were collected without headspace in 1.0 L dark glass bottles containing 100 µL of 6.0 M HCl from 114 basins in the Han, Nakdong, Gum, and Youngsan rivers. The sampling sites were selected to uniformly represent all streams of the rivers.

2.3. Extraction procedure

2.3.1. DI Procedure

A pH modifier with a volume of 10.0 µL (10 mM

HCl) and 25.0 μL of the internal standard (0.1 mg/L) were added to 1.0 mL of a sample. The solutions were passed through 0.20 μm PTFE syringe filters from Advantec (Tokyo, Japan). A 20.0 μL aliquot of the solution was injected into the UPLC–MS/MS system.

2.3.2. SPE procedure

The method was developed and optimized using ultra-pure water spiked with working standard solution to produce concentrations of 50.0 ng/L for two analytes in the spiked sample. The efficiency of the SPE cartridges to extract the compounds from water was tested. For the optimum pH–value of the water sample, cartridges were preconditioned with 5.0 mL of methanol, and then with ultra-pure water (3 × 5 mL) with a pH–value of 1, 2, 3, 4, 5, 6, 7, 8, or 9 depending on the pH–value of the water sample that is subsequently applied to the column. The water samples were then drained into the cartridges for 50 min after the pH was adjusted with 1.0 M HCl or 1.0 M KOH. After being loaded, the cartridges were cleaned with 1.0 mL ultra-pure water and dried under vacuum for 5 min, and were then eluted to 20 mL test tubes from the sorbents with 6.0 mL of methanol at a flow rate of 1.0 mL/min. The eluants were dried under a nitrogen stream at room temperature. The solution was dissolved with 100 μL of water and 50.0 μL methanol and a 10.0 μL aliquot of the solution was injected into the UPLC–MS/MS system.

For the real sample analysis, a MCX cartridge was preconditioned with 5.0 mL of methanol, and then with ultra-pure water (3 × 5 mL). The water samples were then drained into the cartridges for 50 min after the pH was adjusted to 3.0, after which 1.0 M HCl and 25.0 ng of PDM–d5 were added. After being loaded, the cartridges were cleaned with 1.0 mL ultra–pure water and dried under vacuum for 5 min, and were then eluted to 20 mL test tubes from the sorbents with 6.0 mL of methanol at a flow rate of 1.0 mL/min. The eluants were dried under a nitrogen stream at room temperature. The solution was dissolved with 100 μL of water and 50.0 μL methanol, and a 10.0 μL aliquot of the solution was then injected into the LC–MS/MS system.

The developed method was verified by checking detection limits, recoveries, precision, and accuracy directly or in 0.5 L surface water and drinking water filtered through pre–combusted Whatman glass microfiber GF/F filters (0.7 μm) followed by Advantec membrane filters (0.45 μm) and spiked with various concentrations of the target compounds.

2.4. UPLC-MS/MS

The ultra–performance liquid chromatography was an Agilent 1200 series (Agilent, Santa Clara, CA, USA) equipped with a binary pump, on–line vacuum degassing system, and autosampler. Analytes were separated using a 50 × 2.1 mm Eclipse Plus–C_{18} column with a 1.8 μm pore size (Agilent, Santa Clara, CA, USA). A binary gradient with a flow rate of 0.2 mL/min was used. Mobile phase A contained 0.05 % formic acid in water, while mobile phase B was acetonitrile. The gradient was as follows: B = 20 % at first, increased to 50 % by 3.0 min, increased to 90 % by 4.5 min, increased to 100 % by 6.0 min, and held for 0.5 min. All of the compounds eluted within 10 min.

MS/MS detection was performed on an Agilent 6460 series Triple Quadruple instrument (Agilent, Santa Clara, CA, USA). The mass spectrometer was operated with electrospray ionization in the positive ion mode (ESI +) and negative ion mode (ESI −) alternating between the modes. Capillary voltage was set to 4.0 kV. The source temperature was 120 °C and the desolvation temperature was 350 °C. Nitrogen was used as a desolvation gas (flow 600 L/h). Detection was performed in a multiple reaction monitoring (MRM) mode. Fragment voltage and collision energy were optimized for PDM and DNS, respectively (*Table* 1).

2.5. Calibration and quantification

The calibration curves of PDM and DNS for direct injection were established by adding 10.0 pg – 1.0 ng of PDM and DNS in standard solution (0.001 or 0.01 mg/L in methanol) and 0.25 ng of PDM–d5 internal standard solution (0.01 mg/L in methanol) to

1.0 mL pure water. The solution was directly injected in the UPLC–MS/MS system.

The calibration curves of PDM and DNS for the SPE were established by adding 50.0 pg – 50 ng of PDM and DNS in standard solution (0.001 – 1.0 mg/L in methanol) and 2.5 ng of PDM–d5 internal standard solution (0.1 mg/L in methanol) to 0.5 L pure water. The solutions were extracted with the established SPE method and the extract was injected in the UPLC–MS/MS system.

Ions selected for quantification and confirmation are presented in *Table* 1. The ratio of the peak area of the standard to that of the internal standard was used in the quantification of the compound.

3. Results and Discussion

3.1. UPLC-MS/MS optimization

The positive electrospray ionization MRM mode alternating between the modes was applied to test mass spectrometric performance for PDM and the negative electrospray ionization MRM mode was applied to test mass spectrometric performance for DNS. Acquisition parameters were optimized for each compound (0.1 mg/L with 10.0 μL injection volume), with the best response observed simultaneously in the positive and negative electrospray ionization MRM modes by monitoring the reaction m/z 282 > 212 for PDM, 287 > 213 for PDM-d5 (IS), and 239 > 193 for DNS. *Table* 1 shows MRM transition and individual cone voltage, as well as collision energy voltages applied for the analytes. Precursor ions of $[M+H]^+$ and fragment ions, formed by the loss of $[C_5H_{10}]$ from the PDM $[M+H]^+$ ion, and precursor ions of $[M-H]^-$ and fragment ions, formed by the loss of $[C_3H_{10}]$ from the DNS $[M-H]^-$, were characteristic.

3.2. Optimization of the mobile phase

In this study, a series of preliminary experiments were performed testing different mobile phases in order to achieve good peak shape and high sensitivity. To achieve the optimum resolution with the interference peaks and maximum sensitivity, four different types of mobile phases were evaluated: formic acid, acetic acid, ammonium formate, and ammonium acetate.

The sensitivity of the peaks was improved after the addition of formic acid to water as the aqueous phase. In particular, it was observed that the sensitivity was doubled when the concentration of formic acid was decreased from 0.5 to 0.05 % for PDM detected in the ESI + mode. On the contrary, DNS sensitivity was quadrupled when the concentration of formic acid was increased from 0.005 to 0.05 % for DNS detected in the ESI – mode. Therefore, 0.05 % formic acid was finally chosen as the binary component for the mobile phase in this study. For the LC separation of the analytes, the use of the non-polar stationary phase was found to be efficient.

The retention times of DNS, PDM, and PDM-d5 were 5.441, 5.994, and 5.998 min, respectively, and all of the compounds were analyzed within 7 min.

3.3. Optimization of SPE method

Since PDM and DNS may be present in surface and drinking water at trace levels, preconcentration using an appropriate sorbent can be a necessary step in sample preparation. In this study, three types of cartridges were selected for evaluating the extraction efficiency of the analytes. Methanol was chosen as a common eluting solvent for evaluating the SPE performance. Acceptable reproducibility on Sep–Pak C18 (117 ± 26.5 % for PDM and 94.6 ± 22.7 % for DNS) were observed for PDM and DNS and improved reproducibility and recoveries (109 ± 15.8 % for PDM and 92.2 ± 11.3 % for DNS) were observed on HLB. Waters Oasis MCX copolymer cartridges, which have the property of retaining acidic and basic compounds, generated the best recovery and reproducibility (100 ± 2.94 % for PDM and 105 ± 3.76 % for DNS). Considering recoveries and reproducibilities, MCX was selected for further SPE method development.

The pH–value of the water sample that will result in the highest recovery for the tested analyte was optimized. The selected pH–values were: 1, 2, 3, 4, 5, 6, 7, 8, and 9. The results showed that extraction recovery was optimized at a pH of 2–3 for PDM and at a pH of 3–4 for DNS. Accordingly, pH 3 was chosen as the best pH value for simultaneously determining PDM and DNS.

3.4. Method validation

3.4.1. DI method

In the DI method, the sample preparation was limited to a filtration step to eliminate the particulate matter present in the samples and the internal standard at 2.5 μg/L. Regarding the filtration step, water samples were passed through 0.45 μm membrane filters.

Due to the very low levels of PDM and DNS that may be present in natural water, a pre-concentration procedure as solid phase extraction[10,11,18–21,26,29,31] is necessary in order to obtain the desired levels of analytical sensitivity. As awareness of the development of more sensitive analytical instrument continues to grow, the direct injection of samples has begun to be looked at as a way to improve inefficient laboratory

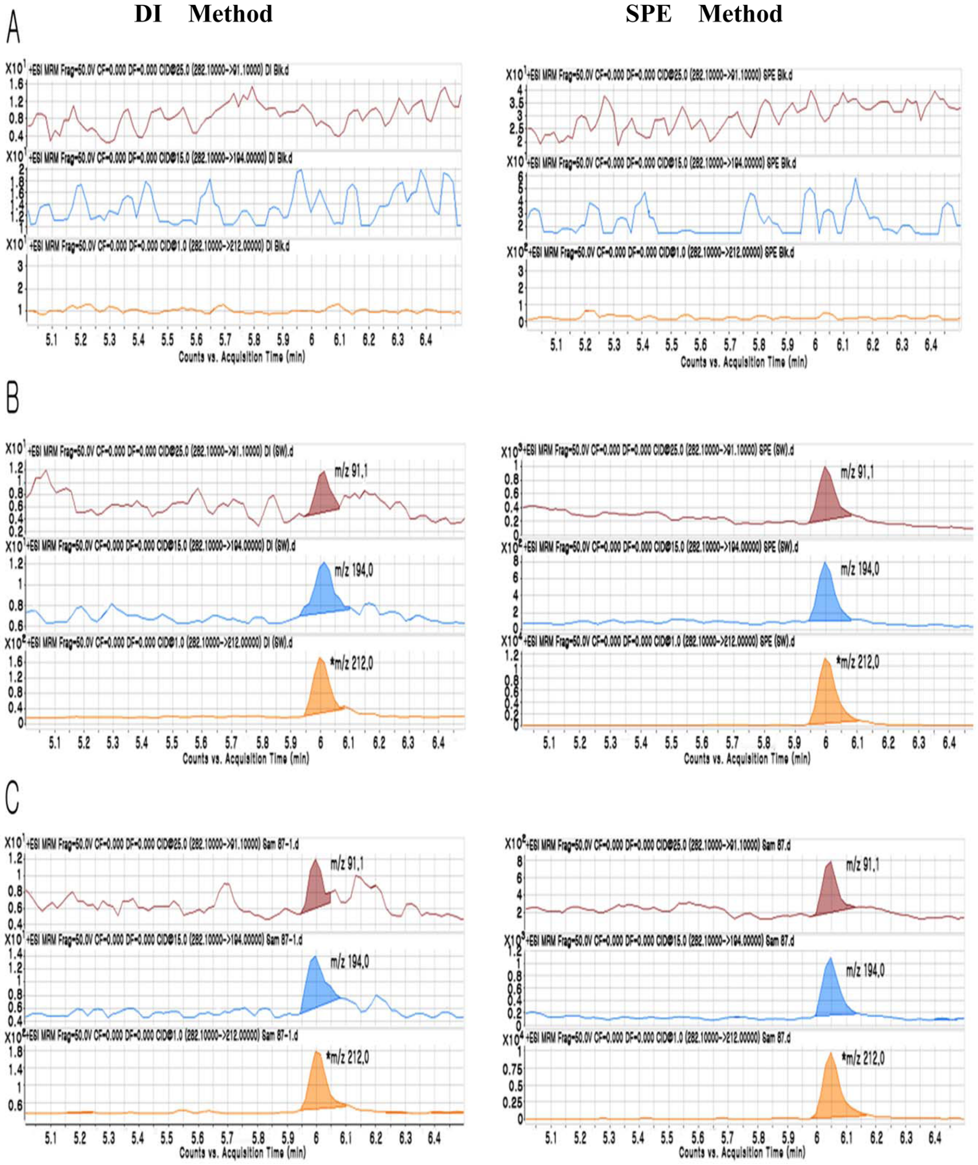


Fig. 1. Comparison of LC-MS/MS chromatograms of PDM by DI and SPE.

procedures for environmental analysis. This method has clear advantages compared to procedures combining concentration and extraction, such as no sample manipulation, smaller sample volume requirements, and an increase in the number of samples that can be processed per unit of time. In addition, this method can be done under severe problems of high interference, short column life time, and ion suppression. All of which further should be improved in order to acquire good quality analytical data.

These developed UPLC–MS/MS conditions were applied to the DI method to detect PDM and DNS in water. *Fig.* 1 and *Fig.* 2 show the UPLC–MS/MS chromatograms of the spiked sample and real sample having the concentration of LOQ. No interfering peak was present close to the retention time of PDM in the chromatograms of *Fig.* 1 when the selected ions were used. Peaks in the chromatogram of the

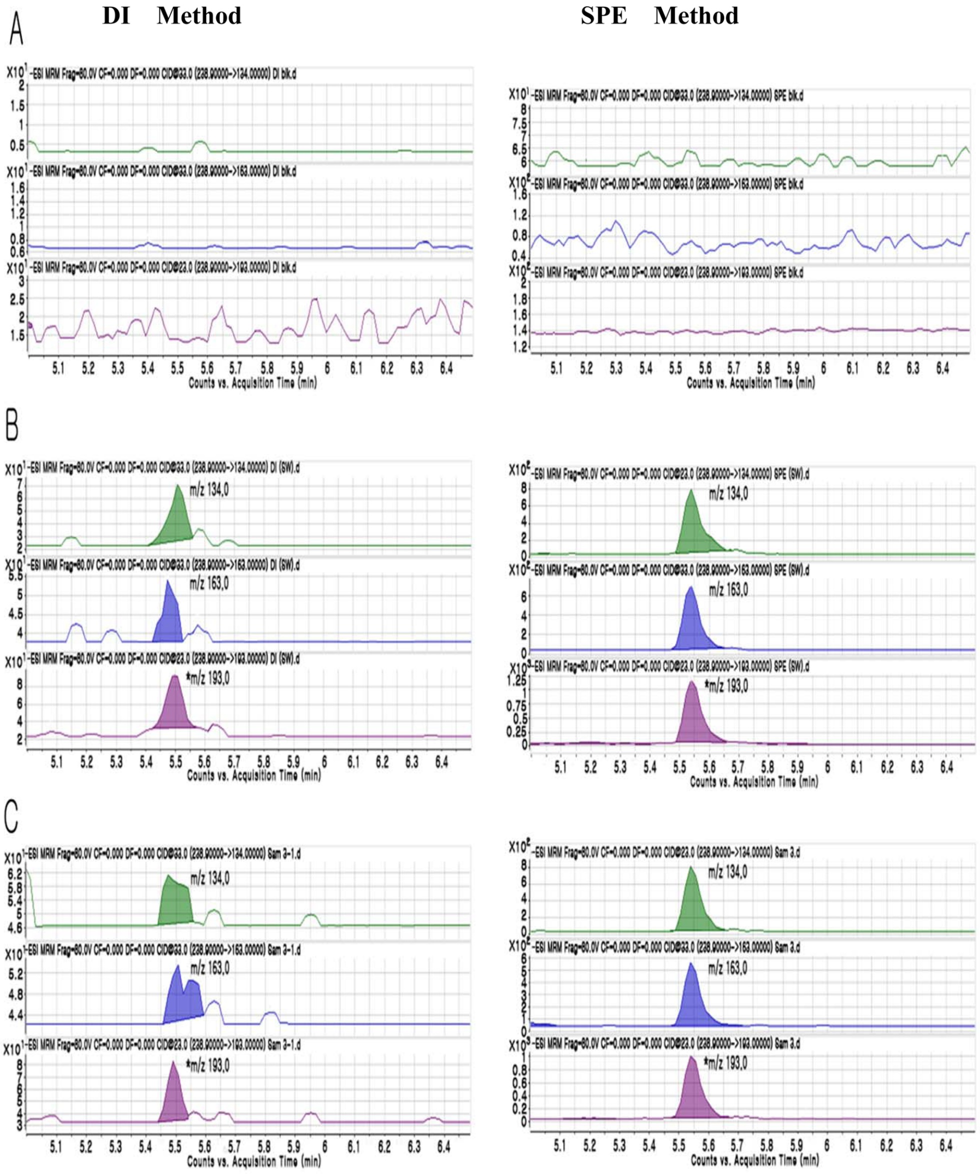


Fig. 2. Comparison of LC-MS/MS chromatograms of DNS by DI and SPE.

selected confirmation ions obtained by DI at levels under 0.03 μg/L of DNS (*Fig.* 2) were not symmetrical, possibly due to overlap with impurity peaks. Otherwise, no interfering peak was present close to the retention time of DNS in the chromatogram of the quantification ion (*Fig.* 2). For exact quantification, the DI–UPLC–MS/MS method is recommended to detect DNS above 0.03 μg/L in surface water.

The LODs and LOQs were determined as the sample concentration producing a peak height 3 and 10 times that of the baseline noise, respectively. The LOQs were subsequently verified using surface water matrix spiked at 0.01 μg/L for PDM and DNS. The LOD and LOQ of PDM and DNS were calculated as 0.003 and 0.01 μg/L by the above defined method. In comparison with other methods, the LOQ was far lower than that with GC–ECD,[8,11] GC–NPD,[13] HPLC,[26] and LC-MS/MS,[31] and was similar to that with GC–ECD,[10] GC-MS,[18–20] or GC-MS following derivatization[23] after extraction and concentration as described in *Table* 2. The results showed that PDM and DNS could be quantified at those concentrations with acceptable precision and accuracy. As observed, the LOQ of the proposed method was about 10 times lower than the maximum level in drinking water established by European legislation[6] and about 3 times lower than the maximum level of DNS in surface water established by the Netherlands.[7]

Using the least-squares fit technique, an examination of the typical standard curve was performed by computing a regression line of peak area ratios for analytes to the internal standard (PDM–d5) on the concentration. This analysis demonstrated a linear relationship with correlation coefficients of above 0.9996. Linear equations were $y = 0.0089x + 0.0110$ in the PDM concentration range of 0.01–1.0 μg/L and $y = 0.0043x - 0.0015$ in the DNS concentration range of 0.03–1.0 μg/L. The standard curve was constructed by computing a regression line of peak area ratios for analytes to the internal standard (PDM–d5) on the concentration. Although PDM–d5 has different chemical properties from DNS, this did not cause any problems with regard to the internal standard.

Accuracy can be assessed by the relative % of the concentration in real samples calculated from a calibration curve constructed with the samples spiked with standard solutions. Intra-day accuracy was evaluated by five spiked samples at concentrations of 0.05 and 0.25 μg/L for PDM and DNS, and inter-day accuracy was determined by their recovery on three different days. The accuracy was in the range of 98.1–102 % and the precision of the assay was less than 5 %.

3.4.2. SPE method

The sensitive determination of PDM and DNS was obtained by high recoveries with MCX and high ion formation by ESI–MS/MS. The LOD and LOQ were defined as in the DI method. The LODs were calculated as 0.00003 μg/L and 0.00007 μg/L for PDM and DNS, and the LOQs were calculated as 0.0001 μg/L and 0.0002 μg/L for PDM and DNS, respectively.

Using the least–squares fit technique, an examination of the typical standard curve was performed by computing a regression line of peak area ratios for PDM and DNS to the internal standard (PDM–d5) on the concentration. The linear equation was $y = 24.53x – 0.0473$ for PDM and there was a linear relationship with a correlation coefficient of 0.9994. For DNS, the linear equation was $y = 14.79x + 0.0845$ and a linear relationship with a correlation coefficient of 0.9979 in the concentration range of LOQ–0.1 μg/L.

Accuracy can be assessed by the relative % of the concentration in real samples calculated from a calibration curve constructed after the extraction of the samples spiked with standard solutions to the spiked concentration. Intra-day accuracy was evaluated by five spiked samples at concentrations of 0.0005 and 0.0025 μg/L for PDM and DNS, and inter–day accuracy was determined by their recovery on five different days. The accuracy was in the range of 96.4–105 % and the precision of the assay was less than 11 % (*Table* 3).

3.5. Real sample analysis

The present developed methods were applied to

Table 3. Intra and inter-day laboratory precision and accuracy results for the direct injection and SPE concentration methods of pendimethalin in water (*n*=5)

Extraction method	Compound	Spiked Conc. (ng/L)	Intra-day measured value			Inter-day measured value		
			Mean ± SD (ng/L)	Accuracy (%)	Precision (%)	Mean ± SD (ng/L)	Accuracy (%)	Precision (%)
Direct Injection	Pendimethalin	50.0	49.6 ± 2.41	99.2	4.86	51.1 ± 2.30	102	4.50
		250	250 ± 10.0	100	4.00	249 ± 9.92	99.7	3.98
	Dinoseb	50.0	50.6 ± 2.30	101	4.55	49.7 ± 2.37	99.5	4.76
		250	254 ± 5.48	102	2.16	245 ± 8.81	98.1	3.59
SPE method	Pendimethalin	0.50	0.49 ± 0.04	98.0	8.54	0.50 ± 0.04	100	7.91
		2.50	2.54 ± 0.17	102	6.68	2.47 ± 0.19	98.9	7.66
	Dinoseb	0.50	0.50 ± 0.05	99.2	10.7	0.50 ± 0.05	101	10.8
		2.50	2.42 ± 0.20	96.9	8.13	2.45 ± 0.23	98.1	9.28

analyze the target compounds in 114 surface water samples. When the SPE extraction method was used, PDM was detected in a concentration range of 0.0002–0.011 μg/L in 31 of the 114 surface water samples. DNS was detected in a concentration range of 0.0005–0.045 μg/L in 17 of the 114 surface water samples.

When the same samples were analyzed by DI and UPLC–MS/MS, PDM was detected in only one of the 114 surface water samples and DNS was detected in a concentration range of 0.012–0.045 μg/L in 9 of the 114 samples. The detected samples were in higher concentrations than the LOQ (0.01 μg/L) of PDM and DNS. The results of the DI and SPE methods were compared as shown in *Fig.* 3. The comparison of the DI method with the SPE method for surface water demonstrated good agreement, within a margin of 21 % in surface water samples.

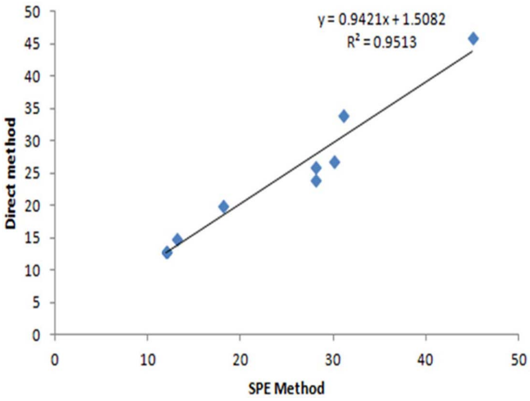


Fig. 3. Comparison of the results of the DI method with the results of the SPE method.

4. Conclusions

A UPLC-ESI-MS/MS method has been developed for the determination of PDM and DNS in surface water and drinking water. The major advantages of the DI UPLC-ESI-MS/MS method are the following: 1) the method allows for determination of PDM and DNS at trace levels lower than the maximum residue values permitted for drinking water and surface water by the EU and the Netherlands 2) the method is very simple and rapid because of the lack of an extracting procedure.

The second result obtained from this study was with regard to the UPLC–MS/MS method that followed clean-up and concentration with MCX. The major advantages of the method are the following: 1) the extraction method of these compounds from water resulted in a high recovery with small variation 2) much lower LOQs (0.0001 μg/L for PDM and 0.0002 μg/L for DNS) were obtained and the LOQs were 150 times lower than the Netherlands guideline values. The SPE UPLC-MS/MS method can be used for the determination of the ultra-trace PDM and DNS residues in environmental water.

Additionally, optimized extraction and instrumental conditions demonstrated that routine analyses of PDM and DNS residues in real surface samples can be carried out sensitively. The developed methods confirmed the existence of PDM and DNS residues in real surface water, providing important tools for evaluating residual herbicides having different chemical properties in environmental water. The data obtained from this method can also be used for the accumulation of monitoring data and risk assessment.

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