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Analysis of polar pesticides in rainwater in Denmark by liquid chromatography–tandem mass spectrometry

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Abstract

A new LC–MS–MS method for analysis of rainwater has been developed and validated for 53 pesticides, degradation products of pesticides and selected nitrophenols. The method was used to monitor the concentration of pesticides in rainwater at one location near Roskilde, Denmark from February 2000 to August 2000. Sampling was done in periods of up to 4 weeks using a cooled wet-only sampler. Water samples were extracted by solid-phase extraction on Oasis HLB columns. The analysis of the extracts was performed by LC–MS–MS with electrospray ionization. All samples were analysed in negative and in positive ionization mode, respectively for acidic and neutral compounds. All analyses were done in the selected reaction monitoring mode in order to obtain a better signal-to-noise ratio. The method has been validated for the following parameters: recovery, detection limit, uncertainty and linearity. Atrazine, terbuthylazine, isoproturon, mechlorprop and (2-methyl-4-chlorophenoxy)acetic acid were measured at concentrations above 0.100 μg/l, mainly during the period of agricultural use. Nitrophenols were measured at high concentrations all year with peaks in the cold season (February–March).

Keywords: Water analysis; Environmental analysis; Pesticides; Nitrophenols

1. Introduction

The main sources for emission of pesticides in the atmosphere and rainfall are volatilization during application, volatilization from crops and soil, and wind erosion from soil. Once pesticides are emitted to the atmosphere, they can be transported long distances from the application site. How far a compound is transported, depends on its half-life in the atmosphere, which in turn depends on the compounds reactivity (e.g. with OH radicals) and its rate of removal by dry and wet deposition.

Several authors [1–13] have reported the occurrence of pesticides in rainwater. The presence of selected pesticides in rainfall in Denmark has been previously reported. Lindane [γ-hexachlorocyclohexane (γ-HCH)], a persistent organic compound, has been chosen in a study [8] as a model compound in order to estimate long range transport, as this chemical is forbidden in Denmark.

In another study [14], the authors have used phenoxyalkanoic acids [mechlorprop, (2-methyl-4-chlorophenoxy)acetic acid (MCPA) and dichlorprop] and isoproturon as model compounds. These pesticides are extensively used in Denmark and they have also been found in precipitations in neighboring countries [15].

In the present study, we have chosen 53 pesticides, degradation products and selected nitrophenols representing a broad range of polarity and volatility (Table 1). Most of these pesticides are currently in

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Table 1
Transition ions for the compounds analyzed in negative ionization mode

Compound	Precursor ion (m/z)	Product ion (m/z)
Benazolin	242	170
Bentazone	239	132
Bromoxynil	276	79
Chlorsulfuron	356	139
2,4-D	219	161
2,4-Dichlorophenol	161	125
2,4-Dinitrophenol	183	122
Dichlorprop	233	161
Dinoseb	239	134
DNOC	197	180
Flamprop	320	121
Fluazifop	326	254
Ioxynil	370	127
Lenacil	233	151
MCPA	199	141
Mechlorprop	213	141
3-Methyl-4-nitrophenol	152	122
Metsulfuron-methyl	380	139
p-Nitrophenol	138	108
Triasulfuron	400	139

use in Denmark, while others have been forbidden several years ago. The last type of compounds may give some information about long-range transport from other countries. DNOC (2-methyl-4,6-dinitrophenol) has been previously found in Danish rainwater at high concentrations throughout the year [14], although it has been banned in Denmark since 1989. Therefore nitrophenol, 2,4-dinitrophenol and 3-methyl-4-nitrophenol were included in the monitoring program in order to demonstrate that the presence of DNOC in precipitation is not due to pesticide use, but that it has the same origin as the other nitrophenols. It is well documented that the presence of nitrophenols in the atmosphere is due to photochemical reactions of aromatic hydrocarbons, NO_x and OH^- radicals [26,27]. As a result of their relatively high solubility in water, nitrophenols are effectively scavenged by precipitation.

Most of the modern pesticides and their degradation products are characterized by medium to high polarity and thermal lability. For these reasons, liquid chromatography (LC) is the most appropriate analytical method. In order to quantify and identify the target analytes at trace levels, mass spectrometry (MS) in the selected ion monitoring (SIM) mode has to be employed.

In the last few years LC coupled to MS has been widely used for analysis of pesticides in water [16].

In the case of LC–MS instrument equipped with a single quadrupole, the fragmentation of the quasi-molecular ion is obtained by in-source collision-induced dissociation (CID) [17]. Increasing the voltage applied to the sampling cone between the atmospheric region and the vacuum zone induces fragmentation. Two or more fragment ions produced by in-source CID are chosen for identification of the target compound in SIM.

In tandem mass spectrometry (MS–MS) performed with triple quadrupole instruments CID of a precursor ion selected in the first quadrupole takes place in the second quadrupole, which is actually the collision cell. A selected typical product ion is then analyzed in the selected reaction monitoring (SRM) mode in the third quadrupole. Even though a large part of the ions selected by the first quadrupole is lost during collision in the second quadrupole, the overall sensitivity in SRM mode is high due to increased signal-to-noise ratio. The presence or absence of a target compound is based on LC retention time compared to that of a standard, and the selection of one or more product ions from the corresponding precursor ion.

LC–MS–MS has recently been reported for the analysis of pesticides in environmental samples [18–21].

This paper describes the validation and application of a multiresidue method for determination of 53 polar pesticides, pesticide degradation products and selected nitrophenols in rainwater. LC–MS–MS in the SRM mode with electrospray ionization (ESI) has been employed for quantitative and qualitative determination of the target compounds. The analytes were divided into two main groups, acidic and neutral compounds. Acidic compounds were analyzed in negative ionization mode and neutral compounds in positive ionization mode. The investigated compounds are listed in Table 1. SPE on a polymeric phase has been employed for pre-concentration of water samples. The method has been applied to monitoring pesticides in Danish rainwater.

2. Experimental

2.1. Sampling method

Rain was collected with a cooled wet-only collector of the type NSA 181/KE made by G.K. Walter Eigenbrodt Environmental Measurements Systems (Königsmoor, Germany) at the National Environmental Research Institute (NERI) near Roskilde, Denmark (55° 42′ N, 12° 6′ E). It consists of a glass (Duran) funnel of diameter of about 500 cm^2 connected to a glass bottle that is kept in a dark refrigerator below the funnel at a constant temperature of 4 °C. The temperature in the room is recorded with a battery powered HOBO H8 Pro temperature logger during the sampling period (Onset Computer Corp., Bourne, MA, USA). A conductivity sensor is activated when it starts to rain and then the lid on top of the funnel is removed. At the end of the rain period the lid is again moved back onto the funnel. In this way no material can dry deposit to the funnel during dry periods. The functioning of the lid mechanism is monitored with a battery powered HOBO H6 state logger, which uses an internal magnetic reed switch (Onset Computer Corp.). The samples were changed about every month. The minimum sampling volume needed for the analysis of all compounds was 200 ml, which is about 4 mm of precipitation. After collection of samples, the glass funnel was rinsed with 1 l distilled water followed by 500 ml acetone. The washings were analysed in order to check the effectiveness of the cleaning method. Only for those compounds occurring at high concentrations in the rainwater samples (e.g. nitrophenols) traces were found in both water and acetone washes, but still at concentrations below 0.1% of the concentrations measured in the rainwater sample.

2.2. Chemicals

Methanol, acetonitrile (LC grade), glacial acetic acid and ammonium acetate (analytical grade) were purchased from Merck (Darmstadt, Germany). Propylene glycol and formic acid (analytical grade) were from Fluka (Buchs, Switzerland). For LC mobile phases and standard dilution, deionized water was further purified with a Milli-Q water purification system (Millipore, Bedford, MA, USA).

The pesticides and pesticide degradation products were purchased from Dr Ehrenstorfer (Augsburg, Germany) in ampoules as mixed stock standard solutions. Calibration standards were prepared by appropriate dilution of the mix stock solutions with methanol–water (10:90). These standards were kept at 4 °C and used within 2 weeks.

Isotopically labeled 2,4-D (D_3) and atrazine (D_5) from Cambridge Isotope Labs (Woburn, MA, USA) were used as surrogate standards. A stock solution (100 μg/ml) was prepared in acetonitrile. A 50 ng/ml solution in methanol–water (10:90) was prepared from the stock solution and used for sample fortification. For MS calibration a solution containing polypropylene glycols (PE Applied Biosystems, Foster City, CA, USA) was used.

2.3. Liquid chromatography

The HPLC system consisted of a Perkin-Elmer Series 200 pump and a Perkin-Elmer Series 200 autosampler (Perkin-Elmer, Norwalk, CT, USA). The analytes were separated on a Hypersil BDS C_{18} column, 250×2.1 mm, 5-μm particle size (Hypersil, Cheshire, UK) at a constant temperature of 30 °C. The sample injection volume was 50 μl. A binary mobile phase gradient was used for analyte separation at a flow-rate of 200 μl/min. The gradient was programmed as follows: linear from 100% A to 50% A in 3 min; linear from 50% A to 100% B in 27 min; maintaining 100% B for 3 min; linear to 100% A in 3 min. Equilibration time prior to the next injection was 14 min.

For separation of acidic pesticides mobile phase A was methanol–water (10:90) with 0.1% acetic acid added, and mobile phase B was 100% methanol with 0.1% acetic acid added. For separation of neutral pesticides mobile phase A was methanol–5 m*M* ammonium acetate (1:99) with 0.1% formic acid added and mobile phase B was methanol–5 m*M* ammonium acetate (90:10) with 0.1% formic acid added.

2.4. Mass spectrometry

A bench-top triple quadrupole mass spectrometer model API 2000 (PE Sciex, Concorde, Canada) equipped with a Sciex turbo ion spray (TISP) probe was employed in this study. The TISP probe corresponds to the commonly named electrospray interface. Mass calibration of both resolving quadrupoles was carried out by continuous infusion of a solution of polypropylene glycols (PPGs) via the system's built-in infusion pump. For each analyte, the values of the voltages applied to the sampling cone, focusing lenses, collision cell and quadrupoles were optimized in the SRM mode by continuous infusion in order to achieve the highest sensitivity as possible.

For LC–MS–MS analysis the nebulizing and auxiliary gas pressures were set at 60 p.s.i. and the curtain gas pressure was set at 30 p.s.i. (1 p.s.i.= 6894.76 Pa). The TISP probe was maintained at 375 °C with a spray voltage of −4500 V for negative ionization mode and +5500 V for positive ionization mode. The electron multiplier was set at 2600 V.

LC–MS–MS analyses were carried out in time-scheduled SRM mode. The chromatographic run was divided into time intervals, where one or more precursor–product transition ions were monitored. Scan time was 1 scan/s and the dwell time ranged from 180 to 1000 ms, depending on the number of ions monitored in the single time interval.

2.5. Sample preparation

For recovery experiments, tap water samples (500 ml) were fortified with the analytes at concentration levels of 0.1, 0.5 and 0.02 μg/l. Deuterated standards (2,4-D and atrazine) were added at a concentration of 0.100 μg/l. The samples were filtered through a glass fiber filter type GC/C (Whatman, Maidstone, UK) and the filter was rinsed with 5 ml methanol, which was added to the sample.

Oasis HLB (200 mg) solid-phase cartridges from Waters (Milford, MA, USA) were used for sample preparation. The cartridges were attached to a 12-position vacuum manifold (Waters), conditioned by adding 10 ml methanol and washed with 20 ml water. The samples were passed through the cartridges using Visiprep large volume samplers (Supelco, Bellefonte, PA, USA) at a flow-rate of 20 ml/min. The bottles containing the samples were rinsed with 20 ml water and the rinses were pulled through the cartridges. Air was passed through the cartridges for 30 min to remove residual water. The cartridges were either eluted immediately or stored at −20 °C. The analytes were eluted with 10 ml methanol at a flow-rate of 1 ml/min. The eluate was evaporated to dryness with pure nitrogen at a temperature of 37 °C after the addition of 50 μl propylene glycol as a keeper. The residue was re-dissolved in 1 ml methanol–water (10:90). Each recovery experiment consisted of three fortified samples and one blank.

3. Results and discussion

3.1. LC–MS–MS analysis

Continuous infusion of each compound was carried out in positive and negative ionization mode. Full scan mass spectra were recorded in order to select the most abundant mass-to-charge-ratio (m/z). The relative intensity for the most abundant m/z was used to evaluate the performance of each ionization mode.

Full scan daughter mass spectra were obtained with continuous infusion of each analyte in product ion scan mode, keeping Q1 locked on the m/z value corresponding to the protonated or deprotonated molecule. The most abundant product ion for each compound was chosen for LC–MS–MS analysis in the SRM mode. The transition ions for acidic and base–neutral compounds are listed, respectively in Tables 1 and 2.

Identification of the target analytes in unknown samples was based on: (a) LC retention time compared to that of a standard (±30 s) and (b) the unique combination of a precursor–product ion.

The stability of the signal intensity was estimated for each compound by injecting 10 times a 50 ng/ml standard and the precision was evaluated by calculating the relative standard deviation (RSD) of the replicate injections. The standard was re-analyzed three times (10 replicates each time) with a 2-day interval to estimate the inter-day precision. RSD values ranged between 0.8 and 9.8% for the inter-day

Table 2
Transition ions for the compounds analyzed in positive ionization mode

Compound	Precursor ion (m/z)	Product ion (m/z)
Atrazine	216	174
Azinphos-ethyl	346	132
Azinphos-methyl	318	132
Carbofuran	222	123
Chloridazone	222	104
Cyanazine	241	214
Desethylatrazine	188	146
Desethylterbuthylazine	202	146
Desisopropylatrazine	174	104
2,4-Dichlorobenzamide	190	173
Dimethoate	230	125
Diuron	233	72
Fenitrothion	278	125
Fenpropimorph	304	147
Hexazinone	253	171
Hydroxyatrazine	198	156
Hydroxysimazine	184	114
Hydroxyterbuthylazine	212	156
Isoproturon	207	72
Linuron	249	160
Metabenzthiazuron	165	150
Metamitron	203	104
Metazachlor	279	135
Metoxuron	229	72
Metribuzin	215	187
Primicarb	239	72
Propachlor	212	170
Prochloraz	376	308
Propyconazole	342	159
Propizamide	256	173
Simazine	202	132
Terbuthylazine	230	174
Triadimenol	296	70

precision and between 1.0 and 12.6% for the intra-day precision.

3.2. Method validation

The method has been validated for the following parameters: recovery, uncertainty, detection limit, and linearity.

3.2.1. Recovery

Recoveries were calculated from triplicate extractions of water samples spiked at 0.100 μg/l. The results are shown in Table 3 for acidic pesticides and Table 4 for neutral pesticides. The percent recovery ranged from 13 to 106%. For nine compounds, the recoveries were lower than 50%. The recoveries listed in Tables 3 and 4 were calculated by comparison to a standard without matrix components. Therefore, the low recoveries of some compounds may be due to matrix signal suppression instead of low efficiency of the extraction method. Suppression of the signal intensity due to matrix components with LC–ESI-MS has been previously reported and explained by theoretical models [22,23]. In order to overcome this problem, a number of different solutions have been proposed involving the use of dual on-line pre-column separation [18], clean-up on strong anion-exchange [24] or the use of internal standard [25]. However, the matrix components have often the same physio-chemical properties of many of the analytes. For multi-residue methods including a broad range of analytes from very acidic to slightly basic compounds, it is often impossible to eliminate the matrix effect without losing the analytes.

As matrix effect reduces signal intensity, the concentration of the analytes in the sample may be significantly underestimated if the calibration is performed with standards without matrix components. It is therefore advisable to perform calibration by extracting procedural standards, i.e. fortified water.

3.2.2. Uncertainty

The uncertainty of measurement of the method was determined using the MODUS (Model for Modular Evaluation of Uncertainty) method [28]. With the MODUS method it is not necessary to know all components of uncertainty isolated one by one. A budget for the uncertainty of an analytical method can be made using estimates for the combined uncertainty of the underlying components. The budget for the uncertainty (u_{total}) for the method here described was divided into the following three estimates: intermediate precision (u_{a}), traceability (u_{b}) and sample volume (u_{c}).

The following formula was used:

$$u_{\text{total}} = \sqrt{u_{\text{a}}^2 + u_{\text{b}}^2 + u_{\text{c}}^2}$$

3.2.2.1. Precision

The results obtained from the recovery experiments were used to estimate the precision of the

Table 3
Mean percentage recovery, uncertainty and limits of detection (LODs) for acidic compounds

Compound	Recovery (%) ±RSD (%)	Uncertainty (%)	LOD (μg/l)
Benazolin	22±4	28	0.027
Bentazone	66±7	19	0.048
Bromoxynil	84±11	22	0.040
Chlorsulfuron	45±5	19	0.006
2,4-D	82±4	9	0.002
2,4-Dichlorophenol	91±9	17	0.015
2,4-Dinitrophenol	64±12	32	0.017
Dichlorprop	89±5	9	0.003
Dinoseb	96±8	14	0.008
DNOC	76±6	14	0.059
Flamprop	83±14	27	0.055
Fluazifop	75±4	10	0.009
Ioxynil	79±8	17	0.039
Lenacil	18±4	32	0.024
MCPA	83±4	9	0.007
Mechlorprop	91±5	10	0.007
3-Methyl-4-nitrophenol	45±7	27	0.009
Metsulfuron-methyl	39±6	27	0.008
p-Nitrophenol	44±5	21	0.011
Triasulfuron	36±5	26	0.009

method. The recovery samples go through all steps in the analytical method. This means that the standard deviation of recovery samples analyzed on different days, using different calibration curves and standards will reflect all the underlying components of uncertainty. The variation of the recovery samples includes both the variation in the sample preparation step and in the LC–MS–MS analysis as well as the variation from using different dilutions of standards. To obtain a reliable estimate of the relative standard deviation on the recovery samples 3–5 series of 3–5 recovery samples are needed.

The precision of an analytical method is generally a function of the concentration of the analytes. Recovery experiments are often conducted at high concentrations, resulting in very low standard deviations, which does not reflect the conditions of real samples. In this study, the recovery experiments were done at the 0.100 μg/l level.

3.2.2.2. Traceability

The traceability is in practice the uncertainty linked to the reference material used for calibration. As the standards used for calibration were directly prepared by dilution of standard mix contained in ampoules, the uncertainty of the traceability was calculated from the certificate of the supplier (0.5%).

3.2.2.3. Sample volume

As the sample volume in this work was determined by weighing the uncertainty of the sample volume was considered to be negligible.

3.2.3. Detection limit

The detection limit was determined by performing extraction of five water samples spiked at a concentration of 0.040 μg/l, i.e. 2–5 times the expected detection limit. The detection limit was calculated as three times the standard deviation of the results (Tables 3 and 4). For all compounds, the detection limit is under 0.100 μg/l, which is the maximum allowed concentration of a single pesticide in drinking water according to the European legislation.

3.2.4. Linearity

The linearity of the method was investigated in the range 0.020–0.200 μg/l. For all compounds, the correlation coefficients were >0.98. However, for

Table 4
Mean percentage recovery, uncertainty and limits of detection (LODs) for neutral compounds

Compound	Recovery (%) ±RSD (%)	Uncertainty (%)	LOD (μg/l)
Atrazine	74±3	8	0.008
Azinphos-ethyl	85±5	10	0.006
Azinphos-methyl	79±8	18	0.003
Carbofuran	50±9	33	0.023
Chloridazone	63±3	10	0.015
Cyanazine	109±6	9	0.009
Desethylatrazine	81±4	10	0.008
Desethylterbuthylazine	81±3	7	0.006
Desisopropylatrazine	83±7	12	0.006
2,4-Dichlorobenzamide	87±10	21	0.006
Dimethoate	64±3	8	0.007
Diuron	82±3	7	0.009
Fenitrothion	74±6	15	0.014
Fenpropimorph	95±5	9	0.009
Hexazinone	73±2	6	0.006
Hydroxyatrazine	59±6	18	0.008
Hydroxysimazine	72±6	15	0.008
Hydroxyterbuthylazine	66±3	8	0.008
Isoproturon	79±4	9	0.006
Linuron	86±4	9	0.008
Metabenzthiazuron	80±4	9	0.010
Metamitron	65±3	9	0.008
Metazachlor	75±3	7	0.009
Metoxuron	68±3	8	0.009
Metribuzin	69±4	11	0.011
Primicarb	49±2	6	0.008
Propachlor	74±3	21	0.004
Prochloraz	77±9	8	0.007
Propiconazole	95±5	10	0.006
Propyzamide	88±5	10	0.007
Simazine	69±3	8	0.008
Terbuthylazine	76±3	9	0.005
Triadimenol	96±5	9	0.006

some compounds the linear regression graph clearly presented a tendency to flatten at concentrations above 0.075 μg/l. The example shown in Fig. 1 for bentazone illustrates this problem. In this case the analyte response is no longer directly proportional to concentration because of saturation of the signal. This phenomenon occurs mainly for compounds analyzed by ESI in the negative ionization mode and it is highly compound-dependent, as previously observed for matrix ion suppression.

Therefore, if analyte concentrations in the sample were over the calibration range, samples were appropriately diluted and run again. As the concentrations of nitrophenols were constantly high, samples were run directly without preconcentration for quantification of these compounds.

3.3. Analysis of rain samples

The analytical procedure described above was used for the analysis of rain samples collected between February and August 2000 at NERI near Roskilde on Zealand. Twenty of the 49 pesticide and degradation products analysed were found at concentrations ranging from 0.001 to 0.730 μg/l. Atrazine, isoproturon, terbuthylazine, MCPA and mech-

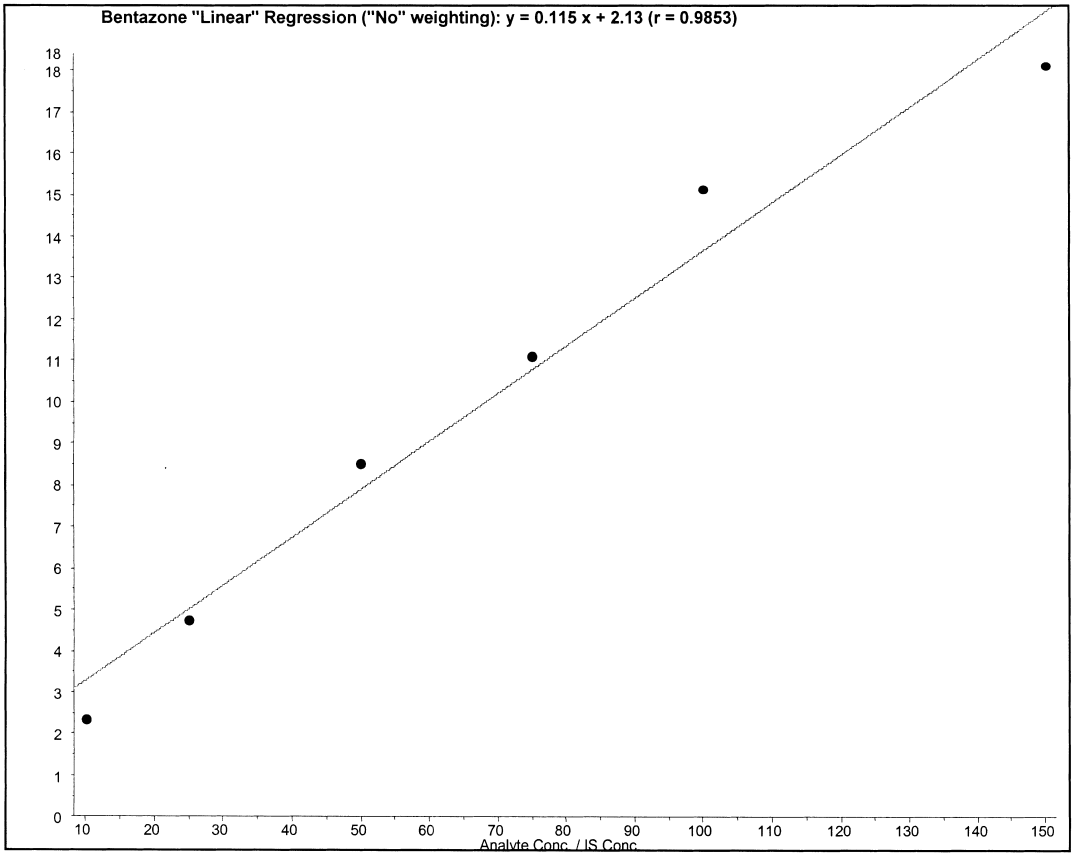

Fig. 1. Linear regression graph for bentazone.

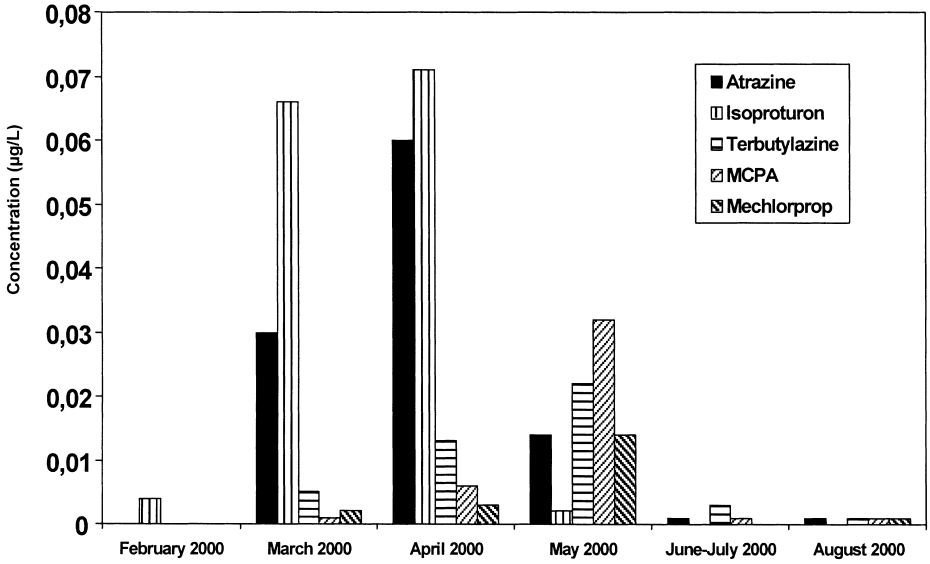

Fig. 2. Concentration of selected pesticides in rainwater collected at Roskilde (Zealand, Denmark).

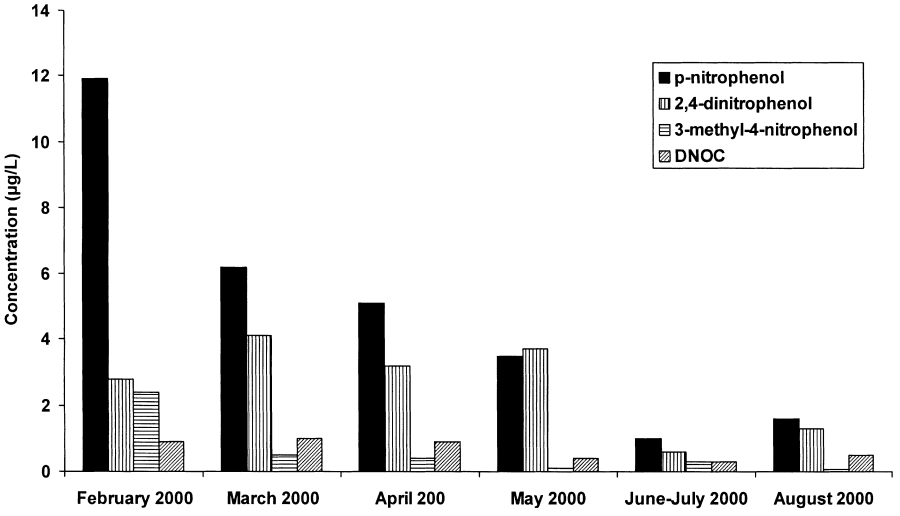

Fig. 3. Concentration of nitrophenols in rainwater collected at Roskilde (Zealand, Denmark).

lorprop were found at concentrations over the detection limit (Fig. 2). The concentrations of nitrophenols ranged from 0.300 to 11.9 μg/l. The results for nitrophenols are summarized in Fig. 3.

4. Conclusions

This work presents for the first time the application of liquid chromatography–mass spectrometry to the analysis of pesticides, their degradation products and selected nitrophenols in rain samples. The method allows quantitative determination of 53 compounds at detection limits lower than 0.100 μg/l. The method has been validated and applied to the analysis of rainwater samples collected at one location in Denmark between February and August 2000.

The method employed has been shown to be suitable for monitoring polar compounds in rainwater for screening purposes. As the method has been designed to cover a large number of analytes belonging to different chemical classes, recoveries and detection limits were not optimal for all compounds.

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