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Liquid chromatographic–tandem mass spectrometric determination of nonylphenol polyethoxylates and nonylphenol carboxylic acids in surface water

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Abstract

This paper presents a new LC–MS–MS method for the determination of the concentration of nonylphenol ethoxylates (NPEOs) and nonylphenol carboxylic acids (NPECs) in surface and drinking water using a reversed-phase column, which is fast and specific by nature. This method allows the simultaneous analysis of the two families of compounds in the same extract. Liquid–solid extraction of 100 ml of sample is performed on graphitized carbon black (GCB) cartridges. Reversed-phase chromatography is performed on a C_8 column with isocratic elution. The electrospray interface is used to monitor the $[M+NH_4]^+$ ion for NPEOs and the $[M-H]^-$ ion for NPECs. Detection limits range from 0.01 to 0.05 μg/l for NP(1–17)EOs and are 0.01 μg/l for NP(1–2)ECs. Mean recoveries range from 78 to 107% with relative standard deviations ranging from 6 to 16%. Applicability of the method is demonstrated by results from a monthly sampling of river water at 11 sampling points located downstream of suspected polluting industries in Quebec (Canada).

Keywords: Water analysis; Tandem mass spectrometry; Nonylphenol polyethoxylates; Nonylphenol carboxylic acids; Surfactants

1. Introduction

Alkylphenol polyethoxylates (APEOs) are non-ionic surfactants which are widely used in the industry, mainly by textile plants, pulp and paper plants, manufacturers of petroleum and leather products, and producers of household and industrial detergents [1]. World production is estimated to be 300 000 tons per year and approximately 7000 tons are used annually in Canada. About 80% of the APEOs produced are nonylphenol polyethoxylates (NPEOs), while the remaining 20% is essentially octylphenol polyethoxylates (OPEOs). Waste water treatment plants degrade APEOs by shortening of the ethoxylate chain, ultimately to alkylphenol. Aerobic degradation may also transform the alcohol group into a carboxylic group to form the alkylphenol carboxylic acid (APEC) [2]. These products are widely found in the environment: sediments, sludge-amended soils, drinking water, duck, fish, fresh

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water, ground water, plants, marine sediments, etc. [3]. Determination of the concentration of NPEOs and NPECs in surface and drinking water is of primary importance because of the lack of data on both the human and aquatic organisms exposure to these compounds, which are proved to have estrogenic activity [4–9].

NPEOs are normally determined by liquid chromatography (LC). Sometimes, a reversed-phase column will be used, separating the ethoxylates by the alkylphenol group. More commonly, a normal-phase column will be used to separate the alkylphenols by the length of the ethoxylate chain. An extensive review has been published on this subject by Lee [10]. Detection may be done with a UV detector set at 277 nm, but a more sensitive and selective detection can be achieved with a fluorescence detector set at 230 nm for excitation and 300 nm for emission. However, any compound containing a benzene ring will respond to these wavelengths, causing a selectivity problem. To overcome this, various LC–mass spectrometry (MS) methods have been published: particle beam (PB) [11], electrospray (ES) [12–17], and atmospheric pressure chemical ionization (APCI) [18]. The PB method uses reversed-phase chromatography and an electron impact (EI) source, which fragments the molecules, thus requiring extensive concentration of the sample (sample size of 500 l and concentration factors of 1 000 000) in order to achieve satisfying detection limits. ES source produces minimum fragmentation. Some methods published to date use reversed-phase chromatography and thus, do not separate the oligomers. One method [13] uses normal-phase chromatography, but introduces a post-column modifier, which induces dilution. This method monitors the $[M+Na]^+$ ion in single MS mode, with less selectivity than MS–MS. Ferguson et al. [17] monitored the sodium adduct and separated the oligomers by reversed-phase chromatography. Selectivity is still a problem, namely because of potential doubly-charged ions. Some authors use the ammonium adduct, but with LC–MS (single stage) this leads to relatively high detection limits. The APCI method was developed to determine the oligomer distribution of a commercial mix, and uses no chromatographic separation.

NPECs are usually determined by gas chromatography. Derivatization is necessary in order to make the molecules volatile and to improve detection. Methods have been published with flame ionization detection or electron-capture detection, but nowadays, MS detection is widely used [19–22]. Gas chromatography is also used to detect nonylpenol (NP), the ultimate degradation product of NPEOs. Chromatograms of NP, NP1EC or NP2EC exhibit a group of peaks, due to the presence of different isomers of the nonyl group [23]. Again, lack of selectivity and sensitivity are the major drawbacks of this method. Some LC–MS methods have been published for the analysis of NPECs [15,16,24]. They use single-stage LC–MS which lack sensitivity for the compounds we are interested in [15,16]. Jonkers et al. used LC–MS–MS for the confirmation of identification of the metabolites [24].

This paper presents a new LC–MS–MS method that overcomes the main drawbacks of existing methods. It involves simultaneous extraction and determination of both NP(1–17)EOs and NP(1–2)ECs in water, thus being less time consuming, more specific and more sensitive. We take advantage of MS–MS and use reversed-phase chromatography, giving little separation of the analytes, but reducing the time required for determination.

2. Experimental

2.1. Chemicals

All chemicals were of analytical grade or better. Nanopure water was used in all experiments. NPEO standard was kindly prepared and provided by Carter Naylor (Hunstman, Austin, TX, USA). NPEC standards and NP2EO-$^{13}C_6$ were obtained from Cambridge Isotope Laboratories (Andover, MA, USA), dichloromethane from EM Science (Cincinnati, OH, USA) and methanol (Optima), formic acid, hydrochloric acid and ammonium acetate from Fisher Scientific (Napean, Canada).

2.2. Apparatus

The LC–MS–MS system consists of a HP 1100 LC (binary pump and automatic injector) from Hewlett-Packard (Palo Alto, CA, USA), coupled to a

Quattro Ultima triple quadrupole mass spectrometer equipped with the electrospray interface, from Micromass (Manchester, UK). Argon is used as the collision gas and nitrogen as the nebulizer gas.

2.3. Chromatographic conditions

The sample (10 μl) is injected onto a 150×4.6 mm I.D., 5 μm Zorbax C_8 column (Agilent Technologies, Palo Alto, CA, USA) held at room temperature. Mobile phase consists of methanol–0.1% formic acid (98:2) and 10 mmol ammonium acetate solution in water. Flow-rate is set at 0.3 ml/min. Run time is 9 min.

2.4. Mass spectrometry conditions

The interface is set at 350 °C and the source at 120 °C. Transitions from the $[M+NH_4]^+$ ions for the NPEOs and transitions from the $[M-H]^-$ ion for the NPECs are monitored. The $[M+NH_4]^+$ ion was chosen for the NPEOs, because the molecular ion was of low intensity when no modifier is added to the mobile phase (Fig. 1A). The most intense ion is the sodium adduct, but it cannot be used with great efficiency in the MS–MS mode, as it is too stable, and does not tend to give relevant fragmentation. This is why the ammonium adduct is forced by incorporating ammonium acetate in the mobile phase (Fig. 1B). This adduct gives reproducible fragmentation under the conditions listed in Table 1. The $[M-H]^-$ is very intense for the NPECs and is enhanced by incorporating formic acid in the mobile phase. For positive and negative modes, the capillary is maintained at 3.0 kV and the cone at 50 V. Nitrogen flows are 70 l/h for the cone gas and 650 l/h for desolvation gas.

2.5. Sampling

Water is sampled in a 1-l glass bottle, previously washed with methanol and water. A 10-ml volume of 37% formaldehyde is added as a preservative. The samples are refrigerated at 4 °C and protected from light until the extraction, which is performed within 12 days after sampling.

2.6. Extraction

Extraction is performed on the whole sample, that is no filtration or centrifugation of the water is performed prior to the extraction process. Sample homogeneity is essential in order to assure reproducibility of the results. The Supelclean ENVI-Carb SPE cartridge (0.5 g, 6 ml) is conditioned by rinsing two times with 5 ml of dichloromethane, and two times with 5 ml of dichloromethane–0.1% formic acid (90:10, v/v). It is then dried and 5 ml methanol followed by 20 ml of water at pH 3 (acidified with HCl) are passed on the column. A portion of 100 ml of the acidified sample (pH 3 with HCl, just prior to extraction) is then added, followed by 20 ml of methanol–water (1:1). The column is air-dried and washed with 1 ml of methanol. NPEOs and NPECs are eluted with 7 ml of dichloromethane–0.1% formic acid (90:10, v/v). The eluate is evaporated to dryness and kept frozen until the analysis. It is then reconstituted in 2 ml of methanol containing the internal standard (NP2EO-$^{13}C_6$).

3. Results and discussion

3.1. Standards

Individual standards are not commercially available for all the NPEOs oligomers. It was thus decided to use the modified commercial mix kindly provided by Carter Naylor, the NPE9 mix. The LC–fluorescence method provided by Naylor was used to determine the concentration of each oligomer in the mix. This method is based on the assumption that molar response factors of individual oligomers are rather constant [25]. The only commercially available standards for NPECs are for NP1EC and NP2EC. Standards for NPEOs and NPECs are not mixed, but injected separately, because it was found that the NPEC standard is contaminated by traces of NPEOs. Carbon-13 labeled injection standard is incorporated in each solution.

3.2. Blanks

The method blanks showed traces of NPEOs, but no NPECs. Table 2 is showing the range of typical

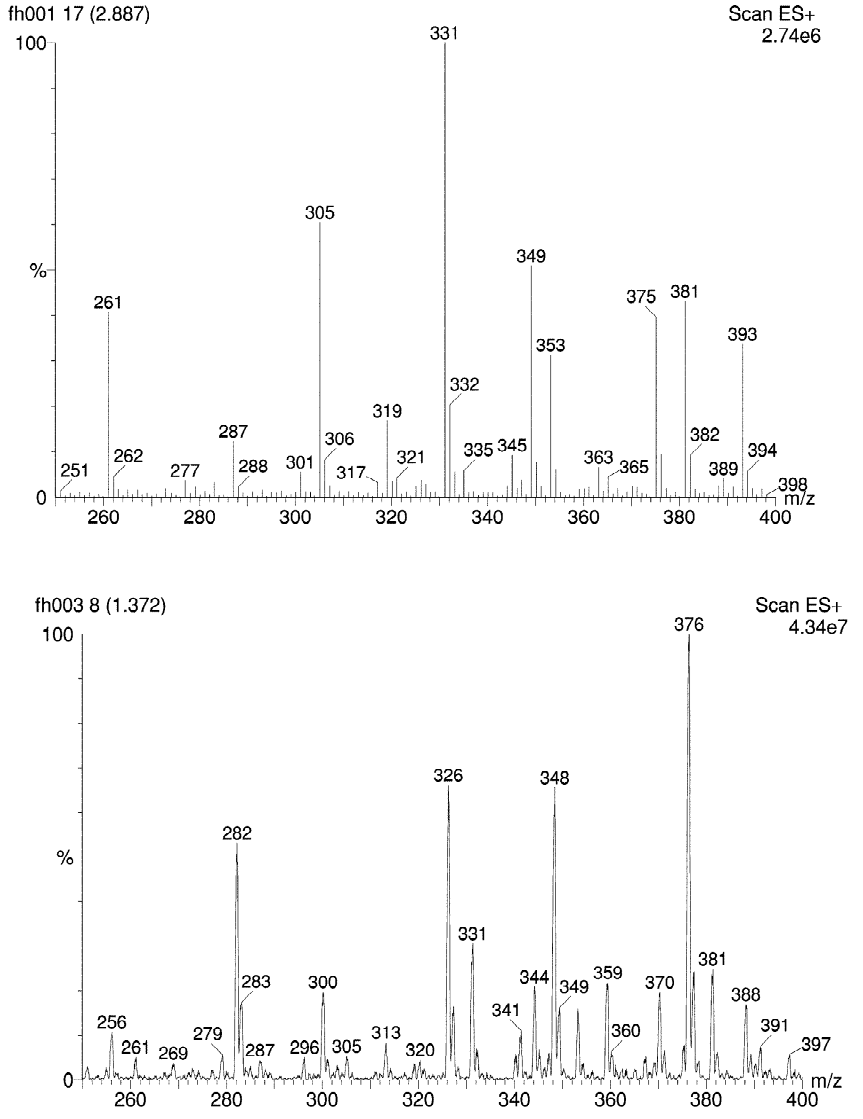

Fig. 1. (A) Mass spectra resulting from infusion of a solution of NP1EO and NP2EO in MeOH–water. Quasi-molecular ions ($[M+H]^+$) at m/z 265 for NP1EO and at m/z 309 for NP2EO. Sodium adducts of NP1EO at m/z 287 and of NP2EO at m/z 331. (B) Mass spectra resulting from infusion of a 1 ppm solution of NP1EO and NP2EO in MeOH–10 mmol ammonium acetate. Ammonium adducts of NP1EO at m/z 282 and of NP2EO at m/z 326.

blank contamination. When observed, this contamination is in the order of one to three times the detection limit. Several procedures were used to eliminate this contamination, without any success. The first hypotheses was methanol contamination. Purification of the methanol by filtration through carbon black does eliminate methanol contamination, as shown by concentration and injection of purified solvent. Cleaning of all the glassware with this filtrated methanol did not completely eliminate the contamination as shown by injections of extraction blanks. The source of this constant contamination is

Table 1
MS–MS parameters (NPEOs: ammonium adducts in positive mode, NPEC: quasi-molecular ion, negative mode)

Oligomer	Parent mass (m/z)	Daughter mass (m/z)	Collision energy (eV)
NP1EO	282.4	127.2	9
NP2EO	326.3	183.2	12
NP3EO	370.3	227.2	12
NP4EO	414.3	271.2	15
NP5EO	458.3	315.3	16
NP6EO	502.3	359.3	18
NP7EO	546.4	291.3	23
NP8EO	590.4	291.3	25
NP9EO	634.5	291.3	26
NP10EO	678.5	291.3	30
NP11EO	722.5	291.3	30
NP12EO	766.5	291.3	30
NP13EO	810.6	291.3	32
NP14EO	854.6	291.3	34
NP15EO	898.6	291.3	34
NP16EO	942.6	291.3	35
NP17EO	986.7	291.3	35
NP2EO-$^{13}C_6$	332.4	253.4	12
NP1EC	277.2	219.2	17
NP2EC	321.2	219.2	12

Dwell time is 0.1 s for every transition, except for NP1EO (0.3 s).

Table 2
Blank contamination ($n=5$)

Oligomer	Mean concentration (μg/l, in extract)	SD
NP1EO	3.1	2.4
NP2EO	3.2	1.4
NP3EO	2.2	1.3
NP4EO	2.0	2.0
NP5EO	2.5	2.8
NP6EO	3.1	3.2
NP7EO	3.4	3.4
NP8EO	2.9	3.1
NP9EO	2.6	2.8
NP10EO	2.2	2.4
NP11EO	1.7	1.7
NP12EO	1.3	1.2
NP13EO	0.9	0.8
NP14EO	0.6	0.5
NP15EO	0.2	0.4
NP16EO	0	0
NP17EO	0	0

still unknown. Considering the detection limit of the method, subtraction of the blanks is a critical point for the quantification of unknown samples.

3.3. Method performance

The performance of the method is summarized in Table 3. Recoveries (in surface water, $n=14$) are near 100% with standard deviations (SDs) below 12% for all compounds, except NP1EO. The sample used was virtually free of particles, as for all the samples analyzed in this study. For samples exhibiting higher level of particles, filtration would be required, in order to assure reproducibility of the data.

Instrumental detection limits were calculated by a signal-to-noise ratio of 3, from the multiple reaction monitoring (MRM) chromatogram of standard solutions. The detection limit of the different oligomers in the sample were derived from the instrumental limit of detection (LOD), taking into account the volume of the sample, the volume of the extract and the recovery rates of spiked samples. These detection limits can be compared with those of other methods. Using LC–MS, Cohen et al. [14] reported detection limits of 1 to 10 μg/l for the individual compounds in water. The detection limits of the method proposed here are at least 20 times lower. Petrovič and Barceló [15] report an instrumental detection limit of 0.50 ng (injected) for NP7EO, while this method goes down to 15 pg for the same product.

Quantification of NP1EO is challenging with this new analytical procedure due to its low response factor compared to the other oligomers. This explains its higher detection limit. For NP1EO, the ammonium adduct is giving a better S/N ratio in MS–MS mode, but it seems that this daughter ion is less stable or less abundant than the product ions of the other oligomers. Even if the LOD of this oligomer is higher than that of the other compounds, it is comparable to what one can get with the LC–fluorescence method. The LC–MS–MS method also has the advantage of higher selectivity.

The range of concentrations of the various oligomers in the mix, combined with the wide range of response factors, leads to calibration curves with several points, in order to cover the linearity range of

Table 3
Performance of the method

Oligomer	Recovery[a] (n=14) (%)	Detection limit (μg/l)		Relative response factor
		In extract	In sample	
NP1EO	78	2.5	0.05	0.003[b]
NP2EO	105	1.0	0.02	0.5[b]
NP3EO	99	1.0	0.02	1[b]
NP4EO	99	1.5	0.03	0.9[b]
NP5EO	100	1.5	0.03	0.6[b]
NP6EO	103	1.5	0.03	0.3[b]
NP7EO	105	1.5	0.03	0.2[b]
NP8EO	106	1.5	0.03	0.2[b]
NP9EO	106	1.5	0.03	0.2[b]
NP10EO	107	1.5	0.03	0.1[b]
NP11EO	106	1.5	0.03	0.1[b]
NP12EO	105	1.0	0.02	0.1[b]
NP13EO	105	1.0	0.02	0.1[b]
NP14EO	106	0.5	0.01	0.07[b]
NP15EO	103	0.5	0.01	0.06[b]
NP16EO	107	0.5	0.01	0.04[b]
NP17EO	101	0.5	0.01	0.04[b]
NP1EC	89	0.5	0.01	1[c]
NP2EC	87	0.5	0.01	0.6[c]

[a] RSDs: 6–16%, 0.3–1.8 μg/l added.
[b] Based on NP3EO.
[c] Based on NP1EC.

each oligomer. Standards of the NPE9 blend, at concentrations between 4 and 2000 ppb were routinely injected. This represents from 0.02 to 8.5 ppb of NP17EO (the less concentrated oligomer in the NPE9 blend) and from 0.39 to 195 ppb of NP8EO (the highest concentrated oligomer). For the low concentrated oligomers in the mix (NP1EO, NP2EO, NP16EO and NP17EO), the point corresponding to the lowest concentration is excluded of the curve. As well, for the highest concentration oligomers in the mix, the highest concentration standard point is excluded from the calibration curve. This leads to linear calibration curves (r>0.995). If a sample shows concentrations outside of the curves, it is diluted accordingly.

The MS method consists of two alternating functions in time (one in positive electrospray and one in negative electrospray), which allows the monitoring of NPEOs and NPECs in the same injection. The total cycle-time is 2.4 s including positive and negative functions. With a peak width of about 25 s, 10 to 11 points per peak are monitored, which provides an accurate representation of the peak area.

Chromatograms of a sample of contaminated surface water are shown in Fig. 2. Co-extracted compounds is one of the most critical issues in the determination of NPEOs [25]. Problems related to contamination of the extract by phthalates, polycyclic aromatic hydrocarbons, phenolic compounds, or other alkylphenols are eliminated with the MS–MS technique. There is no interference in the MS–MS chromatograms (has seen in Fig. 2), in opposition to what could be observed in LC–fluorescence or LC–UV.

3.4. Internal standard

The chromatographic separation of the different oligomers is not very efficient. Separation is not needed because of the high selectivity of MS–MS. But ion suppression is observed, and for this reason, chromatographic separation was attempted. Ion sup-

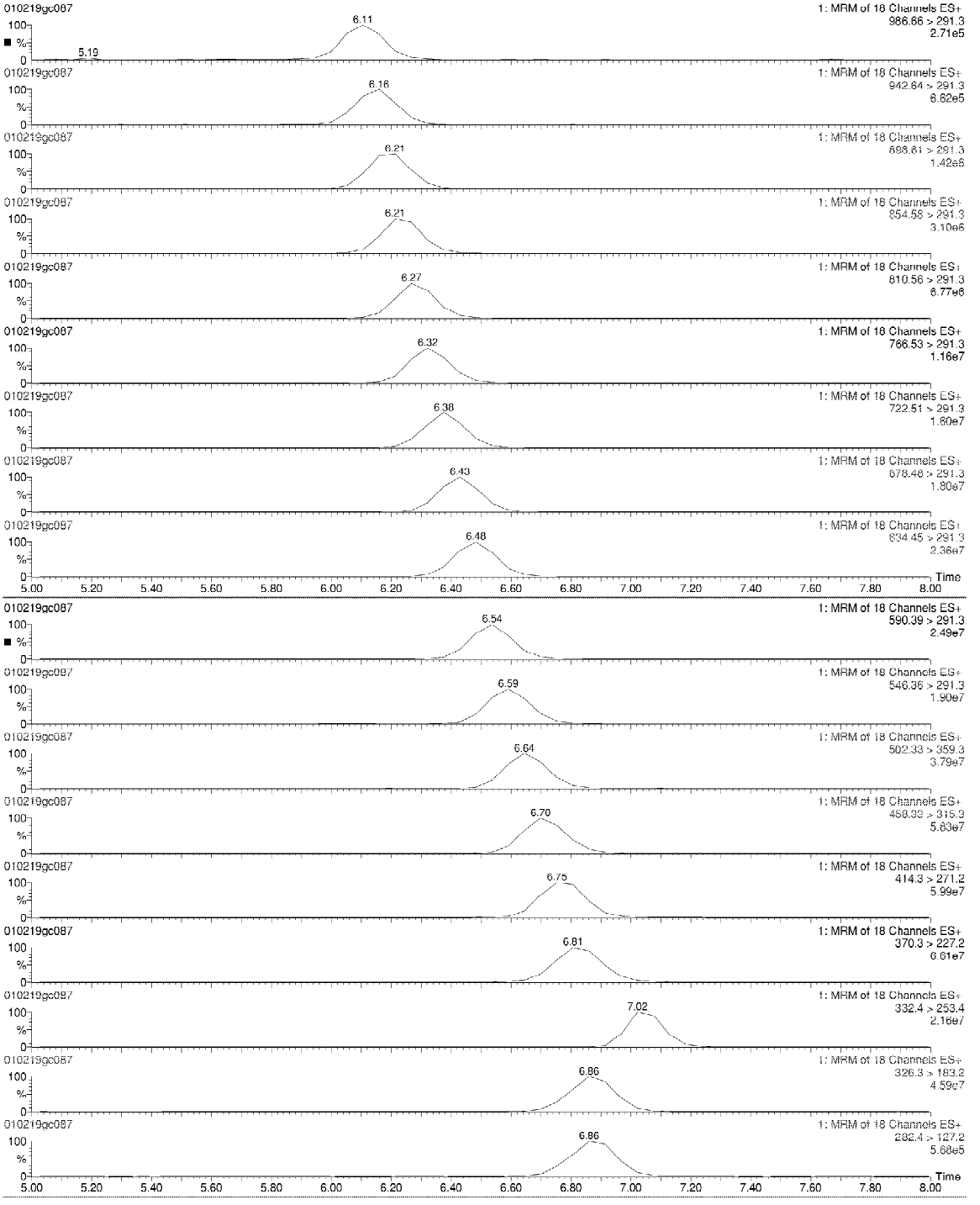

Fig. 2. Chromatograms of a sample of raw water (sample 6, December). Calculated concentrations in the water are as follow: 4.0, 1.8, 1.4, 1.4, 1.8, 1.9, 2.2, 2.5, 2.4, 2.5, 2.0, 1.7, 1.2, 0.75, 0.43, 0.27 and 0.12 μg/l for NP1EO to NP17EO, and 5.5 and 6.3 μg/l for NP1EC and NP2EC. For identification of traces and conditions, see Table 1.

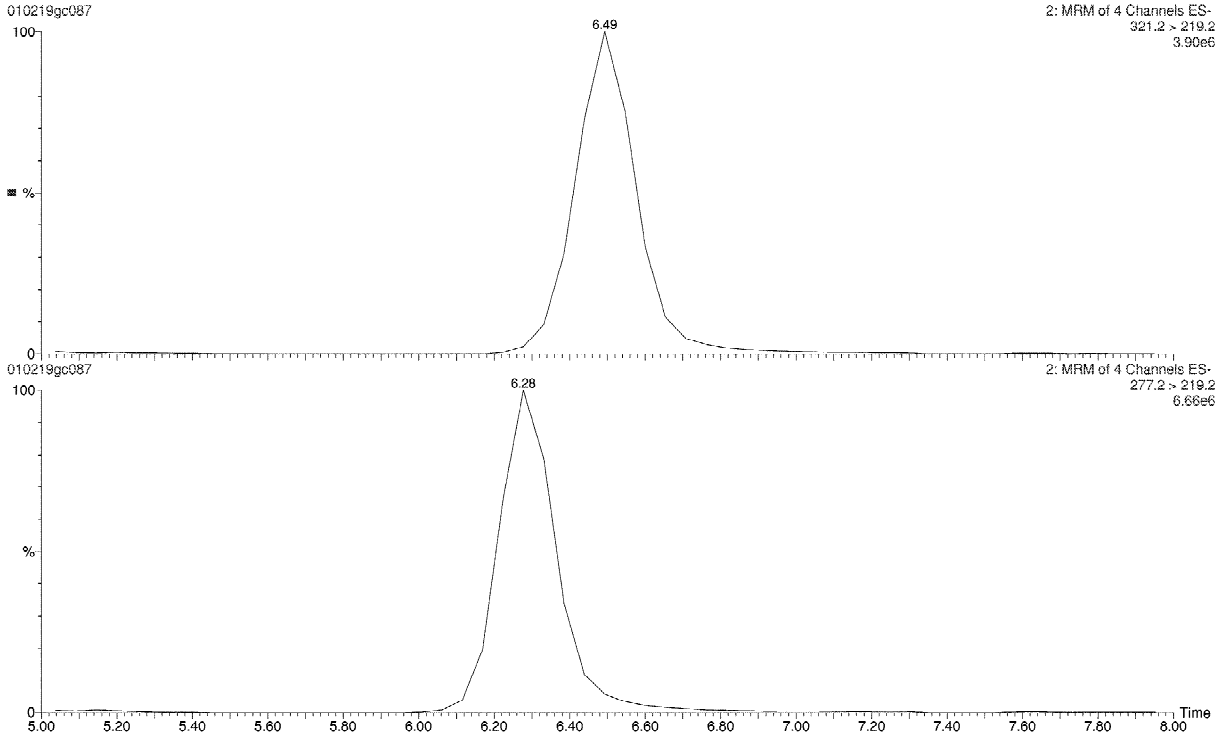

Fig. 2. (*continued*)

pression causes the calibration curves to be linear over a limited range of concentration. The reversed-phase columns are not the best way to separate the NPEOs by their ethoxylate chain. The chromatographic separation reported here is sufficient if an internal standard is used. It will be exposed to the same ion suppression as the components of interest and will hence correct for this phenomena. A carbon 13 labeled NPEO is the best internal standard one can use in this case, because it will elute in the same region as the components of interest and the correction it will apply on the oligomers will then be optimized. The internal standard that was used does not co-elute exactly with the native oligomers, but is one of the only three labelled nonylphenol ethoxylates commercially available, the others being NP1EC-$^{13}C_6$ and NP2EC-$^{13}C_6$. Nevertheless, it will correct for major ion suppression and using it gives a more accurate concentration of the native oligomers present in the matrix. Incorporating NP2EO-$^{13}C_6$ in the routine analysis increases the linear range of the calibration curves. It also corrects the ion intensity of the nonylphenol ethoxylates if an interference elutes at the same time as the main group of ethoxylates.

3.5. Case study

In order to demonstrate that this method can be used to adequately quantify NPEOs and NPECs in real-life surface water samples, this section presents partial results from a survey of nonylphenols in Quebec rivers. A full interpretation of the data set will be presented elsewhere.

Sampling was carried out at eleven sites located downstream of pulp and paper and/or textile effluents. Fig. 3 shows the location of the sampling points.

There are large variations in the total concentrations of these contaminants over time, as shown in Fig. 4a and b. The bars in the graph do not represent a monthly mean, but the results of a single sample (grab samples). Quebec has a very cold winter (from

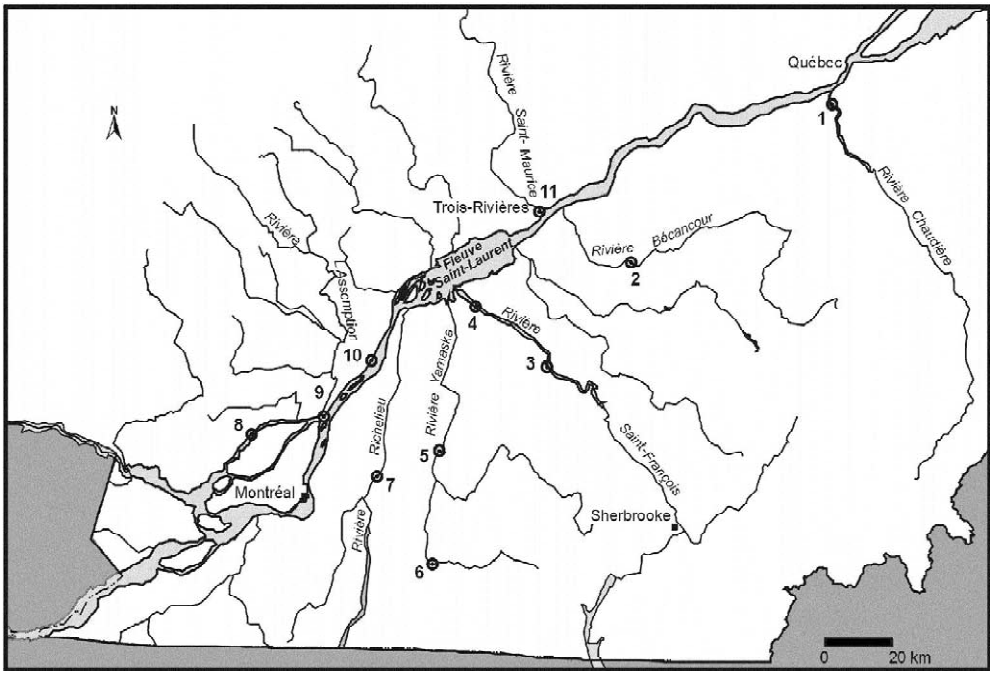

Fig. 3. Map of southern Quebec, showing the sampling points.

December to March) and a warm summer (from June to September). Increases of water temperature, with related increases in microbiological activity, may explain lower concentrations of nonylphenols in summer. Decreases in the concentration of NPEOs in Spring may also be explained by dilution during this high flow season. This seasonal variation is in accordance with the results of other research that demonstrate that degradation of nonylphenols in waster water treatment plants is slower in colder winter conditions (Lee et al. [21]). This leads to higher NPEO concentrations in rivers during winter.

It can be seen in Fig. 4b that two sites (5 and 6) show higher concentrations of NP(1–2)ECs than the others. These sampling points also exhibit elevated level of NP(1–17)EOs. Sampling points 8, 9 and 10 show continuous contamination by the NPEOs, but the results for NPECs are relatively low. This may be explained by different causes: nature of the NPEO sources, distance from these sources, differences in biodegradation rates, etc.

Some sampling was carried out in duplicates in order to evaluate the short-term reproducibility of the data. Results for the sum of NP(1–17)EOs and NP(1–2)ECs are shown in Table 4. Differences between duplicates vary from 2.6 to 32%. The mean error is 12.7%, which is acceptable, considering that it includes the errors related to the sampling technique, the extraction and the instrumental determination of the different compounds. Moreover, it can be concluded that the analytical technique copes well with the particles concern that we discussed earlier, or that the samples were very homogeneous. The 32% error is recorded for the duplicates with the lowest concentrations: mean of 0.83 μg/l. Under these conditions, even if the difference between the duplicates is relatively small (0.27 μg/l), the error percentage is high., As expected, the relative precision is better for samples containing higher concentrations of contaminants.

In Fig. 5, the relative concentration of the oligomers is presented for six selected samples. It can be seen that all oligomers are present, and that the distribution is similar to what is found in commercial mixtures, although some samples exhibit higher concentrations of the lower oligomers (NP1EO,

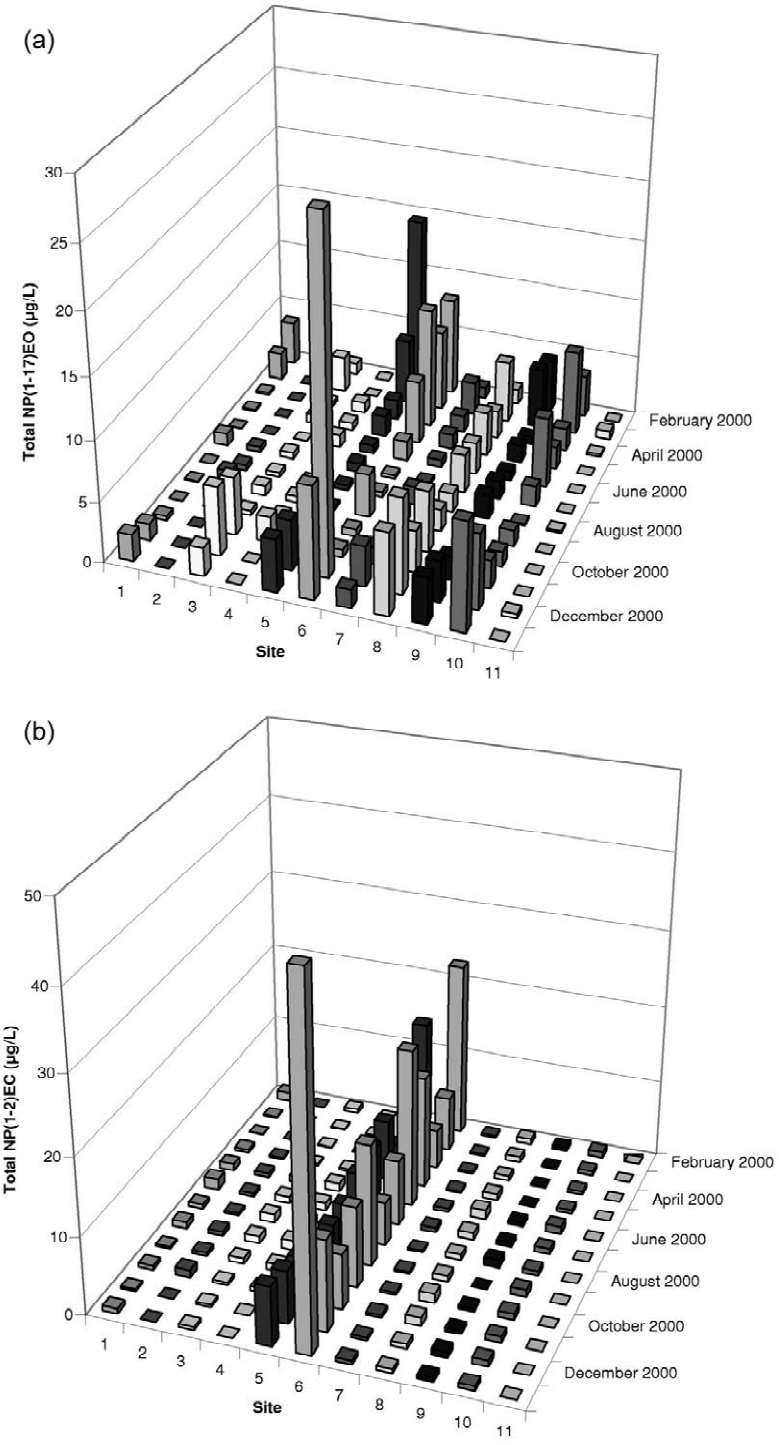

Fig. 4. Summation of the concentration of oligomers at the different sampling points over time. (a) Total NP(1–17)EOs, (b) total NP(1–2)ECs.

Table 4
Difference in concentration between sampling duplicates

Site	Month	Average total concentration of sample and duplicate (μg/l)	Cumulative difference (μg/l)	Error (%)
1	February	5.22	1.11	21
4	August	1.22	0.19	15
5	April	3.52	0.09	2.6
5	July	6.55	0.59	9.0
6	February	30.7	2.94	9.6
8	February	2.01	0.08	4.0
9	April	0.83	0.27	32
9	August	2.99	0.32	11
10	July	2.36	0.22	9.3

Total of the sum of NP(1–17)EOs and NP(1–2)ECs.

NP2EO). These distributions can be compared to the results of Shang et al. [13] where NPEOs were analyzed in sediments. In their case, lower oligomers were dominant, due to hydrolithic shortening of the polyethoxy chain of NPEOs.

4. Conclusions

A new analytical method has been developed for the determination of alkylphenol polyethoxylates and alkylphenol carboxylic acids in water.

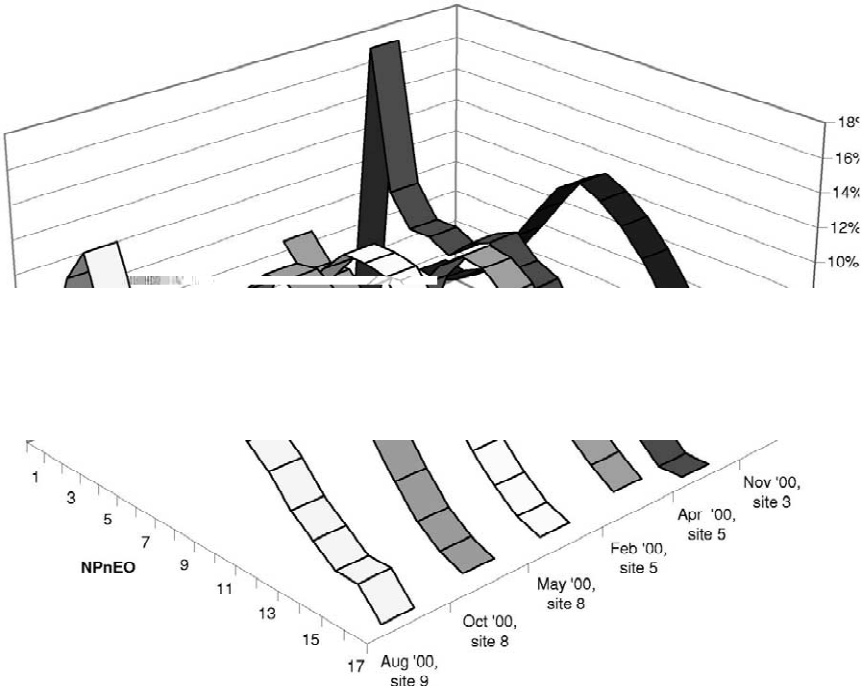

Fig. 5. NPEO concentration distribution for six different samples. The composition is based on the total NP(1–17)EO concentration. The NPEC distribution is approximately 50–50 for NP1EC and NP2EC.

The major improvements over existing methods in faster extraction and analysis, better detection limits and higher selectivity. It is demonstrated that this new method can be used to adequately quantify these compounds in real-life samples of surface water.

Future work includes analysis of octylphenol polyethoxylates and octylphenol carboxylic acids and increasing the number of NPEOs and NPECs monitored, as soon as the standards become available. The method is currently being adapted for the analysis of nonylphenol.

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References

[1] H.-B. Lee, T.E. Peart, Water Qual. Res. J. Canada 33 (1998) 389.
[2] M. Ahel, W. Giger, M. Koch, Water Res. 28 (1994) 1131.
[3] D.T. Bennie, Water Qual. Res. J. Canada 34 (1999) 79.
[4] E.J. Routledge, J.P. Sumpter, Environ. Toxicol. Chem. 15 (1996) 241.
[5] S. Jobling, J.P. Sumpter, Aquatic Toxicol. 27 (1993) 361.
[6] A.M. Soto, H. Justicia, J.W. Wray, C. Sonnenschein, Environ. Health Perspect. 101 (Suppl. 2) (1992) 65.
[7] R. White, S. Jobling, S.A. Hoare, J.P. Sumpter, M.G. Parker, Endocrinology 135 (1994) 175.
[8] A. Blom, E. Ekman, A. Johannisson, L. Norrgren, M. Pesonen, Arch. Environ. Contam. Toxicol. 34 (1998) 306.
[9] C.E. Purdom, P.A. Hardiman, V.J. Bye, N.C. Eno, C.R. Tyler, J.P. Sumpter, Chem. Ecol. 8 (1994) 267.
[10] H.-B. Lee, Water Qual. Res. J. Canada 34 (1999) 3.
[11] L.B. Clark, R.T. Rosen, T.G. Hartman, J.B. Louis, I.H. Suffet, R.L. Lippincott, J.D. Rosen, Int. J. Environ. Anal. Chem. 47 (1992) 167.
[12] C. Crescenzi, A. Di Corcia, R. Samperi, A. Marcomini, Anal. Chem. 67 (1995) 1797.
[13] D.Y. Shang, M.G. Ikonomou, R.W. Macdonald, J. Chromatogr. A 849 (1999) 467.
[14] A. Cohen, K. Kint, S. Bøwadt, P. Persson, J.Å Jönsson, J. Chromatogr. A 927 (2001) 103.
[15] M. Petrovič, D. Barceló, Anal. Chem. 72 (2000) 4560.
[16] C. Hao, T.R. Croley, R.E. March, B.G. Koenig, C.D. Metcalfe, J. Mass Spectrom. 35 (2000) 818.
[17] P.L. Ferguson, C.R. Iden, B.J. Brownawell, Anal. Chem. 72 (2000) 4322.
[18] S. Pattanaargsorn, P. Sangvanich, A. Petson, S. Roengsumran, Analyst 120 (1995) 1573.
[19] W. Giger, E. Stephanou, C. Schaffner, Chemosphere 10 (1981) 1253.
[20] A. Di Corcia, A. Costantino, C. Crescenzi, E. Marinomi, R. Samperi, Environ. Sci. Technol. 32 (1998) 2401.
[21] H.-B. Lee, J. Weng, T.E. Peart, R.J. Maguire, Water Qual. Res. J. Canada 33 (1998) 19.
[22] A. Di Corcia, R. Cavallo, C. Crescenzi, M. Nazzari, Environ. Sci. Technol. 34 (2000) 3914.
[23] H.-B. Lee, T.E. Peart, D.T. Bennie, R.J. Maguire, J. Chromatogr. A 785 (1997) 385.
[24] N. Jonkers, T.P. Knepper, P. de Voogt, Environ. Sci. Technol. 35 (2001) 335.
[25] M. Ahel, W. Giger, E. Monar, S. Ibric, Croatica Chem. Acta 73 (2000) 209.