

# LC–MS–MS analysis and occurrence of octyl- and nonylphenol, their ethoxylates and their carboxylates in Belgian and Italian textile industry, waste water treatment plant effluents and surface waters

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## Abstract

Alkylphenols (APs), alkylphenol ethoxylates (APEOs), ethoxycarboxylate metabolites (APECs) and bisphenol A were determined in surface water using solid-phase extraction (SPE) followed by triple-quadrupole LC–MS–MS. APs were separated by LC from APECs using an acetonitrile–water–gradient without the addition of any buffer. Nonylphenol ethoxycarboxylates (NPECs) interfere in the detection of nonylphenols (NPs) when using an acidic mobile phase, because they produce the same MS–MS fragment ions ( $219 > 133$  and  $147$ ). 4n-NP shows the characteristic transition  $219 > 106$ ; it is well suited as internal standard. Nonylphenol ethoxylates  $\text{NPE}_n\text{Os}$  ( $n = 1–17$ ) were analysed separately in a second run by positive ionization using an ammonium acetate mobile phase. Textile industry discharges, the corresponding wastewater treatment plant (WWTP) effluents and the receiving rivers in Belgium and Italy were analysed. Among the substances investigated,  $\text{NPE}_1\text{C}$  and  $\text{NPE}_2\text{O}$  exhibited the highest concentrations in the water samples, up to  $4.5 \mu\text{g l}^{-1}$   $\text{NPE}_1\text{C}$  in a WWTP effluent and  $3.6 \mu\text{g l}^{-1}$   $\text{NPE}_2\text{O}$  in a river. The highest NP levels were found in the receiving rivers (max.  $2.5 \mu\text{g l}^{-1}$ ). The predicted no-effect concentration (PNEC) for NP of  $0.33 \mu\text{g l}^{-1}$  for water species was frequently exceeded in the surface waters investigated, suggesting potential adverse effects to the aquatic environment.

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## 1. Introduction

Alkylphenol ethoxylates (APEOs) are nonionic surfactants widely used in agricultural, industrial, and domestic applications (Krogh et al., 2003). They are applied in textile industries in auxiliaries formulations (used in pretreatment operations) or in additives as detergents or wetting agents in wool scouring, hydrogen peroxide bleaching and dyeing processes. Because of the poor degradability and toxicity of their metabolites, APEOs have been replaced in household applications in most western countries, mainly by alco-

hol ethoxylates. Among APEOs, nonylphenol ethoxylates (NPEOs) are by far the most commonly used isomers; 80% of the APEO surfactants used are NPEOs, while the remaining 20% are almost entirely octylphenol isomers (OPEOs). Commercial NPEOs are complex mixtures of ethoxy homologues and alkyl isomers (European Commission, 2002, 2003; Petrovic et al., 2002a; Knepper et al., 2003a).

The environmental fate of the metabolites of APEO surfactants is of significant interest because of their potential endocrine effects (Jones-Lepp et al., 2000; Sumpter, 2002). Alkylphenols (APs), short-chain APEO and alkylphenol carboxylate metabolites APEC and other 4-para-alkylphenolic compounds like bisphenol A (BPA) (Staples et al., 1998; Fromme et al., 2002; Hu et al.,

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2002) are weakly estrogenic; they have been shown to couple to the estrogen receptor in *in vitro* tests (Soto et al., 1991; Jobling and Sumpter, 1993; Field and Reed, 1996; Routledge and Sumpter, 1996).

Exposure to xeno-estrogens has been linked to decreased sperm counts, increased testicular, prostate, and breast cancer, and reproductive disorders in humans (Vethaak et al., 2005). It has been shown that effluents of wastewater treatment plants (WWTPs) are estrogenic to fish; feminized male fish were found in UK rivers (Desbrow et al., 1998; Jobling et al., 1998; Lye et al., 1999). Laboratory studies with nonylphenol (NP) have proven its estrogenic activity *in-vivo*, leading not only to typical estrogenic responses, such as elevated vitellogenin, but also to reduced testicular growth in males (Jobling et al., 1996), impaired spermatogenesis, and reduced secondary sexual characteristics (Gimeno et al., 1997; Christiansen et al., 1998). However, these effects are dose-dependent, as NP can cause intersexuality at “high” concentrations (Gray and Metcalfe, 1997), but not at lower concentrations (Nimrod and Benson, 1998; Sumpter, 2002).

APEOs are discharged to WWTPs or directly released into the environment (Gibson et al., 2005; Langford et al., 2005). After secondary wastewater treatment usually more than 95% of the APEOs are degraded; however, more recalcitrant metabolites (APs, APECs) are formed, which are widespread environmental pollutants. An overview on the biodegradation of APEOs can be found in (Ahel et al., 1994; Di Corcia et al., 1998, 2000; Jonkers et al., 2001; Staples et al., 2001; Knepper and Berna, 2003; Petrovic and Barceló, 2003). NP is biodegradable with half-lives in water between several days and weeks (European Commission, 2002); BPA has a reported half-life of 2.5–4 days (Staples et al., 1998).

Analysis of alkylphenolic compounds is complex because of the existence of different ethoxylate oligomers and alkyl-chain isomers. Liquid chromatography–mass spectrometry (LC–MS) is increasingly being used for the determination of the full range of APs (Ferguson et al., 2000; Petrovic and Barceló, 2000; Jeannot et al., 2002; Petrovic et al., 2003b), APEOs (Shang et al., 1999; Ferguson et al., 2000; Petrovic and Barceló, 2000; Jeannot et al., 2002; Shao et al., 2002; Houde et al., 2002; Petrovic et al., 2003b; Berryman et al., 2004) and APECs (Ferguson et al., 2000; Petrovic and Barceló, 2000; Petrovic et al., 2003b). Several LC tandem MS–MS methods have been recently reported for these compounds (Jonkers et al., 2001; Houde et al., 2002; Loyo-Rosales et al., 2003; Petrovic et al., 2003a; Schmitz-Afonso et al., 2003; Jahnke et al., 2004). Also doubly carboxylated compounds CAPEC have been identified (Di Corcia et al., 2000; Jonkers et al., 2001).

The objective of the present study was to investigate LC–MS–MS analysis of alkylphenolic contaminants and their occurrence in effluents and surface waters for the determination of contamination trends in the environment. Special emphasis was placed on method optimization using real environmental samples.

## 2. Experimental

### 2.1. Chemicals and reagents

The technical 4-nonylphenol mixture of chain isomers (Aldrich, no. 29,085-8), 4-*tert*-octylphenol (38,444-5) and bisphenol A (23,965-8) standards came from Aldrich. 4-octylphenoxy acetic acid (OPE<sub>1</sub>C), NPE<sub>1</sub>C (d2), 4-nonyl- and 4-octylphenolmono- and diethoxylate (NPE<sub>1–2</sub>O, OPE<sub>1–2</sub>O), NPE<sub>1</sub>O (d2), and 4n-nonylphenol (native and d8) were delivered by Dr. Ehrenstorfer (Augsburg, Germany, <http://www.analytical-standards.com/>). Nonylphenoxy acetic acid (NPE<sub>1</sub>C) was generously provided by Mira Petrovic (CSIC, Barcelona, Spain). The other long-chain APEOs (OPEO and NPEO) were only available in form of a commercial surfactant mixture of different oligomers with an average number of 9 ethoxy groups (Kao Corp., Barcelona, Spain) (Petrovic et al., 2003b). Standards for NPE<sub>2</sub>C and NPE<sub>3</sub>C were not available. Methanol (SupraSolv), ethylacetate (SupraSolv), acetonitrile (LiChrosolv for HPLC), acetone (SupraSolv), and hexane (SupraSolv) were obtained from Merck (Darmstadt, Germany).

Single standard stock solutions of the analytes in the high mg l<sup>-1</sup> range were prepared by weighing mg amounts of the compounds and dissolving in 10 ml methanol or Milli-Q water. The working standard solutions were prepared by further diluting the stock standard solutions with methanol.

### 2.2. Samples and sample pretreatment

Belgian and Italian waters were investigated (Fig. 1). A water sampling campaign was performed on the 17–18 June 2003 in the textile industry region in Belgium south of Ghent. Effluent samples were taken sequentially at three different times at three textile companies, or the corresponding WWTPs, and the receiving waters (River Schelde, Creek Molenbeek and Creek Gaverbeek). The concentrations given are the average values from the three samples taken. The Italian sampling campaign was performed on 19 November 2003 in the textile industry region south of the city Como and in Milan. The WWTP in Fino Mornasco is a modern WWTP including ozone treatment, treating municipal and industrial (textile industry) effluents. The WWTP in Bulgarograsso discharges in the Creek Lura, which was dry.

Grab water samples were collected in 1 l glass bottles, stored at 5 °C, transported to Ispra (Italy), decanted and the supernatant extracted within one week.

### 2.3. Solid-phase extraction

The water samples were extracted by solid-phase extraction (SPE). The SPE procedure for the clean-up and concentration of water samples was performed automatically using an AutoTrace<sup>®</sup> SPE workstation (Tekmar, Cincinnati, Ohio, USA). 200 mg (6 ml) Oasis HLB columns

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