

Occurrence and fate of alkylphenols and alkylphenol ethoxylates in sewage treatment plants and impact on receiving waters along the Ter River (Catalonia, NE Spain)

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Received 10 January 2007; received in revised form 13 August 2007; accepted 13 August 2007

Whereas partitioning of nonylphenol upon particulate matter and enrichment in sludge has been detected, long chain NPE_nO_s were mainly found in the dissolved phase.

Abstract

The partitioning of alkylphenols in the dissolved and particulate matter of influents, effluents, accumulation onto sludge and the impact of sewage treatment plant upon receiving waters was studied along the Ter River basin (Catalonia, NE Spain). A solid-phase extraction or pressurized liquid extraction followed by liquid chromatography–mass spectrometry was developed and permitted to determine target compounds with high efficiency in waters, particulate material and sludge. Nonylphenol mono- and diethoxylate, nonylphenol and octylphenol partitioned preferably upon particulate matter and sludge, whereas long chain NPE_{3–15}O prevailed in the dissolved phase and was released by effluents. Within the treatment process, a net accumulation of alkylphenols in sludge was found, producing up to 148 g/t/month. The removal efficiency of alkylphenols was of 37–90% and depended on the treatment. Assessment on the fate of these contaminants within STPs is discussed in terms of flow rates, biological oxygen demand and tons of sludge produced.

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Keywords: Liquid chromatography–mass spectrometry; Alkylphenols; Water; Particulate matter; Sewage sludge; Sewage treatment plants

1. Introduction

Endocrine-disrupting compounds (EDCs) are exogenous substances that can cause adverse health effects in an intact organism or its progeny (Soto et al., 1991; Jobling and Sumpter, 1993). They are natural and man-made chemicals found in the aquatic environment, and they have received attention in recent years due to the interactions in the hormonal system of organisms or humans.

Among EDCs, nonylphenol (NP), 4-*tert*-octylphenol (OP) and mono- and diethoxylated nonylphenols (NPE_{1–2}O) deserve

special attention not only because of their disrupting properties but rather for the widespread and high concentrations found in the environment. Alkylphenol ethoxylates (APEOs), introduced as detergents in the United Kingdom in 1944 have excellent surface active properties and are one of the most widely used surfactants in the world, used for industrial, agricultural, and domestic applications (Ying et al., 2002). Since then, the production and use of non-ionic surfactants correspond to 90% of alkylphenols (APs) and APEOs. As an example, NPEOs are used in cleaning products, textiles, petroleum, pulp and paper industry and pesticides formulation (Ying et al., 2002). On the other hand, OP is an important chemical intermediate mainly used for the production of phenolic resins and lacquers.

APEOs and their metabolites were restricted or altogether banned in some countries in Europe (Naylor, 1995), and there

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are significant initiatives to reduce their use or phase them out world-wide (Renner, 1997). Thus, throughout northern Europe (Scandinavian countries, UK, Germany) a voluntary ban on APEO use in household cleaning products began in 1995, and restriction on industrial cleaning applications in 2000 (Renner, 1997). Despite these restrictions, APs are detected in high levels in environmental matrices and specifically, NP and OP are included in the priority list of 33 substances of the Water Framework European Directive (WFD) 2000/60/EC (Directive 2000/60/EC), whereas NP is included in the US EPA as non-priority pollutant list (US EPA (non)priority pollutant list, 2006 <http://www.epa.gov>). The environmental concern of these compounds is mainly because of the endocrine-disrupting effects of two short chain NPEO oligomers (NPE₁O and NPE₂O) and the metabolite NP (Routledge and Sumpter, 1996).

One of the main sources of APs in the environment is by direct urban or industrial input or via sewage treatment plants (STPs) effluents which contribute to the levels of APs in the aquatic system, primarily attributed to incomplete removal during sewage treatment processes (Brunner et al., 1988; Ahel et al., 1994a; Lee and Peart, 1995; Harries et al., 1996; Solé et al., 2000; Snyder et al., 2001). The levels encountered in certain sewage effluents and receiving rivers are sufficient to induce a hormonal response in some fish species (Purdom et al., 1994; Harries et al., 1996; Sumpter et al., 1996; Solé et al., 2000; Tsuda et al., 2000). Ahel et al. (1994a) estimated that at least 60–65% of all nonylphenolic compounds entering the STW are discharged to the receiving waters with the effluent and 51% are released as metabolic products after undergoing mechanical and biological treatment (Ahel et al., 1994a). It is reported that within a biological treatment plant, APEOs can be degraded aerobically and anaerobically generating shorter-chain APEs and APs, which were recalcitrant under aerobic conditions (Ying et al., 2002; Birkett and Lester, 2003; Ying, 2006). To further minimize the release of these compounds towards receiving waters, STPs have been designed with additional treatments rather than aerobic/anaerobic and have been installed in areas with more than 15,000 inhabitants.

Within a monitoring program started in Catalonia with the aim to determine the occurrence and fate of APs and APEOs in surface water and the effect of STPs upon water quality, the

objectives of this study were: (i) to set up an analytical method to determine NP, OP, NPE_{1–2}O and NPE_{3–15}O at trace level in water, particulate matter and sludge and to establish the quality parameters of the technique, (ii) to study the partitioning of these five alkylphenolic compounds in dissolved and particulate matter of the Ter River, including influent and effluent waters, (iii) to evaluate the role and efficiency of STP to remove such compounds and (iv) to estimate the accumulation of APs in sludge.

The study area is the Ter River, which supplies 55% of raw water for drinking purposes to Barcelona city and surroundings. With a 3010 km² of basin surface and 208 km long, it originates in the middle of the Catalan Pyrenees (at 2400 m high) and passes through Girona, and leads to the Mediterranean Sea (Alba-Ter Consortium/Agbar Foundation, 2004). This river receives the direct impact of metallurgic, pulp mill, textile and tannery industries and APs and APEOs have been identified as main contaminants (Espadaler et al., 1997; Céspedes et al., 2006).

2. Experimental

2.1. Chemicals and reagents

Table 1 lists the compounds studied and their physico-chemical properties. NPE_{1–2}O was laboratory-synthesized by Aigües de Barcelona. NPE_{3–15}O contained chain isomers and oligomers with an average number of nine ethoxy units and were from Kao Corporation (Barcelona, Spain). High purity OP, technical grade 4-nonylphenol (NP), and 4-heptylphenol (4-HP, used as the internal standard) were from Aldrich (Milwaukee, WI, USA). The internal standard bis(2-ethylhexyl)phthalate (ring-D₄, high purity 98%) was purchased from Cambridge Isotope Laboratories (Cambridge, MA, USA). Stock solutions of individual standards and standard mixtures were prepared at 1000 µg L⁻¹ in methanol. Working standard solutions were obtained by further dilution of stock solutions with methanol.

HPLC-grade solvents (water, methanol, acetonitrile, acetone and dichloromethane) were from Merck (Darmstadt, Germany). Analytical grade sodium acetate was purchased from Panreac (Barcelona, Spain).

2.2. Sample collection

Water samples were collected during spring 2001 in nine points distributed along the Ter River basin (Catalonia, NE, Spain), including Terri and Gurri tributaries, as well as influent and effluent wastewaters and corresponding sludge of five STPs discharging into the Ter River. Table 2 shows the sampling sites corresponding to surface water samples analyzed along the Ter River basin, the total organic carbon (TOC), suspended particulate material (SPM) and

Table 1
CAS number, formula, molecular weight and physico-chemical properties of the compounds analyzed

Compound	Acronym	CAS-no.	Formula	Molecular weight	Water solubility ^a	log <i>K</i> _{oc} ^b	log <i>K</i> _{oc} ^c
4- <i>tert</i> -Octylphenol	OP	104-66-9	C ₁₄ H ₂₂ O	206	12.6	4.12	5.18
4-Nonylphenol, branched	4-NP	84852-15-3	C ₁₅ H ₂₄ O	220	5.43	4.48	5.39
Nonylphenol monoethoxylate	NP ₁ EO	27986-36-3	C ₁₇ H ₂₈ O ₂	264	3.02	4.17	5.46
Nonylphenol diethoxylate	NP ₂ EO	9016-45-9	C ₁₉ H ₃₂ O ₃	308	3.38	4.21	5.18
Nonylphenol <i>n</i> -ethoxylate	NP _{<i>n</i>} EO (<i>n</i> = 3–15)	na	C ₂₁ H ₃₆ O ₄	na	na	na	na

Water solubility (mg L⁻¹), organic water partition coefficient (log *K*_{ow}) and organic carbon sorption constant (log *K*_{oc}).

na, Not available.

^a Ahel and Giger (1993a).

^b Ahel and Giger (1993b).

^c Ferguson et al. (2000).

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