Available online at www.sciencedirect.com
ScienceDirect
Chemosphere 70 (2007) 281–287
CHEMOSPHERE
www.elsevier.com/locate/chemosphere

Seasonal variation of hydrophobic organic contaminant concentrations in the water-column of the Seine Estuary and their transfer to a planktonic species *Eurytemora affinis* (Calanoïd, copepod). Part 2: Alkylphenol-polyethoxylates

K. Cailleaud [a,b,c], J. Forget-Leray [c], S. Souissi [b], S. Lardy [a], S. Augagneur [a], H. Budzinski [a,*]

[a] *Université Bordeaux 1, ISM-UMR 5255 CNRS, Laboratoire de Physico-Toxico-Chimie de l'Environnement (LPTC), 351 Cours de la Libération, 33405 Talence, France*
[b] *Université des Sciences et Technologies de Lille, Ecosystèmes Littoraux et Côtiers (UMR 8013 CNRS), 32 avenue Foch, 62930 Wimereux, France*
[c] *Faculté des Sciences et Techniques du Havre, Laboratoire d'Ecotoxicologie-Milieux Aquatiques (UPRES EA3222), GDR IMOPHYS, 25 Rue Philippe Lebon, 76058 Le Havre, France*

Received 18 September 2006; received in revised form 28 May 2007; accepted 6 June 2007
Available online 1 August 2007

Abstract

The occurrence and fate of alkylphenols in various matrices of the Seine River Estuary were studied. Nonylylphenols (NP) and nonylphenol polethoxylates (NPEs) were monitored in surface dissolved water, suspended particulate matter (SPM) and in a copepod, *Eurytemora affinis* from November 2002 to January 2004. NPs, nonylphenol mono and diethoxylates (NP1EO, NP2EO) and nonylphenol-ethoxy-acetic-acid (NP1EC) were detected and measured in all dissolved water and SPM samples whereas nonylphenoxy-acetic-acid (NP2EC) was only found sporadically in dissolved water samples. Seasonal variation of total concentrations of NPs and NPEs, ranging, respectively from 399 to 2214 ng l^{-1} and from 405 to 9636 ng g^{-1}, were measured in the dissolved water and in the SPM. Significant decreases were observed in the water-column during the maximum biological activity periods in spring and autumn. Furthermore, increasing levels were observed in the SPM during the winter period. High concentrations of NP1EO and NP were detected in all copepod samples, ranging from 3423 to 6406 ng g^{-1}. This study is the first to report high levels of endocrine disruptors in estuarine copepods.

Keywords: Nonylphenol; Crustacean; Bioaccumulation; Estuary; Water- column; Alkylphenol-polyethoxylates

1. Introduction

Since the 1960s, increasing numbers of environmental organic contaminants have been found in aquatic ecosystems, often with high and increasing concentrations. During recent decades, reproductive and developmental diseases reported for a wide range of aquatic species (Krimsky, 2000; Vos et al., 2000; Yadetie and Male, 2002), have shifted the attention slightly towards other sources of industrial and agricultural contaminants. These adverse effects on the physiology and particularly on the hormonal regulation of exposed organisms are generally ascribed to molecules so-called endocrine disruptors. Depending on their molecular structure, some of these chemicals have been listed as priority compounds by regulating bodies (European Union and the Oslo and Paris Commission). Among all those contaminants, the harmful effects of many surfactants, such as alkylphenol-polyethoxylates and their metabolites, are highlighted due to their endocrine-disrupting properties and because of their increasing concentrations in aquatic ecosystems (Thomas et al., 1999; Ferguson et al., 2003; Isidori et al., 2006).

* Corresponding author. Tel.: +33 5 40006998.
E-mail address: h.budzinski@lptc.u-bordeaux1.fr (H. Budzinski).

0045-6535/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2007.06.012

Alkylphenol-polyethoxylates (APnEs), where n indicates the number of ethoxy units, are high production volume non-ionic surfactants, widely used in various industries and agriculture. Nonylphenol-polyethoxylates (NPnEOs) are by far, the most commonly used and synthesized APnEs, accounting for about 80% of total APnEs (Renner, 1997). The annual worldwide production is about 500 000 tons, with a European annual usage of 73 500 tons (E.U., 1999). These molecules are used in numerous applications (detergents, wetting agents, emulsifiers, pesticide formulations and many industrial sectors). To date, NPnEOs have not been banned in Europe, but their use and sale have been drastically restricted. Therefore, these compounds have been entirely replaced by alcohol-ethoxylates in household detergents in the EU and in the USA.

These contaminants are released directly or through sewage plants, with or without treatment, into aquatic ecosystems. NPnEOs are unstable in aquatic environment and subject to biodegradation. Some degradation pathways have been proposed and studied both in field and laboratory experiments (Ying et al., 2002; Hayashi et al., 2005). Thus, the biodegradation of NPnEOs results in successive formation of lower ethoxylate congeners. On the one hand, during aerobic processes, the polyethoxylate chains are oxidized, producing mainly nonylphenol-ethoxy-acetic-acid (NP1EC), nonylphenoxy-acetic-acid (NP2EC) and nonylphenols (NP) (Ahel et al., 1994; Hayashi et al., 2005). On the other hand, during anaerobic processes, polyethoxylate chains are hydrolyzed into various metabolites (NP1EO and NP2EO) as shown in Fig. 1. Final degradation products (nonylphenol, octylphenol etc.) are more stable and more hydrophobic and thereby preferentially adsorbed on the suspended particulate matter or in the sediments.

Most NPnEOs entering the environment are highly water soluble. Eighty percent of these compounds are detected in the dissolved phase and 20% in the suspended particulate matter (Isobe et al., 2001). The occurrence of NPnEOs in freshwater environments has been substantially reported (Thiele et al., 1997). However, their occurrence, their fate and their transfer to organisms in estuarine systems are less known (Heemken et al., 2001; Stachel et al., 2003). In this respect, microzooplanktonic organisms are key species in the estuarine food-web which could ensure a principal role in the transfer of contaminants to top predators. In addition, the organisms placed on top of food chains could be affected by the presence of APs in their food, as well as in the dissolved phase and in the SPM. These aspects are of particular interest in the Seine River Estuary (France), where organic as well as inorganic pollution from urban and industrial activities has been extensively studied (Chiffoleau et al., 1994; Fernandez et al., 1997). However, no data is available about the contamination by NP and NPnEO. Furthermore, these compounds are known to exhibit higher toxicity than their precursors, and to mimic estrogens in the hormonal regulation. Thereby, NPnEOs, NPnECs and NPs are of toxicological interest, because of their potential bioaccumulation in

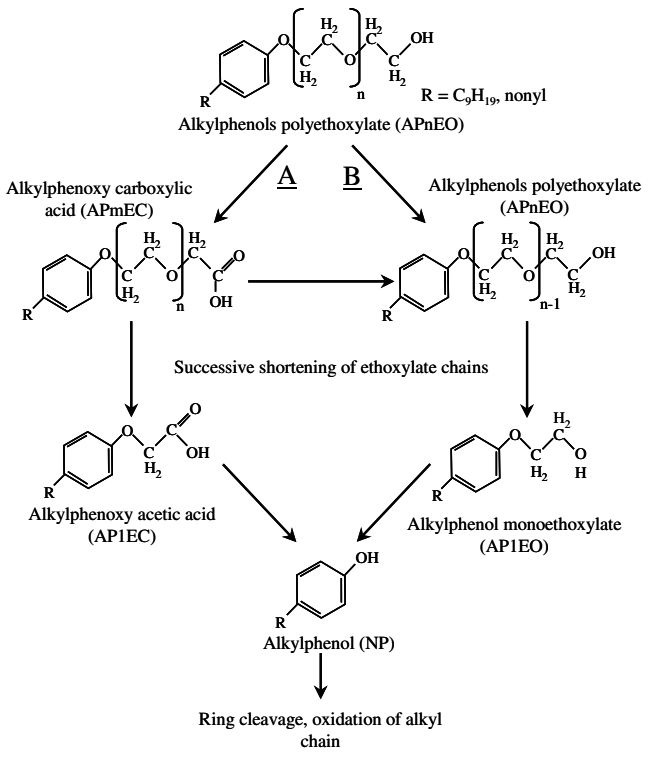

Fig. 1. Biodegradation routes of alkylphenol-polyethoxylates: (a) the oxidative hydrolytic (aerobic) pathway and (b) the non-oxidative hydrolytic (anaerobic) pathway (according to Fenner et al., 2002).

organisms which could be exposed via sediments or via the dissolved phase (Cross-Sorokin et al., 2003), and because of their acute and chronic toxicity (Brown et al., 1999; Forget-Leray et al., 2005).

The present study, which is the second part of a series of two articles, focuses on the occurrence of $NP_{1-2}EOs$, $NP_{1-2}ECs$, and NPs in the water-column of the Seine Estuary and their fate related to seasonal variation. The analysis of various metabolites, and particularly NP/NPEOs and NP/NPECs ratios, gave insight into biodegradation processes involved in this estuary. Besides the potential transfer of these chemicals to a dominant copepod species in many North Atlantic estuaries, *Eurytemora affinis*, has been investigated to estimate the possible endocrine-disrupting hazard of such contaminants on estuarine invertebrates, and the threat to the local food-web integrity.

2. Material and methods

2.1. Sample collection

Surface water and copepod samples were collected from November 2002 to February 2005 at the Tancarville station in the oligohaline part of the Seine Estuary (France) using the Seine-Aval Research Program boat. All the samples were collected 150 m away from the Tancarville sewage treatment plant (STP). The sampling strategy and the environmental parameters of each cruise have been detailed in