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Identification and chemical characterization of specific organic indicators in the effluents from chemical production sites

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ABSTRACT

The structural diversity of the wastewater composition was described by the use of detailed non-target screening analyses of industrial effluents from chemical production sites. Determination of the indicative organic compounds acting as potential molecular indicators for industrial emissions from chemical production industries has been possible due to (i) detailed characterisation of industrial contaminants and identification of compounds with high source specificity, (ii) quantitative determination of the organic constituents in the industrial effluents and (iii) the review of their industrial applications. The determination of potential site-specific markers and industrial molecular indicators corresponding to certain production processes (production of starting materials for manufacturing paper and printing inks, powder coatings as well as epichlorohydrin production) was performed in this work.

The results of this study allowed significant contributions to the chemical characterisation of industrial contaminants and isolation of indicators that can act as representatives of industrial effluents in the aquatic environment.

1. Introduction

Chemical production plants represent a substantial source of contamination introduced into the aquatic environment. They produce a wide range of compounds including pharmaceuticals, plant and crop-protecting agents, solvents, plasticizers, antioxidants, thermal stabilizers, ultraviolet light absorbers, optical brighteners, surfactants and other chemical products. Being emitted at a significant concentration level, organic compounds in the chemical effluents normally possess a high structural diversity and reveal notable ecotoxicological effects. Within a wide range of industrial contaminants associated with synthetic products, and by-products as well as with those formed during wastewater treatment, many of them are unknown as far as structural characteristics and environmental behaviour are concerned. So far the composition of industrial effluents has been investigated comprising industrial sites of various production branches, i.e. paper, textile, tannery and leather industry as well as chemical manufacturing (Smith, 1990; Knepper, 2002; Morisawa et al., 2003; Rojas and Ojeda, 2005; López-Grimau et al., 2006; Soupilas et al., 2008). In a previous study we have made an attempt to identify possible markers for petrochemical industrial activities (Botalova et al., 2009).

Besides a high structural diversity of their constituents, industrial effluents have often had pronounced ecotoxicological effects on aquatic organisms. Investigations on the toxicological and ecotoxicological properties of industrial effluents have been performed in a number of studies (Castillo et al., 2001; Hewitt and Marvin, 2005). Phthalate esters used in the production of various plastics (including PVC) are among the most common industrial

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chemicals. These contaminants together with the food antioxidant butylated hydroxyanisole have revealed estrogenic activity in fish and mammalian tests (Jobling et al., 1995). Genotoxicity of acridine derivatives detected in industrial waters in the Netherlands has been shown by Bobeldijk et al. (2002). The authors reported a first observation in surface water of hexamethoxymethylmelamine, a chemical often used in coating industry. In the effluent from a semi-conductor equipment manufacturer Labunska et al., 2008 found concentrations of 36 μg/L chloroform and 65 μg/L highly toxic and carcinogenic tetrachloromethane, which had been discharged into a river.

There are a number of ecotoxicological studies performed on wastewaters from chemical manufacturing sites (Jop et al., 1991; White et al., 1996; Soupilas et al., 2008). Ecotoxicological investigations have been carried out on complex effluents from a chemical plant in Italy producing synthetic rubbers, latexes of synthetic rubber, acrylonitrile butadiene styrene resins, dimethylcarbonate and derivatives (two-ring phenols, phenolic antioxidants, esters of diethylenglycol), fertilizers (ammonium nitrate, compound fertilizers), etc (Guerra, 2001). The evaluation of ecotoxicological response has been performed in the tests with *Daphnia magna, Vibrio fisheri, Artemia salina, Brachionus plicatillis*. Ecotoxicological investigations were carried out by Swartz et al. (2003) in the wetlands adjacent to an industrial area with a number of chemical factories, i.e. a chlor-alkali plant, located in the Republic of Azerbaijan. The results of the study showed the acute toxicity in fish tests with Russian sturgeon (*Acipenser gueldenstaedti*) as well as potential mutagenicity in Caspian turtles (*Mauremys caspica*).

Determination of specific molecular indicators in wastewaters from certain industrial branches or production processes can be useful to distinguish various industrial pollution sources. Despite numerous investigations performed on the characterisation of effluents discharged by chemical production plants, there is a gap in information on the specificity of contaminants in terms of their molecular structure. This approach does not consider tracing of synthetic products appearing in industrial effluents, which are likely to be found in municipal sewage wastewater as well. It is rather focused on the identification of industrially related contaminants like synthetic precursors, intermediates and by-products in industrial effluents. These particular molecular structures are specific in relation to a certain industrial branch or production process. The aims of this work are (i) to characterise in detail organic chemical composition in the effluents from a set of industrial sites and (ii) to isolate specific compounds that might act as source indicators (site-specific markers and branch-specific indicators). Some compounds are found in the wastewater exclusively from a certain industrial site discharging its effluents into a river. If detected in the water of the same river along the flow only after the discharge point of this industrial site, they can act as site-specific markers. As an important precondition, these contaminants appear neither in the effluents from other industries contaminating the river nor in the river water affected by other industrial discharges. Branch-specific indicators are related to the corresponding production processes taking place at the chemical sites. Monitoring and identification of such molecular indicators would substantially contribute to the efficient point source identification.

2. Methods and materials

2.1. Samples

Samples of wastewaters subject to biological and chemical treatment before their discharge into a river were collected from five chemical production plants (defined as A, B, C, D, and E) situated in North-Rhine Westphalia, Germany. Information on single grab samples provided for the analyses is given in Table 1. Sampling campaigns at industrial complex A took place four times in summer 2007 (27.06; 19.07; 02.08; 15.08). Effluent samples from industrial sites B, C, D and E were collected in November 2007.

The wastewater samples were filled in thoroughly pre-cleaned 1 L aluminium bottles with alumina coated screw caps and stored in the dark at a temperature of 4 °C.

2.2. Chemicals and glassware

Only glass, metal and PTFE equipment were used in the laboratory in order to minimise possible contamination. All glassware was cleaned by ultrasonic agitation in water containing detergent (Extran, Merck, Germany) and rinsed with water followed by high-purity acetone and *n*-hexane. The solvents were purchased from Merck, Germany, and distilled over a 0.5 m packed column (reflux ratio approximately 1:25). The solvent purity was tested by gas chromatographic analyses. Anhydrous granulated sodium sulphate (Merck, Germany) and hydrochloric acid (Merck, Germany) needed for the analytical procedure were cleaned by their extraction with pure acetone. The results of blank analyses indicated that none of the compounds presented in this study was detected in the blank.

2.3. Extraction

The extraction method used has been previously described in detail (Dsikowitzky et al., 2002). Briefly, a sequential liquid–liquid extraction procedure was applied to approximately 500 mL and 1000 mL aliquots of the wastewater and river water samples, respectively, using *n*-pentane, dichloromethane and dichloromethane after acidification to pH 2 with hydrochloric acid. 50 mL

Table 1 – Sampling of the wastewater from chemical production sites.

Site	Sampling locations	Date of sampling
Industrial site A	–Outflow A	4 sampling campaigns: 27.06.2007 19.07.2007 02.08.2007 15.08.2007
Industrial site B	–Outflow B1	08.11.2007
	–Outflow B3	22.11.2007
	–Outflow B4	22.11.2007
Industrial site C	–Outflow C1	21.11.2007
	–Outflow C2	07.11.2007
Industrial site D	–Outflow D1	19.11.2007
	–Outflow D2	
Industrial site E	–Outflow E	12.11.2007