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Identification and chemical characterization of specific organic constituents of petrochemical effluents

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ABSTRACT

Based on extensive GC/MS screening analyses, the molecular diversity of petrochemical effluents discharged to a river in North Rhine-Westphalia was characterised. Within a wide spectrum of organic wastewater constituents, specific compounds that might act as source indicators have been determined. This differentiation was based on (i) the individual molecular structures, (ii) the quantitative appearance of organic compounds in treated effluents and (iii) the information on their general occurrence in the technosphere and hydrosphere. Principally, site-specific indicators have been distinguished from candidates to act as general petrochemical indicators. Further on, monitoring the environmental behaviour of target organic contaminants in an aquatic system shortly after their release into the river allowed a first evaluation of the impact of the petrogenic emission in terms of the quantity and spatial distribution.

The identification of petrogenic contaminants was not restricted to constituents of the effluents only, but comprised the compounds circulating in the wastewater systems within a petrochemical plant. A number of environmentally relevant and structurally specific substances that are normally eliminated by wastewater treatment facilities were identified. Insufficient wastewater treatment, careless waste handling or accidents at industrial complexes are potential sources for a single release of the pollutants.

This study demonstrates the relevance of source specific organic indicators to be an important tool for comprehensive assessment of the potential impact of petrochemical activities to the contamination of an aquatic environment.

1. Introduction

Industrial effluents contribute significantly to the contamination of surface water systems. Since the types of industries discharging waste to rivers and lakes cover a wide range of industrial branches the quality and, consequently, the resulting environmental impact or risk of these effluents is varying. However, generally the industrial wastewaters tend to carry a huge load of organic and inorganic pollutants. In particular, organic pollutants not only appear in industrial effluents at high concentrations but also exhibit a high diversity with respect to their molecular structures. Therefore, a wide range of organic contaminants, comprising for example pesticides, mono- and polycyclic aromatic hydrocarbons, polychlorinated biphenyls (PCBs) as well as many phosphorous- and sulphur-containing compounds have been identified in industrial wastewaters, and their behaviour in natural aqueous systems have been investigated to some extent (Castillo et al., 1998; Alonso and Barceló, 1999; Miermans et al., 1999; Guerra, 2001; Crowe et al., 2002; Dsikowitzky

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et al., 2004a,b; Zhang et al., 2008; Schwarzbauer and Heim, 2005). However, many of these contaminants remain unspecific with respect to the type of industrial effluents. For example, in aqueous (e.g. wastewaters, industrial discharges, treated effluents) and solid samples from a wastewater treatment plant in Italy, 16 PAHs were determined approximately in the 1.12–4.62 μg/L range (Busetti et al., 2006). Determination of non-halogenated solvents (toluene, xylenes, ethylbenzene and diisobutylketone) in textile industrial wastewater was performed with head-space solid phase micro-extraction h-SPME (López-Grimau et al., 2006). Castillo and Barceló reported the appearance of phenol, nonylphenol isomers and phthalate esters in the effluents of a textile industry in Portugal (1999). However, indicative compounds reflecting specific industrial processes and the corresponding chemicals have been reported rarely. The degradation products of azo dyes, such as 6-acetylamino-3-aminonaphthalene-2-sulfonic acid, *N*-(3,4-bishydroxymethylphenyl)acetamide, aromatic amines and anilines can pose a hazard to the aquatic environment (Pinheiro et al., 2004; Bilgi and Demir, 2005).

The environmental impact of industrial effluents has been pointed out by numerous ecotoxicological studies (Burkhard and Ankley, 1989; Burkhard et al., 1991; Hao et al., 1996; Chen et al., 1999; Kungolos, 2005a,b; Hewitt and Marvin, 2005). The identification of a variety of benzothiazoles and more polar organics as major toxic compounds was performed in tannery effluents with *Vibrio fischeri* tests (Fiehn et al., 1997; Reemtsma et al., 1999a,b). Significant amounts of polyethylene glycol, polyethoxylate decylalcohol and linear alkylbenzene sulfonates were found to be major constituents in textile wastewaters. High concentration levels were found for some benzene- (BS) and naphthalenesulfonates (NPS) which are used in the textile industry as dye bath auxiliaries (Castillo and Barceló, 2001). The authors argued that toxicity observed in the effluents from textile industries to *Daphnia magna* can be attributed to nonylphenol isomers, alcohol polyethoxylated, nonylphenol ethoxylates and several phthalates.

Due to the enormously increasing importance of petroleum for the industrial development during the last century, petrochemical effluents have had a significant impact on the pollution of surface water systems. Moreover, petrochemical discharges have been proved to induce notable ecotoxicological effects, e.g. particle-associated genotoxins are released into aquatic environment by emissions from oil industries (White et al., 1996). Mutagenic activity of petroleum hydrocarbons was studied on microbiological cultures obtained from river waters under influence of discharge from petrochemical industrial effluents (Vargas et al., 1993), and in soil receiving the leachate water from petroleum sludge (Brown and Donnelly, 1984). The genotoxicity of the aromatic compounds and PAHs from the wastewater emitted by various petrochemical industries in France was observed directly *in vivo* tests with amphibian larvae by Gauthier et al. (1993). De Lemos et al. (2007) using fish tests proved the genotoxicity of the PAHs and petroleum hydrocarbons in the river water obtaining petrochemical effluents in southern Brasil.

Several studies covering various organic substances of petrochemical origin that affect the aquatic environment have been performed in the last decades (Wise and Fahrenthold, 1981; Clements and Cheng, 1982; Field et al., 1991; Kuo et al., 1996; Castillo and Barcelo, 1999; Olmos et al., 2004; Nadal et al., 2007; Grigoriadou et al., 2008a,b). However, most of these studies focussed on the contamination of aquatic systems and did not analyse the responsible composition of the industrial effluents.

It has to be stated, that there is a lack of systematic investigations on petrogenic pollutants in industrial wastewaters as well as of the information on their environmental relevance. The approach described in this work is not considered by current measures in the field of environmental regulations. Actually, monitoring of industrial emissions are focused predominantly on bulk parameters, such as TOC, AOX, BOD, N, P, heavy metals and selected organic pollutants (chlorinated benzenes, phenols, pesticides, brominated organic compounds, estrogens, PAHs, PCBs, phthalates, tensides) as well as ecotoxicological test systems.. First attempts to take into account individual pollution characteristics are implemented in the EU Water Framework Directive by accounting for specific contaminants in river basins. Therefore, this work is aimed to characterize the composition of petrochemical effluents discharged to a river in North Rhine-Westphalia, and to isolate specific compounds that might act as source indicators. These indicator substances, typical for oil production industries and unique signatures of petrochemical effluents shall allow efficient source identification in polluted aquatic systems.

2. Methods and materials

2.1. Samples

Sewage water samples were taken from two petrochemical industrial sites (designated as A and B) located in North Rhine-Westphalia, Germany. Sampling details are described in Table 1. Wastewater effluent samples from industrial site A were collected on 19.11.2007. This company is producing industrial oil

Table 1 – Sampling of wastewater from industrial sites and water from the river subject to the effluent discharge.

Site	Sampling locations	Date of sampling
Industrial site A	- Outflow	19.11.2007
Industrial site B	- Waste deposit leakage water	3 sampling campaigns:
	- BTX production	07.08.2007,
	- After de-oiling and CO_2 stripping	23.08.2007,
	- Outflow	23.10.2007.
River (under discharge from industrial site B)	- 4 km upstream the industrial source	
	- 0.4 km, 1.3 km, 7.5 km and 15 km downstream the industrial source	10.07.2008