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Toxicity of water and sediment in a small urban river (Store Vejleå, Denmark)

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It is recommended that both chemical and biological methods should be used in risk assessments for sediment toxicity.

Abstract

The urban stream Store Vejleå (Denmark), which receives discharges of urban runoff, was investigated using a combination of biological toxicity tests and chemical analysis. The urban stormwater and road runoff gave low, but statistically significant, effects on the reproduction of the alga *Pseudokirchneriella subcapitata*. In all pre-concentrated water samples toxic effects were found and differences in toxicity depending on time and location of sampling were identified. Undiluted pore water samples from sediments collected in the stream were all toxic towards the algae and dilutions from 4 to 14 times were needed compared to a pore water sample from an unpolluted stream where a dilution factor of only 1.6 was required. A qualitative correlation between the toxicity of the pore water and the degree of pollution as evidenced by the metal concentration was observed, but statistically significant correlations could not be established by ranking procedures of, e.g. metal content or PAH-concentrations versus the observed toxicity.

Keywords: Biotests; Pore water; Solid phase extraction (SPE); Toxicity; Urban storm water

1. Introduction

The environmental impacts of urban stormwater and road runoff are gaining increased attention internationally. In Europe, the adoption of the Water Framework Directive (Directive 2000/60/EC) has emphasised the need for addressing potential problems arising from discharge of urban stormwater. Several studies have described physical, chemical, and biological problems related to these types of discharges (e.g. Maltby et al., 1995a, b; Marsalek et al., 1999). It has been documented that heavy metals and PAHs accumulate in sediments related to urban stormwater and a range of different organic chemicals have been found in the water phase (e.g. Maltby et al., 1995b; Carr et al., 2000). Many of the compounds are known to be toxic to animals and humans and to have potential for carcinogenic, mutagenic and/or allergenic effects (Ledin et al., 2004; Eriksson et al., 2005). However, the potential ecotoxicity of the chemicals present in urban runoff is not well described in the literature, though a number of studies dealing with toxicity assessment of urban wet-weather discharges have been published (review by Marsalek et al., 1999). Wet-weather discharges have complex compositions and an analytical-chemical characterisation may not suffice in explaining the toxic potential (Ellis, 2000). An alternative monitoring strategy using a battery of toxicity tests has been pointed out as a useful tool for screening and assessing potential receiving water impacts (Marsalek et al., 1999), however, only few actual studies have been carried out.

The present study focused on measuring toxicity both in the water and in the sediment phase in the stream Store Vejleå located 20 km west of Copenhagen (Denmark). The water in the

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stream originates primarily from discharges of urban stormwater and road runoff. As a result of previous investigations (Kjølholt et al., 2001) it was expected that the toxicity of stream water was low, but also that organic chemicals were present in the water phase. Therefore, two approaches for toxicity testing were applied to water samples: (1) direct testing of whole samples and (2) testing of samples fractionated and pre-concentrated by solid phase extraction (SPE) in order to quantify the toxicity of non-volatile organic chemical contaminants in the water phase. Furthermore, toxicity testing of pore water from sediments collected in Store Vejleå was included in the study.

The aim of the study was to address the order of magnitude of toxic effects of chemical constituents in water samples, not to make simulations of in situ toxicity. As a consequence of this, all samples were grab samples collected on different occasions and were therefore not flow-, weather-, or time-dependent samples. Standardised toxicity tests were applied. The biotests were used as indicators for toxicity and hazard ranking of both the sediment and the water samples and two freshwater test species, that represent the primary producers and zooplankton, were used throughout the study, i.e. the alga *Pseudokirchneriella subcapitata* and the crustacean *Daphnia magna*.

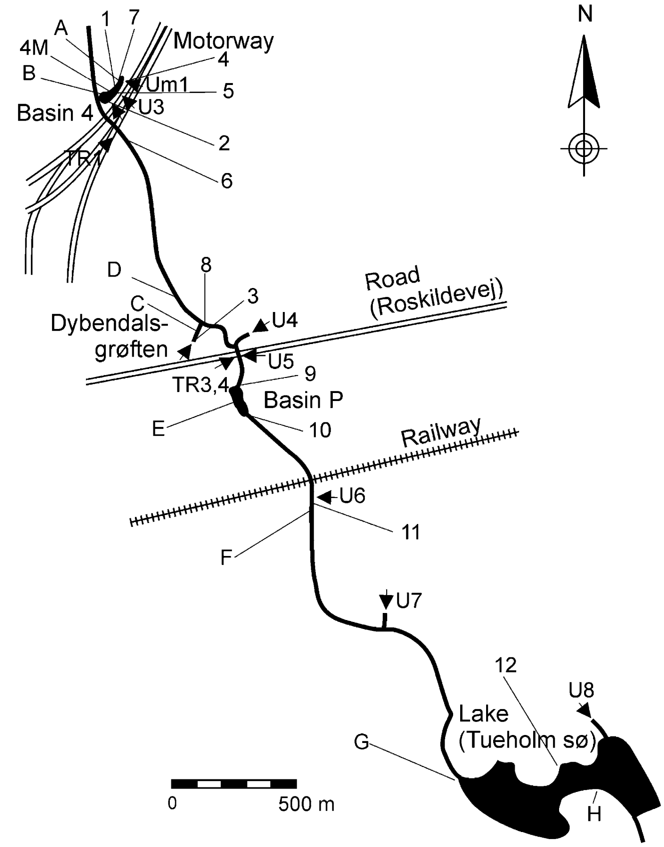

Fig. 1. Map of Store Vejleå, Denmark. Inlets are illustrated with arrows, water samples with numbers (1–12) and sediment samples with letters (A–H, 4M).

2. Materials and methods

2.1. Site description and sampling procedure

The stream Store Vejleå, shown in Fig. 1, is dry most of the year upstream of the inlet from Basin 4. Basin 4 is a detention pond, which receives runoff water from both a motorway and an urban area. About half of the water in the stream originates from Basin 4, and around one third of the water flow in the stream can be attributed to the inlet from "Dybendalsgrøften", which can be characterized as urban runoff. The stream Store Vejleå has several small inlets connected to the urban rainwater system (cf. Fig. 1).

A total of 12 water samples (grab samples on four occasions in 2001) and 9 sediment samples were collected from both the stream and the inlets to the stream (see Fig. 1). Additionally, one water sample and one sediment sample were taken in an unpolluted stream (Fønstrup Bæk, Denmark). Sediment samples were taken with a tube made out of plexiglass, it was carefully pressed down in the sediment and a plug was put on the top of the tube, the top 5 cm were discharged and the next teen centimetres were used for the sample. Each sediment sample consisted of ten increments. All of the samples were collected in acid washed bottles and kept at 4 °C. Sediment samples were sieved in the laboratory (1.5 mm) to remove larger particles. The samples were adjusted to approximately the same dry weight by letting the sediment settle and remove a certain amount of water. The sediment was shaken to ensure homogeneity before samples were taken to biotests and chemical analyses. Biotests were performed immediately after sampling.

2.2. Chemical analyses

Water samples were analysed for general hydro-chemical parameters (pH, electric conductivity, temperature, oxygen, ammonium and chloride) and non-volatile organic carbon (NVOC). Concentrations of benzene, toluene, ethylbenzene, and xylenes (BTEX-compounds) were analysed by GC-FID. In water samples the concentrations of Pb, Cr, Cu and Zn were analysed using an AAS with graphite furnace and all sediment samples were analysed for the metals: Cd, Cr, Cu, Ni, Pb and Zn by AAS-flame. Prior to sediment analysis a known amount (about 1–2 g DM) was mixed with HNO_3 (7 M, 20 ml) followed by autoclaving for 30 min, the samples were filtrated and diluted with water (DS 259, 1982). Furthermore, the concentrations of PAHs were analysed in sediment samples by GC/MS. The extraction procedure prior to GC/MS-analysis was as follows: a known amount (about 5 g) of wet sediment was well mixed with sodium sulphate (anhydrous). n-Pentane (40 ml) was added to the dried sediment in an amber glass bottle. The bottle was shaken for 1 h (100 rpm) in the dark at 20 °C. The pentane was recovered by centrifugation and the extraction procedure was repeated 3–6 times with new solvent until the recovered pentane was clear. The recovered pentane was concentrated by flushing with air.

2.3. Solid phase extraction

Pre-concentration by means of solid phase extraction (SPE) at pH 7.0 followed by biotests, as described by Baun and Nyholm (1996), was used to investigate the toxicity of organic chemicals in the water phase. Isolute ENV+ columns were used as SPE resins.

2.4. Biotests

Two standardized biotests were chosen as indicators of toxicity for hazard ranking of the contaminated samples. Algal bioassays were carried out according to the ISO-standard for algal toxicity testing (ISO, 1989a) applying a mini-scale test version as described by Arensberg et al. (1995). Six untreated controls were included in all tests. The test vials were incubated on a shaker (100 rpm) in continuous white fluorescent light (80–100 μE/m^2 per s) at 20 ± 2 °C. The tests were conducted at pH 8.1 ± 0.2 with typical control growth rates of 1.7–1.9/day. Algal growth rates were determined from acetone extractions as described by Mayer et al. (1997). Concentration–response curves were described by the Weibull equation, which was fitted to data using non-linear regression applying a computer program developed by Andersen et al. (1998). Pore water testing was used to assess the toxic effects of