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First comprehensive screening of lipophilic organic contaminants in surface waters of the megacity Jakarta, Indonesia

L. Dsikowitzky [a,*], M. Sträter [a], Dwiyitno [a,b], F. Ariyani [b], H.E. Irianto [c], J. Schwarzbauer [a]

[a] Institute of Geology and Geochemistry of Petroleum and Coal, RWTH Aachen University, Lochnerstrasse 4-20, 52056 Aachen, Germany
[b] Research and Development Center for Marine and Fisheries Product Processing and Biotechnology (BBP4KP), Ministry of Marine Affairs and Fisheries, Jl. K.S. Tubun, Petamburan VI, Jakarta Pusat 10260, Indonesia
[c] Research Center for Fisheries Management and Conservation, Ministry of Marine Affairs and Fisheries, Gedung Balitbang-2, Jl. Pasir Putih II, Ancol Timur, Jakarta 14430, Indonesia

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ABSTRACT

Jakarta is an Indonesian coastal megacity with over 10 million inhabitants. The rivers flowing through the city receive enormous amounts of untreated wastewaters and discharge their pollutant loads into Jakarta Bay. We utilized a screening approach to identify those site-specific compounds that represent the major contamination of the cities' water resources, and detected a total number of 71 organic contaminants in Jakarta river water samples. Especially contaminants originating from municipal wastewater discharges were detected in high concentrations, including flame retardants, personal care products and pharmaceutical drugs.
A flame retardant, a synthetic fragrance and caffeine were used as marker compounds to trace the riverine transport of municipal wastewaters into Jakarta Bay. These markers are also appropriate to trace municipal wastewater discharges to other tropical coastal ecosystems. This application is in particular useful to evaluate wastewater inputs from land-based sources to habitats which are sensitive to changing water quality, like coral reefs.

1. Introduction

Indonesia is the world's fourth most populous country and a center of marine biodiversity (Roberts et al., 2002). As in many other emerging economies, the rapid economic growth is accompanied by a migration towards the cities. The greater Jakarta area, Jabodetabek, is the main center of the Indonesian economic activity. It accounts for 12% of the GNP, 61% of the country's financial activities and 31% of the domestic industrial output. Moreover, Jabodetabek is the largest concentration of urban population in Indonesia (Nur et al., 2001).

The rapid growth of this coastal megacity strongly enhanced the usage of freshwater resources for domestic and industrial purposes. The 13 rivers which flow through Jakarta City and discharge into Jakarta Bay receive wastewaters from >10 million inhabitants. Wastewaters from flush lavatories are collected in septic tanks and disposed separately. A large proportion of the other wastewaters remains untreated and flows directly from the households into open channels which are connected with the rivers/channels. The Jakarta river systems therefore receive large amounts of untreated or partially treated municipal wastewaters and transport the contaminant loads towards Jakarta Bay.

The occurrence of some organic contaminant groups in water, sediments and economic important mussel species from Jakarta Bay was previously studied. This includes polycyclic aromatic hydrocarbons (PAHs), DDT (bis(chlorophenyl)trichloroethane) and DDT-metabolites, polychlorinated biphenyls (PCBs), tributyltin (TBT), polybrominated diphenyl ethers (PBDEs), hexachlorocyclohexanes (HCHs) and linear alkylbenzenes (LABs) (Williams et al., 2000; Monirith et al., 2003; Sudaryanto et al., 2007a, b, Rinawati et al., 2012; Harino et al., 2012; Falahudin et al., 2013). Dsikowitzky et al. (2014a) reported exceptionally high concentrations of the insect repellent N,N-diethyl-*m*-toluamide (DEET) in river water samples from Jakarta City and also showed the presence of this contaminant in seawater samples taken in the Jakarta Bay.

In contrast to the many studies about organic contaminants in Jakarta Bay, the river pollution in Jakarta City regarding organic contaminants was less intensively investigated. The present study therefore provides the first comprehensive survey of organic contaminants occurring in the rivers receiving wastewaters from the tropical megacity Jakarta. The contaminant spectrum in surface waters of Jakarta City might be completely different from that known from industrial nations of the northern hemisphere. Therefore, we made use of a non-target GC/MS (gas chromatography–mass spectrometry) screening which allows for the identification of a wide range of lipophilic organic contaminants. This allows the identification of those site-specific compounds that represent the major and most harmful contamination

* Corresponding author.
E-mail address: loga-pub@emr.rwth-aachen.de (L. Dsikowitzky).

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of the cities' water resources. The compound spectrum detectable with this approach is restricted to volatile, low-molecular weight non-polar to semi-polar organic substances.

In specific, we addressed the following objectives: i) identification of the most relevant organic contaminants in Jakarta river water in terms of detection frequency and concentrations and assessment of the contamination sources, ii) comparison of the detected contaminant spectrum to that of other urban areas, and iii) assessment of the distribution of selected contaminants in Jakarta coastal waters to identify pollution hotspots and to track the riverine contribution to the pollution of the Jakarta Bay.

2. Experimental

2.1. Study area and sampling

The study area has a tropical monsoon climate. The Northwest monsoon (October–March) brings rainfall to the Jakarta area, whereas the Southeast monsoon (April–September) coincides with the dry season. 13 rivers flow through the greater Jakarta region (called Jabodetabek) and discharge into the relatively shallow Jakarta Bay, of which the Ciliwung River, Citarum River and Cisadane River have the biggest catchment areas (Fig. 1). Modelling results revealed an average total discharge of the rivers entering Jakarta Bay of 204.8 ± 97.4 $m^3 s^{-1}$ in 2012. The water circulation within the Jakarta bay shows a counter clockwise pattern with water masses leaving in north-eastern direction (van der Wulp et al., 2016).

Water samples from the rivers flowing into Jakarta Bay were taken on October 6–7, 2012 (Fig. 1). Water samples were also taken at 22 stations in Jakarta Bay on October 2–4, 2012. The samples were stored at 4 °C at BBP4KP in Jakarta and transported cooled within three days to Germany. At RWTH Aachen University, the samples were stored at 4 °C and processed within three weeks.

2.2. Chemicals, blanks and recovery experiments

Reference materials of the identified compounds were purchased from Sigma-Aldrich, Germany. Blank analyses (n = 2) were run to determine background concentrations of the investigated compounds. They revealed that none of the compounds considered for this study were detected in the blank. Recoveries (n = 3) were determined by spiking 1 L high-purity water (Lichrosolv, Merck, Germany) with concentrations of 5 μg of the respective reference compounds and subsequent execution of the analytical procedure as described in Section 2.3. The experimental results are presented in Table 1 and illustrate the uncertainties associated with the quantitation of the target analytes. Caffeine exhibited a low recovery rate of 23 ± 1% with our method (Table 1). This result would have been better by solvent extraction from an alkalized aqueous matrix. Nevertheless, we included the quantitative data of caffeine because of the good reproducibility of the quantitative results.

2.3. Water sample extraction

Prior to extraction, the samples were filtered through pre-cleaned MNGF-6 glass fiber filters (pore width 0.45 μm). After filtration, 1 L-aliquots of water samples were extracted according to Dsikowitzky et al. (2002), a method that was optimized for the identification and quantitation of a wide range of organic contaminants. Briefly, *n*-pentane (1st fraction), dichloromethane (2nd fraction) and dichloromethane after acidification to pH 2 (3rd fraction) were used for the sequential extraction in a separation funnel. Acidic compounds in the third fractions were methylated by addition of a methanolic diazomethane solution. Thereafter, the 3rd fractions were further separated in two subfractions by liquid chromatography on activated silica gel and by using 2 mL dichloromethane and 2 mL methanol as eluents, respectively. The first two fractions of the water samples were spiked with a surrogate standard solution containing d_{34}-hexadecane (6.0 ng μL^{-1}) and decafluorobenzophenone (7.0 ng μL^{-1}). 200 μL of a surrogate standard containing 4-fluoroacetophenone (14.4 ng μL^{-1}) was added to the third fractions. Prior to GC/MS-analyses, all fractions were concentrated to final volumes of 50 μL (first two fractions) and 200 μL (third fractions).

2.4. Gas chromatography–mass spectrometry (GC/MS)

GC/MS analyses were performed as single measurements with a Trace MS mass spectrometer linked to a Trace GC, scanning at a rate of 2.5 scans $second^{-1}$. Carrier gas (helium) velocity was 42 cm s^{-1}. A ZB-XLB fused silica capillary column was used for gas chromatographic separation (30 m × 0.25 mm ID × 0.25 μm film thickness). Chromatographic conditions were: split/splitless injection (injector temperature 270 °C), splitless time 60 s, GC oven was 3 min. at 60 °C, then programmed from 60 to 310 °C at a rate of 3 °C min^{-1} and kept at 310 °C for 20 min. The mass spectrometer was operated in electron impact ionization mode (70 eV), source temperature 200 °C, scanning from 35 to 700 amu.

Identification of the individual compounds was based on comparison of EI + mass spectra with those of data bases (NIST, Wiley), and was verified with mass spectra of purchased reference compounds

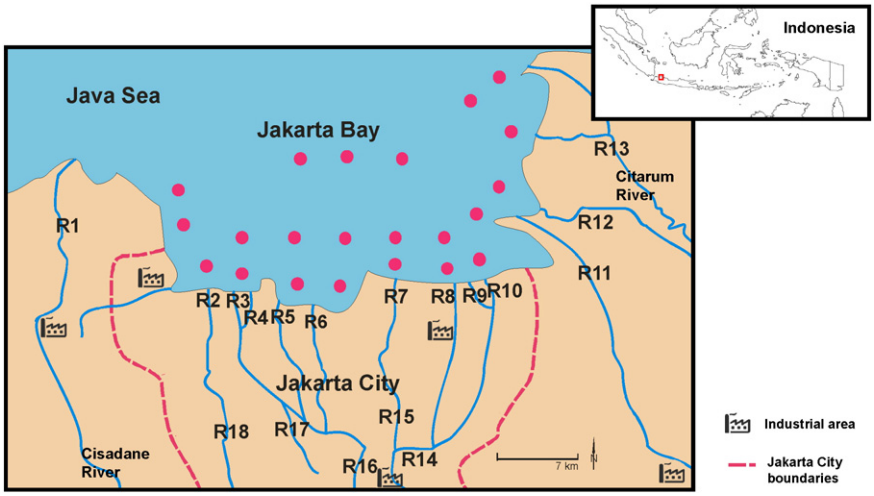

Fig. 1. Schematic sketch of the study area with sampling stations.