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Baseline

Monitoring micropollutants in marine waters, can quality standards be met?

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ABSTRACT

The environmental risks of 33 micropollutants occurring in Belgian coastal zone were assessed as single-substances and as mixtures. Water and sediment samples were taken in harbors, coastal waters and the Scheldt estuary during 2007–2009. Measured environmental concentrations were compared to quality standards such as Predicted No Effect Concentrations (PNECs), Environmental Quality Standards (EQSs), and Ecotoxicological Assessment Criteria (EAC). Out of a total of 2547 samples analyzed, 232 and 126 samples exceeded the EQS and EAC, respectively. Highest risks were observed for TBT, PBDEs, PCBs and the PAHs anthracene, indeno(1,2,3-cd)pyrene, benzo(g,h,i)perylene, benzo(k)fluoranthene, and benzo(b)fluoranthene in the water compartment and for TBT and PCBs in the sediment compartment. Samples taken at all stations during the April 2008 campaign indicate a potential risk of the contaminant mixtures to the aquatic environment (except W06 station). This study argues the need to revise quality standards when appropriate and hence the overall regulatory implication of these standards.

1. Introduction

The marine environment receives inputs of hazardous substances through riverine sources (including harbors), direct discharges and atmospheric deposition (Steen et al., 2001; Noppe et al., 2007). As a result, a large number of micropollutants are present in the marine environment. Organisms living in these ecosystems are thus exposed to a range of substances which may cause adverse effects. During 2007–2009, an extensive monitoring program was performed to analyze the environmental concentrations in the Belgian coastal zone of established specific pollutants or priority compounds, such as those identified by Oslo and Paris Convention (OSPAR), Water Framework Programme (WFP) and the United Nations Economic Commission for Europe (UNECE) list (http://www.vliz.be/projects/inram). Many of the priority substances have previously been measured in the Belgian coastal zone (e.g. Covaci et al., 2005; Roose et al., 2005; Verslycke et al., 2005; Noppe et al., 2007; Schipper et al., 2008; Wille et al., 2010); however, the measured exposure data were not further evaluated in terms of environmental risk of single-substances or mixtures. In this study, the measured environmental concentrations of the above mentioned monitoring campaign will be assessed for the first time against different international quality standards, which have been developed to assess and manage the potential impact of micropollutants in the aquatic environment. The three quality standards to which our data will be compared, are Predicted No Effect Concentrations (PNECs), Environmental Quality Standards (EQSs), and Ecotoxicological Assessment Criteria (EAC). PNECs are used in the context of REACH or Registration, Evaluation, Authorization and Restriction of Chemicals (EC 1907/2006), which is the European Regulation on chemicals and their safe use. PNEC is the concentration of the substance below which adverse effects in the environment are not expected to occur. The EQS is established in the context of the Water Framework Directive (WFD; 2000/60/EC), which aims to achieve a good chemical and ecological water status in European water bodies (lakes, rivers, coastal and transitional waters and groundwater) by 2015. Chemical status refers to priority substances for which EQS have been developed (EC, 2008).

OSPAR contracting parties have agreed on a procedure for the determination of EAC for the following pollutants occurring in water, sediment, and biota: trace metals, poly chlorinated biphenols (PCBs), poly aromatic hydrocarbons (PAHs), tributyl tin (TBT) and some organochlorine pesticides (OSPAR, 1996).

It should be recognized that, in most cases, aquatic organisms are not exposed to a single substance but to a mixture of chemicals. Therefore, there is increasing concern about the potential adverse effect of mixtures since the effect the mixture can be higher than

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the effect of each individual component. To date, the EU has not developed guidelines to address both human health and environmental assessment of chemical mixtures. Experimental mixture studies in ecotoxicology and human toxicology demonstrate that the concept of dose/concentration addition and independent action provide good approximations of observed combination effects (Kortenkamp, 2007). Dose/concentration addition occurs if chemicals in a mixture act by the same mechanism/mode of action. Whereas, independent action occurs if chemicals act independently from each other, usually through different modes of action that does not influence each other. A detailed description of both dose addition and independent action approach can be found in the review by Kortenkamp (2007) and Syberg et al. (2009). In this study, we assessed for the first time, the environmental risks posed by contaminant mixtures occurring in the Belgian coastal waters using the concentration addition approach.

The aims of this study are therefore (i) to evaluate if the concentrations of micropollutants occurring in the Belgian harbors, coastal waters, and the Scheldt estuary, meet the current regulatory requirements by comparing the measured levels to three quality standards: PNEC (REACH), EAC (OSPAR), and EQS (WFD) and (ii) to assess the (*in situ*) mixture toxicity/risk of these micropollutants using the concentration addition approach.

The study area is located in the three Belgian coastal harbors (Oostende, Nieuwpoort, and Zeebrugge), the Scheldt estuary, and the near and coastal zone of the Belgian part of the North Sea. An overview of the study area and sampling stations is given in Fig. 1. Ten Sampling stations were selected in three coastal harbors: four in the harbor of Zeebrugge (ZB01–ZB04), and three in the harbors of Nieuwpoort (NP01–NP03) and Oostende (OO02–OO04) each. In each harbor, one sampling station was selected as representative for the major freshwater inputs into the harbor, the others were located in the middle and at the harbor mouth. An additional station was selected at the Sluice Dock in Oostende (OO01). This enclosed, shallow lagoon is used for aquaculture activities (oyster and mussel culture). The lagoon is supplied with water from the inner harbor of Oostende. Two stations were sampled in the Scheldt estuary: one was located at the river mouth near Vlissingen (S01), the second more upstream near Antwerp (S22). Six sampling stations were chosen in the Belgian coastal area: three (W01, W02, and W03) were located near-shore close to the harbor mouth of Oostende, Nieuwpoort and Zeebrugge; the remaining three (W04, W05, and W06) were situated more offshore, about 5 km from the coast. The sampling campaigns were carried out in 2007 (May/June, July, November/December), 2008 (April), and 2009 (June/July).

The 'Zeekat', a rigid hull inflatable boat, was used for sampling the harbor stations. Coastal and estuarine stations were sampled with the research vessels: 'Belgica', 'Zeeleeuw', or 'Scheldewacht'. Water samples were collected at each sampling site using 10L Go-Flo bottles® (General Oceanics Inc., Miami, Florida, USA) at a depth of approximately 3 m. Samples were stored at 4 °C in the dark, prior to analysis.

Sediment samples were taken with Van Veen grab (0.1 m^2 surface area) and aliquots of the samples were centrifuged to obtain the clay fraction (<63 μm) using a flow-through centrifuge (Biofuge Stratos Heareus, Kendro Laboratory Products, Hanau, Germany).

The following chemicals were considered for risk assessment: perfluorooctane sulfonate (PFOS), TBT, poly brominated diphenyl ethers (PBDEs), PCBs, PAHs, phenols, and organonitrogen pesticides (ONP) (see Table 2).

PFOS, phenols and ONPs were analyzed at the Laboratory of Analysis of Organic Micropollutants of the Flemish Environment Agency (FEA, Ghent, Belgium). PFOS was extracted using solid-phase extraction and detected by liquid chromatography coupled to a time-of-flight mass spectrometer (LC–ToF-MS) (Wille et al., 2010). For sediment samples, PFOS was extracted with methanol before solid-phase extraction and analysis with LC–ToF-MS. For phenols, sample preparation included derivatisation with pentafluorobenzoylchloride and extraction with hexane before detection

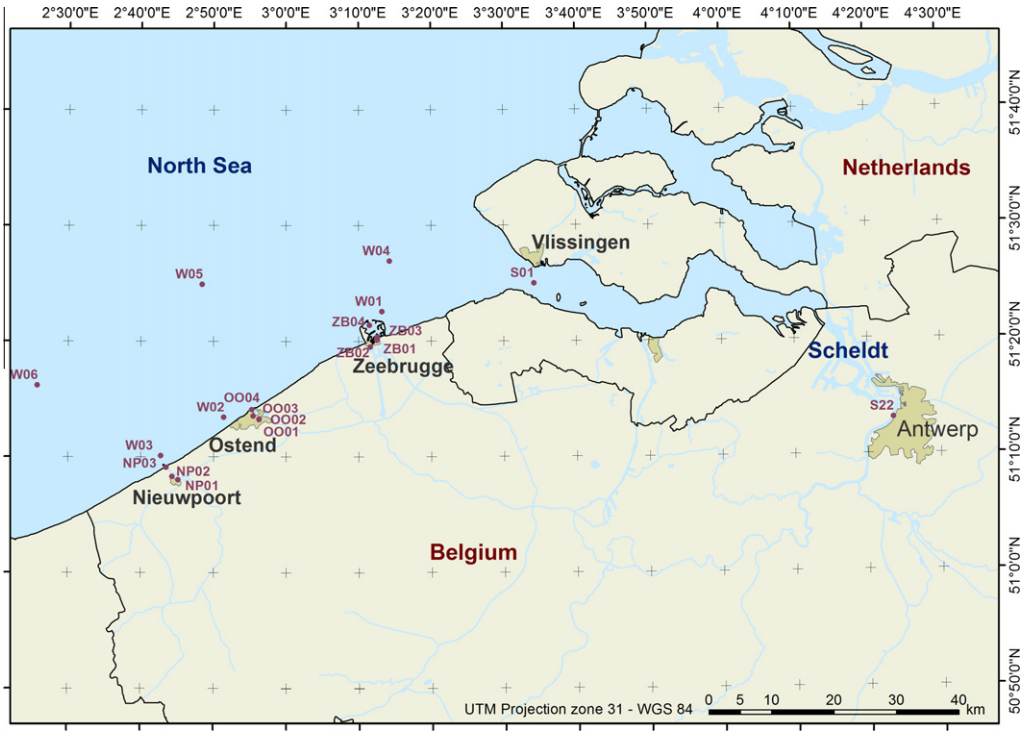

Fig. 1. Sampling stations in the Belgian part of the North Sea (W01–W06), the Scheldt estuary (S01 and S22) and the harbor of Nieuwpoort (NP01–NP03), Oostende (OO01–OO04) and Zeebrugge (ZB01–ZB04).