



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.

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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 m² 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

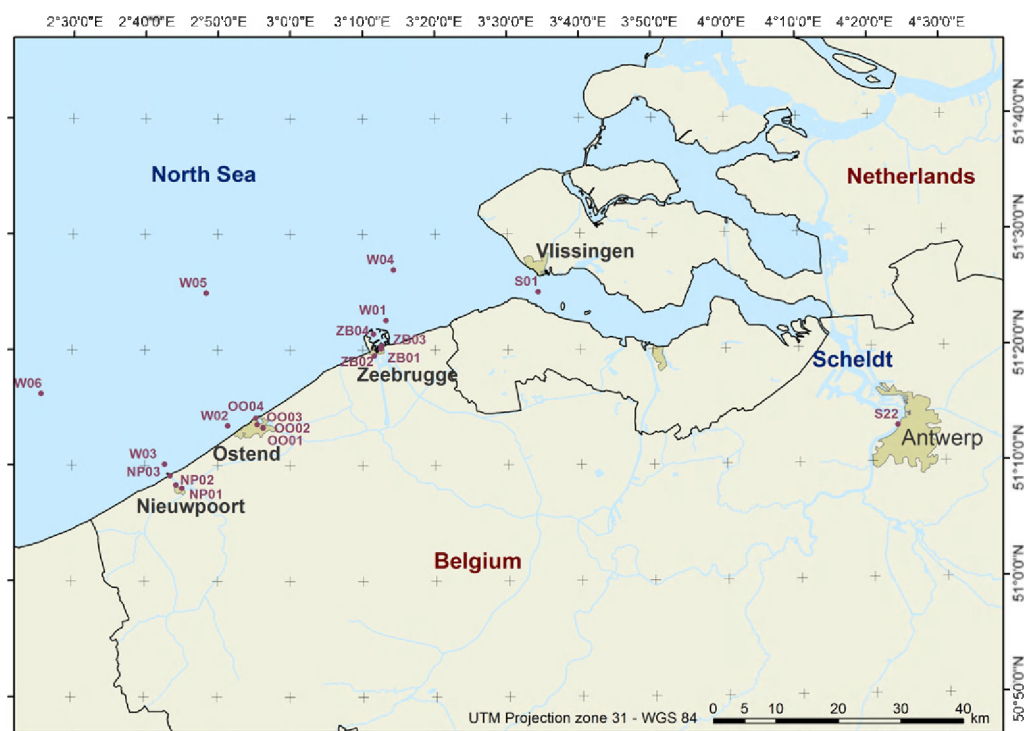


Fig. 1. Sampling stations in the Belgian part of the North Sea (W01–W06), the Scheldt estuary (S01 and S22) and the harbor of Nieuwpoort (NP01–NP03), Oostende (OO01–OO04) and Zeebrugge (ZB01–ZB04).

Table 1

Accuracy of the analytical methods for TBT, PBDEs, PCBs, and PAHs measured in water and sediment. Validation results: reference material or internal standard used, recovery (%), relative standard deviation (RSD %), and limits of detection (LoD ng/g DW for sediment and ng/L for water).

Compartment	Substance	Reference material	Recovery (%)	RSD (%)	LoD (ng/g DW for sediment, ng/L for water)
Sediment	TBT	CRM 646 freshwater sediment water spiked with unethylated standards	98	11	2.0 ng TBT kation/g DW
Water	TBT		105	14	1 ng TBT kation/L
	Acenaphthene		130	5	2
	Acenaphthylene		75	11	3
	Anthracene		99	15	2
	Benz(a)anthracene		75	9	4
	Benzo(a)pyrene		75	11	11
	Benzo(b)fluoranthene		93	14	12
	Benzo(ghi)perylene		84	12	4
	Benzo(k)fluoranthene	QPH069MS marine sediment (Quasimeme standard material used for interlaboratory proficiency testing)	78	14	3
Sediment	Chrysene		93	9	6
	Dibenz(a,h)anthracene		94	6	2
	Phenanthrene		94	10	6
	Fluoranthene		73	8	12
	Fluorene		77	11	2
	Indeno(1,2,3-cd)pyrene		81	12	6
	Naphtalene		99	10	11
	Pyrene		82	8	5
	Acenaphthene		102	9	0,5
	Acenaphthylene	Water spiked with standards	85	11	0,5
	Anthracene		85	5	0,5
	Benz(a)anthracene		80	12	0,5
	Benzo(a)pyrene		79	6	0,5
	Benzo(b)fluoranthene		102	7	0,5
	Benzo(ghi)perylene		85	9	0,5
	Benzo(k)fluoranthene		88	11	0,5
Water	Chrysene		76	8	0,5
	Dibenz(a,h)anthracene		89	31	0,5
	Phenanthrene		84	13	0,5
	Fluoranthene	Internal reference material (marine sediment)	92	9	0,5
	Fluorene		103	11	0,5
	Indeno(1,2,3-cd)pyrene		89	9	0,5
	Naphtalene		117	11	10
	Pyrene		75	11	0,5
Sediment	BDE100		104	10	1,0
Water	BDE47	Water spiked with standards	96	13	1,0
	BDE99		105	9	1,0
Sediment	Σ PCB7	Internal reference material (marine sediment)	85–110	<20	1,0
Water	Σ PCB7	Water spiked with standards	90–110	<20	1,0

by gas chromatography coupled to mass spectrometer (GC–MS). Analysis of the ONPs in filtered samples was performed by gas chromatography coupled to electron ionization mass spectrometer (GC–EI–MS–MS) analysis (Noppe et al., 2007).

TBT, PBDEs, PCBs, PAHs are analyzed with gas chromatography (GC) in a single extract by Management Unit of the North Sea Mathematical Models (MUMM, see Table 1 for accuracy of the analytical methods). For PAHs, PCBs, PBDEs, water samples were extracted using solid-phase extraction. For analysis of TBT, liquid–liquid extraction was used. Detection of PAHs and TBT was done with a mass spectrometric (MS)–quadrupole detector operated in the selected ion monitoring (SIM) election-ionization mode (EI), while detection of PCBs and PBDEs was done with an ion-trap MS in EI–MS–MS mode.

Environmental concentrations measured in this study will be compared to the three quality standards: PNEC, EQS, and EAC. These values are summarized in Tables 2 and 4 for the aquatic and sediment compartment, respectively.

PNECs were taken from EU risk assessment reports which can be found on the European chemical Substance Information System (ESIS) website (<http://ecb.jrc.ec.europa.eu/esis>). PNECs were available for PBDE, 4-n-nonylphenol, and bisphenol A. The PNEC found for PBDE is the PNEC applicable for pentaBDE (CAS nr. 32534-81-9). The PNEC for PFOS was reported in OSPAR (2006).

The methodology to derive a PNEC is described in the EU guidance of information requirements R10 (ECHA, 2008) and is mainly based on the EU technical guidance document TGD (European Commission, 2003).

The EQSs used here were those derived by the European Commission for 33 priority substances (EC, 2008) and additional values set by the Flemish Government (Vlaamse regering, 2010). EQS for PCB is the criteria for the sum of 7 congeners PCB 28, 52, 101, 118, 138, 153, and 180. For PAHs, the EQS for the sum of benzo(b)fluoranthene and benzo(k)fluoranthene and the sum of benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene must be met. The EQS for PBDE is applicable for the congeners 28, 47, 99, 100, 153, and 154.

EACs were taken from OSPAR (2004) and are expressed as a lower and upper level. The lower EAC value is defined as a concentration which will protect all marine species from chronic effects, including the most sensitive species. The upper EAC is defined as the highest concentration that is expected not to cause acute toxic effects. In this study, the lower EAC is used to assess the risk of the different micropollutants. A number of the EACs derived to date are regarded as provisional (see Tables 2 and 4) due to the limited quantity of toxicological data of marine species available (OSPAR, 2004).

For each substance or substance group, the measured Environmental/Exposure Concentration (MEC) was compared to the three

Table 2
Risk assessment with highest aquatic Measured Exposure Concentration (MEC) of all locations (station, campaign) and international standards PNEC, EQS, EAC and the RCRs are expressed as MEC/PNEC, MEC/EQS, and MEC/EAC.

Substance	MEC (µg/L)	Station	Campaign	PNEC (µg/L)	EQS (µg/L)	EAC (µg/L)	MEC/PNEC	MEC/EQS	MEC/EAC
PFOS	0.039	S22	07/07/09	2.5	NA	NA	0.02	NA	NA
TBT	0.044	S22	07/07/09	NA	0.0002	0.00001	NA	220	4400
PBDE: BDE 47	0.005	S22	2008/11	0.53	0.0002	NA	0.009	26	NA
PBDE: BDE99	0.011	W02	2007/29	0.53	0.0002	NA	0.02	57	NA
ΣPCB7	0.031	S22	13/06/08	NA	0.002	NA	NA	16	NA
Nonylphenol	0.79	S22	15/06/07	NA	0.3	NA	NA	2.6	NA
4-n-nonylphenol	0.012	All	All	0.33	NA	NA	0.04	NA	NA
Pentachlorophenol	0.015	All	All	NA	0.4	NA	NA	0.04	NA
BisphenolA	0.18	NP01	16/04/08	0.15	NA	NA	1.2	NA	NA
Alachlor	0.04	NP01	16/04/08	NA	0.3	NA	NA	0.1	NA
Atrazine	0.000077	S22	13/06/08	NA	0.6	NA	NA	0.0001	NA
Chloridazon	1.37	OO02	15/04/08	NA	10	NA	NA	0.1	NA
Diuron	0.45	NP01	30/11/07	NA	0.2	NA	NA	2.3	NA
Isoproturon	0.29	NP01	30/11/07	NA	0.3	NA	NA	0.97	NA
Linuron	0.77	OO02	15/04/08	NA	0.3	NA	NA	2.5	NA
Monolinuron	0.043	ZB02	30/05/08	NA	0.3	NA	NA	0.1	NA
Propanil	0.003	all	all	NA	0.2	NA	NA	0.01	NA
Simazine	0.00006	ZB03	29/11/07	NA	1	NA	NA	0.00006	NA
Acenaphthene	0.16	ZB01	30/05/07	NA	0.06	NA	NA	2.6	NA
Acenaphthylene	0.047	OO03	08/01/08	NA	4	NA	NA	0.01	NA
Anthracene	0.039	S22	13/06/08	NA	0.1	0.001(p)	NA	0.4	39
Benzo(a)anthracene	0.042	S22	13/06/08	NA	0.3	NA	NA	0.1	NA
Benzo(a)pyrene	0.09	S22	13/06/08	NA	0.05	0.01 (p)	NA	1.8	9
Benzo(b)fluoranthene	0.39	S22	13/06/08	NA	0.03	NA	NA	16	NA
Benzo(g,h,i)perylene	0.085	S22	13/06/08	NA	0.002	NA	NA	122	NA
Benzo(k)fluoranthene	0.08	S22	13/06/08	NA	0.03	NA	NA	16	NA
Chrysene	0.06	S22	13/06/08	NA	1	NA	NA	0.06	NA
Dibenzo(a,h)anthracene	0.055	S22	13/06/08	NA	0.5	NA	NA	0.1	NA
Phenanthrene	0.028	S22	13/06/08	NA	0.1	0.5 (p)	NA	0.3	0.06
Fluoranthene	0.076	S22	13/06/08	NA	0.1	0.01 (p)	NA	0.8	7.6
Fluorene	0.02	OO02	31/05/07	NA	2	NA	NA	0.01	NA
Indeno(1,2,3-cd)pyrene	0.16	S22	13/06/08	NA	0.002	NA	NA	122	NA
Naphthalene	0.067	W03	14/05/07	NA	1.2	5	NA	0.05	0.01
Pyrene	0.12	S22	13/06/08	NA	0.04	0.05 (p)	NA	3	2.4

MEC = Measured Environmental Concentration, PNEC = Predicted No Effect Concentration, EQS = Environmental Quality Standard, EAC = Ecotoxicological Assessment Criteria, p = provisional.

quality standards described above. As a worst-case assumption, the MEC (for the sediment or water compartment) used in this study is the highest concentration of the micropollutant measured in that compartment irrespective of location or sampling period.

The risk characterization ratio (RCR) of a single micropollutant was calculated using:

$$RCR = \frac{MEC}{PNEC} \text{ or } \frac{MEC}{EQS} \text{ or } \frac{MEC}{EAC}$$

A value larger or equal to 1 is interpreted as a potential environmental risk.

We used the principles of the concentration addition approach for assessment of mixtures. For a mixture with i micropollutants, the risk characterization ratio of the mixture (RCR_m) is the sum of all the risk characterization ratios of the individual compounds (RCR_i), assuming that concentration addition model is applicable:

$$RCR_m = \sum_{i=1}^n RCR_i = \sum_{i=1}^n \frac{MEC_i}{PNEC_i} \text{ or } \sum_{i=1}^n \frac{MEC_i}{EQS_i} \text{ or } \sum_{i=1}^n \frac{MEC_i}{EAC_i}$$

When the value of the RCR of the mixture is larger or equal to 1 a potential environmental risk is identified.

For the aquatic compartment, the highest Measured Environmental Concentrations (MEC) for each micropollutant observed in the different stations and campaigns and the results of the risk assessment conducted in the context of this 3 years study are presented in Table 2, the shaded cells indicate a $RCR > 1$. The highest RCR values were observed for TBT (MEC/EAC of 4400 and MEC/EQS of 220), and the PAHs benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene (both MEC/EAC of 122) for sampling location S22. The

other chemicals potentially causing a risk at S22 are: BDE47, PCB7, nonylphenol, anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, fluoranthene, and pyrene.

The chemicals that pose an environmental risk at harbor locations NP01, OO02, and ZB01 are: bisphenol A, diuron, linuron, and acenaphthene. The highest concentration of BDE99 was found in the near-shore coastal station W02 (RCR of 57).

Table 3 gives an overview of the % water samples which exceeded the EQS or EAC at the different sampling locations. Out of a total of 2547 samples analyzed, 232 and 126 samples exceeded the EQS and EAC, respectively. The highest % of the samples exceeding RCR of 1 was found for TBT (97% exceeded EQS and 100% EAC). PBDEs BDE47 and 99 exceeded the EQS in 47% and 43% of all samples, respectively. Both substances pose a risk in all sites except for BDE47 where no risk was identified in the stations NP03 and W01.

The other substances with a potential risk in most of the stations (S22, harbors and offshore coastal areas) are the PAHs: benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene (both 68% exceeded EQS); anthracene (38%); benzo(b)fluoranthene and benzo(k)fluoranthene (both 27% exceeded EQS). For all these PAHs, the highest concentration was measured in S22.

The pesticides diuron and linuron have the highest concentrations in NP01 and OO02, respectively where 4% and 1% of the samples exceeded the EQS. The RCR for ΣPCB₇ was exceeded in 7% of the samples in the stations ZB01, OO01, and S22 with the highest concentration found in the latter station. Concentrations of nonylphenol were highest in the harbor stations ZB04 and OO04 with 3% of the samples that exceeded the EQS.

Table 3

% Exceeding of all water samples for each micropollutant with a RCR > 1 for MEC/EQS and MEC/EAC and the stations where the potential risks are observed are presented together with the amount of samples analyzed in the years 2007–2009.

Substance	% exceeding MEC/EQS	STATIONS	% exceeding MEC/EAC	STATIONS	# samples
TBT	97	All	100	All	79
PBDE: BDE47	47	NP01–NP03; ZB01–ZB04; OO01–OO04 S22 ^a ; S01			
PBDE: BDE99	43	W02–W05			60
ΣPCB7	7	All			
Nonylphenol	3	ZB01; OO01 S22 ^a ZB04 ^a OO04 NP01 ^a ; OO02			45
Diuron	4	S22			81
Linuron	1	OO02			81
Acenaphthene	1	ZB01			77
				NP01–NP03; ZB01–ZB04; OO01–OO04 S22 ^a ; S01	
Anthracene	0		38	W04	76
Benzo(a)pyrene	1		10	ZB02–ZB03; OO03–OO04 S22 ^a ; S01	77
		NP01–NP03; ZB01–ZB04; OO03–OO04 S22 ^a ; S01			
Benzo(b)fluoranthene	27	W05–W06 NP01–NP03; ZB01–ZB04; OO01–OO04 S22 ^a ; S01			77
Benzo(g,h,i)perylene	68	W02–W05 NP01–NP03; ZB01–ZB04; OO03–OO04 S22 ^a ; S01			
Benzo(k)fluoranthene	27	W05–W06			77
Fluoranthene	0		12	ZB01–ZB02; OO02, OO04 S22 ^a	
		NP01–NP03; ZB01–ZB04; OO01–OO04 S22 ^a ; S01			
Indeno(1,2,3-cd)pyrene	68	W02–W05			77
Pyrene	1	S22	1	S22	77

^a Highest concentration; MEC = Measured Environmental Concentration, EQS = Environmental Quality Standard, EAC = Ecotoxicological Assessment Criteria.

The % of samples that exceeded the PNEC was not included in Table 3 because only three PNECs were found and only bisphenol A exceeded the PNEC once at the harbor station NP1.

An overview of the risks due to mixture toxicity in the aquatic compartment is given in Fig. 2 for all sampling stations monitored during the April 2008 campaign. Mixture toxicity was assessed using EQS and EAC values but not with PNEC due to the limited number of PNECs available. All stations indicate a potential risk (RCR > 1) of the mixture to the aquatic environment, except for W06 station. However, for this station no TBT measurement was available.

The main substances that have an impact on the risks assessed with EQS are PAHs, PBDEs, and TBT. The highest risks are observed at the stations S22, OO04, ZB02, and OO02 with a RCR ranging from 30 to 450.

When EACs are used, mainly TBT and to a lesser extent PAHs are the drivers for the observed risks. The stations for which the highest risks are observed are the upstream region of the Scheldt near

Antwerp (S22) and the harbors in the following order: OO04, NP01, OO03, ZB02 with a RCR between 200 and 900. For the near- and offshore stations W02–W06, all risk quotients were >1.

Table 4 presents the results of the risks assessed with the highest Measured Environmental Concentration (MEC) of the 33 micropollutants in the sediment compartment of the harbors, Scheldt estuary, and coastal zone stations during 2007–2009 campaigns. EAC standards were found for some of the micropollutants, except for PFOS, phenols, ONPs, and some PAHs. The highest risk was identified for TBT and PCBs with a RCR of 14800 and 157, respectively. Other potential risks with a RCR above 1 were found for PBDE (BDE100) and the PAHs were a EAC was available: anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, chrysene, phenanthrene, fluoranthene, naphthalene, and pyrene. No EQS standards for this compartment were available and only two PNECs were found, i.e. for PBDE and bisphenol A. Due to practical reasons, phenols were not measured in sediment samples.

Table 4
Risk assessment with highest sediment Measured Exposure Concentration (MEC) of all locations (station, campaign) and international standards PNEC, EQS, EAC and the RCRs are expressed as MEC/PNEC, MEC/EQS, and MEC/EAC.

Substance	MEC (µg/kg dw)	Station	Campaign	PNEC (µg/kg dw)	EQS (µg/kg dw)	EAC (µg/kg dw)	MEC/PNEC	MEC/EQS	MEC/EAC
PFOS	16.96	S22	15/06/07	NA	NA	NA	NA	NA	NA
TBT	74	OO01	09/08/07	NA	NA	0.005 (p)	NA	NA	14800
PBDE: BDE 100	98.7	S22	13/06/08	310	NA	62	0.3	NA	1.6
ΣPCB7	157	S22	07/07/09	NA	NA	1 (p)	NA	NA	157
4-n-Nonylphenol	NA			NA	NA	NA	NA	NA	NA
Pentachlorophenol	NA			NA	NA	NA	NA	NA	NA
BisphenolA	NA			24 (ww)	NA	NA	NA	NA	NA
Alachlor	NA								
Atrazine									
Chloridazon									
Diuron									
Isoproturon					NA				
Linuron									
Monolinuron									
Propanil									
Simazine									
Acenaphthene	240	S22	13/06/08	NA	NA	NA	NA	NA	NA
Acenaphthylene	80	S22	13/06/08	NA	NA	NA	NA	NA	NA
Anthracene	600	S22	13/06/08	NA	NA	50	NA	NA	12
Benzo(a)anthracene	620	S22	13/06/08	NA	NA	100(p)	NA	NA	6.2
Benzo(a)pyrene	560	S22	13/06/08	NA	NA	100(p)	NA	NA	5.6
Benzo(b)fluoranthene	660	S22	13/06/08	NA	NA	NA	NA	NA	NA
Benzo(g,h,i)perylene	390	S22	13/06/08	NA	NA	NA	NA	NA	NA
Benzo(k)fluoranthene	290	S22	13/06/08	NA	NA	NA	NA	NA	NA
Chrysene	810	S22	13/06/08	NA	NA	100(p)	NA	NA	8.1
Dibenzo(a,h)anthracene	84	ZB01	30/05/07	NA	NA	NA	NA	NA	NA
Phenanthrene	1400	S22	13/06/08	NA	NA	100	NA	NA	14
Fluoranthene	1710	OO02	31/05/07	NA	NA	500(p)	NA	NA	3.4
Fluorene	580	S22	13/06/08	NA	NA	NA	NA	NA	NA
Indeno(1,2,3-cd)pyrene	370	S22	13/06/08	NA	NA	NA	NA	NA	NA
Naphthalene	1200	S22	13/06/08	NA	NA	50	NA	NA	24
Pyrene	1100	S22	13/06/08	NA	NA	50 (p)	NA	NA	22

MEC = Measured Environmental Concentration, PNEC = Predicted No Effect Concentration, EQS = Environmental Quality Standard, EAC = Ecotoxicological Assessment Criteria, p = provisional.

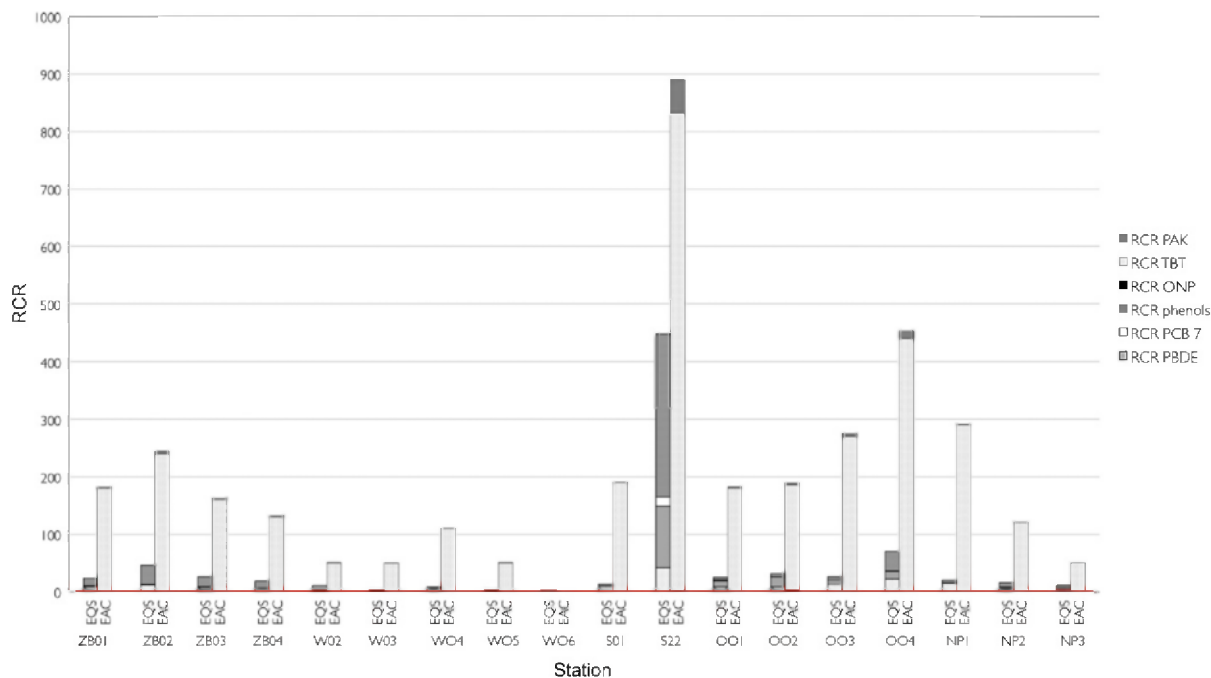


Fig. 2. Assessment of mixture toxicity in all water samples of the campaign in April 2008. Key note: RCR = Risk Characterization Ratio, MEC = Measured Environmental Concentration, EQS = Environmental Quality Standard, EAC = Ecotoxicological Assessment Criteria.

Results from our study of the single substances risk assessment indicate that highest potential risks (RCR > 10) were observed for

TBT, PCBs, PBDEs, and PAHs in Belgian harbors, coastal waters and the Scheldt estuary.

Highest potential risk was observed for TBT, which exceeded the quality standards up to 4400- and 14,800- fold for the aquatic and sediment compartment, respectively. Similar high TBT levels have previously been reported in the Belgian coastal environment and the Western Scheldt (Verslycke et al., 2005; Schipper et al., 2008). Even though a global ban on the use of TBT on large vessels came into force in 2008, historical contamination is still important although TBT levels are decreasing (Morton, 2009; Verhaegen et al., 2012). Also PCBs still represent a potential risk despite production of PCBs was banned in the mid-1980s. Roose et al. (2005) reported the concentrations and patterns of PCBs in the sediment of the Belgian part of the North Sea and the Scheldt estuary for the period 1991–2001. The PCB concentrations in sediment vary between 0.1 and 50 µg/kg dw. A significant downward trend could not be found at any of the stations, which suggests that PCB levels have not changed during the past decade (Roose et al., 2005). In our study, we could confirm this finding since we even measured higher sediment concentrations up to 157 µg/kg dw in the Scheldt estuary. However, Covaci et al. (2005) concluded that concentrations of PCBs in sediment samples from the Scheldt river were found to decline slightly in the last years. Covaci et al. (2005) also reported that concentrations of PBDEs in sediment of the Scheldt river have increased exponentially, in accordance with similar observations worldwide. In this study, the two congeners BDE47 and 99 poses the highest potential risk compared to the other congeners in the aquatic environment of the Belgian coastal zone, e.g. highest RCRs were noted in the 2007 campaigns in all stations of the Belgian part of the North Sea.

From the pesticides measured in this study, diuron and linuron posed a potential risk in the harbors, however, this was only found for 4% and 1% of the measured samples, respectively (see Table 3). Diuron was also found as a major herbicide in Lake Geneva, a large European Lake (Chèvre et al., 2008).

As a general trend from the single substance risk assessment, concentrations of pesticides were observed to be mainly higher in the marine environment than the Scheldt estuary (S22). Concentrations of PFOS, TBT, PCBs, and PAHs were generally higher in S22 compared to the marine sampling locations. This could indicate that the Scheldt estuary is a source of contamination of the latter micropollutants for the North Sea.

Internationally, the same substances are reported to be of concern to the marine environment as those found in our study. PCBs, TBT, PBDEs, and the PAHs benzo(g,h,i)perylene and benzo(k)fluoranthene are also one of the substances that caused adverse effects in the Baltic Sea with RCR above 1 in respectively 20%, 9%, 1%, 1%, 1% of the 137 samples studied (Law et al., 2006; HELCOM, 2010). The data in the integrated risk assessment were primarily from biota and only secondarily from sediment or water. Borchers et al. (2011) reported that a chemical monitoring program was put in place between 2009 and 2011 in Irish surface waters, i.e. in 70 lake sites and 180 river sites. The 33 priority substances of the WFD and 14 potential local relevant pollutants were monitored where 18 substances are the same as in our study. Only six substances are present in concentrations above the EQS in ten or more samples: mecoprop, glyphosate, sum of benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene, sum of benzo(b)fluoranthene and benzo(k)fluoranthene, benzo(a)pyrene, and fluoranthene. The latter two substances do not pose a risk and the first two were not measured in our study. TBT and PBDEs were not measured by Borchers et al. (2011) since no sufficiently sensitive methods were available to quantify concentrations at or below the EQS.

Several authors have shown that mixture effects can be of environmental concern even if all single substances are present under their respective no-observed effect concentrations (NOEC); see for example Backhaus et al. (2000), Faust et al. (2001), Silva et al. (2002), Faust et al. (2003), Bellas (2008), and Breitholtz et al.

(2008). In our study, quality standards were already exceeded in single substance risk assessment for several chemicals. It is therefore not surprising that mixture risk assessment lead to even higher potential risks. All the sampling sites further of the coast, which serve as control sites (least polluted), exceeded the EQS and EAC when risks of mixtures were assessed (Fig. 2). This underlines the need for the development of a regulatory mixture risk assessment methodology.

Quality standards (PNEC, EAC, EQS) are frequently used in environmental management. They are derived according to standardized procedures, e.g. by the application of assessment factors (e.g. 10, 50, 100 or 1000) to experimental ecotoxicity values or, for data rich substances, species sensitivity distributions and the determination of a critical percentile protective for the ecosystem (European Commission, 2003). The establishment of these quality standards is typically associated with a large degree of uncertainty. Once these values are set, risk managers and decision makers will use them, however, often with insufficient background on how these quality standards were developed and what level of conservatism is included (Sijm et al., 2001; Verdonck et al., 2007). Scientist should need to clarify the derivation and the accuracy of the quality standards to these decision makers. Sometimes quality standards are so low that chemical analysis is analytically very difficult or impossible, e.g. TBT, PBDE, PAHs (Lepom et al., 2005; Borchers et al., 2011). In this case it is even more important to understand and analyze the derivation and conservatism of the environmental protection value. For WFD, Member States have stressed the need for more guidance on implementation of monitoring requirements of substances with low quality standards (Borchers et al., 2011).

For the sediment compartment, the shortage of relevant and high quality ecotoxicological effect data is even higher than for the pelagic compartment. The quality standards for this compartment are often derived from the values for water applying the equilibrium partitioning method. Ecological effects assessment in this compartment may thus be less reliable and lead to over- or underestimating of environmental risks (Sijm et al., 2001). Establishment of more reliable quality standards through the generation of more effects data and/or new, more ecologically relevant, derivation methods can have important management consequences. It has, for instance, been shown that a slight increase of the EQS can result in a large reduction of sediment remediation costs (Henning-de Jong et al., 2009). The new European chemical legislation REACH may be an opportunity to refine quality standards since more ecotoxicological data will become available.

It can be concluded that the quality standards such as EQS and EAC were frequently exceeded in the single substance risk assessment in the Belgian coastal and estuarine area. It is therefore not surprising that mixture risk assessment lead to even higher potential risks. All stations sampled in April 2008 indicate a potential risk of the mixture to the marine environment. The study also shows that the quality standards are often so low that they cannot be detected or quantified by most well-equipped laboratories. We thus conclude that some of the current quality standards should be refined in time, e.g. when new (eco)toxicity data becomes available to decrease the degree of uncertainty. Furthermore, we stress that there is an urgent need to develop regulatory guidance for the assessment of mixtures while avoiding accumulating unwanted uncertainty.

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