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Additive modelling reveals spatiotemporal PCBs trends in marine sediments

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ABSTRACT

We developed generalised additive mixed models (GAMMs) to infer spatiotemporal trends of environmental PCB concentrations from an extensive dataset ($n = 1219$) of PCB concentrations measured between 1991 and 2010 in sediments of the Belgian Coastal Zone (BCZ) and the Western Scheldt estuary. A GAMM with time, geographical zone, periodicity and the organic carbon – water partition coefficient as covariates explained 49% of the variability in the log transformed PCB sediment concentrations. The time trends unraveled two to threefold PCB concentration decreases in the BCZ during the last 20 years. However, in the Western Scheldt estuary, time trends were spatially heterogeneous and not significantly decreasing. These results demonstrate that international efforts to cut down emissions of PCBs have been effective to reduce concentrations in open water ecosystems like the BCZ but had little effect in the urbanised and industrialised area of the Scheldt estuary.

1. Introduction

The environmental fate and toxicity of persistent organic pollutants (POPs) are of global concern. POPs concentrate in fatty tissues and magnify in food chains due to their hydrophobic and lipophilic properties (Jones and de Voogt, 1999). Their persistence facilitates their transport to and impacts on regions far from their sources (Muir et al., 2000). International conventions, such as the United Nations Environment Programme (UNEP) Stockholm convention on POPs, aim for cross-border governance of this problem by controlling the primary POP sources and eliminating POP emissions globally by 2020 (UNEP, 2001). To quantify their spatiotemporal distribution and evaluate the success of regulations, monitoring activities intensified at the beginning of the 1990s (Lamon et al., 2009; Lohmann et al., 2012). In particular, spatiotemporal trend analyses of hazardous substances are stipulated as a key priority by the OSPAR commission and data collection frameworks such as the Coordinated Environmental Monitoring Programme (CEMP) were initiated (ICES, 2004).

Polychlorinated biphenyls (PCBs) are often used as model compounds to study the environmental behaviour of POPs (Schuster et al., 2010; De Laender et al., 2010). PCB time trend studies performed in air (e.g. Schuster et al., 2010; Venier et al., 2012), seawater (e.g. Gioia et al., 2008), biota (e.g. Roose et al., 1998; De Laender et al., 2011; Weijs et al., 2012) and polyethylene pellets (e.g. Ryan et al., 2012) indicate decreasing PCB trends, suggesting legislative efforts have been successful (Lohmann et al., 2007). However, site-specific hotspots of PCBs (Wurl and Obbard, 2005; Gioia et al., 2008) have been detected, making it unsure if global PCB decreases are also occurring near densely populated industrialised sites (de Wit et al., 2006; Gedik et al., 2010; Van Ael et al., 2012) and in estuaries (Danis et al., 2004; Carroll et al., 2007; Webster et al., 2011).

The southern part of the North Sea and the Western Scheldt estuary are globally amongst the most intensively monitored marine and estuarine regions. Despite the high degree of industrialisation and urbanisation present in this region (Hesse, 2010), Breivik et al. (2007) has simulated decreasing congener-specific primary atmospheric PCB emissions between 1991 and 2010. However, the question is whether the decreasing atmospheric PCB concentrations are also reflected in other environmental compartments (e.g. water, sediment and biota). For instance, Berrojalbiz et al. (2011) found that different environmental compartments do not always follow identical trends. Additionally, we ask if different PCB congeners follow similar trends. In case of primary point source pollution, it is hypothesised that dissimilar trends will be observed per congener. However, under secondary diffuse source pollution, similar trends across congeners are expected.

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In this paper we analyse one of the longest and most complete data sets of PCBs using a regression-based technique in order to compare the levels and time trends of marine and estuarine PCB sediment concentrations between and within the Belgian Coastal Zone (BCZ) and the Western Scheldt estuary. We used 1219 monthly averages of PCB sediment concentrations, representing 10 PCBs measured in a twenty-year period. To test the robustness of the inferred time trends, we compared these trends to 614 independent monthly averages of PCB concentrations. Finally, in order to compare different environmental compartments, the PCB sediment time trends inferred in this research were compared to PCB emission estimates of Breivik et al. (2007).

2. Data and models

2.1. Data

Sediment concentrations of polychlorinated biphenyls (PCBs) in the sediment fraction smaller than 63 μm along the Belgian Coastal Zone (BCZ) and the Western Scheldt estuary were obtained from the online database of the Belgian Marine Data Centre (BMDC, http://www.mumm.ac.be/). In total, 4297 PCB concentrations representing 10 congeners were extracted from the BMDC. The study area was divided in eight zones: four in the Western Scheldt estuary and four at the BCZ (Fig. 1).

Prior to the modelling, we detected three outliers by means of Cleveland dotplots (Table S1, Figs. S1–S10) and removed these from the data. Furthermore, we discarded 376 values that were below the detection limit. Next, the remaining 3921 sediment concentrations (μg/g) were log10 transformed (Zuur et al., 2010) and, based on the reported latitude and longitude of the sampling location, assigned to one of the eight zones (Fig. 1). Monthly averaging of the reported sediment concentrations (μg/g on a dry weight basis) resulted in a dataset comprising of 1833 records representing monthly mean sediment concentrations of 10 PCBs measured between 1991 and 2010. Two thirds of this dataset ($n = 1219$) was randomly selected for model fitting, the remaining one third ($n = 614$) was used to assess the trends we found (Tables S2–S5).

2.2. Statistical modelling

The overall objective of our research was to infer PCB time trends for the BCZ and the Scheldt estuary and to verify which PCB congeners show similar spatiotemporal gradients. To this end, additive modelling was selected; a nonparametric alternative to the more conventionally used generalised linear models (GLMs). Generalised additive models (GAMs) only differ from GLMs in that GAMs use nonparametric smooth functions of the explanatory variables whereas GLMs use products between the regression coefficients and the explanatory variable (Wood, 2006):

$$g^{-1}[E(Y_i|X_{ij})] = \alpha + \sum_{j-1}^{k} f_j(X_{ij}) \qquad (1)$$

where g specifies the link function between the expected value of Y_i (PCB concentration) and the explanatory variables X_{ij}, with $i = 1$ to n the number of the observations and $j = 1$ to n the number of explanatory variables. The smoother function $f_j(x_{ji})$ quantifies the effect of the jth explanatory variable on Y_i and α represents the estimated regression coefficient. The number of knots of $\mathrm{f_j}$ represents the amount of smoothing applied to the data (Wood and Augustin, 2002). A smoother with two knots is linear, has little variability and may be biased since there is only one piecewise function (Keele, 2008). Increasing the number of knots allows more flexibility, but may result in overfitting. The optimal number of knots depends on sample size; for sample sizes above 100, five knots provide a good compromise between flexibility and overall fit (Keele, 2008). For smaller samples, below 30, the use of three knots is a good starting point. Keele (2008) report that four to five knots is appropriate for most applications. In our analysis, the number of knots for the smoothing curves was fixed to four. All additive models were fitted using the mgcv package in R (R Development Core Team, 2010).

2.3. Model fitting

We considered three different model configurations to fit to the data, only differing in the covariates they contained (Table 1). All three models included time (as year and month), zone and periodicity as covariates. Time and zone (Fig. S11) were included because our objective was to quantify spatiotemporal trends. Periodicity was represented by a period τ and an amplitude A, because an interannual repetitive fluctuation was observed during data exploration. In essence, the effect of periodicity is the same for two concentrations separated in time by a multiple of τ years, i.e. $f(x + \tau) = f(x)$. However, when the time interval is not a multiple of τ, periodicity affects two concentrations differently, depending on the amplitude. We used a cycling period of eight years as shorter or longer cycling periods proved to fit less well to the observed

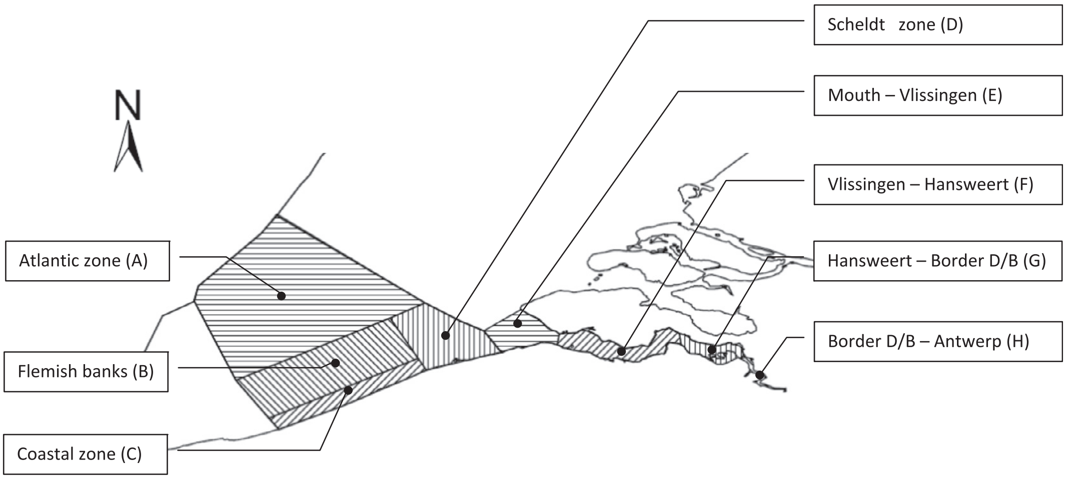

Fig. 1. Eight subzones delimited in our study area: the Atlantic zone (A), the Flemish banks (B), the coastal zone (C), and the Scheldt zone (D), the mouth of the Scheldt (E) and three trajectories from Vlissingen to Hansweert (F) from Hansweert to the Dutch–Belgian border (G) and from the border to Antwerp (H).

Table 1
Different modelling approaches used to infer time trends of the POP sediment concentrations. The predictors available are listed in columns, per modelling approach the significance of the predictors included is shown by means of its *p*-value.

	Model 1	Model 2	Model 3
Model formulation	$C_{sed} \sim$ s(Year|Zone) $+s$(Periodicity) +Substance +Zone	$C_{sed} \sim$ s(Year|Zone) $+s$(Periodicity) $+s(\log K_{oc})$ +Zone	$C_{sed} \sim$ s(Year|Zone) $+s$(Periodicity) $+s(\log K_{oc})$ +Zone
Predictors			
Time	$2.0 \times 10^{-16} < p < 2.1 \times 10^{-1}$	$2.0 \times 10^{-16} < p < 3.2 \times 10^{-1}$	$2.3 \times 10^{-14} < p < 4.3 \times 10^{-1}$
Zone	$<2.0 \times 10^{-16}$	$<2.0 \times 10^{-16}$	$<2.0 \times 10^{-16}$
Periodicity	1.4×10^{-15}	2.2×10^{-9}	1.5×10^{-13}
Substance	$<2.0 \times 10^{-16}$		
$\log K_{oc}$		$<2.0 \times 10^{-16}$	$<2.0 \times 10^{-16}$
CorCAR1			$\varphi = 0.14$
Predictive power			
R^2	0.69	0.47	0.47
AIC	556	1210	1169

periodicity in the data (Fig. S12). Apart from time, zone and periodicity, the first model (model 1) also included the chemical name of the PCB (termed "Substance") as a fourth covariate, allowing for PCB-specific time trends (Table 1). In the second model (model 2), the variable "Substance" (in model 1; Table 1) was replaced by the log10 organic carbon–water partition coefficient ($\log K_{oc}$; in model 2; Table 1). The $\log K_{oc}$ values were obtained from the freely available EPI Suite™ v4.10 application (http://www.epa.gov/oppt/exposure/pubs/episuitedl.htm). Due to the typical trade-off between model accuracy and general applicability (Guisan and Zimmermann, 2000), we expected model 2, including the descriptor $\log K_{oc}$, to have a lower predictive power than model 1 (Table 1). Lastly, because modelling marine data can result in misleading predictions due to autocorrelation of the samples (Merckx et al., 2011), we tested if accounting for this autocorrelation resulted in a better model by comparing the Akaike Information Criterion (AIC) of model 2 to the AIC of a third model that explicitly included autocorrelation (model 3). The AIC rewards proximity to the data but penalises model complexity. Lower AIC values indicate a better model. Because sampling occurred irregularly in time, a continuous correlation structure was selected (Table 1). The correlation coefficient (φ) of this structure was fitted to the data and its value was used to evaluate the strength of autocorrelation in the data. Positive φ values indicate that data at any particular point in time are positively related to preceding time points (Wood, 2006). The closer this value is to 1, the more autocorrelative the data are (Zuur et al., 2009).

2.4. Residual diagnostics and model robustness

When analyzing environmental data using a regression-based technique, it is particularly important to test the underlying assumptions (i.e. homogeneity and normality) based on the residuals of the fitted model (Zuur et al., 2009). Homogeneity was concluded if the variability of the residuals was similar across the range of fitted values. Normality was assessed using graphical diagnostics such as the QQ plot (residuals should be on a straight line) and the histogram of the model residuals (a bell-shaped curve is expected; Wood, 2006; Zuur et al., 2009). The model configuration combining a low AIC and acceptable residual diagnostics (see Zuur et al., 2009) was selected as the optimal model configuration. The robustness of the model was assessed by applying it to the independent data ($n = 614$), i.e. data that were not used for model calibration. To this end, every PCB concentration in the independent data set was compared to the corresponding prediction.

2.5. Time trend interpretation using emission data

The time trends we inferred between 1991 and 2010 were compared to the PCB emission trends for the same period published in Breivik et al. (2007). The latter dataset contains yearly global congener-specific atmospheric PCB emission predictions for a 1° × 1° grid between 1930 and 2100. The PCB emission estimates are based on population density within the grid square. In accordance to Schuster et al. (2010), the grid square at the emission data were chosen closest to the geographical position of the studied zone. The PCB time trends in the BCZ and the Scheldt estuary were compared to the PCB emission trends for grid 51.5° × 2.5° and grid 51.5° × 3.5°, respectively. The nonparametric Spearman correlation coefficient was used and assessed at a 0.01 level of significance.

3. Results and discussion

3.1. Model selection

Model 1, including one intercept and one time trend per polychlorinated biphenyl (PCB), indicated that the periodic oscillation and zone-specific temporal averages were significant covariates of PCB sediment concentrations (Table 1). The congener-specific intercepts of model 1 increased with the log10 organic carbon – water partition coefficient ($\log K_{oc}$; Figs. 2 and S13), most notably for PCBs with $\log K_{oc}$ smaller than 5. For more hydrophobic substances ($\log K_{oc} > 5$), this increase was less evident. High lipophilicity often reflects large molecule sizes, causing a decrease in the chemical's potential to adhere to environmental matrices due to steric hindrance (Fisk et al., 2001; Jonker and Koelmans, 2002; Hung et al., 2010).

Although, the fit of model 2, including the $\log K_{oc}$ of the PCB as a covariate, was lower than the fit of model 1 (Table 1), the time trends were similar, i.e. PCB concentrations decreased in the Belgian Coastal Zone (BCZ) and were relatively stable in the estuary. The fact that the $\log K_{oc}$ could successfully replace the "Substance" covariate indicates that the 10 PCB congeners studied followed the same trend. As such, the $\log K_{oc}$ can be used to understand the behaviour of those 10 congeners. Since the 10 congeners followed the same trend, no primary point sources are expected in the BCZ and Scheldt estuary as in case of point sources we would expect congener specific trends.

Model 3, including an autocorrelation structure ($\varphi = 0.14$), indicated that the data were only slightly auto-correlated. However,

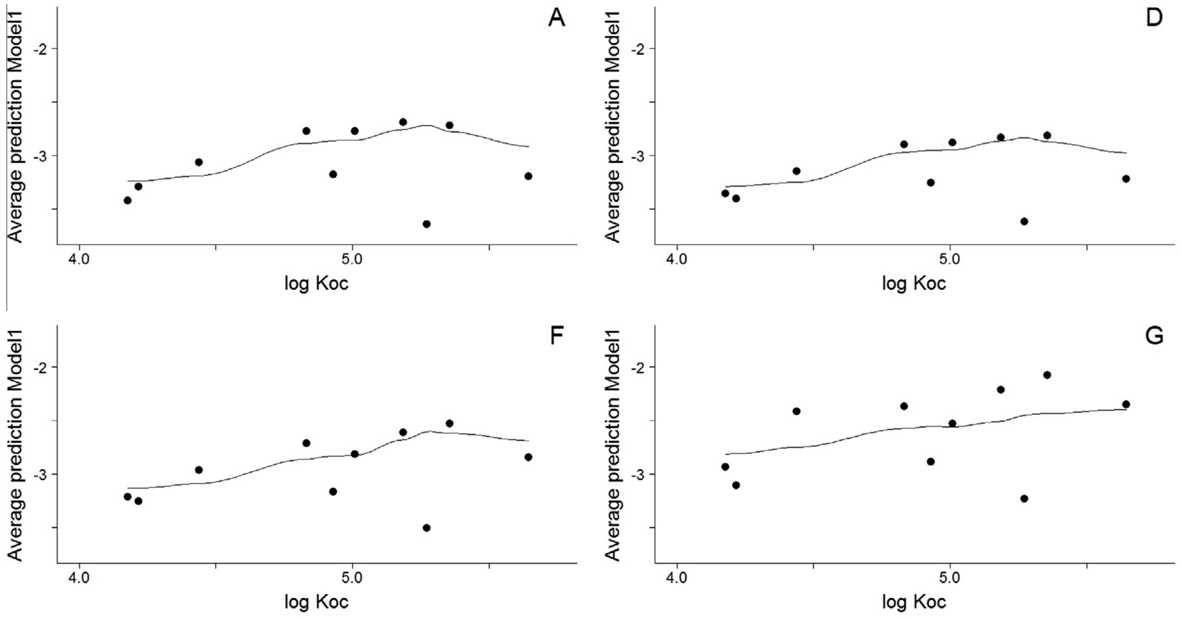

Fig. 2. Per PCB, the intercept of the additive model was extracted and plotted against its log10 organic carbon–water partition coefficient (log K_{oc}) by zone: the Atlantic zone (A), the Scheldt zone (D), and two trajectories from Vlissingen to Hansweert (F) and from Hansweert to the Dutch–Belgian border (G). The lower the log K_{oc}, the lower the intercept of the model. However, at the highest log K_{oc} values the log K_{oc} effect is limited. In one substance class, log K_{oc} – intercept relations are similar for the different zones. Therefore, we concluded that is valid to replace the grouping variable "Substance" by the numerical variable log K_{oc}.

the AIC of model 3 (AIC = 1169) was lower than that of model 2 (AIC = 1210), indicating the data were explained better when including the autocorrelation structure (Table 1). The residuals of model 3 follow a normal distribution (Fig. S14) and when plotting the residuals versus the covariates no patterns were observed (Fig. S15). This indicates that the normality and homogeneity assumptions, and therefore the derived *p*-values, were valid. Testing of model 3 against independent data demonstrated that the model was capable of capturing zonal differences in PCB sediment concentrations (Fig. 3). Except for the lowest and highest sediment concentrations (which were slightly over- and underestimated, respectively), the time trends we found based on model 3 deviate less than one order of magnitude of those reflected by the independent data set, showing that the inferred time trends are robust within the study region (Fig. 3). Considering the effect of analytical variation between laboratories on measured PCB concentrations (Wells and de Boer, 2006) and the environmental variation of PCB concentrations (Lohmann et al., 2012), which both may be as high as two to three order of magnitude, the accuracy of the inferred time trends was considered adequate.

3.2. PCB time trends and levels

The time trends indicated decreasing PCB sediment concentrations in the BCZ (Fig. 4). In 1991, PCB concentrations were on average two to threefold times higher than today and currently vary around 0.56 ± 0.46 ng/g (on a dry weight basis). The decreasing PCB sediment concentrations in the BCZ corroborate with what has been described for other coastal and estuarine regions (e.g. Konat and Kowalewska, 2001; Johannessen et al., 2008; Hong et al., 2010) and other environmental compartments (e.g. Roose et al., 1998; Schuster et al., 2010; De Laender et al., 2011).

In contrast with the time trends for the BCZ, PCB time trends in the Scheldt estuary differed among zones. In general, PCB concentrations in the Scheldt estuary remained stable between 1991 (3.08 ± 3.46 ng/g) and 2010 (2.79 ± 3.99 ng/g). This was reflected by the smoothers for zone F, G and H. In zone F, PCB concentrations did not change with time (0.87 ± 0.54 ng/g in 1991 versus 1.59 ± 0.25 ng/g in 2009). In the zone between Hansweert and the Dutch–Belgian border (zone G), PCB concentrations decreased up to the year 2000, but then increased again. In the zone closest to the port of Antwerp (zone H) the PCB concentrations remained relatively unchanged (7.22 ± 3.78 ng/g in 1991 versus 6.78 ± 5.15 ng/g in 2006; Fig. 4). The inferred time trend at the mouth of the river Scheldt (zone E, neighbouring the BCZ) followed the same pattern as the time trends found in the BCZ. The PCB sediment concentrations in zone E decreased threefold between 1992 (0.85 ± 0.45 ng/g) and 2010 (0.26 ± 0.15 ng/g).

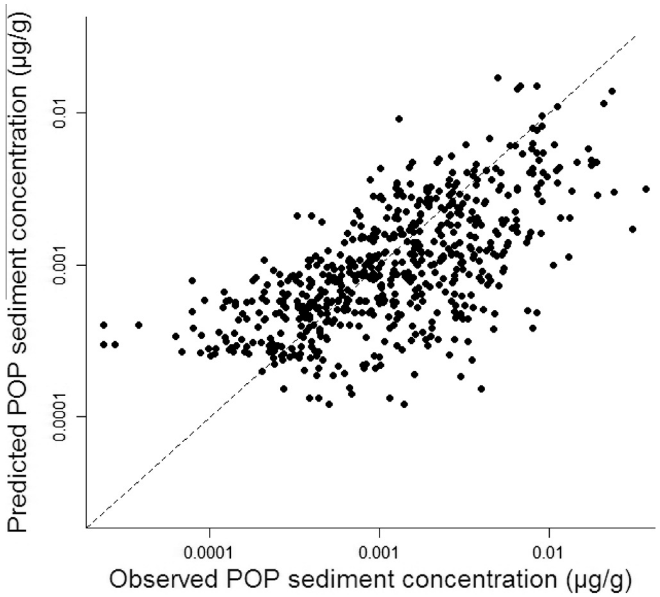

Fig. 3. Application of model 3 on the independent data set ($n = 614$). The estimated PCB sediment concentrations are compared with the observed concentrations. The dotted line represents the first bisector.

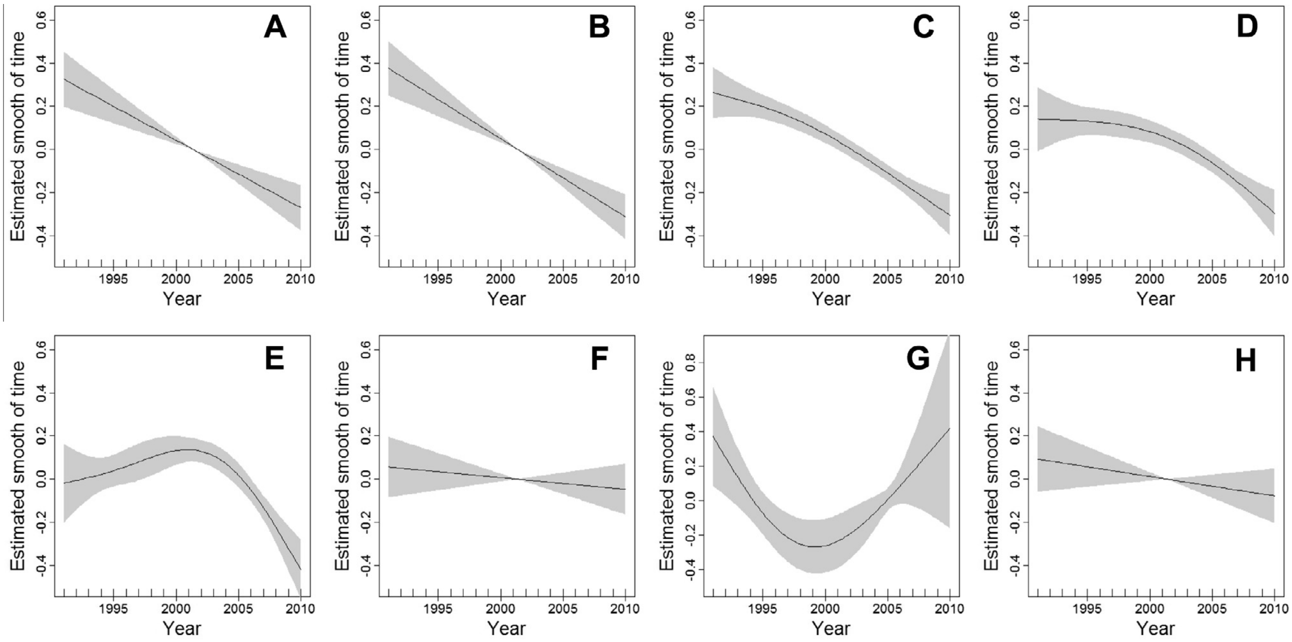

Fig. 4. Zone dependent time smoothers for the model 3: the Atlantic zone (A), the Flemish banks (B), the coastal zone (C), and the Scheldt zone (D), the mouth of the Scheldt (E) and three trajectories from Vlissingen to Hansweert (F), from Hansweert to the Dutch–Belgian border (G) and from the border to Antwerp (H).

The PCB sediment concentrations in the Western Scheldt estuary always exceeded the concentrations in the BCZ (Fig. S11). This has already been reported for PCBs (Danis et al., 2004) and for dissolved metal concentrations (Baeyens et al., 1998). In 2004, Voorspoels et al. (2004) reported an inverse relation between the POP concentrations in benthic species and the distance between sampling points and the port of Antwerp. Also in Korea, Hong et al. (2010) found a positive correlation between the distribution and levels of organochlorine contaminants and shipping and industrial activities. More recently, Webster et al. (2011) concluded that the PCB sediment concentrations in the Clyde estuary (Scotland) exceeded those of the open sea and related this to the fact that the estuary was subject to (in)direct inputs.

Although the PCB congeners studied were identical (i.e. same breakdown rates) for both regions, dissimilar time trends were observed in the BCZ and the Scheldt estuary (Fig. 4). This suggests the presence of PCB inputs in the estuary, which can be indirect from other environmental compartments based on the PCB partitioning characteristics or direct via the industrial activities in the port of Antwerp (e.g. commodity-throughput, oil refinery, petro chemistry). Although the port of Antwerp is the largest chemical cluster in Europe (Hesse, 2010), direct inputs via point sources are unlikely as the PCB congeners studied followed identical trends (see Section 3.1). This suggests that mainly indirect diffuse inputs are the main sources of PCBs. However, Breivik et al. (2007) simulated decreasing atmospheric PCB concentrations and we found relatively stable PCB sediment concentrations in the Scheldt estuary. This was reflected in the non-significant correlation coefficients between the PCB sediment time trends inferred and the emission estimates of Breivik et al. (2007); Table 2). This indicates that other PCB sources than the atmospheric deposition contributed to those stable PCB levels. The latter can be explained by the dredging activities, which are permanently carried out to maintain the maritime fairway to the harbour of Antwerp (Plancke et al., 2008). These activities consist of dredging natural sills in the fairway and relocating the dredged sediment (Pynaert and Speleers, 2004). Polluted sediment has been previously identified to control the concentrations in the other environmental compartments (Lohmann et al., 2007; Ishaq et al., 2009). Also, Schulzbull et al. (1995) observed surprisingly high PCB concentrations in the southern part of the Baltic Sea and related this the relocation PCB polluted sediment. In the Indiana harbour and ship canal in Lake Michigan dredging resulted in release and redistribution of PCBs in the environmental compartments (Martinez et al., 2010). Overall, due to the myriad of activities going on, the proximity of urbanised and/or industrialised areas may lead to higher PCB levels and different PCB trends compared to the open sea (de Wit et al., 2006; Choi et al., 2011; Yang et al., 2011). The PCB inputs are mainly from diffuse secondary origin and therefore the regulatory efforts, which have successfully reduced the preliminary PCB sources in many ecosystems, should now focus on the secondary pollution sources.

Superimposed on the spatiotemporal effect, we found an interannual oscillation of the sediment PCB concentrations (Fig. 5). After attempting various oscillation periods (5–11 years), the best fit

Table 2
Spearman correlation analysis between the PCB time trends found based on model 3 and the PCB emission estimated by Breivik et al. (2007).

	CB28	CB31	CB52	CB101	CB118	CB138	CB105	CB153	CB156	CB180
Flemish banks	0.91*	0.91*	0.91*	0.91*	0.91*	0.91*	0.91*	0.91*	0.91*	0.91*
Scheldt zone	0.74*	0.74*	0.74*	0.74*	0.74*	0.74*	0.74*	0.74*	0.74*	0.74*
Atlantic zone	0.89*	0.89*	0.89*	0.89*	0.89*	0.89*	0.89*	0.89*	0.89*	0.89*
Coastal zone	0.86*	0.87*	0.87*	0.87*	0.86*	0.86*	0.86*	0.86*	0.86*	0.86*
Mouth of the Scheldt	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.34
Section Vlissingen–Hansweert	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34
Section Hansweert-border	−0.26	−0.25	−0.25	−0.25	−0.25	−0.26	−0.25	−0.25	−0.25	−0.25
Section border-Antwerp	0.51	0.51	0.51	0.52	0.51	0.51	0.51	0.51	0.51	0.51

* Significance codes: 0.01.

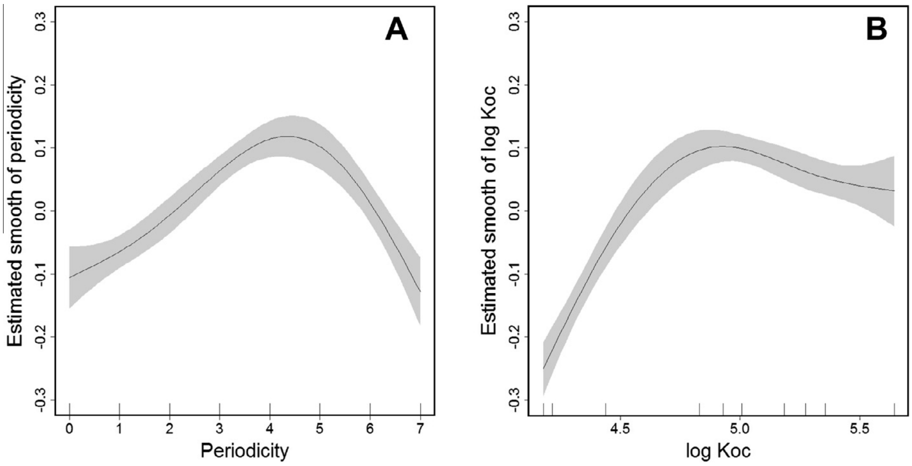

Fig. 5. Smoothers for the periodicity (A) and the log10 organic carbon–water partition coefficient (log K_{oc}) (B) of model 3. The small vertical lines above the *x*-axis in 4B indicate the log K_{oc} values present in the dataset.

was obtained with an oscillation period of eight years (Fig. S12), which is similar to the period of the North Atlantic Oscillation (NAO; Hurrell and Van Loon, 1997). The NAO influences temperature and precipitation across the North Atlantic basin, exerts a major impact on marine ecosystems (Hurrell, 1995) and has been shown to influence PCB concentrations in the Canadian Arctic atmosphere (Hung et al., 2005). The mechanism allegedly explaining the relationship between the NAO and the distribution of POPs suggests that positive phases of the NAO (i.e. high temperatures) enhance the volatilisation of POPs and thus influence their environmental behaviour (Pelley, 2004). In 2010, Ma et al. concluded that the interannual fluctuations in POP time trends are related to climate variability caused by the NAO and the El Nino-Southern Oscillation (ENSO). Also in the freshwater environment, POP concentrations measured around the Great Lakes during the 1990s showed a strong association with climatic oscillation patterns (Ma et al., 2004).

4. Conclusions

Environment legislation (e.g. OSPAR convention) successfully reduced PCB concentrations in the BCZ. The 10 PCB congeners we considered followed the same trend, suggesting that no point sources are present in our study area for these congeners. The main PCB input is from indirect, diffuse origin, preventing the decreasing PCB sediment levels in the highly industrialised and urbanised estuaries.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.marpolbul.2014.01.002.

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