Chemosphere 156 (2016) 172–180

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Chemical analyses of dredged spoil disposal sites at the Belgian part of the North Sea

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HIGHLIGHTS

- PCB concentrations in Belgian marine sediments not decreasing since 2005.
- Zn and Cu concentrations at dredged spoil disposal sites possibly affected by shipyards.
- Dredged spoil disposal site monitoring essential to identify adverse time trends.

ARTICLE INFO

Article history:
Received 27 December 2015
Received in revised form
5 April 2016
Accepted 30 April 2016
Available online 10 May 2016

Handling Editor: Caroline Gaus

Keywords:
Dredged spoil disposal
Heavy metals
PCB
PAH
Pollution control measures

ABSTRACT

The chemical status of five dredged spoil disposal sites in the Belgian Part of the North Sea is evaluated. A linear mixed-effect model was applied to PCB, PAH and heavy metal data from 2005 to 2014. No decrease in PCB concentrations was found, with even an increase at two disposal sites. Hg/AL ratios increased with 62% at one disposal site (BR&WS2) from 2005 to 2006 to 2013–2014. Cu and Zn concentrations increased at two disposal sites. Additional harbour sampling suggests that the latter is possibly linked to antifouling paints. Based on OSPAR environmental assessment criteria, the current chemical status of the sites suggests no chronic effect of dredged spoil disposal. However, increasing time trend data for PCB, Hg, Cu and Zn demonstrate the importance of monitoring to identify adverse trends.

1. Introduction

Marine dredging can be divided in maintenance dredging works (to safeguard navigation in ports, harbours and channels), and capital dredging works (to deepen channels or ports, construct and burry cables). When strict quality criteria are met, dredged sediment can be disposed at sea. As dredged spoil disposal is potentially harmful to the marine environment, a strict monitoring of biological and chemical impact is obliged (OSPAR, 2009a). On the Belgian Part of the North Sea (BPNS), five dredged spoil disposal sites are defined, and monitored two times a year.

The current chemical monitoring of dredged spoil disposal sites at the BPNS routinely includes measurements of polychlorobiphenyls (PCB), polycyclic aromatic hydrocarbons (PAH) and heavy metals (Al, Fe, Cd, Cr, Cu, Hg, Ni, Pb and Zn). Monitoring of these compounds is also included in the European Marine Strategy Framework Directive (MSFD 2008/56/EC). Within descriptor 8, it is described that these pollutants may not give rise to pollution effects. Within MSFD, chemical concentrations in sediments of the BPNS are assessed against OSPAR environmental assessment criteria (EAC).

Large amounts of PCB were manufactured between 1930 and 1983 and reach the environment through disposal, leakage,

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http://dx.doi.org/10.1016/j.chemosphere.2016.04.124

evaporation and accidents (Roose et al., 2005). Although PCB were banned in the mid-1980s, sources still remain, e.g. within waste disposal, PCB-containing equipment, by remobilisation from sediments or by formation of by-products in thermal and chemical processes (OSPAR, 2012). Contradictory information can be found on PCB time trends at the BPNS after 1990. Roose et al. (2005) did not find a significant decrease from 1991 to 2001 for the PCB CB153 (no decrease of more than 20%). Due to good concentration correlations between various marker PCB, the authors considered CB153 representative for other marker CBs. The OSPAR quality status report 2010 (OSPAR, 2010a) indicates no significant decrease for more than 80% of PCB time series from 1998 to 2007 in OSPAR zone II, including the BPNS. Assessment was done by identifying linear trends in the log concentration over a 10 years period at the 5% significance level. In contrast, Everaert et al. (2014) report a decrease of 50–66% in the BPNS between 1991 and 2010 while concentrations at the nearby Scheldt estuary revealed no decreasing trend.

PAH may enter the marine environment by offshore activities, oil spills, river discharges and atmospheric transport (OSPAR, 2012). A predominantly downward trend is noticed in biota throughout the OSPAR area, but is less pronounced in marine sediments (OSPAR, 2010a). Heim and Schwarzbauer (2013) estimated an increase of PAH fluxes since 1996 due to an increased energy consumption. PAH levels in the Scheldt estuary did not decrease in 2000–2009 (Gao et al., 2013).

Stringent pollution control measures have led to substantial reductions in heavy metal pollution by industrial combustion processes, metal production, transport and waste streams (OSPAR, 2010a). OSPAR reports a strong reduction in biota and sediments during the 1990s followed by a slowdown (OSPAR, 2010a). This is consistent with data from the Scheldt estuary and Belgian coastal zone reported by Gao et al. (2013) and Baeyens et al. (2005), covering the time window of respectively 1978–1998 and 1985–2000.

In the present study, time series of PCB, PAH and heavy metals, obtained from dredged spoil disposal site monitoring in the BPNS, are analysed by a linear mixed-effect model. In addition to the identification of significant time trends, the aim is to evaluate if trends are affected by dredged spoil disposal. Additional harbour monitoring was performed to estimate the effect of antifouling paints from leisure boats on Cu and Zn contamination. Since the ban of tributyltin (TBT), Cu made a revival as an antifouling, while several new products (Irgarol, Zn Pyrithione) contain Zn.

2. Materials and methodology

2.1. Description of sampling sites

The BPNS contains five disposal sites (Fig. 1). Near the port of Zeebrugge, disposal sites BR&WS1, BR&WS2 and BR&WZE equal an area of 7.07, 0.88 and 1.77 km^2 with an average dredged spoil disposal rate of 0.78, 2.05 and 1.79 ton dry matter (ton DM).m^{-2}.y^{-1} from April 2004 to March 2014, respectively. BR&WOO near port Oostende and LNP near port Nieuwpoort receive less dredged spoil, respectively 0.36 and 0.09 ton DM.m^{-2}.y^{-1} for an area of 1.77 km^2 each (Lauwaert et al., 2014).

From April 2004 to March 2014, all disposal sites mainly received maintenance dredged spoil, ranging from 83% (BR&WS1) to 100% (LNP). With exception of Br&WS2, there are no large fluctuations in yearly disposal rates (Table S1). Differences in chemical load between disposal sites can be expected since BR&WS1, BR&WS2 and BR&WZE mainly receive dredged spoil from the industrialized port of Zeebrugge (42.5 million tons of freights in 2014, Anon, 2015a) and the shipping track to the Western Schelde which connects the port of Antwerp (199 million tons of freights in 2014, Anon, 2015b). At port Oostende, 1.4 million tons of freights were handled in 2014 (Anon, 2015c) while this port also contains a significant leisure boat harbour. Nieuwpoort is especially a leisure boat harbour.

2.2. Sampling and sample preservation

Sediment samples at the BPNS were taken two times a year, i.e. in February/March and September/October. In this publication, results of PCB and heavy metal data from 2005 to 2014 are included. PAH time series are limited since systematic data are only available since 2008. Five disposal sites (BR&WS1, BR&WS2, BR&WZE, BR&WOO, LNP) are monitored with three zones for each disposal site: (1) the actual disposal site (DIS), (2) the directly impacted zone (IMZ), i.e. outside but less than 0.3 nautical mile away from the actual disposal site and (3) reference samples taken on longer distance from the disposal site (REF). Trend modelling (§2.4) includes the three zones and was performed on the raw data. In the discussion, focus is on the actual disposal site: average concentrations, increase or decrease percentages are given for DIS, unless otherwise mentioned. For heavy metals, changes in concentration were discussed, relative to the Al concentration. A map locating disposal sites and sampling points is shown in Fig. 1. Coordinates of sampling locations are provided as supplementary information. All samples were taken by a Van Veen grab (0.1 m^2) and immediately deep frozen (−20 °C) on board the research vessel Belgica. In the lab, samples were wet sieved on a 63 μm sieve, followed by freeze drying and ball milling. The proportion of the <63 μm fraction is on average 5.1, 1.3, 45.2, 5.0 and 7.1% for BR&WS1, BR&WS2, BR&WZE, BR&WOO and LNP, respectively.

Additional sampling was performed at the harbours of Nieuwpoort (HNP) and Oostende (HOO) in November 2013 and April 2014. Samples were taken by small Van Veen grabs (0.03 m^2) from the rigid inflatable boat Zeekat (Nieuwpoort) or from the quaysides (Oostende). Fig. 1 gives an overview of the sampling locations, while coordinates are provided in Table S3.

2.3. Contaminant analysis

For the analysis of PCB, the sum of 7 PCB, suggested by OSPAR for environmental monitoring (OSPAR, 2010b), was made. This sum includes IUPAC numbers CB28, CB52, CB101, CB118, CB138, CB153 and CB180. Two distinct methods were applied. All samples until 2012 were analysed by a Soxhlet extraction on freeze dried sediment with hexane:acetone (3:1) for 6 h at 90 °C. This was followed by desulfurization by tetrabutylammonium sulphite, dissolved in deionized water. After phase separation, the solvent phase was dried by Na_2SO_4. Clean-up was done on a column with deactivated aluminium oxide as stationary phase and hexane as mobile phase, followed by fractionation on a glass column with silicon oxide and hexane as mobile phase. Tetrachloronaphthalene was added as an internal standard before splitless injection at 210 °C on a gas chromatograph with electron capture detection (GC-ECD). Separation was done on a capillary HT8 column (SGE, 50 m, 0.22 mm, 0.25 μm) with hydrogen (Parker hydrogen generator) as carrier gas and with a temperature program starting at 90 °C for 2 min, up to 180 °C at 20 °C min^{-1} to 285 °C at 2.8 °C min^{-1} which was held for 10 min. Flow rate was constant at 0.8 ml min^{-1}. Detector was set on 300 °C with 25 ml min^{-1} Ar-CH_4 (95:5) as make-up gas.

Freeze dried samples from 2013 and later were analysed by pressurized liquid extraction (PLE) at 100 °C with hexane:acetone (3:1) as extraction solvent. Florisil was added to the cell for clean up. CB29, CB112 and CB140 were added in the extraction cells as calibration standards. Three extraction cycles of 5 min static time