Ecotoxicological effects of Dutch harbour sediments

Stronkhorst, J.

2003

VRIJE UNIVERSITEIT

Ecotoxicological effects of Dutch harbour sediments

The development of an effects-based assessment framework to regulate the disposal of dredged material in coastal waters of the Netherlands

ACADEMISCH PROEFSCHRIFT

ter verkrijging van de graad van doctor aan
de Vrije Universiteit te Amsterdam,
op gezag van de rector magnificus
prof.dr. T. Sminia,
in het openbaar te verdedigen
ten overstaan van de promotiecommissie
van de faculteit der Aard- en Levenswetenschappen
op dinsdag 11 maart 2003 om 15:45 uur
in de aula van de universiteit,
De Boelelaan 1105

door

Jozua Stronkhorst

geboren te Amersfoort

promotor: prof.dr. A. Brouwer
copromotor: dr. A.G.M. van Hattum

Chapter 11

Summary

11.1 Introduction

Aim of the thesis

This thesis describes the development of an effects-based assessment framework for contaminated harbour sediments that is proposed for disposal in coastal waters of the Netherlands. Until recently, the environmental regulations governing the disposal of contaminated dredged material was based on chemical analysis of a suite of traditional compounds in the sediments and a comparison with numerical action levels. However, laboratory toxicity tests or bioassays might provide a more accurate identification of hazardous dredged material that should be excluded from open water disposal. Bioassays are useful as they enable the adverse biological effects of the combination of toxic substances in sediment to be assessed directly. The research described in this thesis sets out to:

- Investigate the feasibility of using laboratory bioassays to determine adverse biological responses in marine sediments from Dutch harbours;
- Evaluate the present status of toxicity and contamination of Dutch marine harbour sediments;
- Identify individual or groups of compounds that contribute to observed sediment toxicity and
- Develop an integrated chemical/biological assessment framework that could be used when considering the disposal of harbour sediments in Dutch coastal waters.

Chemicals of concern

Most of the annual volume of ca. 25 million m^3 material dredged from Dutch waterways and harbours consists of fine-grained sediments. Under the former chemical assessment framework the action levels are frequently exceeded – especially for copper, zinc and polycyclic aromatic hydrocarbons (PAHs); approximately 7% of the volume of sediment proposed for disposal in the open sea was rejected and had to be stored in confined depots. The former framework did not consider tributyltin, an active ingredient of the anti-fouling paints used on sea-going vessels. This highly toxic chemical leaches from the paints and binds to fine sediments, where it can persist for a long time.

The status of the contamination of dredged material was re-evaluated after a period in which emissions from point sources had been greatly reduced (see chapter 2). Data on sediment chemistry from 1999 and 2000 were assessed against screening levels selected from sediment quality guidelines used in other countries and representing a low probability of adverse biological effects. This yielded a ranking of the environmental hazard of 22 contaminants. About 34 % of the volume of dredged material exceeded one or more screening levels. The contaminants of concern were tributyltin (TBT), mineral oil (petroleum hydrocarbons), polychlorinated biphenyls (PCBs) and mercury. The PCB and mercury contamination is the legacy of historical inputs; the TBT and oil contamination is often related to present-day shipping activity. Concentrations of trace metals, rare earth elements, organochlorine pesticides and PAHs were low and apparently of minor environmental concern. Little is known about the group of planar PCBs and dioxins that are of particular concern for marine top predators.

11.2 Feasibility of bioassays

Selection of bioassays

Bioassays are generally suggested as tools that can address the adverse biological effects of (i) the cocktail of contaminants associated with sediment, (ii) the differences in bioavailability of the contaminants and (iii) the presence and effects of compounds that have been overlooked by chemical analysis.

From a list of candidate toxicity tests, the National Institute for Coastal and Marine Management/RIKZ has developed several bioassays into standard operating procedures (SOPs). The SOPs were applied in an inter-laboratory comparison in order to check the reproducibility of test methods (see chapter 3). Bioassays that had acceptable inter-laboratory variability were selected for the test-battery and include:

- Survival of the amphipod *Corophium volutator* (a species abundant in North Sea estuaries) after 10 days' exposure to the whole sediment;
- Survival and re-burrowing of the heart urchin *Echinocardium cordatum* (a species found throughout the North Sea) after 14 days' exposure to the whole sediment;
- Metabolic (bioluminescence) inhibition of the bacterium *Vibrio fischeri* after 20 minutes' exposure to a sediment suspension (the Microtox solid phase bioassay);
- Dioxin-like mode of action of sediment-extracts when exposed to a cell-line called DR-CALUX assay (Dioxin Receptor, Chemical Activated LUciferase gene eXpression).

Observed biological responses in harbour sediments

The four selected bioassays were applied to sediments collected during extensive surveys in 1999 and 2000 in harbours and reference sites along the Dutch coast (see chapter 4 and 5). All test results were validated against criteria for test performance. The modifying or confounding influence of natural factors in the silty marine sediments was considered in detail. For instance, some 15% of the amphipod results were rejected because high ammonia levels developed over the 10 days' exposure period of the test. Microtox results were mathematically corrected for the modifying influence of fine sediment particles. After quality assurance and quality control procedures, the proportions of results of the amphipod, heart urchin, bacterium and DR-CALUX bioassays approved were 81%, 90%, 99% and 100%. The remaining data were considered to be false-positive results.

The bioassays clearly distinguished between harbour sediments that cause adverse effects and those that do not. The lower and upper thresholds for biological effects were set at respectively 24% and 30% mortality for amphipods, 27% and 35% mortality for heart urchins, 24 and 48 Toxic Units for the Microtox SP and 25 and 50 ng TEQ/kg dry weight for the DR-CALUX bioassay. These thresholds either mark the point at which biological effects are always significantly higher than in clean control sediment or are the 95th percentiles of the biological effects observed in coastal reference sediments. The upper and lower thresholds for the amphipods were exceeded in 9% to 17% of the sediment samples, for the heart urchins in 33% to 40%, for the bacteria in 23% to 50% and for the DR-CALUX in 3% to 12% for the of the cases. The strongest effects in the heart urchin and bacterium tests were observed in sediments from the northerly harbours; there was significantly less response in sediments from the Delta Region and the port of Rotterdam. The highest CALUX-TEQ values were found in sediments from several inner harbours of the port of Rotterdam.

11.3 Cause-and-Effects

Advanced chemical analyses were applied to identify the dioxin-like compounds responsible for the response in the DR-CALUX bioassay. On average, polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofuranes (PCDFs), accounted for 50% of the DR-CALUX activity and planar PCBs for 6%; the rest of the DR-CALUX response is attributable to other compounds with a dioxin-like mode of action, such as chlorinated naphthalenes (chapter 5). Three different approaches were used to investigate the cause-and-effect relationships between sediment chemistry and the data of the other bioassays.

In order to discriminate between the effects of persistent constituents and non-persistent constituents, chemical manipulations were applied to toxic samples of interstitial water according to so called Toxicity-Identification-Evaluation procedures (see chapter 6). The manipulated samples were tested for toxicity with four bioassays: the amphipod *Corophium volutator* (survival as an endpoint), the sea urchin *Psammechinus miliaris* (fertilisation, embryo development) and the bacterium *V. fischeri* (bioluminescence inhibition). The gradual pH manipulations identified the prominent toxicity of ammonia in the amphipod and sea urchin embryo tests, and also sulfide toxicity in the bacterium test. A small but significant reduction in the toxicity of the interstitial water was achieved by removing persistent compounds through C_{18} solid phase extraction. Moreover, EDTA chelating also resulted in a slight detoxification of the interstitial water but this was not related to any measured trace metals. Divalent metals were not bioavailable in these silty anaerobic harbour sediments, due to the high levels of acid-volatile sulfide. So, despite the presence of toxic levels of ammonia and sulfide in the harbour sediments, adverse biological effects of persistent constituents were observed in the samples.

Experiments with TBT spiked sediments were conducted to determine the toxicity to amphipods and heart urchins of this important contaminant (see chapter 7). TBT was highly toxic for the benthic species investigated. However, because sorption in the silty sediment sharply reduced the bioavailability of the compound, toxicity was observed at a relatively high TBT concentration in the bulk sediment.

Regression analysis between concentrations of a suite of contaminants were found to be significantly correlated with bacterial bioluminescence inhibition but had little correlation with the heart urchin mortality (see chapter 8). The amphipod mortality was not correlated with any chemical or physico-chemical parameter. Sediments that passed the chemical quality guidelines showed a low frequency of adverse effects in the amphipod, Microtox SP and DR-CALUX bioassays and a gradual increase in significant toxicity results at higher levels of contamination. This was not the case for the heart urchin bioassay. A substantial proportion of sediments contaminated with mineral oil had a better amphipod and heart urchin survival than was expected from the median lethal concentration for mineral oil of these species. The most likely reason for the lower toxicity is weathering of the oil components. As far as TBT is concerned, no causal relationship was established between the observed TBT levels and acute toxicity in the harbour sediments. It was concluded that assessments of slightly contaminated and very contaminated sediments showed redundancy among bioassays and sediment chemistry, but in moderately contaminated sediments both types of measurements are complementary.

11.4 Integrated assessments

Monitoring at dumping sites in the North Sea

The environmental impact and recovery associated with the disposal of large volumes of moderately contaminated dredged material from the port of Rotterdam was studied at two dumping sites close to each other in the North Sea (see chapter 9). During the period of dumping, very few benthic invertebrates were found at the sites. Concentrations of cadmium, mercury, PCBs, PAHs and TBT were double to triple those at a reference site. In four different bioassays with marine invertebrates the sediments showed no acute toxic effects. In tissue (pyloric caeca) of resident starfish *Asterias rubens*, the residual levels of mercury, zinc, PCBs and dioxin-like activity were never more than twice those at the reference site. Four different biomarkers were used on the starfish tissues, but no significant differences were found. Minor pathological effects were observed in resident dab *Limanda limanda*. One year after dumping had ceased, a significant increase in the species richness and abundance of benthic invertebrates and a concomitant decrease in the fine sediment fraction of the seabed was observed. After 8.2 million m^3 of moderately contaminated dredged material had been dumped at the new dumping site Northwest, the species richness and abundance of benthic invertebrates declined. This correlated with a shift in sediment texture from sand to silt. It is concluded that marine benthic resources at and around the dumping sites have been adversely affected by physical disturbance (burial, smothering). However, no causal link could be established with sediment-associated contaminants.

An effects-based assessment framework

A novel effects-based assessment framework has been developed to more accurate identify hazardous dredged material that should be excluded from disposal into coastal waters of the Netherlands and stored in confined disposal facilities. The ecotoxicological and chemical parameters it requires cover a range of environmental hazards. An amphipod survival bioassay (*Corophium volutator*) and bacterial metabolic inhibition test (Microtox Solid Phase) are used to assess non-specific toxicity of the mixture of contaminants in harbour sediments. Persistent compounds with a dioxin-like mode of action are tackled by using the DR-CALUX bioassay and analysis of Ó$_7$-PCBs. As tributyltin (TBT) and polycyclic aromatic hydrocarbons are not adequately addressed by any of the bioassays considered, bulk sediment analysis in combination with sediment quality guidelines is used for both compounds. Chemical analyses are also required for mineral oil and trace metals but not for organochlorine pesticides because these compounds are no longer of concern.

The effects-based quality criteria for TBT and bioassays are frequently exceeded and require new solutions for sediment quality management in the coming years. A weight-of-evidence approach is proposed to balance between the ecological hazards of open water disposal and the socio-economic costs of confined disposal. A hazard quotient H was defined that weights all lines of evidence from the measured endpoints. Approximately 62% of the volume of the dredged material was not hazardous and directly acceptable for unrestricted open water disposal. Exceeding the effects-based quality criteria to some degree results in an acceptable volume of harbour sediments that requires confined disposal. At the same time a reduction in marine pollution is achieved thanks to a better selection of hazardous material when using the new assessment scheme.

11.5 Conclusion

More than half the dredged material from Dutch harbours suggested for disposal in coastal waters is of any environmental concern. The remaining part is slightly to moderately contaminated through present-day activities or through historic inputs. Several bioassays are applicable to assess the toxicity in these silty marine sediments. Using a test battery with four bioassays adverse biological effects were observed in a substantial parts of the sediments. The identification of compounds that contribute to the observed sediment toxicity appears to be a difficult task. Chemical analysis of the sediments showed (statistical) relationships with responses in some but not all bioassays.

On the basis of the research presented in this thesis an effects-based assessment framework was developed that could be used to improve the regulation on the disposal of contaminated harbour sediments into Dutch coastal waters thanks to a more accurate identification of hazardous dredged material.