ORIGINAL ARTICLE

Ecological risk assessment of contaminated sediments in a harbour site

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Key words

Marine sediments • Environmental and ecological risk • Geostatistical tool • Heavy metals • Organic pollution

Summary

During major dredging operations in the harbour of Genoa, one of the largest in Italy, a monitoring study was carried out on the quality of marine sediment output, with a view to identifying possible pollutants engendering environmental and ecological risk. The concentration range of all the pollutants evaluated fell within acceptable limits. The only pollutant with concentrations approaching ecological risk levels was nickel. Differences in concentrations of pollutants were mapped and related to specialized areas of harbour activity.

Introduction

Pollution of the marine environment is due to human exploitation of the sea shore and reaches a peak in harbours [1, 2]. Periodic dredging of harbours is associated with the migration and dispersion of pollutants in the water and the land bordering harbour areas. In 2005, extensive monitoring of marine sediments was carried out in Genoa harbour during major dredging work on the harbour bed. Soil pollution can be evaluated by using standard guidelines for analysing environmental and ecological risk. Environmental risk analysis concerns pollutants in residential and industrial areas; Ecological Risk Assessment (ERA), which is based on risk analysis guidelines [3], concerns the toxic effects of pollutants on the biological community. The quotient method, which was drawn up by Jones et al. in 1999, can be used at a screening stage to detect chemicals of potential ecological concern (COPECs) [4] and to identify geographic areas exposed to potential risk [5]. The Kriging method is used to map the local distribution of pollutants.
The aim of this study was to assess the environmental and ecological risk due to organic and inorganic pollution of the top 50 cm of sediment.

Materials and methods

STUDY AREA AND SAMPLING PLAN

Genoa harbour, one of the largest in Italy, extends for 20 km along the Ligurian coast of Northern Italy (Lat. 44°24'15''N; Long. 8°54'15''E). It can accommodate ships of any tonnage and handle all kinds of goods in its 13 cargo terminals. It also has a ferry and cruise terminal.
The 2005 monitoring campaign was carried out in the central area of the harbour according to the following sampling plan [6]: 199 sediment cores were collected from different harbour areas (Fig. 1). Each core was divided into 50-cm-thick sections. The sediment cores were extracted from a square mesh of 100 x 100 m or 50 x 50 m, by a core barrel with penetration ranging from 0.5 m to 5 m [3]. The 922 samples obtained were evaluated for the following chemical parameters: polycyclic aromatic hydrocarbons (PAHs), polychlorobiphenyls (PCBs) and heavy metals (As; Cd; Cr; Cu; Pb; Hg; Ni; Zn).

ENVIRONMENTAL RISK

Environmental risk was calculated in terms of the limits laid down by Italian law (D.L.152/06); the mean, minimum and maximum concentrations (mg/kg) are shown in Table I. There is an environmental risk when the mean values of the experimental data exceed the legal limits.

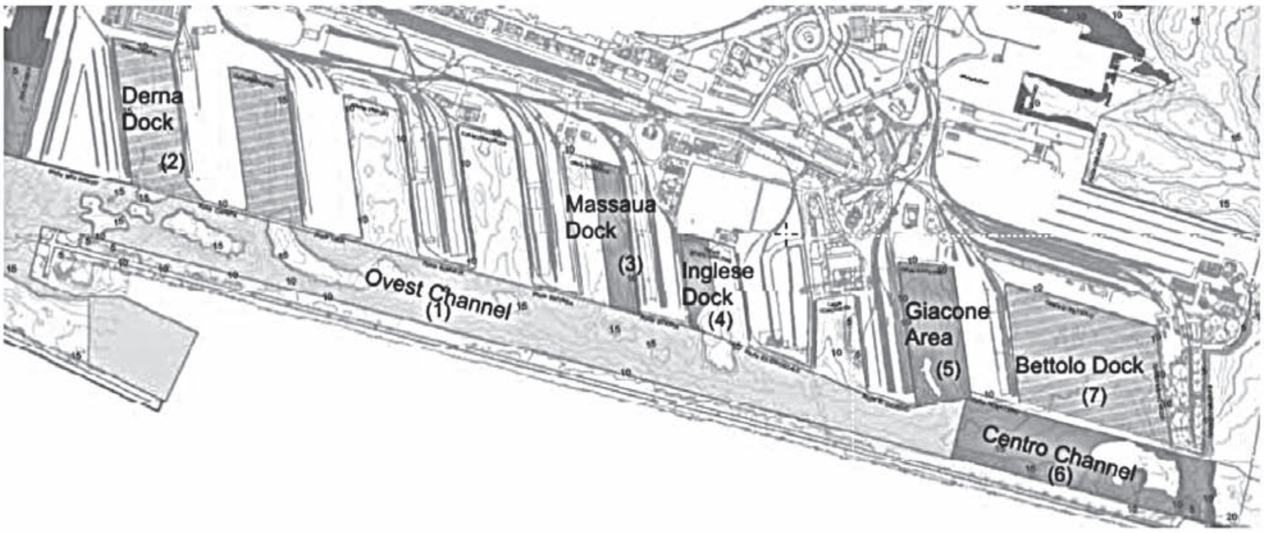
GEOSTATISTICAL TECHNIQUE

The "Kriging" geostatistical technique [7, 8] was used to obtain the spatial relationships from the pollutant values. The Kriging technique and spatial distribution maps of the pollutants were derived by means of the *Surfer® 8* software [5]. The final spatial distribution maps of the pollutants were used to estimate the amount of pollutants in the surface sediment.

ECOLOGICAL RISK

The ERA procedure applied in this study was developed by the U.S. Environmental Protection Agency on the ba-

Fig. 1. Map of central area of Genoa harbour: (1) heavy traffic of freighters (2) miscellaneous goods; (3) coffee, cocoa and chemical products; (4) cement, coal, steel products and forest products; (5) storage of kaolin, aluminium, coal and fertilizers; (6) heavy traffic of freighters; (7) miscellaneous goods.



sis of the risk analysis guidelines drawn up by the U.S. National Academy of Science.

ERA screening was used to establish the ecological condition of Genoa harbour. The ERA procedure identifies COPECs and estimates quantitative risk. COPECs were defined by means of the quotient method [4]. In this study, the quotient values were estimated as the ratio between the mean concentration of each pollutant and the toxicological benchmark concentration [4]. With ratio values > 1, potential acute toxicity can be expected.

Risk was characterized by means of two methods [5]: the first consists of comparing the cumulative distribution of the exposure to each pollutant (i.e. the cumulative frequency of the contaminants in sediment) with the corresponding toxicological benchmark for risk to the benthic community. The benchmarks applied were Sediment Quality Guidelines (SQGs), as defined by the National Research Council [3]: Effect Range Low (ERL), Effect Range Median (ERM), Threshold Effect Level (TEL) and Probable Effect Level (PEL) [4, 9, 10]. This procedure, which is recognized by the Society of Environmental Toxicology and Chemistry [11], has been widely adopted. The second method is geostatistical analysis of the estimated risk indexes in order to create a visual representation of risk [12]. A risk index is assigned to each station on the basis of the number of pollutants that exceed the corresponding TEL and PEL benchmarks. On the TEL risk map, pollutants with ERLquotient ≥ 1 (QERL ≥ 1) were considered, whereas on the PEL risk map, pollutants with ERMquotient ≥ 1 (QERM ≥ 1) were considered. The spatial distribution map obtained (risk map) allowed easy identification of the main areas of risk for the benthic community [5].

Results and discussion

As shown in Table I, the presence of pollutants fell within the limits imposed by law. With regard to chemical pollutants, concentrations (mean) were below the legal limits; environmental risk can therefore be defined as negligible in this area of study.

The quotients QERL and QERM were calculated for all pollutants considered: only nickel showed ERL and ERM quotients above 1 (Fig. 2). Therefore, the greatest danger for the benthic community stems from

Tab. I. Minimum, maximum and mean concentrations of heavy metals, PAHs and PCBs in the port of Genoa and the residential and industry legislation limits.

	As	Cd	Cr	Hg	Ni	Pb	Cu	Zn	PAH_s	PCB_s
Mean [mg/Kg]	4.35	0.32	81	0.5	55	139	70	220	11	0.04
Minimum [mg/Kg]	0.07	0.02	6.2	0.02	1.86	6	5.2	17.2	0	0
Maximum [mg/Kg]	19.2	2.3	304	2.80	166	1213	4921	1930	1171	1.75
Residential DL.152/06 value [mg/Kg]	20	2	150	1	120	100	120	150	10	0.06
Industrial DL.152/06 value [mg/Kg]	50	15	800	5	500	1000	600	1500	100	5

Fig. 2. Quotient values for heavy metals in sediments from Genoa harbour.

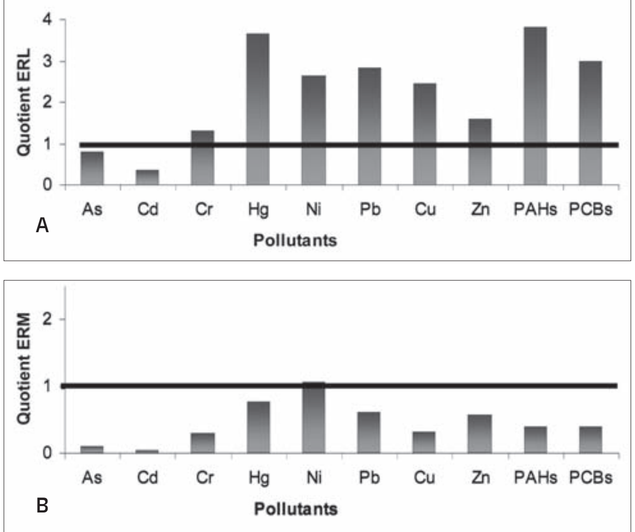
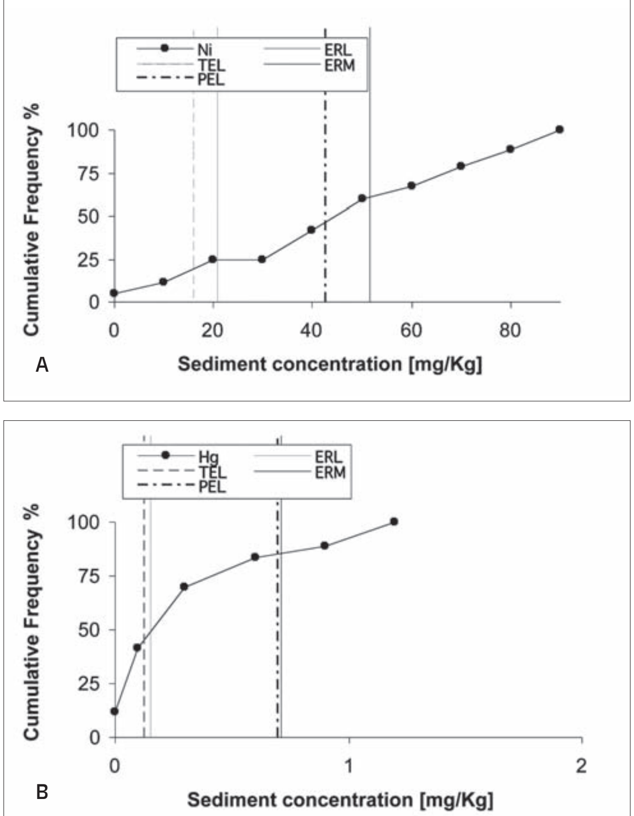


Fig. 3. Nickel and mercury risk estimation based on cumulative distribution comparing with the SQGs.



the presence of nickel, which is regarded as a COPEC. However, it should be noted that the value of the ERM quotient for mercury was close to 1.

Topic maps were created for all pollutants by means of the "*Kriging*" geostatistical technique; these showed that pollution was more concentrated in Bettolo Dock than in the other areas of the port of Genoa. Comparison of the recorded values of each pollutant with those specified in the guidelines reveals that the values of nickel are high and that many of these exceed the ERL limit (20.9 mg/kg) and ERM limit (51.6 mg/kg), particularly in Bettolo Dock, the Ovest Channel and the Giacone Area. This is probably due to industrial activities in the area.

The highest concentrations of mercury were found in close proximity to the Bettolo Dock-Centro Channel, where shipping traffic is heaviest, and close to Massaua Dock-Inglese Dock, where the industrial terminal is located. The maximum concentration recorded was 2.8 mg/kg.

While the highest concentrations of lead (1213 mg/kg), copper (4921 mg/kg), zinc (1930 mg/kg) and PCBs (1.75 mg/kg) were found close to Bettolo Dock, the highest concentration of PAHs (1171 mg/kg) was recorded in the Ovest Channel. The concentrations of the other pollutants were low and their distribution homogeneous.

The risk engendered by nickel and mercury, as estimated by comparing their cumulative frequency with the sediment quality guidelines, is shown in Figure 3. A graph of these metals is depicted since these are more dangerous for benthic organisms than other pollutants. However, the risk of exposure to all pollutants was also assessed.

Nickel concentrations exceeded the ERL and TEL values (the benchmarks associated with a low probability of adverse effects) in 75% and 80% of the sampling stations, respectively. Moreover, they exceeded ERM and PEL values (the benchmarks associated with a significant risk) in about 46% and 54% of the sampling stations, respectively.

Mercury concentrations above the ERL and TEL were found in 50% of the sampling stations and above the ERM and PEL in 30% of the stations. Similar values were recorded for lead, copper and chromium.

Zinc displayed a low potential risk; indeed, ERM and PEL values were exceed in fewer than 30% of sampling stations. On applying the same criteria adopted for the other pollutants (As, Cd, Cr, PCBs and PAHs), the risk was seen to be lower than 20%.

Figures 4 and 5 show risk maps based on the classes obtained from the TEL and PEL, respectively. On the TEL risk map (Fig. 4), the highest risk class (class 8) is located in the Ovest Channel, particularly at the western end, where the steelworks are located; in Massaua Dock, where the industrial terminal is situated and where heavy metals (Ni, Zn, Cu) are treated, and in some areas of Bettolo Dock, where the traffic of commercial ships is heavy. The most frequent risk class is class 5.

On the PEL risk map (Fig. 5), the maximum risk corresponds to class 2 and is seen in Bettolo Dock; in the Giacone Area and in some parts of the Ovest Channel, the highest class is 1. The only pollutant that is present in the entire area is nickel. When nickel is associated to other pollutants, in this case mercury, risk class values increase. A high concentration of nickel can lead to

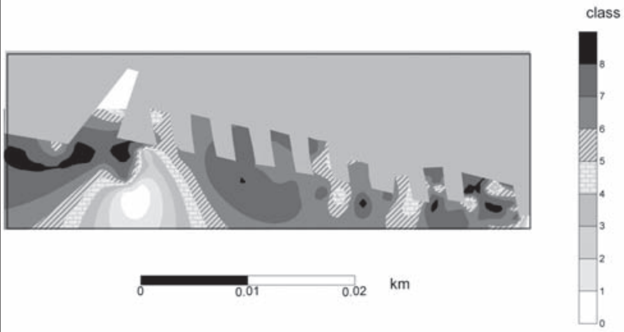


Fig. 4. Spatial distribution of indexes of risk for the benthic community; each risk class represents the number of pollutants exceeding the corresponding TEL benchmark value.

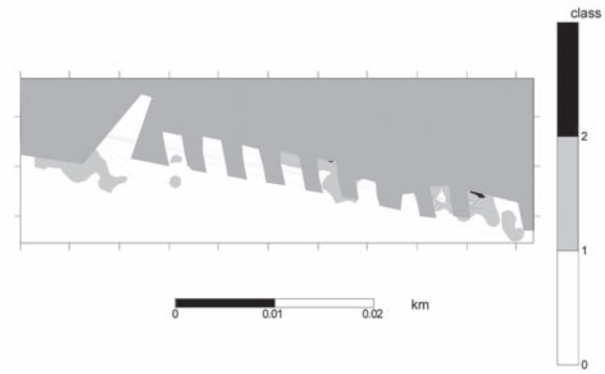


Fig. 5. Spatial distribution of indexes of risk for the benthic community; each risk class represents the number of pollutants exceeding the corresponding PEL benchmark value.

the death of microorganisms, and may affect the food chain [13].

Conclusions

According to Italian law, the harbour of Genoa is not a polluted area, since the mean values of our experimental data never exceeded the commercial and industrial limits imposed on pollutants.

These results can be used as a starting point to assess ecological risk in the port of Genoa. Our data enabled us to locate the areas with the highest ecological risk and to identify the COPECs present; the area at greatest risk is Bettolo Dock, and nickel is the most dangerous substance. In conclusion, the dredging work does not appear to have caused major problems, since the SQGs were exceeded only in Bettolo Dock and, in this area, removal of the sediment from the seabed is not foreseen.

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