Sedimentation and chronology of heavy metal pollution in Oslo harbor, Norway

Aivo Lepland a,*, Thorbjørn J. Andersen b, Aave Lepland a, Hans Peter H. Arp c, Elisabeth Alve d, Gijs D. Breedveld c, Anders Rindby e

a Geological Survey of Norway, Leiv Eirikssons vei 39, 7491 Trondheim, Norway
b Department of Geography and Geology, University of Copenhagen, Oester Voldgade 10, 1350 Copenhagen, Denmark
c Norwegian Geotechnical Institute, P.O. Box 3930 Ullevål Stadion, 0806 Oslo, Norway
d Department of Geosciences, University of Oslo, P.O. Box 1047 Blindern, 0316 Oslo, Norway
e Cox Analytical Systems, Östergårdsgatan 7, SE-43153, Mölndal, Sweden

A R T I C L E   I N F O

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A B S T R A C T

Stratigraphic profiles of Cu, Cd and Hg in ten sediment cores from the Oslo harbor, Norway, combined with results of radiometric dating demonstrate that pollution by these metals peaked between 1940 and 1970. Dating results indicate that Hg discharges peaked between 1940 and 1950, Cd reached maximum ca. 1955–1960, and Cu has the highest concentration in sediment interval corresponding to ca. 1970. Geochemical profiles and maxima of Cu, Cd and Hg concentrations can be used as chronostratigraphic markers for sediment cores from the Oslo harbor. Acoustic backscatter and sediment core data indicate that propeller wash affects the seabed in the Oslo harbor. The propeller-induced turbulence causes erosion, and in places exposes and remobilizes contaminated sediments that accumulated in the harbor during previous decades. Such re-exposure of contaminated sediments could be detrimental to local ecosystems and offset remediation efforts, warranting further impact studies and potential mitigation strategies to prevent redistribution.

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1. Introduction

Anthropogenic contaminants discharged into water-bodies can cause detrimental effects to marine ecosystems, which above certain threshold levels can lead to species loss, fishing restrictions and dietary restrictions on seafood. Such consequences are particularly of concern in urbanized and industrial harbors. Regardless whether discharges originate from air, rivers, urban runoff or effluent pipes, contaminants such as heavy metals and organic pollutants are typically scavenged by suspended, fine-grained, mineral and organic particles in the marine environment, and are concentrated in hydrodynamically quiet basins where muddy sediments accumulate. Sheltered estuaries, fjords, bays and harbors that border densely populated industrial areas are thus particularly sensitive to contaminated sediment loadings (Bryan and Langston, 1992; Birch and Taylor, 1999; Vaalgamaa, 2004). Because of a quiet hydrodynamic regime but relatively high sediment supply from nearby landmasses, such sheltered basins may have a continuous and relatively high sedimentation rate, unless disrupted by dredging, dumping or disturbance due to propeller wash. Sediment profiles from such basins have thus the potential of providing a high-resolution historical contamination record that can be used for reconstructing past environmental changes (Valette-Silver, 1993; Callaway et al., 1998; Alve et al., 2009). Reliable deciphering of contamination histories requires, however, a control upon the accumulation and flux rates (Croudace and Cundy, 1995), and related sediment chronology that have most commonly been determined by the $^{210}$Pb radiometric dating method (Goldberg, 1963; Koide et al., 1973; Ruiz-Fernández and Hillaire-Marcel, 2009). A temporal framework of sediment profiles can also be established by using man-induced chemical tracers including radionuclides ($^{137}$Cs), and on the local scale by using heavy metals or other compounds which release into the environment is known from historical records (Kilby and Batley, 1993; Alve et al., 2009).

Although the marine basins in the vicinity of urbanized and industrialized areas have been acting as sinks for contaminants, stratigraphic profiles from several harbors and estuaries show decreasing abundances of metal contaminants in the most recent sediments (Hornberger et al., 1999; Cearreta et al., 2000; Mason et al., 2004; Alve et al., 2009). This indicates that contaminant control measures and other changes (e.g. changes in energy production) can lead to an improvement of environmental status. In areas experiencing such improvement, the ongoing natural accumulation of cleaner sediments has been burying heavily contaminated sediments, thereby limiting the bioavailability of earlier accumulated pollutants. However, such natural isolation of con-
taminated sediments is not the case everywhere where discharges have been reduced. Physical disturbance of the seabed due to bioturbation, dredging or propeller wash may expose and re-suspend heavily contaminated particles (Cundy et al., 2003; Granberg et al., 2008) from previous decades. Thus, contaminated sediments that have been buried under cleaner sediments through natural sedimentation processes are still vulnerable, as seabed disturbances can cause remobilization of contaminants. Relatively shallow harbors that are being navigated by powerful ships are likely to be particularly susceptible to environmental effects of contaminant remobilization by re-suspension.

Sound management of impacted basins and planning of remediation strategies require a thorough understanding of the sedimentation regime (both natural and man-induced) as well as knowledge of the pollution history and distribution of contaminants in the sediments. In this paper we examine the stratigraphic and spatial trends of selected heavy metals (Cu, Cd and Hg) in bottom sediments of the Oslo harbor, Norway. The radiometric dating results are used for reconstructing the contamination history of individual metals and to assess the potential of concentration maxima of individual metals as local chronostratigraphic markers. Acoustic seabed reflectivity data, combined with sediment sample observations, are here used for textural characterization of the seabed and for defining areas that are affected by propeller wash and related sediment re-suspension.

2. Inner Oslofjord and Oslo harbor

Oslo harbor is located in the northernmost end of the inner Oslofjord, a fjord system consisting of two main basins, Vestfjord and Bunnefjord with a water depth exceeding 150 m in both basins (Fig. 1). The microtidal (ca. 20 cm range) inner Oslofjord is separated from the outer fjord system and the Skagerrak Sea by a shallow sill (19 m) at Drøbak. The circulation in the inner Oslofjord is estuarine with a halocline at about 20 m water depth (Baalsrud and Magnusson, 2002). Seabed topography in the inner Oslofjord is largely controlled by the Early Paleozoic stratified metasedimentary rocks (Dons and Larsen, 1978; Olaussen et al., 1994) that form the bedrock in a majority of the area. Selective erosion of less resistant strata within the package of NE–SW-striking metasediments has formed a pattern of NE–SW trending depressions and ridges at the seabed (Fig. 1). Numerous faults, fractures and mafic dykes cut the Early Paleozoic metasediments nearly perpendicular to the strike, and create another set of depressions and ridges that extend in NW–SE direction (Fig. 1). Glacial and post-glacial unconsolidated sediments occur mainly in depressions, and have thus a patchy distribution. Bedrock ridges that form submarine topographic highs typically have a thin (<2 m) sediment cover or are completely bare of sediments. Sediment thicknesses within individual basins are highly variable with maximum thickness in excess of 100 m in the deep Bunnefjord basin. Glacial diamictite that is exposed in some places at the seabed is interpreted to form the base of the sediment succession in depressions. The diamictite is overlain by glaciomarine and Holocene mud. Distinct seismic reflectors at ca. 10–15 m depth are observed in many depositional basins, and are interpreted to mark the contact between glacial till and glaciomarine sediments (NGU, unpublished data). The uppermost part of the Holocene sequence is typically very loose and rich in organic matter, and has a strong smell of H₂S, especially in basins close to Oslo city. Anoxic conditions developed at the bottom of several deep basins during the course of the last century, as a consequence of restricted deep-water renewals, and eutrophication resulting from a high supply of municipal waste, organic material, pollutants and nutrients. Such discharges into the fjord have considerably decreased over the last few decades as a result of governmental regulations and extensive sewage water treatment. As a consequence the anoxic conditions have been reduced both in spatial and temporal extent (Baalsrud and Magnusson, 2002). The fine grain-size and fluffy surface character of sediments in depositional basins indicate weak bottom currents and limited bottom transport. Pockmarks, i.e. 5–8 m deep crater-like depressions with ca. 60 m diameter that form in connection with fluid escape from underlying sediments and bedrock, are common in many sedimentary basins, particularly those with fault zones in underlying bedrock (Webb et al., 2009).

The area of the Oslo harbor investigated in this study is located around the island of Hovedøya and between the island and Oslo city (Fig. 2). It comprises a flat-bottom main basin at 20–23 m water depth with shallowing embayments at Pipervika and Bjørvika (Fig. 2). Bathymetric high-resolution data obtained in 2004 showed the presence of numerous dredging tracks, anchor scars, and wavy, filling-related loading bulges, indicating that the seabed in the area bears a strong physical anthropogenic imprint. The modern sedimentation regime in the area is influenced by big cruise ships and ferries that navigate in the basin and harbor at two different piers (Fig. 3). Small circular depressions representing pockmarks occur at several places around Hovedøya (Fig. 2).
The seabed in Pipervika and Bjørvika has been significantly altered during the course of the Oslo Harbor remediation project (2006–2008). Within the frame of this project, heavily contaminated surface sediments (Cornelissen et al., 2006, 2008; Oen et al., 2006) in shallow areas (<15 m water depth) of these embayments have been removed by dredging whereas the contaminated seabed in the water depth range from 15 to 20 m has been capped by sand and clay (Breedveld et al., 2009). Contaminated sediments in the deeper (>20 m water depth), main harbor basin were beyond the scope of the Oslo Harbor remediation project, but a possible later capping has been considered.

3. Methods and materials

3.1. Sediment sampling

Sediment cores from ten sampling stations around Hovedøya (Fig. 2) were obtained outside the dredging and capping areas during cruises in May 2005 and December 2006 using the Geological Survey of Norway (NGU) R/V Seisma and University of Oslo R/V Trygve Braarud respectively. A modified Niemistö corer (Niemistö, 1974) was used as a sampling device. The sediment penetration depth ranged from 0.45 to 0.9 m and never exceeded the length of the sampling tube (7 cm inner diameter). Seawater that occurred above the sediment surface was kept in the sampling tube to limit disturbances at the sediment–water interface. Retrieved cores were capped using rubber caps, and were handled and stored in an upright position. Duplicate cores were collected at each location during the 2006 cruise. One core set from the 2006 cruise has been utilized in this study, whereas the other core set was used for carbonaceous particle and organic contaminant analyses that are presented in a parallel publication (Arp et al., submitted for publication). Because of the very soft nature of the top 0.1–0.3 m sediment interval that greatly complicates undisturbed subsampling of wet sediment cores, the cores were frozen before further handling at the NGU’s laboratory. Frozen sediment cores were split lengthwise by a diamond rock saw. One half of the split core was used for geochemical analyses whereas the other half of two selected cores was subsampled for radiometric dating.

3.2. XRF core logging

The frozen split cores were imaged optically and radiographically, and XRF scanned for Cu (and several other elements that are not reported here) using an Itrax Core Scanner (cf. Croudace et al., 2006) at the Itrax factory in Gothenburg, Sweden. A few mm of the surface of the split cores was melted with a heat lamp, and smoothed with a spatula prior to scanning. This pre-treatment provided an ice crystal free, smooth sediment surface, and brought about the real sediment color. The scanning was undertaken at room temperature hence additional melting occurred during the course of analyses, but the bulk of the split core remained frozen.

![Fig. 2. Depth-colored shaded-relief image of the seabed in the Oslo harbor. Red dots indicate the locations of ten sediment cores studied in this paper. Arrows indicate the positions of pockmarks that occur in the seabed sediments.](image-url)
were determined by the Perkin Elmer Optima 4300 Dual View 
Cu (and many other elements not reported here) concentrations 
Gray to olive gray sediments in lower parts of cores were subsam-
17–19, 21–23, etc. down to the base of the dark colored section. 
obtained for intervals (cm) 0–1, 1–2, 2–3, 3–4, 5–7, 9–11, 13–15, 
grey to black), organic-rich section in the upper part of cores were 
geochemical analysis. Subsamples from the distinctly dark (dark 

clasts.

areas correspond to coarse-grained, higher density sediments or 
allow recognition of sedimentary structures and textural variations 
by small-scale variations in the sediment matrix. Because various 
geochemical elements absorb X-rays differently, the radiographic images 
illustrate the sediment texture in high (P0503007) and low (P0503009) backscatter amplitude areas. Dashed lines indicate the main navigation paths (from the web map service of the Norwegian Coastal Administration). The backscatter data are superimposed on the shaded-relief image.

X-rays, which in this study were generated by a Mo tube at 30 kV and 50 mA, are, in the Itrax system, focused to a 20 × 0.2 mm rectangular beam (size of irradiated area) with the long axis perpendicular to the axis of the sediment core. The XRF logging was done using a 2 mm step size and a 2 s counting time on eight of the cores, and using a 0.5 mm step size and a 1 s counting time on the remaining two cores (0609070, 0609071). The presented profiles show the down-core variations in Cu concentrations in relative arbitrary units (counts per second). The Cu profiles were smoothed using a 1 cm running average to suppress spikes caused by small-scale variations in the sediment matrix. Because various sediment types absorb X-rays differently, the radiographic images allow recognition of sedimentary structures and textural variations along the core. On grey-scale radiographic images, the lighter areas typically relate to fine-grained, low density sediments and darker areas correspond to coarse-grained, higher density sediments or clasts.

3.3. Inductively coupled plasma-atomic emission spectrometry (ICP-AES), atomic absorption (AA) and SC analyzer

After XRF scanning, the frozen split cores were sliced for further geochemical analysis. Subsamples from the distinctly dark (dark gray to black), organic-rich section in the upper part of cores were obtained for intervals (cm) 0–1, 1–2, 2–3, 3–4, 5–7, 9–11, 13–15, 17–19, 21–23, etc. down to the base of the dark colored section. 
Gray to olive gray sediments in lower parts of cores were subsam-
ples at 10 cm intervals by isolating 2 cm thick slices. Al, Fe, Mn and 
Cu (and many other elements not reported here) concentrations 
were determined by the Perkin Elmer Optima 4300 Dual View 
ICP-AES, Hg concentrations were determined by the CETAC M-
6000A atomic absorption cold vapor Hg Analyzer, and Cd concen-
trations were determined by the Perkin Elmer graphite furnace 
atomic adsorption system SIMAA 6000. Detection limits for re-
ported metals were the following (mg/kg): Al (20), Fe (2), Cu 
(0.5), Mn (0.2) Cd (0.02) and Hg (0.01). Precision was better than 
10 % (RSD) for all metals. For all these analyses acidified aqueous 
sample solutions were obtained by leaching 1 g of freeze-dried 
sediment with 7 N HNO3 in an autoclave at 120 °C for 1 h (Norsk 
Standard NS 4770). Note that this nitric acid leach does not attack 
resistant silicates hence the metal values given are not total con-
centrations. This acid leach typically dissolves metals that are car-
ried and scavenged by organic matter, clay minerals and authigenic 
precipitates as well as those that are scavenged by resistant min-
eral particles. The contents of total carbon (Ctot), organic carbon 
(Corg) and total sulfur (S) were determined with a Leco SC-444 an-
alyzer using 100–350 mg of sediment. Carbonate was removed with 
an excess 10% HCl prior to Corg measurements. The content of car-
bonate carbon (Ccarb) was calculated as the difference between Ctot 
and Corg. Detection limits for S, Ctot, Corg were 0.01%, 0.07% and 
0.1%, respectively, and the precision was <2.5% (RSD) for Ctot, and 
<10% (RSD) for S and Corg.

3.4. Dating of sediment cores

Radiometric dating of sediments using the 210Pb and 137Cs-
metho was undertaken on two cores by analyzing 36 subsamples 
collected from the second half of frozen cores. The subsampling scheme for dating included 2 cm intervals from the sediment–water interface down to 18 cm core depth, followed by selected 2 cm intervals further down-core (Table 1). The subsamples were analyzed for the activity of 210Pb, 226Ra and 137Cs via gamma spec-
trometry at the Gamma Dating Center, Department of Geography 
and Geology, University of Copenhagen. The measurements were 
carried out on a Canberra ultra low-background Ge-detector. 
210Pb was measured via its gamma-peak at 46.5 keV, 226Ra via 
the granddaughter 214Pb (peaks at 295 and 352 keV) and 137Cs via its peak at 661 keV. Contribution of unsupported 210Pb in mea-
sured samples was calculated by subtracting supported 210Pb from total 210Pb. Supported 210Pb was determined using 228Ra activity 
assuming equilibrium between these two isotopes. Radiometric 
dates were calculated from unsupported 210Pb records applying a 
modified CRS model (Appleby, 2001), forced by a chronostrati-
graphic marker (1963) derived from the 137Cs profiles. Standard 
CRS-model dates were older than the modified, reference year 
(1963) forced chronologies. In core 0503035 the 1963 peak was da-
ted to 1950; in core 0503036 it was dated to 1956. The reason for 
the discrepancy is not known but may be related to the rather 
coarse vertical sampling resolution and relatively low activity of unsupported 210Pb, which increases the standard errors on calcul-
ated dates based on this isotope. The chronologies based on a 
combination of 210Pb dating and 137Cs peaks were thus considered 
the more reliable. The reliability of 137Cs peaks in bottom sedi-
ments from the Oslofjord has later been confirmed by the dating 
results of other studies (E. Alve, unpublished data).

3.5. Interferometric sonar

The seabed in the Oslo harbor was mapped during a cruise in 
June 2004 with NGU’s research vessel RV Seisma using the Geo-
Acoustics 250 kHz GeoSwath interferometric sonar (see Lepland 
et al. (2009) for technical specifications). This sonar produces 
high-resolution bathymetric and backscatter data from the water 
depth range of 0–80 m. The sonar has two transducers, which are 
equipped with one transmitter stave and four phase differencing 
interferometric and sidescan receiving staves. All four receiving
Table 1

$^{210}$Pb and $^{137}$Cs activities, calculated radiometric dates (modified CRS model (Appleby, 2001)) and sediment accumulation rates for cores 0503035 and 0503036.

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<th>$^{210}$Pb total error (Bq kg$^{-1}$)</th>
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<th>$^{210}$Pb unsupported error (Bq kg$^{-1}$)</th>
<th>$^{137}$Cs (Bq kg$^{-1}$)</th>
<th>$^{137}$Cs error (Bq kg$^{-1}$)</th>
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staves record time series of the returning echo from the ensonified area. The calculation of the distance to the scattering location at the seabed is done by determining the angle of the returning echo and the elapsed time. The amplitude of the signal provides backscatter information, which is a measure of the relative texture and hardness of the seabed (Countrey and Shaw, 2000; Collier and Brown, 2005; Lepland et al., 2009). The across track sampling density of the GeoSwath system is 1.5 cm, and the vertical resolution of bathymetric data is estimated to be ± < 2 cm (GeoAcoustics, 2004).

4. Results and discussion

4.1. Seafloor backscatter and sediment texture

The acoustic data show that the majority of Oslo harbor comprises seafloor of relatively low backscatter amplitude (Fig. 3), consistent with the occurrence of fine-grained, cohesive sediments in the studied cores (Fig. 4a). However, the seabed in front of the piers and in areas being navigated by big ferries and cruise ships is acoustically highly reflective (high backscatter amplitude) in contrast with the rest of the harbor. Sandy and gravelly sediments occur within these high backscatter amplitude areas (Fig. 4b). The spatial position of these coarse-grained sediments right in front of piers indicates that they represent lag deposits formed by propeller wash. The high-amplitude zone with sandy and gravelly sediments extends from piers down to ca. 21 m water depth, defining the water column thickness that is strongly affected by propeller wash turbulence. Zones with intermediate backscatter amplitude extend from the high-amplitude patches at piers into the main harbor basin along the ship navigation pathways (Fig. 3). Such slightly elevated seabed backscatter amplitude within the navigation areas suggests a moderate propeller-induced effect that results in erosion and exposure of older, slightly more consolidated sediments and/or a development of a lag deposit with slightly coarser (more reflective) texture. The backscatter data thus indicate that propeller wash affects the seabed in the Oslo harbor down to at least a water depth of 23 m.

Fig. 4. Box core photos illustrating (a) the muddy texture and very soft nature of sediments in low backscatter amplitude areas (P0503009), and (b) coarse, gravelly-sandy sediment texture in high backscatter amplitude areas (P0503007). See Fig. 3 for locations of box cores.

Fig. 5. Stratigraphic distribution of Cu, Cd, and Hg concentrations (7 N HNO₃ leach on subsamples) in sediment cores around Hovedøya, Oslo harbor. Cores are arranged in a geographic sequence; see Fig. 2 for core localities. Dashed lines connect the maximum concentrations of individual metals, and highlight the systematic stratigraphic separation of Cu, Cd and Hg maxima in the studied cores. The positions of Cu correlation line (blue) in cores 0503035 and 0609075 are corrected (shifted ca. 5 cm upwards) based on the XRF core logger data, which show that the actual Cu maxima position in these cores are ca. 5 cm shallower than indicated by the subsample profiles.
4.2. Geochemical profiles

4.2.1. ICP-AES, AA and SC analyzer data

Geochemical characteristics show a distinct difference between the upper and lower parts of the sediment columns. The upper parts are variably enriched with heavy metals, Fe, C$_{\text{org}}$, C$_{\text{carb}}$ and S, but depleted in Al (Figs. 5 and 6) and other lithogenic elements (not shown). These characteristics reflect a strong anthropogenic imprint, and accumulation during periods of significant discharges of contaminants and nutrients. Nutrient discharges increased primary productivity, which in turn led to high contents of C$_{\text{org}}$ and C$_{\text{carb}}$ (largely calcareous biogenic debris), and promoted sulfate

![Graphical representation of geochemical profiles](image-url)
reduction with abundant Fe-sulfide precipitation (Fig. 6). The high abundance of carbonaceous, calcareous and sulfidic components effectively dilutes the detrital minerogenic components, and explains suppressed Al levels in upper parts of sediment columns (Fig. 6). The lower parts of sediment columns exhibit stable profiles of elements, representative of natural sediments in the area, and thus predate the anthropogenic influence on the Oslo harbor sedimentary environment.

Cu, Cd and Hg exhibit broadly similar stratigraphic profiles in all studied cores, characterized by distinct subsurface enrichments and a decrease towards the sediment–water interface (Fig. 5). Concentrations of Hg (6.2–19.3 mg/kg) and Cu (448–1490 mg/kg) within the maximum intervals in individual cores significantly exceed the threshold values of what is considered a severely contaminated sediment (Fig. 7) as defined by the Norwegian Climate and Pollution Agency (KLIF) (Bakke et al., 2010). Although the Hg and Cu concentrations are considerably lower in the surface sediments compared to the subsurface intervals (Fig. 5), they still fall within levels considered significantly to severely contaminated by KLIF (Fig. 7). It is noteworthy that Hg levels in sediments of Oslo harbor are up to an order of magnitude higher compared to some other harbors and industrialized estuaries (cf. Mason et al., 2004; Hammerschmidt et al., 2008). Cd concentrations reached the level of moderate to significant contamination (8.5–47.3 mg/kg) during the pollution maximum, but in the surface sediments Cd concentrations are typically within the limits of the minor contamination class (Fig. 7). The peak to surface ratios of metal concentrations for all cores except 0609072 range between 2.2 and 7.7 for Cu, 3.7 and 9.5 for Hg and 6.3 and 27.2 for Cd, and manifest a distinct decrease in surface sediments. These ratios are, however, relatively low (1.4, 1.5 and 1.4, respectively) in 0609072 due to anomalously high surface concentrations of metals in this core (Fig. 5). The depth of subsurface maxima of individual metals is geographically variable, but most cores show a stratigraphic separation of Hg, Cd and Cu peaks. Among these three metals Hg typically exhibits its maximum concentration in the deepest sediment interval, followed respectively by Cd and Cu maxima in shallower intervals (Fig. 5). For some cores, however, the sampling intervals (every second 2 cm interval analyzed from 5 cm core depth downward) are insufficient to resolve individual maxima (0503035, 0609075; Fig. 5).

4.2.2. XRF core logger Cu profiles

The resolution limitations that may occur while working with stratigraphic data obtained on a set of subsamples with gaps can be overcome by complementing the subsample dataset with stratigraphically continuous XRF core logger data on the same cores. It has to be noted, however, that the XRF counts reflect the total concentration of Cu whereas the 7 N HNO₃ leach leaves resistant silicates untouched, and this Cu fraction is not quantified. Under the condition that the Cu concentrations in the resistant silicate fraction is relatively low and stratigraphically stable, the trends seen on the XRF core logger profiles largely reflect the variations of non-silicate, 7 N HNO₃ extractable Cu. Thus, the XRF core logger counts, and the concentration data obtained using 7 N HNO₃ leachate can be considered comparable with a minor systematic offset due to resistant silicates.

Fig. 8 presents the comparison of Cu profiles obtained by two methods, and demonstrates that profile shapes and maxima positions generally agree. Still, in cores 0503035 and 0609075, the concentration maxima of the subsample dataset are stratigraphically ca. 5 cm deeper than suggested by the XRF core logger data (Fig. 8). Such inconsistencies are explained by the relatively coarse subsampling scheme which, as illustrated by these profiles (Fig. 8), may result in masking of specific features on subsample profiles. The XRF core logger data should thus be preferred in an attempt to define the stratigraphic position of Cu maxima.

Fig. 7. Comparison of Cu, Cd and Hg contamination levels in surface sediments (small dots) and in sediment intervals corresponding to the maximum contamination (large dots behind the small ones) using the environmental quality classification of the Norwegian Climate and Pollution Agency (Bakke et al., 2010). According to this classification, the sediments of Oslo harbor were severely contaminated by Cu and Hg and moderately to significantly by Cd at their contamination maximum. Although the metal concentrations have been decreasing significantly in most recent sediments (Fig. 5), the abundances of Hg and Cu in surface sediments still exceed the limit for severe contamination in some cores.

Whereas the Cu count rates in the studied cores were mostly above the detection limit of the applied XRF method, the concentrations of Hg and Cd were too low to be detected with the counting times used. Core logger data are therefore not available for Hg and Cd.
4.3. Sediment chronology

The obtained $^{210}$Pb and $^{137}$Cs records from two dated cores, 0503035 and 0503036, (Table 1; Fig. 6) show a gradual decrease of unsupported $^{210}$Pb with depth, and exhibit a two-peak profile for $^{137}$Cs. These well-defined $^{137}$Cs peaks are considered reliable chronostratigraphic markers, corresponding to atmospheric fallout from the 1986 Chernobyl accident and from testing of nuclear weapons that culminated in 1963 (DeLaune et al., 1978). Dating results from the lower part (below 22 cm) of core 0503036 are uncertain because of a clear indication of disturbance due to dumping of Fe-rich slag (dark, X-ray opaque interval on the radiograph; Fig. 8) that has apparently been heavily altered during diagenesis resulting in precipitation of abundant authigenic sulfides and carbonates (Fig. 6). Sediment dating indicates a relatively high though variable sedimentation rate during the middle of the last century until ca. 1960 (up to ca. 3 kg m$^{-2}$ year$^{-1}$, but note relatively large calculated errors (Table 1)), when sediments that were severely contaminated with the heavy metals accumulated (Fig. 6). Sediment dating indicates a relatively high though variable sedimentation rate during the middle of the last century until ca. 1960 (up to ca. 3 kg m$^{-2}$ year$^{-1}$, but note relatively large calculated errors (Table 1)), when sediments that were severely contaminated with the heavy metals accumulated (Fig. 6). Sedimentation rates may also be influenced by the ship traffic induced sediment dispersal, and the deepening of the wash zone during the last 4 decades.

4.4. Chronology of heavy metal contamination

Systematic relationships between Cu, Cd and Hg profiles in studied cores with concentration maxima of individual metals in consistent stratigraphic order (Fig. 5) may reflect (i) the temporal differences in discharge of metal contaminants or (ii) post-depositional redistribution of metals during diagenesis. Diagenetic alterations that may influence metal mobility are primarily driven by the oxidation of organic matter (Ridgway and Price, 1987), a process in which a variety of electron acceptors are used in a thermodynamic sequence, and by the precipitation of authigenic phases, most importantly sulfides (Zwolsman et al., 1993). Although there is a considerable overlap in progression of early diagenetic reactions, the oxidants (electron acceptors) of organic matter are generally consumed in the order: oxygen > nitrate > manganese oxides > iron oxides > sulfate, determining the diagenetic zonation (Froelich et al., 1979; Berner, 1980). Considering that remobilized metals are typically retained in sediments as sulfide precipitates (Ridgway and Price, 1987), the sediment interval in which effective metal mobility may occur extends from the sediment surface down to the base of the diagenetic sulfate reduction zone. Although no direct pore water measurements were undertaken to define the base of the sulfate reduction zone, the stratigraphic profiles of redox sensitive elements such as Fe, Mn, C$_{org}$ and S (Fig. 6) and the strong odor of H$_2$S in shallow subsurface sediments suggest that
sulfate is effectively consumed within the top few centimeters of the sediment column. The absence of distinct Mn and Fe enrichments at the surface, which would indicate oxyhydroxide precipitation, suggest that sediment columns are anoxic throughout. The thickness of the inferred sediment interval in which metals may have been remobilized and diagenetically fixed is thus considerably smaller than the stratigraphic separation of the Cu, Cd and Hg maxima that, though variable, typically exceeds 10 cm (Fig. 5). It appears therefore unlikely that the stratigraphic separation of Cu, Cd and Hg maxima is significantly influenced by diagenetic remobilization. Low abundances of Hg and Cu in an altered slag layer in core 0503036, which is extremely rich in authigenic sulfides and carbonates (Fig. 6), likewise indicates that the precipitation of these diagenetic phases does not concentrate Hg and Cu and alter sediment profiles, consistent with generally low dissolved Hg levels observed in estuarine pore waters (Gagnon et al., 1997). Precipitation of authigenic phases may have a minor influence upon diagenetic redistribution of Cd, as indicated by its elevated concentration in the precipitate-rich layer (Fig. 6). It appears, however, unlikely that Cd profiles bear a notable diagenetic overprint aside from the precipitate-rich layer, because Cd profiles as well as Hg and Cu profiles do not correlate with redox sensitive elements or with each other (Fig. 6). Instead, the development of well-defined metal maxima in stratigraphic order most likely reflects the temporal differences in discharges of individual metals that culminated first for Hg, and were followed respectively by Cd and Cu during more recent times. It has to be noted however that in basins where recent sedimentation rates have been variable, the maximum metal concentrations, if observed within intervals of slow sedimentation, may not always correspond to maximum discharges but can also be explained by low sediment dilution (Crouard et al., 1995).

Integration of metal profiles with the dating results allows the assignment of chronologic constraints on individual maxima. The Cu maximum occurs in core 0503036 slightly above the lower $^{137}$Cs peak (Fig. 6), and the same is evident in core 0503035 when the XRF core logger Cu profile is used instead of the subsample data (Figs. 6 and 8). The dating results using activities of both unsupported $^{210}$Pb and $^{137}$Cs thus suggest that sediments most enriched in Cu accumulated in the Oslo harbor in ca. 1970. Using the available dataset it is difficult to assess whether the Cu maximum in studied cores reflects the maximum of Cu discharges at ca. 1970, or is (partly) caused by low sediment accumulation rate after ca. 1960 as described above. If the change in accumulation rates is found to be crucial, an earlier culmination (ca. 1960–1965) of Cu discharges would be suggested.

Maxima of Cd and Hg both occur within sediment intervals associated with high accumulation rates (Fig. 6), hence it is likely that these maxima are indicative of maximum contamination by these metals. The heaviest Cd contamination, which pre-dates the Cu peak, reached its culmination in ca. 1955–1960. The maximum Hg contamination is interpreted to have occurred in ca. 1940–1950. However, this time estimate is rendered somewhat uncertain. This is because the corresponding sediment interval in core 0503036 is disturbed by the slag dumping as described earlier, and in core 0503035 the Hg peak is broad, complicating the exact definition of the Hg maximum using the available subsample dataset. Still, the inspection of metal profiles in all studied cores clearly reveals the regular stratigraphic sequence and relatively consistent spacing between the metal maxima in individual cores. Allowing the time span from Cd to Cu maxima to be 10–15 years, a slightly shorter time span can be suggested for the sediment interval between Hg and Cd maxima because of the change in accumulation rate at ca. 1960 as described above. Hence it appears reasonable to suggest that the peak Hg contamination occurred in the Oslo harbor within the time interval 1940–1950. Considering the importance of heavy metal maxima as useful chronostratigraphic markers in the Oslo harbor, additional high-resolution geochronology and geochemistry studies on sediment cores are needed for more accurate age dating of the characteristic features of the heavy metal profiles. The chronostratigraphic potential of other environmentally significant metals such as Pb, Zn, Cr, which are also enriched in the Oslo harbor sediments (data not presented), should likewise be assessed in future studies. However, the stratigraphic trends of these metals in the studied cores are not as systematic and do not show distinct maxima as observed for Cu, Cd, and Hg. This is possibly due to a greater variability of sources, hence the applicability of Pb, Zn and Cr as chronology indicators may turn out to be more limited.

4.5. Sedimentation in the Oslo harbor

The sediment thickness on top of the Cu maximum can be used for assessing the rate of deposition in different parts of the Oslo harbor since 1970. Fig. 5 indicates that the 1970 level is at a relatively shallow sediment depth in cores that were collected close to the ship navigations paths between Bjørvika and Hovedøya (0503035, 0609072, 0503036, 0503037; Figs. 2, 3 and 5). Westward, the 1970 level deepens in cores both north (0609071) and south (0609073, 0609074) of Hovedøya, and then shallows again in the most distant stations from the harbor (0609070, 0609075, 0609076). The core 0609073, which has the deepest Cu maximum and thickest sequence of contaminated sediments (Fig. 5) was collected from the pockmark, a depression that acts as a local sediment trap. The deep Cu maximum in 0609073 is thus partly related to the specific depositional conditions in the pockmark. Consequently the 0609073 is not fully comparable with other cores, and should be excluded in a general assessment of the sedimentation regime in the area. Still, the apparent high post-1970 sedimentation rate in cores 0609071 and 0609074 (i.e. both north and south of Hovedøya) is intriguing, particularly because there is no obvious natural reason for the higher sedimentation at these stations compared to ones closer to the harbor, which are more proximal to the main natural sediment source in the area, the Akerselva River (Fig. 2). The high recent sedimentation rate at 0609071 and 0609074 can, however, be explained by sediment sourcing from the adjacent navigation paths where propeller-induced disturbances and wash occur. Considering that the high sedimentation at 0609071 and 0609074 is due to sediment supply from the propeller wash areas, these (re)suspended sediments do not apparently get transported very far as indicated by shallow Cu maxima at nearby 0609070 and 0609076 (Figs. 2 and 5).

Anomalously high heavy metal concentrations at the sediment–water interface in core 0609072 (10 mg/kg Hg, 9.6 mg/kg Cd, 520 mg/kg Cu; Fig. 5), and a very shallow Cu maximum, suggest that erosion has occurred at this site, and this has re-exposed old (possibly from 1970s or early 1980s) contaminated sediments at the seafloor. Considering the unlikelihood of storm related erosion at 23 m water depth in relatively sheltered Oslo harbor, the most likely cause for this erosion at the site of core 0609072 is propeller wash, which is consistent with the intermediate backscatter amplitude in the area (Fig. 3). The soft character of muddy sediments at the surface of core 0609072, and a lack of any obvious lag deposit which would hinder sediment re-suspension, indicate that the seabed in this particular area is susceptible for further erosion that may expose and remobilize contaminants from even deeper, more severely impacted intervals. The acoustic backscatter data presented above (Fig. 3) indicate that sediment re-suspension and erosion due to the propeller wash is apparently a widespread phenomenon in the Oslo harbor. The areal extent of the seabed where the propeller wash reworks old, heavily contaminated sediments in the Oslo harbor is currently unknown, but this poten-
tially important contaminant source has to be accounted for within the context of environmental management. Quantification of contaminant remobilization due to propeller wash is particularly important now, after the completion of the Oslo harbor remediation project, in which shallow areas (<20 m) of the harbor have recently been cleaned up by dredging and capping. Positive environmental effects of this remediation could be offset by the input of remobilized contaminants from the propeller wash areas. To minimize these risks, mitigation strategies such as capping of the seabed within the navigation paths in the main basin of the Oslo harbor should be considered.

5. Conclusions

Systematic trends in Cu, Cd, and Hg concentrations with stratigraphically separated maxima and decrease towards the surface in sediment cores from the Oslo harbor reflect the time difference in anthropogenic discharges of these individual metals. The maxima in Cu, Cd and Hg profiles serve as chronostratigraphic markers, and can be used for a temporal framework and for correlating sediment cores in the Oslo harbor.

The modern sedimentation regime in the Oslo harbor is strongly influenced by ship traffic. Turbulence due to the propeller wash limits the sedimentation within the navigation paths of cruise ships and big ferries, and locally causes erosion of the seabed. This propeller-induced erosion has a negative effect on the environmental conditions as it exposes and remobilizes sediments from previous decades that are severely enriched with various contaminants.

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