An investigation of trace metals and oil contamination in Southampton Water sediments: the distribution and influence on organisms

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Abstract. An investigation was conducted on 21st April 2012 in Southampton Water sediment, with the aim of detecting the contaminants distribution and the influence on the living organisms. Among the sampling sites, station 3 and 4 are most close to Fawley oil refinery, where contaminants with respect to trace metals, Cu and Zn, and oil are observed with highest concentrations. Metals contained in the sediments are in forms of weakly bounded compounds, such as carbonates and oxides, or strongly bounded complex, including organic metals and sulphide. High values of organic matter concentration in sediment at station 3 agree with the oil release from Fawley. Chlorophyll a concentrations are lowest at station 4, corresponding to the high pollution around.

1. Introduction  
Trace metals are necessary nutrients, including Fe, Zn, Cu, Mn, Co, Ni, Mo, etc., for all living organisms in extremely small amounts. They are essential components of important enzymes catalysing many crucial biochemical reactions. Some of the metals have pairs of oxidation states with similar free energy and are well suitable for the functions of storage, transport and transfer of energy[1] and maintenance of reduction states within cells through redox reactions. For instance, Fe-S rich ferredoxin is ubiquitous in electron transfer in all biological systems[2]; Cu-Zn superoxide dismutase is an important antioxidant in eukaryotes cytoplasm and Fe-Mn superoxide dismutase in mitochondria and in prokaryotes[3]. Cells take up various trace metals in particular amounts by active transport to satisfy their own need, although, to some extent, the ambient concentrations and ratio of these metals vary. However, when the changes are extremely high, above the tolerable limits, which organisms can no longer resist, these trace nutrients can be toxic ingested in excess quantities.

Because of human activities, large inputs of many metals and the organic loading into the oceans have modified the abundances and the cycling processes of trace metals hence enhanced the biological availability, leading to adverse influence on marine biota. Mining and processing of metals directly increase the emission of various metals into the oceans; land use change enhances the inputs of metals by leading to the desertification causing dust storms over the oceans; and eutrophication in coastal areas due to agriculture increases organic matter and decreases oxygen in seawater, which indirectly affects the bioavailability of various trace metals[3]. Concentrations of metals in sediments are higher than those in the overlying waters by 3 – 5 orders of magnitude, and the organometallic states of...
several metals in the sediments also increase the bioavailability and toxicity\cite{4}, which means benthic communities suffer more severe ambient metal contamination than other marine organisms.

An investigation of the trace metals and oil contamination in Southampton Water sediments was conducted on 21st April 2012 by *R.V. Callista*. The aim of the study is detecting the distribution of the trace metals, Cu and Zn, and oil released from Fawley oil refinery into the sediment, and the impacts on the living organisms.

2. Methodology

Fourteen stations were set up along Southampton Water and the River Hamble near the Fawley oil refinery (Figure 1). Site coordinates are summarized in Table 1.

![Google map](image_url)

**Figure 1.** Sampling sites along Southampton Water and the River Hamble.

| Station | Latitude      | Longitude     | Station | Latitude      | Longitude     |
|---------|---------------|---------------|---------|---------------|---------------|
| 1       | 50°52.780 N   | 1°23.812 W    | 7       | 50°49.287 N   | 1°18.561 W    |
| 2       | 50°51.794 N   | 1°22.190 W    | 8       | 50°51.238 N   | 1°18.547 W    |
| 3       | 50°50.995 N   | 1°20.655 W    | 9       | 50°52.432 N   | 1°18.538 W    |
| 4       | 50°50.759 N   | 1°20.112 W    | 10      | 50°50.837 N   | 1°19.408 W    |
| 5       | 50°49.939 N   | 1°19.351 W    | 11      | 50°51.788 N   | 1°20.715 W    |
| 6       | 50°49.530 N   | 1°18.902 W    | 12      | 50°52.380 N   | 1°21.613 W    |
| 7       | 50°49.287 N   | 1°18.561 W    | 13      | 50°52.628 N   | 1°22.220 W    |

Sediment sample was collected at each station; surface samples were scraped from the grab samples and stored in the Sterilin tubes; relatively undisturbed sediment cores were obtained from the grab samples at 6 stations (station 2, 3, 6, 9, 11 and 13). Overlying water was collected at each station by a through flow device on the hull of the *R.V. Callista*.

Pore-water density was assumed of about 1.026 g cm\(^{-3}\). The porosity and water content were derived by the following formulas\cite{5}. Each sample was preprocessed with HCl and HNO\(_3\). The copper and zinc contents were derived by measuring the absorptions of the samples using the Flame Atomic Absorption Spectrophotometer (F-AAS) at the wavelength of 213.9 nm for Zn determination and 324.7 nm for Cu\cite{6}. The fluorescence of each preprocessed sample was measured using LS55.
Fluorometer. And the oil concentrations were calculated using standard curve[7]. The carbon and nitrogen contents were determined using automatic CN-analyzer following the partitioning of inorganic and organic carbon phase by acidification with 25% HCl in situ within silver sample cups[8]. Chlorophyll a samples were collected by the Glass Fibre Filters and extracted using 90% acetone. Measurements were conducted using 10-AU-Fluorometer.

\[
\text{Porosity} = \frac{\text{Wet weight} - \text{Dry weight}}{1.026} \times \frac{1}{2}
\]

(1)

\[
\text{Water content} = \frac{\text{Wet weight} - \text{Dry weight}}{\text{Wet weight}}
\]

(2)

3. Results and discussion

3.1 Sediment porosity and water content

Porosity is the parameter describing the amount of open space in a geologic material. Sediment porosity consists of open space between sediment grains filled with pore water. Water content is the proportion of water in the sediment by mass. Figure 2 shows the porosity and water content of the sediments from fourteen stations. Porosity values from all these stations are higher than 0.6, and water content is ranging from 35%-62%, suggesting large open space and high pore water content in the sediment.

![Figure 2. Sediment porosity (by volume) and water content (by mass) of each station.](image)

There is an obvious mistake on porosity data at station 9, since porosity values should not exceed one, which may result from operation error or record mistake; those from station 8 and 13, which are relatively high, may also lack of reliability. Besides, assuming the density of pore water is 1.026 g cm\(^{-3}\) and a constant density of sediment, porosity and water content values should be direct proportioned. However, the obvious mismatch between porosity and water content indicates potential mistakes possibly due to sampling or operation error. Otherwise, this mismatch may imply high variations of pore water density and sediment density from different stations. Further investigation and more accurate work are needed to confirm the argument.

These porosity data are used in the following data analysis to convert the concentration or percentage per mass of wet sediment into those per mass of dry sediment. Assuming that each wet sample has a uniform density \(\rho\), the scaling factor can be expressed as:

\[
\frac{1}{1 - \text{Porosity}}
\]

(3)

which is derived from the formulas as below:
3.2 Copper and zinc content

Oceanic Cu concentrations are about 0.1 μg/L, and in UK estuaries are with values of 2 – 3 μg/L in the Bristol Channel – Severn Estuary, and 3 – 176 μg/L in Restronguet Creek. In the sediments of UK estuaries, Cu concentrations range from 10 – 2000 μg/g, from clean areas to heavy polluted regions like Restronguet Creek[9]. The concentrations of Zn in the open ocean are less than 1 μg/L and those in estuaries and coastal areas are much higher. Zn concentrations in the Bristol Channel – Severn Estuary are about 11 – 23 μg/L, and in Restronguet Creek range from 20 – 20460 μg/L. Sediments in UK estuaries contain Zn ranging from less than 100 μg/g to over 3000 μg/g[10]. Data from Bryan and Langston[4] show an average valued 31 μg/g of Cu concentration and 105 μg/g of Zn concentration in Hamble sediments. Average concentrations of Cu and Zn in surface sediment in the investigating area are about 46 μg/g and 103 μg/g. Figure 3 shows Cu and Zn concentrations in surface sediments by both HCl and HNO₃ leaching.

![Figure 3. Cu and Zn concentrations (μg/g) in dry sediments along fourteen stations. Some data were lost during the experiment and the absence was compensated by interpolation while plotting.](image-url)

Remarkable high concentrations of both Cu and Zn are found at station 9 (Cu-HCl 405 μg/g, Cu-HNO₃ 173 μg/g, and Zn-HCl 571 μg/g; Zn-HNO₃ data is lost). As mentioned before, concentrations in dry sediments are derived by using porosity data. Since the porosity at station 9 exceeds 1, which is impossible, these concentration values are therefore unreliable. High value of Cu by HNO₃ leaching occurs at station 3 (241 μg/g) which is expected due to the adjacency to Fawley. Compared with the low value from HCl leaching, the difference may suggest strongly bounded Cu at this site, because weakly bounded metals such as metallic oxides or carbonates can be extracted by acid; while organic metals or metallic sulphide can be extracted by concentrated HNO₃ due to its strong oxidising ability. This also explains that values from HNO₃ extracts are mostly larger than those from HCl leaching (ignoring station 9). Sediment characteristics, with sulphur smell and no life, at this station also agree with metal behavior. A small peak of Cu-HNO₃ at station 13 (101 μg/g), as well as Zn-HNO₃ at station 2 (250 μg/g), which is far away from Fawley, suggests other process or inputs than just diffusion from Fawley. Otherwise, it may be due to any sampling or operation error, as the porosity of station 13 is lack of reliability. Station 4 and 10, which are near Fawley, see unexpected low concentrations for both Cu and Zn. Vertical profiles of metal concentrations in sediment cores are shown in Figure 4 (Cu) and Figure 5 (Zn). Difference between Cu-HCl and Cu-HNO₃ at station 2, 3 and 11 suggests the existence of organic and sulphide bounded Cu. High values at station 3 are due to the adjacency to Fawley, but the remarkable peak at station 13 at the depth of about 3 cm is puzzling. Since other points are much lower and several data are absent, this point may be inaccurate. The consistency of
Zn-HCl and Zn-HNO₃ suggests little organic bounded Zn in the sediment. Station 9 misses most of the data and can hardly show the vertical profile of the metal concentrations in the sediment.

Figure 4. Cu concentrations in dry sediments (μg/g) with depth (cm) at station 2, 3, 6, 9, 11 and 13. Concentration scales were modified consistently (400 μg/g) to better illustrate the changes between different cores. Some data were lost during the experiment.

Figure 5. Zn concentrations in dry sediments (μg/g) with depth (cm) at station 2, 3, 6, 9, 11 and 13. Concentration scales were modified consistently (500 μg/g) to better illustrate the changes between different cores. Some data were lost during the experiment.
3.3 Oil concentrations

Oil distribution in sediment along Southampton Water and the River Hamble is shown in Figure 6. The average value of oil concentration is about 1.10 mg/g. Highest value of 4.29 mg/g is found at station 9, but as mentioned before, concentrations in dry sediment from station 9 are inaccurate due to its wrong porosity. The reliable peak at station 3 with the value of 3.33 mg/g, and the other high value of 2.68 mg/g at station 4 clearly show hydrocarbon introduction by Fawley. Sediment samples at these sites are oily and sticky, with sulphur smell and no life existing, which are consistent with the high oil distribution.

![Figure 6. Oil concentrations in dry sediments (mg/g) along fourteen stations.](image)

3.4 Organic carbon, nitrogen and chlorophyll a

Figure 3.4 shows the result of C-N analysis. Higher values with respect to both C and N at station 3 than those at station 11 clearly indicate the influence of hydrocarbon discharge from Fawley.

![Figure 7. Percentage (%) of organic carbon and nitrogen in dry sediment with depth (cm) at station 3 and 11. Percentage scales were modified consistently (0.031\%) to better compare the change between the two cores.](image)

Contaminants within sediments dissolve in the pore water and diffuse to the overlying water then affect organisms especially plants in the overlying water. Chlorophyll a is often used to analyse plant distribution. Figure 8 shows the concentrations of chlorophyll a in overlying water of the fourteen stations.

![Figure 8. Chlorophyll a concentrations (μg/L) in overlying waters along fourteen stations.](image)
stations. The average value is about 0.5 μg/L. Highest value of 0.939 μg/L is found at station 6 where is far from Fawley, Lowest value (0.066 μg/L) is at station 4 where is near Fawley and with high trace metals and oil concentrations, suggesting that contaminants from Fawley adversely affect the living organisms. The abnormally low values at station 1 and 2 may probably attribute to sampling or operation error since seaweed exists in those sediment samples.

4. Conclusion

Among the sampling sites, station 3 and 4 are most close to Fawley oil refinery, where contaminants with respect to trace metals, Cu and Zn, and oil are observed with highest concentrations. Metals contained in the sediments are in forms of weakly bounded compounds, such as carbonates and oxides, or strongly bounded complex, including organic metals and sulphide. High values of organic matter concentration in sediment at station 3 agree with the oil release from Fawley. Chlorophyll a concentrations are lowest at station 4, corresponding to the high pollution around.

Some unexpected values that are hard to explain may imply other factors, but may be also due to sampling and operation errors. A lot of data absence and mistakes pose more difficulties to the data analysis. Further studies are needed to improve the accuracy of the experiment operation, as well as to obtain finer data along Southampton Water and the River Hamble for comprehensive and profound analysis in order to help fully understand the contaminants behavior in the sediments and overlying water and the impacts of Fawley on the local environments.

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