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Innovative treatment by bioremediation of contaminated sediments from the Venice Lagoon, Italy: the Arsenale Vecchio case study.

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ABSTRACT

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Sediments in industrialized and/or urbanized coastal shallow waters have reached an alarming and harmful level of contamination that requires the development of new cost effective technologies. We report on the in situ forced aeration experiment in the Arsenale shipyard dock basin of the Venice Lagoon, Italy.
This study follows the promising results obtained by similar experiment carried out in the Industrial Harbor of Marghera, where sediment reworking and mixing are strong. The study site of the Arsenale shipyard was chosen in order to test a new forced aeration system aimed at oxygenating the surficial sediments with a minimum of reworking and mixing.
The aeration technique, chosen for the oxygenation of the highly polluted bottom sediments, is unique due to its innovative use of a system of porous pipes laid on the bottom sediments, therefore it is non intrusive and does not obstruct harbor activities.
Forced aeration consists in the introduction of a great quantitative of oxygen at the surficial sediment-water column interface with the aim of stimulating aerobic bacterial communities to create an adapt environment for the biodegradation of organic and inorganic pollutants. The general reduction of organic pollutants and heavy metals in the surficial sediments resulted in the documented return of small fish to the area as an indication of a less polluted environment. The experiment has indicated that tangential forced aeration could represent a non intrusive and cost effective way for reducing organic and heavy metal pollutants in coastal environments where other techniques may not be environmentally and/or economically feasible.

ADITIONAL INDEX WORDS: *Geochemistry, bioremediation ,surficial sediments, innovative technology, heavy metal contamination*

INTRODUCTION

Marine and fresh water systems all over the world in recent years are under environmental stress due to increased urban, industrial and agricultural development and related pollution, becoming a worldwide issue. Sediments are described as the last sink or storage place for pollutants and their accumulation process in sediments creates an internal reservoir that might influence the overlaying water column. The remediation of contaminated sediments requires urgent action that, in turn, represents major financial costs. The choice of the proper methods and technology for the environmental recovery of polluted water systems is fundamental in order to accomplish the sediment remediation with the lowest financial impact and with technologies non intrusive to the environment. The high level of contamination found in surficial sediments of highly urbanized and/or industrialized areas required an in depth understanding of the contamination problem and the development of new, cost effective and environmentally non-intrusive techniques. Although the use of many contaminants have been restricted or banned, past contaminants persist for many years in the surficial and sub-surficial sediments of water bodies, both inland and in coastal areas, and become potential hazard to human health and to the environment. Through the years, interest and concern for these extremely distinct ecosystems have increased the scientist efforts to find new cost-effective technologies to recover contaminated sediments in water body ecosystems. Two different approaches for the recovery of contaminated sediments are used: *ex situ* and *in situ* treatment. *Ex situ* treatment is always preceded by dredging and transportation of the sediments far from the original site:

dredging can lead to re-suspension of sediments and further contamination of the water column while spills and volatilization may occur during transportation. To minimize these risks, sediments can be treated *in situ* using different techniques such as: natural attenuation, oxygenation, bioremediation, capping, solidification, confinement and so forth.

In general, most modern techniques applied to recover polluted water environments are related to long-term results. Of the several techniques available, oxygenation by forced aeration, chosen for this experiment, represents a quite innovative and promising approach, with almost immediate results (Bonardi et al., 2004).

The forced aeration technique consists in the introduction of a great quantitative of oxygen at the surficial sediment-water column interface with the aim of: a) stimulating the growing of aerobic bacterial communities by supplying them with oxygen (electron acceptor for aerobic metabolism), b) creating an adapt environment for the biodegradation of inorganic and organic pollutants. Many of these are particularly resistant to biodegradation due to the presence of one or more aromatic rings in their molecular structure, in the presence of appropriate oxygenation condition however, several species of bacterial can break the aromatic ring through particular enzymes called cyclo-oxygenase. Bioremediation is in fact the process that uses microorganisms or their enzymes to restore contaminated environments to their original condition.

The aim of our experiment was to determine: a) the effect of forced aeration and oxygenation on bottom and sub-bottom sediments, b) the inorganic pollutant content variations with time, c) the relation between sediment textural, mineralogical and geochemical characteristics and the content of contaminants.

STUDY AREA: THE ARSENALE VECCHIO OF THE LAGOON OF VENICE

The Lagoon of Venice, located in the northern part of the Adriatic Sea (Figures 1, 2) is a shallow basin with a surface area of about 550 Km^2 and an average depth of 0.6 m. The Arsenale area, located in the eastern part of Venice covers an area of about 46 ha, of which 11ha are water. Presently under the Italian Navy jurisdiction, the Arsenale are dates back its origin to the XI century when shipyard activities started with peak expansion during the XV century. The Arsenale Vecchio shipyard dock basin (Figure 3) was chosen for our experiment because of its limited size and reduced boat traffic.

Geological setting

The sediments underlying the Arsenale area, as for the Venice Lagoon, consist mainly of unconsolidated sand, silt, clay and peat. Mud layers with different level of consolidation are present within this sequence (Serandrei et al. 2003). The present bottom sediments of the test area consist mainly of the original marine-lagoonal sediments mixed with the polluted landfill material from the surrounding reclaimed marsh and with the recent contaminated material from the past shipyard activities and the more recent Navy operations.

THE FORCED AERATION SYSTEM

The forced aeration apparatus, supplied by SAPIO Industries (Figure 4) was located on the dock adjacent to the experiment area. It consists of a 20 000 liter cryogenic evaporator, a main distribution conduit (Figure 5), and a set of 19 porous pipes 21 m long laid on the bottom floor of the basin (Figure 6). The gas from the liquid oxygen was automatically distributed during the night through the porous pipes.

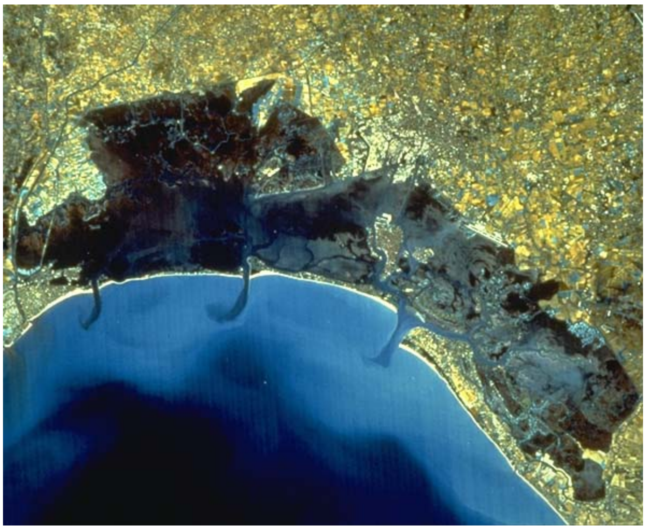


Figure 1 . The Venice Lagoon

Figure 2 . The Venice urban area

Figure 3 . The Arsenale Vecchio shipyard dock basin experiment area

Figure 4 . The 20 000 liter cryogenic evaporator

Figure 5 . The main distribution conduit

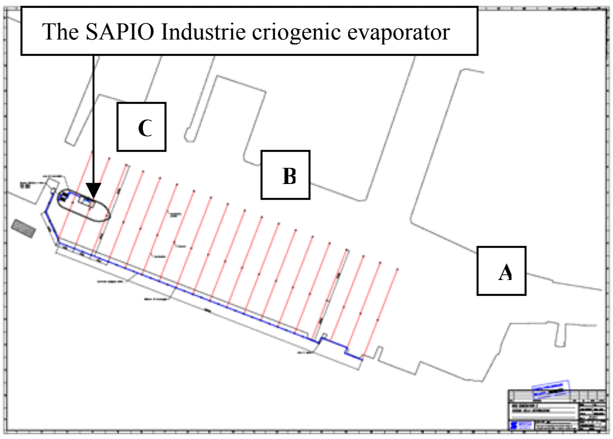


Figure 6 . The porous pipe system and coring site locations A, B, C

MATERIALS AND METHODS

The oxygenation experiment by forced aeration, took place during a 6-month period, from June to December 2005.

A preliminary sedimentological study was carried out in order to obtain a general overview of the study area and the coring sites (A,B,C) were selected with site B located 10 m in front of the pipe system, while site A and site C at 50 and 30 m respectively. A detailed sedimentological study was carried out in order to evaluate the impact of forced oxygenation on bottom sediments and on the water column above. A set of 3 cores 50 cm long was collected before (A2, B2, C2), during (A3, B3, C3) and after (A4, B4, C4) the aeration. An additional 11 m long core (ARS EXM) was collected nearby with the aim of obtaining the natural concentration of the heavy metals to be used as natural sediment reference base.

In order to minimize any possible mixing the cores obtained, carefully kept upright, were frozen in order to avoid any additional artificial mixing of the top part that, being in direct contact with the water column above, is very fluid and mixing could easily occur.

All the cores were photographed and described for their lithology, stratigraphy, color variability and macrofossil content. The frozen cores were then sliced every 2 cm for the top 20 cm in order to obtain sufficient sub-samples for grain-size, mineralogical and geochemical composition determination. Following the organic matter removal with H_2O_2, the sand fraction was determined using a vertical settling tower, while the mud fraction was analyzed using a FRITSH Analysette 20 SediGraph.

X-ray powder diffraction analysis of bulk material was performed in order to determine the mineralogical composition of each sample. An Inductively Mass Spectrometer (ICPMS) was use for the major, minor and traces element determination.

In order to determine the effect of forced oxygenation by aeration on the surficial sediments in direct contact with the water column above, several samples were analyzed with a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS).

RESULTS AND DISCUSSIONS

All samples of the surficial sediments from the three coring sites and from the reference core present similar grain size and mineralogical compositions. In general grain size varies from sandy-silt to clayey-silt to silty-clay. The average mineralogical composition of the samples from site B, reported in Figure 7 is fairly similar for all sediment samples from the three sites and, as expected, no remarkable variation was detected during the experiment. Dolomite prevails over calcite and quartz as major mineralogical components, while muscovite, ankerite, plagioclase, kaolinite, gypsum are minor.

The porous pipe of the aeration system are laid on the surface of bottom sediments in contact with the water column above, therefore a probable sediment mixing that may occur is limited to the top 5-10 cm of sediments. As expected the effect of force oxygenation is limited to the 10-15 top cm of each core. In general the comparison of the average of the heavy metal content of the top 10 cm of each core collected before during and after the forced oxygenation shows a negative trend. In fact the heavy metal content is higher in the samples collected before the aeration and lower in those collected soon after the aeration. The general reduction of heavy metal concentration (Figure 8) is higher for samples from site B located close to the porous pipe system, while samples from the farther located sites A and C show a lower impact of the forced oxygenation on the surficial sediments.

Of particular interest are the results of the SEM-EDS detailed investigation of the first 2 mm sediments of each core, directly in contact with the water column above and where the impact of the forced oxygenation is more direct. It is known that framboidal pyrite is characteristic of an anoxic environment . "According to Deer, Howie and Zussman (1966) raspberry-like aggregates of tiny spherical particles of pyrite are referred to as framboidal and their presence in sediments has been attributed to the action of micro-organisms, or sometimes to colloidal deposition". The SEM Figure 9a of a top 2mm sample from site B obtained during the aeration shows abundant granules of framboidal pyrite while fewer granules are present in the sample collected after 40 days (Figure 9b) at the end of the aeration as effect of the oxygenation. Similarly the two components pf pyrite: Fe and S, show a decreasing content with the increase of the oxygenation (end of the aeration). Further evidence of the effect of the forced aeration is given in Figure 10 showing oxygenation induced traces of erosion on the surface of the cubic crystals of a framboidal pyrite granule. A further evidence of the environmental recovery of the Arsenale Vecchio shipyard basin is given by the return of small fish (Acquatelle) (Figure 11) in the test area.

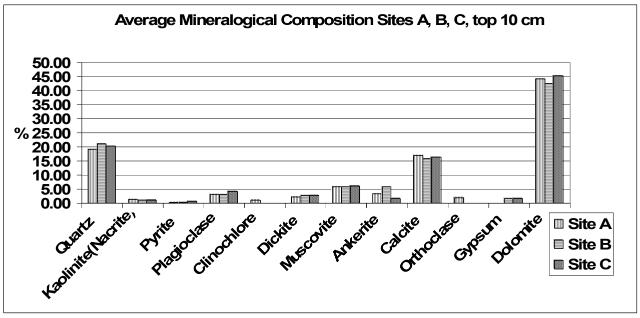
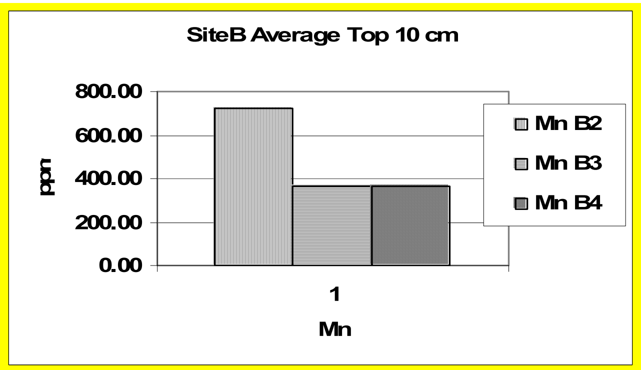
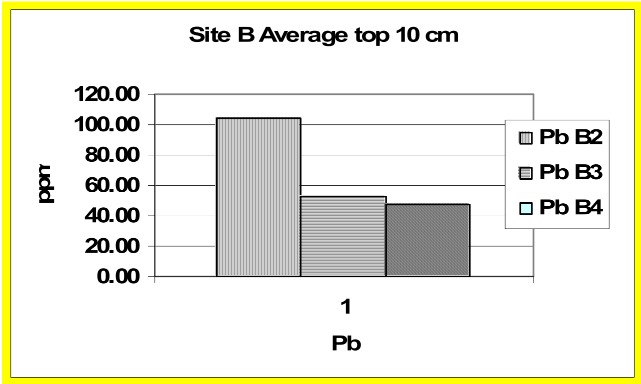
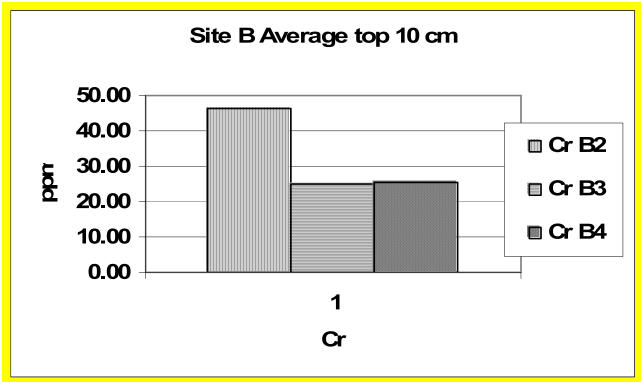
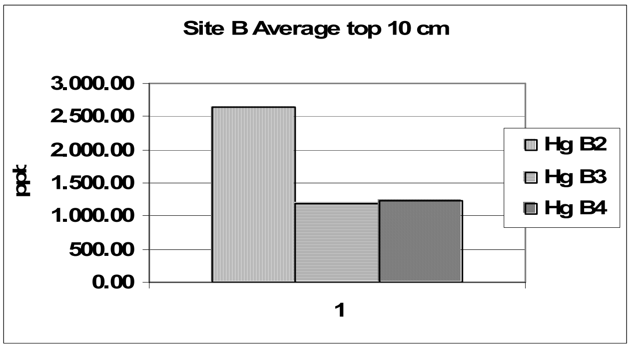


Figure 7 . Average Mineralogical composition of sites A, B, C









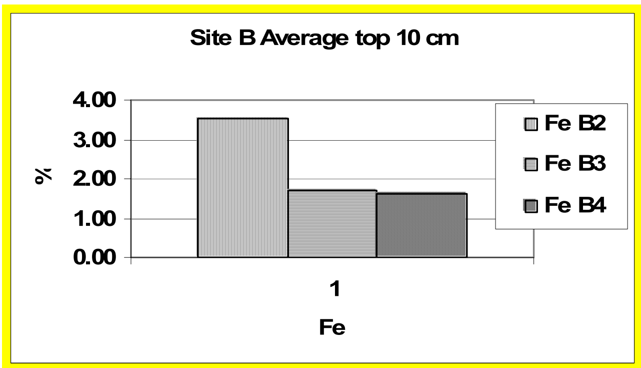


Figure 8 . Some examples of heavy metal variations following the forced aeration at the contact bottom sediment/water column above.

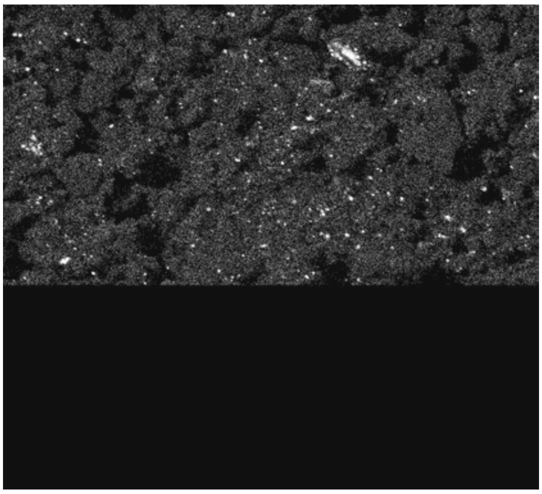


Figure 9a

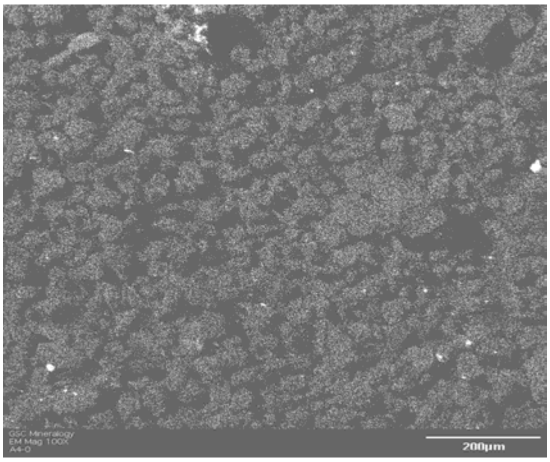


Figure 9b

Figures 9a,9b . High resolution x-ray map of Sulfur (S) (bright white areas). Photo a: sample taken during the aeration campaign. Photo b: sample taken after the aeration campaign. The Sulfur bright white areas are less abundant in Photo b as effect of the aeration. All spots checked by EDS: the chemistry is Fe and S (Pyrite)

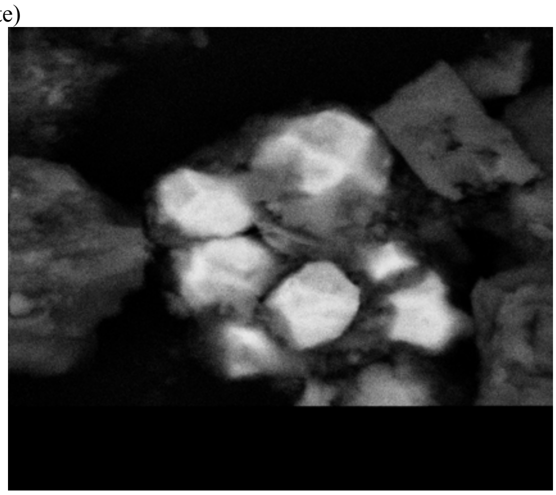


Figure 10 . Oxygenation induced traces of erosion on the surface of the cubic crystals of a framboidal pyrite granule from site B.

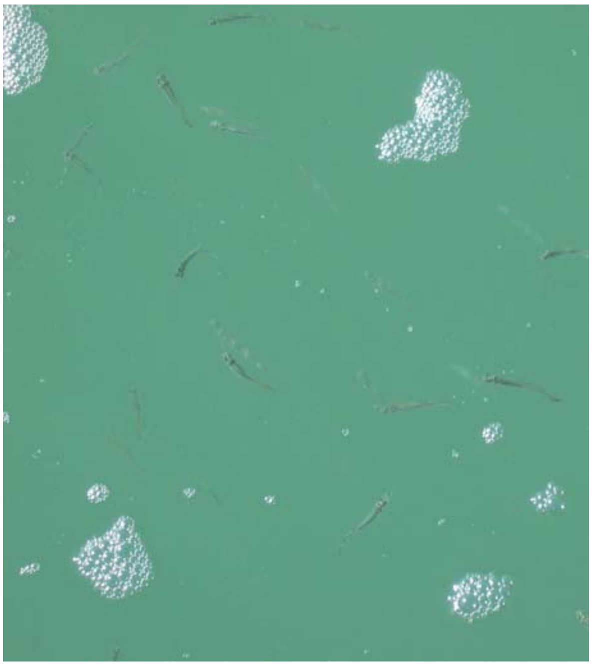


Figure 11 . Acquatelle (small fish) and Air bubbles from forced aeration

CONCLUSIONS

The oxygenation of the Arsenale Vecchio shipyard basin by mean of a forced aeration system has indicated that: a) is effective in reducing the heavy metal content in the top surficial sediments; b) is also effective in the recovery of the water body above; c) is is not obtrusive, allowing the daily normal navigation; d) its effects are fast obtainable; e) bottom sediment mixing is reduced and limited to the top 5-10 cm; f) forced aeration could represent a cost effective way of environmental recovery in situations where removing, or in situ treatment of bottom sediments may not be feasible; e) finally and not less important, the bioremediation of the water body above the bottom sediment favor with time the formation of a clean capping over the bottom contaminated sediments.

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