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Laboratory tests for the phytoextraction of heavy metals from polluted harbor sediments using aquatic plants

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ABSTRACT

The aim of this study was to investigate the concentrations and pollution levels of heavy metals, organochlorine pesticides, and polycyclic aromatic hydrocarbons in marine sediments from the Leghorn Harbor (Italy) on the Mediterranean Sea. The phytoextraction capacity of three aquatic plants *Salvinia natans*, *Vallisneria spiralis*, and *Cabomba aquatica* was also tested in the removal of lead and copper, present in high concentration in these sediments. The average detectable concentrations of metals accumulated by the plants in the studied area were as follows: $>3.328 \pm 0.032$ mg/kg dry weight (DW) of Pb and 2.641 ± 0.014 mg/kg DW of Cu for *S. natans*, $>3.107 \pm 0.034$ g/kg DW for *V. spiralis*, and $>2.400 \pm 0.029$ mg/kg DW for *C. aquatica*. The occurrence of pesticides was also analyzed in the sediment sample by gas chromatography coupled with mass spectrometry (GC/MS). Due to its metal and organic compound accumulation patterns, *S. natans* is a potential candidate in phytoextraction strategies.

1. Introduction

With the Industrial Revolution and subsequent development, heavy metal pollution of the environment has become a global crisis, disturbing the natural biogeochemical cycles (Khan et al., 2007).

Among all marine environments worldwide, harbors have long served as sinks for contaminants produced by navigation. In addition, the surrounding industrial and urban settlements are also a source of contamination in these areas (Taylor et al., 2004). Dredging of sediments from such harbors is necessary not only for flood prevention and optimal shipping traffic but also for remediation purposes in areas posing a high risk to the environment and health (SedNet, 2013). Sediments have played an important role in the transport of nutrients, metals, and other contaminants through river systems to oceans and seas (Gibbs, 1977).

Heavy metals in marine sediments have natural and anthropogenic (human) origins: their distribution and accumulation are influenced by sediment texture, mineralogical composition, reduction/oxidation state, and adsorption/desorption processes (cycles) as well as physical transport. Moreover, metals can be adsorbed from the water column onto the surfaces of fine particles and transported thereafter to sediments. As metals participate in various biogeochemical mechanisms with significant mobility, they can affect ecosystems through bioaccumulation and biomagnification processes (Manahan, 2000). The metal concentrations are generally much higher in sediments than in water, acting as a source of chemicals in the water column, as well as having direct adverse toxic effects on sediment-dwelling organisms (Martinez et al., 2007; Sawasdee et al., 2011). The high Pb concentration in the marine environments is attributed to several sources such as boat exhaust systems, oil spills, and petroleum compounds from motor boats used for fishing and from sewage effluents discharged into the sea (Laxen, 1983). Lead from different industrial sources is transported to the inlets via mixed wastewater effluents or by boat engine fuel spills, thus accumulating in these areas (Abu-Zied et al., 2012).

Lead is one of the most ubiquitous toxic metals, but with no known biological necessity; it is lethal at high levels for most living organisms (Goyer, 1991, 1993). Lead undergoes methylation in the environment; organ-lead species are considered to accumulate more readily than inorganic species (Moore, 1991). Copper enters the marine environment from different sources, including mining, smelting, domestic, and industrial activities, as well as from algaecides and an antifouling agent used in boat hulls (Fabrizio and Coccioni, 2012). Copper is naturally found in rocks, water, and air, and it is an essential element for plant growth. It is an important constituent of many enzymes of oxidation–reduction reactions (Lepp, 1981). However, high intake of copper is known to cause adverse health problems (Gorell et al., 1997).

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Contamination by organochlorine compounds has spread worldwide, which is detected in a wide range of environmental media including water, sediments, and fish (Tanabe et al., 1994). Organochlorine pesticides used on land enter the aquatic environment by runoff or atmospheric deposition (Colombo et al., 1990; Fushiwaki and Urano, 2001). Plants provide several potential defense mechanisms at the cellular level, which are involved directly in detoxification, with the additional ability of surviving even at high metal concentrations (Macnair, 1990). Moreover, plant species vary significantly in their ability to accumulate metals and other organic elements from contaminated soils and waters (Raskin et al., 1994).

The phytoremediation process uses living green plants that are capable of fixing or adsorbing toxic contaminants, thus reducing or eliminating them (Shen and Chen, 2000). The accumulation of these contaminants in plants can cause some physiological and biochemical changes (Perry et al., 2002; Dhir et al., 2004). Submerged aquatic plants are particularly useful in removing organic and inorganic pollutants from water or reducing their levels (Dunbabin and Bowmer, 1992; Mishra and Tripathi, 2009). They do not migrate and attain equilibrium with their surroundings within a short period (Raskin et al., 1994). Aquatic plants are unique bioindicator species in the evaluation of water quality and subsequent risk assessment. The absorption and accumulation of elements by these plants occurs through two different paths: the root system and the leaf area (Sawidis et al., 2001).

The aims of this study were as follows: (1) to quantify the concentrations of heavy metals (Cd, Pb, Ni, Cr, Zn, and Cu) in the marine sediments (Mediterranean sea, harbor of Leghorn, Italy), (2) to apply and test the ability of three aquatic plant species (i.e., *Salvinia natans*, *Vallisneria spiralis*, and *Cabomba aquatica*) to translocate and accumulate heavy metals in their different parts, (3) and to assess the concentration of organochlorides, pesticides, and polycyclic aromatic hydrocarbons (PAHs) present in these sediments.

2. Materials and methods

2.1. Description of study areas

Sediment samples were collected from the Leghorn Harbor (Italy) on the Mediterranean Sea. Polluted marine sediments were dredged in February 2014 from the sea bottom at a depth of approximately 7 m (43° 33′ 2″ N; 10° 17′ 39″ E) (Fig. 1). The studied area experiences a Mediterranean climate, which is characterized by warm to hot, dry summers and mild to cool, wet winters. The average annual precipitation is about 759 mm. The coldest month is January with an average annual temperature of 15.5 °C, whereas the warmest month is July, with an average monthly temperature of 23.8 °C, reaching an absolute average maximum of 37.8 °C (Doni et al., 2015).

2.2. Analysis of organochloride pesticides, polychlorinated biphenyls, PAHs, and heavy metals

2.2.1. Reagents and standards

In this study, reagents such as n-hexane, n-acetone, trimethylpentane, methanol, and anhydrous sodium sulfate were of analytical grade and obtained from Sigma Aldrich (Darmstadt, Germany), in addition to deionized water.

In order to determine the content of organochloride pesticides and PAHs, the sediment was dried at room temperature for 48 h. OCP (Open Core Protocol)-standard acenaphthene, acenaphthylene, acenaphthylene-D8, anthracene, anthracene-D10, benzo(a)anthracene,

Fig. 1. Map of the study location and sampling sites in the Leghorn area of Italy.

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