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

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Keywords: Marine sediments, heavy metals, aquatic plants, organochlorine pesticides, polycyclic aromatic hydrocarbons, polychlorinated biphenyls

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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* were also tested in order to remove lead and copper, present in high concentration in these sediments. The average metal concentrations accumulated by the plants in the studied area, detectable in the extracting solutions were:  $>Pb$  ( $3.328 \pm 0.032$  mg/kg D.W) and  $Cu$  ( $2.641 \pm 0.014$  mg/kg D.W) for *S.natans*,  $>3.107 \pm 0.034$  g/kg D.W for *V. spiralis* and  $>2.400 \pm 0.029$  mg/kg DW, *C. aquatica*, respectively. Pesticides occurrence was also analyzed sediments sample being performed by gas chromatography coupled with mass spectrometry. According to the metal and organic compounds accumulation patterns of *S.natans*, this species seemed to be valuable for application in the phytoextraction strategies.

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Graphical abstract



### **Highlights:**

- Livorno harbor marine sediment characterization,
- Phytoextraction of heavy metals from marine sediments and optimization aspects of process parameters,
- Application of new bioremediation methods for the removal of heavy metals from marine sediments using different aquatic plant species,
- Determination of some organic (pesticides) compounds in marine sediments.

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4 **Laboratory tests for the phytoextraction of heavy metals from**  
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8 **polluted harbor sediments using aquatic plants**  
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43  
44 **ABSTRACT**

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47 The aim of this study was to investigate the concentrations and pollution levels of heavy metals,  
48 organochlorine pesticides and polycyclic aromatic hydrocarbons in marine sediments from the  
49 Leghorn harbor (Italy) on the Mediterranean Sea The phytoextraction capacity of three aquatic  
50 plants *Salvinia natans*, *Vallisneria spiralis* and *Cabomba aquatica* were also tested in order to  
51 remove lead and copper, present in high concentration in these sediments. The average metal  
52 concentrations accumulated by the plants in the studied area, detectable in the extracting  
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4 solutions were: > Pb ( $3.328 \pm 0.032$  mg/kg D.W) and Cu ( $2.641 \pm 0.014$  mg/kg D.W) for *S.natans*,  
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6 > $3.107 \pm 0.034$  g/kg D.W for *V. spiralis* and > $2.400 \pm 0.029$  mg/kg DW, *C. aquatica*,  
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8 respectively. Pesticides occurrence was also analyzed sediments sample being performed by gas  
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10 chromatography coupled with mass spectrometry (GC/MS).  
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14 According to the metal and organic compounds accumulation patterns of *S.natans*, this species  
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16 seemed to be valuable for application in the phytoextraction strategies.  
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18  
19 *Keywords:* Marine sediments, heavy metals, aquatic plants, organochlorine pesticides, polycyclic  
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21 aromatic hydrocarbons, polychlorinated biphenyls  
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## 24 25 **1. Introduction**

26  
27 During the industrial revolution and development, the environmental pollution by heavy  
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29 metals became a serious problem, disturbing the natural biogeochemical cycles (Khan et al.,  
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31 2007).  
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34 Worldwide, in marine environments, harbors have had a long history in acting as sinks  
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36 for contaminants produced by navigation. Beside this, the surrounding industrial and urban  
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38 settlements were also a contamination source of these areas (Taylor et al., 2004). Dredging of  
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40 sediments from such harbors was necessary to prevent flooding and allow shipping traffic  
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42 efficiency, but also for remediation purposes, where the risk to the environment and health might  
43  
44 be high (SedNet, 2013). Sediments have played an important role in the transport of nutrients,  
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46 metals and other contaminants through river systems to the world's oceans and seas (Gibbs,  
47  
48 1977).  
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54 Heavy metals in marine sediments have natural and anthropogenic (human) origins: the  
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56 distribution and accumulation are influenced by sediment texture, mineralogical composition,  
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58 reduction/oxidation state, and adsorption/desorption processes (cycles) as well as physical  
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4 transport. Moreover, metals can be absorbed from the water column onto fine particles surfaces  
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6 and moved thereafter towards sediments; participating in various biogeochemical mechanisms  
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8 with significant mobility, it can affect the ecosystems through bio-accumulation and bio-  
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10 magnification processes (Manahan, 2000). Metal concentrations in sediments are generally much  
11  
12 higher than in water and may act as a source of chemicals in the water column and also,  
13  
14 adversely, affect sediment-dwelling organisms through direct toxicity (Martínez et al., 2007;  
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16 Sawasdee et al., 2011). The high Pb concentration in the marine environments is attributed to  
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18 several sources such as boat exhaust systems, oil spill, and petroleum compounds from motor  
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20 boats employed for fishing and sewage effluents discharged into water (Laxen, 1983). Lead  
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22 pollution derived from different industrial sources is expected to be carried to the inlets via  
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24 mixed wastewater effluents or by boat-engine fuel spills, thus accumulating in these areas (Abu-  
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26 Zied et al., 2012).  
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34           Lead is one of the most ubiquitous toxic metals and has no known biological necessity; in  
35  
36 high levels, it is lethal for most living organisms (Goyer, 1993; Goyer, 1991). Lead undergoes  
37  
38 methylation in the environment; organ-lead species are thought to accumulate more readily than  
39  
40 inorganic species (Moore, 1991). The input of copper into marine environment comes from  
41  
42 different sources, including mining, smelting, domestic and industrial activities and from  
43  
44 algaecides and an antifouling applied to boat hulls (Fabrizio and Coccioni, 2012). Copper is  
45  
46 naturally found in rocks, water, and air, being an essential element for plant growth. It is an  
47  
48 important constituent of many enzymes of oxidation–reduction reactions (Lepp, 1981). However,  
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50 a high intake of copper is known to cause adverse health problems (Gorell et al., 1997).  
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56           Contamination by organochlorine compounds has spread all over the globe and continues  
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58 to be detected in a wide range of environmental media including water, sediment and fish  
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4 (Tanabe et al., 1994). The application of organochlorine pesticide on land enters in aquatic  
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6 environment by runoff or atmospheric deposition (Colombo et al., 1990; Fushiwaki and Urano,  
7  
8 2001). Plants provide a large range of potential defense mechanisms at the cellular level, which  
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10 are involved directly in the detoxification, and also have the ability to survive even to high metal  
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12 concentrations (Macnair, 1990). Moreover, plant species vary significantly in their ability to  
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14 accumulate metals and other organic elements from contaminated soils and waters (Raskin et al.,  
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16 1994).  
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21           The phytoremediation process stands for the use of living green plants which are able to  
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23 fix or adsorb toxic contaminants, contributing to their reduction or disappearance (Shen and Chen,  
24  
25 2000). The accumulation of these contaminants in plants can cause some physiological and  
26  
27 biochemical changes (Perry et al., 2002; Dhir et al., 2004). The submerged aquatic plants are  
28  
29 particularly useful in the abatement, monitoring reduction and removal of organic and inorganic  
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31 pollutants from water (Dunbabin and Bowmer, 1992; Mishra and Tripathi, 2009). They do not  
32  
33 migrate and attain equilibrium with their surroundings within a short period (Raskin et al., 1994).  
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35 Aquatic plants are unique bioindicator species for the evaluation of water quality and subsequent  
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37 risk assessment. The absorption and accumulation of elements by these plants can follow two  
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39 different paths, for example, the root system, and leaf area (Sawidis et al., 2001).  
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45           The aim of this study was (1) to quantify the concentrations of heavy metals (Cd, Pb, Ni,  
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47 Cr, Zn and Cu) in the marine sediments (Mediterranean sea, harbour of Leghorn, Italy), (2) to  
48  
49 apply and to test the ability of three aquatic plant species (i.e. *Salvinia natans*, *Vallisneria*  
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51 *spiralis* and *Cabomba aquatica*) to translocate and accumulate heavy metals in their different  
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53 parts, (3) and to assess the concentration of organochlorides, pesticides and polycyclic aromatic  
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55 hydrocarbons presents in these sediments.  
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## 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 of approximately 7 m to depth (43°33'2''N; 10°17'39''E), (Fig. 1). The climate in the studied area belongs to the Mediterranean climate, which is characterized by warm to hot, dry summers and mild to cool, wet winters. The precipitate annual average is about 759 mm. The average annual temperature is 15.5°C in the coldest month (January), while July is the warmest month, with an average monthly temperature of 23.8°C, reaching an absolute average maximum of 37.8°C (Doni et al., 2015).

### 2.2. Organochloride pesticides, polychlorinated biphenyls, polycyclic aromatic hydrocarbons and heavy metals analysis

#### 2.2.1. Reagents and standards

Reagents used in the research comprised the following: n-hexane, n-acetone, trimethylpentane, methanol, anhydrous sodium sulfate were of analytical grade and were obtained from Sigma Aldrich (Germany) and de-ionized water

In order to determine the organochloride pesticides and polycyclic aromatic hydrocarbons content, the sediment was dried at room temperature for 48 h. All the OCP standards acenaphthene, acenaphthylene, acenaphthylene-D8, anthracene, anthracene-D10, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chlordane, chlorpyrifos, crysene, p-p'DDD, p-p'DDE, p-p'DDT, dibenzo(ah)anthracene, dibenzo(ah)anthracene-D14, dieldrin, endosulfan sulfate, phenanthrene, fluoranthene, fluorene, naphthalene, PCB052, PCB101, PCB 118, PCB128, PCB138, PCB170,



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4 PCB180, PCB187, PCB194, PCB206, pyrene, indeno(1,2,3-cd)pyrene, simazine and trifluralin  
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7 were purchased from O2SI Smart Solution, (USA).  
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9 Standard solutions were prepared in acetone at a concentration of 100 µg/mL and diluted  
10  
11 with acetone when necessary. The entire glassware was cleaned with laboratory detergent,  
12  
13 sequentially rinsed with de-ionized water, acetone, and methanol and heated in an oven at 300 °C  
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15 for 12 h.  
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### 18 19 *2.2.2. Sample extraction for GC/MS analysis* 20

21 A quantity of 2 g of dried sediment was extracted by adding 3 mL of acetone and was  
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23 placed in an ultrasound bath for 10 minutes, followed by the addition of 3ml hexane and  
24  
25 subjected afterwards to another 10 minutes of ultrasound treatment. The extraction procedure  
26  
27 was repeated two times to improve the efficiency of recovery. The organic extracts were  
28  
29 combined, added of 2 mL of trimethylpentane and concentrated by a nitrogen stream for the  
30  
31 elimination of acetone and hexane. In order to remove the sulphur compounds, trimethylpentane  
32  
33 solution was shaken with 1 mL of 2-propanol and 1 mL of TBA-sulfite reagent for 1 min.  
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35 Afterwards, 5 mL of water was added and the test tube was shaken for another minute, followed  
36  
37 by centrifugation, and the trimethylpentane phase was transferred to a test tube (Jensen et al.,  
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39 1977). The trimethylpentane phase was finally concentrated to 1 mL and purified on activated  
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41 silica stationary phase. The repeatability of the method was assessed on the basis of 3 parallel  
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43 determinations of pesticides.  
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### 50 51 *2.2.3. GC/MS conditions* 52

53 Mass spectrometry analyses were performed with an Agilent 7010 GC/MS instrument  
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55 (Palo Alto, CA, USA) equipped with a DB-5MS fused-silica capillary column (30 m × 0.25  
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57 mmI.D., film thickness 0.25 µm; J&W Scientific). Helium was used as the carrier gas at a flow  
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4 rate of 1.0 mL/min. A 1- $\mu$ L sample was introduced by split-mode injection (split ratio 10:1).  
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6 Triple quadrupole GC /MS is the most sensitive GC/MS/ MS system with the lowest, 0.5 fg. The  
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8 mass spectrometer was run in electron ionization (EI) mode with an electron energy of 70 eV,  
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10 scanning a range of 50-550 amu. The manifold temperature was kept at 230 °C. For sample  
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12 monitoring and confirmation analysis, SIM mode was used with a dwell time of 50 ms for each  
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14 ion. All OCPs were identified by retention time and specific ions. They were quantified by  
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16 comparison to the internal standard.  
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### 21 *2.3. Heavy metals from dredged marine sediments*

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25 The concentration levels of heavy metals (Cu, Cr, Ni, Pb, Zn and Cd) was detected in  
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27 sediments samples by extraction, using the following extracting solutions: HCl (1M), double  
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29 distilled water, NaCl (36‰) and concentrate HNO<sub>3</sub> (67 %). The sediment contains most studied  
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31 forms of heavy metals in oxidative status 0, in order to determine the amount of heavy metals;  
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33 their existence was passed in the salt form by treatment with acids. In this in order to be able to  
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35 determine the amount of heavy metals existence was passed in the salt form by treatment with  
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37 acids.  
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42 In particular, 200 g of sediment was stirred for 6 hours in 200 mL of extracting solutions  
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44 (each in separate solution). At the end of the predetermined time, the suspension was filtered and  
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46 the resulting solution was analysed by inductively coupled plasma optical emission spectrometer  
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48 (ICP–OES, Optima 5300 DV, Perkin–Elmer, USA). The measured heavy metal concentrations  
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50 are summarized in (Table 1).  
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54 Heavy metals (Cu, Cd, Zn) detected in sediment samples were below the limit of  
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56 detection, except lead and copper, which were in higher concentrations.  
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### 59 *2.4. Plant material and growing conditions for phytoextraction studies*

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4 Three submerged aquatic plants species were used in the present study: fanwort  
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6 (*Cabomba aquatica*), tape grass (*Vallisneria spiralis*), and floating fern (*Salvinia natans*). The  
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8 plants' growth experiments were performed in a hydroponic greenhouse system (at University of  
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10 Agricultural Sciences and Veterinary Medicine in Cluj-Napoca, Romania), with an addition of  
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12 fertilizer (Complex 3, 0.5 %). Plants aged 50 days, were selected for the phytoremediation  
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14 experiments. The plants were kept under laboratory conditions for an acclimatization period of 4  
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16 days in modified Hoagland nutrient solution with the following chemical composition: 1 mM  
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18  $\text{KNO}_3$ ; 1 mM  $\text{Ca}(\text{NO}_3)_2 \times 4\text{H}_2\text{O}$ ; 1 mM  $\text{NH}_4\text{H}_2\text{PO}_4$ ; 1 mM  $\text{MgSO}_4 \times 7\text{H}_2\text{O}$ ; 25 mM KCl; 12.5 mM  
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20  $\text{H}_3\text{BO}_3$ ; 1 mM  $\text{MnSO}_4 \times \text{H}_2\text{O}$ ; 1 mM  $\text{ZnSO}_4 \times 7\text{H}_2\text{O}$ ; 0.25 mM  $\text{CuSO}_4 \times 5\text{H}_2\text{O}$ ; 0.25 mM  $\text{H}_2\text{MoO}_4$   
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22 (85%  $\text{MoO}_3$ ) with Fe(III) citrate (Taiz and Zeiger, 2002) as iron source, at room temperature (21-  
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24  $23^\circ\text{C}$ ) with a 14/10 h (light/dark) photoperiod. The plants were cultivated in 250 mL Erlenmeyer  
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26 flasks (5 g), containing 100 mL of lead solution of sediment and 100 mL Hoagland solution.  
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33 The phytoremediation experiments were carried out for 10 days. The sediments resulted  
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35 from the solution's heavy metal content was checked by Atomic Absorption Spectrometer  
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37 (SensAA Dual GBC Scientific Equipment, Australia).  
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41 The phytoremediation process was analysed at various operational parameters in the  
42  
43 following conditions: a) effect of initial lead concentration:  $C_i = 2.5-4$  mg/L (initial metal  
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45 concentration),  $m_{\text{plant}} = 5-11$  g fresh weight plant, the volume of solution:  $V = 0.2$  L, room  
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47 temperature:  $T = 21 - 23$  °C; b) effect of initial pH 3-5,  $m_{\text{plant}} = 5$  g fresh weight plant,  $C_i = 2.5-5$   
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49 mg/L,  $V = 0.2$  L,  $T = 21-23$  °C. During the experiments, water samples were collected at regular  
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51 24 hour intervals from the nutrient solution in order to determine the heavy metal content for  
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53 sediment.  
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4 The characterization of the phytoremediation process was realized through the  
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6 determination of the phytoremediation efficiency and capacity using the following equation:  
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$$E,(\%) = \frac{C_i - C_f}{C_i} \cdot 100 \quad (1)$$
  
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15 
$$q_{\max} (mg / g) = \frac{(C_i - C_f) \cdot V}{m} \quad (2)$$
  
16  
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18  
19 where E, (%) represents the efficiency, C<sub>i</sub> and C<sub>f</sub> the initial and final concentration of lead  
20  
21 (mg/L) in the aqueous solution, the q<sub>max</sub> (mg/g) represents the amount of heavy metals adsorbed  
22  
23 onto unit weight of plant, V (L) means the volume of heavy metals aqueous solution and m (g)  
24  
25 the plant quantity.  
26  
27

### 28 29 30 *2.5. Digestion of plant material and determination of heavy metal content* 31

32 At the end of the experiment, plant samples were dried for 12 h at 60°C in a forcedly –  
33  
34 drought oven. The dried plant samples (approximately 0.2 g) were digested in 8 mL of  
35  
36 concentrated nitric acid (Merck, Germany) at 40°C for 8 h. After digestion, the solutions were  
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38 filled up to volume with distilled water to 50 mL. Determinations of heavy metal concentrations  
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40 in all samples were carried out by the Atomic Absorption Spectrometer.  
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### 44 45 *2.6. The bio-concentration factor (BCF)* 46

47 The bio-concentration factor (BCF) is defined as the ratio of the total concentration of  
48  
49 elements accumulated in plants to the heavy metal concentrations in experimental solutions (the  
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51 heavy metals from the experimental solutions were extracted from the analyzed sediments)  
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53 representing an important parameter in the heavy metal uptake studies (Dunbabin and Bowmer,  
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55 1992).  
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4 The BCF is calculated using the formula:  $BCF = \frac{\text{Concentration of metal in the plant}}{\text{Concentration of metal in water}}$  (Jitar et al., 2015).  
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## 8 9 *2.7. Statistical analysis*

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11 The standard deviation was calculated from three replicated concentration values using  
12 the Microsoft Excel's statistical package. Each treatment was replicated three times and all data  
13 are expressed as the means  $\pm$  S.D. The data obtained were compared with *t* test to confirm any  
14 significant differences. The results are considered significant at  $P < 0.05$ .  
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## 21 **3. Results and discussion**

### 22 23 24 *3.1. Sediment characteristics*

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26 The sediment samples were used for the analysis of the physicochemical parameters.  
27 There were analyzed the sediments taken from a depth of 7 m with a pH 7.65, using the  
28 ISO10390: 2005 method. The chloride concentration in our solution was measured by  
29 potentiometric titration with  $AgNO_3$ . All the experiments were realized at room temperature. The  
30 moisture content of the sediment was calculated, taking into consideration the weightless of the  
31 sample after being heated at  $105^\circ C$  during 24 h. The results of physicochemical properties of the  
32 investigated sediments are presented in (Table 2).  
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### 44 *3.2. Metal accumulation in the aquatic plants tissues*

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46 In the phytoextraction studies, the bioaccumulation of lead and copper in aquatic plants  
47 was monitored. The results of this study indicate that the extent of heavy metal accumulation is  
48 differed among the aquatic plant species. Relatively high amounts of accumulated Pb and Cu is  
49 observed in the order *Salvinia natans* > *Vallisneria spiralis* > *Cabomba aquatica*. The highest  
50 concentrations of Pb in the aquatic plants are associated with the high concentrations in the  
51 surrounding sediments. In some cases, copper has not been detected.  
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4 As Table 3 shows, all the plants accumulated copper only from the solution with HNO<sub>3</sub> in  
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6 Hoagland. However the highest removal amount (2.641±0.014 mg/kg) was obtained at *Salvinia*  
7  
8 *natans*. Rahman and Hasegawa (2008) reported that the highest concentrations of arsenic in this  
9  
10 aquatic plant (*Salvinia natans*) were 2.400 ±0.02 μmol (g dry weight)<sup>-1</sup> respectively, over 5  
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12 days.  
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16 The concentrations of lead in the sediments have an initial concentration of 3.5 mg/L, and  
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18 can be detected from all solutions. The measured *Pb* concentrations varied between 3 mg/kg and  
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20 0.250 mg/kg DW at different experimental solutions, where the highest concentration of lead  
21  
22 was accumulated by *Salvinia natans* (3.328 ±0.032 mg/kg DW), and using sodium chloride with  
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24 Hoagland nutrient solution. Aquatic plants *V. spiralis* and *C. aquatica* had a very low rate of  
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26 accumulation, demonstrating a decreased survival in this experimental condition.  
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31 Marques et al. (2009) observed maximum *Pb* concentrations of 1178 mg/kg in the roots  
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33 and 149 mg/kg dry weight in the leaves of *R. ulmifolius*, over 16 days. According to the  
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35 literature, a lower concentration of heavy metals is proving to be more easily accumulated in the  
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37 plant and opposite (Dhir, 2009).  
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41 The above results indicate that these aquatic plants might accumulate large amounts of  
42  
43 lead and copper in their tissues. These results are similar to the findings of Dhir (2004) who  
44  
45 reported that *Salvinia natans* is a metal hyperaccumulator plant which was able to tolerate and  
46  
47 bioconcentrate high quantities of Fe<sup>2+</sup>, Cr<sup>6+</sup>, and Ni<sup>2+</sup> metals (Chorom et al., 2012).  
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51 Plants can uptake the heavy metals via their roots and in certain cases, such as  
52  
53 submerged plants, by their leaves. The metal uptake occurred by two pathways: first step  
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55 extracellular (apoplastically), which is a fast one followed by intracellular (simplistically),  
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57 which is a slow level. The heavy metals' uptake in the fast stage was possible by physical and  
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4 chemical sorption (adsorption) as well by ion exchange processes. The slower stage is the  
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6 intracellular uptake and transport of the metals into the cells (Raskin et al., 1994).  
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9 Metal concentrations in plants vary by plant species. Plant uptake of heavy metals from  
10  
11 sediments occurs either passively with the mass flow of water into the roots, or through active  
12  
13 transport across the plasma membrane of root epidermal cells. The bioavailability of trace  
14  
15 elements to plants is ultimately controlled by the nature of the sediments, their total  
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17 concentration in the sediments and their chemical forms (Favas et al., 2014).  
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### 21 3.3. The bio-concentration of metals (BCF)

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23 The determined bioconcentration values by *Salvinia natans*, *Vallisneria spiralis* and  
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25 *Cabomba aquatic* for Pb is represented in (Fig. 2).  
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28 BCF was used to assess the availability of heavy metals in the used experimental  
29  
30 solution. BCF values of heavy metals, determined in the three plant species, originated from  
31  
32 various types of wetlands, reflecting their heavy metals accumulation ability in the surrounding  
33  
34 environments. The plant bioaccumulation factor (*Salvinia natans*, *Vallisneria spiralis* and  
35  
36 *Cabomba aquatica*) for lead is shown in Fig. 2. Based on the values calculated, BCF plants are  
37  
38 classified as follows: *Salvinia natans* > *Vallisneria spiralis* > *Cabomba aquatica*. The highest  
39  
40 values (25 µg/L) recorded in this study were observed at experimental solution, using NaCl with  
41  
42 Hoagland nutrient solution, in all cases. The lowest values of BCF in plants were registered in  
43  
44 the case of *Cabomba aquatica* (<1) (Qui et al., 2001). This can be explained by the fact that the  
45  
46 plant has a decreased lead bioaccumulation capacity.  
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52 Therefore, it can be concluded, that *Salvinia natans* possess a higher accumulative ability  
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54 in the above-mentioned experimental solution in comparison with the other two plant species.  
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### 57 3.4. Organochlorine pesticides polycyclic aromatic hydrocarbons and polychlorinated biphenyls

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4 Unlike heavy metals, all chlorinated hydrocarbons are anthropogenic in origin. Non-  
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6 persistent pesticides are very unlikely to contaminate the marine environment significantly, since  
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8 they will be degraded before reaching it (Michael, 1978). The highly chlorinated hydrocarbons  
9  
10 are found in the deeper sediments and are more readily adsorbed on sedimenting particles. On  
11  
12 the other hand, the less-chlorinated hydrocarbons are more easily decomposed.  
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16 PAHs are included in the organic compound class containing two or more benzene rings. PAHs  
17  
18 in the marine environment may be of different origins: pyrolytic (forest fires, volcanic eruptions,  
19  
20 waste incineration and combustion of fossil fuels), petrogenic (from petroleum and its  
21  
22 fractionation products), or diagenetic (diagenetic transformation of biogenic precursors on  
23  
24 marine sediment) (Nikolaou et al., 2009).  
25  
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29 They are characterized by high toxicity, persistence and the ability to bioaccumulation in  
30  
31 the environment. Due to their molecular weights, they can be divided into low molecular weight  
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33 compounds (LMW), e.g., naphthalene, acenaphthylene, fluorene, phenanthrene, and pyrene, and  
34  
35 high molecular weight compounds (HMW), e.g., benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene,  
36  
37 and coronene (Boonyatumanond et al., 2007).  
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41 The distribution of various pesticides in the sediment from the three locations sampled is  
42  
43 summarized in Fig. 3.  
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45  
46 Only seven PAHs compounds (4–6 aromatic ring specie), benzo(a)anthracene, benzo(a)  
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48 fluoranthene, benzo(b)fluoranthene benzo(k)fluoranthene benzo(a)pyrene, benzo(g,h,i)  
49  
50 perylene, dibenzo(a,h)anthracene) were detected above the determination limits. No PAHs with  
51  
52 six or more aromatic rings were observed to be present above the detection limits, although it has  
53  
54 been shown that the particle fraction of “Asian Brown Cloud” can carry a significant amount of  
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56 PAHs to mountain region (Loewen et al., 2005).  
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4 Benzo(b)fluoranthene was present in the highest concentration in sediment samples, in all  
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6 studied pesticides average levels of up to 0.2633 ng/g. Benzo(a)anthracene, benzo(a)  
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8 fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)  
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10 perylene, dibenzo(a,h)anthracene concentrations was however lower than benzo (b)fluoranthene  
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12 ranging in all sediments samples studied.  
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16 The detection limit was 0,0008ng/g of aldrin and 0.0005 ng/g of dieldrin, detected in  
17  
18 sediment samples. Statistically, the differences in the mean concentrations of aldrin and dieldrin  
19  
20 for the studied sites were significant ( $p < 0.05$ ). Doong et al. (2002) reported a concentration  
21  
22 range of 0.05–0.15  $\mu\text{g kg}^{-1}$  for aldrin and 0.12–5.8  $\mu\text{g kg}^{-1}$  for dieldrin. In the present study,  
23  
24 however, the concentration of detected dieldrin was much higher while aldrin was lower than the  
25  
26 one in the study. Another study by Darko et al. (2008) reported lower concentrations of aldrin  
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28 and dieldrin - 0.65  $\mu\text{g g}^{-1}$  ( $\mu\text{g kg}^{-1}$ ) and 0.072  $\mu\text{g g}^{-1}$  ( $\mu\text{g kg}^{-1}$ ) in Lake Bosomtwi in the Ashanti  
29  
30 region of Ghana. The absence of aldrin in the analyzed sediments samples may be attributed to a  
31  
32 cessation of their use in the area and also to their decomposition in the environment. The import  
33  
34 of aldrin pesticides, widely used in the 1950's and 1960's, has been banned in Morocco since the  
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36 1984 National implementation plan for Stockholm Convention on Persistent Organic Pollutants  
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38 (POPs). Directorate for surveillance and risk prevention. Rabat, Morocco (Ministry of Territory  
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40 Management, Water and Environment, 2006).  
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48 Endosulfan sulfate concentrations detected in the sediment samples were relatively low,  
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50 as compared with those reported by Mensah (2012), wherein the measured endosulfan sulfate  
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52 concentration in sediment was of 0.06 ng/g. Endosulfan sulfate concentration was relatively low  
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54 and the absence of alpha-endosulfan indicated a high rate of degradation of the compound.  
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4 From the sediment samples studied, p-p'DDD, p-p' DDE and p-p'DDT levels were  
5 significantly lower than p,p-DDT. The concentration of p-p'DDD, p-p' DDE and p-p'DDT ranged  
6 from 0.0015 ng/g to 0.0053 ng/g to 0.0018 ng/g, among the studied samples with the highest  
7 mean concentration being p-p'DDE. Some p-p' DDT metabolites were detected in sediments but  
8 did not exceed permissible limits. In this research pp'-DDT concentrations in sediment are  
9 lower, in comparison with other years, when the DDT concentration was much higher, indicating  
10 a slow degradation process for DDT. DDT has been banned from agricultural use and restricted  
11 for public health purposes, under the Stockholm convention in which Ghana is a signatory. The  
12 present investigation therefore gives an indication on the restricted use of DDT for agricultural  
13 and vector control purposes in Ghana (Mensah et al., 2012).  
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28 The mean distribution of polychlorinated biphenyls (PCB) from sediment is shown in  
29 Figure 3. Usually the lower chlorinated (tri and tetrachlorobiphenyls) are the ones with the  
30 highest removal rates from contaminated soils (Erickson, M.D., 1997). It was also observed an  
31 increase in the concentration of PCB101 (20 %), PCB 138 (40 %), PCB170 (41 %), PCB 180 (45  
32 %) and PCB 194 (64 %). In this sediment samples most of the PCB was below the detection  
33 limit. PCB has very low water solubility ( $0.0027\text{--}0.42\text{ ng/L}^{-1}$ ) and is very hydrophobic (Gomes et  
34 al., 2014).  
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#### 45 **4. Conclusions**

46 The purpose of this research was to analyze the concentration of heavy metal pollutants  
47 the concentration of heavy metal pollutants and organic compound levels in the sediments  
48 collected from Leghorn harbor (Italy) on the Mediterranean Sea. The phytoextraction possibility  
49 was studied in order to asses a new alternative method for multimetal remediation purposes.  
50 Three plants, namely *Salvinia natans*, *Vallisneria spiralis* and *Cabomba aquatica* were tested for  
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4 the removal of lead and copper from the sediment. These three plants proved to be highly  
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6 effective in absorbing Pb at different concentrations. The correlation between the final metal  
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8 concentration in the water and the metal concentration in the plant indicated that these plants can  
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10 be used effectively for the removal of heavy metals from a solution with various concentrations.  
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12 The amount of heavy metals accumulated in plants showed a potential use for application in  
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14 waters contaminated with Pb which are widely used from basic household items to complex  
15  
16 industrial technologies. In the present investigation there were not registered changes in the  
17  
18 levels for the DDT because it was taken out of use only specific classes of pesticides show the  
19  
20 changes. benzo(a)anthracene, benzo(a)fluoranthene, benzo(b)fluoranthene,  
21  
22 benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i) perylene, dibenzo(a,h)anthracene  
23  
24 concentrations were however lower than benzo(b)fluoranthene ranging in all the studied  
25  
26 sediments samples. The obtained results showed the presence of chlorinated organic pesticides  
27  
28 polycyclic aromatic hydrocarbons and ploclorobifenili in low concentrations.  
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32 In addition, the results of this study suggested that *Salvinia natans* was a good candidate  
33  
34 for removing Pb and Cu from the polluted aquatic environments.  
35  
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49  
50 professional development in an international and interdisciplinary environment”.  
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### 53 54 55 **References**

56  
57  
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59  
60  
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63  
64  
65

- 1  
2  
3  
4 Abu-Zied, R., Basaham, A., El-Sayed, M., 2012. Effect of municipal wastewaters on bottom  
5  
6 sediment geochemistry and ben thic foraminifera of two Red Sea coastal inlets, Jeddah,  
7  
8 Saudi Arabia. *Environ. Earth Sci.* 68, 451-469.  
9
- 10  
11 Boonyatumanond, R., Wattayakorn, G., Amano, A., Inouchi, Y., Takada, H., 2007.  
12  
13 Reconstruction of pollution history of organic contaminants in the upper Gulf of Thailand  
14  
15 by using sediment cores: first report from Tropical Asia (TACO) project. *Marine Pollution*  
16  
17 *Bulletin.* 54, 554–565.  
18  
19
- 20  
21 Chorom, M., Parnian, A., Jaafarzadeh, N., 2012. Nickel removal by the aquatic plant  
22  
23 (Ceratopyllum demersum L). *Int. J. Environ. Sci. Dev.* 3.(4), 372.  
24  
25
- 26 Colombo, J.G., Khalil, M.F., Horth, A.C., Catoggio, J.A., 1990. Distribution of chlorinated  
27  
28 pesticides and individual polychlorinated biphenyls in biotic and abiotic compartments of  
29  
30 the Rio de La Plata. *Environ. Sci. Technol.* 24, 498–505.  
31  
32
- 33 Darko, G., Akoto, O., Opong, C., 2008. Persistent organochlorine pesticide residue in fish,  
34  
35 sediment and water from Lake Bosomtwi, Ghana. *Chemosphere.* 72, 21–24.  
36  
37
- 38 Dhir, B.P., 2009. *Salvinia: an Aquatic Fern with Potential Use in Phytoremediation*, *Environ. We*  
39  
40 *Int.J. Sci. Tech.* 4, 23-27.  
41  
42
- 43 Dhir, B.P., Sharmila, P., Saradhi, P.P., 2004. Hydrophytes lack potential to exhibit cadmium  
44  
45 stress induced enhancement in lipid peroxidation and accumulation of proline. *Aquatic*  
46  
47 *Toxicol.* 66, 141–147.  
48  
49
- 50 Doni.S., Macci. C., Peruzzi. E., Iannelli. R., Masciandaro. G., 2015. Heavy metal distribution in  
51  
52 a sediment phytoremediation system at pilot scale. *Ecological Engineering.* 81, 146–157.  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

- 1  
2  
3  
4 Doong, R.A., Sun, Y.C., Liao, P.L., Peng, C.K., Wu, S.C., 2002. The distribution and fate of  
5  
6 organochlorine pesticides residues in sediments from the selected rivers in Taiwan.  
7  
8  
9 Chemosphere. 48, 237–246.  
10  
11 Dunbabin, J.S., Bowmer, K.H., 1992. Potential use of constructed wetlands for treatment  
12  
13 industrial waste water containing metals. *Sci. Total Environ.* 111, 151–168.  
14  
15  
16 Erickson, M.D., 1997. *Analytical Chemistry of PCBs*, CRC Press, Boca Raton, Florida. pp.87.  
17  
18  
19 Fabrizio, F., Coccioni, R., 2012. The response of benthic foraminiferal assemblages to copper  
20  
21 exposure: a pilot mesocosm investigation. *J. Environ. Protect.* 3, 342-352.  
22  
23  
24 Favas, J.C., João Pratas, J., Varun, M., D'Souza, R., S. Pau. M., 2014. Accumulation of  
25  
26 uranium by aquatic plants in field conditions: Prospects for phytoremediation. *Science of*  
27  
28 *the Total Environment.* 470-471, 993-1002.  
29  
30  
31 Fushiwaki, Y., Urano, K., 2001. Adsorption of Pesticides and then biodegraded products on clay  
32  
33 minerals and soils. *J. Health Sci.* 47 (4), 429-432.  
34  
35  
36 Gibbs, R.J., 1977. Transport phases of transition metals in the Amazon and Yukon rivers. *Geol.*  
37  
38 *Soc. Am. Bull.* 88, 829-843.  
39  
40  
41 Gomes, H.I., Dias-Ferreira, C., Ottosen, M.L., Ribeiro, B., 2014. Electrodialytic remediation of  
42  
43 polychlorinated biphenyls contaminated soil with iron nanoparticles and two different  
44  
45 surfactants. *Journal of Colloid and Interface Science.* 433, 189–195.  
46  
47  
48 Gorell, J.M., Johnson, C.C., Rybicki, B.A., 1997. Peterson, E.L., Kortsha, G.X., Brown, G.G.,  
49  
50 1997. Occupational exposures to metals as risk factors for Parkinson's disease. *Neurology*  
51  
52 48, 650–658.  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

- 1  
2  
3  
4 Goyer, R.A., 1991. Toxic effects of metals. In: Casarett and Doull's toxicology. The basic  
5 science of poisons, 4th ed., ed. Amdur, M. O., Dull, J., and Klassen, C. D. New York:  
6 Permagon Press.  
7  
8  
9  
10  
11 Goyer, R.A., 1993. Lead toxicity: current concerns. *Environ. Health Perspect.* 100, 177–187.  
12  
13  
14 Jensen, S., Renberg, L., Reutergardh, L., 1977. Residue Analysis of Sediment and Sewage  
15 Sludge for Organochlorines in the Presence of Elemental Sulfur Soren Jensen," Lars  
16 Renberg, and Lars Reutergardh, *Analytical Chemistry.* 49, (2).  
17  
18  
19  
20  
21 Jitar. O., Teodosiu. C., Oros. A., Plavan., Nicoara. M., 2015. Bioaccumulation of heavy metals in  
22 marine organisms from the Romanian sector of the Black Sea. *New Biotechnology.* 32,  
23 369-378.  
24  
25  
26  
27  
28 Khan, M.A., Ahmad, I., Rahman, I., 2007. Effect of environmental pollution on heavy metals  
29 content of With aniasomnifera. *J. Chin. Chem. Soc.* 54, 339–343.  
30  
31  
32  
33 Laxen, D.P.H., 1983. The chemistry of metal pollution in water. In: *Pollution- Causes, Effects*  
34 *and control.*, edited by Roy. M.Harrison, The Royal Society of Chemistry. London.  
35 WIVOBN. pp. 104.  
36  
37  
38  
39  
40 Lepp, N.W., 1981. In: *Effect of Metal Pollution on Plants, Vol.1.* London. Applied Science  
41 Publishers. pp. 145–170.  
42  
43  
44  
45 Loewen, M.D., Sharma, S., Tomy, G., Wang, F., Bullock, P., Wania., 2005. Persistent organic  
46 pollutants and mercury in the Himalaya. *Aquat Ecosyst Health Manag.* 8, 223–330.  
47  
48  
49  
50 Macnair, M. R., 1990. The genetics of tolerance in natural populations. In: Shaw J (ed) *Boca*  
51 *Raton, Heavy metal tolerance in plants: evolutionary aspects.* CRC Press, 235–254.  
52  
53  
54  
55 Manahan, S.E., 2000. *Environmental Chemistry Seventh Edition.* Lewis Publishers, CRC Press  
56 LLC. 898.  
57  
58  
59  
60  
61  
62  
63  
64  
65

- 1  
2  
3  
4 Marques, A., Moreira, H., Rangel, A., Castro, P., 2009. Arsenic, lead and nickel accumulation in  
5  
6 *Rubus ulmifolius* growing in contaminated soil in Portugal. J. Hazard. Mater. 165, 174–  
7  
8 179.  
9
- 10  
11 Martinez. L , Gibert. X; Marti. O ., Díez, S., Romo, J., Bayona, J.M., de Pablo, J., 2007.  
12  
13 Distribution of polycyclic aromatic hydrocarbons (PAH) and tributyltin (TBT) in  
14  
15 Barcelona harbour sediments and their impact on benthic communities. Environ. Pollut.  
16  
17 149 (1), 104–113.  
18  
19
- 20  
21 Mensah, H., Atiemo, S., Palm, L.M., Blankson-Arthur, S., Tutu. A., Fose, P., 2012.  
22  
23 Determination of organochlorine pesticide residue in sediment and water from the Densu  
24  
25 river basin, Ghana. Chemosphere. 86, 286-292.  
26  
27
- 28  
29 Michael, B., 1978. Heavy metals and chlorinated hydrocarbons in the Mediterranean. Ocean  
30  
31 Management. 3, 253-313.  
32
- 33  
34 Ministry of Territory Management, Water and Environment, 2006. National implementation plan  
35  
36 for Stockholm Convention on Persistent Organic Pollutants (POPs). Directorate for  
37  
38 surveillance and risk prevention. Rabat, Morocco.  
39
- 40  
41 Mishra, V.K., Tripathi, B.D., 2009. Accumulation of chromium and zinc from aqueous solutions  
42  
43 using water hyacinth (*Eichornia crassipes*). J. Hazard. Mater. 164, 1059–1063.  
44
- 45  
46 Moore, J.W., 1991. Inorganic Contaminants of Surface Water: Research and Monitoring  
47  
48 Priorities. Springer-Verlag, New York.  
49
- 50  
51 Nikolaou, A., Kostopoulou, M., Lofrano, G., Meric, S., 2009. Determination of PAHs in marine  
52  
53 sediment: analytical methods and environmental concerns. Global Nest J. 11, 391–405.  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

- 1  
2  
3  
4 Pavlikova, D., Pavlík, M., Staszková, L., Motyka, M., Štávková, J., Tlustos, P., Balík, J.,  
5  
6 2008. Glutamate kinase as potential biomarker of heavy metal stress in plants. *Ecotox.*  
7  
8 *Environ. Safe.* 70, 223–230.  
9
- 10  
11 Perry, A.R.R., Flammarion, P., Vولات, B., Bedaux, J.J.M., Kooijman, S.A.L.M., Garric, J., 2002.  
12  
13 Using biology based model (Debtox) to analyse bioassays in ecotoxicology: opportunities  
14  
15 and recommendation. *Environ. Toxicol. Chem.* 21, 459–465.  
16  
17
- 18  
19 Qui, Y.W., Yu, K.F., Zhang, G., Wang, W.X., 2001. Accumulation and partitioning of seven  
20  
21 trace metals in mangroves and sediment cores from three estuarine wetlands of Hainan  
22  
23 Island, China. *J. Hazard. Mater.* 190, 631-638.  
24  
25
- 26  
27 Rahman, M A., Hasegawa, H., Ueda, K., Maki, T., 2008. Influence of phosphate and iron ions in  
28  
29 selective uptake of arsenic species by water fern (*Salvinia natans* L.). *Chemical*  
30  
31 *Engineering Journal.* 145, 179-184.  
32
- 33  
34 Raskin, I., Nanda, K. N., Dushenkov, S., Salt, D.E., 1994. Bioconcentration of heavy metals by  
35  
36 plants. *Curr. Opin. Biotech.* 5, 285–290.  
37
- 38  
39 Sawasdee, B., Köhler, H.R., Triebkorn, R., 2011. Histopathological effects of copper and  
40  
41 lithium in the ramshorn snail, *Marisa cornuarietis* (Gastropoda, Prosobranchia).  
42  
43 *Chemosphere* 85, 1035–1039.  
44
- 45  
46 Sawidis, T., Chettri, M.K., Papaionnou, A., Zachariadis, G., Stratis, J., 2001. A study of metal  
47  
48 distribution from lignite fuels using trees as biological monitors. *Ecotoxicol. Environ.*  
49  
50 *Safety.* 48, 27–35.  
51
- 52  
53 Sayed, El., Basaham, M.A., 2004. Speciation and mobility of some heavy metals in the coastal  
54  
55 sediments of Jeddah, eastern Red Sea. *J. Environ. Sci.* 27, 57-92.  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65



- 1  
2  
3  
4 SedNet, 2013. Contaminated Sediments in European River Basins. European Sediment Research  
5  
6 Network.[http://www.sednet.org/download/Sednet\\_booklet\\_final.pdf](http://www.sednet.org/download/Sednet_booklet_final.pdf).  
7  
8  
9 Shen, Z.G., Chen, H.M., 2000. Bioremediation of heavy metal polluted soils. Rural Eco-  
10  
11 Environment. 16(2), 39-44.  
12  
13  
14 Taiz, L., Zeiger, E., 2002. Plant Physiology, Third ed., Sinauer Associates, Inc Chapter 35, 68-  
15  
16 72.  
17  
18  
19 Tanabe, S., Hisato, I., Tatsukawa, R., 1994. Global organochlorine and their ecotoxicological  
20  
21 impact on marine mammals. Sci.Total Environ. 154, 163–177.  
22  
23  
24 Taylor, S.E., Birch, G.F., Links, F., 2004. Historical catchment changes and temporal impact  
25  
26 on sediment of the receiving basin, Port Jackson, New South Wales. Aust. J. Earth Sci. 51,  
27  
28 233-246.  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
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**Table 1.** Heavy metals concentrations in the four extracting solutions

Sample	Cu	Pb	Zn	Ni	Cd	Cr
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
HCl 1M	ND	3.5	0.51	1.8	0.20	0.42
H <sub>2</sub> O	ND	0.57	0.038	0.26	0.055	0.028
NaCl						
36 ‰	ND	2.52	0.040	1.99	0.33	0.33
HNO <sub>3</sub>						
67 ‰	0.48	2.35	2.74	2.48	0.44	2.274

\*ND-non-detected

**Table 2.** General characteristics of the sediments.

<b>Characteristics</b>	<b>Values</b>
pH sediment	7.65
Electrical conductivity (dS m <sup>-1</sup> )	3.54
Determination of chlorine in the sediment (Cl <sup>-</sup> ) g/mol	35.453
NaCl (g/mol)	58.44
Water salinity (%)	3.5
Porosity (%)	35
Density (kg/m <sup>3</sup> )	1750
Moisture (%) <sup>a</sup>	32.4
Cl <sup>-</sup> concentration in the sediment extract (M)	0.0282
Cl <sup>-</sup> (1 Kg/sediment) (g\Kg)	6.2

<sup>a</sup> The percentage is calculated on dry mass

**Table. 3** The amount of Pb and Cu accumulated by aquatic plants during the 10-day exposure.

Aquatic plant species	Heavy metal concentration	Experimental solutions	Pb content in plant (mg/kg DW)	Cu content in plant (mg/kg DW)
<i>Salvinia natans</i>	3 mg/L Pb	NaCl with Hoagland	3.328 ±0.032	ND
	3 mg/L Pb	NaCl without Hoagland	3.247±0.020	ND
	2.8 mg/L Pb	HNO <sub>3</sub> with Hoagland	2.852 ±0.013	2.641±0.014
	0.8 mg/L Cu			
	3.5 mg/L Pb	HCl with Hoagland	1.938±0.013	ND
<i>Vallisneria spiralis</i>	3 mg/L Pb	NaCl with Hoagland	3.107 ±0.034	ND
	3.5 mg/L Pb	NaCl without Hoagland	3.061±0.028	ND
	2.8 mg/L Pb	HNO <sub>3</sub> with Hoagland	2.640 ±0.034	2.409±0.048
	0.8 mg/L Cu			
	3.5 mg/L Pb	HCl with Hoagland	1.935 ±0.048	ND
<i>Cabomba aquatica</i>	3 mg/L Pb	NaCl with Hoagland	2.400 ±0.029	ND
	3 mg/L Pb	NaCl without Hoagland	1.965 ±0.183	ND
	2.8 mg/L Pb	HNO <sub>3</sub> with Hoagland	0.205 ±0.003	1.941±0.028
	0.8 mg/L Cu			

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3.5 mg/L	HCl with Hoagland	1.780±0.005	ND
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ND- non-detected concentration (mg/L)

DW- dry weight (mg/Kg)

Fig. 1



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Fig.2

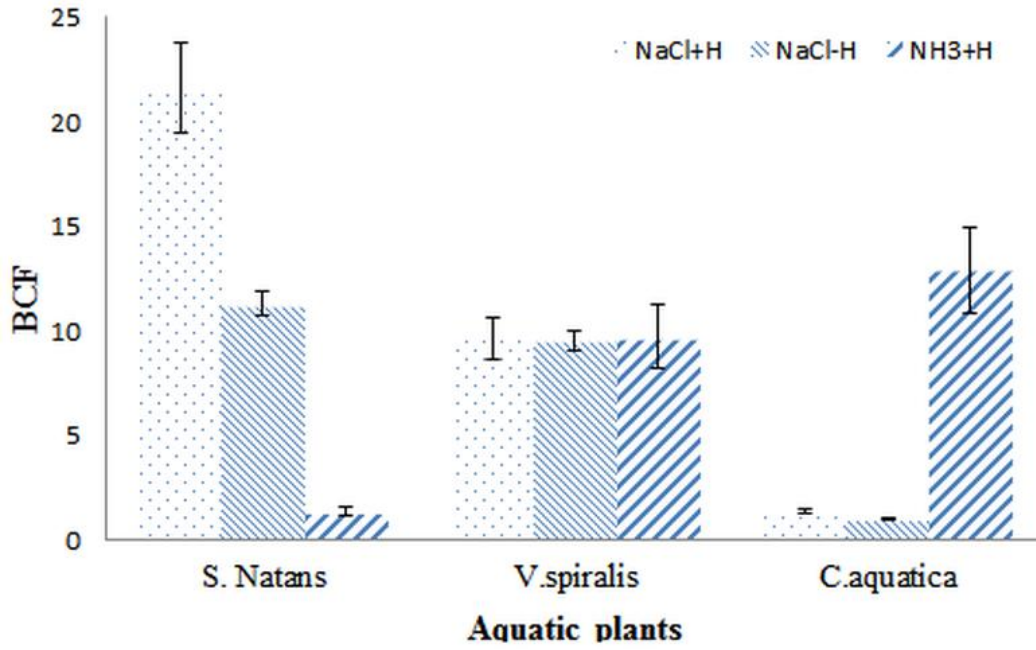
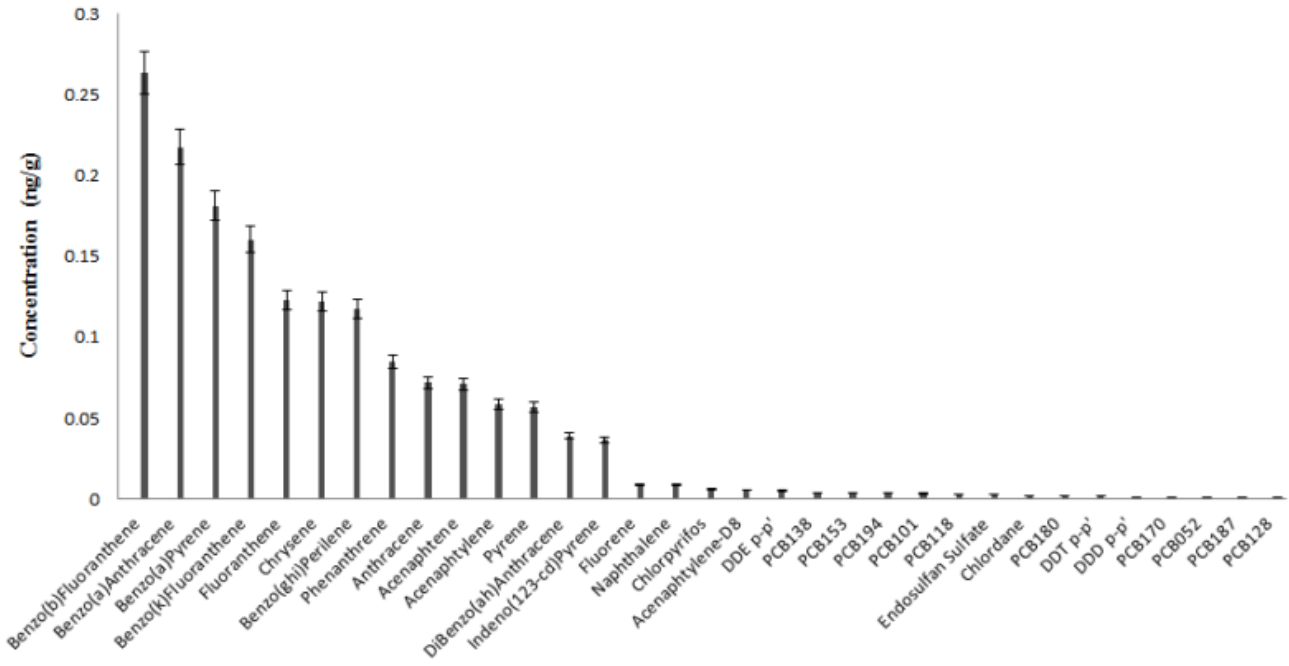


Fig. 3





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**Figure captions**

**Figure 1** Map of the study location and sampling sites in the Leghorn area of Italy

**Figure 2** Bioconcentration factors for *Salvinia natans*, *Vallisneria spiralis* and *Cabomba aquatica* in different experimental solutions. Results are expressed as means  $\pm$  S.D ( $n=3$ )

**Figure 3** The distribution of various pesticides in the sediment from the three locations sampled is summarized

**Table 1.** Heavy metals concentrations in the four extracting solutions

Sample	Cu mg/L	Pb mg/L	Zn mg/L	Ni mg/L	Cd mg/L	Cr mg/L
HCl 1M	ND	3.5	0.51	1.8	0.20	0.42
H <sub>2</sub> O	ND	0.57	0.038	0.26	0.055	0.028
NaCl 36 ‰	ND	2.52	0.040	1.99	0.33	0.33
HNO <sub>3</sub> 67 ‰	0.48	2.35	2.74	2.48	0.44	2.274

\*ND-non-detected

**Table 2.** General characteristics of the sediments.

<b>Characteristics</b>	<b>Values</b>
pH sediment	7.65
Electrical conductivity (dS m <sup>-1</sup> )	3.54
Determination of chlorine in the sediment (Cl <sup>-</sup> ) g/mol	35.453
NaCl (g/mol)	58.44
Water salinity (%)	3.5
Porosity (%)	35
Density (kg/m <sup>3</sup> )	1750
Moisture (%) <sup>a</sup>	32.4
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ND- non-detected concentration (mg/L)

DW- dry weight (mg/Kg)

Fig. 1



Fig.2

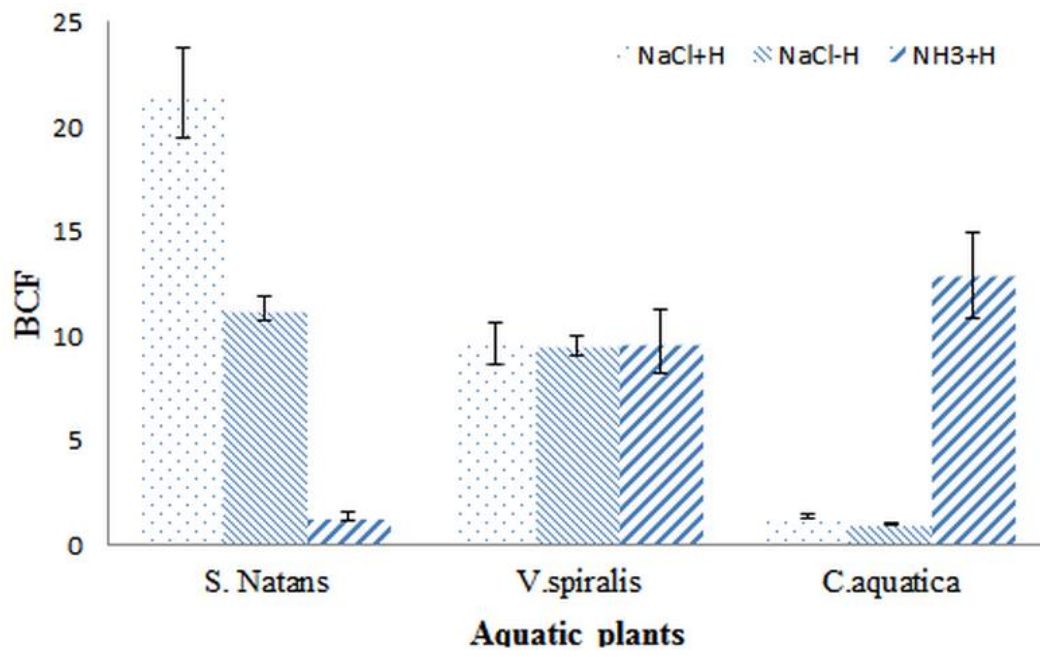


Fig. 3

