Chemosphere 183 (2017) 371–379

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

The effectiveness and efficiency of phytoremediation of a multicontaminated industrial site: Porto Marghera (Venice Lagoon, Italy)

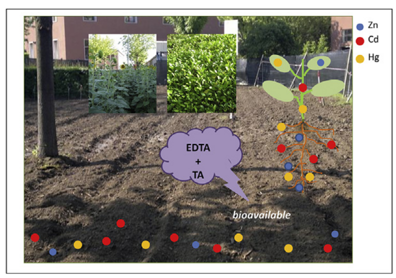
C. Guarino, R. Sciarrillo*

University of Sannio, Department of Science and Technology, via Port'Arsa 11, 82100 Benevento, Italy

HIGHLIGHTS

- The microcosms and mesocosms tests are applied to *in-situ* phytoextraction process.
- *Helianthus annuus* L. and *Brassica juncea* (L.) Czern. were used.
- The EDTA and Ammonium Thiosulfate increase the removal of Cd, Hg, Zn.
- *B. juncea* was able of removing more than twice respect to *H. annuus.*
- The synthetic chelator additions resulted in bioavailable metal order of Zn > Cd=Hg.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 March 2017
Received in revised form
15 May 2017
Accepted 16 May 2017
Available online 19 May 2017

Handling Editor: T Cutright

Keywords:
Multicontaminated industrial site
EDTA
Ammonium thiosulfate
Helianthus annuus L.
Brassica juncea (L.) Czern

ABSTRACT

The Venice Lagoon is worldwide considered as a typical example of the human impact on the surrounding ecosystem. The development of the industrial zone of Porto Marghera begun in 1917 as an extension of the Venice Port, in order to sustain activities related to oil and coal, as well as to exploit the railway system. Despite the recent decrease in the number of employees, Porto Marghera is still one of the most important chemical districts in Italy. This study reports early results from the ongoing *in-situ* phytoextraction of potentially toxic elements (Cd, Hg, Zn) within the industrial area of Porto Marghera. Two agronomic plant species with high annual biomass yield (*Helianthus annuus* L., *Brassica juncea* (L.) Czern.) were used. This paper also reports the microcosms and mesocosms tests to evaluate the efficacy of the treatments to be applied to the *in-situ* phytoextraction process of the polluted site. The combined use of EDTA and Ammonium Thiosulfate during phytoextraction increases the efficiency of Cd, Hg, Zn removal from contaminated soil.

1. Introduction

Industrial activities often represent an important source of pollution by potentially toxic elements (PTEs), which can be introduced into the atmospheric, terrestrial and aquatic ecosystems (Passariello et al., 2002).

In literature many cases of chemical contamination have been described in former industrial areas, where significant amounts of elements were mobilized by weathering and leaching (Iavazzo et al., 2012; Nadal et al., 2004; Pravdić, 1995; Remon et al., 2005).

* Corresponding author.
E-mail address: sciarrillo@unisannio.it (R. Sciarrillo).

http://dx.doi.org/10.1016/j.chemosphere.2017.05.102

The Venice Lagoon is worldwide considered as a typical example of the human impact on the surrounding ecosystem (Gieskes et al., 2015). The development of the industrial zone of Porto Marghera begun in 1917 as an extension of the Venice Port, in order to sustain activities related to oil and coal, as well as to exploit the railway system. Despite the recent decrease in the number of employees, Porto Marghera is still one of the most important chemical districts in Italy (Zonta et al., 2007). Major industrial activities consist of several basic chemical products, oil refining and storage, shipbuilding, metal extraction and metallurgy, as well as energy production and distribution, waste water treatment, and hazardous waste incineration (Pavoni et al., 1992; Bellucci et al., 2002; Region of Veneto and ARPAV, 2004). This broad industrial activity affected the surrounding environment, leading to a well documented contamination of air, soil, groundwater and inner tidal canals (Frignani et al., 2001, 2004; Alcock et al., 2002; Scazzola et al., 2004; Dalla Valle et al., 2005; Rapaglia, 2005; Rossini et al., 2005).

Based on a study carried out by the Province of Venice (2015), main anthropogenic activities affecting air quality in Venice are the followings: (i) oil refining; (ii) metallurgy, lately confined to Al production; (iii) chloro-soda cycles, discharging dichloroethane (DCE), vinyl chloride monomer (VCM) and polyvinylchloride (PVC); (iv) power generation (oil and coal); (v) urban waste incineration, and (vi) traffic emissions. The Italian law 426/1998 defined the industrial area of Porto Marghera as a high environmental hazard site and listed it as a contaminated Sites of National Interest (SIN) which needs to be reclaimed.

In recent years, the disposal of former industrial sites has widely become a key subject of interest in terms of reclamation in order to promote their different use for the community.

Frequently, techniques for the reduction of potentially toxic elements (PTEs) content in heavily contaminated soils involve either onsite management or excavation and subsequent disposal to a landfill site. This approach results very expensive and simply shifts the problem elsewhere along with the hazards associated with transportation of polluted soil and migration of contaminants into the nearby environment (Juwarkar et al., 2010).

An alternative environmental friendly and potentially cost-effective approach consists in the so called *green-technologies*. Such technologies were developed of direct extract pollutants (cleanup) or promote their stabilization through the use of biological structures (plants, fungi, bacteria) (Salt et al., 1995; Raskin et al., 1997; Chaney et al., 1997; Marchiol et al., 2013; Onwubuya et al., 2009; Guarino and Sciarrillo, 2017; Guarino et al., 2017).

Phytoextraction is the *green-technology* typically used to tackle metals and metalloids accumulated in the aerial parts which can be removed by harvesting and burning of the biomass (Juwarkar et al., 2010; Tangahu et al., 2011). Basically, the application of phytoextraction technologies is limited to low contamination levels (gentle remediation), while for heavily contaminated sites, phytostabilization seems to be probably the preferable option to restore ecosystems (Schwitzguébel et al., 2009; Vangronsveld et al., 2009).

The success of phytoremediation is strictly dependent on the potential of the plants to accumulate contaminants in below or aboveground biomass, withstand the metal stress and yield high biomass; moreover high efficiency of water use, fast growth and adaptation to pedoclimatic and edaphic conditions are also parameters affecting the plant selection. Besides, a crucial point of plant remediation efficiency is related to the mobility and bioavailability of PTEs and the phytoextraction rate is limited by solubility and diffusion to the root surface (Rajkumar et al., 2012).

In order to overcome this problem, soil washing techniques with the addition of natural and/or chemical chelating agents can be helpful for metal extraction from the solid phase to a liquid matrix enhancing the cleanup of soil contaminated by PTEs (Wu et al., 1999; Thayalakumaran et al., 2000; Pastor et al., 2007; Quartacci et al., 2007) although a potential leaching of the PTEs as a consequence of the higher mobility induced by the use of chelating agents must be assessed. In fact, despite the potential usefulness of this technology, some concerns have been expressed regarding the potential risk of leaching of metals to groundwater (Nascimento and Xing, 2006; Evangelou et al., 2007). Moreover, some chemical chelating agents (e.g., EDTA) are not only phytotoxic but also toxic to beneficial soil microorganisms that play an important role in plant growth (Chen and Cutright, 2001; Mühlbachová, 2009; Ultra et al., 2005; January et al., 2008; Munn et al., 2008; Bolan et al., 2014).

This paper reports early results from the ongoing *in-situ* phytoextraction of PTEs (Cd, Hg, Zn) within the industrial area of Porto Marghera in the province of Venice (Italy). Two agronomic plant species with high annual biomass yield (*Helianthus annuus* L., *Brassica juncea* (L.) Czern.) were used. This paper also reports the microcosms and mesocosms tests to evaluate the efficacy of the treatments to be applied to the *in-situ* phytoextraction process of the polluted site.

2. Materials and methods

2.1. Site description

The industrial area of Porto Marghera, located on the border of the Venice Lagoon (549 km^2), is characterized by an extension of almost 12$km^2$and employs more than 10,000 people (Zonta et al., 2007). The *in-situ* phytoremediation process was carried out in an area owned by Venezia Tecnologie Spa company, on the basis of the final remediation project of the Syndial site (D. Lgs. 152/06) approved by the Italian Ministry of Environment, Land and Sea in 2008.

A preliminary survey was carried out identifying and selecting a total of 7 representative sampling points in order to assess soil properties and contamination (1 m of depth) (Supplementary Fig. 1a–b).

2.2. Soil: chemical analyses

Soil samples were analyzed in order to characterize their main physical and chemical properties; in particular, the following parameters were studied: humidity at 105 °C, pH, EC at 25 °C, total carbonates, CEC, organic Carbon, total N, C/N, and total content of, Cd, Hg, and Zn.

Soil samples were oven-dried at 105 °C for 24 hand acid-digested in a microwave oven (CEM, MARSXpress) according to the USEPA method, (USEPA, 1995a,b). After mineralization, soil extracts were filtered (0.45 m PTFE), diluted and analyzed. Total content of Cd, Hg, and Zn in soils extracts were determined by an ICP-OES (Varian Inc., VistaMPX). The mean concentrations of Cd, Hg and Zn in soil were always higher than the permissible threshold values for residential soils (Table A of D. Lgs. 152/06).

The accuracy of the analytical procedure adopted for ICP-OES analysis was checked by running standard solutions every 20 samples. Yttrium was used as the internal standard. A reagent blank and certified reference material (NIST SRM®2710 a Montana soil