AES BIOFLUX

Advances in Environmental Sciences - International Journal of the Bioflux Society

Study on optimal application of the ex-situ soil washing method to remove metals from polluted soils

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Abstract. Overcoming the concentration of heavy metals in soil due to various polluting activities becomes a major problem. Soil washing is a remediation method that uses water, inorganic or organic acids and chelating agents, becoming increasingly used for soil rehabilitation. Determination of the site`s characteristics is the most important factor which depends on the soil washing method. Extraction of heavy metals with the soil washing method is influenced by geological and hydrological characteristics, soil type and composition, pH, organic matter content, distribution of pollutants in soil, soil physical and chemical characteristics and pollution source. The present paper is a study on the conditions in which the extraction of metals from soil may be applied to obtain the best results and propose a suitable alternative site remediation method by washing for heavily contaminated soils with heavy metals existing in our country.
Key Words: soil washing, heavy metals, soil remediation.

Rezumat. Depăşirea concentraţiei metalelor grele din sol datorită diferitelor activităţi poluatoare devine o problemă majoră. Spălarea solurilor este o metodă de decontaminare care utilizează apă, acizi anorganici sau organici şi agenţi de chelare devenind tot mai utilizată pentru reabilitarea solului. Determinarea caracteristicilor sitului este cel mai important factor de care depinde aplicarea metodei de spălare a solului. Extragerea metalelor grele din sol prin metoda spălării este influenţată de caracteristicile geologice şi hidrologice ale solului, tipul şi compoziţia solului, pH, conţinut în materie organică, distribuţia poluanţilor în sol, caracteristicile fizice şi chimice ale solului precum şi de sursa de poluare. Prin prezenta lucrare se face un studiu asupra condiţiilor în care extragerea metalelor din sol se poate aplica pentru a se obţine cele mai bune rezultate şi se propune o variantă adecvată de depoluare prin spălare pentru siturile puternic contaminate cu metale grele, existente în ţara noastră.
Cuvinte cheie: spălarea solului, metale grele, remedierea solului.

Introduction. Intensive industrial development has led to the accumulation of high concentrations of metals in the soil, which represent the largest percentage of pollutants in soil as results from the European Environment Agency report in 2007 (Fig.1) (www.epa.gov) (http://themes.eea.europa.eu). Once they reached the soil they won't biodegrade from natural processes and therefore remain in the ecosystem (Moutsatsou et al 2006).

Soil pollution by metals is of great importance because of the reactivity, toxicity and mobility of the metals in soil and their potential to bio-accumulate. Metals are present in soil in different forms, and they are retained by the soil depending on its characteristics such as pH, soil type, ion exchange capacity, organic matter content, age of contamination (Ting Xie 2000).

To remedy the contaminated soil several technologies can be applied, such as incineration, thermal desorption, vitrification, electrokinetic extraction, solidification/stabilization, soil washing, bioremediation, phytoremediation.

Further a study will be made on the remediation technology of soils contaminated with metals by ex-situ soil washing.

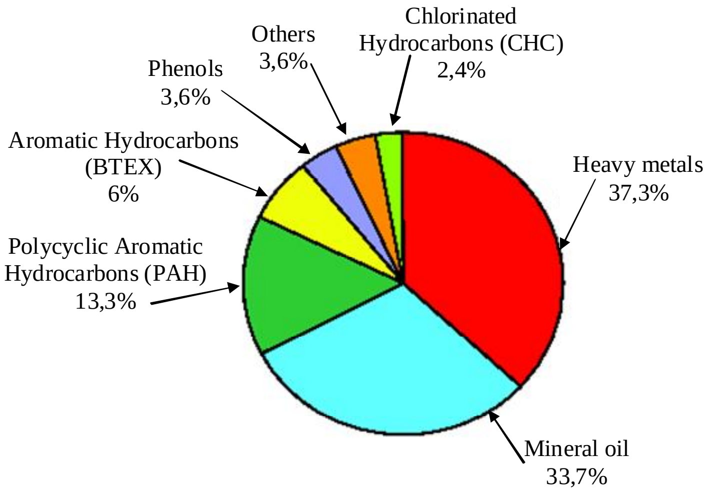


Figure 1. Overview of contaminants affecting soil and groundwater in Europe (http://themes.eea.europa.eu)

Soil washing of metals from contaminated soils. Soil washing is an ex-situ remedial technology (Fig.2, U.S. EPA, 2001, https//:portal.navfac.navy.mil). This method has as a principle pollutant removal from soil matrix by its solubilization in a washing solution. Soil washing technology can be applied for remediation of sites contaminated with heavy metals, hydrocarbons and semi-volatile organic compounds (Micle 2009; Micle & Neag 2009).

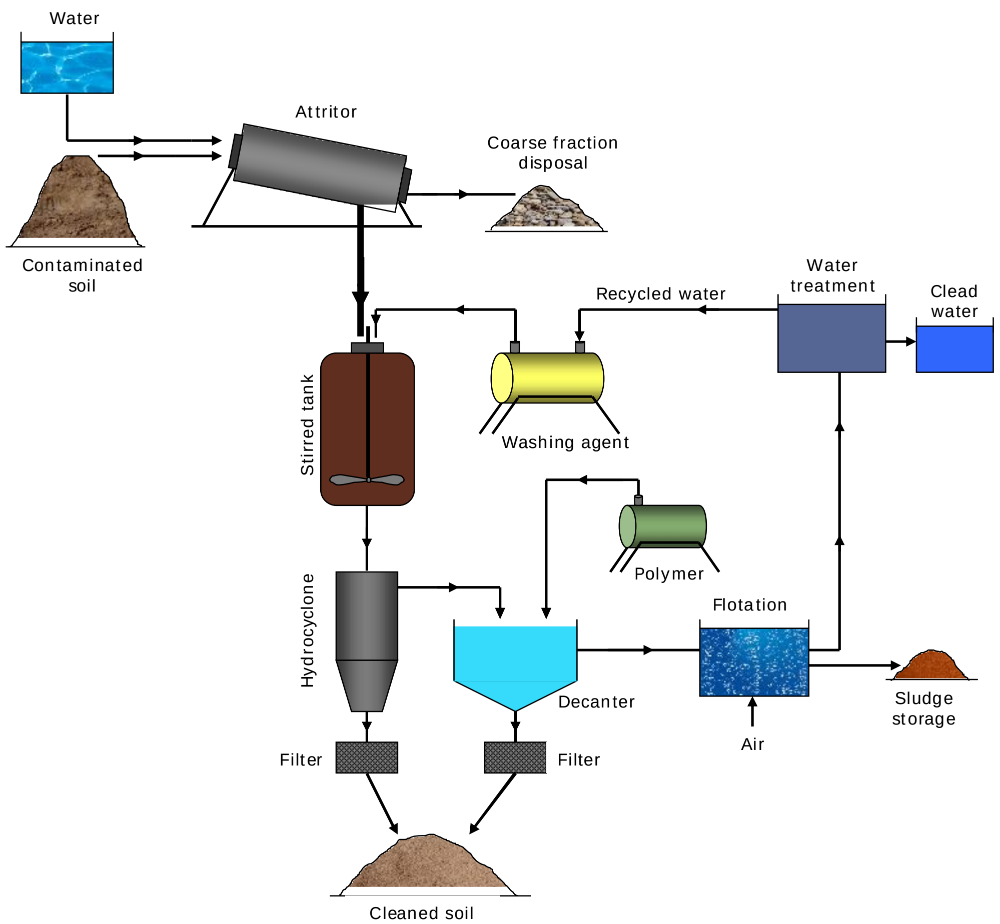


Figure 2. Schematic diagram of soil washing.

In the case of pollutants with low solubility in aqueous solution the presence of additives such as acids, bases, surfactants, solvents, chelating or separation agents is necessary in order to achieve an effective remediation (Moutsatsou et al 2006).

Soil washing process involves:

- excavation of polluted soil;
- mechanical size grading to remove coarse fraction;
- separation process to separate the coarse fractions from the fine;
- treatment of these fractions (soil washing);
- resulting water treatment;
- resulting waste management (Mann et al 1993; U.S. EPA 2001);

In the choice of soil washing technology for the rehabilitation of polluted sites several factors should be taken into account, such as:

- site characteristics, these being among the most important factors to be analyzed (Reddy & Chinthamreddy 2000); in this case is necessary information on site geology and hydrogeology, the distribution of pollutants in soil, soil type, its composition on deep soil chemistry. Soil washing efficiency increases with increasing sand content in it, but it is not economically recommended for soils with a clay content of 30-50%;
- contaminant characteristics, such as type of pollutant, concentration and distribution on the vertical and horizontal, this technology can be applied to a wide range of contaminants;
- necessary space varies according to soil washing system construction, system transfer rate and site logistics. A quantity of 20 tons per hour can be placed on a surface of 2,023 m^2, including staging area for treated and untreated soils. In some systems additional space may be need, depending on system design (Mann et al 1993; Sogorka et al 1997).

The ability to extract metals from soil depends on the presented factors but also on the extractive agent's chemistry and processing conditions. To get more relevant results all these factors are taken into account.

In Figure 3, according to Mann et al (1993), are presented opportunities for the application of soil washing according to different contaminants and soil type.

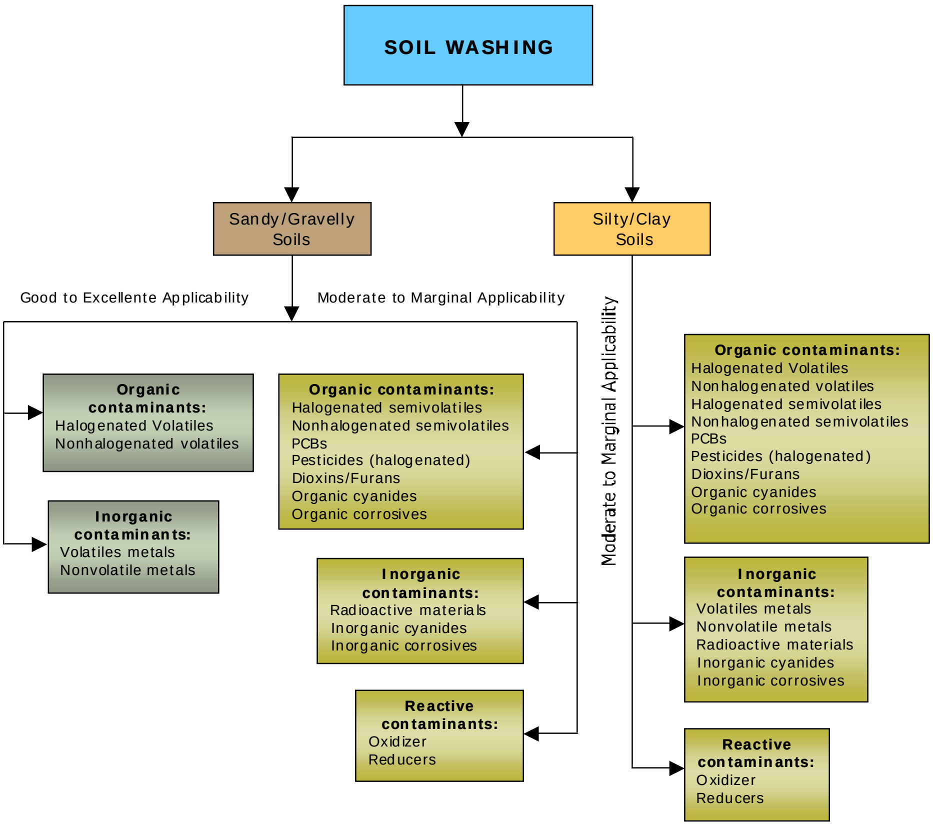


Figure 3. Applicability of soil washing to general contaminant groups for various soils.

Mobilization of metals from the soil matrix can be achieved by:

- changing the acidity;
- changing the ionic solution strength;
- redox potential change;
- complex formation (Moutsatsou et al 2006).

Remediation of soil contaminated with metals by the application of soil washing technology can be achieved by three ways:

a) Physical separation: the technology uses machinery from the mineral processing industry. In applying this variant the fact that it is used for metal particles found in soil as an individual or for those that are attached to soil particles is taken into account, generally not an appropriate method for metals absorbed into soil particles. The degree of release of the mineralogical phase containing metals is an important factor in the application of physical separation. This factor refers to the availability of the metal phase to separate from the soil particles. The degree of extraction of metals from soil depends on soil particle mineralogical aspects such as shape, morphology and mineralogy bonds. Mineralogical speciation aspects and solid phase speciation of metal bearing particles can be analyzed microscopically or spectroscopically. The efficiency of the process of physical separation depends on soil characteristics, such as: particle shape, size distribution, clay content, soil moisture, humus content, magnetic properties, soil matrix heterogeneity, density difference between soil matrix and metal and hydrophobic properties of the particles from the surface. Physical separation may not apply if:

- metal particles are strongly bond to the soil;
- density difference between particles and surface properties are not significant;
- wide range of chemical forms of the metal;
- the metal is present in all particle size fractions of contaminated soil;
- soil contains less than 30-50% clay;
- soil has a high humus content;
- soil contains organic compounds with high viscosity (Dermont et al 2008).

Soil particle sizes affect the efficiency of physical separation, the yield being lower if the soil contains very fine particles, it is recommended that particle size is between 63 and 2000 µm (Dermont et al 2008).

b) Chemical extraction: this method uses a fluid containing chemical reagents such as acids, bases, surfactants, chelating agents, salts or redox agents to transfer metal from the soil in an aqueous solution. The efficiency of extraction of metals from soil by this method depends on the geochemistry of soil (texture, cationic exchange capacity, buffering capacity, organic matter content), metal contaminant characteristics (type, concentration, metals fractionation and speciation, extraction agent dosage and chemistry and metal extraction conditions, pH, detention time, the number of successive steps of extraction, how the reagent is added, the ratio liquid / solid etc) (Dermont et al 2008).

Factors to be taken into account in the application of chemical extraction technology are:

- metal speciation (distribution of chemical species) and fractionation (fractions depending on the specific soil substrates bonds) in the soil;
- type of metal and its valence, cationic metal extraction capacity increases if the pH decreases;
- if metal is not under an adsorbed form, the extraction efficiency depends on solubility of the metal in the washing solution (Dermont et al 2008).

The applicability of chemical extraction is limited by:

- high clay content;
- high humus content;
- a high content of Fe and Ca;
- high calcium content and high buffering capacity;
- simultaneous contamination with cationic and anionic metals;
- high soil heterogeneity;
- metals are associated with residual soil forms (Dermont et al 2008).

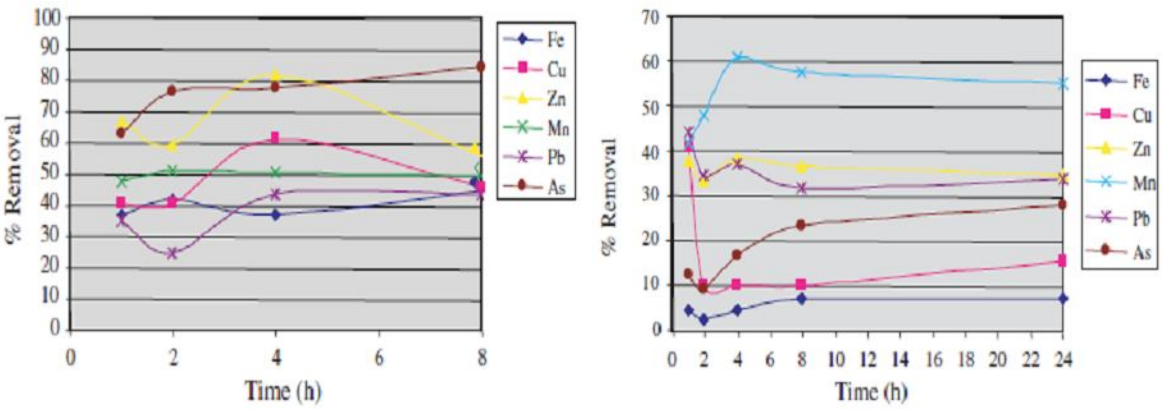
c) Physico-chemical separation: it is the most used version for the remediation of soils contaminated with metals. This version is a combination of the previous two and therefore the first step physical separation occurs, seeking metal concentration in a small volume of soil, after which it is subjected to chemical extraction of dissolved metals. (Dermont et al 2008).

Soil washing has the following advantages:

- reducing the volume of soil to be decontaminated, thus reducing costs;
- physical separation allows simultaneous treatment of metal and organic pollutants;
- recovered metal can be reused;
- treated soil can be redeposited on site;
- metals adsorbed to soil particles can be treated;
- generally pollutant removal efficiency is between 60-90%;
- costs are relatively low ($ 187 and $ 70 for small sites to large sites) (Mann et al 1993; Dermont et al 2008) (www.frtr.gov).
- The main disadvantages of soil by washing are:
- the need of a space big enough for the equipment;
- the need for wash water treatment;
- the use of washing agents increase the cost of the process and may cause problems related to reuse of treated soil;
- the technology is not suitable for soils with high clay content (Mann et al 1993; Dermont et al 2008) (www.frtr.gov).

Analysis of factors influencing soil washing. Soil washing is based on the ability of water or water with various additives to mobilize metals from the soil. This requires the factors affecting metal mobility in soil to be known. These factors are: pH, organic matter content, metal content in soil, soil adsorption capacity, washing time, also the extraction of additives and the presence of different inorganic pollutants (Moutsatsou et al 2006).

One of the important factors influencing the extraction of metals from soil is the washing time and the type of additive. Moutsatsou et al (2006) conducted a study on the influence of time on the extraction of metals from soil from washing it with a 1M HCl solution (Fig. 3a) and 0.1 M EDTA solution (Fig. 3b). As this study shows that Zn, Cu, Pb are best extracted from a washing time of 4 hours, with HCl, As and Fe for 8 hours, and Mn after 2 hours. Washing in the presence of EDTA led to the conclusion that Mn and Zn can be best extracted after a wash of 4 hours, Pb and Cu after 2-hour washes, Fe after 8 hours, while As after 24 hours.



a) b)

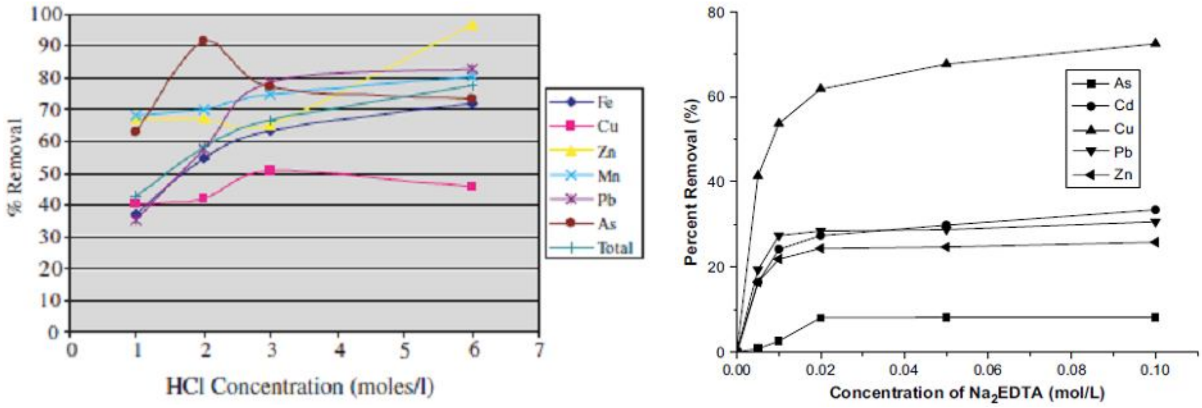
Figure 3. a) Mobilization of metals under 1 M HCl as a function of time. b) Mobilization of metals under 0.1 M EDTA as a function of the time (Moutsatsou et al 2006).

The concentration of extraction additives is another factor affecting the efficiency of soil washing. Influence of HCl concentration on the soil washing has been studied by

Moutsatsou et al (2006) (Fig. 4a), and the cleaning function of the concentration of Na_2EDTA has been studied by Zelí Zou et al (2009) (see Fig. 4b).

In case of using HCl most metals (Mn, Pb, Zn, Fe) studied can be extracted at a concentration of 6 mol/L, while As at the concentration of 2 mol/L with the best mobility and Cu with the concentration 3 mol/L.

Use of Na_2EDTA to remove the metals by washing has the best yield of extraction and concentration of 0.10 mol/L for Cu and Cd, and for As, Pb and Zn concentration value of 0.02 mol/L.



a) b)

Figure 4. a) Mobilization of metals as a function of HCl concentration (Moutsatsou et al 2006). b) Extraction efficiency of diferent concentrations of Na_2EDTA (liquid/solid=20, 24h) (Zeli Zou et al 2009).

One of the factors influencing the results of washing is also the pH. Its influence was studied by Moutsatsou et al (2006) (Fig. 5). From this analysis it appears that Cu and Pb can be extracted at an almost neutral pH (pH=7.1) and Mn, Fe, Pb are better dissolved at pH values higher than 8.1. The mobilization of Zn does not show significant variations with the increase of pH.

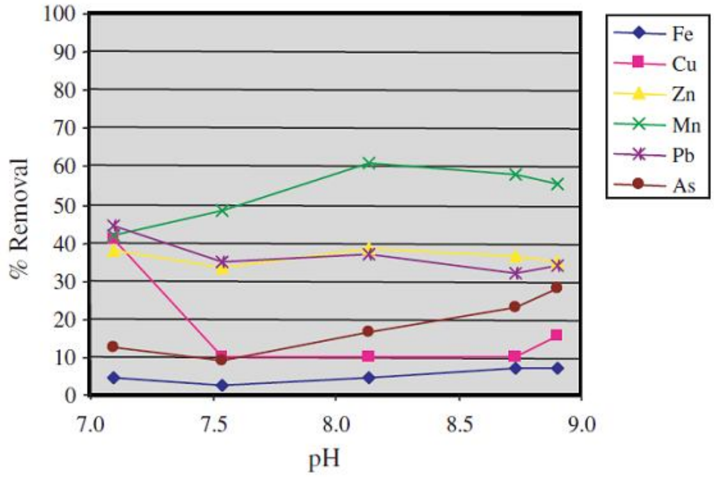


Figure 5. Metals mobilization under 0.1M EDTA as a function pH (equilibrium) for a 24 h of mixing (Moutsatsou et al 2006).

Conclusions. Using soil washing for remediation of sites contaminated with metals requires a very thorough analysis of site characteristics (soil type, soil chemistry, horizontal and vertical extent of the pollutant, particle size analysis etc) and the pollutant (speciation and fractionation of the metal bonds between soil particles and metal matrix, etc). This analysis shows to what extent the application of soil washing is recommended to fix the desired area. When choosing the method of soil washing as a remediation method it should be applied with confidence because of the advantages it presents.

Ex-situ soil washing efficiency is relatively higher for sandy soils and a low pH. Depending on the soil contaminants and additives that are used the washing duration varies, observing that the use of chelating agents means less time than with the use of acids. The concentration of additives is also very important and should be chosen depending on the characteristics and properties of the pollutant.

Even in highly contaminated soils, where by washing the pollutants cannot be removed, the technology is used to reduce the volume of soil to be treated by other methods, significantly reducing costs.

Acknowledgements. We thank the distinguished authors Moutsatsou A., and Protonotarios V., for their amiability of giving us the acceptance for using some data from their article. Paper prepared for the Project "Doctoral studies in engineering sciences to develop knowledge-based society-SIDOC", Contract POSDRU/88/1.5/S/60078.

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Received: 17 March 2011. Accepted: 01 July 2011. Published online: 18 July 2011.

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How to cite this article:
Szanto M., Micle V., Prodan V.C., 2011 Study on optimal application of the ex-situ soil washing method to remove metals from polluted soils. AES Bioflux **3**(2):83-90.