



Short Communication

Removal of chlorinated pesticide contamination by soil washing with sole water

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Received: 7 January 2020 / Accepted: 27 February 2020 / Published online: 5 March 2020
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Abstract

Chlorinated pesticide soil contamination still affects large territories due to past extensive use, poor solubility in water and scarce biodegradability of these agro-chemicals. In particular, this is noticeable for dichloro-diphenyl-trichloroethanes and their derivatives, globally referred as DDX contaminants. Presently, containment or immobilisation is a dominant approach to limit contamination, and remediation has been tried mainly at laboratory scale with contradictory results. Soil washing has been reported as a possible remediation treatment, although environmental effects of employed synthetic co-solvents or surfactants remain unclear. A soil washing treatment with sole water has been set up at laboratory scale, obtaining promising results on a contaminated soil with DDX level of 5050 mg/kg.

Keywords Attrition · DDT · Clay · Remediation · Silt · Soil

1 Introduction

Production and use of chlorinated pesticides have been favoured by their effectiveness in limiting the spread of harmful insects. On the other hand, the poor solubility in water and scarce biodegradability of these agro-chemicals have caused their accumulation in soil of sites involved in chemical or agricultural activities. Relevant environmental [1, 2] and human health issues [3] still affect large territories. In particular, this is noticeable for dichloro-diphenyl-trichloroethanes (DDTs) and their derivatives dichloro-diphenyl-dichloroethanes (DDD), dichloro-diphenyl-dichloroethenes (DDEs) globally referred as DDX contaminants. Their persistence has been reported after decades from their ban from the market [4]. Different approaches have been proposed in presence of chlorinated pesticide-contaminated soil including containment, immobilisation, desorption, flushing, chemical or biological degradation [5, 6]. Effectiveness of most of them has

been reported only at laboratory scale while containment or immobilisation is extensively practised [6]. Soil washing has drawn attention for its successful implementation in presence of organic [7] and inorganic [8] contaminants even mixed together [9]. Its limited environmental impact in terms of greenhouse gas emissions in comparison with other soil remediation treatments has been pointed out as additional benefit [10]. In general, it entails operations of excavation, separation of coarse fraction, attrition scrubbing, washing, separation of remediated fractions from contaminated fractions and treatment or disposal of the latter ones as wastes [11]. In particular, attrition scrubbing is an operation derived from mining industry, consisting in an energetic stirring of soil with a proper liquid, run by machines with helical impellers or opposite blades. Friction produced among soil particles results in mobilisation of contaminants adhered to particle surface and disaggregation of particle agglomerates. In practice, attrition scrubbing promotes concentration of contaminants in

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liquid [12] or in silt [13] improving soil washing effectiveness. In general, soil particle size distribution is not affected although additional silt can be produced by comminution in case of attrition operated in presence of added abrasive powders [14]. Soil washing optimisation is mainly empirical depending on several microscopic phenomena involved (e.g., mobilisation, disaggregation, comminution, sorption, dissolution), contaminated soil and apparatus peculiarities [15]. In particular, the literature on chlorinated pesticide-contaminated soils is scarce although careful extrapolation can be done considering other organic contaminants. In general, synthetic co-solvents or surfactants have to be employed [5, 6]. The latter ones can affect soil microbial population acting as poisons or nutrients. Furthermore, information on their regeneration when exhausted is lacking, pointing to the risk of additional dangerous waste production [6]. According to that, great environmental benefits could derive from setting up soil washing treatments based on sole water. Promising results on DDX contaminated soil obtained at Eni S.p.A. laboratories within a remediation project managed by Eni Rewind S.p.A. (former Syndial S.p.A., Eni S.p.A. subsidiary for environmental activity) are reported [16].

2 Material and methods

Raw soil was sampled from a disused Italian industrial site previously devoted to agro-chemical production and storage [1]. It was air dried for 8 h at room temperature and atmospheric pressure till weight invariance and screened to isolate the fraction of particles with size less than 2 mm, referred as screened soil. The latter one was 99 wt% of the raw soil. Moisture loss was about 10 wt%. For balance purposes, an aliquot was further screened to isolate the fractions of particles with size larger and smaller than 0.63 μm , respectively, referred as sand and silt. The latter one was about 20 wt% of the screened soil. Then, 3 kg of screened soil were placed in an Erweka PRS™ planetary stirrer (holding capacity of 5 dm³) assembled on an Erweka AR403™ apparatus and 900 g of tap water were added (pH of 7.0 measured by Macherey-Nagel pH-Fix 0–14 PT™ strips, electrical conductivity of 422 $\mu\text{S}/\text{cm}$ measured by a Hach sensION+™ instrument equipped with a Hach 50–70™ electrode). The mixture was stirred for 120 min at 90 min⁻¹ obtaining a dense paste with no appreciable pH variation. It is noticeable, that solid-to-liquid ratio was within the range recommended in the literature on attrition scrubbing while rotation speed was lower [17]. These mild conditions were adopted to avoid production of further silt, emulsion and heating due to friction. Afterwards, 600 g of the aforementioned paste was diluted with tap water up to a total volume of 900 cm³. The diluted paste was

stirred for 30 min at room temperature in a Velp Scientifica Rotax 6.8™ rotary stirrer at 5 min⁻¹ and then kept without stirring for further 30 min. Afterwards, it was filtered on a Carlo Erba FPE204250™ buchner filter equipped with a polyethersulphone membrane with porosity of 0.22 μm . Recovered soil was air dried for 8 h at room temperature and atmospheric pressure till weight invariance and underwent to screening to isolate the silt. The latter one was still about 20 wt% of the recovered soil, pointing to unappreciable particle comminution. All screening operations were run by a Retsch AS200™ apparatus equipped with Endecotts stainless-steel screens.

DDX level quantification on solids and liquids was carried out using gas chromatography coupled with mass spectrometry (GC–MS) according to standard methods, respectively, EPA 3545A [18] and EPA 8270D [19] by an external laboratory.

Further physical–chemical characterisation was carried out on solids.

Structural analysis was performed by x-ray powder diffraction (PXRD). A PANalytical Empyrean™ diffractometer equipped with a real-time multiple strip (RTMS) PIXcel 3D™ detector was employed. Data were collected in the angular range from 3° to 70° with 0.03° 2 θ step and 10 s/step accumulation time. The CuK α radiation with wavelength of 1.54178 Å was used. Powdered samples were loaded into a boro-silicate glass capillary which was spun during data collection to minimise preferred orientation phenomena. Qualitative analysis was carried out with a search–match method developed in the PANalytical X'Pert HighScore™ software package.

Microscopic observations were performed using a Reichert Jung Polyvar MET™ microscope in reflection mode. Samples were embedded into epoxy resin and polished with silicon carbide papers. Diamond paste was used for final polishing.

Particle size distribution was evaluated by static light scattering (SLS) using a Coulter Beckman LS 13 320™ analyser equipped with an aqueous liquid module Coulter Beckman ALM™. Solids were suspended in a 1 wt% ethylene glycol aqueous solution (Carlo Erba Reagents RPE™ grade). Data collection was replicated six times in order to smooth the noise due to presence of clay agglomerates.

3 Results and discussion

Whole soil washing treatment was replicated on two different raw soil lots from the same site and average results have been reported in this study.

Silt has been noticed as the most contaminated fraction of screened soil. In fact, DDX level in screened soil has been 5050 mg/kg while in silt has been 11,300 mg/

kg, corresponding to about 45 wt% of raw soil DDX contaminants.

After soil washing treatment, DDX level in silts has increased to 24,950 mg/kg, corresponding to about 99 wt% of raw soil DDX contaminants. In other words, large part of DDX contaminants has been concentrated in a limited fraction of raw soil. Furthermore, DDX level in tap water has been less than $1.0 \mu\text{g}/\text{dm}^3$, according to DDX poor solubility in water.

Structural analysis has pointed to quartz and feldspar (albite) as the main phases of screened soil with kaersutite and clay minerals (muscovite and chamosite) as minor phases (Fig. 1). Virtually identical mineralogical composition has been noticed in recovered soil and silt after soil washing treatment, with the latter one slightly enriched in clays. It agrees with marked affinity among chlorinated pesticides and clay sorbents referred in the literature [20].

Microscopic observations were carried out on screened soil before the attrition and on the two different fractions obtained after the mechanical treatment. Microscopic observations of screened soil before soil washing have shown particles with irregular shape and different sizes, ranging from few up to $100 \mu\text{m}$ (Fig. 2a). After soil washing, particles with larger size have been still present in sand (Fig. 2b) while fines have been removed and concentrated in silt (Fig. 2c). Particles have retained their initial irregular shape with sharp edges and corners, confirming unappreciable comminution. In other words, no further silt has been produced, minimising dangerous wastes to treatment or disposal.

Particle size evaluation basically agrees with these evidences pointing to average particle sizes of about $129 \mu\text{m}$, $43 \mu\text{m}$ and $131 \mu\text{m}$, respectively, on recovered soil, silt and sand.

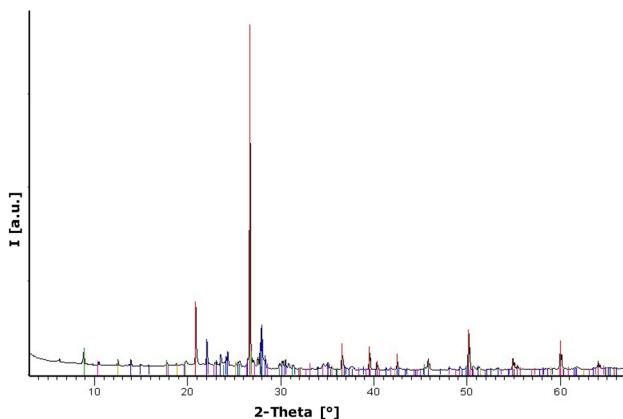


Fig. 1 XRD pattern of screened soil before soil washing. Theoretical peaks of identified phases are subtended: quartz in red, albite in blue, muscovite in green, chamosite in yellow and kaersutite in fuxia

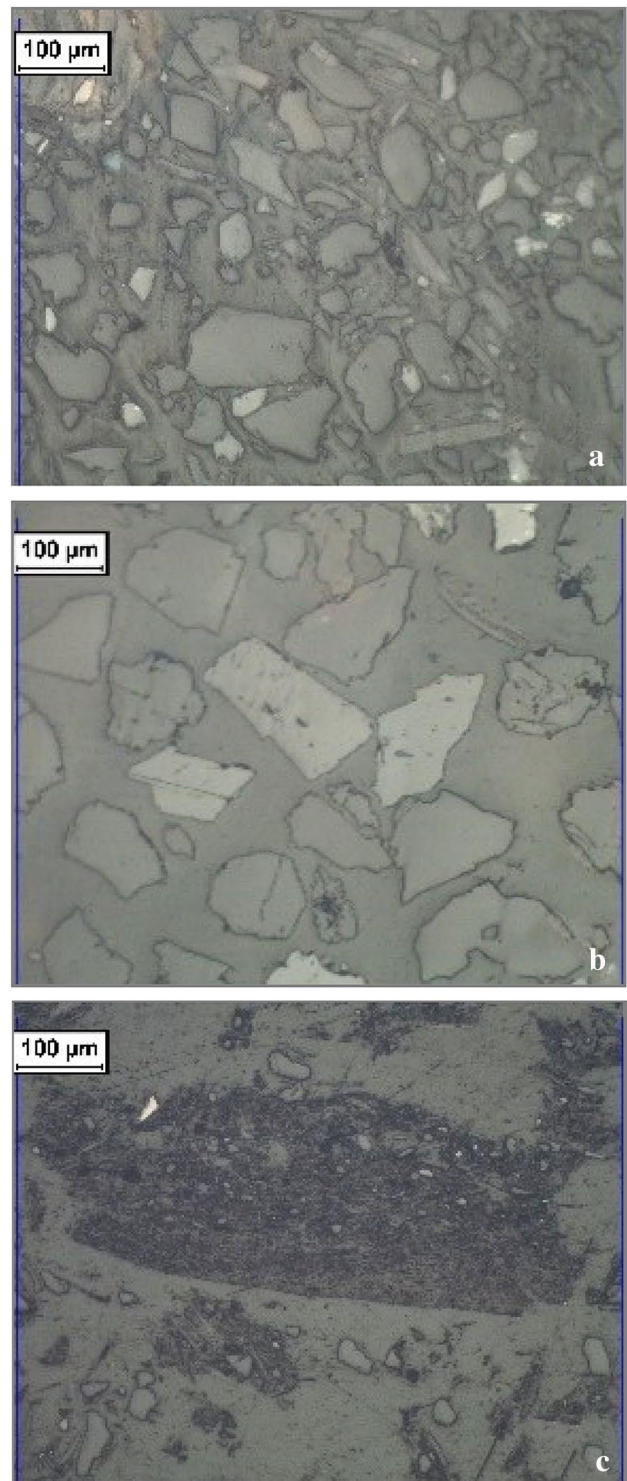


Fig. 2 Microscopic images of **a** screened soil before soil washing; **b** sand from soil recovered after soil washing; **c** silt from soil recovered after soil washing

According to that, DDX contaminant mobilisation and their sorption on clays can be inferred as working microscopic phenomena involved in proposed soil washing treatment.

4 Conclusion

A soil washing treatment with sole water has been set up at laboratory scale, obtaining promising results on a contaminated soil with DDX level of 5050 mg/kg. In particular, about 99 wt% of DDX contaminants has been concentrated in silt, representing only about 20 wt% of raw soil. According to that, it can be considered a possible step to DDX contaminated soil remediation and reuse. Economic benefits can be expected from drastic reduction in amount of DDX contaminated soil sent to disposal or further treatment. Indicatively, the following average Italian market costs can be traced: 0.98 k€ for each transport by truck of DDX contaminated soil (load of about 28 t; distance of 400 km); 0.80 k€/t for DDX contaminated soil incineration. DDX contaminant mobilisation and their sorption on clays present in silt can be inferred as working microscopic phenomena while any further hypothesis has to be considered too speculative at actual level of definition. Further clues could come from a deeper soil physical–chemical characterisation, especially in terms of chemical species potentially acting as co-solvents or surfactants.

Author contributions All authors contributed to the study. Data collection and analysis were performed by Manuela Grande, Sara Perucchini, Michela Bellettato and Erica Montanari. The first draft of the manuscript was written by Marco Tagliabue. All authors contributed to revision and approved the final version.

Compliance with ethical standards

Conflict of interest All authors are employees of Eni S.p.A. Marco Tagliabue is one of the inventors of a relevant patent application [16].

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