Extraction of pentachlorophenol from soils using environmentally benign lactic acid solutions

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ABSTRACT

Soil contamination with pentachlorophenol (PCP) is widespread across the globe. Soil washing/extraction is a common technique to remove this compound. Several soil washing/extraction solutions have been used but a majority of them have the problem of persistence in the environment due to their low biodegradability. Our aim was to investigate mixed solutions of lactic acid and water as potential alternatives to surfactant solutions or organic solvent systems used for the removal of PCP from three soils: montmorillonite, a natural sediment (with organic matter), and the same sediment without organic matter (ignited sediment). This study included the optimization of the concentration of lactic acid in water for maximum extraction efficiency and the determination of linear desorption constants for removal of PCP from the three soils with lactic acid. The effect of soil/sediment organic matter on the extraction efficiency was also studied. Initial experiments showed that 24 h was the optimum extraction time. High extraction efficiencies were obtained for montmorillonite (40–80%) and ignited sediment (~90%). The natural sediment exhibited low PCP extraction due to presence of organic matter, while high desorption coefficient values (~23 L/kg) were obtained for the ignited sediment. For all soils, a decrease in extraction was observed at higher concentrations of lactic acid. The specific surface area of soil/sediment was also found to be an important factor affecting the extraction of PCP.

1. Introduction

Of all techniques available for the remediation of soils, solvent extraction is an efficient process for removing organic contaminants [1–5]. Various groups of organic contaminants like chlorinated phenols, pesticides, herbicides, and polycyclic aromatic hydrocarbons (PAHs) have been reported to be removed by this process. Soil extraction or soil washing can be done *in-situ* or *ex-situ*. The former process involves washing of soil at its source using *in-situ* solvent circulation system while the latter requires excavation of soil from the site.

Several solvents have been used in the past for both laboratory scale experiments and *in-situ* remediation processes. In general soil washing/extraction processes require water miscible solvents, due to the presence of soil moisture where partially miscible or immiscible solvents hinder mixing during the extraction process and hence reduce effectiveness. *In-situ* processes utilize dilute solutions of solvents. As a result, different solvents have been investigated as

mixed solvent systems. Such systems involve varying concentrations of a miscible organic solvent in water. The organic co-solvent added enhances the solubility of the organic contaminants in the aqueous phase exponentially [6]. Ethanol [2,7], and methanol [3] co-solvent mixtures have been investigated for the removal of pentachlorophenol (PCP) and naphthalene, respectively. The presence of water, especially for *in-situ* flow systems, increases the transport of the contaminants.

Cyclodextrins [4,5], rhamnolipids [8], surfactants [9,10], chelating agents like ethylene diamine tetra acetic acid (EDTA) [4], organic acids like citric acid [4], ionic liquids, specifically butyl imidazolium hexafluorophosphate (bmim [PF$_6$]) and butyl imidazolium chloride (bmim [Cl]) [11], and polymeric solvents [12] have also been investigated. However, of all these solvents used so far, several possess environmental concerns. The solvents need to be environmentally friendly and biodegradable if they have to be used for soil washing especially *in-situ* treatment. They should not persist in the soil environment. If there are traces of solvent residue in the soil, they should not be toxic. The focus of our recent work is to investigate novel, environmentally friendly, biodegradable solvents which are easily available and comparatively inexpensive.

PCP is a highly recalcitrant chlorinated organic compound found extensively in soils, sediments and aquatic systems [13]. The main

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sources of PCP contamination include its use as an antiseptic, herbicide and wood preservative agent. PCP has a half life of 45 days in the soil environment [14]. It is very hydrophobic (log K_{ow} = 5.0) and hence tends to persist in soil and sediments. PCP exhibits specific organ toxicity towards liver, kidneys and the central nervous system. Published human and animal toxicity data report PCP half-lives in blood of 15 h in rats, 78 h in monkeys, and 30–50 h in humans [15]. Since PCP biodegrades very slowly, it is required to apply various remediation techniques for its removal. In order to effectively apply these techniques, PCP interaction with soil, mineral and organic matter should be studied. Chiou et al. [16–18] have studied the bonding of PCP with soils and soil organic matter extensively. The main factor affecting the sorption of organic compounds in soil is the soil organic matter [19]. Other factors like pH [20], specific soil surface area [21], particle size, CEC (cation exchange capacity), and soil moisture also influence PCP adsorption on soil. Hence, the extraction of these hydrophobic organic compounds from soils is mainly interactions between soils, solvents and the PCP.

PCP adsorption onto mineral soils like montmorillonite has also been investigated extensively. Various studies [16,22,23] have established that the retention of organic contaminants including chlorophenols is strongly dependent on soil organic matter (SOM). Clay minerals are comparatively less important except when there is no water content [23]. Karichkoff and co-workers [24] established that the bonding of various HOCs with soil minerals was a direct function of the compounds polarity. The sorption was also dependent on the availability of reactive sites on the surface of the mineral clays. These reactive sites are sometimes occupied by mineral oxides. In this case, PCP sorption is dependent on the ions affinity for PCP. This was studied by various researchers [25,26] who investigated this phenomenon by saturating montmorillonite with various cations. PCP sorption onto soil minerals has also been attributed to the swelling potential of the soils [23].

1.1. Background

Lactic acid is an organic, alpha hydroxyl acid produced by fermentation of corn steep liquor. Lactic acid has a low volatility [27] and is completely miscible with water. Driven by the need of overcoming the environmental implications of the aforementioned extraction solvents, and searching for an extracting solvent that could be used both in *in-situ* and *ex-situ* processes, this work explores an alternate soil extraction solvent using solutions of lactic acid. The basic criteria of selection of lactic acid are its biodegradability, non toxicity and environmental benignity. It completely biodegrades in less than 5 days making it a good material for manufacture of biodegradable polymers. [27]. It is almost non-toxic in the aquatic environment producing no effects in goldfish exposed to as high as 430 ppm for >100 h [28]. U.S. EPA has classified both lactic acid and its ethyl and butyl esters as Class 4A inert compounds. Such a classification is given only to chemicals that have no toxicity and other environmental concerns [29]. Lactate esters have been found to be good cleaning agents for the removal of oils, greases and paints as well as having excellent solvation properties for pesticides and fertilizers [30]. The presence of lactic acid in soil has been found to affect and enhance biodegradation of highly toxic compounds like toxaphene [31]. After the immobilization of PCP in the lactic acid phase, combined biological treatment can be carried out with lactic acid as a primary substrate. Lactic acid has been previously tested for the removal of phenanthrene as well as heavy metals from soil [4]. The basic criteria of selection of lactic acid are its non toxicity and environmental "greenness". Hence, here we explore the solvent extraction properties of lactic acid from an environmentally benign standpoint.

Table 1
Properties of soils and sediments.

Characteristic	Method used for determination[*]	Value	
		CC	MT
Inorganic: sand (%)	ASTM D422	49.2	19
Silt (%)	ASTM D422	34.1	50
Clay (%)	ASTM D422	16.7	31
Organic matter (%)	ASTM D2974	3.4	nil
pH	ASTM D4972	7.4	3.9

[*] http://www.astm.org/Standards/D4972.htm.

The resemblance of its structure to that of the components of soil organic matter has lead to studies on its effects on PCP adsorption/desorption in soil [32]. Tam et al. [32] investigated adsorption of PCP in various soils in the presence of indigenous organic matter as well as addition of lactic acid and reported the enhancement of PCP adsorption in the presence of organic compounds. There is no prior published literature about interaction of lactic acid in co-solvent systems with water. Such studies are beyond the scope of this paper whose main objective is to investigate the effectiveness of lactic acid co-solvent systems for extraction of PCP from soils. An attempt has been made here to explain effects of soil organic matter on extraction.

2. Materials and methods

2.1. Soils

Montmorillonite (MT) (Fisher Scientific) is commercially available clay with high surface area. The characteristics of these soils are presented in Table 1. These analyses were conducted by HC Nutting Company using the methods outlined by American Society for Testing and Materials (ASTM) standards. CC soil was ignited to remove soil organic matter. Following the procedure suggested by Tam et al. [32] a known weight of soil was ignited in a furnace at 700 °C. Then the soil was left to cool in the hood. After this, the PCP was spiked into the soil (see Section 2.3). The weight of soil used in extraction was twice that of the other soils. This soil is referred to as ignited soil (IGN) in throughout this paper.

2.2. Extractants

Lactic acid (Aldrich Chemicals – 95% purity) in different concentrations was tested as a mixed solvent extractant system. Acetone, dichloromethane and methanol were obtained from Aldrich and their purity was HPLC grade or greater.

2.3. Spiking procedure

Concentrated stock solutions of PCP were prepared in acetone. A certain amount of the PCP solution was added to water–soil mixtures. Spiking was carried out in 125 mL glass vials with Teflon caps. The vial was filled up to the top to minimize headspace loss. The vial was tumbled for 3 weeks at room temperature. Then it was air-dried in the dark in a fume hood for 3–5 days. The final moisture content was maintained at 6% for MT and 8% for CC and IGN. The initial loading was 100 mg/kg PCP for all soils. In order to study the effect of soil organic matter on a higher PCP concentration, a batch of soil with 600 mg/kg concentration was also spiked. This concentration was chosen because heavily contaminated soils have been found to have a concentration 600 mg/kg [33]. Control experiments were performed at each step to quantify for loss due to evaporation and adsorption onto glassware.

2.4. Soil extraction

All batch shaking experiments were conducted in polyethylene (PE) centrifuge tubes. Soil and solvent were added to the tubes at soil: solvent extraction ratios of 1:5, 1:10 and 1:20 (g:mL). 10, 20 and 50 mL size tubes were used for the extraction experiments based on the soil:solvent ratios. The samples were vortexed on a lab mixer (vortexer) until they were well mixed. Then they were placed inside a rotating tumbler and tumbled for 24 h at 20 rpm at room temperature. After shaking, the two phases were separated by centrifuging at 5000 rpm for 30 min. The liquid extract was filtered through 0.45 μm filter. The liquid extract was analyzed for PCP using high performance liquid chromatography. Most experiments were performed in triplicates except a few of those involving the Caeser's Creek sediment and ignited soil owing to restricted quantity of soil available. The tube was weighed before and after extraction and the weight of the soils was recorded before and after extraction for mass balance calculations. The volume of solvent was also measured for extraction calculations.

2.5. Analysis of PCP

Quantitative analysis of PCP in lactic acid was conducted using a high performance liquid chromatography (HPLC) (Agilent 1100 series). A reverse phase amide column (RP-16 Discovery Supelco) and a UV–vis diode array detector were used for HPLC analysis. A mixture of (0.01N sulfuric acid) and acetonitrile in the ratio 30:70 at a flow rate of 1.5 mL/min was used as the mobile phase. The detection wavelength used was 254 nm.

2.6. BET surface area of the soils

The BET surface area of the three soils was measured by Tristar 3000 (Micromeritics Corp, GA), using nitrogen adsorption/desorption studies.

2.7. Soxhlet extraction

In order to determine the initial PCP concentration in the soil, a soil sample weighing 2 g was placed into a cellulose extraction thimble (Whatman). The Soxhlet apparatus consisted of a 250 mL round bottomed flask, a Soxhlet extraction tube, and a bulb type Allihn condenser. The PCP was extracted with a 100 mL of methanol for a period of 24 h, according to USEPA method 3540C [34]. After the extraction cycle was completed, the solvent remaining in the flask and tube was measured. The samples were concentrated to 2 mL using a rotary evaporator before analysis by HPLC.

2.8. Sonication

Sonication has been used as a standard procedure for extraction of soils. This procedure was used to determine the initial concentration of PCP in soil, and the results were compared with the Soxhlet procedure. About 2 g of the soil sample was sonicated with 30 ml of methanol for 30 min. The sample was placed in a water bath to dissipate the heat produced by the sonicator tip and minimize loss of solvent by evaporation. The power was adjusted at 60 Hz. As in the other extractions, the sample after extraction was measured and weighed. Table 2 gives the initial concentrations obtained from these methods.

3. Results

3.1. Extraction from montmorillonite (MT)

The results for extraction of PCP from montmorillonite using different concentrations of lactic acid at various soil:solvent ratios

Table 2
Initial concentrations of PCP in the soils.

Sample	PCP concentration (mg/kg)
MT	100
CC	137
	602
IGN	95

MT: montmorillonite. CC: Caeser's creek sediment. IGN: ignited soil.
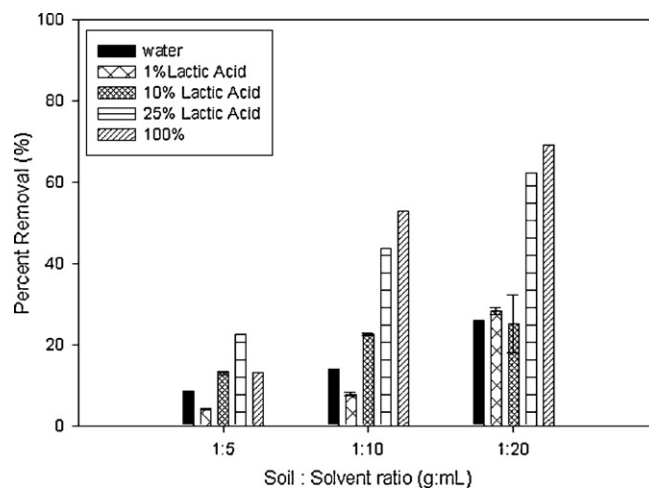

Fig. 1. Extraction of PCP from montmorillonite (MT) (100 mg/kg spike).

are shown in Fig. 1. The results from Fig. 1 show that at the soil:solvent ratios of 1:10 and 1:20, the 100% lactic acid produced higher recoveries than the other concentrations evaluated. Lowest PCP recoveries were obtained with water and 1% lactic acid. The 10% and 25% lactic acid solutions produced intermediate extraction efficiencies between those obtained with 1% and 100%. The PCP extraction efficiencies of the 25% and the 100% were comparable at higher soil:solvent ratios. Greater efficiencies at higher solvent content (i.e., the higher soil:solvent ratios) indicate increased solvent effectiveness. Since MT has no organic matter, the extraction can be attributed most exclusively to surface interactions.

3.2. Extraction from CC sediment

The comparison of extraction of PCP from this type of soil is shown in Fig. 2. The 1% lactic acid was as effective as the higher
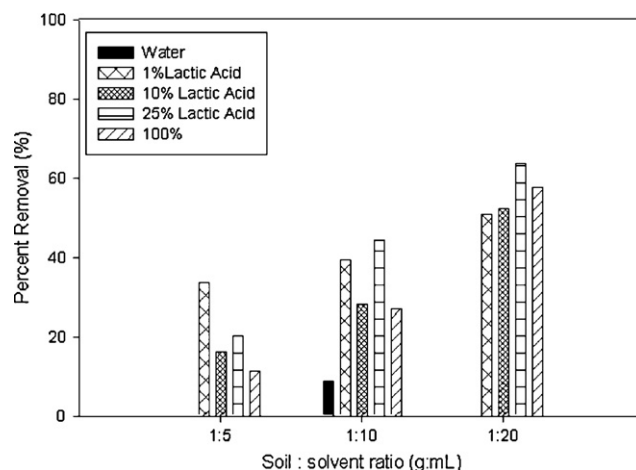

Fig. 2. Extraction of PCP from Caesar's Creek sediment (CC) (137 mg/kg).
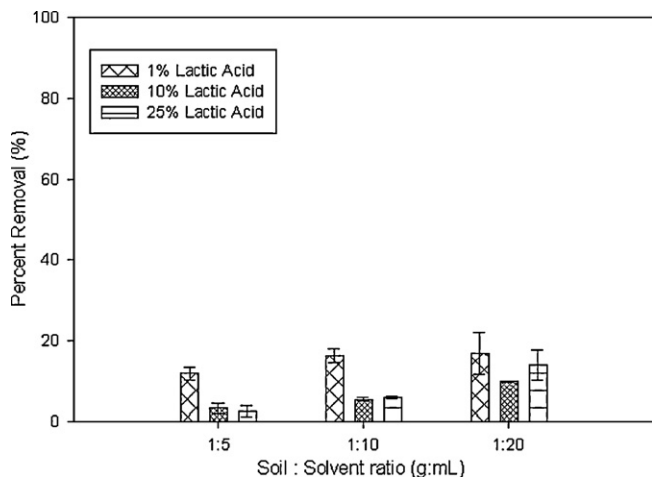
Fig. 3. Extraction of PCP from CC (601 mg/kg spike).

concentrations at higher solvent content. At a ratio of 1:5 (g:mL), the extraction efficiency at 1% lactic acid concentration was considerably higher than those of the other concentrations. At this soil:solvent ratio, the lowest extraction efficiency was obtained for the 100% lactic acid solution. The highest extraction efficiency was observed in the case of the 1:20 soil:solvent ratio and 25% lactic acid solution.

The extraction efficiency to extract PCP from the CC soil with a greater level of PCP contamination (600 mg/kg) in the CC soil (with 1%, 10% and 25% lactic acid concentrations) was also investigated. The results are shown in Fig. 3. The extraction efficiencies were not comparable with the 100 mg/kg spike of the same soil. As presented in the results, the extraction efficiencies were the lowest of all the soils studied.

3.3. Extraction from ignited CC sediment

In order to study the effect of soil organic matter alone, the CC sediment was burnt off to remove organic matter. The extraction data of this type of soil are represented in Fig. 4. The process of soil organic matter removal by ignition is a common procedure that has been reported by Tam et al. [32] and has been discussed under Section 2.1. The extraction efficiencies of 1% and 25% lactic acid are comparable at a soil:solvent ratio of 1:20 g:mL. Extraction with water also exhibits efficiencies of about 40–80%.
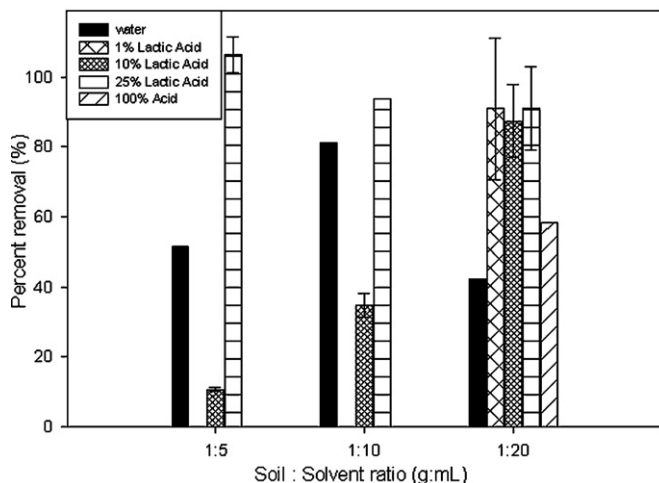

Fig. 4. Extraction of PCP from ignited soil (IGN).

Table 3
Values of the desorption coefficient (K_D).

Solvent (lactic acid fraction)	K_D (L/kg)		
	MT	CC	IGN
Water (0%)	8.40	4.25	5.00
1%	0.06	11.71	8.00
10%	5.87	7.43	22.28
25%	19.21	13.19	13.57
100%	0.35	3.58	3.77

MT: montmorillonite. CC: Caesar's creek sediment. IGN: ignited soil.

3.4. Linear desorption coefficients

Batch extraction data of the three soils at the different soil:solvent ratios of 1:5, 1:10 and 1:20 (g:mL) with lactic acid solutions were used for these calculations. Distribution coefficients for desorption of PCP was calculated using the following equations [20,35]:

$$q_e = K_D C_e + I \tag{1}$$

where q_e is the PCP remaining in soil after extraction (mg/kg), K_D is the distribution coefficient (L/kg), I is the inextractable PCP remaining in the soil and the y is the intercept of the plot of q_e versus C_e, which is the aqueous concentration of PCP in the solvent (mg/L). The K_D is determined from the slope of the plot of q_e versus C_e. The value of q_e can be determined by mass balance calculation:

$$q_e = q_0 - C_e \left(\frac{V}{M} \right) \tag{2}$$

where q_0 is the initial concentration of PCP in the soil, obtained from Soxhlet or sonication. V (L) and M (kg) are the volume of liquid extract and mass of the extracted soil, respectively. The K_D values obtained by this method are shown in Table 3.

The extraction at the 1% lactic acid for the CC sediment was close to that of the 25% lactic acid concentration. The inextractible fraction I was also calculated using Eq. (1). The values of I were the largest for the montmorillonite extracted with a 1% lactic acid and was found to be 93 mg/kg. Proportionally high values were also obtained for the 600 mg/kg spike (504–551 mg/kg). The ignited soil exhibited the least amount of the inextractible PCP, ranging from 56 to 76 mg/kg.

3.5. Solution pH

The pH of the lactic acid mixed solvent was measured before and after the extractions for the 1:5, 1:10 and 1:20 soil:solvent ratios. The pH of the different concentrations of the clean lactic acid ranged from 1.13 to 2.8 for the 100% to a 1% lactic acid concentration, respectively. The solution pH data after extraction show that an increase affected by contact with soil. The solution pH for all the soils after extraction was found to be in the range of 4.27–4.34 for the three soils at the different soil:solvent ratios.

4. Discussion

4.1. Desorption coefficients

The linear desorption coefficients indicate an increase in extraction of PCP from both montmorillonite and the ignited CC sediment with increasing the lactic acid concentration up to 25% followed by a decrease in PCP extraction from both soils for the 100% lactic acid. In the case of the CC sediment, the highest extraction also occurred for the 25% lactic acid solution, but there was a decrease in extraction for the 10% lactic acid solution. All three soils showed a decrease in extraction with 100% lactic acid, with the largest decrease occurring for montmorillonite.

For montmorillonite, there was an increase in extraction of PCP with increasing lactic acid from 0% to 25% in the mixed solvent. This soil had no organic matter. As shown in Table 3, the K_D was largest for the 25% lactic acid solution (19.2 L/kg), considerably higher than the K_D for the CC sediment at the same concentration of lactic acid indicating higher extraction of PCP from montmorillonite than from the CC sediment. The highest extraction occurred with the 10% lactic acid solution for the ignited CC sediment (22.28 L/kg). Lower extraction of PCP from the CC sediment could be attributed to the presence of organic matter in the CC sediment. For montmorillonite and ignited CC sediment, which had no or negligible organic matter, the difference in the BET specific surface area is more than one magnitude. The desorption coefficients indicate a significant increase in the extraction of PCP from the ignited CC sediment, showing that the difference in soil surface area played an important role in extraction even in the absence of soil organic matter. Khodadoust et al. [7] studied the extraction of PCP from montmorillonite, Ottawa sand and Edison soil using mixed solvents of ethanol–water, and found that the extraction of PCP from Ottawa sand and montmorillonite was not dependant on the soil specific surface area in the absence of organic matter. However, the main reason for this observation in our study could be the physical changes in the CC sediment due to ignition.

4.2. pH effect

In the partitioning of PCP onto soils, pH of the soil–solvent systems plays an important role. The sorption of the ionic form of PCP on soils is mainly due to hydrophobic interactions but pH effects could cause electrostatic forces to dominate [36]. Solution pH effects have been determined in various systems of mixed solvents [20,35]. In systems of ethanol–water and methanol–water, it was assumed that the pK_a values of PCP increased with increasing fraction of alcohols in the mixtures. In our case, the solution pH of the lactic acid decreased from 2.5 at 1% lactic acid to 1.13 at 100% lactic acid solution. Lower pH values result in lower dissociation of PCP at the higher lactic acid concentrations (with lower solution pH). The pH of the lactic acid–water mixed solvents after extraction with ignited soil, montmorillonite and Caesar's Creek sediment was 4.27, 4.34 and 4.43, respectively. This indicates that the majority of the extracted PCP from all three soils was in the neutral form. In a previous study that investigated the effect of amendments like oil and surfactants on PCP adsorption, Fall et al. [37] found that a 0.2-unit decrease in pH had the same effect on the desorption coefficient K_D as increasing the soil organic content by 1% for the pH range of 3–7.

4.3. Irreversible sorption

The value of I in the linear desorption isotherm equation refers to the irreversibly adsorbed PCP. Irreversible adsorption/desorption is a phenomenon that has been observed in organic compound adsorption onto soils [19]. It is that fraction of the organic compound that is irreversibly adsorbed and cannot be removed by these extraction methods. It has been attributed to various factors namely, pore defects, entrapment into the soil organic matter, and other factors. Desorption hysteresis has also been linked to intercalation of the HOCs in soils, especially in the case of mineral soils like montmorillonite. Where only physical sorption processes and surface ion exchange govern PCP adsorption, in homoionic clays like K-montmorillonite, intercalation has been attributed to the fact that the basal spacing of the clays was just optimum to facilitate adsorption and prevent its interaction with any water or solvents [38,39]. The highest I value for MT in our study ranged was 93 mg/kg. In the absence of soil organic matter, this irreversibly adsorbed PCP could be attributed to intercalation and associ-

ated mechanisms. Further characterization procedures would be required to confirm this phenomenon which is beyond the scope of this paper. In their studies of PCP adsorption using ten soils, He et al. [40] observed higher desorption hysteresis when the difference between the solute concentration in the solid and aqueous phase was significantly greater. This has also been observed in our study, in the case of the Caesar's Creek sediment spiked with 600 mg/kg where the values of I range between 504 and 551 mg/kg. Another study, Banerji et al., [19] found a higher I value with soils spiked with 500 mg/kg of PCP using successive extractions of water and propanol. Irreversible sorption, among other factors, depends heavily on the soil type. The value of I is the smallest for the ignited soil (56 mg/kg for extraction by 10% lactic acid) and the largest in the case of extraction with Caesar's Creek (72–87 mg/kg), thus attributing the inextractible PCP to the presence of soil organic matter.

In the sorption of HOCs onto SOM, He et al. [23] reported sorption hysteresis after removing SOM using H_2O_2 treatments. Their results indicated that the hysteresis effects decreased after treatment of H_2O_2 indicating that SOM was related to the sorption/desorption capacities. These results are in accordance with a study by Lee et al. [20] who reported that irrespective of pH and other associated mechanisms, sorption increased with increasing soil organic carbon content, except in case of montmorillonite or kaolinite where sorption is due to functional groups. In fact, such clays have been suggested as natural matrix systems to capture and sequester PCP and other HOCs in the environment.

4.4. Soil surface area

One of the factors affecting PCP sorption in soils is the specific soil surface area. BET analysis determined a specific surface area of 6.3 m^2/g for the ignited soil as compared to 3.34 m^2/g for Caeser's Creek. The BET surface area for montmorillonite was measured to be 25 m^2/g. The burning of the Caesar's Creek sediment caused some pore size transformations that resulted in an increase in the specific surface area. Ignition of soil also causes various other surface changes like aggregation of clay into sand, increase in pH at higher temperatures, and decreasing CEC and organic content with higher temperatures. These effects were observed by Giovanni and Lucchesi [41] who studied burning of soils at various temperatures to study the changes in physiochemical properties of the soils. For soils with no organic matter, the extraction data indicate greater desorption of PCP from ignited soil than from montmorillonite, where the specific surface area of ignited soil was smaller than that of montmorillonite. The lowest PCP extraction occurred for Caesar's Creek sediment which contained organic matter, indicating that PCP desorption from Caesar's Creek sediment was due to the solvent interaction with the soil organic matter. In the case of the ignited soil where PCP extraction was greatest, the specific soil surface area was between that of montmorillonite and Caesar's Creek sediment, showing that in the absence of organic matter, higher PCP extraction may be attributed to the lower soil surface area. This observation is in agreement with Khodadoust et al. [7] in the extraction of PCP from montmorillonite, Ottawa sand and Edison soil using mixed solvents of ethanol–water, they found that the extraction of PCP from Ottawa sand and montmorillonite was not dependant on the soil specific surface area in the absence of organic matter.

4.5. Soil–solute–solvent interactions

The extraction of PCP increased with an increase in the lactic acid concentration in the mixed solvent. In all three soils studied, there was a decrease in the extraction with 100% lactic acid. These findings are similar to those reported by Khodadoust et al. [2] who investigated removal of PCP from various soils using water–ethanol

co-solvents. The decrease was very sharp for montmorillonite. This shows that desorption was not due to the solubility of PCP in the solvent. For montmorillonite, the desorption was due to soil–solvent interactions. The soil property data show that the surface area of montmorillonite is one magnitude higher than that of ignited soil but desorption from this soil is higher. In the case of the ignited soil, water yields an extraction efficiency of 40–80% indicating that the extraction is mainly a soil–solvent interaction.

In the previous study conducted by Khodadoust et al. [2] investigating extraction of PCP using water–ethanol mixtures, they reported leaner solutions of ethanol being as effective as or more effective than stronger ethanol solutions. It was also observed that in higher soil:solvent ratios, water and 100% ethanol were very effective. In our study, at higher solvent content, water and 100% lactic acid exhibited increased extraction efficiency. When the liquid phase is dominant, as in case of the higher solvent content, the solvent capacity may contribute entirely to the extraction efficiencies. In the absence of prior published literature about interaction of lactic acid in soil–water systems, based on the above results, lactic acid co-solvent systems behave similar to water–ethanol co-solvent systems in the extraction of PCP from soils.

Lower extraction of PCP from Caesar's Creek sediment with higher lactic acid concentrations in the lower solvent content was due to the effect of the organic acid on soil organic matter, which is purely a soil–solvent interaction. In this case, even the highest solvent content, 100% lactic acid was not the most effective contrary to the observations with the other soils without organic content. 25% lactic acid seems to be most effective in this case, leading to progressively higher extraction over the various soil:solvent ratios.

The natural organic matter present in soil has been compared to a semi-polymeric material that exists as glassy and rubbery states [42]. Desorption of organic compounds from such soils involves washing them out of the pores present in the rubbery state. The soil–solvent interaction is greatly affected by the ability of the solvent to extract from the NOM (natural organic matter)/SOM (soil organic matter). The desorption of PCP from soil is thus affected by factors including the type of its bonding with soil. Tam et al. [32] reported that the possible mechanism of PCP adsorption in soils in the presence of organic matter is by electrostatic interactions between the soil surface and organic acids. PCP has also been found to form intermolecular hydrogen bonds with COOH groups found in the soil organic matter [43]. The addition of lactic acid to a soil with organic matter may have increased the number of COOH groups for PCP bonding, hence decreasing desorption.

5. Conclusions

Lactic acid used in mixed solvent systems of lactic acid–water was effective for the extraction of PCP from montmorillonite and natural sediment. The extraction increased with increasing concentration of lactic acid in the mixed solvent up to 25% lactic acid and then decreased for higher lactic acid concentrations up to 100% lactic acid. The decrease in extraction with the more concentrated lactic solutions was observed in the Caesar's Creek sediment and was attributed to the presence of organic matter. In this case, maximum efficiencies were observed with 1% lactic acid. PCP extraction from the CC sediment increased with an increase in specific soil surface area and the removal of organic matter after ignition. In the absence of organic matter (montmorillonite and ignited CC sediment), the extraction of PCP was greater from the soil with the lower specific surface area (ignited CC sediment).

The designation of "green solvents" has been recently applied to ionic liquids that were "green" only due to lack of vapor pres-

sure and hence air pollution problems. Lactic acid can be thought to be a "green" solvent from a broader environmental standpoint – non volatility, environmental benignity and non-toxic nature. Produced from biological materials, lactic acid can be manufactured in completely "green" processes with no harmful by products. This study assessed the effectiveness of lactic acid in a laboratory scale soil washing process. Further site specific and more mechanistic studies are required before field application can be implemented. However, this work can be thought of as the first step towards the development of a soil washing process using lactic acid.

Acknowledgements

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