



## Subcritical water extraction for the remediation of phthalate ester-contaminated soil

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### ARTICLE INFO

#### Article history:

Received 17 November 2010  
Received in revised form 10 June 2011  
Accepted 13 June 2011  
Available online 5 July 2011

#### Keywords:

Phthalate ester  
Subcritical water  
Soil remediation  
Accelerated solvent extraction  
HPLC–UV

### ABSTRACT

Subcritical water has been used as an environment-friendly extraction fluid for many classes of organic compounds. It was used for the removal of phthalate esters (PEs), such as di-methyl phthalate, DMP; di-ethyl phthalate, DEP; di-iso-propyl phthalate, DIPP; di-n-butyl phthalate, DBP; benzyl butyl phthalate, BBP; di-n-pentyl phthalate, DpentP; di-n-hexyl phthalate, DHXP; di-heptyl phthalate, DheptP; di-2-ethylhexyl phthalate, DEHP; di-n-nonyl phthalate, DNP; di-n-octyl phthalate, DOP; di-n-decyl phthalate, DDP, in soil samples under the optimum condition of 250 °C and 10 MPa in our study. The soil samples cleaned with subcritical water were extracted by homemade accelerated solvent extraction system (ASE) and analyzed by HPLC–UV to check for soil remediation efficiency. Three types of soil collected at different sites in Taiwan have been tested. Although at higher PEs concentration levels, the modification of treatments may be necessary for satisfactory removal of the contaminants, soil samples of different PEs levels treated with subcritical water extraction (SCWE) were analyzed and the results indicated removal efficiency ranges of 80–90% for PEs spiked in soil samples. Soil samples contaminated with native DEHP were treated and gave comparable recovery efficiencies. Our results indicate that the applications of subcritical water as soil remediation for removal of PEs contaminant are feasible.

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### 1. Introduction

Phthalate esters (PEs), a popular group of plasticizers, have already been categorized as environmental hormones by Environment Agency Government of Japan and Environmental Protection Agency of United States (US EPA). Because they can be easily transferred into our environment and cause different harmful effects [1], people have begun to pay attention to these pollutants. In Taiwan, approximate 700 thousand tons per year of PEs, such as DEHP, were produced for industrial uses. Some literatures also indicated the exposure to PEs has already affected the health of many newborns in Taiwan [2]. Recently, varieties of food contamination cases were reported by different media in Taiwan due to the addition of cloudy agents and emulsifiers in food processing, and they were heavily contaminated with PEs, such as DEHP, DOP and DBP. Some of the food products were even exported to many countries, and this severe case was reported to World Health Organization, WHO, by Taiwanese government, indicating that pollution and intensive use of PEs is endangering food safety in human societies. Therefore, cleaning and remediation of land areas heavily contaminated with PEs and other contaminants are important environmental issues. Various techniques for the degradation or reduction of PEs

in environmental samples have been reported, most of them were investigations using methods of biodegradation [3–9].

Water is a polar solvent; it has a critical point of 374 °C and 22 MPa. The high temperature and pressure may keep it in subcritical or supercritical liquid state in a wide range of conditions. Its widely tunable dielectric constant decreases significantly by raising water temperature. The dielectric constant of water at 25 °C is approximately 80, but it reduces to approximately 27 by increasing the temperature of water to 250 °C [10]. With the variation of temperature and pressure, one can control the solvent characteristics of water to a great extent. Under subcritical conditions, it can be a strong solvent for many kinds of organic compound, but not much of harmful effects when cooling down.

Recent studies have demonstrated that raising the temperature of water allows one to quantitatively extract a wide variety of organic solutes from many different matrices. Examples include the extraction of polycyclic aromatic hydrocarbons (PAHs) or polychlorinated biphenyls (PCBs) from contaminated soils, sludge or sediments [11–14]. For the analyses of subcritical water extracts of organic compounds, most studies used solid-phase trapping or microextraction for pretreatment followed by HPLC determination. In our study, eco-friendly subcritical water extraction was used as the remediation tool to reduce PEs contents in soil. A homemade accelerated solvent extraction (ASE) and HPLC–UV system were utilized for the quantification of residual PEs in both water and soil sample extracts. We therefore recommend a useful combination of

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tools to access the efficiency of soil remediation using subcritical water extraction.

## 2. Experimental

### 2.1. Chemicals and reagents

All solvents used were HPLC grade and purchased from Tedia (Tedia Company, Inc., Fairfield, OH, USA). The PE standards (dimethyl phthalate, DMP; di-ethyl phthalate, DEP; di-iso-propyl phthalate, DIPPP; di-n-butyl phthalate, DBP; benzyl butyl phthalate, BBP; di-n-pentyl phthalate, DpentP; di-n-hexyl phthalate, DHXP; di-heptyl phthalate, DheptP; di-2-ethylhexyl phthalate, DEHP; di-n-nonyl phthalate, DNP; di-n-octyl phthalate, DOP; di-n-decyl phthalate, DDP) were products of Polyscience Inc., USA, and the purities of standards were near 100%. 2-Methyanthracene (purchased from ChemService Inc., USA), near 100% purity, was selected as the internal standard which showed as an easily recognizable peak in the chromatogram. The PE stock standards, 1000  $\mu\text{g}/\text{mL}$ , were prepared using acetonitrile as solvent. The calibration working standards range from 1.0 to 100  $\mu\text{g}/\text{mL}$  were prepared daily by dilution from stocks.

### 2.2. Soil samples

Standard soil stocks, for the preparation of standard soil samples were supplied by Environmental Resource Associated, USA. Based on supplier's information the semi volatile blank soil used in this study was examined by methods such as SW846, 8270 °C and 8310 to be contamination free. However, other chemical and physical properties of soil were not supplied due to possible differences among batches. Standard soil samples were then prepared by spiking the PE standard solutions into blank soil (purchased from Environmental Resource Associated, USA) using a slurry process as follows: 5 g of the blank soil were mixed with different concentrations of PE and internal standard (5 mL of 6  $\mu\text{g}/\text{mL}$ ) solutions followed by a mixing process using a Heidolph rotary evaporator for over 48 h under atmospheric pressure to ensure homogeneity, and the solvent was allowed to evaporate at room temperature until dried. The dried soils were stored in tightly closed brown glass bottles at room temperature until required. Several different kinds of real soil samples were sampled from known sites in Taiwan and transported to the laboratory where they were air-dried for 24 h

prior to sieving through a 2 mm mesh at room temperature. The soil samples were then stored in brown air-tight containers until used. If needed, the real soil samples may be spiked with PEs working standards with the same procedure as the preparation of standard soil samples.

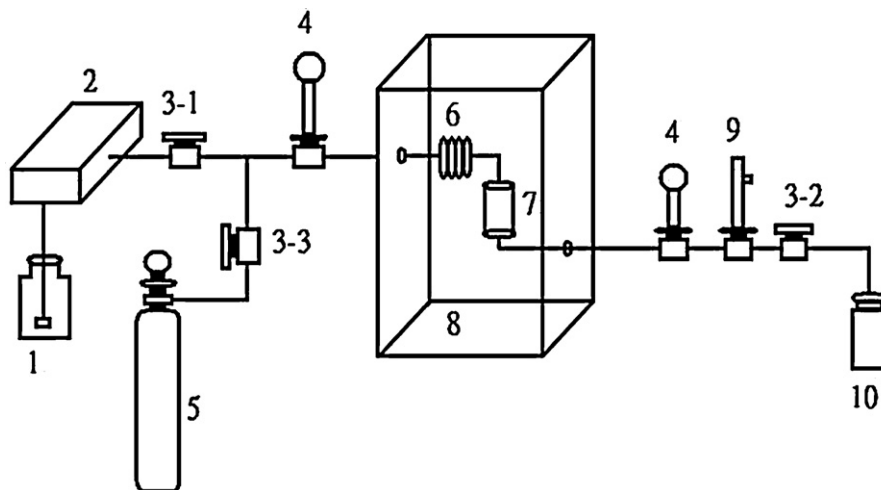
### 2.3. Apparatus for subcritical water extraction

The homemade SCWE and ASE system is depicted in Fig. 1 [15]. A Jasco PU-980 pump (Jasco, Japan) was used to pump the reagent water or acetonitrile into 3 mL stainless steel sample extraction cell (Suprex, Pittsburgh, PA, USA). The cell, located in an oven (used in Shimadzu GC-14A), is connected to a nitrogen cylinder operated to purge the sample and residual solvent at recovery stage.

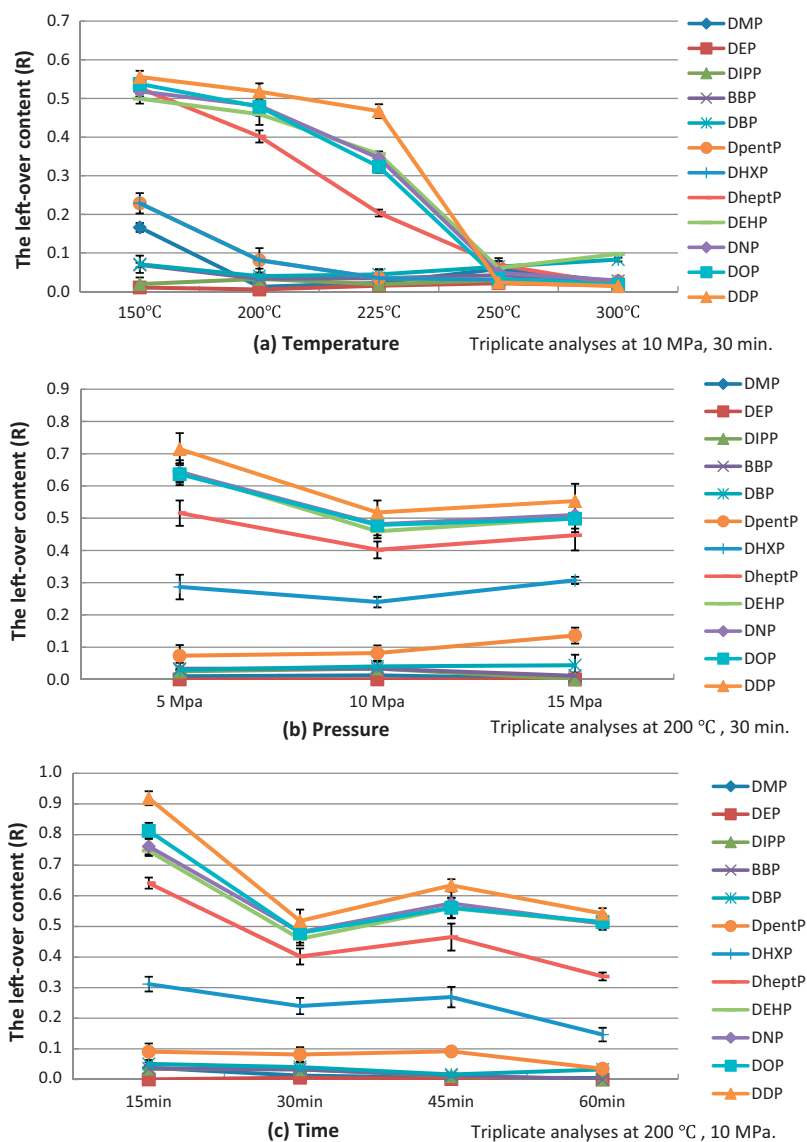
### 2.4. Procedures

The SCWE remediation process of PE-contaminated soil consisted of seven steps: (a) filling up the cell containing 1.0 g soil sample with reagent water until the cell was full, (b) pressuring the extraction cell to the desired pressure, (c) preheating the cell at selected temperature followed by equilibration at preset pressure for 10 min, (d) static extraction at selected pressure and temperature for a selected period of time, (e) after static extraction, the cell was allowed to cool off to room temperature, (f) then both valves 3-1 and 3-2 were opened and solvent pump was turned on to flush the cell for the collection of PEs, (g) finally nitrogen from cylinder was introduced to remove all the residual solvent from the system. To be free of cross contamination, the ASE system should be cleaned at experimental temperature and pressure for at least 5 min using the extraction fluid and blank tests should be carried out followed by confirmation with HPLC/UV. One should be aware of the danger of water in subcritical state which is slightly corrosive. Based on our experience, it is advisable to reach the desired temperature before increasing the pressure to the needed level for easier, safer and faster maneuver.

Ten milliliters of aqueous effluent from SCWE was re-extracted with solid phase extraction (SPE) membrane ( $\text{C}_{18}$ -SPE, 47 mm diameter, 3 M), and eluted with the optimum condition of 8 mL (4 mL  $\times$  2 mL) dichloromethane for the collection of PEs. Then the eluate was blown with nitrogen to dryness, and 1 mL acetonitrile was added for quantification. The recoveries of PEs using aforementioned method ranged from 68% (DMP) to 78% (DIPPP).



**Fig. 1.** Apparatus of ASE or SCWE: (1) solvent reservoir, (2) pump, (3) two-way valve, (4) pressure gauge, (5)  $\text{N}_2$  cylinder, (6) preheated coil, (7) extraction cell, (8) oven, (9) pressure relief valve, (10) collection vial.



**Fig. 2.** Effects of SCWE by changing (a) temperature, (b) pressure and (c) static extraction time. The left-over content ( $R$ ) =  $(A_{SCWE}/A_{IS})/(A/A_{IS})$ , where  $A_{SCWE}$  is the area of PE after SCWE analysis by ASE/HPLC/UV;  $A$  is the area of PE analysis by ASE/HPLC/UV;  $A_{IS}$  is the area of I.S. analysis by ASE/HPLC/UV; DMP, di-methyl phthalate; DEP, di-ethyl phthalate; DIPP, di-iso-propyl phthalate; DBP, di-n-butyl phthalate; BBP, benzyl butyl phthalate; DpentP, di-n-pentyl phthalate; DHXP, di-n-hexyl phthalate; DheptP, di-heptyl phthalate; DEHP, di-2-ethylhexyl phthalate; DNP, di-n-nonyl phthalate; DOP, di-n-octyl phthalate; DDP, di-n-decyl phthalate.

Five levels of extraction temperature (60, 80, 100, 120 and 140 °C), five levels of extraction pressure (3.5, 7.0, 10.5, 14.0 and 17.5 MPa) as well as five levels of extraction time (2, 5, 10, 15 and 20 min) were tested to optimize the ASE system and the performance was evaluated using HPLC/UV. The SCWE-treated soil was extracted again with ASE using the optimum conditions as followed: acetonitrile as extraction solvent, 120 °C static extraction temperature, 10.5 MPa pressure, 5 min extraction time. The elu-

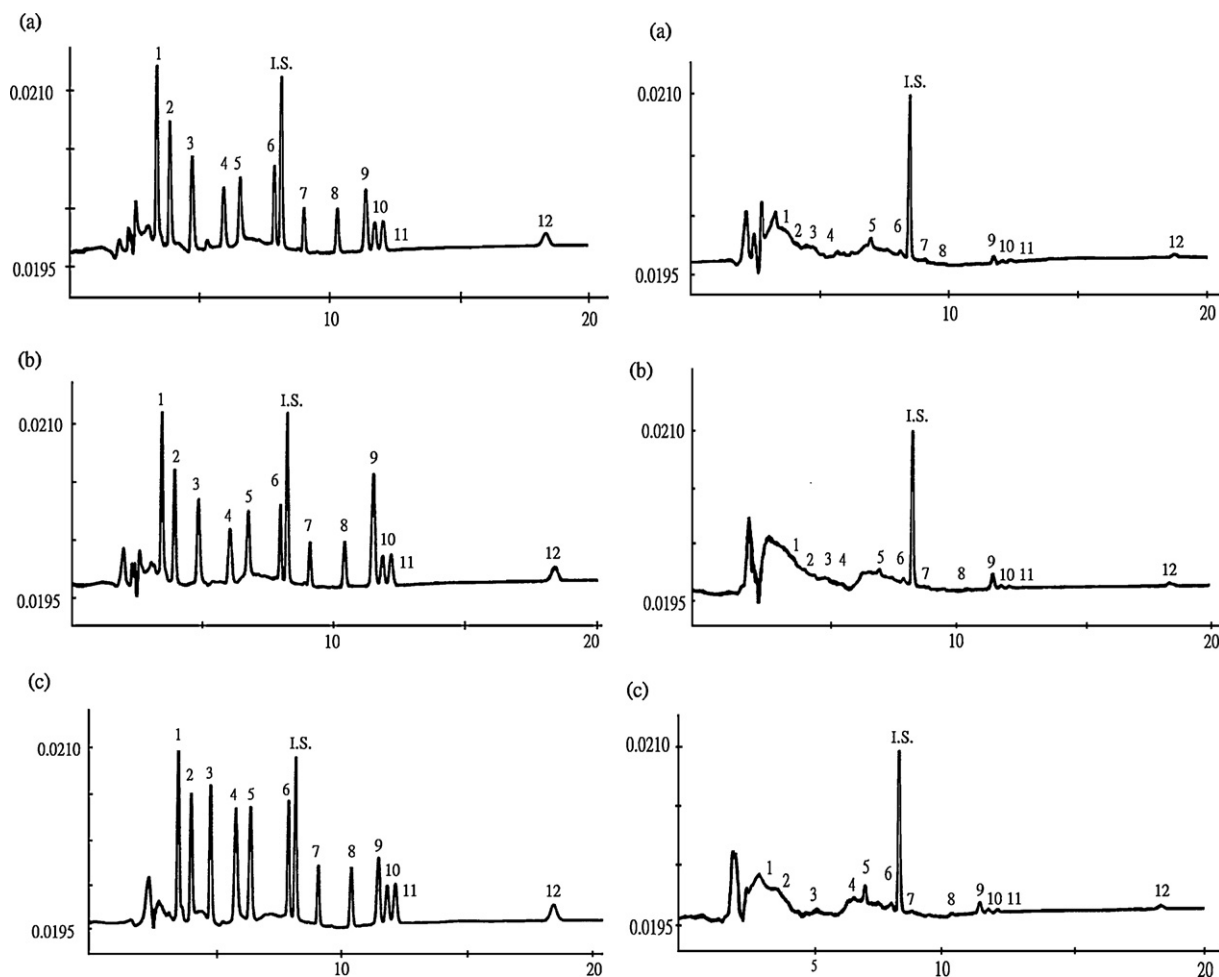
ate was then concentrated to 1 mL with evaporator for HPLC–UV analyses to check for the efficiencies of SCWE as a tool for soil remediation.

### 2.5. Instrumental analyses

The HPLC system used in our study included a Perkin-Elmer model series 200 gradient pump, and a Soma UV/VIS detector

**Table 1**  
Physical and chemical properties of the three soil types in the experiment.

Soil	pH	Particle size fraction (g/kg)				CEC cmol(+)/kg	OM %	Free Fe <sub>2</sub> O <sub>3</sub> g/kg
		Sand	Silt	Clay	Texture			
Pinchen	3.8	52	397	551	C	9.5	2.53	27.9
Chingchung	6.9	161	559	280	SiCl	8.6	2.19	6.1
Taikang	8.1	102	257	641	C	18.8	2.61	17.9



**Fig. 3.** The comparison of soil sample chromatograms without SCWE and chromatograms of soil samples after SCWE: (a) Pinchen; (b) Chingchung; (c) Taikang. Unit: x-axis: retention time (min); y-axis: absorbance intensity.

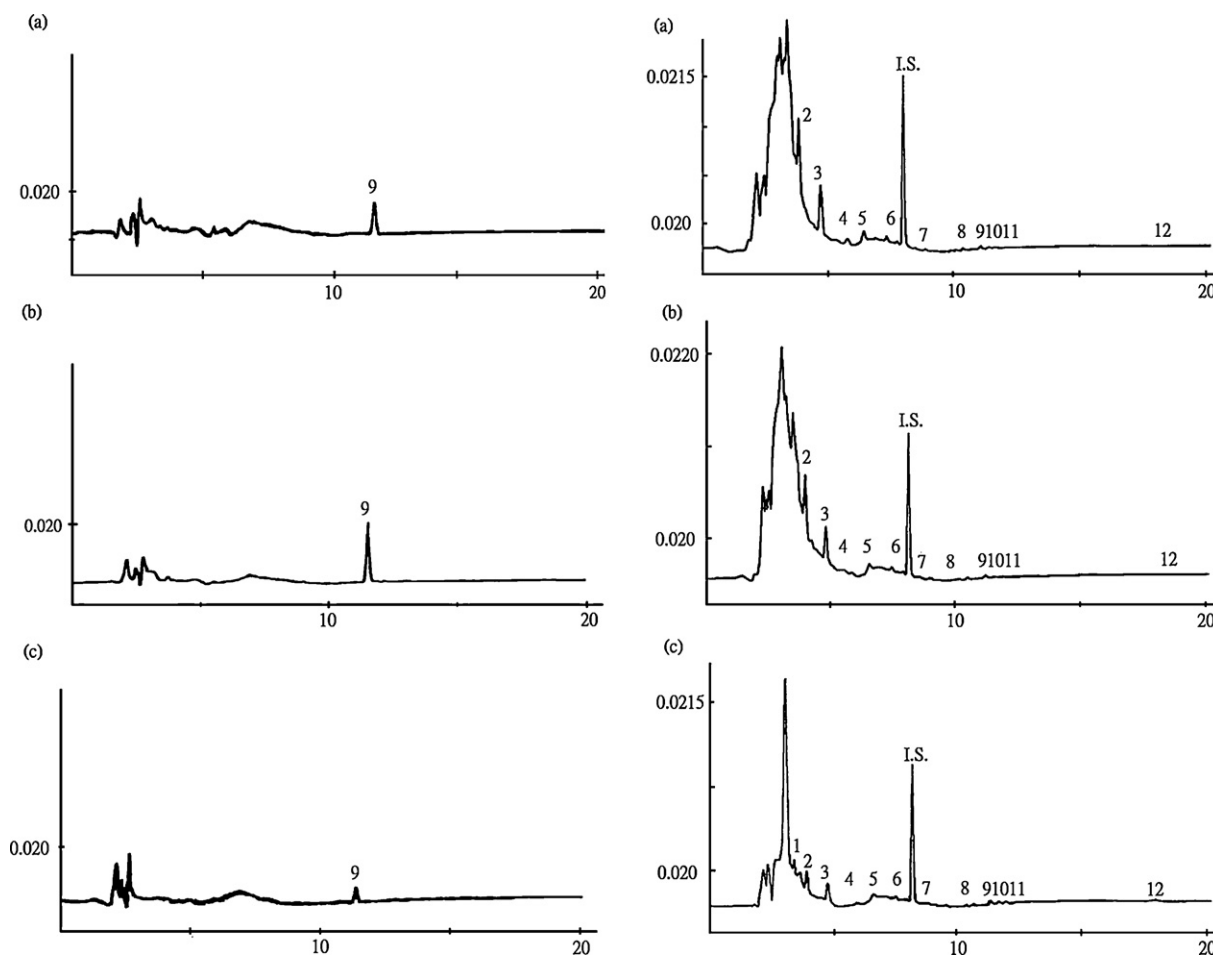
model s-3702 equipped with a Merck LiChroCART RP-18 column (4 mm × 250 mm × 5 μm). The gradient program in the study used the mobile phase started with 20% water and 80% acetonitrile for 3 min of 0.7 mL/min of flow rate, followed by 100% acetonitrile for 17 min of 1.0 mL/min of flow rate. Injection volume of sample was 20 μL. The UV detector was set in 223 nm wavelength for the absorbance of PEs for more sensitive detection. The retention times of PEs in HPLC/UV system were utilized for identification. Photodiode-array detector is applied for the identifications of analytes, based on an independent method developed in our laboratory [16]. A performance check PEs standard solution was prepared separately to check of HPLC/UV system. The limits of detection ranged from 0.14 (DpentP) to 1.70 μg/g (DEP). Although soil matrix will affect the limits of detection (LOD) determined for real samples, in this study, LOD of PEs were established for PE-spiked standard soil using ASE/HPLC/UV. After SCWE process, the soil matrix could be reduced in real soil sample, and then we might easily observe the analyte signals that could not be detected. Due to the LOD of PEs in different real soil samples should be different due to matrix effects. We therefore estimated the concentration of PEs and the left-over contents in real soil sample using the known LODs established using PE-spiked standard soil after SCWE. The recoveries of PEs were from 82 (DheptP) to 92% (DEP) using ASE/HPLC/UV in this study. The uncertainties of quantification of PEs within 95% confidence intervals were estimated from 0.08 μg/g (DIPP) to 0.21 μg/g (BBP).

### 3. Results and discussion

#### 3.1. Optimization of SCWE conditions for PE-contaminated soil

##### 3.1.1. Extraction temperature effect

According to the specification of the oven manufacturer and our calibration, the uncertainty of the temperature is ±1%. The accuracy of GC oven temperature was verified by the manufacturer. Based on our experience, the temperature of GC oven is well controlled in the system and calibrated with a thermocouple at two temperature points, 150 and 250 °C. The extraction temperatures were changed from 150 to 300 °C to select the optimum one throughout the whole study. After the SCWE and the collection of extracts, we further analyzed the extracted soil samples using ASE-HPLC/UV to check for the left-over contents and remediation efficiencies. As indicated in Fig. 2(a), we thought that the temperature was the major factor influencing SCWE efficiency for PE-contaminated soil samples, because the left-over contents could easily be decreased in greater magnitudes when the temperature was over 250 °C. The left-over contents decreased gradually while the temperature increased from 150 °C to 250 °C, especially for the PEs with longer hydrocarbon side chains, such as DEHP, DNP, DOP and DDP. Although some compounds showed good extraction efficiencies around 200 °C. The temperature of 250 °C was chosen for this study as the optimum one. The left-over contents were not easily to be observed and quantified due to the small signal responses



**Fig. 4.** The chromatograms of the blank in real soil samples and effluent after SCWE: (a) Pinchen; (b) Chingchung; (c) Taikang. Unit: x-axis: retention time (min); y-axis: absorbance intensity.

and the high removal efficiencies. So we had to fix the temperature at 200 °C to evaluate the effects of pressure and extraction time on the efficiencies of the extraction process. However, 250 °C was still the optimum parameter found in this study.

Raising of temperature can enhance the extraction efficiency due to two factors, the solubility and mass transfer effects. With the increasing of temperature which reduces the dielectric constant of water, solubilities of organic compounds can then be increased. Another factor is the breaking of interaction between solute and matrix due to high temperature.

### 3.1.2. Extraction pressure effect

The pressure gauge used in this study was verified by the manufacturer. According to the specification of the oven manufacturer and our calibration, the uncertainty of the pressure is  $\pm 2.5$  bar, verified with a pre-calibrated pressure meter. The purpose of maintaining certain high pressure was to keep water in the liquid state to avoid vaporization when the temperature was increased. Notwithstanding, extraction pressure is not considered as a major factor for extraction efficiency according to some references [9–13], we still optimized it by changing it from 5 to 15 MPa. As shown in Fig. 2(b), there were no obvious enhancements in extraction efficiency for most PEs except for long-chain PEs (DNP, DOP, DDP) when pressure was raised from 5 to 15 MPa. The pressure was finalized to be 10 MPa.

### 3.1.3. Static extraction time

To minimize solvent use for the remediation of PE-contaminated soil, we investigated static extraction scheme. We discussed four

parameters including 15, 30, 45, 60 min extraction time while the other factors were fixed. Fig. 2(c) shows the relationship between the left-over contents and static extraction times. Increasing the static extraction time obviously decreased PE contents in soil samples. We discovered that 15 min of extraction gave good efficiency for most of PEs in soils, especially for short chain compounds, such as DMP, DEP and DIPP; however, it was not good enough for the rest. For the entire study 5–8 mL reagent water was used as extraction solvent, after the optimization of the static extraction time the condition of 250 °C, 10 MPa and 30 min static extraction was decided to be the most acceptable for the remediation of PE-contaminated soils in this study.

### 3.2. The removal using SCWE in real soil samples

Three types of real soil samples from Taiwan (Table 1.) were spiked with PE standards at three different concentration levels (12, 50 and 100  $\mu\text{g}/\text{mL}$  in 5 g of soil samples) with the same processes described in 2.2. After SCWE with optimum conditions, we analyzed the extracted soils using ASE followed with HPLC/UV. Results were showed in Table 2. Even at high concentration levels, the signals of DMP, DEP, and DIPP in these soils were negligible, indicating successful removals. By comparing the results from the spiked samples and real samples contaminated by DEHP, we observed about less than 10% removal efficiency difference. This may be due to different degrees of interactions between DEHP and soil matrices. For DEHP, 84–89% removal from original soil samples was achievable at low concentration level. But for soil contaminated with high concen-

**Table 2**  
Efficiency of subcritical water treatment of soils for PEs at different concentration levels.

Soil classification	Pinchen soil			Chingchung soil			Taikang soil			LOD in standard soil μg/g
	L	M	H	L	M	H	L	M	H	
1. DMP	–	–	–	–	–	–	–	–	–	1.05
2. DEP	–	–	–	–	–	–	–	–	–	1.70
3. DIPP	–	–	–	–	–	–	–	–	–	0.50
4. BBP	–	–	2.21 (1.89)	–	–	–	–	–	–	1.06
5. DBP	–	–	1.42 (0.66)	–	–	2.00 (0.01)	–	3.25 (1.02)	2.65 (0.80)	1.30
6. DpentP	4.92 (0.17)	1.22 (0.60)	1.38 (1.00)	–	0.90 (0.09)	3.69 (0.14)	2.00 (0.34)	2.70 (0.70)	4.56 (0.11)	0.14
7. DHXP	3.82 (0.18)	1.20 (0.76)	3.86 (0.25)	5.59 (0.31)	1.45 (0.52)	5.95 (0.05)	2.57 (0.27)	2.51 (0.74)	8.15 (0.22)	0.22
8. DheptP	8.55 (0.65)	3.33 (2.88)	13.46 (0.76)	6.03 (0.26)	3.17 (1.24)	12.00 (0.52)	3.54 (0.32)	4.63 (1.91)	15.50 (0.13)	0.27
9. DEHP	16.30 (1.44)	11.00 (2.45)	33.02 (1.55)	11.11 (2.09)	10.05 (2.01)	25.20 (0.96)	12.59 (0.88)	12.82 (1.99)	30.82 (1.09)	0.18
10. DNP	8.06 (0.10)	10.20 (2.36)	36.62 (2.58)	6.65 (0.41)	7.94 (1.90)	22.45 (1.12)	8.45 (0.85)	11.13 (1.44)	31.44 (1.22)	0.29
11. DOP	11.10 (1.29)	7.88 (4.41)	29.37 (0.72)	4.62 (0.42)	5.26 (1.50)	17.50 (0.87)	4.79 (0.24)	7.04 (1.76)	23.88 (0.14)	0.26
12. DDP	14.09 (0.43)	15.31 (0.11)	50.07 (0.11)	7.24 (0.28)	11.22 (0.21)	29.60 (2.01)	11.54 (0.39)	13.54 (0.73)	38.76 (1.69)	0.35

Unit: relative left-over percentage, (%) of PEs in soil samples compared with original PEs quantities in samples.

Relative left-over percentage =  $(C_{SCWE}/C) \times 100\%$ , where  $C_{SCWE}$  is the Concentrations of PEs in soils after SCWE calculated by calibration lines using ASE/HPLC/UV, and C is the Concentrations of PEs in soils calculated by calibration lines using ASE/HPLC/UV.

L: low concentration; M: medium concentration; H: high concentration; –: <LOD, cannot be identified or quantified; (x): % standard deviation, triplicate analysis.

**Table 3**  
Results of analyses of collected SCWE extracts.

Soil classification	Pinchen soil			Chingchung soil			Taikang soil			LOD in standard soil μg/g
	L	M	H	L	M	H	L	M	H	
1. DMP	–	–	–	–	–	–	–	–	–	1.05
2. DEP	–	–	–	–	–	–	–	–	–	1.70
3. DIPP	5.64 (0.85)	17.9 (4.19)	23.78 (3.18)	5.31 (0.11)	11.79 (3.23)	42.32 (2.04)	2.24 (0.29)	12.29 (2.11)	14.25 (4.48)	0.50
4. BBP	–	–	1.37 (0.08)	–	–	3.11 (0.36)	–	–	2.41 (0.40)	1.06
5. DBP	–	1.64 (0.01)	3.76 (0.08)	–	1.85 (0.16)	4.91 (0.05)	–	1.59 (0.43)	3.22 (0.01)	1.30
6. DpentP	0.30 (0.01)	0.35 (0.04)	0.62 (0.08)	0.19 (0.01)	0.57 (0.01)	1.35 (0.03)	–	0.31 (0.11)	1.69 (0.02)	0.14
7. DHXP	0.46 (0.02)	0.49 (0.02)	0.72 (0.07)	0.29 (0.13)	1.17 (0.14)	1.40 (0.03)	–	0.28 (0.01)	1.91 (0.06)	0.22
8. DheptP	0.45 (0.11)	0.57 (0.01)	0.69 (0.06)	0.28 (0.06)	0.37 (0.13)	1.22 (0.02)	–	–	2.23 (0.03)	0.27
9. DEHP	0.41 (0.05)	0.92 (0.08)	1.80 (0.21)	0.21 (0.01)	0.54 (0.03)	1.36 (0.12)	0.50 (0.01)	0.63 (0.02)	2.31 (0.23)	0.18
10. DNP	–	–	0.94 (0.14)	–	0.58 (0.03)	1.15 (0.03)	0.42 (0.04)	0.63 (0.03)	1.99 (0.14)	0.29
11. DOP	–	–	0.75 (0.02)	–	0.51 (0.01)	1.12 (0.09)	0.36 (0.02)	0.47 (0.05)	2.15 (0.03)	0.26
12. DDP	–	–	–	–	–	1.44 (0.06)	–	0.92 (0.01)	2.23 (0.31)	0.35

Unit: μg/mL. Concentrations of PEs in extracts were calculated by calibration lines after SPE and ASE/HPLC/UV. L: low concentration; M: medium concentration; H: high concentration; –: <LOD, cannot be identified or quantified; (x): ±standard deviation, triplicate analysis.

tration levels of DEHP, larger quantities of subcritical water may be needed for better removal percentages.

### 3.3. The analyses of collected extracts after SCWE

PEs are hydrophobic with low solubility in water. Direct injection of collected extract into HPLC system may be hindered due to great solubility change after the release of subcritical conditions to create an inhomogeneous sample phase. We used C<sub>18</sub> SPE membrane to back extract the PEs from SCWE extracts. We established the SPE parameters by changing elution volume to gain the optimum recoveries with analyses using HPLC/UV. It was then determined that 8 mL (4 mL × 2 mL) of dichloromethane gave satisfactory results. After removal of dichloromethane to near dry, the sample volume was adjusted to 1 mL with acetonitrile for quantification. The recoveries of PEs were found to be around 70% after HPLC/UV analyses; however, some minor signals appeared in the chromatograms. Therefore, we suspected that some of the PEs may be broken down during the subcritical water extraction environment. Therefore, the amounts of PEs in the collected aqueous extracts did not meet the expected quantities. Fig. 3 demonstrates the comparison of chromatograms from soil samples before and after SCWE, using ASE followed by HPLC/UV. Fig. 4 compares the chromatograms obtained from blank soil samples using ASE followed by HPLC/UV and those from collected extract analyses using C<sub>18</sub> SPE followed by HPLC/UV. The quantitative results were shown in Table 3. The appearance of some extra signals in chromatograms from 3 to 5 min indicates some possibilities of degradations and transformations of PEs might occur under severe SCWE environment, as discussed in the literature by Krammer and Vogel [17]. Some literatures also indicated that organic matters may be oxidized in the subcritical water condition [18].

In addition, we discovered over 80% removal efficiencies from the samples originally contaminated by DEHP, as shown in Figs. 3 and 4 and Table 2, using SCWE.

Biological degradation using microorganisms is by far the most popular technique for PEs removal, as reported in many literatures. If indigenous species can be located, microbial degradation is the most studied technique for the remediation of PEs-contaminated soils. They usually take more than several hours to days to reach ideal results. Specific microbial species were used to treat specific PEs. By comparing with other methods reported for the removal of phthalate esters in soil samples, this study shows the advantages of less time consuming for PEs removal using a green solvent, water, without the need to locate and culture an effective strain of microbial species. Much time can be saved with the application of SCWE which is free of organic solvent. It may be a potential technique to deal with PEs-contaminated soil in the future. Some literature reported that specific PEs can be degraded using UV irradiation with catalysis in aqueous solution, but it was not established in soil sample.

## 4. Conclusions

We have succeeded to supply data indicated the feasibility of removal twelve PEs in soil samples by using subcritical water as

a possible remediation tool. Although at higher PEs concentration levels, the modification of treatments may be necessary for satisfactory removal of the contaminants, with PEs at low concentration level, most of contaminants in soil samples were reduced to be below 10% of original contents using the optimum treatment conditions. Theoretically, the quantities of PEs left in subcritical water after extraction should explain for the PEs removal efficiencies. However, from the analyses of SCWE effluents, we discovered that the amounts of PEs in the collected extracts did not meet the expected quantities. This may be due to degradations and transformations of PEs during SCWE stage, as demonstrated in Fig. 4.

## Acknowledgment

We thank the laboratory of Dr. Lee Dar-Yuan of the Department of Agricultural Chemistry, National Taiwan University for the collection and supplying some real soil samples.

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