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Determination of pentachlorophenol in wastewater irrigated soils and incubated earthworms

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Abstract

The analyses of low pentachlorophenol (PCP) in soils and earthworms require a sensitive and reliable analytical method. In this paper, several derivatization methods and extraction solvents were compared systematically. The derivatization reagents included acetic anhydride, 2,3,4,5,6-pentafluorobenzyl bromide (PFBBr) and diazomethane. Hexane, acetone, hexane–acetone (1:1), dichloromethane and methanol were used as the extraction solvents. PFBBr derivatization showed the highest sensitivity. The derivatization parameters of PFBBr including the amount of PFBBr, the power and irradiation time of microwave were optimized. As a result, 200 μl of PFBBr (10%) at 150 W of microwave oven for 30 min achieved the best result. The PFBBr derivatization method had the detection limit of 0.07 $\mu g\,l^{-1}$ of PCP. Extraction by a mixture of hexane and acetone (1:1) showed the best recoveries. The recommended method was used to determine the low PCP in soils irrigated by wastewater and earthworms incubated in the corresponding soils. The concentrations of PCP in soils were in the range of 1.38–179 $ng\,g^{-1}$, while those in earthworms were 11.2–262 $ng\,g^{-1}$. The recoveries of the surrogate standard (trichlorophenol) ranged from 81.1% to 107%, demonstrating the merit of the method.

Keywords: Pentachlorophenol; Derivatization; Extraction; Soils; Earthworms

1. Introduction

Pentachlorophenol (PCP) is listed as the 31st most hazardous substance in the US Federal Register of 1991 [1], but has been used worldwide for more than 50 years as a general biocide [2]. Its major application today is in the treatment and preservation of wood products [3]. The widespread use of PCP and its recalcitrant nature results in the global environmental contamination. It has been detected in air, soil, groundwater and surface water near some industrial discharges [4].

Wastewater irrigation is a common practice for agriculture in China as well as in arid and semi-arid areas. Various pollutants could be introduced and accumulated in the soil environment after long-term wastewater irrigation because of mismanagement and improper treatment of wastewater. Much attention has been paid to the accumulation and bio-transfer of heavy metals in the soil system as a consequence of wastewater irrigation [5,6]. However, accumulation of persistent organic pollutants, such as PCP and the associated ecological consequences after wastewater irrigation has not been emphasized sufficiently [7]. Earthworms comprise the largest part of the soil fauna biomass and are able to accumulate various organic contaminants [8,9]. Accumulation of organic contaminants in earthworms implies a risk not only for the earthworm population itself, but also for many vertebrate species feeding on earthworms. Therefore, the quantitative determination of PCP in soil and incubated earthworms is of high interest with regard to soil quality and remediation of contaminated soils. To this end, the accurate determination of low PCP-content is required [10,11].

Many methods have been described for the determination of PCP in the environment [11–20]. As PCP needs to be determined at trace level, the first step of the protocol consists of an extraction procedure. Several extraction techniques have been proposed. Although some assistant methods, such as supercritical fluid [15], sonication [10,16,21,22], and microwave [23] extraction were adopted, Soxhlet extraction is still applied as an effective and economic one [14,24,25]. As far as the extrac-

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tion technique is concerned, extraction solvent is a key factor [26]. Among the solvents ethanol [21], dichloromethane [14,25], methanol [27,28], toluene [13,16,17], hexane [10,22], acetone [29] and a mixture of hexane and acetone [25] were frequently used.

GC is a favorite determination technique for organic pollutants. However, some organic compounds, especially chlorophenols, do not have favorable gas chromatographic properties because of their relative polarity, thermal instability and low volatility, thereby causing adsorption and tailing of chromatographic peaks [30]. These shortcomings can be overcome to a large extent by derivatization, such as methylation [12,30], pentafluorobenzylation [31,32] and acetylation [10,13,33]. However, different detection limits are reported by different analysts even the same derivatization method was used. For example, the detection limits of PFBBr derivatization were described to be 1–4 $\mu g\,l^{-1}$ [31], 10 $\mu g\,l^{-1}$ [34], and 100 $\mu g\,l^{-1}$ [35]. Thus, it is important to make overall comparison of different derivatization methods.

The aim of this study is to compare different derivatization procedures and extraction solvents in detail, thus to establish a suitable routine GC-ECD method for the sensitive determination of low PCP content in wastewater irrigated soils and earthworms; it is significant to assess environmental risk of wastewater irrigated soil.

2. Materials and methods

2.1. Sample collection and earthworm incubation

2.1.1. Soil sample collection

Soil samples were collected from 10 sites in a representative wastewater irrigated farmland downstream in the suburb of Beijing, China. The sampling sites were allocated along the irrigation channels. The wastewater consists of effluents from the sewage plant and untreated wastewater from a coal plant. At each site, four cores of the topsoil at the depth of 10 cm were taken at random and pooled together in the field. All soil samples were air-dried, ground and screened through a 2-mm stainless sieve to remove stones, plant roots and other large particles.

2.1.2. Earthworm incubation

Fifteen clitellate earthworms (*Eisenia fetida*), average 0.3 g of each, were kept in uncontaminated background soil for 1 week before being introduced to 1 kg moistened wastewater irrigated soils (40% on water-holding capacity). Five soils were selected randomly from 10 soil samples for this purpose. Each soil has triplicate experiments. The beakers covered with wet filter paper were kept in the dark at $22 \pm 2\,^{\circ}C$ and de-ionized water was added daily to compensate for water loss due to evapotranspiration during the incubation. After 15 days, the earthworms were removed, rinsed with water, and kept in wet filter paper for 24 h to allow the gut to empty. Then the earthworms were rinsed with water again and stored at $-20\,^{\circ}C$ prior to the determination of PCP.

2.2. Apparatus

Gas chromatograph, equipped with a ^{63}Ni electron capture detector (GC-ECD) (Hewlett Packard 6890, USA) and a HP-5 fused silica capillary column (film 0.32 μm, i.d. 0.25 mm, length 30 m) (J&W, USA), was used for PCP determination. Chromatographic data were collected and recorded using a HP Chemstation. A home microwave oven (Midea, PJ21C-BI, 800W, China) was used in the PCP derivatization by PFBBr.

2.3. Reagents and standards

All the organic solvents were commercial available. Dichloromethane, methanol, *n*-hexane (Mallinckrodt, USA), and acetone (Merck, USA) were of pesticide grade. Acetic anhydride (Merck, USA), 2,3,4,5,6-pentafluorobenzyl bromide (Acros, NJ, USA) and anhydrous potassium carbonate (Beijing Chemicals, China) were of analytical grade. Anhydrous sodium sulphate (pesticide grade, Merck, China) was heated at 130 °C for 24 h before use.

Reference standards of PCP (AccuStandard Inc., New Haven, USA), internal standard 2,4,6-tribromophenol (AccuStandard Inc., New Haven, USA) and surrogate standard 2,4,6-trichlorophenol (AccuStandard Inc., New Haven, USA) were made in *n*-hexane, stored in sealed containers and preserved in 4 °C. The containers were weighed and the volatile solvents were compensated before use. Working solutions were prepared by diluting stock solutions in derivatization medium.

2.4. Comparison of three derivatization methods

2.4.1. Methylation using diazomethane solution

PCP was derived according to the method of Zuin et al. [12]. Briefly, 1 ml of a diazomethane solution (freshly prepared by distillation of 2.14 g *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide with 10 ml KOH 96% in ethanol and 30 ml ethyl ether) was added to 1 ml standard solution. Then, the yellow mixture remained at room temperature for about 60 min for a complete methylation. The volume was reduced to 1 ml by evaporation under a gentle stream of N_2.

2.4.2. Acetylation using acetic anhydride

The development of this procedure was based on the method of Buhr et al. [13]. Acetic anhydride was used for derivation of PCP to PCP–acetate. Ten milliliters of 0.1 mol l^{-1} K_2CO_3 solution were filled in a 20 ml flask, then 1 ml PCP was added. The derivation procedure at room temperature was as follows: stirring for 10 min – addition of 0.25 ml acetic anhydride – stirring for 10 min – addition of 0.25 ml acetic anhydride – stirring for 10 min. Then 9 ml hexane was added. The solution was stirred for 10 min and set for 10 min. The organic phase was separated, dried over Na_2SO_4 for 5 min. Then, 5 ml of organic phase was removed and reduced to 0.5 ml by evaporation under a gentle stream of N_2.

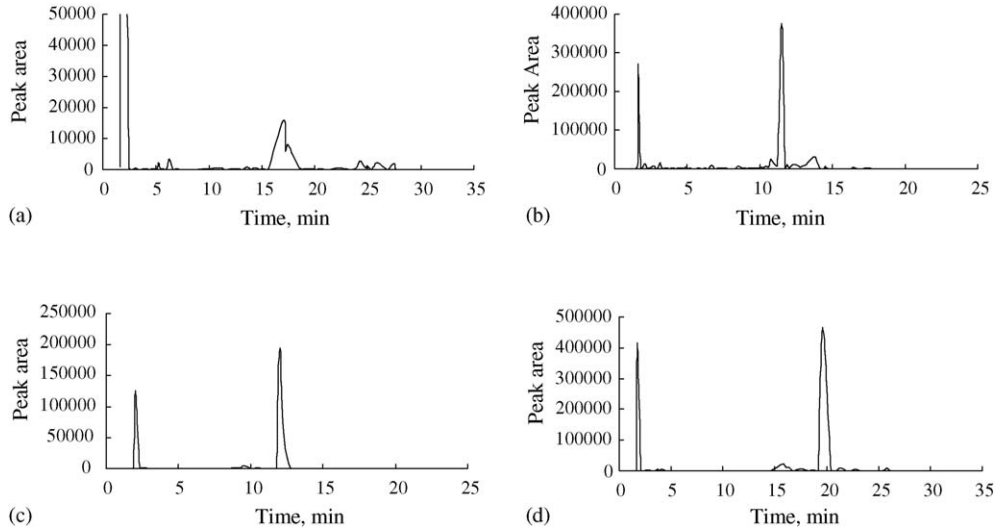

Fig. 1. Comparison of chromatograms of PCP with and without derivatization using different derivatization reagents, PCP concentration was set at 1 μg ml^{-1}: (a) without derivatization, retention time: 17.03 min; (b) diazomethane, retention time: 11.47 min; (c) HAc, retention time: 12.01 min; (d) PFBBr, retention time: 19.65 min.

2.4.3. Pentafluorobenzylation using PFBBr

The experimental conditions of Fu and Xu [35] were followed. Briefly, 5 ml acetone, 0.1 g K_2CO_3, and 0.5 g Na_2SO_4 were added into 10 ml flask, together with 1 ml PCP standard solution. After stirring vigorously for thoroughly intermixing, 100 μl 10% PFBBr was added. Then the flask was stirred vigorously again, sealed well, placed in a microwave oven, and derivatized at 150 W for 4 min. After cooled down, removed from the flask to a concentrator, washed with 5 ml acetone three times, the organic phase was reduced to 1 ml by evaporation under a gentle stream of N_2.

2.4.4. Gas chromatographic analysis and calibration

One microliter of the solution containing PCP derivative was injected into a split/splitless injector (splitless mode). For determination of derivatized PCP by acetic anhydride and diazomethane, the injector temperature was set at 250 °C; detector temperature was 300 °C; the initial column temperature was 55 °C, programmed at 55 °C for 1.75 min, then from 55 to 280 °C at 20 °C min^{-1}, and maintained at this temperature for 8 min. The total analytical time was 21 min. For determination of derivatized PCP by PFBBr, the injector temperature was 250 °C; the initial column temperature was 55 °C, programmed at 55 °C for 1.75 min, then from 55 to 230 °C at 15 °C min^{-1}, and maintained at this temperature for 5 min, then from 230 to 280 °C at 5 °C min^{-1}, and maintained at 280 °C for 2 min. The detector temperature was 300 °C. The total analytical time was 30.42 min.

Calibration was performed for the concentration range from 5 to 1000 ng ml^{-1}. One hundred nanogram of 2,4,6-tribromophenol was used as an internal standard.

2.5. Analysis of PCP in soil and earthworm samples

Soxhlet extraction was used in this study. Earthworms were frozen at −20 °C and ground with a mortar and pestle. Ten grams of soil or 3–5 g of ground earthworm tissue were mixed with 10 g anhydrous Na_2SO_4 in paper extraction thimbles and then extracted with 100 ml hexane–acetone for 48 h at 10 min cycle^{-1}. The extract was carefully concentrated to 2 ml by rotary evaporator. The residue was transferred to a column (1 cm i.d. × 5 cm) prepared by packing silica gel (60–80 mesh), covered by a 2 cm layer of sodium sulfate, and then washed with 30 ml hexane and 30 ml acetone. The eluate was reduced to 1 ml volume for analysis. PCP in the extract was reacted with 200 μl 10% PFBBr for derivatization. The microwave oven power was set at 150 W, and the reaction time was 30 min. After derivatization, extraction solvent was removed. The residue was washed with 3 ml hexane–acetone (1:1) three times. The liquid was evaporated to 1 ml. One microliter of derivatized PCP was injected into GC-ECD for analysis.

To assure quality of the proposed analytical method, the method blank was analyzed in each analytical batch. The blank values of the analytical procedure were determined by extracting an empty cellulose thimble by the same method as the real sample. No chromatographic peak of derivatized PCP was found in chromatograms of the procedural blank. 2,4,6-Trichlorophenol was used as surrogate standard to monitor the performance of the extraction, cleanup, analytical system and the effectiveness of the method, which was added to the samples before Soxhlet extraction. 2,4,6-Tribromohenol added before sample derivatization was used as internal standard to quantitatively evaluate the amounts of PCP.

3. Results and discussion

3.1. Comparison of three derivatization method

In this study, a systemic comparison was made among acetic anhydride, PFBBr and diazomethane derivatization methods in terms of the peak shape, the linearity of the calibration curves, the detection limit and the stability of the three derivatives.

Table 1
Regression equation and linear correlation coefficients of three derivatization methods

Method	Regression equation	Correlation coefficient	Detect limit ($\mu g\,l^{-1}$)
Methylation	$y = 371.27x$	0.998*	0.5
Acetylation	$y = 255.07x$	0.999*	0.7
Pentafluorobenzylation	$y = 473.71x$	0.999*	0.4

* Significant at 0.01 probability level.

3.1.1. The chromatograms of three derivates

The gas chromatogram (Fig. 1) demonstrated that after derivatization PCP's unfavorable gas chromatographic properties (Fig. 1a) were overcome, and symmetrical chromatographic peaks were obtained, and the tailing was decreased. Most importantly, the detection limit of PCP in GC was improved effectively.

3.1.2. Linearity of the calibration curves and the detection limits

The linearity of the derivatives was compared when diazomethane, acetic anhydride and PFBBr were used as derivatization reagents. The data points were fitted to a simple straight-line model $y_i = ax_i$. When the linear two-parameter model, $y_i = ax_i + b$, was used, the quality of the fit was not significantly improved on a probability level of 99%. As shown in Table 1, all the three derivatization methods had good linearity, with correlation coefficients greater than 0.998. The linear range of PCP was from 5 to 1000 ng ml^{-1}. Based on the detection limits defined as the signal-to-noise (*S/N*) ratio of 3, the PFBBr had the lowest detection limit, while acetylation had the highest (Table 1). The relative standard deviation (R.S.D.) of six measurements was at the range of 1.3–4.8%, respectively.

3.1.3. Stability of the three derivatives

In order to examine the stability of acetic anhydride, PFBBr and diazomethane derivatives, each derivative was injected into GC-ECD repeatedly. The concentration of PCP for this purpose was 100 ng ml^{-1}. The calibration curves were constructed newly everyday. The derivatives were preserved in dark at 4 °C. The PFBBr derivative was quite stable within 2 days. No distinct decrease was observed for acetic anhydride derivative after 1 day, however, after 2 days, the recovery decreased by 8%. The diazomethane derivative is instable, and the recovery decreased more than 10% after 2 days.

3.2. Optimization of the derivatization conditions

Although in the previous comparison, PFBBr derivatization method was proven to be effective; still, the PFBBr derivatization was further optimized including amount of PFBBr used, derivation time and microwave power in order to obtain higher sensitivity. The concentration of PCP for this purpose was set at 100 ng ml^{-1}.

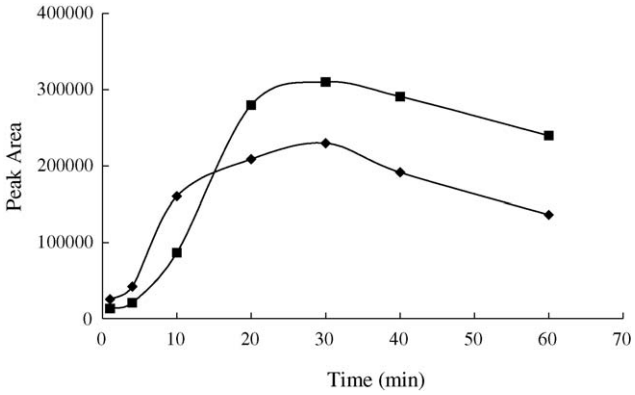

Fig. 2. Effects of PFBBr derivatization time and microwave power on the derivatization efficiency: (■) 150 W and (♦) 300 W.

3.2.1. Effect of the PFBBr amount on the derivation efficiency

Fu and Xu [35] deemed that the volume of 10% PFBBr should not exceed 100 μl, otherwise, more PFBBr could lead to the contamination of GC-ECD. However, the volume of PFBBr recommended by USEPA [32] was 250 μl. Therefore, the effect of 10% PFBBr volume on the derivatization efficiency was studied from 50 to 250 μl. When the volume of PFBBr solution increased, from 50 to 150 μl, the peak area of PCP derivatives increased obviously. The peak area of 150 μl was four times larger than that of 50 μl. When the volume was further increased from 150 to 250 μl, the peak area remained almost the same. In addition, no contamination of GC-ECD was observed. Thus, 200 μl 10% PFBBr was used in the following study.

3.2.2. Effect of the microwave oven power and reaction time on the derivation efficiency

A 150 W microwave oven power and 4 min reaction time were recommended by Fu and Xu [35] for PFBBr derivatization. They found that higher microwave oven power and longer reaction time could sacrifice the recovery. In this study, the effect of microwave oven power and reaction time were reevaluated. As shown in Fig. 2, the peak area of PFBBr derivative obtained at 150 W microwave oven power was higher than that at 300 W. Under the condition of microwave oven power of 150 W, the peak area increased with the reaction time increased from 1 to 20 min, and maintained unchanged from 20 to 40 min. After that it dropped down when the reaction time was further increased to 60 min. Therefore, the microwave oven power and reaction time were set at 150 W and 30 min in the remaining experiment.

The determination sensitivity of PCP was increased greatly under the optimized conditions. The detection limit of 0.07 $\mu g\,l^{-1}$ was obtained by the present study, which is much lower than Gurka et al.'s (10 $\mu g\,l^{-1}$) [34], Boucharat et al.'s (1–4 $\mu g\,l^{-1}$)[31], and Fu and Xu's (1 $\mu g\,l^{-1}$)[35].

3.3. Comparison of the extraction solvents

The effects of various extraction solvents, such as hexane, dichloromethane, methanol, acetone and the mixture of hexane and acetone were evaluated for the extraction of PCP from the

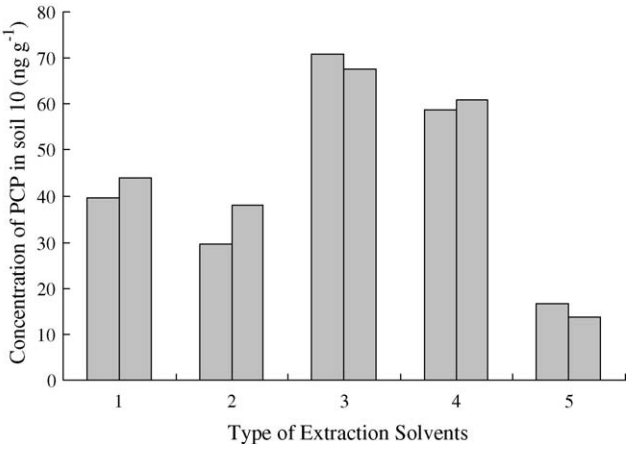

Fig. 3. Effect of different extraction solvents on the extraction efficiency of PCP from soils: (1) hexane; (2) acetone; (3) hexane and acetone (1:1); (4) dichloromethane; (5) methanol.

soil samples before PFBBr derivatization. As shown in Fig. 3, the highest concentration was obtained when the mixture of hexane and acetone was used as extraction solvent, while low extraction efficiencies were obtained when hexane, dichloromethane, acetone were used separately. Our results were supported by Polese and Ribeiro [10], who compared the extraction ability of PCP from soils between hexane and hexane–acetone (1:1), and found that better recoveries were obtained when hexane–acetone (1:1) was applied as extraction solvent. Although methanol was reported as the best solvent to extract PCP in wood [13], however, the lowest peak area was obtained when methanol was used in this study.

3.4. Determination of PCP in soil and earthworm samples

The determination of PCP in soils irrigated by wastewater and earthworms incubated is given in Table 2. The PCP concentrations in soils and earthworms were in the range of 1.38–179 and 11.2–262 ng g^{-1}, respectively. The recoveries of the surrogate standards were at the range of 81–107%, showing sufficient reliability and validity of the method.

So far, there is no Chinese soil quality criterion of PCP available. According to the EPA of Denmark [36], the soil quality criterion of PCP is 150 ng g^{-1}, while the eco-toxicological soil quality criterion of PCP is 50 ng g^{-1}. Among the 10 soils we determined, the PCP concentrations in soil 7 and 10 were higher than the eco-toxicological soil quality criterion. Moreover, the concentrations of PCP in all earthworms were higher than those in the corresponding soils, indicating the accumulation of PCP in earthworms and the high risk of wastewater irrigation.

Table 2
Concentration of PCP in soils and earthworms ($n = 6$)

Soil	PCP in soils (ng g^{-1})	TCP recovery (%)	PCP in earthworms (ng g^{-1})	TCP recovery (%)
1	5.53 ± 0.23	85.6	–	–
2	32.9 ± 1.2	92.0	71.6 ± 6.5	82.3
3	1.38 ± 0.12	81.1	–	–
4	18.9 ± 0.09	89.9	47.6 ± 2.6	92.0
5	6.46 ± 0.20	89.6	–	–
6	8.54 ± 0.06	87.0	–	–
7	179 ± 8	90.6	262 ± 14	84.1
8	4.02 ± 0.24	85.2	11.2 ± 1.1	89.9
9	20.2 ± 1.5	107	57.3 ± 3.0	102
10	70.8 ± 4.0	90.4	182 ± 16	87.0

4. Conclusion

Three derivatization procedures and various extraction solvents were compared and optimized in order to search for the best method for analysis of low-content PCP in soils irrigated with wastewater and earthworms incubated. The PFBBr derivatization and hexane–acetone extraction method revealed lower detection limit, higher reproducibility and better recovery, thus making the determination of PCP in soils and earthworms at nanograms per gram levels feasible. The accumulation of PCP in soils and earthworms were found, which showed that the wastewater irrigated area presented a critical situation, offering risks to different environmental compartments and local population.

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