LEGUME-GRASS INTERCROPPING
PHYTOREMEDIATION OF PHTHALIC ACID
ESTERS IN SOIL NEAR AN ELECTRONIC
WASTE RECYCLING SITE: A FIELD STUDY

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LEGUME-GRASS INTERCROPPING PHYTOREMEDIATION OF PHTHALIC ACID ESTERS IN SOIL NEAR AN ELECTRONIC WASTE RECYCLING SITE: A FIELD STUDY

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A field experiment was conducted to study the phytoremediation of phthalic acid esters (PAEs) by legume (alfalfa, Medicago sativa L.)-grass (perennial ryegrass, Lolium perenne L. and tall fescue, Festuca arundinacea) intercropping in contaminated agricultural soil at one of the largest e-waste recycling sites in China. Two compounds, DEHP and DnBP, were present in the soil and in the shoots of the test plants at much higher concentrations than the other target PAEs studied. Over 80% of ‘total’ (i.e., all six) PAEs were removed from the soil across all treatments by the end of the experiment. Alfalfa in monoculture removed over 90% of PAEs and alfalfa in the intercrop of the three plant species contained the highest shoot concentration of total PAEs of about 4.7 mg kg\(^{-1}\) DW (dry weight). Calculation of phytoextraction efficiency indicated that the most effective plant combinations in eliminating soil PAEs were the three-species intercrop (1.78%) and the alfalfa monocrop (1.41%). Phytoremediation with alfalfa was effective in both monoculture and intercropping. High bioconcentration factors (BCFs) indicated the occurrence of significant extraction of PAEs by plants from soil, suggesting that phytoremediation may have potential for the removal of PAEs from contaminated soils.

KEY WORDS: phthalic acid esters, phytoremediation, intercropping, monoculture, bioconcentration factor

INTRODUCTION

Phthalic acid ester (PAE) compounds are the most extensively used plasticizers worldwide and have become ubiquitous pollutants with widespread distribution in the environment (Zeng et al. 2008). PAEs can severely retard crop growth, lower the quality of crop products, and impact soil animals and microorganisms, and their toxicity in ecosystems can include adverse effects on reproductive development and other genetic effects in...
mammals (Rhee 2002; Shono and Suita 2003; Takeuchi et al. 2005; Kondo et al. 2006; Fu et al. 2007; Kusu et al. 2008; Saito et al. 2010; Suzuki et al. 2010). PAEs interact with androgen and thyroid receptors more than estrogen receptors (Shigeki et al. 2001). Their possible accumulation in edible vegetables from soils and potential harm to humans via the food chain has also aroused public concern (Zeng et al. 2008). The remediation of PAE compounds in contaminated soils is therefore an issue of active concern.

Uncontrolled e-waste recycling at Taizhou, Zhejiang province, one of the largest e-waste dismantling sites in China, has led to combined soil contamination by substances such as potentially toxic elements (including heavy metals), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins/dibenzo-p-dioxins (PCDD/Fs), and polybrominated diphenyl ethers (PBDEs), and this has led to great public concern for the environment and human health (Wang et al. 2006; Chen et al. 2008; Li et al. 2008; Ni et al. 2008). PAEs can be found in the ash formed from the open burning of electric wires (Liu et al. 2009). PAEs tend to have high lipophicity and this accounts for their ready adsorption to organic matter in contaminated soil and sediment particles (Zheng et al. 2007; Xu and Li 2008). Furthermore, during the last two years the soil total concentrations of five PAE compounds were reported to range from 12.6 to 46.7 mg kg\(^{-1}\), concentrations much higher than the allowable soil concentrations in the United States (Liu et al. 2009; Liu et al. 2010; Zhang et al. 2010a,b). They have been nominated in the list of 129 prior pollutants in the United States and as environmental endocrine disruptor chemicals by USEPA and we therefore selected them to be the target pollutants in our investigation.

Potential advantages of phytoremediation compared with other remediation approaches include the preservation of soil texture and structure, the utilization of solar energy, the involvement of an active soil microbial biomass, and low cost (Schnoor et al. 1995; Chekol et al. 2004; Huang et al. 2004). The use of higher plants for effective remediation has become a topic of increasing interest (Cunningham et al. 1996; McIntire and Lewis 1997). Environmentally friendly phytoremediation using plant species such as alfalfa, perennial ryegrass and tall fescue has been employed for PCBs, PAHs and other soil pollutants (Chekol et al. 2004; Rezek et al. 2008; Cheema et al. 2009; Shen et al. 2009; Cheema et al. 2010; Tang et al. 2010; Xu et al. 2010a) and in preliminary greenhouse tests for PAEs in our laboratory. However, phytoremediation of phthalate compounds has so far received little attention. The aims of the present work were therefore to compare the concentrations and components of PAEs in an agricultural soil under different treatments in an experimental field area, to check the efficiency of phytoremediation to PAE target pollutants and determine the concentration of total and individual PAE compounds in the shoots of different plant species, and to evaluate different plant species combinations for their suitability for larger scale remediation.

**MATERIALS AND METHODS**

**Chemicals**

A mixed standard solution of 6 PAE compounds (1 mg ml\(^{-1}\)) was prepared, namely dimethyl phthalate (DMP), diethyl phthalate (DEP), butyl benzyl phthalate (BBP), di-n-butyl phthalate (DnBP), bis (2-Ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DnOP), and the internal standard benzyl benzoate (BB, 5 mg ml\(^{-1}\)) which were all obtained from AccuStandard, Inc., New Haven, CT, USA. The six target pollutants were selected for
study because they were nominated as priority pollutants by USEPA. Certified reference material CRM 136–100 (Base Neutral Acids: BNAs – Clay 1) was purchased from RT Corp., Laramie, WY, one of the original Proficiency Test providers recognized by USEPA.

Analytical grade solvents (acetone and hexane) obtained from chemical reagent companies in Nanjing were re-distilled in an all-glass system to remove trace impurities before use. HPLC grade hexane was purchased from Tedia Company Inc., Fairfield, OH. Anhydrous sodium sulfate (NaSO₄, reagent grade), neutral alumina (Al₂O₃, 400 mesh and reagent grade), neutral silica gel (100–200 mesh) and sulphuric acid (H₂SO₄, guaranteed reagent) were obtained from National Pharmaceutical Group Chemical Reagent Co., Ltd., Shanghai, China. The three column packing materials were dried in a muffle furnace at 400°C for 6 h and stored in desiccators before use.

**Plant Materials**

Seeds of the three plant species alfalfa (*Medicago sativa* L.), perennial ryegrass (*Lolium perenne* L.) and tall fescue (*Testuca arundinacea*) were purchased from the Institute of Agricultural Science and Technology, Jiangsu province, east China.

No plastic equipment was used during sample collection and preparation to minimize background contamination in PAE analysis. Glassware was washed by the following procedure prior to analysis. After immersion and washing with soapy water in a laboratory ultrasonic washer and air drying, glassware with tick marks was immersed in sulfuric acid (H₂SO₄, 98%, reagent grade) and washed with tap water, then rinsed with ultrapure water before oven dry at 50°C. Glassware without tick marks was baked for 6 h at 400°C in a muffle furnace. All glassware was then thoroughly rinsed with acetone:hexane (1:1 v/v) before use.

**Phytoremediation Experiment**

The field experiment was located on agricultural land about 250 m from an electronic waste dismantling site at Taizhou, Zhejiang province, east China for a period of two years. The average total concentrations of target PAEs were 1032.6 ± 311.8 µg kg⁻¹ in October 2008 and 2389.5 ± 370.4 µg kg⁻¹ in October 2010 in the control treatments. The pH value of the soil was 5.56, with an organic matter content of 36.5 g kg⁻¹, and total nitrogen, phosphorus and potassium concentrations of 1.96, 0.56 and 23.1 g kg⁻¹, respectively.

The planting regimes consisted of an unplanted control treatment (CK), alfalfa monoculture (A), perennial ryegrass monoculture (P), tall fescue monoculture (T), alfalfa and perennial ryegrass intercrop (AP, seed ratio 1:1), alfalfa and tall fescue intercrop (AT, seed ratio 1:1) and alfalfa, perennial ryegrass and tall fescue intercrop (APT, seed ratio 1:1:1). There were 4 replicate plots of each treatment, each 2.4 × 2.4 m, giving 28 plots in total in a fully randomized design. All three plant species were sown by broadcasting at the start of the experiment.

**Sample Processing**

Two years after the establishment of the experiment the soil and shoots of individual plant species in each plot were sampled. Soil samples were collected to 15 cm depth using a soil corer. Five cores were collected from each plot and combined to give a composite sample. All of the plant shoots were collected by cutting just above ground level within each
SOIL PHTHALIC ESTER PHYTOREMEDIATION BY LEGUME-GRASS INTERCROPPING

plot for biomass measurement and five random shoots were selected for further analysis. Fresh plant samples were taken to the laboratory, immediately washed with tap water and rinsed with distilled water and wiped dry with paper tissue before freeze-drying with the soil samples in a Free Zone 2.5 Liter Freeze Dry System (Labconco Corp., Kansas City, MO, USA). Soil samples were air dried and sieved through a 60-mesh screen after drying and plant samples were homogenized in liquid nitrogen prior to storage at –20°C and further analysis.

10.00 g of soil (or 1.00 g of plant sample) was placed in a clean glass centrifuge bottle, mixed on a vortex mixer for 1 min, and immersed in 30 ml of acetone:hexane (1:1 v/v) overnight. Spiked samples were prepared by adding 1 ml of 1 mg l\(^{-1}\) standard solution of 6 target PAEs to the soil (or 0.1 ml to the plant sample) before analysis following the same procedure. Ultrasonic extraction was carried out the next day in a water bath at 25°C for 30 min at 100% power before centrifuging at 1500 rpm for 5 min. The three supernatants were all filtered into a round bottom flask after another two extractions with 20 ml of acetone:hexane (1:1 v/v) for 15 min each. About 70 ml of liquid in the flask was reduced by rotary evaporation to 1–2 ml (350 mbar, 40°C water bath, 80 rpm). Hexane (3–4 ml) was added to the remaining solvent and rotary evaporation was continued to less than 1 ml but not to dryness.

Column chromatography was performed in a glass column (1 × 26 cm) with 2 g of NaSO\(_4\), 6 g of neutral Al\(_2\)O\(_3\) and 12 g of neutral silica gel (from bottom to top). Pre-washing was with 15 ml of hexane and 15 ml of acetone:hexane (1:4 v/v) mixture before sample loading and elution with 40 ml of acetone:hexane (1:4 v/v). All the washing solutions were collected and reduced to less than 1 ml by rotary evaporation as described above. Plant samples were further washed with sulphuric acid (Meng et al. 1996) and concentrated to less than 1 ml. 10 \(\mu l\) of internal standard, BB, was added before hexane (HPLC grade) was added to bring the final volume to 1 ml. Samples were transferred to brown sample bottles and stored at -20°C before further analysis.

**Instrumental Analysis and Quality Control**

Analysis of individual PAEs in samples was performed by a modification of USEPA method 8270C (USEPA 1996) with an Agilent 7890GC-5975 MSD gas chromatograph-mass spectrometer. Samples were resolved on a DB-5 (30 m × 0.25 mm × 0.25 \(\mu m\)) fused-silica capillary column with helium (purity >99.999%) as carrier gas at 1.2 ml min\(^{-1}\). The injector temperature was set at 250°C. The GC temperature program featured an initial column temperature of 50°C which was held for 1 min, with a ramp of 15°C min\(^{-1}\) to 200°C which was held for 1 min, then 8°C min\(^{-1}\) ramp to 280°C which was held for 3 min. Post run was at 285°C for 2 min. Under selected ion monitoring mode, non-pulse injection with a volume of 1.0 \(\mu l\) each in split-less mode was carried out. The GC-MS transfer line was set at 280°C.

During analysis, whole procedure blanks, soil matrix blanks, spiked soil matrix and parallel samples were all employed, together with analysis of the certified reference material. The recovery rates of spiked soils matrix at 100 \(\mu g\) kg\(^{-1}\) (DW) were between 75.88% and 107.61%, with an RSD of 3.88–8.91. Instrument detection limits (IDLs) for the 6 target compounds were 0.11–0.35 \(\mu g\) l\(^{-1}\), and method detection limits (MDLs) were 68–135 \(\mu g\) kg\(^{-1}\). Linearity of response between 0.02 to 2 mg l\(^{-1}\) showed \(R^2\) (correlation coefficient) values of the calibration curve >0.999. BB was used as the internal standard to allow high accuracy and sensitivity. Analysis of the CRM also showed the reliability of the
results (Tables S1 and S2). For every 16 samples, 2 whole procedure blanks, 2 soil matrix blanks and 1 CRM 136–100 were analyzed.

**Statistical Analysis**

The removal rates of 6 PAEs were calculated as:

$$R\% = (1 - \frac{Cat}{Cac}) \times \frac{Cac}{Ctc},$$

where, $R$ is the removal rate of an individual PAE compound, $Cat$ is the residual concentration of an individual target compound under different treatments, $Cac$ is the concentration of an individual target compound in the control treatment, and $Ctc$ is the total concentration of the 6 target compounds in the control treatment.

All the data were processed with Microsoft Excel 2003 and the SPSS v.14.0 software package. The data were analyzed for significant differences from the control treatment or between treatments using one-way analysis of variance.

**RESULTS AND DISCUSSION**

**Soil Concentrations and Composition of six Target PAE Compounds**

PAE concentrations in soil samples under the different experimental treatments were determined by assaying for the six target pollutants remaining in the soil (Figure 1). Compared to the control treatment, PAE concentrations in all experimental treatments were substantially reduced with highly significant differences ($p < 0.01$), indicating that effective remediation had been achieved by using the three test plant species. The concentrations of the six PAE compounds were much lower than the soil allowable concentrations listed by USEPA (Table 1) after remediation, even though the concentrations of individual PAEs in the control were near the listed allowable concentrations (Zhang et al. 2010a). The highest

![Figure 1](image-url)  
**Figure 1** Concentrations of six PAE compounds in soil under the different treatments ($\mu$g kg$^{-1}$ DW). For treatment abbreviations see the Phytoremediation Experiment section (Materials and Methods). Each point is the mean of three replicates. Double asterisks in columns show highly significant difference at $p < 0.01$ level compared to control soil.
removal rate was observed in the alfalfa monoculture, with a total removal rate of over 90%, and the removal rates of all the other treatments also exceeded 80% (Figure 2). There are a number of factors that might explain the greater effectiveness of alfalfa monoculture compared with the other planting combinations in eliminating PAE pollutants. Alfalfa is a legume and is likely to form a nitrogen fixing symbiotic system with rhizobia in the soil. This may promote plant growth and accelerate microbial multiplication by increasing the nitrogen supply in the rhizosphere and thus contribute to phytoremediation. Root nodules with a healthy appearance were observed on roots of alfalfa when the soil samples were collected from the field plots, indicating that alfalfa was capable of dinitrogen fixation in our experiment. The large shoot biomass of alfalfa could also be an explanation because it removed 22.8 ± 0.67 mg total PAE per plot, the highest removal rate of the different experimental treatments investigated (Table 2). The PAE removal rates of the different treatments followed the order alfalfa monoculture > alfalfa/ryegrass > ryegrass monoculture > alfalfa/ryegrass/fescue > alfalfa/fescue > fescue monoculture. It has been reported that intercrops of different remediating plant species have a distinct advantage in eliminating hydrophobic pollutants such as PAHs compared with monocultures (Maila et al. 2005; Wu et al. 2007), a trend which was not apparent in the present study.

**Table 1** Soil allowable concentrations and cleanup objectives of the six PAE compounds in the US

<table>
<thead>
<tr>
<th>Compound</th>
<th>Allowable concentration (mg kg$^{-1}$)</th>
<th>Cleanup objective value (mg kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMP</td>
<td>0.020</td>
<td>2.0</td>
</tr>
<tr>
<td>DEP</td>
<td>0.071</td>
<td>7.1</td>
</tr>
<tr>
<td>DnBP</td>
<td>0.081</td>
<td>8.1</td>
</tr>
<tr>
<td>BBP</td>
<td>1.215</td>
<td>50.0</td>
</tr>
<tr>
<td>DEHP</td>
<td>4.350</td>
<td>50.0</td>
</tr>
<tr>
<td>DnOP</td>
<td>1.200</td>
<td>50.0</td>
</tr>
</tbody>
</table>

![Figure 2](https://example.com/figure2.png) Percentage of six target PAE compounds removed from test soil under different treatments ($\mu$g kg$^{-1}$ DW). Each point is the mean of three replicates.
Table 2  Shoot biomass of test plants under the different treatments

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Shoot biomass, kg DM per plot</th>
<th>PAE removal by plant shoots, mg per plot</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6.78 ± 0.20a</td>
<td>22.78 ± 0.67</td>
</tr>
<tr>
<td>P</td>
<td>2.58 ± 0.11c</td>
<td>8.01 ± 0.34</td>
</tr>
<tr>
<td>T</td>
<td>1.49 ± 0.03d</td>
<td>4.55 ± 0.09</td>
</tr>
<tr>
<td>AP-A</td>
<td>4.09 ± 0.04e</td>
<td>12.32 ± 0.12</td>
</tr>
<tr>
<td>AP-P</td>
<td>0.96 ± 0.04f</td>
<td>2.75 ± 0.11</td>
</tr>
<tr>
<td>AT-A</td>
<td>2.28 ± 0.06g</td>
<td>7.41 ± 0.20</td>
</tr>
<tr>
<td>AT-T</td>
<td>0.67 ± 0.02b</td>
<td>1.60 ± 0.05</td>
</tr>
<tr>
<td>APT-A</td>
<td>2.97 ± 0.09h</td>
<td>14.10 ± 0.43</td>
</tr>
<tr>
<td>APT-P</td>
<td>0.65 ± 0.02b</td>
<td>2.71 ± 0.08</td>
</tr>
<tr>
<td>APT-T</td>
<td>0.32 ± 0.02i</td>
<td>1.23 ± 0.08</td>
</tr>
</tbody>
</table>

For treatment abbreviations see the Phytoremediation Experiment section (Materials and Methods).
Each biomass value is the mean of four replicates ± standard derivation (SD).
Different letters in columns denote significant difference at $p < 0.05$ level between treatments.

DEHP and DnBP were found to be major PAE compounds in all the soil samples. Their initial proportions in control soil were about 90% and 7%, respectively. DEHP was the compound most effectively removed of the six target pollutants, usually with over 60% total removal except in the control. This agrees with previous conclusions regarding the relationship between structure and characteristics of PAE compounds. Compounds with longer alkyl chains are more readily adsorbed and accumulate as time proceeds. The second most effectively removed pollutant, DnBP, had total removal rates >5% (individual removal of over 70%) in the various experimental treatments (other than the control), which might be regarded as an acceptable result for phytoremediation. Alfalfa monoculture and alfalfa/ryegrass intercrop were more competitive than the other treatments, especially in elimination of DEHP. The two grass species, perennial ryegrass and tall fescue, demonstrated little difference in the removal of DEHP and DnBP in this experiment. The grasses extracted slightly more DnOP than the legume even when they were intercropped with the leguminous species.

Our results indicate the feasibility of phytoremediation of the contaminated soil irrespective of whether monoculture or intercropping was used, although the process requires a longer time period, usually more than one year, than biodegradation by microorganisms and other remediation methods such as photocatalytic degradation within 24 h (Zeeb et al. 2006; Xu et al. 2010). Alfalfa may be considered to be useful for the removal of both total PAEs and typical PAE pollutants in the soil.

Concentrations of Six PAE Compounds in Plant Shoots

Figure 3 lists and compares the concentrations of the six target pollutants in plant shoots in the different treatments. Total concentrations of the six PAE pollutants in individual plant species were high in the three-species intercrop, alfalfa/ryegrass/fescue, with almost all present at >4 mg kg$^{-1}$ (DW) in the individual species. However, alfalfa monoculture removed the largest amount of total PAE per plot of 22.8 ± 0.67 mg (Table 2) with the help of its large shoot biomass. This is equivalent to a removal rate of about 1.7 ± 0.05 mg g ha$^{-1}$ to a depth of 15 cm. Alfalfa shoots accumulated the highest concentrations of the
Figure 3 Concentrations of six PAE compounds in shoots under different treatments (µg kg⁻¹ DW). Each point is the mean of three replicates. Different letters on bars denote significant difference at $p < 0.05$ between treatments.
target pollutants. DEHP and DnBP also comprised the bulk of the total concentrations, especially in alfalfa shoots across treatments.

PAE concentrations in plant roots were not included in the study because the large root systems are difficult to sample quantitatively without soil contamination after two years of plant growth. However, variation between individual plant species might be due, at least in part, to different capacities of their root systems to take up PAEs, as this has been found to be true for PCBs (Schnoor et al. 1995). From a scientific perspective it would be preferable to include the roots to elucidate the dynamics of the pollutants in the whole soil-plant system. However, in practice the plant shoots are more important because phytoremediation involves harvesting the plant shoots and removing them from the site.

The extent of assimilation in the plant shoots depends on both extraction from contaminated soil and absorption from the atmosphere. Previous studies have suggested that atmospheric absorption is a principal route of absorption in vegetables in agricultural land near plastics manufacturing industries (Wang et al. 2010) and DEHP was absorbed mainly through the leaves (Schmitzer et al. 1988). Foliar absorption may therefore make a contribution to plant PAE absorption at our experimental site at Taizhou.

**Bioconcentration Factors in Plant Shoots**

Comparing the BCFs of PAE compounds in the shoots of the different plant species indicates that direct absorption and metabolism might be the main mechanisms by which PAE-contaminated soil is phytoremediated. The sum of the BCFs of alfalfa in the three-species intercrop was found to be the largest among all the shoot samples (Figure 4). The large biomass of alfalfa shoots may have increased the capability of this species to accumulate PAE compounds to the aboveground parts (Table 2). An advantage of intercropping is indicated by the observation that alfalfa intercropped with the other species showed larger BCFs than did alfalfa in monoculture.

**Figure 4** BCFs of six PAE compounds in shoots under different treatments (µg kg⁻¹ DW). Each point is the mean of three replicates.
Figure 5  Phytoextraction efficiency of soil PAEs under different treatments. Different letters on bars denote significant difference at $p < 0.05$ level between treatments.
The BCF of DnBP was relatively low in the three-species intercrop whereas that of DEHP was relatively low in monoculture treatments of the three plant species. An interesting observation is the large BCF of DnOP in all treatments, especially in alfalfa in the three species intercrop. The large shoot biomass of alfalfa in this treatment may have promoted the accumulation of DnOP from the atmosphere as it is present at low concentration in the soil but high in the shoots.

The BCFs of the different compounds indicate that phytoremediation can be adapted to local conditions, and alfalfa/ryegrass and alfalfa/ryegrass/fescue might be particularly useful combinations, especially for soil highly contaminated with DEHP and DnOP.

**Phytoextraction Efficiency**

Figure 5 indicates that the phytoextraction efficiency of the experimental treatments followed the order alfalfa/ryegrass/fescue > alfalfa monoculture > ryegrass monoculture > fescue monoculture > alfalfa/ryegrass > alfalfa/fescue and ranged from 1.18 to 1.78%. The three-species intercrop appeared to greatly increase the efficiency of phytoextraction compared with the monocultures. The major finding is the relatively high capability of alfalfa in removal of PAEs, but all species combinations showed some phytoremediation capacity.

**CONCLUSIONS**

Both alfalfa in monoculture and the three-species intercrop gave satisfactory removal of PAEs from the contaminated soil and intercropping appeared to make alfalfa more effective. DEHP and DnBP were the two pollutants that were present at the highest concentrations and gave the highest removal rates in soil and plant samples. Calculated BCFs indicate the substantial potential of these plant species to accumulate PAEs and the results also indicate that the atmosphere was an important source of PAEs to the plants. The ability of grasses and legumes to take up PAEs emphasizes the environmental risk from these compounds in terms of contamination of the human food chain and possible endocrine disrupting effects.

**ACKNOWLEDGMENTS**

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**REFERENCES**


**SUPPORTING INFORMATION**

**Table S1** Analysis parameters of the six PAE target compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>IDL (µg l⁻¹)</th>
<th>MDL (mg kg⁻¹)</th>
<th>Linear Equation</th>
<th>Correlation Coefficient (R²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMP</td>
<td>0.35</td>
<td>0.089</td>
<td>(y = 136.97x + 47.33)</td>
<td>0.9994</td>
</tr>
<tr>
<td>DEP</td>
<td>0.19</td>
<td>0.068</td>
<td>(y = 506.27x + 328.78)</td>
<td>0.9993</td>
</tr>
<tr>
<td>DnBP</td>
<td>0.17</td>
<td>0.097</td>
<td>(y = -598.73x + 166.04)</td>
<td>0.9995</td>
</tr>
<tr>
<td>BBP</td>
<td>0.25</td>
<td>0.073</td>
<td>(y = -2588x + 88.91)</td>
<td>0.9990</td>
</tr>
<tr>
<td>DEHP</td>
<td>0.21</td>
<td>0.118</td>
<td>(y = -2913x + 139.23)</td>
<td>0.9993</td>
</tr>
<tr>
<td>DnOP</td>
<td>0.11</td>
<td>0.135</td>
<td>(y = -245.2x + 163.77)</td>
<td>0.9991</td>
</tr>
</tbody>
</table>
Table S2 QA/QC report of PAE spiked matrix samples

<table>
<thead>
<tr>
<th>Compound</th>
<th>Recovery of EPA-8270 (%)</th>
<th>Recovery (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Given Confidence Interval (mg kg&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Determined Value (mg kg&lt;sup&gt;-1&lt;/sup&gt;)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMP</td>
<td>93.18</td>
<td>75.88 ± 4.30</td>
<td>2.85 – 3.4</td>
<td>2.72 ± 0.14</td>
</tr>
<tr>
<td>DEP</td>
<td>95.75</td>
<td>78.09 ± 3.88</td>
<td>1.29 – 1.64</td>
<td>1.55 ± 0.22</td>
</tr>
<tr>
<td>DnBP</td>
<td>90.77</td>
<td>81.20 ± 3.91</td>
<td>0.64 – 0.797</td>
<td>0.767 ± 0.19</td>
</tr>
<tr>
<td>BBP</td>
<td>91.21</td>
<td>92.33 ± 4.57</td>
<td>6.61 – 8.32</td>
<td>7.32 ± 0.19</td>
</tr>
<tr>
<td>DEHP</td>
<td>94.20</td>
<td>99.87 ± 8.91</td>
<td>0.821 – 0.961</td>
<td>0.927 ± 0.49</td>
</tr>
<tr>
<td>DnOP</td>
<td>89.90</td>
<td>107.61 ± 7.47</td>
<td>4.78 – 5.71</td>
<td>5.62 ± 0.28</td>
</tr>
</tbody>
</table>

<sup>a</sup> Mean value of recovery ± standard deviation (SD) at 0.1 mg kg<sup>-1</sup>; n = 7.  
<sup>b</sup> Mean value of recovery ± SD; n = 6.