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The thermal degradation and soil recovery of thermal treatment of field-weathered decabrominated diphenyl ether-contaminated soil

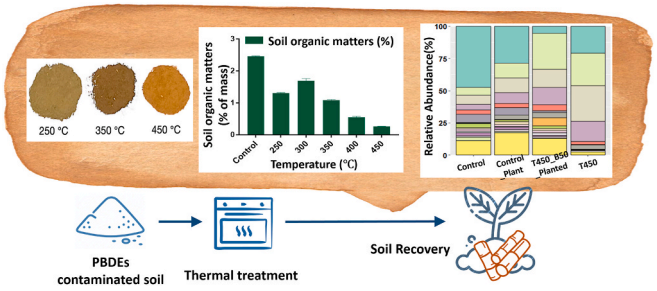
Jennifer Ia Wen Wen Liu [a,1], Yu-Jie Lin [a,1], Chi-Fong Ko [a], Jiann-yuan Ding [b], Yang-hsin Shih [a,*]

[a] Department of Agricultural Chemistry, National Taiwan University, No. 1, Sec. 4, Roosevelt Rd., Taipei, 10617, Taiwan
[b] Center of General Education, Wenzao Ursuline University of Languages, Kaohsiung, 80793, Taiwan

HIGHLIGHTS

- The thermal removal of PBDE contaminated soil in the field is debromination mechanism.
- Soil properties and soil microbial composition are related to temperature for thermal treatments.
- Sugarcane bagasse, one of agricultural residues, recovers soil functions by evaluating plant growth.
- This study achieved the goals of green remediation and environmental sustainability.

GRAPHICAL ABSTRACT



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ABSTRACT

A farm at Taoyuan in Taiwan was highly contaminated with decabrominated diphenyl ether (BDE-209), a widely used commercial brominated flame retardant and persistent in the environment, more than 10 years. Since crops are able to absorb and accumulate BDE-209 from soils in our previous research, posing a hazardous risk for humans, it is essential to develop a practical method of soil treatment. Thermal treatment was studied among different approaches. In our previous study (Ko et al., 2022), we found that heating to 450 °C for 30 min achieved a complete removal of BDE-209 in soil. However, the high temperature significantly decreased the original soil organic matter (SOM) from 2.47% to 0.27%, altering the soil texture, damaging microbial biomass, and thus affecting the revegetation after the thermal treatment. Sugarcane bagasse, a common agricultural residue, served as an amendment to restore soil fertility. Current results indicate that 2.5% bagasse can improve the SOM in soil by up to 2.73% and restore its bacterial composition, making the plant growth conditions similar to those of the untreated contaminated soil. In light of the high removal efficiency provided by the 450°C-thermal treatment and the high recovery efficiency of sugarcane bagasse, the strategy presented in this study serves to be a promising method for sustainable remediation.

* Corresponding author.
E-mail address: yhs@ntu.edu.tw (Y.-h. Shih).
[1] Equal contribution.

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1. Introduction

Polybrominated diphenyl ethers are brominated flame retardants (BFRs), a group of synthetic chemical additives that are added to polymeric components in numerous consumer products, such as plastics, textiles, electronic equipment, and furniture, to enhance their fire resistance. PBDEs are directly mixed into industrial/commercial products rather than chemically bonded to them. Once these products are discarded into landfills, PBDEs easily migrate and contaminate the surrounding soil and groundwaters (Zhang et al., 2021). PBDEs are aromatic compounds containing bromine atoms and are comprised 209 homologs. Of all the 209 kinds of PBDE congeners, only three major types of technical PBDE mixtures (Penta-BDE, Octa-BDE, Deca-BDE) are commercially available. Furthermore, Deca-BDE contains polybrominated dibenzodioxins and dibenzofurans (PBDD/Fs) as impurities both in its production and in the products (Ren et al., 2011; Sindiku et al., 2015). The highest brominated decabromodiphenyl ether (BDE-209) makes up the majority of total PBDE production because of its lower price and superior performance (Sjödin et al., 1999). Consequently, BDE-209 is the most abundant PBDE congener in aquatic environmental matrices (Zhu et al., 2014), including water, soil, sediment, plants, the human body, etc. (Sun et al., 2013). Our earlier researches revealed that there was a significant amount of PBDE pollution, primarily BDE-209, in farmlands near a northern Taiwan factory, which lingered in the soil (Chou et al., 2019) and accumulated in crops at an even higher level (Yang et al., 2018). Being so ubiquitous, BDE-209 may pose risks to not only ecosystems but also human health, and BDE-209 has been linked to possible human cancers such as kidney cancer (Li et al., 2014), papillary thyroid cancer (Hoffman et al., 2017), and breast cancer (He et al., 2018). Therefore, there is an urgent need to research its removal from environmental matrices given its persistence, bioaccumulation, and toxicity. Several degrading strategies have been revealed for the removal of PBDEs from contaminated soil (Sahu et al., 2021; Yao et al., 2021), including adsorption (Zhu et al., 2016), direct photolysis (Pan et al., 2016), photocatalytic reductive debromination and oxidative degradation (Huang et al., 2013; Li et al., 2014), nanoscale zero-valent iron (Shih and Tai, 2010a,b), phytoremediation (Deng et al., 2016), microbial transportation and degradation (Chen et al., 2018), and thermal treatment over synthesized Fe–Al oxide composites (Yang et al., 2016).

Among the currently available remediation solutions on PBDEs mentioned above, thermal treatment shows the most promise as it can remediate soil quickly and reliably (Ko et al., 2022); however, there is limited research on thermal treatment alone without any additional composite and the underlying mechanism has not been completely understood. Furthermore, thermal treatment as a forceful technology may impede land reuse as it can damage soil properties. The effects of thermal treatment on soil organic matter (Kornochalert et al., 2014), soil texture, soil cation exchange capacity, soil water holding capacity, and soil pH can have a substantial impact on soil fertility and subsequent agricultural production: heating to 620 °C for 180 min can reduce SOM by more than 90% (Vidonish et al., 2016), and the alteration of soil organic matter (SOM) from thermal treatment may also abate the uptake of available nutrients by plants.

As part of the “sustainable remediation” concept, which emphasizes the importance of incorporating sustainability principles into remediation activities, we used agricultural waste such as sugarcane bagasse, a common agricultural residue, in this study. With 0.28 tons of sugarcane bagasse generated for every ton of sugarcane produced, 448 million tons of bagasse are generated each year worldwide (Schmitt et al., 2020), and finding a useful application of bagasse waste would be extremely valuable. Composed predominantly of cellulose, hemicellulose, and lignin, sugarcane bagasse is hydrophilic (Thiangtham et al., 2019), which gives it a high capacity for water and ion uptake, thus making it an ideal material for recovering thermally damaged soils. Sugarcane bagasse could also be recognized as a soil amendment because of its promising ability to increase the availability of phosphorus in soil. Dotaniya and Datta (2014) showed that combining rice straw with bagasse and press mud increased the availability of phosphorus in soil by 68%. In addition, sugarcane bagasse could also serve as an organic carbon source for microorganisms (Mustafa et al., 2020), accelerate the microbial activities in soil, and thus improve soil microbial diversity. With the advantages mentioned above, sugarcane bagasse shows great potential to restore thermal-treated soil. To evaluate the suitability of sugarcane bagasse for cultivation, we used *Ipomoea aquatica*, a widely cultivated vegetable in Asia, as a bioindicator.

The aim of this study was to investigate the mechanism of PBDE degradation in its contaminated soil by thermal treatment, explore how the treatment alters soil properties, and propose a soil function restoration strategy.

2. Material and methods

2.1. Site description and soil collection

A sampling site for PBDE-contaminated land has been described previously (Chou et al., 2019; Ko et al., 2022; Yang et al., 2018). In short, the soil sample was retrieved from Taoyuan, Taiwan, with geographical location 121.2° E in longitude and 25.1° N in latitude. The farmland is near a factory, which historically utilized BFRs - mainly BDE-209 - in its products. The exhaust gas released from the manufacturing vent, whose air outlets face the primary contaminated location, is the cause of PBDE pollution. According to the soil sampling approach we specified (Chou et al., 2019), soil samples were collected from the site for this study.

2.2. Thermal treatment

Thermal treatment was performed in a box furnace with a programmable controller (Nabertherm, B-150, Germany) as described in our previous study (Ko et al., 2022). In brief, an appropriate amount (less than 1000 g) of the soil sample was placed in a heat-resistant container and heated in an electric furnace for a thermal treatment test after drying, grinding, and sieving. The effects of temperature on the elimination of PBDEs were examined in this study using temperatures between 100 and 450 °C, adjusted in steps of 50 °C.

2.3. Quantification of PBDEs and qualification of byproducts

Sample extractions were performed in accordance with USEPA 1614 (U. S. EPA, 2007), with a slight modification as covered in our previous study (Yang et al., 2018; Chou et al., 2019; Ko et al., 2022). In short, 2 g of soil samples were extracted using a 3 mL combination of *n*-hexane and acetone (1:1, V:V) numerous times until the concentration of PBDEs in the extract was below the detection limit. PBDEs in the extracts were analyzed by an Agilent 6890 gas chromatograph (GC) equipped with a micro electron capture detector (μECD). Samples were injected to a 300 °C injection port in splitless mode and separated on a DB5-HT column capillary column (15 m × 250 μm × 0.1 μm) with nitrogen as the carrier gas at a flow rate of 7 mL/min. The oven was held initially at 110 °C for 5 min, increased to 200 °C at 25 °C/min and then increased to 300 °C at 10 °C/min and held for 5 min. The byproduct identification during degradation was determined with a GC–MS (Agilent 5975 inert MSD), using column and chromatographic conditions identical to those of the GC-μECD system (Peng et al., 2013; Shih et al., 2012; Shih and Tai, 2010a,b; Shih and Wang, 2009). Considering the low concentration of byproducts in the contaminated soil samples after thermal treatment, soil samples were additionally spiked with 43.7 ± 7.63 mg/kg BDE-209 for byproduct identification. De-brominated products in samples after thermal treatment were identified by setting the retention time ranges for each congener group using the isotope ^{13}C-labeled surrogate standards of the PBDEs (MBDE-MXG) purchased from Wellington Laboratories (Ontario, Canada).

Quality assurance and quality control (QA/QC) were performed during the experiments. Average recoveries of the $^{13}C_{12}$ labeling of PBDEs as internal standard for BDE-28, -47, −100, −99, −126, −154, −153, −183, −197, −207, −209 and their detection limit of congeners were the same as we presented in our previous papers (Chou et al., 2019; Ko et al., 2022). For quality control, sample blank was carried out in each analysis along with the sample collection. Instrument blanks were also performed every 10 sample injections.

2.4. Soil analyses

Soil texture was determined using a hydrometer via the Bouyoucos Method. The water holding capacity (WHC) was measured by soaking 15 g of soil samples in 15 mL water for 1 week and then allowing the water to drain for 1 week. Soil pH and electrical conductivity were recorded using an EXstik pH/Conductivity meter (EXTECH, USA) after an hour of extraction in a soil:water mixture (1:1). Soil organic content (SOC) was analyzed using an elemental analyzer (Vario Microcube, Bruker, Germany). The contaminated soil from the site was clay loam, consisting of 37% sand, 29% silt and 34% clay. The pH value of the soil was 7.74, and its estimated content of soil organic matter was 2.3%.

2.5. Thermal-treated soil restoration

Sugarcane bagasse was purchased from Taiwan Sugar Corporation (Tainan, Taiwan) and was employed in the soil samples after thermal treatment. The percentage of nitrogen (N), total phosphorus (P_2O_5), total potassium (K_2O), and organic matter in the sugarcane bagasse was determined to be 1.0%, 0.6%, 0.8%, and 56%, respectively. For the soil restoration experiment, 1 kg soil samples were treated with 25–200 g of sugarcane bagasse and mixed properly before planting.

2.6. Ipomoea aquatica growth experiment

All experiments were conducted in growth chambers with a 16/8 h light/dark cycle and held at a constant temperature of 25 °C. Each pot (8.5 cm diameter × 7 cm height) contained 1 kg soil (dry weight). Seeds of *Ipomoea aquatica* were purchased from Green Orchids Corporation (New Taipei City, Taiwan). Seeds subjected to germination were sterilized in 75% ethanol for 10 min and then in 0.1% sodium hypochlorite for 5 min, followed by rinsing with sterilized distilled water. Five seedlings were transferred to each pot after germination in sterile petri dishes at 25 °C for 3 days. The treatments were fully randomized and repositioned weekly. The soil moisture content was maintained by watering every other day. The shoot length of *I. aquatica* and the number of leaves for each seedling were recorded as an indication of growth performance.

2.7. Microbial analysis

Soil DNA was isolated using a DNeasy PowerSoil Pro Kit from Qiagen Inc. (Hilden, Germany) and amplified using a 341F-805R primer set (341F: 5′-CCTACGGGNGGCWGCAG-3′, 805R: 5′-GACTACHVGGGTATCTAATCC-3′), designed to target the V3 and V4 regions of the bacterial 16S rDNA. The 450–500 bp fragments amplified by PCR were excised during gel extraction and purified using a QIAquick Gel Extraction Kit (Hilden, Germany). Sequencing libraries were generated using a TruSeq Nano DNA Library Prep Kit from Illumina (San Diego, USA) following the manufacturer's recommendations. The Illumina Miseq platform was used in sequencing and 300 bp paired-end reads were generated at Genomics BioSci & Tech Ltd., (New Taipei City, Taiwan).

Paired-end reads were trimmed using the Cutadapt program, merged with FLASH v1.2.11, and analyzed by FastQC v0.11.5 and MultiQC v0.9 for quality control. The operational taxonomic unit (OTU) was picked with Mothur v.1.39.5 that had 97% identity. Chimera sequences were identified using UCHIME v4.2 using the Gold database for reference data. The sequences from various OTUs were compared with representative sequences from the SILVA database to perform species annotation (Pedregosa et al., 2011). The statistical number of sequences in each sample at each level of classification was estimated based on species annotation. The dominating bacterial taxa (>2%) were expressed in terms of their relative abundances (percentage of each OTU in the total OTUs) at the phylum and family levels.

2.8. Statistical analyses

Statistical analyses were performed in R version 4.1.2 (R Core Team, 2021). Differences in the microbial community composition associated with each sample were visualized using the packages vegan (Dixon, 2003), phyloseq (McMurdie and Holmes, 2013), ggplot2 (Villanueva and Chen, 2019), and dplyr (Wickham et al., 2021). Significance levels were tested using Fisher's Least Significant Difference (LSD) test with a threshold of $P < 0.05$.

3. Results and discussion

3.1. Removal efficiency

The initial concentration of BDE-209 in the soil samples was 1.472 mg/kg. As described in our previous work (Ko et al., 2022) and Fig. 1, the heating temperature at 450 °C for 30 min was efficient to completely remove the contaminant from the soils. For temperature at 250 °C, 300 °C, 350 °C, and 400 °C for 30 min, the average removal efficiencies were 59.7%, 75.6%, 89.9%, and 98.1%, respectively (Fig. 1). However, after heating soils to 450 °C for 30 min, the content of SOM in soils reduced more than 89%. For temperature at 250 °C, 300 °C, 350 °C, and 400 °C for 30 min, SOM decreased 46.7%, 31.1%, 55.9%, and 77.8%, respectively. The thermal degradation of this field-weathered decabrominated diphenyl ether-contaminated soil was also observed not only PBDEs. Furthermore, some studies have also shown that higher temperatures cause more damage to the soil during the heat treatment (Song et al., 2019), not to mention their higher energy requirements. Lowering the temperature is beneficial for saving energy and alleviating the damage to soil properties while still achieving a good removal efficiency of the pollutants (Ren et al., 2020).

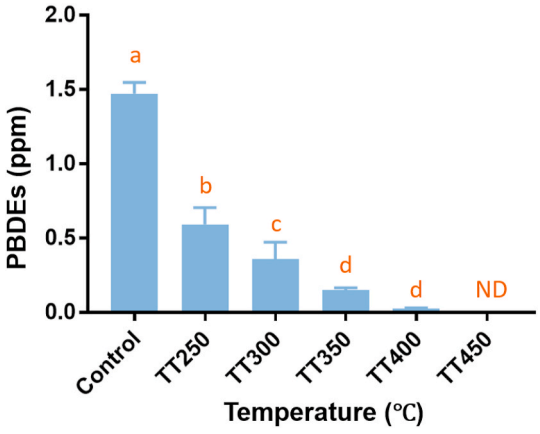

Fig. 1. Effects of temperature on the removal of PBDEs in the contaminated soil (Ko et al., 2022). The initial concentration of PBDEs in contaminated soil was 1.472 mg/kg. Thermal treatment was conducted at different temperature and held for 30 min. Data represent mean values (±SD) of three replicates. Values denoted by the same letter are not significantly different according to the Fisher's (LSD) test at $P \leq 0.05$.

3.2. Thermal degradation mechanism of PBDEs in soil

Since only the detection of bromide ions was investigated in our previous work (Ko et al., 2022), the PBDE degradation mechanism in soil was previously not studied. To investigate the byproducts of thermal degradation, the soil samples were artificially contaminated with DBDE, achieving a final concentration of 43.7 ± 7.63 mg/kg, and all soils samples were treated from 250 °C to 450 °C for 1 h.

At a temperature of 250 °C, three byproducts were observed: BDE-208, BDE-209, and Mono-BDE. For the 300 °C trial, byproducts from Mono-to Octa-BDE could be observed in the spectra, with the exception of Tri-BDE. At 350 °C, byproducts from Mono-to Penta-BDE remained. For the 400 °C treatment, Mono-DBE, Di-BDE and Tri-BDE were observed, while at 450 °C, Mono-DBE, Di-BDE, Tri-BDE, and Penta-BDE by-products were observed (Fig. 2). According to these observations, at lower temperatures, DBDE starts to lose few bromine at time, identifying structures with high number of bromines bound, and when elevating the temperature, more Br–C bond is broken, releasing more bromines from PBDE structures and leaving behind less brominated structures. This Br–C bond breakage was observed in our previous work by detection of bromide ions in the samples (Ko et al., 2022) and explains the increase of the bromide ions with increasing temperature.

Research on thermal treatment for PBDE removal is rather rare, and thermal treatment of PBDEs-contaminated soil without any composite was even rarer. Hydrothermal treatment for BDE-209 degradation was reported to decompose BDE-209 by more than 99% after 10 min at 300 °C (Nose et al., 2007). On the other hand, thermal treatment using synthesized materials such as Fe–Al composite oxides (Yang et al., 2016) and flowerlike LiαTiOx micro/nanostructures (Li et al., 2017) were reported to successfully degrade PBDEs through hydrodebromination. Furthermore, Weber and Kuch (2003) indicated that pyrolysis of BFRs can produce considerable amounts of PBDD/Fs. Buser (1986) reported the highest yields of PBDD/Fs from pure PBDEs at around 600 °C in his short term experiments of 60 s, with a total yield of 10%. As a gas phase reaction (Striebich et al., 1991), this temperature range for the optimal formation of PBDD/Fs during PBDE pyrolysis is 600–700 °C. A stepwise formation pathway of PBDDs from oxidation of PBDEs by quantum chemical calculations (Altarawneh and Dlugogorski, 2013) is consistent with the experimental results of the pyrolysis of PBDEs only (Liang et al., 2020). Under these high temperature, dioxin-like compounds were formed. However, in the temperature range of 250–450 °C we applied in this weathered PBDEs-contaminated soil in this study, we cannot analyze these dioxin-like compound due to our limited resource of instruments and standards. Lu et al. (2017) indicated that PBDFs were produced at extreme high levels when ball milling equipment was operated at 270 °C in the destruction of Deca-BDE in soil; however, no PBDD/Fs was observed when the temperature was cooled to 60 °C. It remains to be investigated whether dioxin-like compounds such as PBDD/Fs can be generated at the temperatures we provided in our study.

The temperature we applied in this study was lower than studies in the absence of any media or synthesized composite materials. A similar phenomenon was observed in the in low-temperature pyrolysis of pentachlorophenol (PCP)-contaminated soil (Thuan et al., 2013). PCP decomposition did not occur in the absence of soil during pyrolysis in the temperature range of 200–400 °C. This indicated that soil is essential for decomposition of contaminants in this temperature range. Considering soil components, such as iron, aluminum, and manganese, could serve as catalysts, and soil organic matter could serve as hydrogen donors. Therefore, soil components play a key role in thermal decomposition, and the natural soil components may act as catalysts such as the synthesized composite material but there are more complicated processes in soils.

3.3. Effects of heating temperature on the color and composition of contaminated soil

Fig. 3 shows the changes in the physical appearance of soil samples when exposed to elevated temperatures. As depicted in the figure, the PBDE contaminated soil samples changed from a brown/gray to a brown/red hue as the temperature was raised from 250 °C to 400 °C. Redness in soil may be caused by elevated temperatures transforming iron oxides (Sumner, 1999). When the heating temperature was extended to 450 °C, there were no further significant changes in the soil color.

The soil texture shifted from clay loam to loam when heated to 250 °C, and remained loam as the temperature increased to 450 °C. For the 450 °C thermal treatment, the clay content decreased from 34% to 21%, whereas the silt and sand content increased from 29% to 36% and from 37% to 43%, respectively. As shown in Fig. 3b, the soil organic matter content gradually but not consistently decreased as the heating temperature increased. Due to the soil heterogeneity and low thermal conductivity of soil, the temperature had risen but the decomposition of soil carbon may not increase correspondingly. Overall, the soil

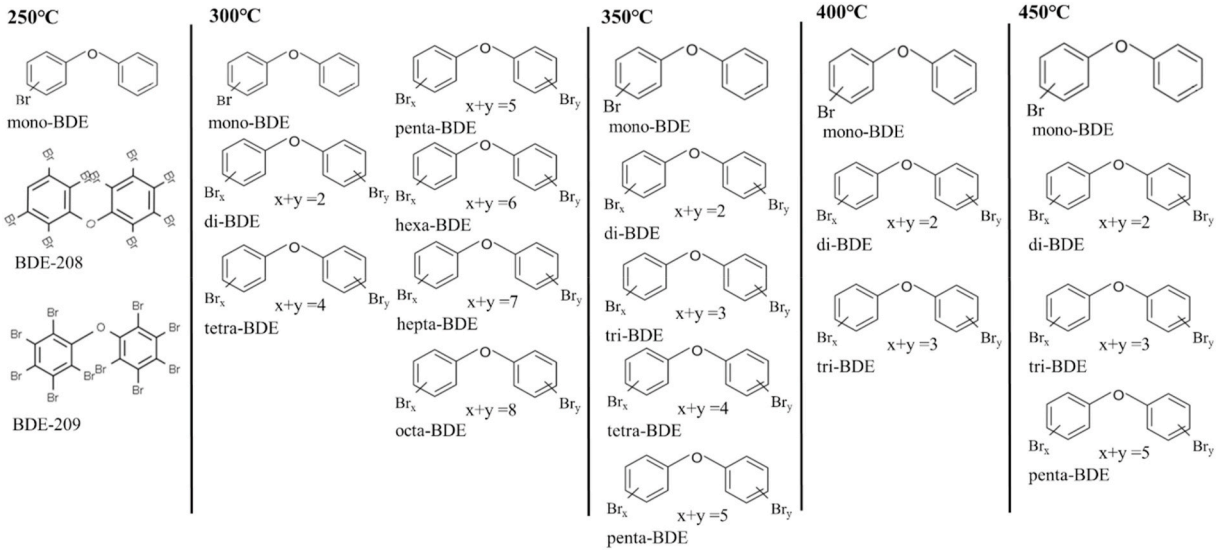

Fig. 2. Thermal degradation by-products of BDE-209 identified at various temperatures. De-brominated products were identified by setting the retention time ranges for each congener group using the 13C-labeled surrogate standards of the PBDEs.

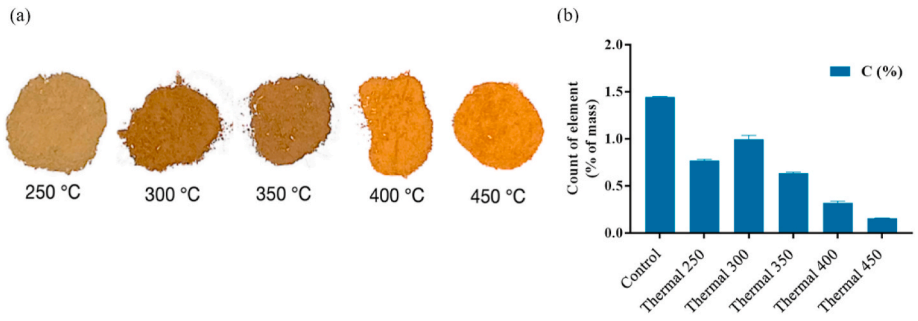

Fig. 3. Effects of heating temperature on soil physiochemical properties. (a) Difference in color. (b) Difference in soil organic matters. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

degradation of this thermal treated PBDE-contaminated soil was significantly found.

3.4. Soil recovery with the application of sugarcane bagasse

Generally, the soil texture was loam after the 450 °C thermal treatment and the changes caused by sugarcane bagasse were not significant. Soil pH did not change significantly after applying sugarcane bagasse; however, sugarcane bagasse from 2.5% to 10% resulted in an increase in electrical conductivity from 2.54 to 3.86 μS. Although soil organic matter declined immediately following the 450 °C heating, with the spike of sugarcane bagasse, its recovery was rapid (Table S1). In response to sugarcane bagasse application, the soil organic matter increased significantly (Fig. 4). Compared with the 450 °C-treated soil samples, the soil organic matter improved up to 2.73% under 2.5% sugarcane bagasse treatment, and with the addition of 10% sugarcane bagasse, the soil organic matter ameliorated 18-fold. Essential elements, including carbon, nitrogen, and hydrogen, in the soil significantly increased with the application of sugarcane bagasse, compared with the 450 °C-treated samples. However, there were no further significant increases in these essential elements when the doses of sugarcane bagasse increased further.

3.5. Plant growth trials

Ipomoea aquatica was grown in each of the soil treatments (PBDE contaminated controls, 450 °C thermal treatments, and bagasse-applied treatments) to quantify the effects of soil changes on plant growth (Fig. 5). All the plants thrived and none of them died during the experiment. A significant difference in shoot length was observed after applying sugarcane bagasse for 21 days. After its application to the 450 °C-treated soils for 9 days, 2.5% sugarcane bagasse helped recover up to 100% of *I. aquatica* shoot length, as compared to the controls. When its concentration was increased to 10%, the sugarcane bagasse

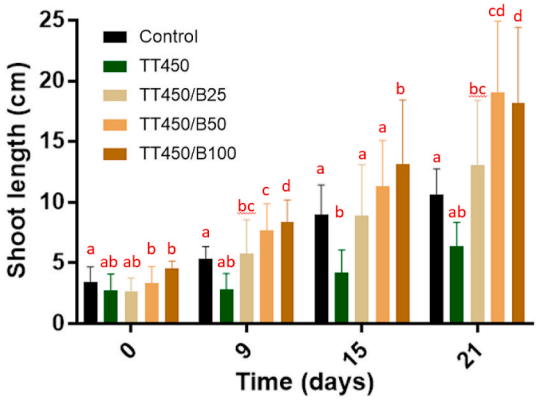

Fig. 5. Effect of sugarcane bagasse on the height and base diameter of *Ipomoea aquatica* seedlings. Data represent mean values (±SD) of three replicates. Values denoted by the same letter at each time point are not significantly different according to the Fisher's (LSD) test at $P \leq 0.05$.

enhanced plant growth by up to 2.98-fold. Moreover, a dose-dependent effect on shoot elongation was observed after 15 days. The application of sugarcane bagasse at 2.5%, 5.0%, and 10% for 15 days increased shoot length by 10.5%, 67.5%, and 112%, respectively. However, the absence of the dose-dependent effect after 21 days may have resulted from *I. aquatica* reaching its growth limitation. The effect of 2.5–10% sugarcane bagasse on the growth of shoots indicates that sugarcane bagasse could be a rapid recovery treatment for recovering soil function.

3.6. Changes in bacterial composition

After sequencing and quality filtering, we obtained a total of 356,331 high-quality 16S rRNA sequence reads across all soil samples; to achieve and maintain the sequencing quality, samples of 450 °C thermal

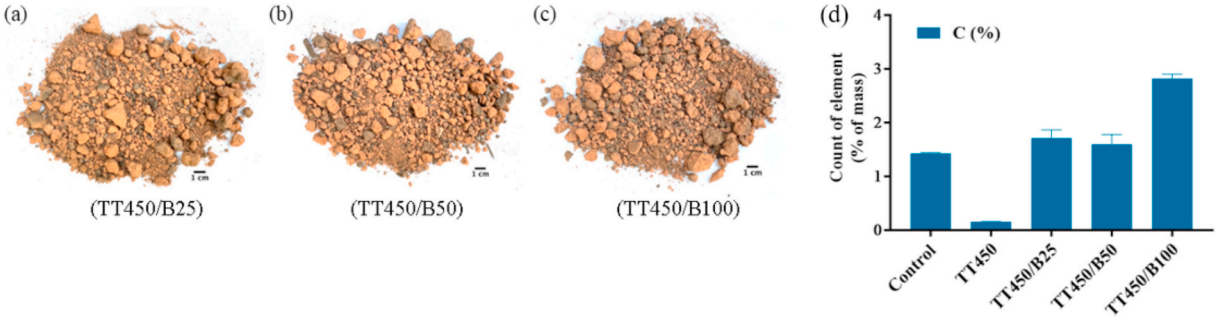

Fig. 4. Dose effect of sugarcane bagasses addition on 450 °C-treated soil physiochemical properties. (a–c) Color of different soil samples (TT450/B25: 25 g sugarcane bagasses in 1 kg 450 °C-treated soil; TT450/B50: 50 g sugarcane bagasses in 1 kg 450 °C-treated soil; TT450/B100: 100 g sugarcane bagasses in 1 kg 450 °C-treated soil). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

treatment and 50 g sugarcane bagasse application were omitted. As 450 °C thermal treatment nearly eliminated all the microorganisms in the soil, we barely collected any microbial biomass from samples immediately after the 450°C-treatment and the subsequent bagasse application. The total soil DNA concentrations in the control, 250°C-treatment, and 450°C-treatment were determined to be 63.4 ng/μL, 3 ng/μL, and non-detectable, respectively. Therefore, 250 °C treated samples were used in place of 450 °C treated samples for the microbial community analysis, and a significant difference was noticed in the 250 °C thermal treated samples. Despite the fact that soil heating is detrimental to microorganisms, heating at lower temperatures such as 250 °C or below may not sterilize the soil but rather eliminate specific bacteria and pose an increase in other species (van der Voort et al., 2016).

In Fig. 6, the microbial composition of untreated contaminated soil (control), untreated contaminated soil planted with *I. aquatica* (control_plant), contaminated soil spiked with 5% sugarcane bagasse after 450°C-thermal treatment (t450_B50_plant), and contaminated soil after 250°C-thermal treatment (thermal250) were compared to investigate the effect of thermal treatment and sugarcane bagasse addition on soil restoration. Major bacterial phyla and classes of Bacilli, Actinobacteria, Chloroflexia, Thermoleophilla, and alpha-, gamma- and delta-proteobacteria were present in all treatments and their relative abundances in different treatments differed. Relative abundances of Bacilli decreased in all the treatments compared to the control, and the decline in the relative abundance of Bacilli was related to a concomitant increase in the abundance of Actinobacteria (up 4.61-fold in the 250°C-thermal treated samples) suggesting that organisms in the class of Actinobacteria tend to recover from the thermal treatment more rapidly than organisms in the class of Bacilli. In addition to Actinobacteria, thermal treatment significantly enhanced the relative abundance of alpha-proteobacteria - by 3.91-fold compared with the control (Fig. 6A). Notably, Proteobacteria was reported to be enriched in the BDE-209 treatments (Zhang et al., 2016), which demonstrates a discrepancy with our finding that the relative abundance of Proteobacteria, including alpha-proteobacteria, delta-proteobacteria, and gamma-proteobacteria subsided when BDE-209 was eliminated through thermal treatments.

Bray-Curtis dissimilarity is one of the most commonly-used metrics for beta diversity. The dissimilarity matrix compares the abundances of microbes that are shared between two treatments and the number of microbes found in each. As shown in Fig. 6b, at genus level, the community pattern was similar in the control groups (PBDE contaminated soils before and after *I. aquatica* cultivation). As expected, the bacterial composition in thermal treated soils was significantly altered. However, only a slight dissimilarity between the samples spiked with 5% sugarcane bagasse after 450°C-thermal treatment and *I. aquatica* cultivated control was revealed. This suggests sugarcane bagasse application along with *I. aquatica* cultivation could gradually restore soil bacterial community structures (Fig. S1).

Despite several reports that total soil microbial biomass can persist in field conditions heated up to 200 °C (Acea and Carballas, 1999), or up to 300 °C-400 °C (Bárcenas-Moreno and Bååth, 2009), we found most of the soil microbial biomass was lost in this study. Soil samples heated at 250 °C lost 62% of their biomass, and microbial biomass in samples was hardly detected when heated at 450 °C. However, microbial biomass was estimated at 84.7 ng/μL, suggesting microbial biomass was restored after the sugarcane bagasse application and *I. aquatica* cultivation for 21 days. Changes in relative abundance supported this observation as well; the combination of *I. aquatica* with sugarcane bagasse amendment resulted in a similar pattern in relative abundance at class level compared with the planted control (Fig. 6a). In addition, alpha diversity indices showed bacterial diversity was higher in the planted treatments, and highest in the combination of *I. aquatica* and sugarcane bagasse treatments than in all the other treatments. These results indicated that thermal treatments not only deteriorate the bacterial biomass, but also cease the bacterial diversity. In contrast, the application of sugarcane bagasse significantly improved the bacterial diversity. Previous studies have found several types of microorganisms such as fungi (Peng et al., 2021), bacteria (Zhou et al., 2021), and microalga (Nguyen et al., 2018) that have been cultured on sugarcane bagasse, attesting to the fact that sugarcane bagasse is a carbon source for a wide range of microorganisms. Aside from sugarcane bagasse, we found that the cultivation of *I. aquatica* played a crucial role in altering soil bacterial composition.

4. Conclusion

A farm in Taoyuan is highly contaminated with BDE-209 (1.472 mg/kg). Since crops were found to absorb and accumulate BDE-209 from contaminated soils, it is crucial to establish a feasible treatment method to remove BDE-209. Thermal treatment by heating soil at 450 °C for 30 min achieved a complete removal of BDE-209. By-products of thermal degradation were also identified: at 450 °C, Mono-DBE, Di-BDE, Tri-BDE, and Penta-BDE by-products were observed.

Regarding the efficiency of PBDE removal provided by thermal treatment, the high temperature altered soil properties. For thermal treatment at 450 °C, the clay content of the soil decreased from 34% to 21%, whereas the silt and sand content increased from 29% to 36% and from 37% to 43%, respectively. The 450 °C thermal treatment also significantly decreased soil organic matter, damaged microbial biomass, and changed soil color. The thermal degradation of soil properties was obvious. To amend the soil, adding agricultural material leftovers, such

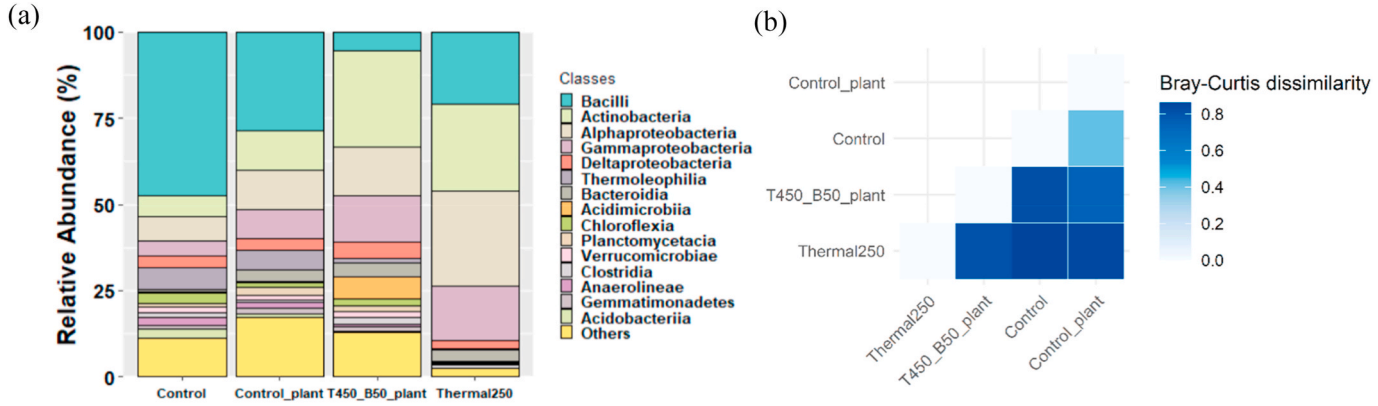

Fig. 6. Bacterial community response. (a) Relative OTU abundance at the class level. (b) Heatmap illustrating Bray–Curtis similarities (β-diversity) based on taxonomic assignments (genus level). Control: untreated contaminated soil, control_plant: untreated contaminated soil planted with *I. aquatica*, t450_B50_plant: contaminated soil spiked with 5% sugarcane bagasse after 450°C-thermal treatment, thermal250: contaminated soil after 250°C-thermal treatment.

as 2.5% bagasse, could increase SOM in soil by up to 2.73% and make the plant growth conditions similar to those of untreated contaminated soil. *Ipomoea aquatica* was grown in each of the soil treatments to quantify the effects of soil changes on plant growth. A significant difference in shoot length growth was observed after applying 2.5% sugarcane bagasse for 21 days, suggesting sugarcane bagasse to be a promising fertilizer for soil restoration. Bacterial community response was also illustrated: organisms in the class of Actinobacteria tended to recover from the thermal treatment more rapidly than other classes. Other than relative abundance, from the Bray-Curtis dissimilarity analysis, a remarkable difference was detected in bacterial composition in thermal treated soils, and the sugarcane bagasse application seemed to restore the bacterial composition.

Author contributions

Jennifer Ia Wen Wen Liu: Conceptualization, Methodology, Validation, Investigation, Writing- Original draft preparation; **Yu Jie Lin**: Formal analysis, Investigation, Data curation, Visualization, Writing-Original draft preparation; **Jiann-yuan Ding:** Data Curation, Reviewing and Editing; **Yanghsin Shih**: Supervision, Writing- Reviewing and Editing, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2023.137736.

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