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Identification of dioxin and dioxin-like polychlorbiphenyls in plant tissues and contaminated soils

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Abstract

The environmental analysis laboratory (EAL) of the Taiwan environmental protection administration (TEPA) has been monitoring certain sites polluted in southern Taiwan by pentachlorophenol manufacture. The analytical results revealed peculiarities in the concentration distributions in plant tissues. There are no available data on dioxin and dioxin-like polychlorbiphenyls (DL-PCBs), which can be taken up from contaminated soils by plant tissues. Thus, the aims of this study were to identify, understand, and to validate these dioxin and DL-PCBs concentrations in plant tissues of the contaminated soils. This research analyzed ten species of plant tissues, including tappa (*Boussonetia papyrifera*) and common jasmin orange (*Murraya paniculata*) from sites in southern Taiwan, with different levels of contamination. Dioxin concentrations in these plant tissues ranged from 12.7 to 2919 ng WHO-TEQ_{DF}/kg dry weight (d.w.), with average of 463 ng WHO-TEQ_{DF}/kg d.w. ($n = 16$). The DL-PCBs concentrations ranged from 0.236 to 1.75 ng WHO-TEQp/kg d.w., with an average of 0.605 ng WHO-TEQp/kg d.w. ($n = 8$). Tappa is one of the most common and fastest growing plants in Taiwan. It also shows the highest tolerance to environmental contaminants and accumulates dioxin and DL-PCBs. This is one of the best species to take up dioxins and DL-PCBs effectively. It can be recommended as a candidate for dioxin and DL-PCB phyto-remediation. These data are useful to evaluate bioaccumulation of dioxin and DL-PCBs, and to study the capability of phyto-remediation in contaminated soils.

Keywords: Bioaccumulation; Contaminated soils; Dioxin; Dioxin-like polychlorbiphenyls (DL-PCBs); Phyto-remediation; Plant tissues

1. Introduction

A review of recent studies on organic pollutant accumulation in plants, the resource air pollutions [1] and soil dusts [2] sorbed by foliages [3,4] indicate that there has been little consideration of phyto-remediation for dioxin pollution. The reports of dixion accumulated in plants included fruits [5], vegetable [6], bayan leaves [7], pine (*Cedrus deodara*) needles [8–10], grass and weeds [11], and needles of spruce tree [12]. Particles and associated particle-bound PCDD/Fs would sorb to leaf surfaces, and are subject to removal via wash off. However, in areas where emissions to air are not very notable, vapor absorption would be the principal source of vegetation pollution. The results of this investigation can have a potential interest in risk assessment studies and environmental fate models.

The environmental analysis laboratory (EAL) of Taiwan environmental protection administration (TEPA) has been monitoring certain sites polluted by pentachlorophenol manufacture, finding a peculiar distribution of plants in southern Taiwan. We observed both a single plant zone and zone where symbiosis occurred. For a better understanding of the implicit effects behind these observations, EAL initiated a project to collect ten kinds of plants, including tappa (*Boussonetia papyrifera*), common jasmin orange (*Murraya paniculata*), in several specific contaminated soils. There are no available data on the uptake of dioxin and dioxin-like polychlorbiphenyls (DL-PCBs), by plant tissues of contaminated soils. Thus, the aims of this study were to identify, understand, and to validate these dioxin and DL-

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PCBs concentrations in plant tissues of the contaminated soils. The EAL conducted a research project, sampling and analyzing 10 plant species, including tappa (*B. papyrifera*), common jasmin orange (*M. paniculata*), in areas with different levels of contamination.

2. Materials and methods

2.1. Plant tissues

Ten plant species and contaminated surface soils (0–15 cm) were collected from dioxin-polluted sites in the southern Taiwan that were characterized as medium (four plant tissues) and highly (six plant tissues) contaminated areas in 2002 (e.g., interior report of the TEPA). All plant tissues were cleaned with double distilled water (DDW) before further pre-treatment.

2.2. Analytical methods

USEPA Method 1613B [13] and Method 1668A [14] were used as analytical methods in this study. Plant tissues were chopped, homogenized, dried, ground into fine particles and passed though a 20 mesh sieve. An appropriate amount (5–10 g) of ground samples was accurately weighed and placed in a Whatman glass microfiber thimbles (43 mm × 123 mm) to avoid any interference. Isotope standards (IS) (M1613-IS for dioxin and M1668-IS for PCBs) were added to each thimble, respectively. Then, the thimble was extracted in a Soxhlet extractor with acetone/*n*-hexane (1:1) at 70 °C for 24 h. The extract was concentrated with a vacuum concentrater (rotary evaporator). After adding clean-up standards of M1613-CS to monitor the clean-up procedures, the concentrations of dioxins were analyzed with acidic silica gel and sulfuric acid/silica gel column, followed by 8% AX-21/celite 545 carbon column eluted with 50% benzene/methylene chloride which were collected for recovering DL-PCBs, and then reverse the carbon column eluted with toluene for recovering dioxins. Then, these elute solvent flux were blow dried with nitrogen gas. After adding recovery standards of dioxin M1613-RS for the dioxin part and of the DL-PCBs M1668-RS for DL-PCBs part, the final sample extracts were analyzed for dioxins and DL-PCBs using a high resolution gas chromatograph/high resolution mass spectrometer (HRGC/HRMS). The instrument model was the Micromass Ultima AutoSpec with a resolution of 10,000 (10% valley). Electronic resource was selected for the ion-monitoring mode, and the source temperature was 280 °C. The GC used was an Agilent 6890/CTC auto-sampler, equipped with a split/splitless injection port at 300 °C and a 60 m long DB-5MS column (J&W Scientific). Helium was used as carrier gas at the flow rate of 1 mL/min. The temperature program of dioxin analysis was as follows: initial temperature 150 °C (3 min), rate: 30 °C/min raise to 210 °C (15 min), then rate: 1.5 °C/min until 230 °C (5 min), then final rate: 15 °C/min raise to final temperature 310 °C (12 min). The DL-PCBs analysis temperature program was as follows: initial temperature at 150 °C (1.5 min), then rate: 30 °C/min raise to 210 °C (15 min) and rate: 1.5 °C/min till 230 °C (5 min), final rate: 15 °C/min raise to final temperature 310 °C (8 min).

3. Results and discussion

The dioxins concentrations in ten plant tissues ranged from 1000 to 1,100,000 ng I-TEQ/kg, for the following plants: (1) tappa (*B. papyrifera L.*), (2) common jasmin orange, (3) *Casuarina equisetifolia*, (4) *Albizia lebbeck*, (5) *Bidens chilensis*, (6) *Momordica charantia.* The dioxin concentrations ranged from 152 to 1784 ng WHO-TEQ_{DF}/kg dry weight (d.w.), for the following tissues of: *B. papyrifera* (*L.*) root, *B. papyrifera* (*L.*) leaf, *M. paniculata Jack. Var. paniculata* leaf, *M. paniculata Jack. Var. paniculata* stem, *Momordica* sp. stem and leaf, *Momordica* sp. leaf, *Bidens pilosa L.* stem and leaf, *Bidens pilosaL.* leaf, *C. equisetifolia Forst.* leaf, *C. equisetifolia Forst.* stem, and *A. lebbeck* (*Willd.*) *Benth* leaf. We found that leaf dioxin concentrations of *B. papyrifera* (*L.*) are higher than root concentrations [8,10–12]. Four kinds of plant samples collected from areas of medium contamination, with concentration range of dioxins in the soil of 100–900 ng I-TEQ/kg, were *Phargmites communis* (*L.*) *Trin* (reed), *Zoysia* sp. (sandbur), *Physalis angulated* and *Solanum nigrum L.* , (nightshade).

The concentrations of dioxins in plant tissues ranged from 12.7 to 632 ng WHO-TEQ_{DF}/kg d.w. The dioxin concentration in the *Physalis angulatal* roots is higher than that in leaves, as shown in Table 1. The highest concentration was found in the leaf of *B. papyrifera* (*L.*), which was 2919 ng WHO-TEQ_{DF}/kg d.w., followed by the root of *P.angulatal*, of 1136 ng WHO-TEQ_{DF}/kg d.w. The percentage contribution of each polychlorinated dibenzo-*p*-dioxins (2,3,7,8-PCDDs) and polychlorinated

Table 1
Dioxin concentrations (ng WHO-TEQ_{DF}/kg d.w.) in different plant tissues at different concentration range of contaminated area

Concentration range of contaminated soils	Species name	Root	Stem and leaf	Leaf	Stem	Full plant	Average
1000–1,000,000 ng I-TEQ_{DF}/kg d.w.	*Boussonetia papyrifera* (*L.*)	649	–	2919	–	–	1784
	Murraya paniculata Jack. Var. paniculata	–	–	602	190	–	396
	Momordica sp.	–	172	331	–	–	252
	Bidens pilosa L.	–	152	–	–	–	152
	Casuarina equisetifolia Forst.	–	–	315	44.7	–	180
	Albizia lebbeck (*Willd.*) *Benth*	–	–	258	–	–	258
100–1000 ng I-TEQ_{DF}/kg d.w.	*Phargmites communis* (*L.*) *Trin*	–	–	–	–	21.0	21.0
	Zoysia sp.	–	–	–	–	12.7	12.7
	Physalis angulatal	1136	127	–	–	–	632
	Solarium nigrum L.	401	79.5	–	–	–	240

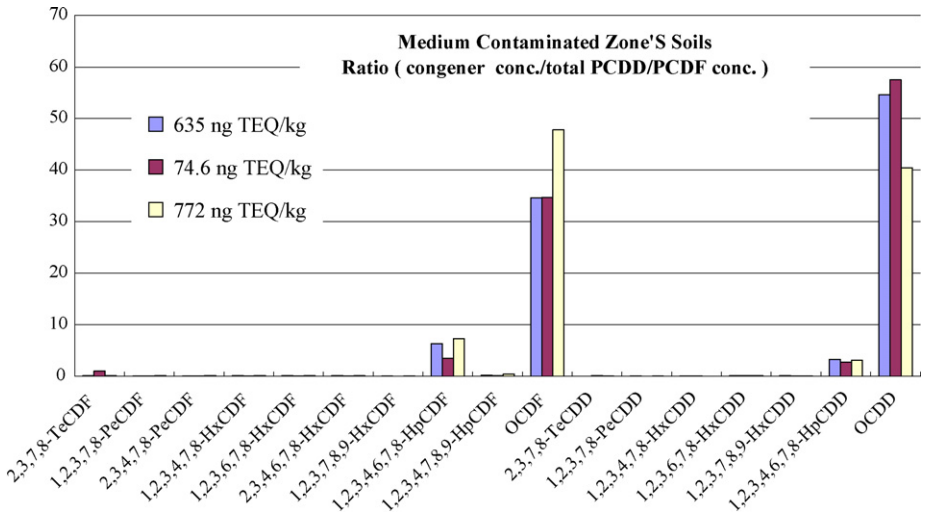

Fig. 1. Percentage contribution of each 2,3,7,8-substituted PCDD/F in soils from areas of medium contamination.

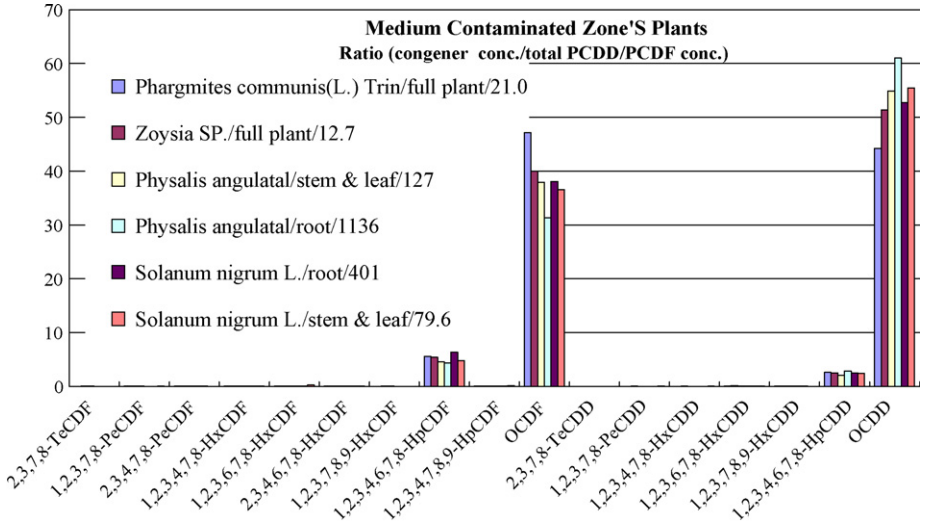

Fig. 2. Percentage contribution of each 2,3,7,8-substituted PCDD/F in plants from areas of medium contamination.

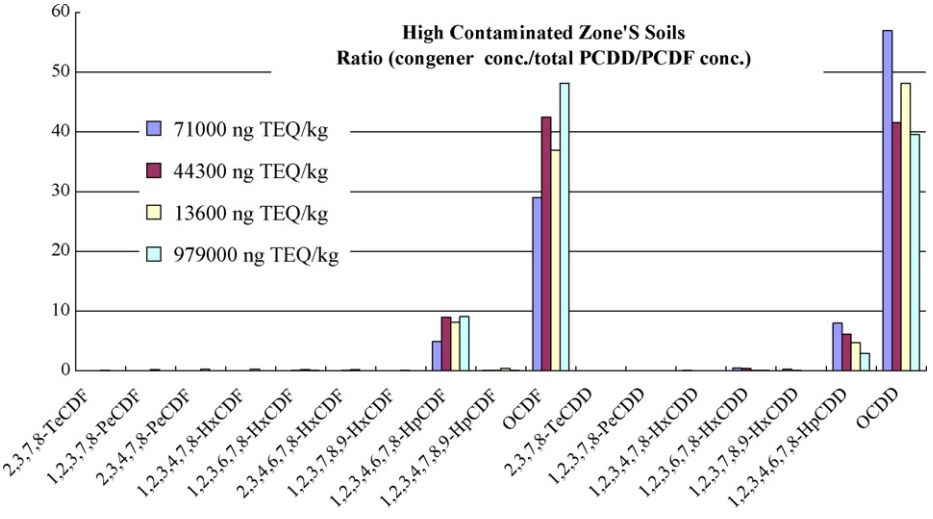

Fig. 3. Percentage contribution of each 2,3,7,8-substituted PCDD/F in soils from areas of high contamination.

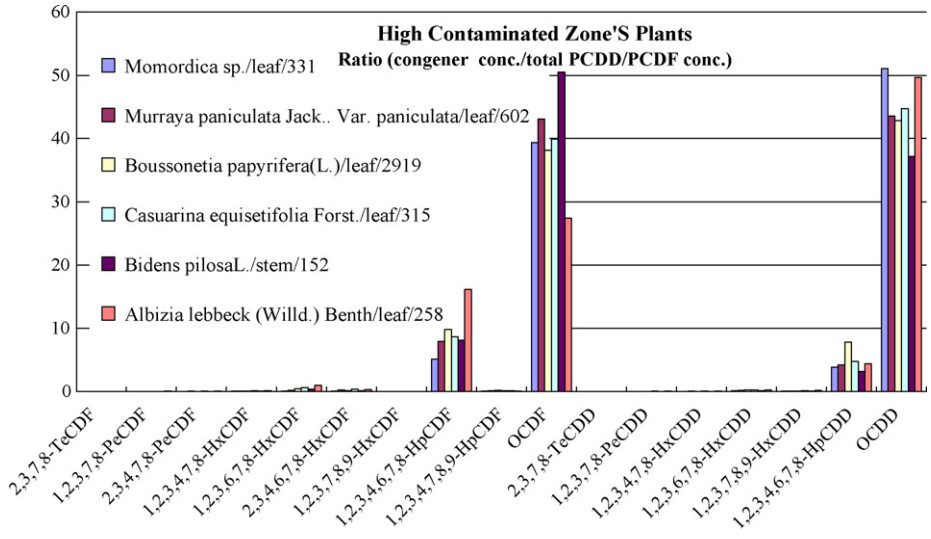

Fig. 4. Percentage contribution of each 2,3,7,8-substituted PCDD/F in plants from areas of high contamination.

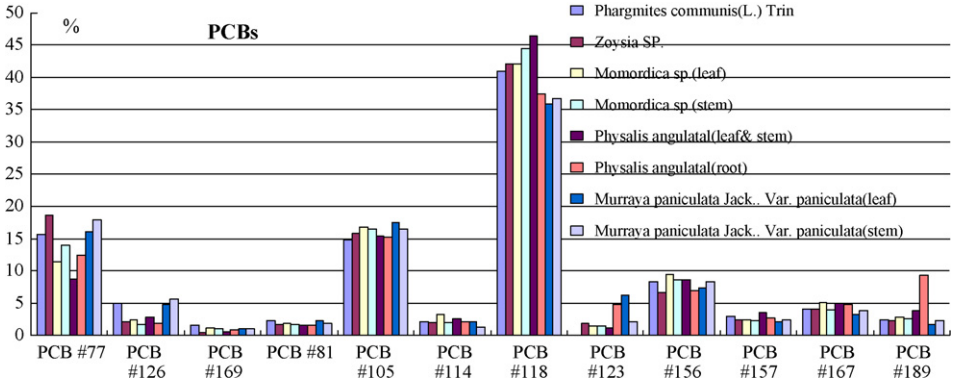

Fig. 5. Percentage of each DL-PCBs congener to total concentration.

dibenzofurans (2,3,7,8-PCDFs) in plants and soil samples from medium and higher concentration areas are shown in Figs. 1 and 2 indicating the resources of dioxins congener are similar in both contaminated areas. The concentrations and distributions of dioxin and DL-PCBs congeners in plant tissues are correspond to soil concentrations, as indicated by the similar resources of the highly contaminated dioxin areas with four soil samples and six plant tissues (Figs. 3 and 4). Fig. 5 shows the percentages of different PCB distributions in the highly contaminated area. The highest concentrations are octachloro dibenzo-*p*-dioxin (OCDD) and octachloro dibenzo-*p*-furan (OCDF) followed by 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,7,8,9-HpCDF. The ratios of DL-PCBs to dioxin were around 0.037 to 2.67% as shown in Table 2 with eight tissues of five plants following two sequential extraction (A and B), indicating the high efficiency of extraction techniques and high recovery percentages, ranging from 1.00 to 11.8% (Table 3). The raw dioxins and PCBs congener analytical data of eight tissues of five plants with two extractions (A and B) is shown in Table 4. The concentrations and contributions of DL-PCB congener to

Table 2
Concentration of dioxin (ng WHO-TEQ_{DF}/kg d.w.) and DL-PCBs (ng WHO-TEQp/kg d.w.) in different plant tissues

	Name of plant							
	Phargmites communis (*L.*)	*Zoysia* sp.	*Momordica* sp.		*Physalis angulatal*		*Murraya paniculata Jack. Var. paniculata*	
			Leaf	Stem	Leaf and stem	Root	Leaf	Stem
$\sum TEQ_F$[a]	13.4	7.30	152	82.5	87.0	681	367	115
$\sum TEQ_D$	7.61	5.43	179	89.3	39.8	455	235	74.6
$\sum TEQ_{DF}$(A)	21.0	12.7	331	172	127	1136	602	190
$\sum TEQ_{PCBs}$(B)	0.560	0.330	0.618	0.236	0.360	0.426	1.75	0.509
((B)/(A)) × 100%	2.67	2.59	0.187	0.138	0.284	0.037	0.291	0.269

[a] TEQ: ng WHO-TEQ/kg d.w.

Table 3
Comparison of dioxin and DL-PCBs concentrations with two extractions

Number of test	Name and part of plant								Average
	Boussonetia papyrifera(L.)		*Casuarina equisetifolia Forst.*		*Solatium nigrum L.*		*Bidens pilosaL*	*Albizia lebbeck (Willd.) Benth*	
	Leaf	Root	Leaf	Stem	Stem and leaf	Root	Stem	Leaf	
lst Time (A)	2919[a]	649	315	46.2	79.6	152	401	258	602
2nd Time (B)	46.4	6.57	2.64	1.59	2.24	5.68	53.6	2.67	15.2
Total (C)	2965	655	318	47.8	81.9	158	455	260	618
((B)/(A)) × 100%	1.59	1.01	0.838	3.44	2.81	3.7	13.4	1.04	3.48
((B)/(C)) × 100%	1.56	1.00	0.831	3.33	2.74	3.6	11.8	1.03	3.23

[a] TEF: WHO-TEF;UNIT: ng WHO-TEQ_{DF}/kg d.w.

Table 4
Dioxin and DL-PCBs congener concentrations (ng/kg) of plant samples

	Scientific name and part of plant							
	Phargmites communis(L.) Trin	*Zoysia* sp.	*Momordica* sp.		*Physalis angulatal*		*Murraya paniculata Jack. Var.paniculata*	
	Full plant	Full plant	Leaf	Stem	Leaf and stem	Root	Leaf	Stem
2,3,7,8-TeCDF	1.85	1.45	6.22	4.70	15.8	46.8	22.1	4.53
1,2,3,7,8-PeCDF	3.09	3.00	11.1	8.80	32.1	125	28.1	11.1
2,3,4,7,8-PeCDF	3.82	3.08	18.0	15.1	48.1	241	111	30.3
1,2,3,4,7,8-HxCDF	8.33	5.15	83.6	45.5	59.5	373	214	72.0
1,2,3,6,7,8-HxCDF	5.02	4.91	87.9	45.7	38.0	267	422	129
2,3,4,6,7,8-HxCDF	7.25	6.01	166	92.4	53.8	517	537	163
1,2,3,7,8,9-HxCDF	1.46	1.32	17.4	15.5	21.3	117	46.1	9.03
1,2,3,4,6,7,8-HpCDF	812	341	9725	4923	3863	38837	17287	5785
1,2,3,4,7,8,9-HpCDF	13.3	629	162	90.4	70.7	645	318	80.7
OCDF	6898	2531	74526	40414	31923	278377	93775	28617
2,3,7,8-TeCDD	0.24	0.34	4.61	2.07	1.17	7.68	4.51	1.75
12,3,7,8-PeCDD	1.03	1.82	39.6	16.1	6.51	47.6	53.1	17.9
12,3,4,7,8-HxCDD	1.65	1.76	68.4	38.3	9.54	98.2	98.7	30.8
12,3,6,7,8-HxCDD	14.3	8.07	311	152	68.5	663	432	137
12,3,7,8,9-HxCDD	3.06	3.58	139	54.9	22.3	164	230	66.3
12,3,4,6,7,8-HpCDD	380	160	7325	4150	1748	25311	9193	2852
OCDD	6467	3253	96692	51279	46190	541981	94861	29010
PCB#77	16.5	272	26.3	16.7	10.3	25.0	56.5	15.4
PCB#126	5.34	3.03	5.58	2.08	3.36	3.81	16.7	4.89
PCB#169	0.96	0.643	246	1.11	0.665	1.64	3.38	0.885
PCB#81	1.86	2.56	4.25	2.00	1.76	3.08	7.71	1.55
PCB#105	20.67	232	38.4	19.7	182	30.6	61.6	14.2
PCB#114	2.7	2.79	7.53	2.43	2.94	4.35	7.31	1.10
PCB#118	40.41	61.5	96.3	53.3	54.9	75.2	126	31.7
PCB#123	10.6	2.64	3.39	1.66	1.34	9.67	21.8	1.78
PCB#156	8.402	9.79	21.7	102	102	13.9	25.8	7.17
PCB#157	2.75	3.40	5.37	2.62	421	5.37	7.50	2.09
PCB#167	4.79	6.06	11.5	4.75	5.92	9.53	112	3.28
PCB#189	2.90	329	6.37	3.00	4.44	18.7	5.78	1.99

the total concentration are shown in Fig. 5. The concentrations of DL-PCB follow the order of PCB#118 > PCB#105 > PCB#77.

4. Conclusions

Persistent organic pollutants (POP), such as dioxins, PCBs and PAHs may migrate into the air or soil through various pathways and are then taken up by plant tissues. Eventually, they can influence human health through food chain. It has also been found that the concentrations of toxic chlorinated organic chemicals with structures similar to dioxin, such as DDT, DDE, and DDD, are astonishingly high in the vascular strands of the plants. These findings imply that the dioxin contents in plants may closely relate to the surrounding environments where plants grow. Tappa is one of the most common and fastest growing plants in Taiwan. It shows the highest tolerance to environmental contaminants and it accumulates dioxin and DL-PCBs. This is one of the best species that can effectively take up dioxin

and DL-PCBs. It can be recommended as a potential plant for dioxin and DL-PCBs phyto-remediation. *P. angulatal* also shows potential adaptive characteristics. When we extensively plant these species, they will be capable, as potential phyto-remediation plants, of removing dioxins from the surface layer of polluted soil. The efficiency of dioxin uptake by these plants merits further study.

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