Environ Earth Sci (2011) 64:581–588
DOI 10.1007/s12665-011-1164-z

ORIGINAL ARTICLE

Phytoremediation of pentachlorophenol-contaminated sediments by aquatic macrophytes

Liangyuan Zhao · Chi Zhu · Chuangxin Gao · Jinhui Jiang · Jiaoyan Yang · Shao Yang

Received: 20 February 2011 / Accepted: 23 June 2011 / Published online: 20 July 2011

Abstract Capability of three species of aquatic macrophytes to remediate pentachlorophenol (PCP)-contaminated sediments starting with initial concentration of 2,000 μg kg^{-1} dw (dry weight) was investigated. Negative effect of PCP on the plant growth, chlorophyll contents and root activities ($p > 0.05$) of the three species of aquatic macrophytes during remediation was not observed. PCP removal was significantly enhanced in the phytoremediated sediments in comparison with the control sediments after 90 days treatment ($p < 0.05$), and the removal rates of PCP in the sediments planted with *P. communis* Trin, *T. orientalis and S. validus* Vahl were 90.35 ± 0.03, 99.23 ± 0.02 and 99.33 ± 0.01%, respectively, while the rate was 29.87 ± 0.05% in the control sediments. Bioaccumulation by three macrophytes was confirmed; the maximum PCP contents in the roots of *P. communis* Trin, *T. orientalis* and *S. validus* Vahl were 419.50 ± 0.71, 1,833.33 ± 7.37 and 2,090.00 ± 2.65 μg kg^{-1} at the 30th day, respectively. In conclusion, *P. communis* Trin, *T. orientalis* and *S. validus* Vahl may act as promising tools for the PCP phytoremediation in aquatic environment, especially *S. validus* Vahl.

Keywords Pentachlorophenol · Phytoremediation · Aquatic macrophyte · Sediment

L. Zhao and C. Zhu contributed equally to this work.

L. Zhao · C. Zhu · C. Gao · J. Jiang · J. Yang · S. Yang (✉)
College of Life Sciences, Central China Normal University, Wuhan 430079, People's Republic of China
e-mail: mryangshao@gmail.com

Introduction

Pentachlorophenol (PCP, C_6Cl_5OH) is a polychlorinated aromatic compound that has been widely used as wood preservative and pesticide (Jiang et al. 2006). PCP is toxic to all forms of life, because it is an oxidative phosphorylation inhibitor (Yang et al. 2009). Owing to its toxicity, widespread distribution and its impurities, PCP has been listed as a priority pollutant or restricted by the environmental protection agency (EPA) of USA and many other countries (e.g., dioxin, furans and hexachlorobenzene) (Cooper and Jones 2008; Dams et al. 2007). However, PCP continues to be widely used for the treatment of utility poles, wharf pilings, and railroad ties and other uses, so it still represents an environmental hazard (Terry and Elisa 2005).

PCP and its salts were used extensively for fighting against schistosomiasis and as pesticides in China in the last decades (Zhang et al. 2001; Schecter et al. 1994), resulting in wide occurrence of PCP at relatively high concentrations in aquatic environment (Yan et al. 2005; Ling and Gao 2004; Fang et al. 2008; Wen et al. 2008). PCP contamination level of sediments in China reported before indicated that it is more severe than that in many other countries (Ling and Gao 2004; Qi et al. 2007; Kobayashi et al. 2008; Dmitruk and Piascik 2008). For example, pentachlorophenol residues in sediments in Wuhan of the Yangtze River catchment, China, ranged from 0.64 to 12.78 ng g^{-1} (Tang et al. 2007). The average PCP concentration in sediments samples surveyed in the Pearl River Delta in China was 7.93 ng g^{-1} and the highest concentration of 163.15 ng g^{-1} was found in fish pond sediments in Zhongshan (Hong et al. 2005). PCP in sediments and suspended particles of Dongting Lake ranged from 0.18 to 48.3 μg g^{-1} (Zhang et al. 2001). PCP owns a low biodegradation rate and a tendency to accumulate in

sediments (Anandarajah et al. 2000). Therefore, there may be a risk of toxicity in PCP-contaminated aquatic environment for a long time. Developing effective methods for remediation of PCP-contaminated sediments is thus urgent.

Compared with conventionally expensive, invasive, and sometimes ineffective techniques for PCP dealing, such as excavation, dredging and some chemical methods, in situ treatment strategies are more effective at reducing risk and decreasing expenditures on management (Kao et al. 2004; Maria et al. 2000; Männistö et al. 2001; Ken et al. 2001; Yang et al. 2009). Among the in situ treatments, bioremediation (microbial remediation and phytoremediation) is thought to be capable in permanent pollutants elimination at low cost (Susan et al. 2007; Monika et al. 2005). However, effectiveness of microbial remediation is limited by the appropriate sediment conditions for microbial activity, recalcitrance of pollutants to biodegradation, and formation of metabolites that may be more toxic than the parent contaminant (Boopathy 2000). Furthermore, microorganisms that show highly efficient biodegradation capabilities under laboratory conditions may not perform equally well at actual contaminated sites (Goldstein et al. 1985). Therefore, phytoremediation has received more attention in the last decade. Phytoremediation is applicable owing to its aesthetic value, environment friendly, manipulation in situ and economic benefit (Susan et al. 2007; Qi et al. 2006; Steven and James 1999; Macek et al. 2000). However, the previous phytoremediation studies mostly focused on the use of terrestrial plants and remediation of heavy metals (Casterline et al. 1985; Takashi et al. 2004; Steven and James 1999; Tessa et al. 2006). Sediments in aquatic environment are regarded as ultimate sink of organic contaminants (Davies et al. 1999; Škrbic and Đurišic-Mladenovic 2007), but little information is available on the possibility of use of aquatic macrophytes for remediation of organic toxicants in aquatic environment. It is, therefore, necessary to develop phytoremediation method of PCP by using aquatic macrophytes.

The aim of this study was to assess the capabilities of three species of common macrophytes, *P. communis* Trin, *T. orientalis* and *S. validus* Vahl to remediate PCP-contaminated sediments. Plant growth, chlorophyll contents, root activities and removal rates of PCP in sediments and accumulations of PCP by the macrophytes were tested. The following hypotheses were studied: (1) PCP inhibited the growth of the three species of macrophytes. (2) Three species of macrophytes can effectively remove PCP from the contaminated sediments. (3) Three species of macrophytes may have different removal capacities to PCP. The research results are believed to benefit the application of indigenous macrophytes to remediate PCP-contaminated sediments in aquatic environment and will be favorable in establishing the successful and sustainable aquatic macrophyte-based remediation strategies.

Materials and methods

Chemicals

PCP of chromatographic grade (purity ≥98.5%) was purchased from QingPu institute of new products (Shanghai, China). Chromatographic reagents were used for gas chromatograph analysis. All other chemicals were of analytical grade and of the highest purity available.

Plant materials

Three species of aquatic macrophytes (*P. communis Trin, T. orientalis* and *S. validus* Vahl) used in the experiment were collected from a local lake in Wuhan, Hubei province, China (30°25′17.17″N, 114°21′51.24″E). All the plants were cultured in the artificial pond for 10 days before the experiments. The macrophytes were grown for 4 months and initial heights of the macrophytes were 172.6 ± 10.6, 176.9 ± 8.1 and 169.1 ± 4.7 cm for *P. communis Trin, T. orientalis* and *S. validus* Vahl, respectively.

Experimental design

The sediments were collected from the top 20 cm layer of PCP-free soil at the Experimental Station (30°30′40.79″N, 114°21′15.14″E). The pH value was 7.24 and the organic matter content was 1.58%. The sediments were air dried and sieved through a 2 mm mesh to remove the large particles. The sediments were then spiked with PCP in ethanol. After the ethanol was evaporated off, the uniformly mixed sediments were loosely packed into experimental pools (6 m long × 1 m wide × 0.6 m deep) and then equilibrated for 4 days before the addition of water. Three treatments were established:

1. Sediments with PCP at 2,000 μg kg^{-1} but without macrophytes (sediment control).
2. Sediments with macrophytes but without PCP (plant control).
3. Sediments with PCP at 2,000 μg kg^{-1} and macrophytes (treatment group).

Fifty individuals were transplanted to experiment pools at initial stage. The exposure experiment was carried out at natural conditions with average daylight intensity of 350 μE s^{-1} m^{-2}, and temperature of 30–35°C/20–25°C (day/night). Tap water was then added and kept at 4 cm above the sediments surface. The experiment ran for 3 months (90 days).

Sampling, growth measurements and chemical analyses

Sampling

In the case of the planted treatments, ten individuals in each replicate were randomly harvested together with the sediments. Roots were cut and collected carefully from the sediments, and then washed with tap water and distilled water to remove the adherent sediments particles. After that, clean roots were dried at 80°C for 24 h and weighed for further PCP analysis. Shoots of each individual harvested were also washed and dried in the same way as roots for PCP analysis.

Sediments were collected using sampling spade. Rhizosphere sediments were sampled by vigorously shaking and rolling the roots to remove any remaining sediments. Then the sediments collected were oven dried, grounded, homogenized and passed through a 60 mm mesh standard sieve.

All the samples above were collected monthly.

Measurement of plant height, chlorophyll content and root activity of the macrophytes

Plant height of the macrophytes was determined by measuring the above-ground part of the main stem of the plant. Chlorophyll content (a + b) of fresh shoot tissue was determined by colorimetry (Arnon 1949), and activities of the young roots were determined by α-naphthylamine oxidation method (Ota 1970).

The plant height of three macrophytes was measured every 15 days; chlorophyll content and root activities were recorded monthly.

Analysis of PCP content in plants and sediments

Extraction methods for the sediments or plants were ensured by efficiency of the recovery tests. Recovery rates ranged from 83.1 to 99.5% with the relative standard deviation (RSD) less than 2.88% ($n = 4$) for the PCP-contaminated sediments and from 81.7 to 95.0% with RSD less than 4. 53% ($n = 4$) for the aquatic macrophytes.

Samples (5 g) were extracted by cyclotron oscillation in 26 mL (25:1, v/v) solution of petroleum ether and 6 mol L^{-1} sulfuric acid for 90 min. The upper extract (15 mL) was purified with the ultrafiltration membrane (0.45 μm) and placed in the separating funnel, and then washed with 5 mL oil of vitriol twice and 10 mL water once. Upper organic phase was collected and 8 mL of 0.10 mol L^{-1} sodium carbonate was added. After agitating for 3 min and kept until statically stratified, the organic phase was collected and was repeatedly treated by the above process. The water phase was collected and combined in another separating funnel, and 5 mL water phase was mixed with 0.3 mL acetic anhydride (300 μg L^{-1}) and 4 mL petroleum ether. The mixed solution were kept in water bath (35°C, 20 min), followed by centrifugation (3,000 rpm, 2 min) and statically placed for 120 min. Finally, upper solution was concentrated to 1 mL and prepared for GC analysis.

GC analyses used a gas chromatograph (Agilent, 6890, USA)equipped with a HP-5 capillary column (30 m length, 0.25 mm ID, 0.32 μm film thickness) and Microcell electron capture detector (μ-ECD). GC conditions were set as: injector temperature, 250°C; starting oven temperature, 100°C (hold 1 min); and ramp, from 15°C min^{-1} to 240°C (hold 1 min). Detector temperature was 300°C. N_2 was used as the carrier gas at a flow rate of 1.0 mL min^{-1} and a split ratio of 10:1 was used. Sample injection volume was 1 μL and makeup flow was 60 mL min^{-1}.

Data collection and statistical analysis

The absolute growth rate (AGR) of three macrophytes was calculated as: AGR (cm $days^{-1}$) = $(H_{i+1} - H_i)/(t_{i+1} - t_i)$, where H_{i+1}, H_i was the plant height of t_{i+1} and t_i. Removal rate of PCP was calculated as: Removal rate (%) = (Ci–Ce) × 100/Ci, where Ci was the initial sediment concentrations of PCP, and Ce was the residual concentrations after 90 days treatment (Ling and Gao 2004). BCFs (Bioconcentration factors) were defined as the ratio of PCP contents in the roots and the sediments on a dry weight basis (Ling and Gao 2004).

One-way ANOVA was performed during the data analysis of PCP removal rates, PCP accumulation capacity among all the treatments, by using turkey test as multiple comparisons. Differences of PCP removal rates and PCP accumulation between plant species were analyzed by independent-samples *t* test (two-tailed). The plant height, GV, chlorophyll content, root activity and unknown peak between planted treatments and corresponding control at different remediation time were compared by independent-samples *t* test (two-tailed). Normal distribution of data was confirmed by the Kolmogorov–Smirnov test and the homogeneity of variances was examined by Levene's test. All statistical analyses were performed by using SPSS version 13.0 and GraphPad Prism 5.0 at 0.05 significance level.

Results

Effect of PCP on plant growth

The presence of PCP in sediments at 2,000 μg kg^{-1} dw had no significantly negative effect on the height of

P. communis Trin during the whole experimental period ($p > 0.05$, Fig. 1). It also showed no significant effect on the plant height of *T. orientalis* and *S. validus* at 30 and 60 days, respectively ($p > 0.05$). In contrast, PCP (2,000 μg·kg^{-1} dw) in the sediments greatly increased the plant height of *T. orientalis* and *S. validus* from 60 to 90 days ($p < 0.05$). At 90th day, the height of *T. orientalis* and *S. validus* in the treatment group was 5.82 and 8.10% larger than that in the plant control group, respectively ($p < 0.05$). The average AGR throughout 90 days experiment for the *P. communis* Trin, *T. orientalis* and *S. validus* of the treatment group were 1.18 ± 0.31, 0.87 ± 0.05 and 0.79 ± 0.15 cm day^{-1}, which were 1.69% ($p > 0.05$), 9.09% ($p < 0.05$) and 20.02% ($p < 0.05$) larger than that in the plant control group, respectively.

Chlorophyll content and root activity of the macrophytes

PCP in the sediments showed no significant effect on the chlorophyll content of *P. communis* Trin during the whole experimental periods ($p > 0.05$, Table 1), while it had a positive effect on its root activity from 60 to 90 days ($p < 0.05$). As for *T. orientalis*, the chlorophyll content of treatment group was higher than that of plant control from 30 to 60 days ($p < 0.05$). Root activity at the treatment sediments of *T. orientalis* was higher at 30th and 60th day while lower at 90th day than that at the plant control sediments ($p < 0.05$). PCP at the test concentration significantly increased the chlorophyll content of *S. validus* Vahl at 30th day ($p < 0.05$) and root activity from 30 to 60 days ($p < 0.05$).

Removal of PCP in sediments

The results showed that residual concentrations of PCP in the sediments declined steadily in the control (sediment control) over the experimental period (Fig. 2). PCP removal was much faster in the sediments of treatment group in the early 30 days of the experiment compared to that in the control ($p < 0.05$). The removal rates of PCP in the presence of three macrophytes varied among species. *S. validus* Vahl has the greatest overall PCP removal efficiency (99.33 ± 0.01%) compared with *T. orientalis* (99.23 ± 0.02%, $p < 0.05$) and *P. communis* Trin (90.35 ± 0.03%, $p < 0.05$). while the PCP removal rate of control was only 29.87 ± 0.05%.

PCP accumulation in aquatic macrophytes

Accumulation of PCP was undetectable in the above-ground parts of the three macrophytes in this experiment, while PCP accumulation in roots was evident. The maximum PCP contents in roots of three macrophytes reached 419.50 ± 0.71, 1,833.33 ± 7.37 and 2,090.00 ± 2.65 μg kg^{-1} for *P. communis* Trin, *T. orientalis and S. validus* Vahl at 30th day, respectively. *S. validus* Vahl showed the greatest accumulation capacity among three macrophytes ($p < 0.05$, Fig. 3).

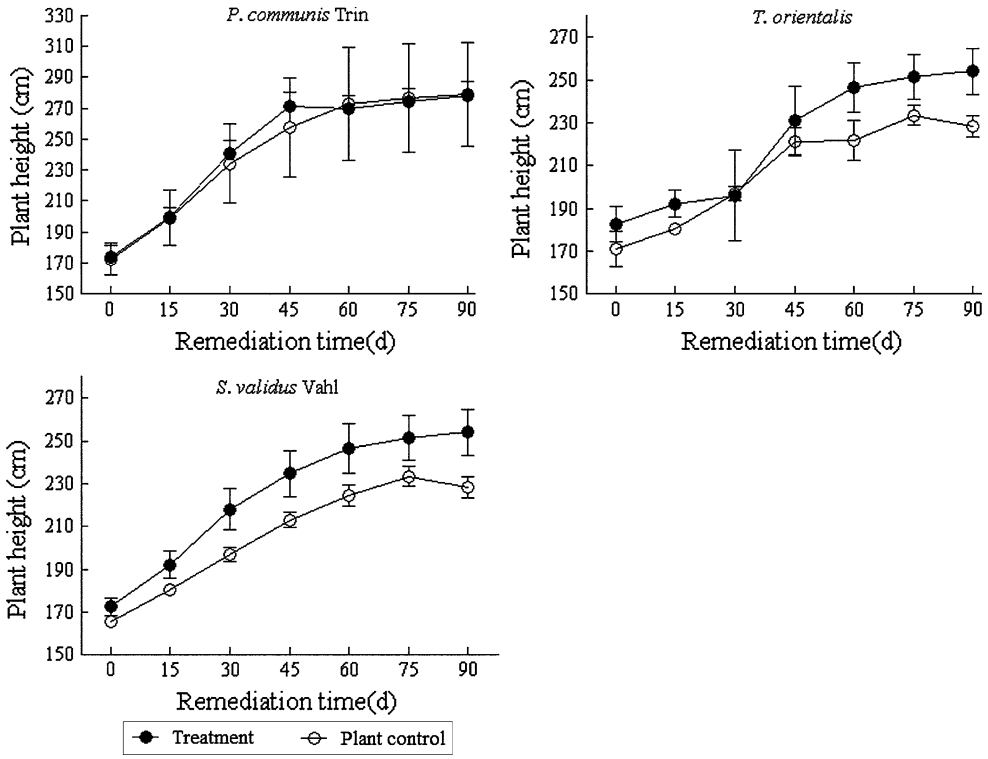

Fig. 1 Plant height of three aquatic macrophytes in treatment group and plant control

Table 1 The chlorophyll contents and root activities of the macrophytes of treatment group and control groups

	Chlorophyll content (mg g^{-1} fw)				Root activity (μg g^{-1} h^{-1} dw)			
	Remediation time (days)				Remediation time (days)			
	0	30	60	90	0	30	60	90
P. communis Trin (plant control)	2.076 ± 0.059	2.113 ± 0.048	2.087 ± 0.084	1.265 ± 0.077	6.258 ± 0.424	6.294 ± 0.283	4.351 ± 0.071	3.752 ± 0.354
P. communis Trin (treatment)	2.068 ± 0.106	2.257 ± 0.084	2.367 ± 0.115	1.498 ± 0.089	6.650 ± 0.919	7.321 ± 0.707	8.372 ± 0.283	6.331 ± 0.147
p(*P. communis* Trin)	0.3109	0.2714	0.2582	0.4582	0.5391	0.0797	<0.0001	0.0003
T. orientalis (plant control)	1.197 ± 0.086	0.927 ± 0.114	1.087 ± 0.210	0.357 ± 0.054	6.558 ± 0.212	9.746 ± 0.283	7.828 ± 0.161	7.088 ± 0.140
T. orientalis (treatment)	1.271 ± 0.087	1.300 ± 0.136	1.645 ± 0.238	0.625 ± 0.187	6.843 ± 0.141	10.921 ± 0.707	8.650 ± 0.247	6.050 ± 0.212
p(*T. orientalis*)	0.354	0.022	0.038	0.076	0.1245	0.0557	0.0085	0.0021
S. validus Vahl (plant control)	0.678 ± 0.035	0.746 ± 0.018	0.921 ± 0.032	0.970 ± 0.064	5.450 ± 0.071	6.215 ± 0.283	4.352 ± 0.071	1.758 ± 0.324
S. validus Vahl (treatment)	0.680 ± 0.033	0.889 ± 0.072	1.095 ± 0.108	1.122 ± 0.100	5.750 ± 1.061	7.518 ± 0.711	6.000 ± 0.566	2.752 ± 0.552
p(*S. validus* Vahl)	0.9460	0.0289	0.0555	0.0909	0.505	0.0420	0.0075	0.0547

p denotes the significant differences between planted and uncontaminated sediments

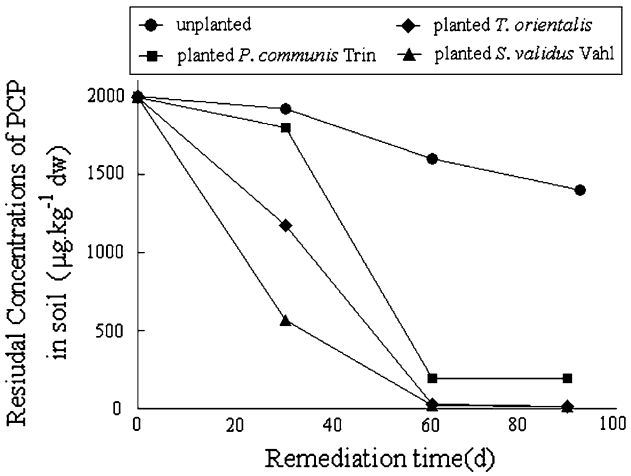

Fig. 2 Residual concentrations of PCP in sediments of treatment group and sediment control

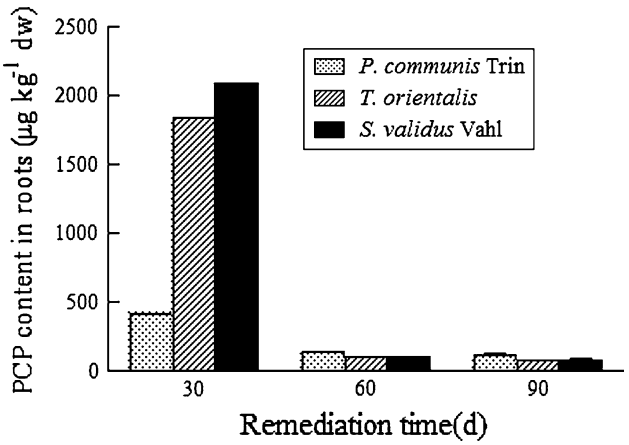

Fig. 3 PCP contents in roots of three macrophytes

The maximum PCP accumulation capacities of the macrophytes are positively related with removal rates ($R^2 = 0.9823$, $p < 0.05$). Due to the removals of PCP in sediments, the PCP contents in macrophytes decreased greatly at 60th and 90th day ($p < 0.05$). *P. communis* Trin exhibited the higher accumulation capacity compared with other two species ($p < 0.05$) from 60 to 90 days. At 90th day, the lowest PCP concentrations (117.50 ± 3.54, 73.33 ± 2.52 and 79.33 ± 6.03 μg kg^{-1}, respectively) were observed in the roots of *P. communis* Trin, *T. orientalis and S. validus* Vahl ($p < 0.05$).

BCFs of *S. validus* Vahl was significantly higher than *T. orientalis* and *P. communis* Trin throughout the experiment ($p < 0.05$, Fig. 4). BCFs of PCP increased with the extension of time ($p < 0.05$). The maximum BCFs of PCP in the roots of the three species of aquatic macrophytes were *P. communis* Trin (0.71 ± 0.01), *T. orientalis* (4.80 ± 0.22), *S. validus* Vahl (4.83 ± 0.11) at 60th, 90th and 60th day, respectively ($p < 0.05$).

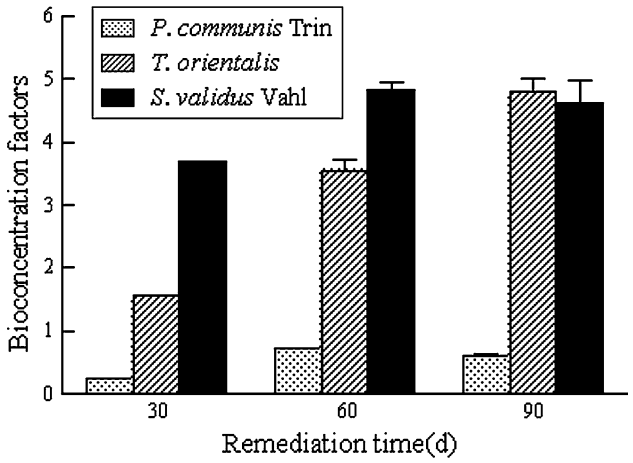

Fig. 4 Bioconcentration factors (BCFs) of PCP in three macrophytes

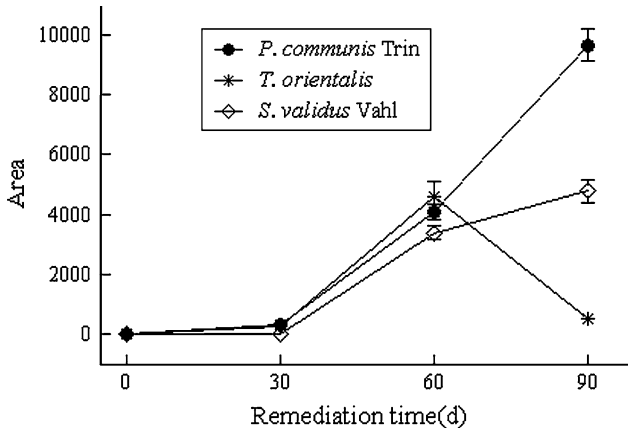

Fig. 5 The content of unknown metabolite product in roots of three macrophytes as a function of time

An unknown peak (retention time was 16.5 min, Fig. 5) was observed in extraction from root tissue of phytoremediation treatment groups, which was not detected in the plant control samples. It was supposed to be the biotransformation product of PCP. The contents of unknown compound kept increase in the experiment periods, but in *T. orientalis* the content of unknown compound increased in early 60 days whereas decreased thereafter ($p < 0.05$), indicating that it was metabolized or transferred out from roots.

Discussion

PCP was the most ubiquitous chlorophenols detected in 92.1% of sediments sampled in the lakes and rivers of 22 major cities in China (Median = 1,210 μg kg^{-1}; range <11,360 μg kg^{-1}) (Wang and Peng 2002). Previous study showed that poplar and willow could not survive at PCP concentrations above 250 mg kg^{-1} in soil, but unfortunately, such PCP concentration was unrealistically environmental levels (Tessa et al. 2006). In this study, PCP of 2,000 μg kg^{-1} dw in the sediments was an environmentally relevant concentration and showed no significantly negative effect on the growth, chlorophyll content and root activity of *P. communis* Trin, *T. orientalis* and *S. validus* Vahl. Root activity refers to the oxidation ability of plant material (Zhang et al. 2009). The results indicated that the three species of aquatic macrophytes could adapt easily to PCP in sediments up to such level. Similar results were observed on ryegrass under lower concentration (8,000 μg kg^{-1}) of PCP (Yan et al. 2005). Furthermore, unlike the previous research, PCP concentrations of 2,000 μg kg^{-1} even increased the growth of *T. orientalis* and *S. validus* Vahl significantly at 90th day ($p < 0.05$). Such enhanced growth may result from the facilitation of soil microbe in roots of the macrophytes, such as the plant growth-promoting bacteria (Siciliano and Germida 1999). The positive influence of microbe may be caused by the PCP directly or indirectly, mechanisms involved still need to be elucidated (Burd et al. 2000; Takashi et al. 2004). Based on the unlimited growth by PCP, establishment of long-term PCP phytoremediation using the three aquatic macrophytes is feasible.

To our knowledge, phytoremediation of PCP-contaminated sediments using aquatic macrophytes has not yet been reported. The results of this study demonstrated significant acceleration of PCP removal in sediments by aquatic macrophytes. The removal rate of PCP in sediments excelled 90% for all the species after 90 days of remediation, which was far more than that in the control ($p < 0.05$). The removal rates are also more than that in previous reports of PCP phytoremediation using terrestrial plants, such as Chinese chive (40%, 28 days), ryegrass (78–82%, 53 days) and rice (63–81%, 82 days) (Takashi et al. 2004; Yan et al. 2005; Terry and Elisa 2005).

Uptake of POPs by plants can contribute to the loss of target compounds from soil (White 2002; Huang et al. 2010). The early reports demonstrated that plant could remediate the PCP-contaminated soil by uptake PCP into root tissue. Total PCP accumulation in the roots of 80 ryegrasses was 6 and 9 μg at the soil PCP concentrations of 8.7 ± 0.5 and 18 ± 0.5 mg kg^{-1}, respectively, which represents 1.5% of the initial amounts of PCP added (Yan et al. 2005). Amount of PCP in Chinese chive was less than 0.53 ± 0.16 μg in plant biomass (3.76 g)(Takashi et al. 2004). The root fraction of the rice treatment had the highest PCP concentration, but accounted for only 0.015 μg of the added $^{[14C]}$PCP of 75 μg (Terry and Elisa 2005). PCP uptake was confirmed in this study by PCP accumulation in root tissue of the macrophytes, and the PCP accumulation is supposed to be higher than the

previous reports though the experimental conditions and data expression were different. However, PCP accumulation by the macrophytes was greatly different between species, *S. validus* Vahl has the greatest accumulation of PCP comparing to *T. orientalis* ($p < 0.05$) and *P. communis* Trin ($p < 0.05$). PCP contents in the roots of the three macrophytes reduced in the late period of experiment, which may result from biotransformation (Takashi et al. 2004). In this study, PCP was undetectable in the aboveground part of the macrophytes, which was accordant with the previous research on ryegrass and rice (Yan et al. 2005; Terry and Elisa 2005). The main reason for this evidence might be the physicochemical characteristics (i.e., the octanol–water partition coefficient) of PCP (Chen et al. 2004). Organics that is most likely to be taken up by plants are moderately hydrophobic compounds with Log K_{ow} ranging from 0.5 to 3 (Alkorta and Garbisu 2001). Since the Log K_{ow} of PCP was 5.01, which might made it difficult to transport from root tissue to upper part tissue. Nevertheless, the result showed the accumulation of PCP by the macrophytes especially *S. validus* and *T. orientalis* played an important role in phytoremediation.

Plant uptake might not be the only principle way in phytoremediation of organic pollutants including PCP (Yan et al. 2005). Dams believed that soil microbes could play a key role in the metabolism and degradation of organic contaminants in soil including PCP (Dams et al. 2007). Plants may stimulate the microbes to degrade the organic chemicals in the rhizosphere by releasing the root exudates and enzymes to build up of organic carbon in the soil (Anderson et al. 1993; Burken and Schnoor 1996). The effect of plant roots in the rhizosphere has been shown to select microbial communities capable of dissipation of organic pollutants (Bollag et al. 2003; Aken et al. 2010; Sun et al. 2010). Therefore, the removal of PCP in sediments can be the combined effects of plants and microbes, and sometimes the effect of microbes may contribute the most (Huang et al. 2010). However, in this study the role of microbes in PCP phytoremediation still needs further analysis.

PCP also can be metabolized by plant such as chinese chive and the metabolite was identified as tetrachlorocatechol (TCC) (Takashi et al. 2004). In this study, it was interestingly found that an unknown new chromatographic peak in the extracts of roots in phytoremediation group, which was highly possible a metabolite of PCP produced by enzymatic system of the macrophytes or by the biodegradation of microorganisms in rhizosphere and then taken up by macrophytes. But the relevant qualitative and quantitative research of this metabolite needs to be further studied.

In China, PCP was used mainly for fighting against schistosomiasis and as pesticide, so the PCP contamination tends to distribute mostly in trench, brook, and riparian zone of river and lake, where aquatic macrophytes including emergent macrophytes can grow and form community. The results of this study demonstrated phytoremediation of PCP in sediments by using aquatic macrophytes; especially *S. validus* may function as an efficient in situ remediation method.

Conclusions

By a phytoremediation experiment of PCP-contaminated sediments by aquatic macrophytes (*P. communis* Trin, *T. orientalis and S. validus* Vahl), it was demonstrated that three species of aquatic macrophytes tested were tolerant to PCP contamination with concentration of 2,000 μg kg^{-1} dw. The PCP removals in treatment groups were evidently enhanced (>90%) by three macrophytes compared to control sediments after 90 days treatment. The macrophytes accumulated PCP efficiently in roots and BCFs of PCP in the roots were *P. communis* Trin (0.71 ± 0.01), *T. orientalis* (4.80 ± 0.22), *S. validus* Vahl (4.83 ± 0.11). In addition, PCP metabolite was detected in the extracts of roots. The results indicated that phytoremediation by aquatic macrophytes, especially *S. validus* Vahl is a promising way for the PCP remediation in aquatic environment.

Acknowledgments This work was financially supported in part by Key research projects of Hubei province of science and technology (Grant No. 2008CDA101) and National major science and technology projects for water pollution control and river management project (Grant No.2008ZX07211-003, 2008ZX07105-004).

References

Aken BV, Paola A, Correa, Schnoor JL (2010) Phytoremediation of polychlorinated biphenyls: new trends and promises. Environ Sci Technol 44(8):2767–2776

Alkorta I, Garbisu C (2001) Phytoremediation of organic contaminants in soils. Bioresour Technol 79:273–276

Anandarajah K, Kiefer PM, Donohoe BS, Copley SD (2000) Recruitment of a double bond isomerase to serve as a reductive dehalogenase during biodegradation of pentachlorophenol. Biochemistry 39:5303–5311

Anderson TA, Guthrie EA, Walton BT (1993) Bioremediation in the rhizosphere: plant roots and associated microbes clean contaminated soil. Environ Sci Technol 27:2630–2636

Arnon D (1949) Copper enzymes in isolated chloroplasts polyphenoloxidase in Beta vulgaris. Plant Physiol 24:1–15

Bollag JM, Chu HL, Rao MA, Gianfreda L (2003) Enzymatic oxidative transformation of chlorophenol mixtures. J Environ Qual 32:63–69

Boopathy R (2000) Factors limiting bioremediation technologies. Bioresour Technol 74(1):63–67

Burd GI, Dixon DG, Glick BR (2000) Plant growth-promoting bacteria that decrease heavy metal toxicity in plants. Can J Microbiol 46:237–245

Burken JG, Schnoor JL (1996) Phytoremediation: plant uptake of atrazine and role of root exudates. J Environ Eng 122:958–963

Casterline JL Jr, Barnett NM, Yuoh K (1985) Uptake, translocation, and transformation of pentachlorophenol in soybean and spinach plants. Environ Res 37(1):101–118

Chen YX, Chen HL, Xu YT, Shen MW (2004) Irreversible sorption of pentachlorophenol to sediments: experimental observations. Environ Int 30:31–37

Cooper GS, Jones S (2008) Pentachlorophenol and cancer risk: focusing the lens on specific chlorophenols and contaminants. Environ Health Perspect 116(8):1001–1008

Dams RI, Paton GI, Killham K (2007) Rhizoremediation of pentachlorophenol by *Sphingobium chlorophenolicum* ATCC 39723. Chemosphere 68:864–870

Davies NA, Edwards PA, Lawrence MAM, Taylor MG, Simkiss K (1999) Influence of particle surfaces on the bioavailability to different species of 2, 4-dichlorophenol and pentachlorophenol. Environ Sci Technol 33:2465–2468

Dmitruk U, Piascik M (2008) Persistent organic pollutants (POPs) in bottom sediments of the Vistula river, Poland. Water Air Soil Pollut 36(2):222–229

Fang LP, Zheng MH, Xiao KY, Yang Y (2008) Tissue-dependent distribution and bioaccumulation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in vegetation samples collected from Dongting Lake, China. Environ Toxicol Chem 27(1):49–56

Goldstein RM, Mallory LM, Alexander M (1985) Reasons for possible failure of inoculation to enhance bioremediation. Appl Environ Microbiol 50:977–983

Hong HC, Zhou HY, Luan TG, Lan CY (2005) Residue of pentachlorophenol in freshwater sediments and human breast milk collected from the Pearl River Delta, China. Environ Int 31:643–649

Huang HL, Zhang SZ, Peter C, Wang S, Xie M (2010) Behavior of decabromodiphenyl ether (BDE-209) in the soil–plant system: uptake, translocation, and metabolism in plants and dissipation in soil. Environ Sci Technol l44:663–667

Jiang XY, Zeng GM, Huang DL, Chen Y, Chen X, Huang GH (2006) Remediation of pentachlorophenol-contaminated soil by composting with inoculation of white rot fungi. Huan Jing Ke Xue 27(12):2553–2557

Kao CM, Chai CT, Liu JK, Yeh TY, Chen KF, Chen SC (2004) Evaluation of natural and enhanced PCP biodegradation at a former pesticide manufacturing plant. Water Res 38(3):663–672

Ken KC, Lo SL, Jerry Wang WH (2001) Pilot study of in situ thermal treatment for the remediation of pentachlorophenol-contaminated aquifers. Environ Sci Technol 35(24):4910–4915

Kobayashi J, Sakai M, Kajihara H, Takahashi Y (2008) Temporal trends and sources of PCDD/Fs, pentachlorophenol and chlornitrofen in paddy field soils along the Yoneshiro River basin, Japan. Environ Pollut 156(3):1233–1242

Ling WT, Gao YZ (2004) Promoted dissipation of phenanthrene and pyrene in soils by amaranth (Amaranthus tricolor L.). Environ Geol 46:553–560

Macek T, Macková M, Ká J (2000) Exploitation of plants for the removal of organics in environmental remediation. Biotechnol Adv 18:23–34

Männistö MK, Salkinoja-Salonen MS, Puhakka JA (2001) In situ polychlorophenol bioremediation potential of the indigenous bacterial community of boreal groundwater. Water Res 35(10):2496–2504

Maria L, Belen B, Rafael C (2000) Determination of phenols in soils by in situ acetylation headspace solid-phase microextraction. J Microcolumn Sep 12(1):25–32

Monika W, Kirsty SH, Don M, Grant N (2005) Laboratory trials on the bioremediation of aged pentachlorophenol residues. Int Biodeterior Biodegradation 55:121–130

Ota Y (1970) Diagnostic method for measurement of root activity in rice plant. Jpn Agr Res Quart 5:1–6

Qi L, Wang ZW, Song M, Chen YX (2006) Evaluation of dissipation mechanisms by *Lolium perenne* L, and *Raphanus sativus* for pentachlorophenol (PCP) in copper co-contaminated soil. Sci Total Environ 368(2–3):814–822

Qi L, Shen KL, Zhao HM, Li WH (2007) Growth response of Zea mays L. in pyrene–copper co-contaminated soil and the fate of pollutants. J Hazard Mater. doi:10.1016/j.jhazmat.2007.04.132

Schecter A, Jiang K, Päpke O, Fürst P, Fürst C (1994) Comparison of dibenzodioxin levels in blood and milk in agricultural-workers and others following pentachlorophenol exposure in China. Chemosphere 29(9–11):2371–2380

Škrbić B, Đurišić-Mladenović N (2007) Principal component analysis for soil contamination with organochlorine compounds. Chemosphere 68(11):2144–2152

Steven DS, James JG (1999) Enhanced phytoremediation of chlorobenzoates in rhizosphere soil. Soil Biol Biochem 31:299–305

Sun TR, Cang L, Wang QY, Zhou DM (2010) Roles of abiotic losses, microbes, plant roots, and root exudates on phytoremediation of PAHs in a barren soil. J Hazard Mater 176:1–3

Susan E, Sudhir S, D'Souza SF (2007) Advances in development of transgenic plants for remediation of xenobiotic pollutants. Biotechnol Adv 25(5):442–451

Takashi N, Takayuki M, Yoshikatsu S, Isamu Y (2004) Biotransformation of pentachlorophenol by Chinese chive and a recombinant derivative of its rhizosphere-competent microorganism, *Pseudomonas gladioli* M-2196. Soil Biol Biochem 36(5): 787–795

Tang ZW, Yang ZF, Shen ZY, Niu JF (2007) Pentachlorophenol residues in suspended particulate matter and sediments from the Yangtze River catchment of Wuhan, China. Bull Environ Contam Toxicol 78(2):148–152

Terry M, Elisa MD (2005) $^{[C\text{-}14]}$Pentachlorophenol mineralization in the rice rhizosphere with established oxidized and reduced soil layers. Chemosphere 61(1):48–55

Tessa M, Barbara A, Siva S, Grant N, Iris V, Brett R, Cara N (2006) Phytoremediation and long-term site management of soil contaminated with pentachlorophenol (PCP) and heavy metals. J Environ Manage 79:232–241

Wang CH, Peng B (2002) analysis of micro organic compound pollution in major city river reaches of the main stem of the Changjiang river. Yangtze River 33(z1):4–9 in chinese

Wen S, Yang H, Yang FX, Liu ZT, Xu Y (2008) Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in surface sediment and bivalve from the Changjiang Estuary, China. Chin J Oceanol Limnol 26(1):35–44

White JC (2002) Differential bioavailability of field-weathered *p*, *p*-DDE to plants of the Cucurbita and Cucumis genera. Chemosphere 49:143–152

Yan H, Xu JM, Tang CC, Wu YP (2005) Facilitation of pentachlorophenol degradation in the rhizosphere of ryegrass (*Lolium perenne* L.). Soil Biol Biochem 37(11):2017–2024

Yang SY, Shibata A, Yoshida N, Katayama A (2009) Anaerobic mineralization of pentachlorophenol (PCP) by combining PCP-dechlorinating and phenol-degrading cultures. Biotechnol Bioeng 102(1):81–90

Zhang B, Zheng M, Liu P, Bao Z, Xu X (2001) Distribution of pentachlorophenol in Dongting Lake environmental medium. China Environ Sci 21(2):165–167 (in chinese)

Zhang WW, Zheng FX, Wang XK, Feng ZZ, Ouyang ZY (2009) Effects of ozone on root activity, soluble protein content and antioxidant system in *oryza sativa* roots. China J Plant Ecol 33(3):425–432 (in chinese)