Distribution of HCHs and DDTs in the soil–plant system in tea gardens in Fujian, a major tea-producing province in China

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1. Introduction

Organochlorine pesticides (OCPs), including hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs), have caused great concerns for decades and have been banned for about 30 years in China due to their persistence in the environment, bioaccumulation through food chains (Nakata et al., 2002), and high toxicity to humans and biota (Willett et al., 1998). A total of 4.9 million tons of HCHs and 0.4 million tons of DDTs were produced from the 1950s through 1983 in China (Li et al., 2006). The spatial distribution characteristic of pesticide application in China has been reported as follows: southeast > central > northwest (Wang et al., 2005). Many HCHs and DDTs were disposed of in an uncontrolled manner in most of the farmland, causing contamination to nearby ecosystems.

Vegetation constitutes an important OCP sink in the ecosystems, and OCPs can accumulate in different plant tissues (Simonich and Hites, 1994). OCPs come into plants through two possible routes: (i) root uptake and adsorption from the soil and subsequent transfer to the aerial tissues (Pereira et al., 2006, 2008; Mikes et al., 2009), (ii) vapor uptake from the surrounding atmosphere and then translocation into various plant parts (Bacci et al., 1990; Simonich and Hites, 1995b; Barber et al., 2004). The first pathway is usually the predominant one for low-volatility organic contaminants, especially the adsorption on roots for those with high n-octanol–water partitioning coefficients (log Kow > 3). In the terrestrial environment, the uptake of semivolatile lipophilic compounds into plants has been studied by numerous studies (Simonich and Hites, 1995a; McLachlan, 1999; Mikes et al., 2009). High levels of contaminants in plant tissues have been attributed to accumulation of contaminants from the atmosphere (McLachlan, 1999; Barber et al., 2004). The uptake of contaminants from soil to root surfaces, however, has been investigated far less.

Tea (Camellia sinensis L.) is a traditional Chinese merchandise for export. The area of tea plantations and the scale of tea production in China rank first in the world, and tea production of Fujian, locating at the southeastern China, ranks top in China in 2010. The leaves of the tea plant are thin and tender, and the surface area per unit weight of leaf is relatively larger than that of other crops. Thus compared to other crops, the residue level of pesticide on tea leaves is higher under the same concentration of contaminants (Chen and Wan, 1997). European Tea Committee (ETC) have established very stringent maximum residue levels (MRL) of pesticides in tea, with the MRL of 20 ng g⁻¹ for HCH (sum of isomers except γ-HCH), 50 ng g⁻¹ for lindane and 100 ng g⁻¹ for total DDT (ETC, 2005). It is urgent to figure out the distribution and source of HCHs and DDTs in tea garden.

In the present study, we sought to elucidate the possible source and distribution of HCHs and DDTs in tea gardens and the accumulation of these compounds in tea plants. To accomplish the goals, the concentrations of HCHs and DDTs were measured in soils and different tea plant tissues in 7 tea gardens.

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2. Materials and methods

2.1. Site description and sample collection

Seven tea gardens were selected in southeastern China’s Fujian province (Fig. 1). All the tea gardens distribute among the hills or low mountains and are far away from the pollution sources, and all seven gardens were operated for 5–7 years. Three sites were selected at the top, middle and foot of each tea garden, and root, old branch, young branch, old leaf and young leaf were collected from 20 tea plants at each site, then the plant samples were rinsed, lyophilized and ground for posterior analysis. Upper 0–30 cm of the soils were collected adjacent to the roots, then the soil samples were air-dried and sieved. All the samples were collected in July, 2009.

2.2. Extraction and analysis

A mixture of 2,4,5,6-tetrachloro-m-xylene (TCmX) and decachlorobiphenyl (PCB209) was added as surrogate standards to 20 g soil samples. The spiked soil samples were Soxhlet-extracted with dichloromethane (DCM) for 72 h, then the extracts were concentrated, purified with silica–alumina cartridge, further concentrated to 0.2 ml, and added with appropriate amount of pentachloronitrobenzene (PCNB) as an internal standard prior to instrument analysis.

About 5 g plant samples spiked with TCmX and PCB209 were Soxhlet-extracted, concentrated to 2 ml for gel permeation chromatography (GPC) cleaning described as those reported by Hu et al. (2008). The cleaning extracts were concentrated and purified in a Silica–Alumina–Florisil cartridge, and then the cartridge were eluted and treated as the soil samples.

GC-ECD (Model 7890, Agilent Technologies, USA) equipped with a HP-5 silica capillary column (30 m × 0.32 mm i.d. × 0.25 μm film thickness) was employed for HCHs and DDTs analysis. Briefly, the oven temperature was maintained at 80 °C for 0.5 min, and then increased to 180 °C at 10 °C min⁻¹, then to 280 °C at 3 °C min⁻¹, and finally to 315 °C at 10 °C min⁻¹ for 15 min. Injector and detector temperature was maintained at 280 °C and 315 °C. Nitrogen (purity > 99.999%) was employed as the carrier gas at the flow rate of 1.5 ml min⁻¹.

2.3. Statistical analysis

All statistical analysis was carried out using the SPSS. Student’s t test and analysis of variance (ANOVA) were applied to test for significant differences in the results.
3. Results and discussion

3.1. HCHs

3.1.1. Levels and distribution of HCHs in soils and plants

The concentrations of total HCHs (ΣHCHs) in soils varied within a wide range, with isomers γ-HCH being the most abundant (Table 1), and the concentrations in soils were significantly lower than those in typical agricultural soils (Chen et al., 2005; Zhang et al., 2011; Yang et al., 2012). ΣHCHs in plant tissues soils were significantly higher than those in soils (Table 1), and the concentrations of old leaves were significantly higher than those in other plant tissues, with γ-HCH being the most abundant and having a wider range than those in soils (from 0.019 ng g⁻¹ to 9.5 ng g⁻¹), but they were much lower than the MRL of the ETC (50 ng g⁻¹).

The relative distribution of the different isomers to total HCHs differed significantly in soils and plant tissues, with γ-HCH being the predominant one (36–83%) (Fig. 2). The ratios of γ-HCH to total HCHs in soils were in agreement with those reported by Gong et al. (2007), who found that most of the ratios were higher than 0.5 in sediments from Quanzhou Bay in Fujian. The relative distribution of β-HCH was the lowest for all the HCH isomers and decreased in the plant tissues (Fig. 2), which might be explained by the fact that, β-HCH is the most persistent isomer to transfer and has the lowest volatility (Willett et al., 1998).

3.1.2. Accumulation and sources of HCHs

Linear regressions can be used to quantify relations between concentrations in soil and plants. The slope of the regression between the soil and the plant concentrations can be interpreted as the plantbioconcentration factor (BCF), and the correlation coefficient (r) describes how much of the concentration variance in plants is explained by the concentration variance in soil (Mikes et al., 2009). In the present study, the slopes of the regression (BCF) were 2.7, 1.2, 1.5, 3.1 for ΣHCHs in root, old branch, young branch and young leaf respectively, and the correlations were significant (Table 2), especially those for root and young leaf. The results suggested that the HCH concentrations in plant tissues highly depended on soil concentrations, especially for root and young leaf (Pereira et al., 2006; Mikes et al., 2009).

The measured BCF (the concentration in plant tissues to that in soil) differed in different compounds. As shown in Fig. 3, high BCFs were found for α- and β-HCH in roots, with the measured BCFs of 3.9, 3.8, 1.9 and 2.9 for α-, β-, γ- and δ-HCH in root. Plots of HCH concentrations in roots against HCH concentrations in soils showed that correlations were significant between them, and the predicted BCFs were 4.0, 3.5, 3.2, and 2.3 for α-, β-, γ- and δ-HCH. Combined with the higher relative distribution of α- and δ-HCH in roots than that in soils, it could be inferred that the roots had the isomer-selective accumulation of α- and δ-HCH. The accumulation of HCHs in the roots occurs mainly as a result of the hydrophobic partitioning between the aqueous solution and the root surfaces, and Kow was usually employed to estimate the BCF in root. The greater the hydrophobicity of the organic compound, the greater the tendency for it to move from the aqueous solution to the root (Dietz and Schuur, 2001). According to the log Kow (Pereira et al., 2006), the values of each HCH isomers are quite similar, with δ-HCH being a little higher. However, the BCFs were not exactly consistent with the tendency for HCH isomers to the roots. This difference may be explained by the fact that soil conditions is much complex, as in the soil, in addition to water, other components such as clays...
and organic matter compete with root surfaces for hydrophobic compounds (Riederer, 2005).

The mechanism of foliar accumulation has been described for several semivolatile compounds in diverse studies, and it is most probably via air–plant partitioning, following volatilization from the soils (Mikes et al., 2009). The vapor pressure and the octanol–air partition coefficient ($K_{OA}$) may influence the behavior of HCH isomers. According to the log $K_{OA}$ of the different HCH isomers (Pereira et al., 2006), the affinities toward lipidic compounds would follow the order of $\delta > \beta > \gamma > \alpha$, but high accumulation capacity appeared for $\gamma$-HCH in plant’s tissues, especially in old leaf. It might be attributed to the long-term exposure to pesticides containing lindane. Pesticides used in the tea gardens were analyzed and $\gamma$-HCH could be detected, with the values ranging from 3.6 µg ml$^{-1}$ to 10.4 µg ml$^{-1}$, but $\alpha$-, $\beta$-, and $\delta$-HCH were lower than the detection limit. In the present study, HCH isomer concentrations in most of the plant tissues were closely related to those in soils (Table 2), suggesting that the process of root uptake and subsequent translocation to the aerial plant tissues could not be discarded.

The ratios of $\alpha$-$\gamma$/HCH can be used to trace the source and the use history of HCHs. This ratio should be 4–7 for technical HCHs and nearly zero for lindane (Iwata et al., 1995). Low $\alpha$-$\gamma$/HCH ratios in the present study indicated the input of lindane in tea gardens (Table 3). Lower ratios in plant’s aerial tissues than those in the roots implied that aerial tissues were more readily expose to the lindane.

$\beta$-HCH is the most stable one among the HCH isomers and it is reluctant to degrade in the environment, thus $\beta$-HCH will be the most abundance isomer in the environment (Willett et al., 1998).

The ratio of $\beta$/($\alpha + \gamma$)-HCH can be used to identify the possible sources of HCHs, and also its input occurred recently or in the past. Low ratios of $\beta$/($\alpha + \gamma$)-HCH in the present study (Table 3) indicated the possible input of technical HCHs or lindane as pesticide in tea gardens. As discussed above, if there existed recent input of technical HCHs, $\alpha$/-$\gamma$-HCH ratios should be higher than those in the present study. However, $\gamma$-HCH was found to be the major isomers in most of the compartments of the tea gardens, and thus there might be the input of $\gamma$-HCH (lindane) in tea gardens.

### Table 1

Mean, standard deviation, minimum and maximum concentrations (ng g$^{-1}$) of HCHs and DDTs in soil and different plant tissues.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Root</th>
<th>Old branch</th>
<th>Young Branch</th>
<th>Old leaf</th>
<th>Young leaf</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-HCH</td>
<td>0.11 (0.095, 0.02–0.33)</td>
<td>0.36 (0.02, 0.012–3.6)</td>
<td>0.14 (0.013, 0.015–0.62)</td>
<td>0.15 (0.12, 0.014–0.46)</td>
<td>0.14 (0.11, 0.011–0.46)</td>
</tr>
<tr>
<td>$\beta$-HCH</td>
<td>0.11 (0.14, n.d.–0.66)</td>
<td>0.095 (0.11, n.d.–0.38)</td>
<td>0.12 (0.15, n.d.–0.71)</td>
<td>0.13 (0.15, n.d.–0.57)</td>
<td>0.086 (0.055, 0.013–0.25)</td>
</tr>
<tr>
<td>$\gamma$-HCH</td>
<td>0.23 (0.067, 0.13–0.35)</td>
<td>0.47 (0.056, 0.034–2.5)</td>
<td>0.63 (0.039, 0.019–13)</td>
<td>1.2 (0.61, 0.096–2.4)</td>
<td>3.7 (2.6, 0.16–9.5)</td>
</tr>
<tr>
<td>$\delta$-HCH</td>
<td>0.12 (0.073, 0.026–0.32)</td>
<td>0.33 (0.027, 0.045–1.3)</td>
<td>0.30 (0.25, 0.017–12)</td>
<td>0.26 (0.15, 0.042–0.64)</td>
<td>0.15 (0.10, 0.018–0.36)</td>
</tr>
<tr>
<td>$\sum$ HCH</td>
<td>0.56 (0.32, 0.18–1.6)</td>
<td>1.3 (1.6, 0.18–7.5)</td>
<td>1.2 (0.67, 0.19–2.9)</td>
<td>1.7 (0.85, 0.26–3.3)</td>
<td>4.1 (2.6, 0.38–10)</td>
</tr>
<tr>
<td>$\sum$ P,p-DDT</td>
<td>0.16 (0.12, 0.017–0.45)</td>
<td>1.3 (1.3, 0.023–4.5)</td>
<td>2.4 (3.5, 0.070–17)</td>
<td>1.4 (1.3, 0.034–2.6)</td>
<td>1.0 (1.3, 0.040–5.3)</td>
</tr>
<tr>
<td>$\sum$ p,p-DDT</td>
<td>0.13 (1.8, 0.010–0.74)</td>
<td>0.33 (0.44, n.d.–1.5)</td>
<td>0.17 (0.16, 0.010–0.62)</td>
<td>0.22 (0.19, 0.016–0.73)</td>
<td>0.22 (0.25, 0.027–1.11)</td>
</tr>
<tr>
<td>$\sum$ p,p-DDT</td>
<td>0.17 (0.19, 0.016–0.74)</td>
<td>0.42 (0.76, n.d.–1.3)</td>
<td>0.75 (0.80, 0.016–2.7)</td>
<td>0.40 (0.44, 0.018–1.8)</td>
<td>0.22 (0.10, n.d.–1.7)</td>
</tr>
<tr>
<td>$\sum$ o,p-DDT</td>
<td>0.45 (0.38, 0.070–1.4)</td>
<td>0.37 (0.31, 0.022–1.3)</td>
<td>0.61 (0.38, 0.067–1.5)</td>
<td>0.90 (0.75, 0.085–2.6)</td>
<td>1.3 (0.39, 0.235–5.1)</td>
</tr>
<tr>
<td>$\sum$ o,p-DDT</td>
<td>0.052 (0.079, n.d.–0.30)</td>
<td>0.056 (0.084, n.d.–0.29)</td>
<td>0.13 (0.38, n.d.–1.8)</td>
<td>0.038 (0.036, n.d.–0.13)</td>
<td>0.04 (0.034, n.d.–0.14)</td>
</tr>
<tr>
<td>$\sum$ o,p-DDT</td>
<td>0.049 (0.049, n.d.–0.15)</td>
<td>0.063 (0.068, 0.010–0.25)</td>
<td>0.12 (0.19, n.d.–0.71)</td>
<td>0.076 (0.079, n.d.–0.27)</td>
<td>0.041 (0.027, n.d.–0.093)</td>
</tr>
</tbody>
</table>

**Concentration is presented as mean (standard deviation, minimum–maximum).**

n.d.: not detected.

### Table 2

Coefficients of correlation between HCHs and DDTs concentrations in the soil and different plant tissues.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Root</th>
<th>Old branch</th>
<th>Young Branch</th>
<th>Old leaf</th>
<th>Young leaf</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-HCH</td>
<td>0.70$^{**}$</td>
<td>0.70$^{**}$</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
</tr>
<tr>
<td>$\beta$-HCH</td>
<td>0.77$^{**}$</td>
<td>0.94$^{**}$</td>
<td>0.65$^{**}$</td>
<td>0.83$^{**}$</td>
<td>0.62$^{**}$</td>
</tr>
<tr>
<td>$\gamma$-HCH</td>
<td>0.52$^{**}$</td>
<td>n.s.</td>
<td>0.70$^{**}$</td>
<td>n.s.</td>
<td>0.61$^{**}$</td>
</tr>
<tr>
<td>$\delta$-HCH</td>
<td>0.66$^{**}$</td>
<td>0.61$^{**}$</td>
<td>0.60$^{**}$</td>
<td>0.63$^{**}$</td>
<td>0.56$^{**}$</td>
</tr>
<tr>
<td>$\sum$ HCH</td>
<td>0.76$^{**}$</td>
<td>0.63$^{**}$</td>
<td>0.50$^{**}$</td>
<td>n.s.</td>
<td>0.79$^{**}$</td>
</tr>
<tr>
<td>$\sum$ p,p-DDT</td>
<td>0.11 (n.d.–0.36)</td>
<td>0.12 (n.d.–0.57)</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
</tr>
<tr>
<td>p,p-DDT</td>
<td>0.74$^{**}$</td>
<td>0.97$^{**}$</td>
<td>0.73$^{**}$</td>
<td>0.81$^{**}$</td>
<td>n.s.</td>
</tr>
<tr>
<td>p,p-DDT</td>
<td>0.94$^{**}$</td>
<td>n.s.</td>
<td>0.688$^{**}$</td>
<td>n.s.</td>
<td>n.s.</td>
</tr>
<tr>
<td>p,p-DDT</td>
<td>0.94$^{**}$</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
</tr>
<tr>
<td>p,p-DDT</td>
<td>0.68$^{**}$</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
</tr>
<tr>
<td>$\sum$ DDT</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
</tr>
</tbody>
</table>

n.s.: not significant; significant correlation.

$^{*}$ P < 0.05.

$^{**}$ P < 0.01.
3.2.2. Accumulation and sources of DDTs

DDT concentrations in plants were higher than those in soils, and the measured BCFs were of 3.4, 5.6, 3.6, 3.1 and 3.9 for \( \sum \)DDTs in root, old branch, young branch, old leaf and young leaf respectively. However, different from HCHs, there were no correlations between soil DDT concentrations and plant DDT concentrations, suggesting that total DDT concentration in plants did not depend on soil concentration. The BCF differed in different tissues for DDT and its metabolites, and the highest BCF were found for \( p,p' \)-DDE (Fig. 3). High BCF for \( p,p' \)-DDT and the higher relative distribution of \( p,p' \)-DDT in plant tissues than that in soil indicated the selective accumulation of \( p,p' \)-DDT in tea plants. As Table 2 showed, close correlations were only found between soil and root for most of the DDTs and its metabolites (Table 2), and the measured BCFs were 10.5, 3.0, 2.5, 1.1, 2.2, 1.2 for \( p,p' \)-DDT, \( p,p' \)-DDE, \( p,p' \)-DDD, \( o,p' \)-DDE, \( p,o' \)-DDE, and \( o,p' \)-DDE respectively (Fig. 3). As mentioned above, \( K_{ow} \) might be employed to estimate the accumulation of DDTs in roots. According to the log\( K_{ow} \) values (US DHHS, 2003), the tendency should be \( p,p' \)-DDT > \( o,p' \)-DDE > \( p,p' \)-DDE. However, the BCFs in root were not exactly consistent with the \( K_{ow} \), and it may also be attributed to the complex conditions in soils as mentioned above (Riederer, 2005).

Vapor pressure could be employed to explain the relative content in the plant’s aerial tissues (Pereira et al., 2006, 2008). Vapor pressure of \( o,p' \)-DDT and \( p,p' \)-DDT is much lower compared to other DDTs, and so it is unlikely that tea plant’s aerial tissues absorb more \( o,p' \)-DDT and \( p,p' \)-DDT than other DDTs. The significantly higher \( p,p' \)-DDT in aerial tissues, especially those in the young branches and leaves than those in soils might be attributed to the direct input of non-degraded DDTs into the aerial tissues.

\[
\text{DDT}(\text{DDD + DDE}) \text{ ratio can be used to establish whether input occurred recently or in the past and whether degradation is significant or not. DDT/(DDD + DDE) ratio in contaminated soils after a long time of weathering is lower than 1 (Hitch and Day, 1992). The ratios in the present study ranged from 1.8 ± 1.7 in soils to 21 ± 34 in the roots, which were in the range of those reported in the agricultural soils in China (Chen et al., 2005; Yang et al., 2012), but much higher than those reported in the soils of USA (Pereira et al., 1996). The ratios in the soils in the present study indicated the new input of DDTs in the tea gardens. The ratios in the plant tissues were significantly higher than those in soils, which implied the selective accumulation of the DDTs, as shown in Fig. 3.}
\]

\[
\text{o,p' -DDT/p,p' -DDT ratio is about 0.175 in the technical DDT and about 7 in diocfol (Qu et al., 2005), and it can be employed to estimate the input of diocfol in the environment. The ratios in the present study ranged from 0.75 ± 0.71 in roots to 3.8 ± 1.1 in soils (Table 3), higher than those in technical DDT but lower than those in diocfol. The results implied the input of diocfol in the tea gardens. The pesticides used in the tea gardens were analyzed and the concentrations were 7.3–20.5 \( \mu \text{g} \cdot \text{ml}^{-1} \) for \( o,p' \)-DDT and 2.8–5.3 \( \mu \text{g} \cdot \text{ml}^{-1} \) for \( p,p' \)-DDT.}
\]

4. Conclusions

Tea plants can accumulate HCHs and DDTs, with the selective accumulation of \( \alpha \)-HCH, \( \delta \)-HCH and \( p,p' \)-DDT in roots. Higher concentrations of HCHs in the tea plant tissues, especially \( \gamma \)-HCH in the old leaves than those in soils, and the lower ratio of \( \alpha /\gamma \)-HCH implied the possible source and process of HCHs in tea plants. Pesticides containing lindane in tea garden were adsorbed on the plant aerial tissues, and some of the \( \gamma \)-HCH came into the soils and then absorbed by the roots. Higher DDTs concentrations, especially \( p,p' \)-DDT and \( o,p' \)-DDT in plant tissues than those in soils, and the high ratios of DDT/(\( \text{DDD} + \text{DDE} \)) and \( o,p' \)-DDT/p,p' -DDT indicated the fresh input of DDTs and diocfol in pesticides in tea gardens.

The correlation of HCHs and DDTs concentration between soils and plant tissues suggested that most of the plant HCH concentrations highly depended on soil HCH concentration, and soil HCHs tended to accumulate in all the plant tissues. However, only root DDT concentrations depended on soil DDT concentration. The results implied that the process of root uptake and subsequent translocation to the aerial plant tissues could not be discarded.

Acknowledgments

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References


