

Available online at www.sciencedirect.com

ScienceDirect

www.journals.elsevier.com/journal-of-environmental-sciencesJOURNAL OF
ENVIRONMENTAL
SCIENCESwww.jesc.ac.cn

Air–soil exchange of organochlorine pesticides in a sealed chamber

Bing Yang¹, Baolu Han^{1,2}, Nandong Xue^{1,*}, Lingli Zhou¹, Fasheng Li¹

1. State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China

E-mail: yangbing@craes.org.cn

2. Department of Environment and Recourses, Hunan Agricultural University, Changsha 410128, China

ARTICLE INFO

Article history:

Received 14 February 2014

Revised 21 April 2014

Accepted 12 May 2014

available online 20 November 2014

Keywords:

Air–soil exchange

Chamber

Organochlorine pesticides

Passive air sampler

ABSTRACT

So far little is known about air–soil exchange under any sealed circumstances (*e.g.*, in plastic and glass sheds), which however has huge implications for the soil–air–plant pathways of persistent organic pollutants including organochlorine pesticides (OCPs). A newly designed passive air sampler was tested in a sealed chamber for measuring the vertical concentration profiles of gaseous phase OCPs (hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs)). Air was sampled at 5, 15, and 30 cm above ground level every 10th day during a 60-day period by deploying polyurethane foam cylinders housed in acrylonitrile butadiene styrene-covered cartridges. Concentrations and compositions of OCPs along the vertical sections indicated a clear relationship with proximity to the mixture of HCHs and DDTs which escapes from the soils. In addition, significant positive correlations were found between air temperatures and concentrations of HCHs and DDTs. These results indicated revolatilization and re-deposition being at or close to dynamic pseudo-equilibrium with the overlying air. The sampler used for addressing air–soil exchange of persistent organic pollutants in any sealed conditions is discussed.

© 2014 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences.

Published by Elsevier B.V.

Introduction

In China, hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs) were among the most used organochlorine pesticides (OCPs) for pest and malaria control from 1950 to 1983. China stood for 33% and 20% of the global HCH and DDT production, representing more than 4 and 0.46 million tons in that period, respectively (Fu *et al.*, 2003). Although being officially banned since 1980s, HCHs and DDTs persist with high residues in various environmental medias, ecological compartments, and human tissues due to their long half-lives, semi-volatility, and hydrophobicity (Xue and Li, 2011; Zhang *et al.*, 2002).

Soils are a reservoir or source for persistent organic pollutants (POPs) and air–soil exchange plays an important role in controlling the fate of POPs (Schuster *et al.*, 2011; Tao *et al.*, 2003). This is especially the case for agrochemical POPs such as OCPs (Cabrerizo

et al., 2011; Kurt-Karakus and Jones, 2006). Soils act as a predominant sink of OCPs (Tao *et al.*, 2003). With strongly adhering to or being trapped within soil mineral particles and soil organic matter, most of OCPs may store in surface soils at an “aged” state (Arias-Estévez *et al.*, 2008). This “aged” state thus limits vertical transport of the compound. On the other hand, soils act as a secondary source by revolatilizing the residuals to the atmosphere in some cases, since the compounds rather decompose in soils much slower than in atmosphere and water (Pereira *et al.*, 2010; Wang *et al.*, 2012). The revolatilization is strongly depending on environmental factors such as temperature (Odabasi and Cetin, 2012) as well as soil properties such as the reservoir potential of soils for OCPs (Pereira *et al.*, 2010; Shen *et al.*, 2010). In many cases the revolatilization under sealed conditions (*e.g.*, in plastic or glass sheds) is most relevant. This is likely to be rather different compared with open conditions, since

* Corresponding author. ndxue2013@gmail.com (Nandong Xue).

higher air temperatures and lower mobility are expected. As a result, the elevated revolatilization probably leads to an accumulation of highly hydrophobic compounds in crops by leaf adsorption and root uptake (Krauss et al., 2004). To date, however, there have been few investigations of air–soil exchange of OCPs under sealed conditions (Kurt-Karakus and Jones, 2006). The issue is especially important in China mainly because of the large residues of OCPs in agricultural soils (Tao et al., 2003) and widespread use of plastic or glass sheds for crop production since the 1980s. The issue also has huge implications for the soil–air–plant cycling of agrochemical POPs.

In studies of air–soil exchange of OCPs, the focus has mainly been on either the atmospheric boundary layer from tens to hundreds meters (e.g., Farrar et al., 2005; Tao et al., 2007) or near soil surface air from tens to hundreds millimeters (e.g., Meijer et al., 2003; Ruzickova et al., 2008), using active and passive sampling techniques. These studies assume that contaminants between air and soil should be at or close to a partitioning equilibrium, providing quantitative evidences on the atmospheric surface exchange of OCPs. Unfortunately, active samplers inevitably bring about some disturbance of the air mass (Kurt-Karakus and Jones, 2006; Zhang et al., 2009). This could become a more significant issue under sealed conditions. Thus using passive sampling techniques under such conditions may be a good alternative owing to low cost, power-free requirement and easy operation (Namiesnik et al., 2005; Seethapathy et al., 2008). Certainly, optimizing calibration against active samplers must be considered (Wania et al., 2003). Nevertheless, passive air sampler (PAS) at least is an improvement due to use of low-rusting material, which is an advantage under sealed conditions with relative humidity being almost 100%.

We therefore designed and tested a novel PAS (PAS-H), which could be used under sealed conditions, with the intention of seeing to what extent “aged” OCP-polluted soils become a secondary source of HCHs and DDTs to the chamber air. The PAS was made by polyurethane foam cylinders housed in acrylonitrile butadiene styrene-covered cartridges. The main objectives of this study were to: (1) calibrate the PAS-H using a co-deployed sampler that has been validated under chamber and field conditions; (2) measure the vertical concentration profiles of OCPs in gaseous phase in the sealed chamber; and (3) determine the effect of temperature gradients on OCPs atmospheric concentrations.

1. Materials and methods

1.1. Chemicals

A mixture stock of OCP standard solution (purity $\geq 99.5\%$), including α -HCH, β -HCH, γ -HCH, δ -HCH, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT, and *p,p'*-DDE, were purchased from Supelco company, Bellefonte, Pennsylvania, USA. The stock was pre-diluted with *n*-hexane to 2 ng/mL in order to adapt to 0.1–100 ng/mL for analysis and stored in a freezer at -20°C . 2,4,5,6-Tetrachloro-*m*-xylene was used as an internal standard for the pesticides analysis (J&K Chemical Ltd., Beijing, China).

All glassware were cleaned using an ultrasonic cleaner (KQ-500B, Kunshan Ultrasonic Instrument, Kunshan, Jiangsu Province, China) at 40°C for 6 hr. Used solvents included *n*-hexane, acetone and dichloromethane (DCM), and ethyl acetate (chromatographic grade, purity $>98\%$, Merck, Darmstadt, Germany). These solvents were redistilled two times prior to use. Anhydrous sodium sulfate (Na_2SO_4) was supplied by LiuLi Chemical Plant (Beijing, China), dried at 400°C for 4 hr in a furnace and kept in a sealed desiccator. Florisil (60–100 mesh, Supelco Company, Bellefonte, Pennsylvania, USA)

was heated at 450°C for 4 hr, stored in a sealed desiccator, and reactivated at 130°C for 12 hr prior to use. Before use, silica gel (80–200 mesh, Beijing Chemical Reagent Company, China) was activated at 130°C for 18 hr in a shallow glass tray, deactivated to 3.3% with deionized water in a 500 mL glass jar, mixed thoroughly and allowed to equilibrate for 6 hr. Deionized water was prepared using an ultra-pure water system (Labconco, Beijing Liyuan Electronic Instrument Co. Ltd., Beijing, China).

1.2. Tested soil

Approximately 100 kg of subsurface soils (>20 cm) was collected from an abandoned pesticide facility ($119^\circ15'56''\text{E}$, $29^\circ27'53''\text{N}$) in Chongqing City, southwestern China. HCHs and DDTs were the principal products in the facility during the 1950s–1980s. The collected soils were enclosed in a stainless steel box and transported to State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences (SKLECRACRAES) within two days. After removing the gravels and plant roots, the soil was air dried at room temperature, powered by passing through a 60 mesh sieve, and then kept at less than -20°C . Soil sampling was performed following Chinese National Guidelines for Technical Specification for Soil Environmental Monitoring (HJ/T 166-2006). The following parameters were determined for five random subsamples of the soil. The content of total organic carbon was measured using a total organic carbon/total nitrogen analyzer (Multi N/C 3100, Analytik Jena AG, Jena, Germany). Soil pH values were determined in a soil-to-water suspension (1:5, W/V) using a pH meter (DELA320, Mettler-Toledo AG, Schwerzenbach, Switzerland). Soil relative humidity was determined by weighing the sample before and after drying it to constant mass at 105°C .

The means and standard deviations of concentrations of $\sum\text{HCH}$ (sum of $\alpha + \beta + \gamma + \delta$ HCH) and $\sum\text{DDT}$ (sum of *p,p'*-DDD, *p,p'*-DDT, *p,p'*-DDE and *o,p'*-DDT) in the soils were (19.7 ± 3.4) $\mu\text{g/g}$ and (73.0 ± 10.8) $\mu\text{g/g}$, respectively (Table 1). *p,p'*-DDD was the predominant DDT metabolite accounting for 78.4% of the $\sum\text{DDT}$ and its concentration was 57.2 $\mu\text{g/g}$. Concentrations of *p,p'*-DDE, *o,p'*-DDT, and *p,p'*-DDT were 7.5, 4.6, and 3.6 $\mu\text{g/g}$, respectively. This profile is consistent with the fact that DDT in soils is transformed by microbial degradation into more stable metabolites such as *p,p'*-DDD and *p,p'*-DDE. In addition, the soil samples had ratios of *p,p'*-DDE/*p,p'*-DDT >1 , also indicating an aged DDT (Harner et al., 2004). Among the four HCH isomers, β -HCH was dominating with a concentration of 11.9 $\mu\text{g/g}$, contributing 60.3% of the $\sum\text{HCH}$. α -HCH accounted for 23.0% of the $\sum\text{HCH}$, followed by δ - and γ -HCHs with concentrations of 2.4 $\mu\text{g/g}$ and 0.9 $\mu\text{g/g}$, respectively (Table 1). Notably, an obvious difference in the profiles of HCH isomers was found between HCHs in the studied soils and the technical HCHs (Li et al., 2006; Liu et al., 2009). The ratio of α/γ -HCH was 5, indicating a mixture of technical HCHs (Li et al., 2009) in the studied soil. The high percentage of β -HCH in the soil also verified a long-term modification of indigenous technical HCH, rather than current input (Li et al., 2009).

1.3. Experimental design

A novel PAS (PAS-H, China Patent No. ZL201220118062.9), shown in Fig. 1, was designed to collect gaseous phase OCPs in

Download English Version:

<https://daneshyari.com/en/article/4454192>

Download Persian Version:

<https://daneshyari.com/article/4454192>

[Daneshyari.com](https://daneshyari.com)