



Compound specific isotope analysis of organophosphorus pesticides



Langping Wu^a, Jun Yao^{a,1}, Polonca Trebse^{b,*}, Ning Zhang^c, Hans H. Richnow^c

^a School of Civil and Environmental Engineering, and National International Cooperation Based on Environment and Energy, University of Science and Technology Beijing, Xueyuan Road No. 30, Haidian District, Beijing 100083, PR China

^b Laboratory for Environmental Research, University of Nova Gorica, Vipavska 13, Nova Gorica SI-5000, Slovenia

^c Department of Isotope Biogeochemistry, Helmholtz Centre for Environmental Research-UFZ, Permoserstraße 9 15, Leipzig 04318, Germany

HIGHLIGHTS

- First report on stable carbon isotope fractionation of organophosphorus (OP) pesticides.
- Method development for analyzing carbon isotope composition of OP pesticides.
- Isotope fractionation characterising decomposition pathways of OP pesticides.

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ABSTRACT

Compound-specific isotope analysis (CSIA) has been established as a tool to study the environmental fate of a wide range of contaminants. In this study, CSIA was developed to analyse the stable carbon isotope signatures of the widely used organophosphorus pesticides: dichlorvos, omethoate and dimethoate. The linearity of the GC–C–IRMS system was tested for target pesticides and led to an acceptable isotope composition within the uncertainty of the instrument. In order to assess the accuracy of the developed method, the effect of the evaporation procedure on measured carbon isotope composition ($\delta^{13}\text{C}$) values was studied and showed that concentration by evaporation of solvents had no significant isotope effect. The CSIA was then applied to investigate isotope fractionation of the hydrolysis and photolysis of selected pesticides. The carbon isotope fractionation of tested pesticides was quantified by the Rayleigh model, which revealed a bulk enrichment factor (ϵ) of $-0.2 \pm 0.1\text{‰}$ for hydrolysis of dichlorvos, $-1.0 \pm 0.1\text{‰}$ and $-3.7 \pm 1.1\text{‰}$ for hydrolysis and photolysis of dimethoate respectively. This study is a first step towards the application of CSIA to trace the transport and degradation of organophosphorus pesticides in the environment.

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1. Introduction

A growing food demand in the world forces intensive agriculture accompanied by releasing of a variety of agrochemicals into the environment. There are public concerns regarding the use of pesticides and adequate monitoring of the fate of pesticides is an urgent objective. Today, over 500 compounds are registered worldwide as pesticides, or metabolites of pesticides, of which organophosphorus compounds are a highly diverse family of organic chemicals used in high amounts. For example, the annual production of organophosphorus pesticides (OP pesticides) is more than 100,000 t in China, which accounts for more than 80% of total pesticide production (Liu, 2010). In our study we focused on three

representatives from the group of OP pesticides: dichlorvos, omethoate and dimethoate. These three OP pesticides are widely used in China, are of public concern, and are on the list of Priority Monitoring Pesticides published by the Ministry of Environmental Protection of the People's Republic of China due to their high toxicity, frequent use and appearance (Jiang, 1993).

Dichlorvos (2,2-dichlorovinyl dimethyl phosphate) is a volatile organophosphorus insecticide with fumigant and penetrant action. It is predominantly used as a fumigant or spray for stored grain and for grain handling equipment (Onicescu et al., 2010). Dimethoate (O,O-dimethyl S-[2-(methylamino)-2-oxoethyl] dithiophosphate) is an OP pesticide which has both direct and systemic action against a broad range of insect pests. It is considered as 'moderately hazardous, class II' compound by WHO with a permissible limit of 0.006 mg L^{-1} in drinking water. Omethoate (2-[(dimethoxyphosphoryl)sulfanyl]-N-methyl-acetamide) is an structural analog of dimethoate, and appears to play a dominant role in the

* Corresponding author. Tel.: +386 5 331 5238; fax: +386 5 331 5296.

E-mail addresses: yaojun@ustb.edu.cn (J. Yao), polonca.trebse@ung.si (P. Trebse).

¹ Tel./fax: +86 10 62333305.

toxicity of dimethoate for insects and mammals. These pesticides may be characterised by classical analytical methods, like GC and LC in combination with different detection techniques, like FID, ECD, NPD and MS (Pappas and Kyriakidis, 2003; Evgenidou et al., 2006; Priya et al., 2011). The complexity of aquatic systems always makes it difficult to assess degradation based on concentration data alone, especially, to distinguish degradation from dilution processes in the environment.

Recently, CSIA has opened a promising avenue to study the contaminants behaviours in the environment employing isotope fractionation to trace reactivity. The stability of chemical bonds is dependent on the mass of substituent thus higher activation energy is needed to cleave a bond formed by heavy isotopomers leading to kinetic isotope fractionation in chemical processes (Bigeleisen and Wolfsberg, 1958). This principle controls the reactivity of the individual stable isotopes in the environment and determines isotope fingerprints during synthesis of organic compounds. The isotope composition provides clues that can be used to identify sources, transformation reactions, and sinks of organic compounds in the environment (Meckenstock et al., 2004). The coupling of gas chromatographs with IRMS makes it possible to analyse isotope ratios of individual compounds in complex mixtures and is known as CSIA. CSIA has offered novel avenues to trace transformation processes of contaminants in complex environments because it can be used to identify (Hirschorn et al., 2004; Elsner et al., 2005; Fletcher et al., 2009; Hofstetter and Berg, 2011) and quantify (Abe and Hunkeler, 2006; Aeppli et al., 2010) transformation reactions by determining the isotope composition of organic compound. Over recent years, CSIA has become an increasingly valuable tool and has been applied to study several groups of contaminants, mostly including benzene homologues (Mancini et al., 2003; Fischer et al., 2008), chlorinated ethenes (Vieth et al., 2003; Van Breukelen et al., 2005; Nijenhuis et al., 2007), petroleum hydrocarbons (Richnow et al., 2003a, 2003b), and fuel oxygenates (Mckelvie et al., 2007; Rosell et al., 2007, 2010, 2012). CSIA has been developed for several pesticides, such as Lindane (Badea et al., 2009), isoproturon (Penning et al., 2010) and 2,6-dichlorobenzamide (BAM) (Reinicke et al., 2012). However, to our best knowledge, the evaluation of OP pesticides by CSIA has, to date, not been reported.

The aim of this study was to develop a method for the analysis of carbon isotope signatures of three OP pesticides (dichlorvos, omethoate and dimethoate) extracted from aqueous samples and to explore the applicability of CSIA to characterise the transformation of OP pesticides. For each compound, the precision of the method was tested as well as the detection limits of precise isotope analysis. All measurements were initially analysed by GC–FID in order to find appropriate chromatographic conditions. Organophosphorus esters are susceptible to hydrolysis, therefore this is the most common environmental degradation pathway, so the method was then applied to assess their isotope fractionation changes during hydrolysis. Photolytic degradation of dimethoate was conducted to demonstrate that CSIA could be used to explore different degradation mechanisms by isotope fractionation.

2. Materials and methods

2.1. Chemicals

High purity standards of three pesticides were selected: dichlorvos (PESTANAL[®], analytical standard, 98.8% pure), omethoate (PESTANAL[®], analytical standard, 97.0% pure), dimethoate (PESTANAL[®], analytical standard, 99.6% pure) were purchased from Fluka (Sigma–Aldrich, Germany). Methanol of HPLC gradient grade (purity $\geq 99.8\%$) was supplied by J.T. Baker (Netherlands), while

dichloromethane (Assay (GC), purity > 99.9%) were supplied by Fluka (Sigma–Aldrich, Germany). Stock and standard solutions of pesticides were stored at $-4\text{ }^{\circ}\text{C}$. All other chemicals were analytical grade and used without further purification. $2 \times \text{DI}$ water was obtained by a NANOpure[®] ultrapure water system (Barnstead, USA).

2.2. Pesticides extraction

Solid-phase extraction (SPE) using 3 mL DSC-18 cartridges (Discovery[®], Bellefonte, USA) were used for extraction of pesticides from aqueous solution. Before extraction, the SPE cartridges were activated by passing consecutively 5 mL of dichloromethane, 5 mL of $2 \times \text{DI}$ water, and 5 mL of purified water alkalized to pH 10 with 0.1 M NaOH (or acidified to pH 3 with 0.1 M HCl for control experiments) (Demoliner et al., 2010). Cartridges were then loaded with 6 mL samples and eluted with 1 mL of dichloromethane to 2 mL vials. The extracted phase was stored for subsequent analysis. All extractions were performed in two parallels for each time point of all experiments, one of them was immediately analysed by GC–FID as described below, and the other one was stored at $-4\text{ }^{\circ}\text{C}$ for isotope analysis.

2.3. Evaporation experiment

The evaporation test was conducted to quantify the effect of evaporation procedures on isotope fractionation. Standard dichloromethane solutions of dichlorvos, omethoate and dimethoate mixture (100 mg L^{-1} 1:1:1) were evaporated under a gentle stream of N_2 to volume of 15%, 25%, 40%, 60%, 80% and 100%, respectively, and changes in their carbon isotope compositions were determined.

2.4. Analysis methods

2.4.1. GC–FID analysis

An Agilent 6890 series gas chromatograph (GC, Agilent Technologies, Germany) equipped with a flame ionization detector (FID) was used. OP pesticides were separated in a HP-608 column ($30\text{ m} \times 0.53\text{ mm} \times 0.5\text{ }\mu\text{m}$, USA) with helium as the carrier gas (flow of 6.0 mL min^{-1}). The column was initially held at $60\text{ }^{\circ}\text{C}$ for 1 min, ramped at $30\text{ }^{\circ}\text{C min}^{-1}$ to $300\text{ }^{\circ}\text{C}$, and held for 2 min. Injector and detector temperatures were set to $180\text{ }^{\circ}\text{C}$ and $250\text{ }^{\circ}\text{C}$, respectively. The samples were injected in splitless mode with injection volumes of $1\text{ }\mu\text{L}$. Each sample was measured in triplicate. Calibration of three tested pesticides was measured by diluting it with dichloromethane.

2.4.2. EA–IRMS analysis

To validate the results of the GC–IRMS method, the carbon isotope compositions of the reference compounds were determined with an elemental analyser (EuroVector, Milan, Italy) directly coupled via a ConFlo III (open split, Thermo Fisher Scientific, Bremen, Germany) to a MAT 253 isotope ratio mass spectrometer (Thermo Fisher Scientific), as described elsewhere (Badea et al., 2009).

2.4.3. CSIA analysis

The carbon isotope composition of dichlorvos, omethoate and dimethoate was analysed by a GC–IRMS system consisting of a gas chromatograph (Agilent 6890) coupled via a GC/C III interface to isotope ratio mass spectrometer (Finnigan MAT 252, Thermo Fisher Scientific). The oxidation furnace of the GC/C III interface containing (Pt, Ni, CuO) was set to $980\text{ }^{\circ}\text{C}$. A DB-608 column ($30\text{ m} \times 0.32\text{ mm} \times 0.5\text{ }\mu\text{m}$, USA) was used for pesticides separation, with helium as the carrier gas at a flow rate of 1.3 mL min^{-1} .

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