



# Classification of nine malathion emulsion samples by using carbon isotope ratios and the ratio of organic solvents



Nana Suto<sup>1</sup>, Hiroto Kawashima\*

Department of Management Science and Engineering, Faculty of Systems Science and Technology, Akita Prefectural University, Akita Prefecture, Japan

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## ABSTRACT

The compound specific isotope analysis is nowadays an important and powerful tool in geochemical, environmental and forensics field. On November 2013, Aqli Foods Corporation in Japan dealt with complaints about stench from frozen foods produced. Subsequently, very high concentrations of organophosphorus pesticide as malathion, ethylbenzene and xylene were detected in recovered frozen foods. In particular case, we present the method to measure the stable carbon isotope ratio ( $\delta^{13}\text{C}$ ) of nine malathion emulsion pesticides using gas chromatography/isotope ratio mass spectrometry (GC/IRMS) to identify the source. The  $\delta^{13}\text{C}$  values of malathion ranged from  $-30.6\%$  to  $-29.5\%$ . Because malathion used in all malathion emulsions sold in Japan is imported from the same overseas company, Cheminova, Denmark. The  $\delta^{13}\text{C}$  values of ethylbenzene ranged from  $-28.2\%$  to  $-20.8\%$  and those of *m,p*-xylene from  $-28.7\%$  to  $-25.2\%$ . The differences in the  $\delta^{13}\text{C}$  values may be because of the material itself and chemical processing. We also determined the ratio of ethylbenzene to *m,p*-xylene and finally categorized the nine malathion samples into five groups on the basis of this ratio and the  $\delta^{13}\text{C}$  values of ethylbenzene and *m,p*-xylene. The results of isotopic fractionation during volatilization (refrigerate, room temperature and incubator) was negligible small.

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## 1. Introduction

On November 2013, Aqli Foods Corporation (currently Maruha Nichiro Corporation) in Japan dealt with complaints about stench from frozen foods (e.g., pizza and croquette) produced by Aqli Foods Corporation [1–6]. Subsequently, ethylbenzene and xylene were detected in a recovered croquette on December 13th and determined 6 ppm and 3 ppm on December 26th, respectively [7]. On December 27th, very high concentrations of malathion (diethyl 2-[(dimethoxyphosphorothioyl)sulfanyl]butanedioate, CAS No. 121-75-5; Fig. 1) were detected in these foods at a maximum concentration of 2200–15,000 ppm [5]. Malathion, an organophosphorus insecticide, has low toxicity and is sold as a cheap pesticide in Japan (see the properties Table 1). As an agrochemical product, malathion is sold as a dust formulation or emulsifiable concentrate, and 101.1 t of the former and 192.3 t of the latter were produced in 2013 [6]. Malathion emulsions contain organic solvents (ethylbenzene and xylene) to increase storage

stability. Because of the presence of ethylbenzene and xylene, we believe that the above incident was caused by malathion emulsion.

In January 2014, Japanese police identified the suspect as a 49-year-old former contract worker at Aqli Foods Corporation [4]. The man added malathion to frozen food packages on four separate occasions between October 3rd and 7th, 2013 [7]. He expressed his dissatisfaction with the employment system and salary at the factory.

Pesticides can easily be obtained and abused, as evidenced by the above incident. Therefore, it is important to be able to identify the sources of pesticides, which can be achieved by measuring the impurities they contain.

Gas chromatography/isotope ratio mass spectrometry (GC/IRMS) can be used to accurately measure stable isotope ratios of carbon and hydrogen in individual compounds in various media [8,9]. The technique has been used in the fields of geochemistry and forensics around the world [10–13], in particular to determine the origin and fate of organic contaminants [14–32]. For several organic compounds, compound-specific isotope analysis has been performed, such as chlordane, DDT, dieldrin, aldrin, heptachlor, and toxaphene [22], chlorothalonil [23], some herbicides [24], atrazine [25,26],  $\gamma$ -hexachlorocyclohexane (Lindane) [27], 3-(4-isopropylphenyl)-1,1-dimethylurea (isoproturon) [28], diazinon [29], 2,6-dichlorobenzamide (BAM) [30], dichlorvos, omethoate, and dimethoate [31], and methamidophos [32]. Recently, it has been measured organic compounds using new interface (e.g., high temperature conversion-elemental analyzer isotope

\* Corresponding author at: Department of Management Science and Engineering, Faculty of Systems Science and Technology, Akita Prefectural University, 84-4 Ebinokuchi, Tsuchiya, Honjo City 015-0055, Japan.

E-mail address: [kawashima@akita-pu.ac.jp](mailto:kawashima@akita-pu.ac.jp) (H. Kawashima).

<sup>1</sup> Present address: Energy and Environment Research Division, Japan Automobile Research Institute, Japan.

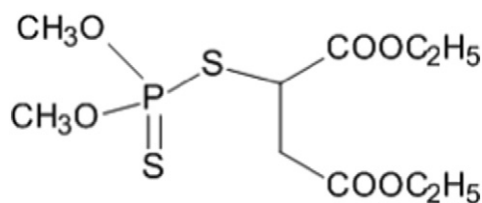


Fig. 1. Chemical structure of malathion.

ratio mass spectrometry (TC-EA/IRMS) and liquid chromatography isotope ratio mass spectrometry (LC/IRMS)). For example, the ibuprofen of pharmaceuticals [33] and glyphosate of pesticides [34] were analyzed using TC-EA/IRMS and LC/IRMS, respectively.

Here, we used GC/IRMS to determine the  $\delta^{13}\text{C}$  values of malathion and organic solvents (ethylbenzene and *m,p*-xylene) in nine malathion emulsion samples produced by Japanese companies. And, we tested for isotopic fractionation during volatilization (refrigerate, room temperature and incubator).

## 2. Materials and methods

### 2.1. Samples

We analyzed the following malathion emulsion samples obtained from Japanese companies: six samples of agrochemical products (1: Sumitomo Chemical Company Ltd., 500 mL; 2: Sumitomo Chemical Company Ltd., 100 mL; 3: Nissan Chemical Industries Ltd., 500 mL; 6: Hokko Chemical Industry Company Ltd., 500 mL; 7: Nihon Nohyaku Company Ltd., 500 mL; 9: Ryukyu Sankei Company Ltd., 500 mL); and three samples of products intended for home garden use (4 and 5: Sumitomo Chemical Garden Products Inc., 100 mL [two samples from different lots]; 8: King Chemical Company Ltd., 100 mL). All malathion emulsions contained 50% malathion and other components (ethylbenzene, xylene, and a surfactant). The companies that produced these samples produce approximately 97% of malathion-containing products in Japan. All samples were purchased from a local distributor between December 30, 2013 and January 29, 2014.

### 2.2. GC/IRMS

Stable carbon isotope ratios were determined by means of GC/IRMS. A gas chromatograph (7890A; Agilent Technologies, Santa Clara, CA, USA) was equipped with a flame ionization detector (FID) and was coupled via a combustion interface to an IRMS instrument (Isoprime, Isoprime Ltd., Manchester, UK).

Carbon stable isotope composition, expressed in  $\delta$  notation in permil (‰) units, was calculated as follows:

$$\delta^{13}\text{C}[\text{‰}] = \left( \frac{\left( \frac{^{13}\text{C}/^{12}\text{C}}{^{13}\text{C}/^{12}\text{C}} \right)_{\text{sample}}}{\left( \frac{^{13}\text{C}/^{12}\text{C}}{^{13}\text{C}/^{12}\text{C}} \right)_{\text{std}}} - 1 \right) \times 1000$$

where  $(^{13}\text{C}/^{12}\text{C})_{\text{sample}}$  and  $(^{13}\text{C}/^{12}\text{C})_{\text{std}}$  are the atomic ratios of  $^{13}\text{C}$  to  $^{12}\text{C}$  in the sample and in the Vienna Pee Dee Belemnite standard, respectively. All samples were measured in triplicate.

Table 1

Physico-chemical properties and structures of the investigated compounds.

Compound	CAS-NO.	Molecular formula	MW/g mol <sup>-1</sup>	Boiling point
Malathion	121-75-5	C <sub>10</sub> H <sub>10</sub> O <sub>6</sub> PS <sub>2</sub>	330.4	156–157
Ethylbenzene	100-41-4	C <sub>8</sub> H <sub>10</sub>	106.2	136.25
Xylene	<i>m</i> -Xylene: 108-38-3 <i>p</i> -Xylene: 106-42-3	C <sub>8</sub> H <sub>10</sub>	106.2	139.1 138.3

The sample (1  $\mu\text{L}$ ) was introduced by on-column injection with a syringe. The oven temperature programs and fused-silica capillary columns were as follows. For malathion: 30 °C for 25 min, ramped to 170 °C at 20 °C/min and held for 10 min, then ramped to 280 °C at 20 °C/min and held for 12.5 min; Rtx-1701 column (30 m  $\times$  0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness; Restek Corporation, Bellefonte, PA, USA). For ethylbenzene and *m,p*-xylene: 60 °C for 0 min, ramped to 100 °C at 1 °C/min and then to 280 °C at 20 °C/min, and held for 5 min; Equity-1 column (60 m  $\times$  0.25 mm i.d., 1  $\mu\text{m}$  film thickness; Supelco, Sigma-Aldrich Japan Inc., Tokyo, Japan). Ultra-high-purity helium (>99.9999%) was used as the carrier gas at a flow rate of 1 mL/min. The combustion furnace temperature was 850 °C, and the combustion interface temperature was 350 °C. We selected CuO grains with 1% Pt and 1% Ni for high accuracy and precision, and we could perform 800–1000 measurements [32].

The shape of the malathion peak is important to obtain precise, accurate  $\delta^{13}\text{C}$  values, but the malathion peak exhibits leading and tailing in the absence of cryofocusing. However, in this study, we installed a liquid nitrogen-cooled cryofocusing system (Cold Trap 9000; Brechbühler, Schlieren, Switzerland) on the capillary line between the combustion interface and the IRMS instrument to improve the malathion peak shape [32]. CO<sub>2</sub> was trapped there at –180 °C and heated rapidly to 60 °C before being introduced into the IRMS instrument. We automated the system using electronic signals from the gas chromatograph, as described below. Cryofocusing with liquid nitrogen was carried out for 150 s before the detection time of the malathion peak because this was the time required for the temperature of the cryotrap to reach –180 °C. After cooling, the trap point was heated to 60 °C for 10 min. Cryofocusing and heating were controlled by switching a valve on the gas chromatography, and the switching time was included in the GC method.

The accuracy and precision of the method were determined as follows. We measured the stable carbon isotope ratios of the fungicide fthalide (4,5,6,7-tetrachlorophthalide, CAS No. 27355-22-2) and the herbicide DBN (2,6-dichlorobenzonitrile, CAS No. 1194-65-6; both from Wako Pure Chemical Industries Ltd., Osaka, Japan) with an elemental analyzer (EuroVector, Jasco International Co., Tokyo, Japan) coupled to the IRMS system. The results of elemental analysis were corrected by using a two-point linear calibration [35]. The following international isotope standards were used: IAEA-600 (caffeine,  $\delta^{13}\text{C} = -27.771\text{‰}$ , International Atomic Energy Agency), LSVEC (lithium carbonate,  $\delta^{13}\text{C} = -46.6\text{‰}$ , International Atomic Energy Agency), and USGS24 (graphite,  $\delta^{13}\text{C} = -16.049\text{‰}$ , United States Geological Survey).

To check instrument stability, L-alanine (Shoko Co., Ltd., Tokyo, Japan;  $\delta^{13}\text{C} = -19.6\text{‰}$ ) was analyzed as a working standard after every nine samples. Then the stable carbon isotope ratios of fthalide and DBN in acetone were measured. The malathion and ethylbenzene or *m,p*-xylene values were corrected every day by using the values for fthalide and DBN, respectively.

We analyzed malathion at a concentration of 1000 ppm in acetone with cryofocusing. The concentration of ethylbenzene and *m,p*-xylene ranged of 662–3040 ppm and 177–2386 ppm in acetone without cryofocusing, respectively. We tested 4 malathion emulsion samples (1, 4, 6, and 8) after keeping them in a refrigerator (2 °C; 3 h), at room temperature (25 °C; 12 h), or in an incubator (60 °C; 1 h or 2 h). After the test, the  $\delta^{13}\text{C}$  of ethylbenzene and *m,p*-xylene in these four samples were analyzed again.

## 3. Results and discussion

### 3.1. Stable carbon isotope ratio of malathion

The  $\delta^{13}\text{C}$  values of malathion ranged from  $-30.6 \pm 0.1\text{‰}$  (5: Sumitomo Chemical Garden Products) to  $-29.5 \pm 0.0\text{‰}$  (6: Hokko Chemical Industry Company), and SD for triple measurement were

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