Chemosphere xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

# Primary risk assessment of dimethyldithiocarbamate, a dithiocarbamate fungicide metabolite, based on their probabilistic concentrations in a coastal environment

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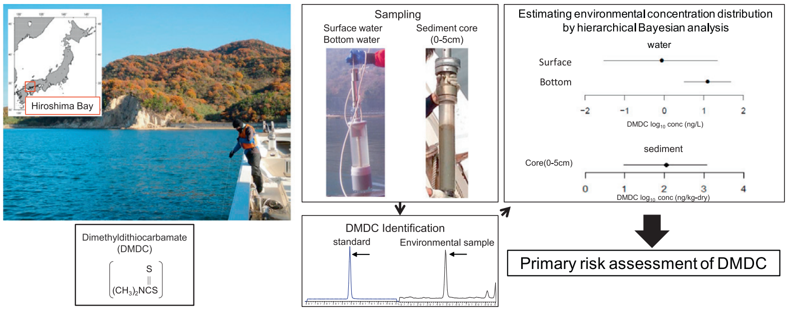
## HIGHLIGHTS

- First report to identify dimethyldithiocarbamate (DMDC) in coastal environments.
- Substantially higher DMDC concentrations in bottom seawater than surface seawater.
- Environmental concentration distributions are estimated by using Bayesian statistics.
- Seasonal concentrations represent temporal variation in the risk to exposed species.
- DMDC levels are likely to be of biological relevance, notably in bottom seawater.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

*Article history:*
Received 17 May 2014
Received in revised form 28 November 2014
Accepted 2 December 2014
Available online xxxx

Handling Editor: Caroline Gaus

*Keywords:*
Dimethyldithiocarbamate
Dithiocarbamate fungicides
Primary risk assessment
Coastal environment
Hierarchical Bayesian analysis
Environmental concentration distribution

## ABSTRACT

The primary ecological risk of dimethyldithiocarbamate (DMDC), a dithiocarbamate fungicide (DTC) metabolite, was evaluated based on their probabilistic environmental concentration distributions (ECDs) in the coastal environment, Hiroshima Bay, Japan. And their behavior and temporal trends was further considered. This is the first report of the identification of DMDC from environmental seawater and sediment samples. DMDC concentrations in bottom seawater were substantially higher than those in surface seawater, which are associated with the leachability from sediments in bottom seawaters, and with photodegradation in surface seawaters. Furthermore, seasonal risks are dominated by higher concentrations from April to June, indicating temporal variation in the risk to exposed species. Hierarchical Bayesian analysis offered DMDC ECD medians and range (5th to 95th percentiles) of 0.85 ng $L^{-1}$ (0.029, 22), 12 ng $L^{-1}$ (3.2, 48) and 110 ng kg $dry^{-1}$ (9.5, 1200) in surface seawater, bottom seawater and sediment, respectively. Considering that DMDC and DTCs have similar toxicological potential to aquatic organisms, the occurrence of the compound in water is likely to be of biological relevance. In summary, this work provides the first demonstration that the ecological risk of DMDC and its derived DTCs in Hiroshima Bay is relatively high, and that DTCs should be a high priority for future research on marine contamination, especially in bottom seawaters.

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http://dx.doi.org/10.1016/j.chemosphere.2014.12.015
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Please cite this article in press as: Hano, T., et al. Primary risk assessment of dimethyldithiocarbamate, a dithiocarbamate fungicide metabolite, based on their probabilistic concentrations in a coastal environment. Chemosphere (2015), http://dx.doi.org/10.1016/j.chemosphere.2014.12.015

## 1. Introduction

Dithiocarbamate fungicides (DTCs) are structurally formed by dimethyldithiocarbamate (DMDC), including thiram, ziram and polycarbamate (Fig. S1 of the Supplementary material), and were originally developed to control diseases in a wide variety of agricultural crops (Davies and White, 1985). Recently, they have become widely used as substitutive antifouling agents on ships and fishing nets following restrictions on the use of organotin antifoulants (Van Wezel and Van Vlaardingen, 2004; Mochida and Fujii, 2009). Due to their wide range of uses, the emissions of respective DTCs are now being reported on a continuous base under the Pollutant Release and Transfer Register (PRTR) system in Japan (The Japanese Ministry of Economy, Trade and Industry, 2011) (Table S1).

For decades, DTCs released into the aquatic environment have been a cause of great environmental concern because of their potential to adversely affect aquatic organisms. Sodium-DMDC, thiram and ziram were shown to impair photosynthesis activity in green algae (*Chlorella pyrenoidosa*), and 96-h $EC_{50}$ levels were reported to be 800, 1100 and 1200 ng $L^{-1}$, respectively (Van Leeuwen et al., 1985a). Thiram was also found to cause wavy distortions of the notochord in zebrafish (*Danio rerio*) from 3 h post-fertilization (hpf) until 24 hpf embryos, giving EC50 values of 1700 ng $L^{-1}$ (Teraoka et al., 2006). Collectively, the predicted no-effect concentration (PNEC) is given as 8.0, 11 and 12 ng $L^{-1}$, in which an assessment factor of 100 is applied to the lowest EC50 of each chemical, indicating that toxicity to aquatic organism is similar between parent compounds and DMDC.

With respect to environmental phenomena of DTCs, it is important to consider their possible fate and degradations. For example, thiram in water and soil is reported to undergo rapid degradation via hydrolysis, photolysis and oxidation to produce a large number of metabolites (Gupta et al., 2012b; Filipe et al., 2013). The half-life of thiram in water was reported to be 2.4 d (pH 8.0; nearly equivalent to seawater in Hiroshima Bay); DMDC is a first metabolite, and appears to be more persistent (Gupta et al., 2012b). The same degradation pathway is expected for ziram to produce DMDC (U.S. Environmental Protection Agency, 2001). Additionally, DMDC seems to have the highest toxicity among the metabolites, and similar to those of parent compounds (Van Leeuwen et al., 1985a). On the other hand, the occurrence of DTCs in coastal environments has not been reported (Mochida and Fujii, 2009), a situation that is attributed to their rapid degradation and to methodological limitations, including its relatively low recovery from the decay of analyte (Gupta et al., 2012b). Thus, in order to conduct a comprehensive risk evaluation of DTCs in the aquatic environment, ambient monitoring of DMDC is a reasonable approach and becomes imperative. Furthermore, environmental behaviors such as partitioning between waters and sediments remain unknown.

Primary ecological risk evaluations have historically used the predicted environmental concentration (PEC) of certain chemicals as a maximum value in monitoring data. However, where there is limited data on environmental occurrence, it is also important to assess the confidence intervals of the environmental concentration distribution (ECD) and its derived quantities. Recently, a hierarchical Bayesian model has been proposed to calculate and quantify the confidence intervals of the ECD (Hayashi and Kashiwagi, 2011). The use of Bayesian statistics for ECD estimation has some advantages, such as explicitly considering the differences between within-site and between-site variations (Qian et al., 2004; Wu et al., 2011). Moreover, the method can also handle environmental concentration data without any arbitrary data manipulation or aggregation, even for data sets that include many ‘not detected’ (N.D.) items (Hayashi and Kashiwagi, 2011). We therefore used a hierarchical Bayesian model to estimate the ECDs of DMDC and its derived DTCs.

The purpose of this study is to estimate probabilistic ECDs of DMDC and its derived DTCs and to comprehensively evaluate the ecological risks by utilizing periodical monitoring data in Hiroshima Bay, Japan, from May 2011 to March 2013. Our study further explored: (1) the estimation of behavior in the coastal environment; (2) consideration of temporal variations in seawaters and sediments.

## 2. Material and methods

### 2.1. Reagents

Organic solvents including dichloromethane, hexane and acetone (dioxin-analysis grade), and analytical grade reagents including DMDC-methyl (100% purity), dimethylsulfoxide (DMSO), ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), L-cysteine hydrochloride monohydrate (L-cysteine), sodium hydroxide, tetrabutylammonium hydrogen sulfate, hydrochloric acid, disodium sulfate and methyl iodide were obtained from Wako Pure Chemical Ltd. (Osaka, Japan).

Throughout the optimization procedure for both water and sediment samples, DMDC was spiked in the form of polycarbamate (95.1% purity: Hayashi Pure Chemical Ltd, Osaka, Japan), which is one of the parent compounds of DMDC (Fig. S1). The standard solution was dissolved in DMSO and diluted with acetone to the required concentrations. An alkaline cleavage solution was prepared by dissolving aliquots of EDTA-2Na and L-cysteine in deionized water, and pH was adjusted to 9.6–10.0 using 12 M sodium hydroxide. The concentrations of both EDTA-2Na and L-cysteine in the solution were adjusted to 5% for seawater and to 15% for sediment.

Working standard solutions of DMDC-methyl were prepared by diluting the stock solutions (100 μg $mL^{-1}$ in acetone) with hexane. $d_{18}$-antrathene was used as an internal standard and was added to each working solution. DMDC and its parent DTC compound were recalculated from DMDC-methyl concentrations.

### 2.2. Instrument conditions

The DMDC-methyl concentrations were determined on a 6890 N (Agilent Technologies, Tokyo, Japan) gas chromatograph system equipped with a 5975 mass spectrometer, which was operated under the selected ion-monitoring mode. The operating conditions of the GC–MS are given in Table S2.

### 2.3. Chemical analysis in water samples

Analytical methodology for water was developed based on previous methods (Kawamoto et al., 2005) with considerable modifications. Briefly, it includes the decomposition of DTCs to DMDC followed by methyl derivatization to DMDC-methyl and 0.5 mL of final concentrate from 500 mL of samples to obtain 1000-fold condensed samples. For method optimization, we used 500 mL seawater sampled from our research institute, which faces Hiroshima Bay (Fig. 1). 50 mL of the 5% alkaline cleavage solution were added to 500 mL of a seawater sample. After 10 min shaking, 12.5 mL of 0.41 M tetrabutylammonium hydrogen sulfate was added and the pH of the water sample was adjusted to between 7.5 and 7.8 using 2 M hydrochloric acid. Methyl derivatization and liquid–liquid extraction were carried out by shaking for 10 min with 40 mL of derivatizing reagent consisting of 0.05 M methyl iodide in dichloromethane and hexane (3:1). The sample

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