Science of the Total Environment 452–453 (2013) 421–426

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

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

Composition, distribution and risk assessment of organochlorine pesticides in soils from the Midway Atoll, North Pacific Ocean

Jing Ge [a], Lee Ann Woodward [b], Qing X. Li [c,*], Jun Wang [a,c,**]

[a] Key Laboratory of Aquatic Botany and Watershed Ecology, Wuhan Botanical Garden, Chinese Academy of Sciences, Wuhan 430074, China
[b] U.S. Fish and Wildlife Service, Pacific Reefs NWRC, Honolulu, HI 96850, USA
[c] Department of Molecular Biosciences and Bioengineering, University of Hawaii at Manoa, Honolulu, HI 96822, USA

HIGHLIGHTS

- Contamination levels of DDTs and HCHs were studied in the Midway Atoll, North Pacific Ocean.
- Potential sources of DDTs and HCHs in soils of the Midway Atoll were investigated.
- Possible degradation modes of o,p′-DDT in soils of the Midway Atoll were analyzed.
- Cancer risks of DDTs and HCHs in soils of the Midway Atoll were assessed.

ARTICLE INFO

Article history:
Received 21 December 2012
Received in revised form 26 February 2013
Accepted 3 March 2013
Available online 27 March 2013

Keywords:
DDTs
HCHs
Midway Atoll
Marine pollution
Risk assessment
Soils

ABSTRACT

Concentrations of legacy organochlorine pesticides (OCPs), including dichlorodiphenyltrichloroethane (DDT) and its metabolites (e.g., DDE and DDD), and hexachlorocyclohexanes (HCHs) were determined in 111 soil samples from the Midway Atoll. OCPs were found in all samples analyzed, with predominance of α-HCH, *p,p′*-DDD and *p,p′*-DDT. The total concentrations ranged from 0 to 127 ng g^{-1} with a median concentration of 17 ng g^{-1} for HCHs and 1.4 to 643 ng g^{-1} with a median concentration of 168 ng g^{-1} for DDTs. The possible degradation pathways and potential sources of DDTs and HCHs were investigated. The total concentrations of DDTs and HCHs were used to evaluate the cancer risk probabilities in humans via ingestion, dermal contact and inhalation of soil particles. Very low cancer risk was found in all soil samples caused by ΣDDTs and ΣHCHs.

1. Introduction

Organochlorine pesticides (OCPs) are synthetic compounds with great chemical stability and listed as persistent organic pollutants (POPs). Due to the wide use throughout the world since the middle of the last century, these compounds are ubiquitous in the environment and pose an environmental and human risk (Ben Hassine et al., 2012; Jones and Voogt, 1999). Some of these pollutants are highly toxic and have a large variety of chronic effects, including endocrine dysfunction, mutagenesis and carcinogenesis. Dichlorodiphenyltrichloroethanes (DDTs) and hexachlorocyclohexanes (HCHs) are hydrophobic and have considerable accumulation potential in organisms and magnification in the food chain. Some of the OCPs are believed to act as endocrine disruptors affecting hormone regulation (Briz et al., 2011; Ray, 2006).

The Midway Atoll (178°W, 28°N) is in the North Pacific Ocean 1100 miles northwest of Pearl Harbor, Hawaii. The atoll consists of two main islands, Sand and Eastern, surrounded by a fringing coral reef (Hope et al., 1997). The Midway Atoll was under Navy jurisdiction from 1903 to 1996. There are many environment contaminants that resulted from 90 years of military operations. Contaminants included polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), petroleum hydrocarbons, pesticides such as DDT and dichlorodiphenyldichloroethane (DDE), and numerous heavy metals (Caccamisea et al., 2012; Hope et al., 1997; Taylor et al., 2009).

Even though heavily modified by human activity nearly hundred years, the islands provide a breeding and feeding habitat for 17 species of seabirds with an aggregate population of nearly 2 million. The Midway Atoll is also a habitat for threatened green sea turtles and Hawaiian monk seals (USFWS, 2010). In order to limit the exposure by ecological receptors, remedies have been implemented. However, those contaminants are not easily degraded. The bulk of the

* Correspondence to: Q.X. Li, 1955 East-West Road, Honolulu, HI 96822, USA. Tel.: +1 808 956 2011; fax: +1 808 956 3542.
** Correspondence to: J. Wang, Key Laboratory of Aquatic Botany and Watershed Ecology, Wuhan Botanical Garden, Chinese Academy of Sciences, Wuhan 430074, China. Tel./fax: +86 27 87510722.
E-mail addresses: qingl@hawaii.edu (Q.X. Li), wangjun@wbgcas.cn (J. Wang).

0048-9697/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.scitotenv.2013.03.015

burden of POPs in the environment resides in soils and sediments where they primarily partition into organic matters. Small changes in the mass of soils/sediments would have a major impact on concentrations in 'adjacent' media, such as air or water (Jones and Voogt, 1999). Many organochlorine POPs have high affinity with soil and are retained in the environment for a long time. They may also be washed in run-off from the land into the ocean.

The objectives of the study were to determine the concentrations of OCPs in the soil of the Midway Atoll, and analyze the potential sources of OCPs in this area. The study was also conducted for a human health risk assessment on cancer, in order to evaluate the potential carcinogenic risk based on the concentrations of OCPs in soil.

2. Materials and methods

2.1. Study area and sample collection

The Midway Atoll is located at the northwest end of the Hawaiian Islands archipelago, at 28.208°N latitude and −177.379°W longitude (Fig. 1). This is approximately 2000 km from Honolulu, Hawaii and 4900 km from Portland, Oregon. The atoll is comprised of two main islands, Sand and Eastern, and one smaller islet, enclosed within a reef approximately 8 km. As part of the Midway Atoll, Sand Island has a long history of use for communication, commercial and military purposes. Midway was a base for military operations between 1941 and the early 1990s. As such, portions of Sand Island were, and continue to be occupied by an airfield, buildings and other structures to support operations and staff that live on the island. One hundred and eleven soil samples were collected in 2006 from the Sand and Eastern islands in the Midway Atoll, North Pacific Ocean. The samples were immediately transferred to the laboratory and frozen at −20 °C until processed for analysis.

2.2. Sample preparation, extraction and cleanup

Soil samples were freeze-dried for 24 h, pulverized and sieved through 80-mesh stainless steel. The sample cell (about 6–12 g) was loaded into an accelerated solvent extractor 200 system (Dionex, Sunnyvale, CA, USA). The extraction was performed with a mixture of acetone and methylene chloride (1:1, v/v) at a pressure of 1500 psi and temperature of 100 °C for three static cycles, a flush volume of 60% of the cell volume and a N_2 purge time of 5 s. A mixture of Ottawa sand and Na_2SO_4 was extracted in the same manner as the sample blank. All samples were extracted in triplicate. After the extract was dried with 30 g of anhydrous sodium sulfate and rinsed with hexane (3 mL), it was concentrated to approximately 3 mL by using a rotary evaporator. The concentrated extract in hexane was cleaned up on an 8 mm i.d. aluminum/silica column. The column was packed, from the bottom to the top, with neutral silica (4 g, 3% deactivated), neutral alumina (2.0 g, 6% deactivated), and anhydrous sodium sulfate (1 cm). The column was eluted with 18 mL of hexane to yield the OCP and other POP fraction. The fraction was concentrated to 20 μL under a gentle stream of high purity nitrogen.

2.3. Gas chromatograph and ion trap MS (GC/ITMS) analysis

The samples were analyzed on a Varian Saturn 2000 gas chromatography/ion trap mass spectrometry (GC/ITMS) system (Varian, Walnut Creek, CA, USA). The column was a capillary column DB-5MS (J&W Scientific, Inc., 30 m × 0.25 mm i.d. × 0.25 μm). Helium was used as the carrier gas and the flow rate was 2 mL min^{-1}. The oven temperature started at 60 °C for 1 min, increased to 290 °C at a rate of 4 °C min^{-1} and held for 10 min. An aliquot of 2.0 μL of the sample was injected in splitless mode with an AS8400 autosampler. The temperatures of injector and ion trap were 280 °C and 250 °C, respectively. The mass spectrometer was operated in the select ion mode with a mass range of

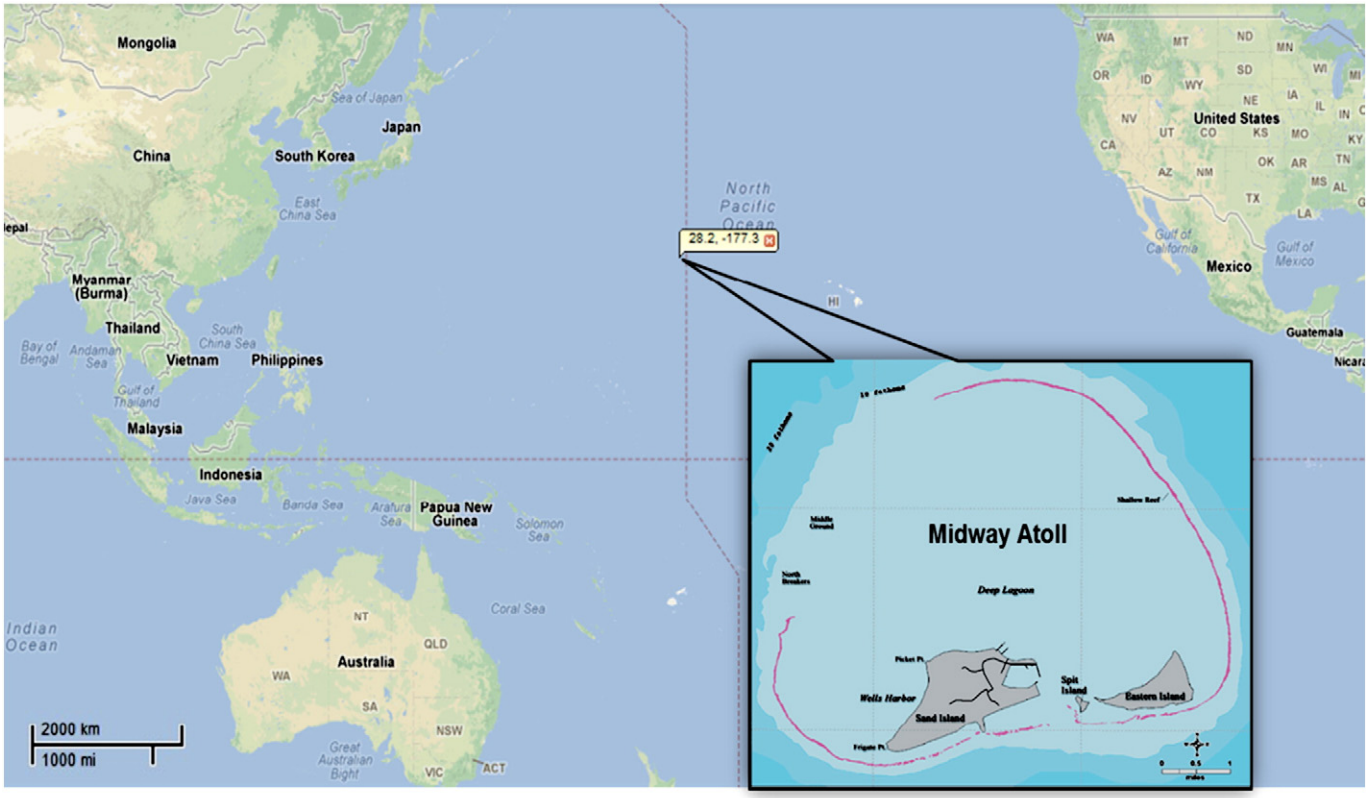

Fig. 1. Locations of study area in the Midway Atoll, North Pacific Ocean.