Deep-Sea Research II 128 (2016) 53–62

Contents lists available at ScienceDirect

Deep-Sea Research II

journal homepage: www.elsevier.com/locate/dsr2

Bioaccumulation of chemical warfare agents, energetic materials, and metals in deep-sea shrimp from discarded military munitions sites off Pearl Harbor

Shelby Koide [a,*], Jeff A.K. Silva [a], Vilma Dupra [a], Margo Edwards [b]

[a] Environet, Inc., 1286 Queen Emma Street, Honolulu, HI 96813, USA
[b] Hawai'i Institute of Geophysics and Planetology, School of Ocean and Earth Science and Technology, University of Hawai'i at Manoa, 1680 East-West Road, Honolulu, HI 96822, USA

ARTICLE INFO

Available online 20 March 2015

Keywords:
Bioaccumulation
Heterocarpus ensifer
Deep-sea shrimp
Discarded military munitions

ABSTRACT

The bioaccumulation of munitions-related chemicals at former military deep-water disposal sites is poorly understood. This paper presents the results of human-food-item biota sampling to assess the potential for bioaccumulation of chemical warfare agents, energetic materials, arsenic, and additional munitions-related metals in deep-sea shrimp tissue samples collected during the Hawai'i Undersea Military Munitions Assessment (HUMMA) project to date. The HUMMA investigation area is located within a former munitions sea-disposal site located south of Pearl Harbor on the island of O'ahu, Hawai'i, designated site Hawaii-05 (HI-05) by the United States Department of Defense. Indigenous deep-sea shrimp (*Heterocarpus ensifer*) were caught adjacent to discarded military munitions (DMM) and at control sites where munitions were absent. Tissue analysis results showed that chemical warfare agents and their degradation products were not present within the edible portions of these samples at detectable concentrations, and energetic materials and their degradation products were detected in only a few samples at concentrations below the laboratory reporting limits. Likewise, arsenic, copper, and lead concentrations were below the United States Food and Drug Administration's permitted concentrations of metals in marine biota tissue (if defined), and their presence within these samples could not be attributed to the presence of DMM within the study area based on a comparative analysis of munitions-adjacent and control samples collected. Based on this current dataset, it can be concluded that DMM existing within the HUMMA study area is not contributing to the bioaccumulation of munitions-related chemicals for the biota species investigated to date.

1. Introduction

In the years following World War II, sea-disposal of excess or obsolete conventional and chemical munitions was a common international practice and significant amounts of chemical munitions and bulk chemical warfare agents (CWAs) were reportedly disposed in the Baltic Sea, Sea of Japan, and Pacific Ocean (Bizzigotti et al., 2009). In the United States waters, the Department of Defense disposed of approximately 29,030 t of CWAs at multiple sites located along the eastern coast, Gulf of Mexico, western coast, and Hawai'i (Department of Defense, Office of the Under Secretary of Defense for Acquisition, Technology and Logistics, 2010). The legacy of this practice has prompted international concern as to the human health and ecological risks associated with the release of munitions chemicals to the marine environment as these munitions corrode on the sea floor.

Bioaccumulation is the process by which contaminant chemicals are taken up by an organism either from the direct exposure to a contaminated medium (absorption) or through consumption of food containing chemicals (ingestion) (Corl, 2001). The degree of bioaccumulation can be affected by a number of factors including the physicochemical properties of the contaminant (*e.g.*, water solubility, octanol-water partition coefficient [K_{ow}]), contaminant bioavailability, the concentration and duration of exposure, and physiology of the organism (United States Environmental Protection Agency [EPA], 2003). The potential for chemicals to bioaccumulate within marine organisms is typically evaluated based on the chemicals' bioaccumulation factor (BAF) (EPA, 2000). BAFs can be measured or estimated with a variety of methods, including empirically driven approaches that rely on measurements of chemical concentrations in aquatic organisms and their surrounding environmental media (water and sediment),

* Corresponding author. Tel.: +1 808 833 2225x1038.
E-mail address: skoide@environetinc.com (S. Koide).

http://dx.doi.org/10.1016/j.dsr2.2015.03.002
0967-0645/

mechanistically driven approaches that rely on food web models in combination with information about the properties of chemicals and ecosystems to estimate bioaccumulation, and empirical relationships based on known or anticipated solution concentration and the hydrophobicity of the contaminant (*e.g.*, K_{ow}). For munitions chemicals, especially CWAs, BAFs available in the existing literature are most often species specific, complicating direct application to alternative species of site-specific interest. Furthermore, there are limitations for prediction when comparing a single chemical property such as the K_{ow}. Evaluation of K_{ow} does not consider factors such as different lipid types, which could have different sorptive capacities and it does not factor in capacities of non-lipid components such as proteins (Endo et al., 2013). Therefore, accurate assessment of risk related to the accumulation of munitions chemicals within a specific aquatic human-food-item biota often requires collection of that organism and direct tissue concentration measurement.

The Hawai'i Undersea Military Munitions Assessment (HUMMA) project was conceived as the most comprehensive deep-water investigation in the United States to catalogue the current condition of chemical and conventional munitions and begin to assess risks posed by the legacy of sea disposal. The HUMMA study area lies within a former sea disposal area south of Pearl Harbor, O'ahu, Hawai'i, that was designated as Hawaii-05 by the Department of Defense. The study area ranges from approximately 450 to 650 m deep with temperatures of 5–6 °C. Sea-disposal operations were poorly documented. However, the site is known to contain both conventional and chemical discarded military munitions (DMM), including 16,000 M47A2 100-pound mustard-filled bombs disposed of by barge some 8 km south of Pearl Harbor between October and November 1944 (Chemical Officer, 1944). A component of the HUMMA investigation is to collect and analyze human-food-item biota to determine the presence or absence of munitions constituents (MC), specifically CWAs, energetic materials, and metals. This study focused on three metals (*i.e.*, arsenic, copper, and lead). The constituents of potential concern (COPCs) are specific MC and associated MC degradation products related to the M47A2 100-pound mustard-filled bombs and the other historically disposed military munitions reported for the study area. Individual COPCs from these sources include a variety of chemicals in the following groups: CWA (*i.e.*, mustard and Lewisite) and their degradation products (*i.e.*, thiodiglycol, 1,4-dithiane, and 1,4-thioxane) from bomb-fill materials; energetic materials from conventional munitions and bursters (*i.e.*, 2,4,6–trinitrotoluene [2,4,6-TNT], picric acid, and Royal Demolition Explosive [1,3,5-trinitroperhydro-1,3,5-triazine]); and metals from munitions casings (*i.e.*, copper and lead) and from CWA degradation products (*i.e.*, arsenic as Lewisite breaks down to forms of arsenic).

In 2010, the State of Hawai'i Department of Land and Natural Resources, Division of Aquatic Resources, reported that approximately 13,456 t of seafood were commercially landed from island waters, of which a portion of approximately 189 t of "other species" were shrimp (State of Hawai'i Department of Land and Natural Resources, 2010). With seafood being an important part of the local diet in Hawai'i, the question arose as to whether or not there are possible impacts from CWA on biota that reside near the disposal sites. HUMMA is an early effort to address this question.

In 2009, the first HUMMA sampling program was conducted in which samples of seawater, sediment, and biota (*i.e.*, shrimp and fish) were collected near conventional munitions and analyzed for CWAs, energetic materials, and metals. During this 2012 HUMMA sampling program, which was conducted in an area southeast of the 2009 HUMMA study area (Fig. 1), M47A2 100-pound mustard-filled bombs were identified, and samples were collected at these munitions to (i) provide data with which to assess the potential for MC bioaccumulation and (ii) serve as a basis for comparison with results from the 2009 HUMMA sampling program, which documented conventional (non-chemical) munitions. Since deep-sea shrimp were observed as being prevalent in very close proximity to munitions (< 1 m) at most of the study sites during the 2009 HUMMA sampling program, the biota species of interest selected for this 2012 study was the commercially landed, deep-sea shrimp, *Heterocarpus ensifer* (State of Hawai'i Department of Land and Natural Resources, 2010). This study will present the analytical tissue results from the 2012 HUMMA sampling program, which was focused on sampling adjacent to disposed chemical munitions, and provide a general comparison against the bioaccumulation findings of other studies, including the 2009 HUMMA sampling program in which sampling occurred near conventional munitions.

2. Materials and methods

2.1. Sampling of specimen

During the 2012 HUMMA sampling program, human occupied vehicles (HOVs) were used to deploy and recover shrimp traps at locations adjacent to the DMM targets of interest and control sites. These traps were deployed at a total of 12 study sites (Fig. 1): three positioned adjacent to likely CWA-containing DMM with casings that appeared minimally breached (less than 5% surface area breached); three positioned adjacent to likely CWA-containing DMM that appeared significantly breached (greater than 25% surface area breached); three positioned adjacent to DMM classified as conventional explosive munitions; and a final three positioned at project sample control sites that were located in excess of 50 m from any munitions-related objects as determined from previous side-scan SONAR surveys of the study area. These category sites are hereafter designated DMMmb (minimally breached), DMMsb (significantly breached), DMMcv (conventional munitions), and CON (control site) throughout this manuscript.

At each study site, the HOV placed the shrimp trap on the sea floor proximal to the main body of the DMM, within 0.5–2 m of the casing. Typically, the traps were left in place for less than 2 h, prior to HOV departure for another site or return to the ocean surface. On board the Research Vessel *Ka'imikai-o-Kanaloa*, shrimp were removed from the retrieved traps following CWA safety clearance by Edgewood Chemical Biological Center (ECBC). The safety clearance involved using a mobile device (*e.g.*, Gas Chromatograph or Mass Selective Detector) or a Civil Defense Simultest kit or equivalent to identify presence/absence of CWA at concentrations that would pose a human health concern, as defined by accepted United States-based environmental screening levels for CWA.

2.2. Shrimp sample handling, processing, and analysis

Shrimp removed from the traps were photographed, inspected for species identification, and the number of shrimp of each species type was documented. Between 14 and 117 *H. ensifer* were recovered from the traps at each of the study sites. This species was identified based on the absence of sharp appendages located on their tails, a characteristic that distinguishes *H. ensifer* from other species (*i.e.*, *H. laevigatus*) common within the study area. A quick guide sheet with photographs of the shrimp species was maintained as a reference for shipboard personnel. Shrimp collected from each trap were also examined for visible lesions or other morphological health indicators present on the exterior of the organism.

Shrimp tissue samples were prepared for analysis in a manner reflective of typical local consumption habits. Shrimp tails were separated from the heads, legs, and carapace. The shrimp were not de-veined nor de-shelled since these parts are commonly consumed. The shrimp tails were placed into pre-cleaned, laboratory-supplied sample containers, properly labeled, frozen, and shipped to the