Journal of Marine Systems xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Marine Systems

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

Heavy metals from Kueishantao shallow-sea hydrothermal vents, offshore northeast Taiwan

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A R T I C L E I N F O

Article history:
Received 26 January 2016
Received in revised form 22 November 2016
Accepted 26 November 2016
Available online xxxx

Keywords:
Heavy metals
Hydrothermal activity
Kueishantao
Spatial distribution
Correlation analysis
Environmental impact

A B S T R A C T

Shallow water hydrothermal vents are a source of heavy metals leading to their accumulation in marine organisms that manage to live under extreme environmental conditions. This is the case at Kueishantao (KST) shallow-sea vents system offshore northeast Taiwan, where the heavy metal distribution in vent fluids and ambient seawater is poorly understood. This shallow vent is an excellent natural laboratory to understand how heavy and volatile metals behave in the nearby water column and ecosystem. Here, we investigated the submarine venting of heavy metals from KST field and its impact on ambient surface seawater. The total heavy metal concentrations in the vent fluids and vertical plumes were 1–3 orders of magnitude higher than the overlying seawater values. When compared with deep-sea hydrothermal systems, the estimated KST end-member fluids exhibited much lower concentrations of transition metals (e.g., Fe and Mn) but comparable concentrations of toxic metals such as Pb and As. This may be attributed to the lower temperature of the KST reaction zone and transporting fluids. Most of the heavy metals (Fe, Mn, As, Y, and Ba) in the plumes and seawater mainly originated from hydrothermal venting, while Cd and Pb were largely contributed by external sources such as contaminated waters (anthropogenic origin). The spatial distribution of heavy metals in the surface seawater indicated that seafloor venting impacts ambient seawater. The measurable influence of KST hydrothermal activity, however, was quite localized and limited to an area of <1 km^2. The estimated annual fluxes of heavy metals emanating from the yellow KST hydrothermal vent were: 430–2600 kg Fe, 24–145 kg Mn, 5–32 kg Ba, 10–60 kg As, 0.3–1.9 kg Cd, and 2–10 kg Pb. This study provides important data on heavy metals from a shallow-sea hydrothermal field, and it helps to better understand the environmental impact of submarine shallow hydrothermal venting.

1. Introduction

Heavy metals are usually recognized as environmental pollutants that raise global concerns both for seawater quality and marine life (Gopalakrishnan et al., 2008; Sfakianakis et al., 2015). Scientists have long realized that seafloor hydrothermal vents emanate hot fluids with high heavy metal contents due to the seawater-rock interaction at elevated temperatures (German and Von Damm, 2006; Koschinsky et al., 2008; Price et al., 2013b; Rona et al., 2013). During that interaction, Fe^{2+}, Mn^{2+}, silica, rare earth elements (REEs), toxic metals (e.g., As, Pb, Cd) and other elements are leached from the host rock, while Mg^{2+} is depleted. Although heavy metals in the vent fluids are consumed by precipitation both in the sub-seafloor due to cooling and when the hot fluids encounter the cold and alkaline seawater (German and Von Damm, 2006; Zeng, 2011), the residual heavy metals still cause contamination of the surrounding ambient seawater. Especially, for the shallow-water hydrothermal fields in water depths of <200 m which are usually located close to the coastline and in zones of high primary production, heavy metals in the vent fluids pose a higher potential impact to the local environment and ecosystem being relevant to humans than those of deep-sea hydrothermal systems. For example, in the shallow-sea hydrothermal fluids off Milos Island, Greece, the As concentration in the high-Cl fluid and low-Cl fluid reached 39 μM and 78 μM, respectively, compared with the background content in seawater of 0.027 μM (Price et al., 2013b). This As occurring in variable speciation can be assimilated into the tissues of marine organisms (Breuer, 2013; Neff, 1997). In the hydrothermal field at

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http://dx.doi.org/10.1016/j.jmarsys.2016.11.018
0924-7963/

Tutum Bay, Ambitle island, Papua New Guinea, As concentrations can be as high as 20.7 μM with dominant speciation of toxic As(III) (Pichler et al., 1999; Price and Pichler, 2005). Studies in the coral reefs in the Tutum Bay indicate that the organisms from the vent area exhibit 2–20 times higher total As contents than that from the control site (Price et al., 2013a). In addition, bioaccumulation of As and Hg have also been found in seaweed and marine copepods from hydrothermal areas at Concepcion Bay, Baja California, Mexico, where toxic metals originate from hydrothermal venting (Leal-Acosta et al., 2013; Villanueva-Estrada et al., 2013).

Kueishantao (KST) is a Holocene volcanic island located offshore northeast Taiwan. There are >30 submarine hydrothermal vents at depths of 5–30 m within 1 km southeast of this island (Fig. 1). Past investigations suggested that the pH values of the vent fluids can be as low as 1.52, and the concentrations of SiO_2, Fe, and Mn are 2–6 orders of magnitude higher than the seawater values (Chen et al., 2005a, 2005b; Han et al., 2014; Kuo, 2001; Wang et al., 2013). Although data on the heavy metals in the vent fluids and ambient seawater are scarce, scientists have noticed that the local marine organisms are influenced by the heavy metals from the vent fluids (Chen et al., 2015; Jiang et al., 2013, 2014). For instance, Peng et al. (2011) investigated the accumulation of trace metals in the crab *Xenograpsus testudinatus* that lives near the vents, and most of the heavy metals accumulated in the gills via respiration pathways. Significant Hg bioaccumulation was found in the marine copepods from KST vent field (Hsiao and Fang, 2013). In addition, the venting activity at KST area may have altered the diversity and abundance of local macrobiota (Chan et al., 2016; Mantha et al., 2013), and even increased the mortality of local plankton (Dahms and Hwang, 2013).

In this study, we studied the heavy metal concentrations in the vent fluids, vertical plumes, and ambient surface seawater of KST field, and estimated the end-member concentrations of heavy metals in the vent fluids. In addition, we studied the possible sources of heavy metals and calculated the annual fluxes of heavy metals emanated from KST hydrothermal vents. This study provides important data on heavy metals from a shallow-sea hydrothermal field. Furthermore, it can help to better assess the environmental and ecological impacts of submarine shallow hydrothermal venting.

2. Samples and methods

2.1. Geological setting

KST shallow hydrothermal field is located offshore northeast Taiwan, within 1 km southeast of the KST islet (121°55′E, 24°50′N) (Fig. 1). KST islet is a Holocene volcanic island that erupted about 7000 years ago (Chen et al., 2001; Kuo, 2001). It is situated at a junction between Okinawa Trough and the Philippine Plate. The magmatic activity underneath KST area is still dynamic because of the westward extension of the Okinawa Trough. Until now, >30 individual hydrothermal vents at depths of 5–30 m have been discovered and the vent number is still increasing as survey continues.

The temperature of the KST vent fluids either fall in the range of 78–116 °C, or was relatively lower at 30–65 °C (Chen et al., 2005a, 2005b; Kuo, 2001). One typical vent with temperature of 110–116 °C (the “yellow vent”) (location: 24.83489° N, 121.96210° E, depth: 8 m) and one lower-temperature vent (the “white vent”) (location: 24.83419° N, 121.96198° E, depth: 13 m) were chosen and investigated in this study (Fig. 2). The distance between both vents was about 86 m (Wang et al., 2013). The fluids from the yellow vent were yellowish and showed pH values as low as 1.52, high fluxes (up to 150 $m^3\ h^{-1}$), and high sulfur contents. The white vent discharged milky white fluids with higher pH ≈ 6 and lower fluxes than the yellow vent (<25 $m^3\ h^{-1}$) (Chen et al., 2005a, 2005b). The yellow vent is one of the most active

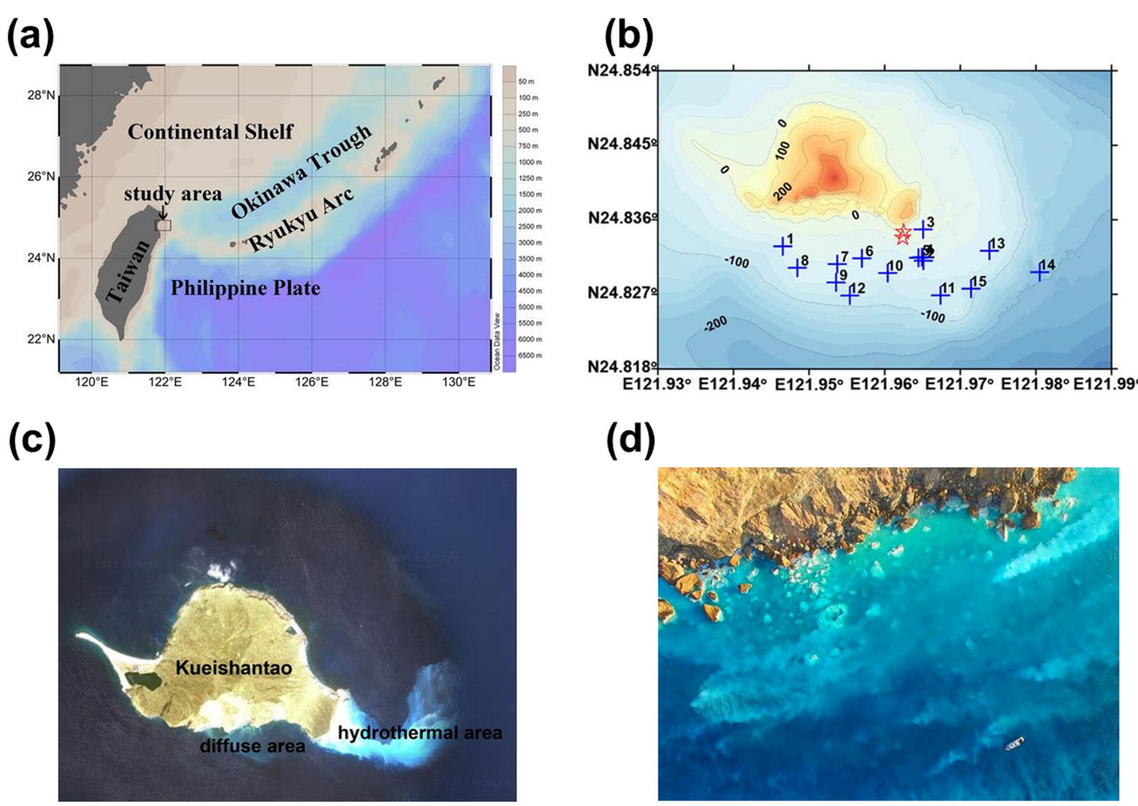

Fig. 1. (a) Geological setting of Kueishantao (KST) area at the southwest end of the Okinawa Trough. (b) Bathymetric map of KST field. The red star symbols show the positions of the white vent and the yellow vent, respectively. The blue “+” symbols with numbers indicate the positions of collected surface seawater samples and their corresponding sample numbers. (c) Satellite image of Kueishantao island and KST hydrothermal field with diffuse and focused fluid areas; (d) aerial view of the KST sampling area (note ship in the lower right corner; courtesy of M. Lebrato). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Please cite this article as: Chen, X.-G., et al., Heavy metals from Kueishantao shallow-sea hydrothermal vents, offshore northeast Taiwan, J. Mar. Syst. (2016), http://dx.doi.org/10.1016/j.jmarsys.2016.11.018