Environmental Pollution 239 (2018) 272–280

Contents lists available at ScienceDirect

Environmental Pollution

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

Thallium contamination of desert soil in Namibia: Chemical, mineralogical and isotopic insights☆

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ARTICLE INFO

Article history:
Received 19 February 2018
Received in revised form
29 March 2018
Accepted 1 April 2018

Keywords:
Soil
Tl isotopes
Mining waste
Contamination

ABSTRACT

We studied arid desert soils from Namibia (Rosh Pinah) that were contaminated with up to 7 mg kg^{-1} of thallium (Tl) via dust emitted from a local flotation tailing dam. Chemical extractions of waste and soil materials indicated that most of the Tl is strongly bound, in accordance with X-ray diffraction and X-ray absorption spectroscopy data that point to the predominant association of Tl with metal sulfides and phyllosilicates. The isotope fractionation factor ε^{205}Tl of the soil samples (from −0.4 to +3.8) shows a positive linear relationship ($R^2 = 0.62$) with 1/Tl, indicative for the mixing of two major Tl pools, presumably anthropogenic Tl and geogenic Tl. The ε^{205}Tl value for the topmost soil samples (~+3) closely matches the ε^{205}Tl value for post-flotation waste particles with a diameter of <0.05 mm, whereas the bulk flotation waste exhibits a significantly larger ε^{205}Tl value (~+6). These variations are in accordance with predominant atmospheric transfer of Tl from the tailings to the adjacent soils via fine (dust) particles. The identified minimal Tl alteration in soils indicates that only a small part of the Tl could be potentially released and passively enter the vegetation, local population and/or food chain in the long term. From this viewpoint, Tl does not represent such an important environmental concern as other (abundant) contaminants at the locality. Furthermore, there could be a relevance for other alkaline desert soils, including those where Tl pollution plays a major role.

1. Introduction

Since thallium (Tl) can be greatly enriched in some sulfides (e.g., sphalerite, ZnS, pyrite, FeS_2; up to 500 mg kg^{-1}) or even act as a mineral-forming element (e.g., lorandite, $TlAsS_2$) (Tremel et al., 1997; Xiao et al., 2004, 2012; Jakubowska et al., 2007; Karbowska et al., 2014; Liu et al., 2016; Vaněk et al., 2016, 2018; Lukaszewski et al., 2018 etc.), crushing, milling, and smelting operations related to these materials play a key role in how Tl could be introduced into local environments. This Tl, when deposited on the soil surface, reacts with other constituents and its fate depends on a number of factors, such as the nature of the original Tl-bearing phases, bulk soil mineralogy, the content and quality of the soil organic matter (SOM), water precipitation and cycles or biological activity. Despite the achievements in environmental Tl geochemistry over the past decade, little is still known about Tl dynamics in arid (desert) soils, nor about the processes that control the mobility

☆ This paper has been recommended for acceptance by Joerg Rinklebe.
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https://doi.org/10.1016/j.envpol.2018.04.006
0269-7491/

of this trace element. Similarly, the question arises as to degree to which the Tl isotope signature may differ between that of the primary Tl source and secondary Tl-bearing phases, and whether the Tl isotope signature is suitable for tracing Tl contamination or its geochemical behavior. Here we describe the combined chemical, mineralogical and Tl isotope record for contaminating wastes and mineral soils in an arid African region historically impacted by Zn-Pb ore mining (Rosh Pinah, Namibia). The results of this study may contribute to better understanding of the fate and cycling of Tl in arid surface/subsurface environments and contribute to the scientific basis for the assessment and remediation of Tl-contaminated sites.

2. Materials and methods

2.1. Study area

The Rosh Pinah site is located in southern Namibia, ~600 km S of Windhoek, the capital of Namibia, and ~20 km N of the Orange River, at the edge of the Namib Desert (Fig. 1). The local climate is arid with a low (and irregular) distribution of precipitation. The rainy season is between April and September, i.e., during the winter; the approximate annual rainfall is 65 mm and the potential evaporation is up to ~2800 mm year^{-1}. Average temperatures in the summer vary between 30 and 40 °C, while the average temperature is 20–25 °C in the winter (Kříbek et al., 2014).

The 740 Ma syngenetic Rosh Pinah Zn-Pb ore deposit is classified as a sedimentary-exhalative (SEDEX) type (Alchin et al., 2005). The ore zone is composed of disseminated to massive sulfides, with sphalerite, pyrite, galena (PbS), and minor chalcopyrite ($CuFeS_2$) as the principal sulfide phases. The strata-bound mineralization is located in silicified black shale, As-bearing feldspars and altered carbonate rocks of the Neoproterozoic Rosh Pinah Formation (Hilda Subgroup of the Port Nolloth Group). There is also significant Ba enrichment linked to barite ($BaSO_4$) (Alchin et al., 2005). The local underground Zn-Pb mine (Trevali Mining Corp., from 3/2017) has been in continuous operation since 1969. The average ore production corresponds to ~700,000 t year^{-1} with 7.9% Zn, 1.7% Pb and 0.1% Cu. Ores from various ore bodies and levels are mixed, then crushed, milled and pulverized to a ≤120 μm fraction and treated in the flotation plant where Zn and Pb concentrates are produced. The dried concentrates are transported by trucks to Lüderitz harbor, from which they are exported overseas. Residual (flotation) tailings are pumped and moved via a pipe to the tailing dam, which is located ~1.5 km S of the processing plant (Fig. 1). Currently, the waste dump covers an area of ~60 hectares and is more than 25 m high (Nejeschlebová et al., 2015). The dam represents the main (point) source of Tl/metal contamination in the area, as its surface tends to be eroded and fine-grained particles may then be easily remobilized and deposited onto soils, including those at more distant locations (>1 km) (Kříbek et al., 2014). At this point, it should be noted that specific remediation practices have been carried out at Rosh Pinah in the past, using vegetation (shrub) plantations, in an attempt to (phyto)stabilize the slope of the tailing dam. Nevertheless, this practice only partially reduced wind (or water) erosion of the material because of the gradual denudation of the plant roots and the vegetation stress caused by the toxicity of the tailings.

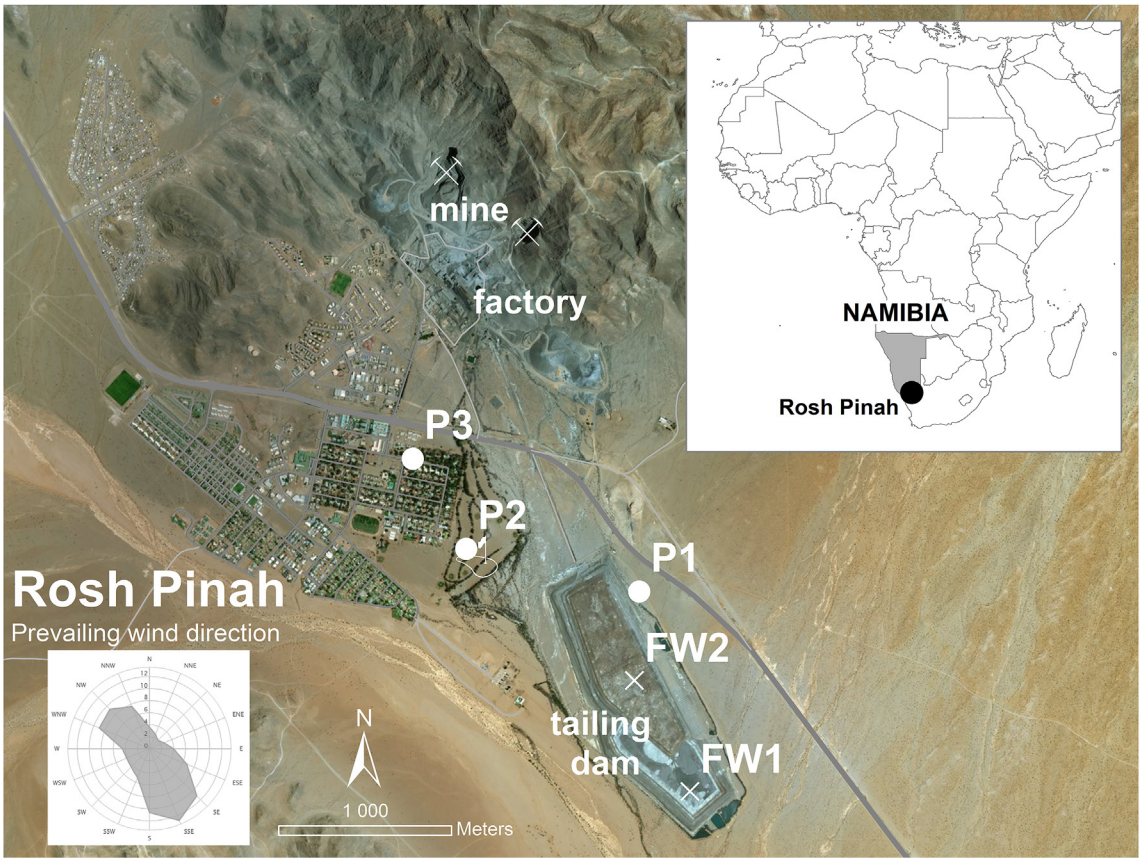

Fig. 1. Study area and sampling sites (P1, P2 and P3 – soil profiles; FW1 and FW2 – flotation waste samples).