Metal(oid) mobility in a hypersaline salt marsh sediment (Sečovlje Salina, northern Adriatic, Slovenia)

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HIGHLIGHTS

- The transfer of metal(oid)s in a hypersaline environment was investigated.
- Availability of metal(oid)s from a health risk perspective was conducted.
- Sediment-water physical and geochemical properties induced limited mobility dynamics.
- Extraction testing in artificial sweat indicate low mobility of metal(oid)s.

GRAPHICAL ABSTRACT
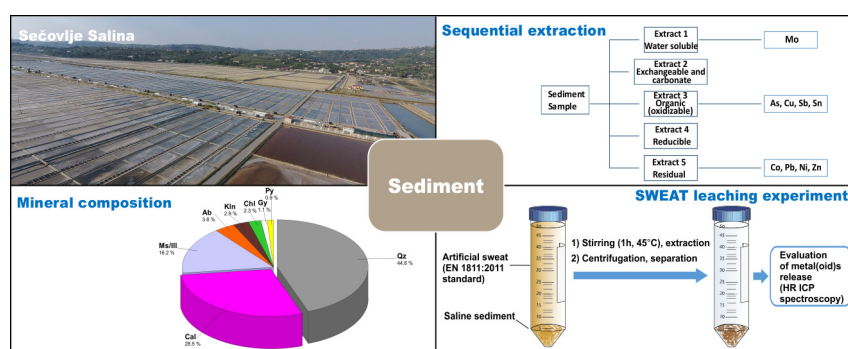
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ABSTRACT

In this research, sediments from the Sečovlje Salina (northern Adriatic, Slovenia) were geochemically investigated in order to decode the mobility of metal(oid)s in the hypersaline environment. The results demonstrated that the concentrations of As, Co, Cu, Mo, Ni, Pb, Sb, Sn and Zn were comparable to those detected in various similar coastal background areas, as well as in the Sečovlje salt marsh core sample. The estimated mobility potential of metal(oid)s in sediment decreases in the following order: Mo > As > Cu > Sb > Sn > Co > Pb > Ni > Zn. Since the hypersaline sediment (e.g. healing mud) is used as a healing factor (it can be applied directly on human skin), the study of metal(oid) bioavailability in an interaction between the hypersaline sediments and the artificial sweat was also performed. It is significant that the metal(oid) contents are leached in very low concentrations and are treated as nontoxic for humans according to international norms for cosmetic products. The study provides information in order to assess the role of metal mobility on the potential health impact of the application of natural healing mud.

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1. Introduction

Metal(oid)s are constantly introduced into marine coastal environments through various routes (e.g. rivers, runoff and land-based point sources) and thus, marine ecosystems are defined as one of the most vulnerable ecosystems on Earth (Gu et al., 2012; Yuan et al., 2004). When metal(oid)s enter into the marine environment, they become incorporated into the sediments and in various biota (organisms), and consequently could pose health risks to marine organisms (e.g. primary producers, fish and invertebrates) and consumers of those organisms, including humans (Wang and Chen, 2000). The majority of metal(oid)

s create a close association with sediment organic matter, Fe/Mn oxides, sulfides, and clays (Wang and Chen, 2000) and their distribution is influenced by sediment mineralogical and chemical composition, various anthropogenic sources, diagenetic processes, etc. (Jain et al., 2005). The evaluation of metal(oid) toxicity and bioavailability to marine (benthic) organisms generally depends on chemical speciation (Besser et al., 2003; Riba et al., 2004; Simpson, 2005; Xiao et al., 2015) and geochemical sediment properties (Rainbow, 2007). Exploring the influences of accumulated metal(oid)s in sediments, their toxicity and bioavailability (biological uptake) in aquatic systems is of critical importance, especially in the hypersaline coastal environments where knowledge is particularly limited (Shumilin et al., 2002; Soto-Jiménez and Páez-Osuna, 2008).

Hypersaline coastal environments in the Mediterranean area, including salinas or inland salt marshes, are characterised by seasonal and spatial variations in tidal high, temperature, solar radiation, evapotranspiration, input of underground and surficial waters, droughts, variable sediment fluxes etc. (Ganju et al., 2017; Reading, 1996). These combinations create very vulnerable/sensitive natural environments with unique environmental and geochemical conditions, depositional and post-depositional processes and mobility behaviour of accumulated metal(oid)s in the hypersaline sediments that must be understood and studied. Few studies have examined metal(oid) distribution and mobility in the northern Adriatic salt marsh systems, which can act both as a sink and sporadically as a possible source for several trace metal(oid)s (Petranich et al., 2017).

Sečovlje Salina Nature Park (SSNP; northern Adriatic, Republic of Slovenia) is recognised as a very valuable hypersaline area and cultural heritage site in the Republic of Slovenia. The SSNP covers a surface area of approximately 6.5 km^2 comprised of habitats with rare, endangered and characteristic plant and animal species. SSNP plays host to one of the only still-functioning artisanal solar salinas (Sečovlje Salina) in the Mediterranean, as well as providing hypersaline sediments (e.g. saline healing mud or fango) and other products (sea water, brine…) for medical treatment, wellness and relaxation purposes to coastal health resorts (Glavaš et al., 2015; Kovač et al., 2013; Neves et al., 2005). This area is therefore of great significance for reasons of natural, ethnological, technical, historical and geothermal resources. Despite the long tradition of thermalism, balneology, climatology and thalassotherapy in Slovenia, there is a lack of scientific studies on the health risks and beneficial effects of natural healing factors, including healing mud.

In this research, the hypersaline Sečovlje sediments were studied in order to better understand the metal mobility potential and bioavailability in the hypersaline system. The main study objectives were (1) to characterise the distribution, concentration and mobility of metal(oid)s in hypersaline Sečovlje sediments; (2) to assign the principal factors affecting the metal concentrations in a hypersaline environment; (3) and to decode metal(oid) transfer dynamics in the Sečovlje sediment - human system.

2. Materials and methods

2.1. Study area

Sečovlje Salina Nature Park (SSNP) is situated in the southwesternmost part of Slovenia, 45°29′N and 13°37′E (Fig. 1) near the Croatian border, in the municipality of Piran. The Sečovlje Salina stretches to the mouth of the Dragonja River in the Piran Bay (Gulf of Trieste, northern Adriatic). In the north-east, it is surrounded by Eocene flysch of the Šavrini Hills, and in the south-west by the Cretaceous limestone of the Savudrija peninsula (Ogorelec et al., 1981). The sediment, mostly deposited there by the Dragonja River, has a very uniform grain size and mineral composition (Glavaš et al., 2017; Ogorelec et al., 1981).

The Sečovlje wetland area is subject to the dynamic natural process of tidal inundation and sea level rise (Ivajnšič et al., 2017) and due to salt

production it is also highly influenced by human-induced hydrological alterations. Throughout the year, especially during salt production season, seawater/brine salinity in the salt making system varies depending on weather patterns, water movements, operational demands and maintenance needs (Kovač et al., 2013; Sau, 2007; Neves et al., 2005). The resulting complex hydrological regime often makes it impossible to adequately follow and monitor the properties and impact of this water phase on the investigated system.

2.2. Sampling

The study was carried out in the crystallisation area of the Sečovlje saltpans with the aim of sampling the sediment which is under the influence of variable saline conditions in connection with the production of salt. This area is also traditionally connected to the sampling and preparation of healing mud. Major sampling including three individual sampling points, was conducted from November 2012 to November 2013 with the exception of collecting the sample used in the sweat leaching experiment, which was collected in 2015. Twelve soft muddy sediment samples were collected with a plastic corer (50 cm length and 10 cm in diameter), the upper 30 cm layer was removed from the corer using a plastic scoop and put in labelled, polyethylene bags for transport to the laboratory. In order to get a representative sample for each station, several samples were collected, mixed together and quartered. Deeper sediment was examined as it is usually used as virgin material for maturation and production of the natural healing muds.

All wet (original, before mixing) samples, with the exception of the uppermost oxidised layer which is a few millimetres in depth, exhibited a dark grey colour. Before sample collection, the salinity of the water overlying sediment was determined using a hydrometer in temperature corrected degrees Baumé and calculated (Ovsyanyi et al., 2004) into mass percent salinity (% S).

2.3. Experimental

2.3.1. Analyses

The granulometric composition of the sediment samples was conducted using a laser granulometer Cilas 920 to measure grain-size via the standard procedure, e.g. a combination of wet sieving and X-ray diffractometry. The grain-size boundaries were calculated and categorised using the GRADISTAT program (version 8.0) developed by Blott and Pye (2012).

The mineral composition of the samples was determined using X-ray powder diffraction (XRD) using a Philips PW3710 X-ray diffractometer equipped with Cu Kα radiation and a secondary graphite monochromator. Data were collected at 40 kV and a current of 30 mA in a range from 2 to 70° 2θ, at a speed of 3.4 2θ/min. Oriented clay mineral aggregate preparation was carried out by a combination of ultrasound dispersion, removal of salt by centrifugation (3 × 3 min at 2500 RPM) and the glass slide method. Samples were next analysed in an ethylene-glycol solvated condition and exposed to the vapour of reagent for at least 24 h at 70 °C. Diffraction patterns were defined using the X'Pert HighScore Plus diffraction software version 4.6 using PAN-ICSD powder diffraction files. Rietveld, a full-pattern fit method, was applied to measure, calculate and compare the profiles.

Total organic carbon (TOC), total nitrogen (TN) and total sulphur (TS) contents were analysed using an Elementar Vario Micro CHNS elemental analyser. Prior to determination, freeze-dried powdered samples were acidified with 6 M HCl to remove inorganic carbon (Sieper et al., 2006). The precision of the method was 3%.

Sediment pH values were measured in situ using a portable pH meter (EUTECH Instruments) and later premeasured in the laboratory in a suspension of sediment in water according to ISO standard 10390:2005. In the laboratory, the sediment samples were frozen, freeze-dried and homogenised before further analyses.