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Baseline

Baseline study on trace and rare earth elements in marine sediments collected along the Namibian coast

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ABSTRACT

Namibia is a fast-growing country with extensive mineral extraction activities used in diamond, fluorspar, uranium, and metals production. To assess the impact of land based human activities on the Namibian coastal marine environment, 25 elements were analyzed in 22 surface sediments samples collected along the coast. After applying a variety of pollution assessment indices (Enrichment Factor, Igeo and Pollution Load Indexes) was concluded that As, Cd and Sb were considerably enriched in the sediments from several sites, while Cu, Pb and Zn showed very high enrichment near the Walvis Bay harbor. Pearson's correlation and Principal Component Analysis were used to investigate common metal sources. Additionally, the determination of Pb isotope ratios confirmed the contribution of land based human activities at Walvis Bay and Lüderitz as sources of pollution. The analysis of REEs did not reveal any important enrichment due to anthropogenic activities, but provides a needed baseline for further investigations.

Sediment analysis is recognized to be a good approach for the assessment of trace elements pollution in marine environments, since it can provide temporally integrated indication of the environmental conditions of a given area (Caccia et al., 2003). Marine ecosystems can become contaminated by trace metals from numerous and diverse sources. However, anthropogenic activities such as mining and industrial processing of ores and metals, still remain a major source of increased amount of trace elements (De Gregori et al., 1996). These anthropogenic inputs accumulate in local sediments up to five orders of magnitude above the overlying water concentrations, (Bryan and Langston, 1992) and then transferred to aquatic organisms, causing direct toxicity to aquatic life and indirect toxicity to human population through consumption of contaminated seafood. Recognizing the importance of this kind of contamination, trace element determination in marine sediment has been included as a standard procedure in marine pollution monitoring programmes at national and regional level since late 70's (Roose et al., 2011) (UNEP regional seas, 2017). However, although important information on the level and temporal trends of trace element concentrations in sediment has been collected for several coastal areas (UN DOALOS, 2016) there are still important geographical gaps around the world that need to be filled up. In the framework of the Convention for Co-operation in the Protection and Development of the Marine and Coastal environment of the West and Central African Region (Abidjan Convention), marine pollution monitoring, is an issue of priority (UNEP, 2011). Unfortunately, marine pollution monitoring programmes have not yet been implemented in most coastal areas of the West and Central African Region; therefore, it is of the upmost importance and a first step to establish baseline information for trace element concentrations in the larger marine environment off the coast of Namibian marine coastal zone.

The Namibian marine environment is remarkable in several ways. It is part of one of the four major eastern boundary regions (Benguela, California, Northwest Africa and Peru) upwelling systems in the world and is exceptionally productive in supporting abundant of marine life (Sakko, 1998). Namibia has an exceptionally low, and geographically very concentrated, coastal population compared to other countries, with five coastal towns on a coastline of 1500 km, including two harbor towns (Walvis Bay and Lüderitz). Potential human threats to Namibian biodiversity, and generally to its marine ecosystem, can be related to naval and fishing activities, diamond and other mining activities

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(Sakko, 1998). The exploitation of minerals and other natural resources has been the backbone of the Namibian economy for many years and the mining sector maintains its importance to the gross national product (Ministry of Environment and Tourism, 2008). Diamond, fluorspar, and uranium continued to be the most significant mineral commodities to Namibia's economy. The country also produces metals such as arsenic, copper, gold, lead, manganese, silver, and zinc, as well as industrial minerals including cement, dolomite, granite, marble, salt, semi-precious stones, sulfur, and wollastonite. In addition to the physical impacts of open pit mining, the consumption, transport and discharge of effluents are key issues from an environmental point of view. Mining and associated activities can have a negative impact on the environment, mainly because of the tailings, mine waste that is generally toxic. Tailings composition is very variable, prone to wind and water erosion; its physical and chemical characteristics favor metals dispersion and mobilization in the environment (Mileusnić et al., 2014). Some studies have dealt with the assessment of environmental consequences related to mining and industrial activities especially soils (Mileusnić et al., 2014) around mining areas. A confirmation that a real threat against human health exists, came from a study of Mapani et al. (2009) whose results point to severe heavy metals contamination with immediate risk for the inhabitants of the Tsumeb area, with almost a century long mining and smelting activities. Namibia's economy heavily depends on fisheries, exploiting one of the most productive fishing grounds in the world, based on the Benguela upwelling current system (FAO, 2007). The catches from the marine capture fishery are landed at two major ports, at Walvis Bay and Lüderitz These two ports has in recent years been expanded dramatically with Walvis Bay as the major Namibian port, connecting the landlocked countries such as Botswana, Zambia, Zimbabwe.

Several major rivers are discharged along the central Namibian marine coastline including the Omaruru River in Henties Bay, Swakop River in Swakopmund and the Kuiseb River in Walvis Bay. Their catchment areas act as collector of sediments and transport particles to the coast during the rainy season. Nevertheless, Namibia has a rather dry and windy climate in the coastal region. The transport of particle is not prerenal, but rather associated to flash flood events or eastward windstorm. Mining and agricultural activities taking place in the catchment areas of these rivers can contribute to the input of contaminants in the coastal area.

To the best of our knowledge, no published data are available on trace elements concentrations in the north Benguela upwelling system (nBUS) off Namibia. In consideration of these aspects, the importance of establishing a new baseline data for future reference is undeniable.

The group of Rare Earth Elements (REEs) was also included in the present study since some mineralogical investigations have confirmed that Namibia may have potential REEs resources (Orris and Grauch, 2002). Additionally, since REEs are naturally associated with U-containing minerals, their determination in these areas with long history of U mining, is of great interest. The distribution patterns of REE has often been applied to geological studies of river and marine ecosystems (Song and Choi, 2009; Rezaee et al., 2010) since they can be used as reliable tool for determining depositional processes and sediment provenance (Xu et al., 2009); Jung et al., 2012). In the last decade the REEs uses in the industry have increased as these elements find application in the production of several modern devices, such as superconductors, electronic components, luminescent materials and car components. As a consequence of their increased widespread use, the potential anthropogenic influence on REEs natural distribution has extended their geochemistry into the field of environmental chemistry (Kulaksiz and Bau, 2011); Hatje et al., 2016), leading scientists to refer to these elements as “new emerging pollutants”.

The aim of this study was then to assess the ecological risk associated to trace elements concentrations in sediments along the Namibian coast and thus provide a record for present and future evaluations of the state of Namibian marine environment. For this purpose, concentrations of selected trace elements including rare earth elements (REEs) and lead isotopic ratios were determined in 22 sediment samples collected along the Namibian coast.

All sample handling was carried out in class 10 laminar hoods. Ultrapure water with resistivity > 18 MΩ was obtained from Milli-Q Element system (Millipore, USA) and was used throughout this work to dilute concentrated acids. Trace grade HNO_3, HF, H_2O_2 and ultrapure HNO_3 were purchased from Fisher Scientific (Hampton, USA). TraceCert standard solutions for Al, Zn, Mn and Fe used for Flame AAS calibration, TraceCert Hg standard solution for AMA calibration and TraceCert multielemental standard for ICP-MS calibration, were purchased from Sigma Aldrich (Buchs, Switzerland) in concentrations of 1000 mg/L (mono-elemental standards) and 10 mg/L (multielemental standard). The Certified Reference Material MESS-2 (Estuarine sediment, National Research Council, Canada) was used for assessing data accuracy. The Standard Reference Material SRM 981 from the National Institute of Standards and Technology (NIST, USA) with the natural Pb isotopic composition was used for correction of the instrumental mass discrimination when measuring Pb isotope ratios. All Teflon and PE lab ware used in the sample preparation and analysis, was pre-cleaned with a procedure consisting of at least 24 h bath in 10% HNO_3 and careful rinsing with MilliQ water.

Following a request for assistance from the Environmental Division of the Ministry of Fisheries and Marine Resources (MFMR), the IAEA Environment Laboratories participated in a scientific sampling expedition in May 2014, during a survey along the Namibian coast, together with the National Marine Information and Research Centre (NatMIRC). Furthermore, additional sediment samples were collected, during the same period, in the frame of a technical cooperation (TC) project between the IAEA and Namibia. The sampling was carried out in various sites along the Namibian coast, between 20°S and 27°S latitude and 11°E and 15°E longitude (Table 3). To facilitate the comparison with existing radioactivity data obtained within the same project, the original sampling coding is also included in Table 3. A total of 22 surface samples have been analyzed in this work and the sampling area was relatively broad (Fig. 1), including sediments collected on the coastal zone, as well as sediments collected in deeper water at the open sea. After collection, sediment samples have been kept frozen during transportation at the laboratory. Later, samples were freeze-dried, sieved at 1 mm and homogenized in agate mortar. Acid digestion was carried out in a microwave system using a Mars X-press Microwave (CEM Mars X-press) equipped with a carousel holding 12 digestion vessels. A quantity of 150 ± 50 mg of dried sample was weighed in Teflon microwave vessels, where 5 mL of ultrapure HNO_3, 2 mL of H_2O_2 and 2 mL ultrapure concentrated HF were added. Each digestion batch included 2 reagent blanks and two replicates of a selected certified reference material. The digestion procedure involves gradual increasing of temperature to 190 °C for 15 min, then additional isothermal treatment for 15 min. After the digestion, obtained solutions were placed on a ceramic heating plate and evaporated to near dryness. The residues were taken up in 2% HNO_3, transferred to 50 mL PE tubes and stored at 4 °C.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was the method used for the determination of trace elements (TE: As, Ba, Be, Cd, Co, Cr, Cu, Li, Mo, Ni, P, Pb, Sb, Sn, Sr, Th, Ti, U, V and Y) and Rare Earth Elements (REE: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) in sediment samples. Measurements were carried out using a quadrupole mass spectrometer, Q-ICP-MS (XSERIES, Thermo Fisher Scientific); instrumental parameters are presented in Table 1. Determination of Pb isotope ratios was performed on digested samples by means of High Resolution Sector Field ICP-MS (NuAttom, NuInstruments Ltd., Wrexham, UK); the instrument parameters are presented in Table 2. Determination of Al, Fe, Mn and Zn was carried out by Flame Atomic Absorption Spectroscopy (ContrAA 700, Analytik Jena, Germany) on the same digested solutions used for ICP-MS, using external calibration. Mercury was determined in sediment samples directly,