HEAVY METAL DISTRIBUTION IN THE SALT PANS OF TUTICORIN, TAMIL NADU, INDIA

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Abstract

In Tuticorin (Thoothukudi), salt is being produced by solar evaporation of brine in ponds. Its industrial environment warrants a heavy metal pollution potential assessment. During the process of solar evaporation, brine is conveyed through reservoir and condenser, to crystallize salt in crystallizer ponds and eventually exit as bittern. In this process, it deposits heavy metals on the pond floors which in turn may adhere to the crystallized salt. Thus, heavy metal quantification and path analysis becomes imperative in terms of pollution potential. The enrichment of heavy metals in salt pan sediments and salt potentials biological risk for the salt pan ecosystem and the consumers of salt. Hence heavy metal distribution was estimated in 16 samples from different pond floors of four salt pans viz. Spic Nagar, Tharuvaikulam, Veppalodai and Roche Park and the description and discussion of the same are presented here. Fe (31.41), Ni (21.76), Pb (15.97), Cu (6.63), Zn (5.07) and Cd (3.27) are the heavy metals observed (with respective average concentrations in mg/kg). In this study, its levels are estimated stage wise, so as to infer it's loading onto the salt produced. These heavy metal pollutants can be traced to effluents of nearby industries and the domestic dumps. Heavy metal presence in the sediments, signals toxicity for the salt consumers.

Keywords: Tuticorin salt pan, salt pan sediments, heavy metal pollution, solar salt farm

1. Introduction

Tuticorin is the largest salt producing district in Tamil Nadu, harvesting around 20 million tons of salt annually. Halite (salt) is one of the major mineral source for human consumption as well as industrial usages. In Tuticorin, the major units of thermal power plants and chemical industries are close to the salt pans. They discharge untreated waste into the ground and the nearest water bodies, which finally reach the ocean. Various disposable materials, fly ash, and some petroleum products are discharged onto the ground (Asha, et al., 2010) and they mix with groundwater and the sediment of salt pans. Heavy metal can be introduced as a dissolved or particulate matter due to natural processes or anthropogenic contributions (Marengo et al. 2006, Tsai et al., 1998, Duzzinet al., 1988, Hamid Reza Pakzadet al., 2014, Santhanakrishnanet al., 2015). Metal contamination of surface sediments can directly affect the seawater and groundwater quality, resulting in potential consequences to the sensitive lowest levels of the food chain and ultimately to human health (Christophoridiset al., 2009). According to Qasimet al., (1988), while Mn, Cu, Fe and Zn are considered as essential micronutrients, mercury, cadmium and lead are not required for any important biological functions of organisms. As such, these heavy metals, if found in abnormal concentrations in salt, can lead to thyroid, liver damage and other harmful effects in consumers (Munoz et al., 2005). Hence, the present investigation is aimed at determining the concentration of Cd, Cu, Fe, Pb, Ni, and Zi, in the sediment samples collected from various ponds of salt pans in Tuticorin district.

2. Methodology

2.1. Geographical setting of salt pans

The etymology of the word "Tuticorin" can be traced back to the period when the locals used to tap drinking water by digging small ponds (Oothu in Tamil). Oothukudi, meaning to dig and drink, later came to be known as Tuticorin. The District covers an area of 4621 sq.km and is bound by the districts of Virudhunagar and Ramanathapuram on the east and by the Gulf of Mannar in the south-east and by Tirunelveli District in the west and south-west. In order to study such an ecosystem of hyper saline nature, the solar farms of salt located in Tuticorin (Lat. 8°45' N and 78°13' E), Tamil Nadu, south India have been considered. The major salt pan areas such as Tharuvaikulam, Roche Park, SPIC Nagar and

Veppalodai have been selected for this study (Fig. 1), based on the pollution input into the salt pan environment through anthropogenic activity, urbanization, industrial and harbor activities. Important major industries in the vicinity are Sterlite, SPIC, Tuticorin Alkali Chemicals, Dharangadhra Chemicals Works, Madura Coats, Kilburn Chemical Industries and the Public Sectors Thermal Power Plant unit (620mm), Heavy Water Plant and Port Trust. The district contributes 70% of the total salt production of Tamil Nadu and meets 30% of the salt requirement of our country.

2.2 Collection of samples

The surface sediment samples were collected from four different major salt pans of Thoothukudi during the year 2013. The samples were taken up to from 20 cm depth from the surface of the ponds (reservoir, condenser, crystallizer and bittern) and were collected separately in polyethylene bags and stored in an ice box, transported to laboratory and frozen at -20p C and later thawed. The samples were dried at 105p C overnight and disaggregated before analysis. The dried samples were homogenized

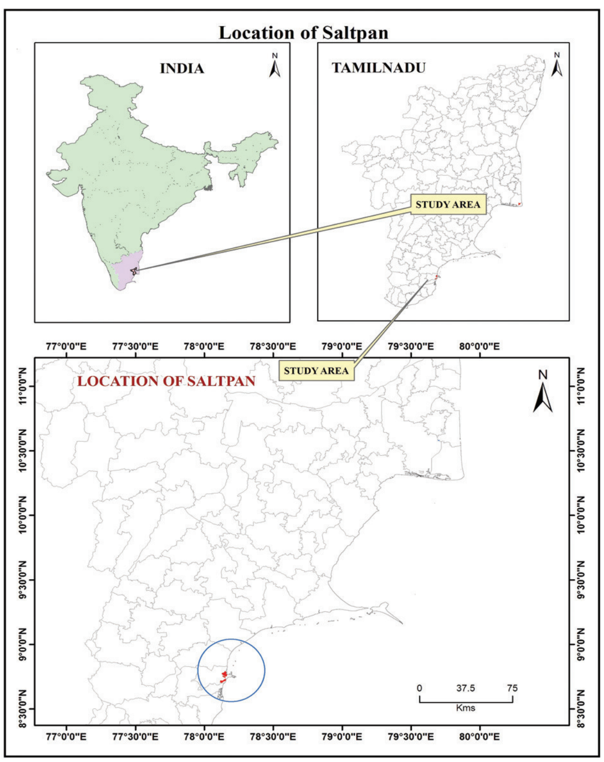

Fig. 1. Location of Saltpan

and sieved to fine powders, and subjected to a wet-digestion. One gram each of the dried powdered sediment samples was used for metal analysis by hot acid digestion method (Bruland et al., 1974).

2.3Analysis of Heavy Metals

One gram each of the powered soil sample was taken, mixed with 1:3 ratio of concentrated hydrochloric acid and nitric acid (2.5 ml: 7.5 ml) and heated at 80ºC for 20 minutes. After the digestion processes was complete. The sample was filtered through a whatman No: 1 filter paper and volume was made to 25 ml using doubled distilled water. Metal concentrations were determined by Perkin Elmer AAS (Model 2380).

3. Results and Discussion

Salt is one of the most important and commonly used food additives throughout the world. Contamination of table salt could results in creating the health hazard for human. Since most of salt the used around the globe comes from mines and solar salterns, it is estimated that heavy metal contamination might be a concern for table salt. Contamination of heavy metals creates a toxic effect on the surrounding biological environment(Jarup, 2003). Yamaguchi and kakzoai, 2001, Christophe Kaki et al., 2011 reported that continuous intake of heavy metal contaminated salt and salted foods could leads to stomach cancer and pre-cancerous effects in humans.

The distribution of heavy metal (mg/ kg) in the sediment samples of all the four saltpans of Tuticorin has been analyzed. Variations of the heavy metals and international and Indian standard values are shown in Table 1.

The concentration of Fe in Tuticorin salt pan surface sediments ranged from 10.94 to 54.08 mg/kg with an average of 31.41 mg/kg (Fig. 2). The highest and lowest values were observed in the condenser and reservoir ponds respectively. Maximum amount of Fe was observed in the condenser ponds of Roche Park and SPIC Nagar salt pans. The hydrogenous fraction of sediments consists chiefly of iron-manganese oxides dispersed as micronodules in the sediments and also present as a coating on sedimentary particles. Iron-manganese oxides are precipitated directly from seawater, they are deposited under oxygenated hydrothermal fluid conditions and

Table 1. Heavy metal analyses of saltpan sediment samples of Tuticorin region.

Heavy metal	Minimum (mg/ kg)	Average (mg/ kg)	Maximum (mg/kg)	Indian Standard (IS 105000: 1991)	WHO Standard (CX STAN 150 – 1985)
	Fe	10.54	31.41	54.08	NGL NGL
Ni	20.13	21.76	24.06	0.02	0.07
Pb	9.68	15.97	21.84	0.02	0.01
Cu	0.38	6.63	13.64	2.0	1.5
Zn	0.37	5.07	19.80	NGL	5.0
Cd	1.98	3.27	3.95	0.01	0.003

NGL - No Guidelines

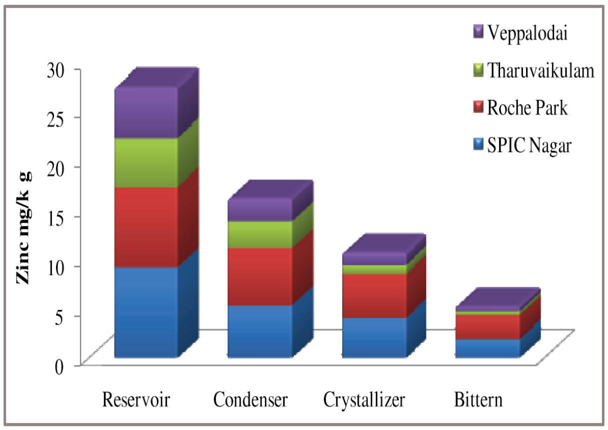

Fig. 2. Zinc concentration in different ponds of all salt pans

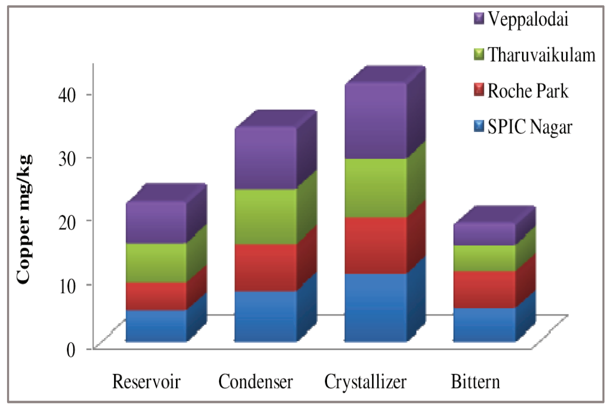

Fig. 3. Copper concentration in different ponds of all salt pans

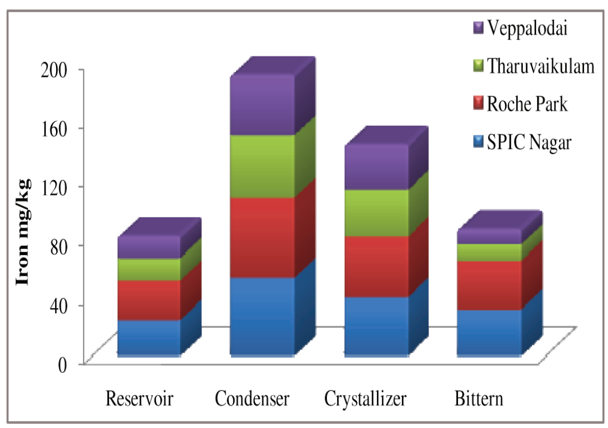

Fig. 4. Iron concentration in different ponds of all salt pans

concentrated as a trace element in condenser ponds (Chen et al., 1996).

Ni concentrations were recorded from 20.13 to 24 mg/ kg with an average of 21.76 mg/ kg (Fig. 3). While Ni is generally reported to be high in all salt pans of Tuticorin, it predominates in bittern. Therefore, it follows to expect a higher amount of Ni in sediment samples. Such higher concentrations of Ni indicate input due to petroleum related activities in the surrounding areas (Muthu Raj and Jayaprakash, 2008).

Pb content in Tuticorin saltpans was found to be 15.15 to 17.18 mg/ kg with an of average 15.97 mg/ kg. Roche Park and SPIC Nagar area salt pans contain higher concentration of Pb than the others (Fig. 4) (Krishna Kumar et al., 2012). Pb contamination is almost certainly from petrochemical industries, metal smelting units, various fertilizer and salt chemical industries, dredging and dumping of sediments from harbours (Ramachandran et al., 1991) and fly-ash (SiO_2, Al_2O_3, Fe_2O_3 and insoluble residues) from the nearby thermal power plant (Smith and Anderson, 1981.,Crecelius, 1985).

Fig. 5 shows, in percent bar graphs, the distribution of Cu in the four stages of salt pans. The average concentration of Cu was found to be 6.58 mg/kg while its concentration varied from 0.38 to 13.64 mg/ kg. The maximum concentration of Cu was recorded in condenser and crystallizer ponds of the salt pans; these ponds indicated the extent of pollution in the sediments of the Tuticorin salt pans. The maximum amount of Cu was deposited in the form of Cu_2S and CuS in condenser and crystallizer ponds. The Roche Park and SPIC Nagar saltpans have increasing trends of Cu occurrences from reservoir to crystallizer, whereas it shows a decrease in bittern. Cu contents of Veppalodai and Tharuvaikulam saltpan sediments reflects the various industrial activities and fly ash dumps of Tuticorin Thermal Power plant (Baskaranet al., 2002).The trace amount of this element is also found associated with white salt, because Cu tends to be absorbed by organic matter and is also a co-precipitate with carbonates (Hamid Reza Pakzad et al., 2014, Morilloet al., 2007, Jenne, 1968, Alloway, 1994, Amdouni, 2009). As stated earlier and by Brookins (1988), Cu could precipitate as Cu, Cu2S and CuS when suitable Eh–pH conditions prevail in mud sediments. Therefore, a noticeable difference is observed between the amounts of this component in the salt samples relative to its average concentration in the mud flat sediments of Tuticorin salt pans (Hamid Reza Pakzad et al., 2014).

The concentration of Zn in Tharuvaikulam and Veppalodai salt pans was 5.07 - 0.45 mg/ kg and in Roche Park and SPIC Nagar salt pans it was 19.5 - 2.16 mg/ kg. These higher concentrations of Zn, recorded in Roche Park and SPIC Nagar salt pans, are mainly due to effluents because of the ore handling in the harbor, heavy water plant and solar alkali plant (Diya et al., 2014). The untreated industrial waste water can form complexes with humic substances which affects the groundwater and sediments. Zn concentration decreases in trend from reservoir to bittern in all the salt pans of Tuticorin (Fig. 6). More amount of Zn was absorbed in algal mats from the reservoir ponds, and in the clay mats beneath these algal mats. It can be attributed to its location in an industrial enclave (of thermal power plant, fertilizers and chemical plants) (Hamid Reza Pakzad et al., 2014). Zn metal commonly appears as Zn2+ in sediment solution and it combines with sulphate and deposits in the form of ZnS. Zn^{2+} which is strongly adsorbed by clay (McBride, 1994) in the salt pans.

Cd is one of the most toxic metals to aquatic biota as well to humans (Neff, 2002). The Cd concentration in Tuticorin salt pans ranges from 1.09 to 4.06 mg/ kg with an average of 3.27 mg/ kg (Fig. 7). It increases from reservoir to crystallizer and finally decreases in bittern. Because Cd is much less soluble in water under a reducing environment, i.e., having less oxygen than the saturated value. So the maximum amount of Cd is observed in condenser and crystallizer ponds. Cd can be accumulated in raw salt from crystallizer ponds. Cd of brine may be due to the discharge of industrial effluents and

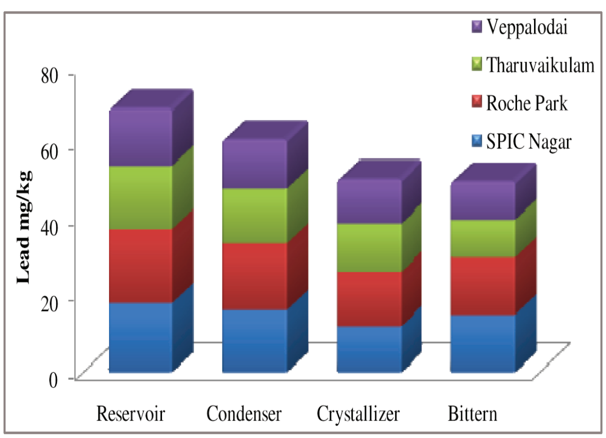

Fig. 5. Lead concentration in different ponds of all salt pans

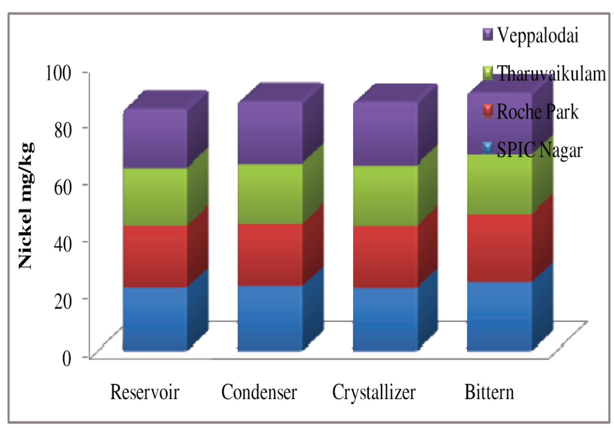

Fig. 6. Nickel concentration in different ponds of all salt pans

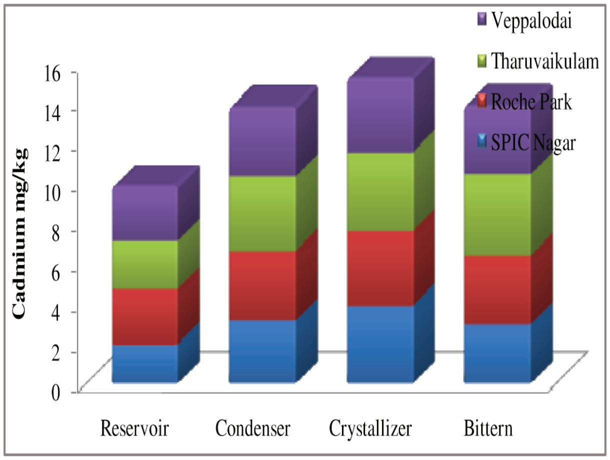

Fig. 7. Cadmium concentration in different ponds of all salt pans

anthropogenic activities. Cadmium occurs generally in lesser amounts in all salt pans compared to other metal (Ni, Pb, Fe, Zn, and Cu) occurrences.

Relative strengths of heavy metals observed in all salt pans are displayed as a radar diagram in Fig. 8 which shows higher concentration of Fe over Ni and Pb. These results indicate metal pollution in salt pans compared within the limits of international standard permissible limits, and also deposition on salt. At low concentrations, copper and iron are essential elements for human health whereas high levels of the same turn toxic. Thyroid and liver problems could arise due to human consumption of solar salt containing these heavy metals. Lead is the smallest mobile heavy metal in sediments under

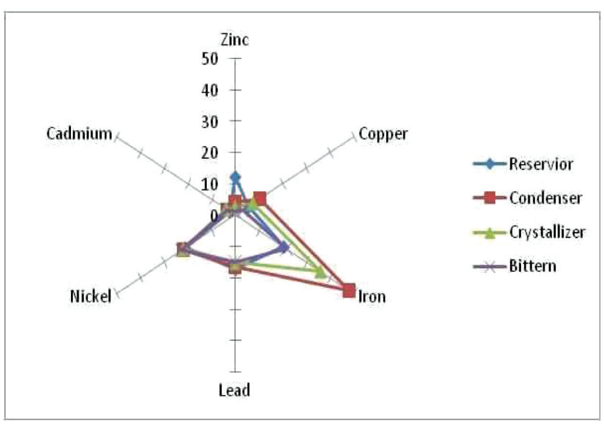

Fig. 8. Heavy metal concentration in Tuticorin salt pans

reducing conditions (Hamid Reza Pakzadet al., 2014 and McBride, 1994) and may become immobilized by organic matter content (Bradl, 2005). This metal is also concentrated in salt samples along with certain clastic minerals and harmful to human. Soylak et al., (2008) reported nearly 1.64µg/g Pb content in Turkey, Egypt, Greece and Brazil and 0.01-0.03, 0.18-0.22 and 0.18-0.19 ìg/g Cd has been reported respectively in Brazil, Egypt and Greece in edible solar salt consumed by humans. As nickel and zinc are also deposited in the sediment of salt pans; toxic recurrence is imminent due to direct intake of solar salt by humans.

4. Conclusion

Presence of toxic elements in salt pans and in turn in salt is confirmed by this study. Hence, it is of paramount importance to contain anthropogenic activities leading to the release of toxic elements to the environment; particularly close to the saltpans. Similarly, it should be seen that industries do not release untreated effluents.

Heavy metals, as assayed from salt pan sediments off different ponds and bittern, show mean values in mg/ kg which are as follows: Fe (31.41), Ni (21.76), Pb (15.97), Cu (6.63), Zn (5.07) and Cd (3.27) in the order of abundance. The higher concentration of heavy metal was encountered in SPIC Nagar and Roche Park saltpans and is attributable to the anthropogenic activities, discharging of industrial sewages and fly ash dumps from the nearby Tamil Nadu Thermal Power Plant etc. However, concentrations of trace elements are below the threshold for sediments at present, a potential risk may emerge in the future, depending on the increased fly ash dumping, disposal of industrial waste and man-made activities. It is predictable that, in future, the Tuticorin solar salt pans may receive a huge amount of heavy metals due to new industrial developments. Further, present values of metals concentrations can be used as baseline data for future comparisons with regard to heavy metal pollution.

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