

ANALYSIS OF ROCK AND SEA SALTS FOR VARIOUS ESSENTIAL S AND INORGANIC ELEMENTS

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Abstract: The present study was conducted to investigate the various essential micro-nutrients and non essential heavy metal concentrations in different sources of salts available in Pakistan. Objective of this study was to know about the nutrient status and potential hazards (if any). There are two types of salts available in the market, sea/lake salt and rock salt. Chemical analyses were carried out in order to know their characteristics. For this purpose, seven samples were collected from different areas of Pakistan and were analyzed for four essential elements (Fe, Zn, Mn and CO) and three non essential heavy metals (Cu, Cd and Ni). The results were compared with permissible limits of WHO required for normal body functions. The edible grade of Khewra appeared to be enriched in Fe with 21.182 mg/kg. Gawadar sea salt was found to be rich in Zn with 28.61 mg/kg. Cobalt was found in Karachi Sea salt and Khewra edible grade with 10.02 and 10.01 mg/kg, respectively. Similarly, the concentrations of non essential heavy metals, like Cu, Cd and Ni were found to be comparatively high in Khewra salt with the average value of 4.04, 79.75 and 8.20 mg/kg, respectively. By comparing the rock and sea salts with different standards, it can be concluded that the concentration of various non essential heavy metals is within the permissible limit. Comparing the two sea salts (Karachi and Gawadar), the concentration of non-essential heavy metals was comparatively less in Gawadar sea salts. The Gawadar salt was found to be enriched in essential micro-nutrients and can be considered as good edible salt.

Key Words: Rock salt, sea salt, micro-nutrients, macro-nutrients, heavy-metals.

Introduction

Salt is a mineral that is mainly composed of sodium chloride. It is an essential part of the diet without which food becomes tasteless. It is required for both plants and animals in small quantities, but harmful when present in excess (Morris *et al.*, 2008). The two major components of salt are chloride and sodium ions while other elements are present in minute quantities like potassium, magnesium, calcium, sulfate ions, iron, zinc, nickel, chromium, cadmium,

manganese, copper & cobalt which are required for normal body functioning (Gong *et al.*, 1997). In Pakistan, two types of salts are available, Sea/lake salt and rock salt. Among these, rock salt is common throughout the country while sea salt is available in coastal areas of Sindh and Balochistan. It is generally agreed that sea salt is more rich in micro-nutrients as it is present in sea water from where it is extracted by evaporation through heating by sunlight (Qadir *et al.*, 2005). Sea salt consists of about 98% NaCl with remaining 2% is constituted

by trace elements like iron, magnesium, sulfur & iodine (Behnke *et al.*, 1997). The air near sea water contains salt particles that control the radioactive properties of clean background atmosphere by scattering sunlight (Clarke *et al.*, 1984). Sea salt is also used in cosmetics & as bathing salt, but takes high concentration of iodine, an essential element for human health (Cole *et al.*, 1999). Because of industrialization, it is usually blamed that due to pollution load it may receive various industrial effluents which are rich sources of heavy metals with negative impact on health like cadmium, nickel, zinc, molybdenum & iron (Khemani *et al.*, 1985).

Rock salt contains natural impurities having calcium sulfate (CaSO_4) and potassium chloride (KCl) as impurities. It is found in deposits of rock salt, brines, saline lakes, marshes, seawater and saline earth (Geo, 1944). The refined salt is mainly sodium chloride which is a part of diets, crystalline solid in color and is obtained by evaporation from sea water or rock deposits while iodized salt is table salt with small amount of potassium iodide (KI), sodium chloride (NaCl) and is used to fulfill the iodine deficiency in human body but in small amounts. The salt regulates the water content in the body, but higher intake may cause health problems including high blood pressure. The Health authorities have recommended limitations for salt intake in terms of per day which are 3400 mg/day for chloride and for sodium is less than 2400 mg/day. The total quantity of salt should be maintained at about 5-6g/day, but people with high blood pressure should limit sodium intake to 1,500 mg per day (Aho *et al.*, 1980; WHO, 2002). So, salt should be used carefully within its permissible limits. Human body needs some essential and non-essential heavy metals in minute quantities. Therefore, it is extremely important to check the salt

quality in terms of essential and non-essential heavy metals as it is the basic food item used in daily routine.

Essential Heavy Metals

Iron (Fe) has been identified as a key factor for lipid metabolism in humans and animals (Cunnane and McAdoo, 1987). The daily intake of iron is 15mg/day (Lenntech, 1998-2009). It is a vital part of hemoglobin that transports oxygen through human body and its deficiency leads to anemia in human beings (Chung *et al.*, 2011) as well as it slow down the level of serum phospholipids which badly effect the fatty acids composition along with impaired de-saturation of saturated fatty acids and give the output in the form of fatigue, diminishe work capacity and anemia (Stangle and Kirchgessner, 1998).

Zinc (Zn) is another trace element that is essential for human health, but excessive concentration of Zn can cause certain health problems like the impairment of growth and reproduction, stomach dis-functioning, skin irritations, vomiting, nausea and anemia, damage the pancreas and disturb the protein metabolism (Oti-boakye, 2011). Zinc deficiency may lead to loss of appetite, decreases sense of taste and smell, slow wound healing and skin sores and in extreme shortage, it cause birth defects. The recommended daily intake for zinc is reported to be 15mg/day (Lenntech, 1998-2009).

Similarly, manganese (Mn) is an essential metal for human health having a big role to maintain function of central nervous-system, bone growth, reproduction and metabolizes cholesterol, carbohydrates. The excessive concentrations of Mn may lead to several health disorders like in unitary laughing, hand tremors, slurred speech, and deadpan expression (Karanja *et al.*, 2010) and some long term adverse health effects like

mental and emotional disturbances and slow and clumsy body movements (Lemos *et al.*, 2008). The daily intake is 5 mg/day (Lenntech, 1998-2009). Manganese is a chemical factor important for life processing, having both structural and enzymatic functions (Lemos *et al.*, 2010).

Molybdenum (Mo) is considered to be important nutritional element to all species. Molybdenum with other trace metals is essential in tiny amounts and can be highly toxic at larger doses (Duyff, 2002). Its deficiency in human and animals slow down the growth and developmental process but too much molybdenum causes fetal deformities and liver dysfunction (Shils *et al.*, 1999). The recommended value for Mo is 0.075 mg/day (Lenntech, 1998-2009).

Cobalt (Co) is termed as beneficial element and required in traces. Co plays a vital role in body functions and considered useful for humans as it is a part of vitamin B₁₂, but toxic in high quantity (Ojeda *et al.*, 2012). The adverse effects of cobalt are vasodilatation, flushing in humans and animals as well as cobalt is also used for anemia treatment (Broding *et al.*, 2009). The total daily intake of cobalt is 7.3 µg to 12µg/day (Dabeka and Mckenzie, 1995).

Non-Essential Heavy Metals

Cadmium (Cd) is tremendously toxic metal generally found in industrial workplaces. Cd can cause lung cancer, kidney dysfunction and produce bone defects in humans and animals (Gopalani *et al.*, 2007). High level of Cd in human may result adverse pulmonary effects like emphysema, bronchiolitis and alveolitis along with renal effects (Yang *et al.*, 2012). The recommended value estimated for Cd is 0.025 mg/day (25µg/kg) (Lenntech, 1998-2009).

Nickel (Ni) is a non essential element and is present in air, water and soil in traces. Recent research shows that Ni has got minor role in plant growth (Brown *et al.*, 1987). The sources which introduce Ni into the environment are metallurgy and refining industries, coal combustion, diesel and fuel oil, sewage, etc. Ni compounds are taken by the human body through inhalation, ingestion and dermal contact (Cempel and Nickel, 2006). Humans are exposed to nickel from food, jewellery, coins, and dental restorations (Vahter *et al.*, 2007). Nickel is carcinogenic and shows many adverse health effects on respiratory tract causing lung cancer, lung inflammation (NTP, 1996), nose cancer, larynx cancer, respiratory-failure, birth-defects, asthma, allergic reactions such as skin rashes, mainly from jewelry and heart disorders (Fischer *et al.*, 2005). The total nickel content in human body is 7µg/kg which is accumulated in bones, parenchymal tissues, myocardium, skin and hair (Wong *et al.*, 2002). The estimated dietary intake of nickel is 2.7µ mol/day (Son *et al.*, 2009).

Copper (Cu) is both, essential and non-essential element. Cu is a micronutrient and is a nutritional component for plants and other living beings required for their growth in small quantities but pose threat to both plant and animal in greater concentrations (Altaher *et al.*, 2001). Along with other minerals copper plays a vital role in the metabolism of farm animals (Zhang *et al.*, 2007). For human life, copper is considered to be important but in higher concentrations it can cause many health problems like anemia, liver and kidney damage, stomach and intestinal irritation while its deficiency has been associated with reduced antibody production (Spears, 2000). The permissible limit of copper is 2 mg/day (Lenntech, 1998-2009).

Chromium (Cr) is a trace metal concerned in metabolism of glucose and lipid and essential for insulin action in human body (Anderson, 1997). In environment, chromium exists in two oxidation states Cr (III) and Cr (IV) which impart it a place in toxic metals (Seema *et al.*, 1997). The toxicity of chromium depends upon its chemical form. Cr (IV) compounds are toxic, mutagenic and carcinogenic in nature while trivalent are less toxic in nature (Goyer *et al.*, 2001). Chromium is mostly used in food industry and in stainless steel. Its deficiency in animals may lead to glucose intolerance and improved fatty acid deposition (Schroeder *et al.*, 1970). The National Research Council, 1989 has recommended daily intake of chromium is 50-200 $\mu\text{g/day}$ (0.96-3.84 $\mu\text{mol/day}$) (Lendinez *et al.*, 2001).

Study Area

The study area is vast including the salt deposition places in Sindh, Punjab & Khyber Pakhtunkhwa. Abundant salt deposits are present in Sindh including sea salt sources in majority of Karachi sea and the largest shipping ports in Pakistan; the Port of Karachi and the Port Qasim. In order to facilitate these ports, plans have been announced recently (Projects, Karachi Port Trust, 2007) but the sea serve as a big deposit for salt from where it is extracted to meet with the human needs and is a good source of the country's income. Khyber Pakhtunkhwa accounts for 10% of Pakistan's GDP, 20% of Pakistan's mining output as well as the important salt mines are also present in different parts of the province like Jatta, Bahadur Khel, Kohat and Karak. All these deposits are accessible by roads from Bannu-Kohat metalled road (ur-Rehman *et al.*, 2010). There are 5 deposits of rock salt in Kohat while the north hills of Kohat are of limestone and hard rock of gypsum series.

There are main deposits of rock salts in Punjab at several places like Khewra, Khushab, Warcha, and Kalabagh from where several thousand tons of salt is being mined and removed by filtration (Qadir *et al.*, 2005). In South Asia, the Khewra salt mines are the oldest ones which are situated in the foothills of the Salt Range about 288 meters above the sea level from where salt has been mined since 320 BC. Khewra salt mine has estimated total of 220 million tons of rock salt deposits while the production from the mine estimated to be 465,000 tons salt per annum, but from here, only 50% salt is extracted while 50% is left as pillars to support the mountain (Talent *et al.*, 2001).

Materials & Methods

Sampling

The representative salt samples were collected during the survey of different mines that were selected on the basis of their quality. In Pakistan, different types of salts are available in market which is derived from rock and sea. Seven samples of salts were collected which are following:

- Kohat rock salt
- Khewra edible salt, crystal white, industrial grade and decoration piece grade.
- Gawadar sea salt
- Karachi sea salt

Analysis

The collected samples were analyzed for different quality parameters including trace elements & heavy metals for which the samples were analyzed in the Central Resource Laboratory (University of Peshawar). The samples were stored in labeled plastic bottles and analyzed through Atomic Absorption Spectrometer, Model AAS (700)

for the determination of different trace elements and heavy metals (Cu, Fe, Ni, Co, Zn, Cr, Mo, Mn & Cd).

Results and Discussion

Essential Heavy Metals

Rock and sea salts consist of some essential trace metals and some non-essential heavy metals as summarized in Tables 1 and 2. In case of essential metals, iron (Fe) was found in rock salt within the range of 12 mg/g to 273 mg/kg, where there was the high concentrations found in industrial grade about 273 mg/kg. In other rock salts, the range was 21mg/kg, 20 mg/kg and 19 mg/kg in Khewra edible, Khewra piece grade and crystal white, respectively. The daily uptake calculated on the basis of 5 g, salt consumed per day was ranged from 0.057 mg/day to 1.366 mg/day and was found below the standard of 15 mg/day (Table-2). The analytical results revealed that all rock salts were found rich in Fe content. In sea salts, the values were in the range of 11 mg/kg to 23 mg/kg in Karachi and Gawader sea salt respectively (Table 1) which shows that Gawader sea salt is enriched in Fe content. As human body needs 15 mg iron per day (Lenntech, 1998-2009), therefore, both types of salts can be considered in terms of availability of iron.

The concentrations of Zn in rock salts were found in the range of 9 mg/kg, 6 mg/kg, 5 mg/kg and 4mg/kg in Kohat rock salt, Industrial grade, Khewra piece grade and Khewra edible salt, respectively. These results revealed that Kohat rock salt was rich

than all of others salts. Zinc contents of all analyzed salts were within the permissible limit (Table-2). Rock salt was comparatively rich in Zn contents but both can be interpreted as good sources of Zn.

In rock salts, manganese (Mn) content was varied between 14 to 26 mg/kg. Highest values of Mn were recorded for industrial grade and Khewra piece grade with average concentration of 26 mg/kg and 23 mg/kg, respectively. The concentration of Mn determined in others salts were in the range of 19 mg/kg, 17 mg/kg and 14 mg/kg for Khewra edible salt, crystal white and Kohat rock salt, respectively. The values of these salts were calculated in terms of 5g of salt consumption per day and were in the range of 0.065 and 0.135 in Karachi and Gawader sea salts, respectively while the range was 0.071 to 0.130 in rock salts (Table-2). All these values were found within the permissible limits (Table-2). Cobalt was found only in Khewra edible salt and Karachi sea salt with concentration of 10.1 and 10.18 mg/kg, respectively (Table-1). In terms of 5g per consumption of salt, the values were found within the permissible limit with range of 0.050 mg/day in both Khewra edible and Karachi sea salts (Table-2). In this regard, both sources are within the limit and are considered as good sources of cobalt as high concentration of cobalt is not good and may damage the human health. Cobalt is doubtful so, it can be considered in both essential and non-essential metals.

Table 1. Concentration of some essential trace elements in salt samples collected from different parts of Pakistan

S.No	Name of sample	Fe (mg/kg)		Zn(mg/kg)		Mn(mg/kg)		Co(mg/kg)	
		Average	Standard Deviation	Average	Standard Deviation	Average	Standard Deviation	Average	Standard Deviation
1	Kohat rock Salt	12.18	1.13	9.05	1.42	14.28	1.76	N.D	N.D
2	Karachi sea	11.34	0.87	3.03	1.11	13.06	1.28	10.02	1.58
3	Khewra edible salt	21.18	1.56	4.10	1.28	19.01	1.31	10.01	1.65
4	Khewra crystal white	19.17	2.11	0.00	0.00	17.10	1.50	N.D	N.D
5	Khewra industrial grade	273.13	23.72	6.00	1.22	26.05	2.01	N.D	N.D
6	Gawadar sea salt	23.05	1.67	5.16	1.06	27.10	1.50	N.D	N.D
7	Khewra piece grade	20.01	0.82	5.06	1.01	23.12	1.16	N.D	N.D

N.D = Not Detected

Table 2. Average daily uptake of essential trace elements calculated on the basis of 5 gram salt consumed/day

S. No.	Name of sample	Fe (mg/day)	Zn (mg/day)	Mn (mg/day)	Co (mg/day)
1	Kohat rock Salt	0.061	0.045	0.071	0
2	Karachi sea	0.057	0.015	0.065	0.050
3	Khewra edible salt	0.106	0.021	0.095	0.050
4	Khewra crystal white	0.096	0.000	0.085	ND
5	Khewra industrial grade	1.366	0.030	0.130	ND
6	Gawadar sea salt	0.115	0.026	0.135	ND
7	Khewra piece grade	0.101	0.025	0.116	ND
8	Permissible limits	15	15	5	0.0073-0.012

Non Essential Heavy Metals

Both sources were also tested for non-essential heavy metals including cadmium (Cd), chromium (Cr) and nickel (Ni). Cadmium was observed in two rock salt samples and in one sea salt sample with the average concentration of 1 mg/kg and 8 mg/kg, respectively for Khewra crystal white and Khewra edible. While in Karachi sea

salt, the average concentration of Cd was 6 mg/kg only (Table-3). Cd was not detected in Gawadar sea salt and other rock salts (Table-3). The recommended value for Cd is 0.025mg/day (Lenntech, 1998-2009). The daily uptake of salt at the rate of 5 mg/day will contribute to 0.005 mg/day to 0.020 mg/day to routine diet and was found below the above mentioned permissible limit.

Similarly, rock salt was also found high in nickel (Ni) content with range of 2.17 mg/g to 8.20 mg/g (Table-2). For rocks salts, the concentration of Ni 8.20 mg/kg and 6.35 mg/kg, respectively for Khewra edible and Crystal white. The concentration of Ni was 6.05 mg/kg 4.30 mg/kg for Industrial Grade and Khewra piece grade, respectively. In Kohat rock salt, the concentration of Ni was comparatively low with average value of 2.17mg/kg (Table-3).

Nickle recorded values for sea salts were in the range of 2.70 mg/g to 8.16 mg/g for Gawader and Karachi sea salt samples, respectively (Table-3). The permissible limit for nickel is 2.7 μ mol/day equivalent to 0.16 mg/day (Christensen, 1995). The result showed that both rock and sea salts are good sources of Ni, but rock salt is richer than the sea salt in Ni content. On the basis of daily salt consumption of 5 g. nickel content was found in the range of 0.014 to 0.041mg/kg in Gawader and Karachi sea salts, respectively while the values were varied in rock salts from 0.011- 0.041mg/kg which conclude that all the rock and sea salts were within the desired limit (Table-4).

Copper (Cu) was found in rock salt in the range of 1mg/kg – 4 mg/kg (Table-2). Khewra edible salt was found high in Cu

contents with average concentration of 4 mg/kg. The concentrations of Cu in others salts were 3, 3, 2 & 1 mg/kg in crystal white, industrial grade, Kohat rock salt and Khewra piece grade, respectively (Table-3). Kohat rock salt and Khewra piece grade were within the permissible limit.

In sea salt, the concentrations of Cu were 0-2 mg/g for Gawadar and Karachi sea salt samples, respectively (Table-3), Karachi sea salt was within the permissible limits and can be termed as a good source of Cu. While the comparison between sea and rock salts showed that rock salt was found comparatively rich in Cu content. The permissible limit of copper is 2 mg/day (Lenntech, 1998-2009), as a result all of the values obtained were within the limit. As Cu is an essential element for human body and rock salt can be considered good for health. High copper doses can cause many health problems like anemia, liver and kidney damage, stomach and intestinal irritation (Suttle *et al.*, 1999). Moreover, chromium and molybdenum were analyzed for both sea and rock salts and were not detected. The recommended daily intake of chromium is 50-200 μ g/day (Lendinez *et al.*, 2001) and Mo is 0.075 mg/day (Lenntech, 1998-2009).

Table 3. Concentration of various trace elements (non essential heavy metals) in salt samples collected from different parts of Pakistan

S. No	Name of Sample	Cu (mg/kg)		Cd(mg/kg)		Ni(mg/kg)	
		Average	SDT	average		Average	
1	Kohat rock salt	2.02	0.81	0.00	0.00	2.17	1.00
2	Karachi sea	2.04	0.79	6.03	1.62	8.16	2.05
3	Khewra edible salt	4.04	1.21	8.00	1.50	8.20	1.56
4	Crystal white	3.08	1.19	1.05	0.27	6.35	1.94

5	Industrial grade	3.01	0.98	0.00	0.00	6.05	1.56
6	Khewra piece grade	1.07	0.32	0.00	0.00	4.30	1.96
7	Gawadar sea salt	0.00	0.00	0.00	0.00	2.70	1.41
	Permissible limit	2 mg/Kg		(25µg/kg)		0.16 mg/day	

Table 4. Average daily uptake of non-essential trace elements calculated on the basis of 5 gram salt consumed/day

S. No	Name of Sample	Cu (mg/Kg)	Cd(mg/Kg)	Ni(mg/Kg)
1	Kohat Rock Salt	0.010	0.000	0.011
2	Karachi sea	0.010	0.030	0.041
3	Khewra edible salt	0.020	0.040	0.041
4	Crystal white	0.015	0.005	0.032
5	Industrial grade	0.015	0.000	0.030
6	Khewra piece grade	0.005	0.000	0.022
7	Gawadar Sea salt	0.000	0.000	0.014
	Permissible limit	2	0.025	0.16

Conclusion

The results showed that in terms of heavy metals, rock salt is good when compared with sea salt. Gawadar sea salt was found good in comparison to Karachi sea salt. The industrial grade of Kewra rock salt is some time used as edible salt. As industrial grade is rich in both essential and non essential heavy metals, therefore, its use as edible salt is not recommended.

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