Technical paper

Chemical Composition of Natural Sea Salt from the Sečovlje Salina (Gulf of Trieste, northern Adriatic)

Nives Kovač,[1,*] Neli Glavaš,[1] Matej Dolenec,[2] Nastja Rogan Šmuc[2] and Zdenka Šlejkovec[3]

[1] *Marine Biology Station, National Institute of Biology, Fornače 41, 6330 Piran, Slovenia*

[2] *University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Geology, Aškerčeva 12, Ljubljana, Slovenia*

[3] *Department of Environmental Sciences, Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia*

** Corresponding author: E-mail: kovac@mbss.org*

Received: 11-01-2013

Abstract

In our research the concentrations of major and minor elements were determined in natural sea salts from the Sečovlje salina (Piran salts, Slovenia) and compared to those of selected samples of commercially available unrefined salts with different geographical origins (Croatia, Austria, Italy, Portugal, India, and Pakistan). In the case of major element contents such as sodium (Na), iron (Fe), aluminum (Al), manganese (Mn), and titanium (Ti) many similarities were observed among the analysed salt samples. On the other hand, Piran salts are characterized by lower silicon (Si) values. Among the salts from the Sečovlje salina, the salt with the trade name *Piran salt* has a higher Mg content while *Flower of salt* has a lower concentration of calcium (Ca). In Slovenian samples the majority of trace element values were lower than 0.5 $\mu g\ g^{-1}$, which was comparable to the results from commercially available unrefined salts. The salt composition differences observed indicate area-specific signatures related to geographic origin and diverse salt production processes. The quality of the studied salt samples is in accordance with standards established by the Codex Alimentarius Commission and the Piran salts are also suitable regarding issues of national food control.

Keywords: northern Adriatic Sea, Sečovlje salina, microbial mat-petola, natural salt, elemental composition

1. Introduction

Sodium chloride or common salt, table salt, or halite is a white crystalline chemical compound with the chemical formula NaCl that is usually observed in a cubic or, rarely, an octahedral crystal form. It is an abundant mineral that is employed for industrial (manufacturing different chemicals), agricultural, and water-conditioning uses as well as a de-icer. Salt is also commonly used in the food industry as a flavour enhancer and it is important as a daily diet requirement of humans. The chemical industry represents the largest consumer of salt (56%) followed by human consumption (22%), road de-icing (12%) and other users (10%).[1]

Salt can be obtained from surface or underground mining of halite deposits (usually former sea beds; underground and surface rock salt) or from solar evaporation of seawater or inland brine. Recently world-wide salt production was estimated to be about 260 million tons per year, of which 100 million t/y was solar salt and 80 million tons rock salt and salt produced from brine.[1]

Salt for human consumption is produced in different forms: salt evaporated as well as cold refined, rock salt, sea salt (refined and unrefined), dendritic (contains ferrocyanide salts), fluoridated salt, and salt fortified with iron. Refined salt usually contains about 99.5–99.9% NaCl and some additives such as whitening and anti-caking agents to keep the salt crystals from sticking together as they absorb moisture from the air (such as ferrocyanide salts, sodium silicoaluminate, magnesium carbonate...). All salts can be iodized, fluoridated and fortified with iron. "Natural" sea salt (unrefined) is not altered by man so contains no additives against caking and is not chemically processed. The salt is naturally evaporated by the sun and wind allowing the sea salt to retain its natural mineral content. The most important thing to remember at this point is that some elements (some trace heavy metals) are significant nutritionally, either for their essential nature or their toxicity.

Elemental salt composition is closely related to salt production techiques and environmental factors. Precipitated salt crystals may contain some organic and inorganic composites (soluble and insoluble). Soluble fractions mainly originate in the mother brine. While the salt crystals grow, small quantities of brine can be trapped within the salt structure. Such fluid inclusions are mostly inorganic with dissolved chemical elements filling inter- and intra-crystalline cavities.[2] Sometimes halophiles are also entrapped within salt inclusions.[3,4] The quantity of fluid inclusion depends on the rate of crystal growth and chemically resembles the mother brine.[2] Additionally, some chemical elements can replace sodium or chlorine in the NaCl crystalline network or be added as fine solid particles (inter- or intra-crystalline).[2,5] The latter mostly originate from atmospheric deposition, brine particulate matter (mostly minerals from concurrent precipitation) and sediment substrates of the crystallization basins.

In the past salt production was one of the main commercial activities in the Gulf of Trieste and Istria (northern Adriatic) but at the present time only the salinas at Sečovlje and Strunjan (Piran salinas) have been preserved. The Sečovlje salina's history goes back to the 9th century[6] but the earliest written sources regarding salt making are dated to the 13th century. In addition to the ancient procedure of salt-making the Sečovlje salina, extending over 6.5 km^2, also provides other aesthetic, cultural and natural values. Because of their exceptional landscape and ecological value, the Slovenian wetlands are also included on the Ramsar list. Today, the company Soline Pridelava soli, d.o.o. (Salt Production Co., Ltd)[7] protects and preserves the natural and cultural heritage within Sečovlje Salina Nature Park[8] and produces and manufactures various salt products.

There have been many studies of flora and fauna in the Sečovlje salina and numerous publications are dedicated to its cultural tradition. However, there is a lack of investigation into the solid (sediment) and aqueous (brine) phases of salinas. The aim of this study was to investigate for the first time the detailed elemental and mineralogical composition of various salt samples from the Sečovlje salina and to compare the results with those of commercially available unrefined salts with various geographical origins.

2. Materials and Methods

2. 1. Sampling Site

The Sečovlje salina (Figure 1) is located in the southern part of Piran Bay (northern Adriatic) on the estuary of the River Dragonja. The recent sediment of the salt pans (up to 90 m deep) is mostly composed of quartz, calcite and clay minerals such as illite, chlorite and kaolinite.[9] Adequate land and favourable climate conditions combine with high seasonal temperatures and winds for the solar evaporation of brine. The annual production of salt in the Sečovlje salina varies from 200 to 4000 tons mainly depending on weather conditions that are important for evaporation (air temperature, wind frequency and intensity, and atmospheric humidity).

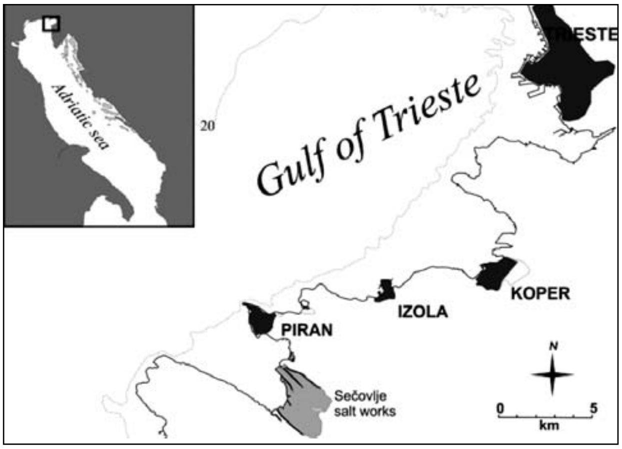

Figure 1: Location of sampling site (Sečovlje salina)

2. 1. 1. Traditional Salt Production in the Sečovlje Salina

The basis for solar salt production is fractional salt crystallization leading to the recovery of NaCl through the natural evaporation and concentration of seawater in crystallization basins. The least soluble salt, calcium carbonate ($CaCO_3$), precipitates first followed by gypsum ($CaSO_4 \cdot 2H_2O$), halite (NaCl) and finally magnesium and potassium salts. The season for salt making usually begins in March with precipitation of NaCl in June/July/August. The salt making process includes the traditional manual technique that has remained virtually the same over time, that is, gathering salt from sea water by moving brine through a series of evaporation ponds until the salt is harvested in crystallization basins. Seawater (brine) salinities in the salt making system vary during the salt production season depending on weather patterns, water movements, operational demands and maintenance needs. The salinity of natural seawater within the intake canals usually equals about 36–38. Sea water is directed into a system of shallow ponds arranged in series. The first series represents the evaporation ponds: I followed by evaporation ponds II and III in successive order of evaporation. Each subsequent evaporation pond is more saline due to the specific operational system and to solar evaporation. Finally the brine is led into the crystallisation basins, covering about 6–7% of all basins, with the help of pumps. Salt precipitated on the crystallizer floor is raked with wooden scrapers into heaps or slopes with the natural inclination allowing surplus water to trickle away. Manually gathered dry salt is then transported in small wagons and stored in special depots. The crucial element in this mediaeval manner of salt-production is a microbial mat called "petola" i.e. a few millimeter thick surface layer[9] covering the mud bottom of the crystallizing basins. In the saline ponds, these biomats (inorganic and organic fractions) have important roles: removing dissolved nutrients from the water, controlling water leakage and infiltration into the mud, immobilising large amounts of elements (also trace elements) and facilitating organic detritus decomposition.[10,11] The petola is mostly composed of an inorganic fraction comprising carbonates, gypsum, quartz and clay minerals[9,12] while organic matter represents a rather low share (organic carbon; 4.3–6.4 wt. %). Petola organic matter originates mainly from a microbial component dominated by cyanobacteria.[9,13,14] During the wet season, organic decay processes and petola cementation lead to the very firm substrate needed for manual salt making.[12] As mentioned above, the petola also prevents the brine and salt from mixing with the muddy floor resulting in the production of white and "natural" sea salt. Therefore special care is dedicated to the cultivation of this biological-chemical facet each year.[14] In this traditional but strictly controlled method of salt production, the Piran salts (i.e. trademark name) are produced. In addition to the daily gathering of the salt on the petola, the artisan salt workers also collect *Flower of salt*. In a thin layer of the surface of the pans' salt basins the salt workers gently gather (by hand) the thin layer of salt crystallizing on the brine surface. The "hopper crystals" (upside down pyramidal structure in shape) of NaCl are typically (in addition to other components) present in that type of salt. Flower of salt is macroscopically characterized by small slightly pink crystals that could also sediment and contribute to salt gathered on the petola. These hopper crystals have fully developed edges and stairstep depressions on, or rather in, each crystal face. In rapidly crystallizing environments (salinas, evaporation lakes,...) the edges of the cubes simply grow faster than the faces, resulting in a series of depressed faces. Hoppering occurs when electrical attraction is higher along the edges of the crystal, causing faster growth at the edges than at the near face centres. This attraction draws the mineral molecules more strongly than the interior sections of the crystal, thus the edges develop more quickly.[15]

2. 2. Samples Characterization

Salt samples from the crystallization ponds of the solar salt works of Sečovlje were randomly selected during the salt production seasons from 2004–2010. Two samples of different salt types (with trademark names *Traditional salt* and *Piran salt*), one sample of *Flower of salt*, one sample of natural bath salt and Piran Bay seawater in powder form were analyzed (indicated by a "PI" mark). Since we wanted to compare their quality with other natural salts, we also analyzed some commercially available unrefined salts with different geographical origins (Croatia, Austria, Italy, Portugal, India, and Pakistan) designated as Salt 1–Salt 6. All samples were stored in polythene bags and taken to the laboratory for further preparation and treatment. They were milled in an agate mortar to a particle size of less than 50 μm and then packed in clean, dry, stoppered glass containers and stored in a refrigerator.

In order to define detailed mineralogical and elemental characteristics of different salt samples, X-ray Powder Diffraction (XRD) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) were employed. The mineral composition of the salt samples was determined by 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/degree, with a speed of 3.0 2 θ/min. The diffraction patterns were identified with the software X'Pert HighScore Plus with an installed PAN-ICSD database.[16]

In the case of the Pakistani salt the elemental analyses (FUS-MS, FUS-ICP, TD-ICP and INNA methods) were conducted by ACTLabs (Activation Laboratories Ltd., Ontario, Canada).[17] The other salt sample results determined by the Aqua Regia Digestion Ultratrace ICP-MS method, were analysed for their detailed elemental composition in an accredited commercial Canadian laboratory (Acme Analytical Laboratories, Vancouver, B.C., Canada).[18] For major elements, a 0.2 g sample was mixed with a mixture of lithium metaborate/lithium tetraborate and fused in a graphite crucible. Fused samples were diluted and analyzed by Perkin Elmer Sciex ELAN 6000/6100/9000 ICP/MS for the major oxides (SiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, TiO_2, P_2O_5) for all samples and selected traces i.e. barium (Ba), beryllium (Be) and strontium (Sr) for the Pakistani salt sample (ACTLab FUS-ICP method). The molten mixture of fused samples were also poured into a 5% nitric acid solution, shaken for 30 minutes until dissolved then run for thorium (Th) and uranium (U) (including bismuth (Bi), gallium (Ga), germanium (Ge), hafnium (Hf), indium (In), molybdenum (Mo) and rubidium (Rb) for Pakistani salt) on a combination simultaneous/sequential Thermo Jarrell-Ash Enviro II ICP (ACTLab FUS-MS method). Samples for copper (Cu) and sulfur (S) detection, including silver (Ag), cadmium (Cd), nickel (Ni), lead (Pb) and zinc (Zn) for Pakistani salt, were digested with four acids and heated in several ramping and holding cycles to incipient dryness. At that point, samples were brought back into solution using aqua regia and analysed with Varian ICP (ACTLab TD-ICP method). For detection of cobalt (Co), chromium (Cr), mercury (Hg), selenium (Se) and gold (Au) in the Pakistani salt sample 1 g aliquot was encapsulated in a polyethylene vial and irradiated with flux wires and an internal standard at a thermal neutron flux. After seven days to allow Na-24 to decay the sample was counted on a high purity Ge detector (ACTLab INNA portion method).

Trace elements (Ag, Ba, Be, Bi, Cd, Co, Cr, Ga, Ge, Hf, Hg, In, Mo, Ni, Pb, Rb, Se, Sr, Zn and Au) present in salt samples S-1, S-2, S-3, S-4, S-5 and Piran salts were detected after aqua regia digestion of equal parts concetrated HCl, HNO_3 and DI H_2O for one hour in a heating block of a hot water bath for low to ultra-low determination using inductively coupled plasma mass spectroscopy (AcmeLabs 1:1:1 Aqua Regia digestion Ultratrace ICP-MS analysis). Quality control and quality assurance (QCQA) of the salt sample analysis were assessed using the reference materials DS8 (AcmeLabs); NIST-694, DNC-1, NIST-1633b, W-2, SY-4, BIR-1A, GXR-1-4-6, SDC-1, JR-1 (ACTLab) and by the results of the duplicate measurements (see Table 1 and 2 for more details).

In the case of high salt samples the important ICP-MS side product represent the $ArCl^+$ (polyatomic interference) which has the same mass-to-charge ratio (m/z = 75) as arsenic (As). Therefore Flow Injection-Hydride Generation-Atomic Fluorescence Spectrometry (FI-HG-AFS) was used to determine arsenic concentrations in salt solutions.[19] Prior to the arsenic analyses the salt samples (0.5 g) were dissolved in 5 ml of MilliQ water. 100 µl aliquots were injected into a stream of mobile phase (15 mmol l^{-1} KH_2PO_4, pH 6.0) via Rheodyne injector and subjected to hydride generation in a PEEK cross. For hydride generation 2 mol l^{-1} HCl, 3.0 ml min^{-1} and 1.5% $NaBH_4$ in 0.1% NaOH, 3 ml min^{-1} were added to convert non-volatile arsenic compounds into corresponding volatile hydrides, which were separated from liquid waste in an A-type gas-liquid separator (PS Analytical, UK), dried in a Perma-pure dryer under the a flow of nitrogen and detected using an Excalibur Atomic Fluorescence Spectrometer (PS Analytical, Kent, UK). Peak areas were compared to the peak area of As(V) standard (1–50 ng ml^{-1}, prepared from Merck Titrisol standard, 1.000 mg ml^{-1}). Detection limits for arsenic were in the range of 0.5–0.8 ng ml^{-1} of injected solution (5–8 ng g^{-1} of salt). The same set-up as above, but with an additional UV-decomposition unit (FI-UV-HG-AFS), in which all potentially present arsenic compounds including organoarsenic compounds are decomposed with persulphate in alkaline conditions (3.0 $K_2S_2O_8$ and 3.0% NaOH) to form As(V) was used to verify the results. Detection limits of this set-up were in the range of 2–3 ng ml^{-1} of injected solution (20–30 ng g^{-1} of salt) so that arsenic in most of the samples was at or below detection limit (data not given).

3. Results and Discussion

The results of X-ray Powder Diffraction (XRD) of the studied samples are presented in Table 1. The mineral composition is characterised by high quantities of halite in all investigated samples, followed by gypsum, bischofite, langbeinite and, in some samples, also by dolomite, calcite, quartz and sylvine. The above mentioned results are also in accordance with mineralogical observations in different salts, shown by the CSIRO Minerals Report.[20]

Table 1: Major minerals found in salt samples

Mineral Name	Chemical Formulae
Halite	NaCl
Gypsum	$CaSO_4 \cdot 2H_2O$
Bischofite	$MgCl_2 \cdot 6H_2O$
Langbeinite	$K_2SO_4 \cdot 2MgSO_4$
Dolomite	$CaMg(CO_3)_2$
Calcite	$CaCO_3$
Quartz	SiO_2
Sylvine	KCl

Elemental analyses showed that six chemical elements sodium (Na), magnesium (Mg), calcium (Ca), potassium (K), sulfur (S), iron (Fe) together with chlorine (Cl) make up the majority of the investigated salt samples. Additionally, silicon (Si), aluminum (Al), phosphorus (P), manganese (Mn), titanum (Ti) contributed with minor concentrations in all salt samples (Table 2). Elemental analyses of selected samples showed similar concentrations in the case of Na, Fe, Al, Mn and Ti with greater differences observed for Mg, Ca, K, S, Al and P. The lowest content of Si was observed in Piran salts and the highest S concentration in the salt samples S-2 (Austria) and S-5 (India).

Regarding the major elements in Piran salts the following sequence was observed: Na > Mg > Ca > S > Fe, K > P > Al > Mn > Ti (*Traditional salt*), Na > Mg > S > Ca > K > Fe > P > Al > Mn > Ti (*Piran salt*) and Na > Mg > S > K > Ca > P > Fe > Al > Mn > Ti (*Flower of salt*). Salt with the trademark names *Traditional salt* and *Piran salt* are both unrefined sea salt that is crystallized from brine, with an approximate density of 26 – 29 °Bè and 28 – 31 °Bè, respectively, and scraped by hand from the crystallization salt basins. Due to higher brine salinity, the *Piran salt* contains higher contents of magnesium components. Bitter salt ($MgSO_4 \cdot 2 H_2O$) contributes to the slightly more bitter taste of *Piran salt*. On the other hand, the lowest Mg concentration was observed in *Flower of salt*. The data from regular quality analyses of salt (internal laboratory reports, Soline Pridelava soli, d.o.o. Company)[21] are in accordance with our results. The main salts composition is presented in Table 3. Bromide concentrations were about 173–271 µg g^{-1} with iodine concentration lower than 0.5 µg g^{-1}. Content of water in the salt samples estimated after the salt draining in storage was lower than 7% and the typical pH value of 20% salt solution was 8.44. The described elemental composition generally reflects the dominant mineral composition (Table 1) in selected samples.

Table 2: Major element content in salt samples (expression of quantities, here and hereafter, according to Coplen 2011)[21]

	Oxide	**SiO_2**	**Al_2O_3**	**Fe_2O_3***	**MnO**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**TiO_2**	**P_2O_5**	**Total**
	Unit	cg g^{-1}	cg g^{-1}	cg g^{-1}	cg g^{-1}	cg g^{-1}	cg g^{-1}	cg g^{-1}	cg g^{-1}	cg g^{-1}	cg g^{-1}	cg g^{-1}
	Detection Limit	0 .01	0.01	0.01	0.001	0.01	0.01	0.01	0.01	0.001	0.0 1	0.01
	Analysis Method	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP
Salt sample	**S-1 (Croatia)**	0.01	0.02	0.03	0.01	0.47	0.43	49.24	0.10	0.001	0.06	50.37
	S-2 (Austria)	0.10	0.04	0.05	0.01	0.24	0.56	49.10	0.39	0.003	0.01	50.51
	S-3 (Italy)	0.02	0.02	0.03	0.01	0.12	0.21	50.19	0.03	0.001	0.04	50.66
	S-4 (Portugal)	0.01	0.02	0.04	0.01	0.87	0.20	46.12	0.21	0.001	0.06	47.53
	S-5 (India)	0.18	0.03	0.05	0.01	1.89	0.26	44.43	0.26	0.002	0.07	47.17
	S-6 (Pa kistan)	0.05	0.03	0.04	0.01	0.24	0.25	49.20	0.21	0.001	0.03	50.05
	PI – Piran salt	<0.01	0.02	0.03	0.01	1.26	0.31	45.92	0.22	0.001	0.04	47.82
	PI – Traditional salt	<0.01	0.01	0.03	0.01	0.60	0.29	50.39	0.02	0.001	0.03	50.85
	PI – Flower of salt	<0.01	0.02	0.03	0.01	0.65	0.10	49.71	0.15	0.001	0.08	50.75
	PI – Natural bath salt	<0.01	0.02	0.04	0.01	0.15	0.16	49.71	0.03	<0.00	10.02	50.13
	PI – Seawater (powder)	<0.01	0.09	0.04	0.01	4.20	1.71	37.34	1.06	<0.00	10.09	44.55
	Average relative error	*1 %*	*2 %*	*2 %*	*4 %*	*6 %*	*2 %*	*3 %*	*8 %*	*3 %*	*11 %*	–
	Conversion factor (c.f.)	*0.467*	*0.529*	*0.699*	*0.775*	*0.603*	*0.715*	*0.742*	*0.825*	*0.600*	*0.436*	–

	Element	**Si**	**Al**	**Fe***	**Mn**	**Mg**	**Ca**	**Na**	**K**	**Ti**	**P**	**S**
	Unit	cg g^{-1}	cg g^{-1}	cg g^{-1}	cg g^{-1}	cg g^{-1}	cg g^{-1}	cg g^{-1}	cg g^{-1}	cg g^{-1}	cg g^{-1}	cg g^{-1}
	Detection Limit	–	–	–	–	–	–	–	–	–	–	0.001
	Analysis Method	–	–	–	–	–	–	–	–	–	–	TD–ICP
Salt sample	**S-1 (Croatia)**	0.005	0.011	0.021	0.004	0.28	0.31	36.54	0.08	0.0006	0.026	0.32
	S-2 (Austria)	0.047	0.021	0.035	0.004	0.15	0.40	36.43	0.32	0.0018	0.004	0.64
	S-3 (Italy)	0.009	0.011	0.021	0.004	0.07	0.15	37.24	0.03	0.0006	0.017	0.11
	S-4 (Portugal)	0.005	0.011	0.028	0.004	0.53	0.14	34.22	0.17	0.0006	0.026	0.32
	S-5 (India)	0.084	0.016	0.035	0.005	1.14	0.17	32.97	0.22	0.0012	0.031	0.64
	S-6 (Pa kistan)	0.023	0.016	0.028	0.005	0.15	0.18	36.51	0.17	0.0006	0.013	0.36
	PI – Piran salt	<0.005	0.011	0.021	0.004	0.76	0.22	34.07	0.18	0.0006	0.017	0.55
	PI – Traditional salt	<0.005	0.005	0.021	0.004	0.36	0.21	37.39	0.02	0.0006	0.013	0.16
	PI – Flower of salt	<0.005	0.011	0.021	0.004	0.39	0.07	36.89	0.12	0.0006	0.035	0.22
	PI – Natural bath salt	<0.005	0.011	0.028	0.005	0.09	0.11	36.89	0.03	<0.0006	0.009	0.12
	PI – Seawater (powder)	<0.005	0.048	0.028	0.004	2.53	1.22	27.71	0.88	<0.0006	0.039	2.37

* – total iron

cg g^{-1} – centigram/gram (%)

c.f. – conversion fa ctor (element = oxide × c.f.)

relative error = [measured value – certified v.]/certified v.

Table 3: Major chemical composition of Piran salts (summarizing the results of internal laboratory reports of Soline Pridelava soli, d.o.o. Company)[21]

Content	Average concentrations Cl	Ca	Mg	SO_4	K
Unit	cg g^{-1}	cg g^{-1}	cg g^{-1}	cg g^{-1}	cg g^{-1}
Method	ISO 2481:1973	ISO 2482:1973	ISO 2482:1973	ISO 2480:1972	ISO 9964:1993
PI – Piran salt	56.20 ± 1.50	0.21 ± 0.05	0.35 ± 0.09	1.07 ± 0.10	0.07 ± 0.00
PI –Traditional salt	56.08 ± 1.07	0.17 ± 0.05	0.28 ± 0.08	0.90 ± 0.21	0.07 ± 0.01
PI – Flower of salt	55.42 ± 1.05	0.06 ± 0.03	0.33 ± 0.05	0.68 ± 0.03	0.11 ± 0.03

While there is no international standard for unrefined sea salt, there is a Slovenian regulation for unrefined seawater (natural) salt (Rules on the quality of salt, OJ RS, No. 70/2003)[23] that determines the quality of unrefined seawater (natural) salt. It must contain not less than 95% of pure NaCl on a dry matter basis, at least 0.1% Ca(II) and 0.2% Mg(II) and not more than 7% of water. The rest of the composition includes natural secondary products and natural contaminants.

Amounts of minor elements detected in selected salt samples are presented in Table 4. Concentrations of Au, Be, Bi, Co, Cr, Ga, Ge, Hf, Hg, In, Mo, Ni, Sc, Se, Th and U in the Piran salts were consistently lower than 0.5 μg g^{-1}, while the average concentrations of Ag, Ba, Sr, Rb and Zn were higher than 0.5 μg g^{-1}. These values are in agreement with the results for commercially available unrefined salts. However, concentrations of trace elements in Pakistani salt were generally higher than the others (Table 4).

Today, there is serious concern about toxic metals present in the environment and in food. As, Cd, Cu, Pb and Hg are the most important heavy metals which may cause different health problems after the consumption of contaminated foods.[24–27] As, Cu and Pb are characterised as both vital and toxic for many biological systems and may enter food materials from soil through the mineralization of crops, food processing or environmental contamination.[24–28] Children are particularly susceptible to Pb exposure due to high gastrointestinal uptake and the permeable blood-brain barrier.[29,30] Cd is a very well-known and widespread environmental pollutant.[24] In humans the biological half-life of cadmium is estimated to be from 10 to 30 years hence it accumulates in biological systems.[31] Hg and most of its compounds are extremely toxic to humans and must be handled with special care.[32] Although the adverse health effects of heavy metals have been known for a long time, exposure to heavy metals continues and in some countries is even increasing.[27]

Food is one of the major routes to widespread heavy metal contamination in the general population. Table salt is one of the most common food additives with a unique place in food consumption. Consequently, maximum limits for the presence of heavy metals in table salt have been established by the Codex of legislation (Codex standard for food grade salt).[33] The Codex standard for food grade salt applies to salt used as an ingredient in food (for direct sale to the consumer and for food manufacturers) and to salt used as a carrier of food additives and/or nutrients. In this case the content of NaCl should comprise at least 97% (exclusive of additives). According to the Codex of legislation, the maximum tolerated amounts of heavy metals in salt are 0.5 μg g^{-1} for As, 0.5 μg g^{-1} for Cd, 2 μg g^{-1} for Cu, 0.1 μg g^{-1} for Hg and 2 μg g^{-1} for Pb. All salt samples are consistent (excluding the Hg and Pb data for the Pakistani salt) with recommended values.

Regarding food-grade salts available in Slovenia, in addition to the National regulations (OJ RS, No. 70/2003; OJ RS, No. 101/2003),[23,34] they also must comply with world regulations.[32] Concentrations of As, Cd, Cu, Hg and Pb in Sečovlje natural salt samples correspond to the allowed maximum limits for the presence of toxic metals in salt. The amounts of heavy metals found in Sečovlje samples were: Cd (<0.01–0.02 μg g^{-1}), Cu (<1–2 μg g^{-1}), Hg (<0.005–0.007 μg g^{-1}), Pb (<0.01–0.46 μg g^{-1}), and As (0.012–0.026 μg g^{-1}). Combining the data from both As measurements (FI- HG-AFS and FI-UV-HG-AFS) indicates that no considerable amounts of non-hydride forming arsenic compounds like, for example, arsenobetaine can be present in the Slovenian and in the other analysed samples. The average values of Au, Be, Bi, Co, Cr, Ga, Ge, Hf, Hg, In, Mo, Ni, Sc, Se, Th and U were lower than 0.5 μg g^{-1} in all investigated salt samples from Sečovlje (PI-samples). Average concentrations of Rb, Sr, Ba, and Zn, Ag, were: 0.1–1.9 μg g^{-1}, 28.6–134.3 μg g^{-1}, <0.5–1.7 μg g^{-1}, <0.1–1.4 μg g^{-1} and <2 μg g^{-1}, respectively.

Soylak et al. (2008)[35] analysed the trace metal content in 28 samples of refined and unrefined salt from Turkey, Egypt and Greece which showed the Cu, Ni, Co, Mn, Pb and Cd concentrations in the range of 0.17–0.47, 0.16–1.57, 0.22–0.48, 0.26–4.68, 0.50–1.64 and 0.14–0.30 μg g^{-1}, respectively. The levels of the previously mentioned element (trace metals) concentrations in unrefined Turkish table salts (rock salt, salt from Salt Lake) were quite comparable to our results except for the Mn and Cu contents being higher in our case.[35] The latter is much more similar to the Cu content (1.16–1.179 μg g^{-1}) determined from the table salt samples from Nigde city (Turkey).[36] Nickel concentrations in the selected natural salts were 0.2–0.9, in the Slovenian salts 0.1–0.4 μg g^{-1} and the nickel content of table salts from Kayseri-Tur-

Table 4: Minor elements found in salt samples

Element	**As**	**Ag**	**Ba**	**Be**	**Bi**	**Cd**	**Co**	**Cr**	**Cu***	**Ga**	**Ge**	**Hf**	**Hg**
Unit	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}	µ g g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}
Detection limit	0.005	0.002	0.5	0.1	0.02	0.01	0.1	0.5	1	0.1	0.1	0.02	0.005
Analysis Method	FI-HG-AFS	Ultra ICP-MS	Ultra ICP-MS	Ultra ICP-MS	Ultra ICP-MS	Ultra ICP-MS	Ultra ICP-MS	Ultra ICP-MS	TD-ICP	Ultra ICP-MS	Ultra ICP-MS	Ultra ICP-MS	Ultra ICP-MS
S-1 (Croatia)	0.018	0.002	<0.5	<0.1	<0.02	<0.01	<0.1	<0.5	<1	<0.1	<0.1	<0.02	<0.005
S-2 (Austria)	0.035	0.005	2.4	<0.1	<0.02	<0.01	<0.1	<0.5	1	<0.1	<0.1	<0.02	<0.005
S-3 (Italy)	0.018	<0.002	<0.5	<0.1	<0.02	<0.01	0.7	<0.5	<1	<0.1	<0.1	<0.02	<0.005
S-4 (Portugal)	0.027	<0.002	<0.5	<0.1	<0.02	<0.01	<0.1	<0.5	<1	<0.1	<0.1	<0.02	<0.005
S-5 (India)	0.022	<0.002	1	<0.1	<0.02	<0.01	<0.1	<0.5	1	<0.1	<0.1	<0.02	0.013
S-6 (Pakistan)*	0.012	<0.500*	4*	<1*	<0.1*	<0.5*	2.3*	<0.5*	2	<1*	<0.5*	0.3*	<1*
PI – Piran salt	0.016	<0.002	1.4	<0.1	<0.02	<0.01	<0.1	<0.5	<1	<0.1	<0.1	<0.02	<0.005
PI – Traditional salt	0.014	<0.002	1.7	<0.1	<0.02	0.02	<0.1	<0.5	2	<0.1	<0.1	<0.02	<0.005
PI – Flower of salt	0.020	<0.002	<0.5	<0.1	<0.02	<0.01	<0.1	<0.5	<1	<0.1	<0.1	<0.02	<0.005
PI – Natural bath salt	0.012	<0.002	1.3	<0.1	<0.02	<0.01	<0.1	<0.5	<1	<0.1	<0.1	<0.02	0.007
PI – Seawater (powder)	0.026	<0.002	1.3	<0.1	<0.02	0.01	<0.1	<0.5	<1	<0.1	<0.1	<0.02	0.007
Relative error	–	*4 %*	*4 %*	*12 %*	*8 %*	*9 %*	*3 %*	*7 %*	*5 %*	*3 %*	*28 %*	*0 %*	*7 %*
** Detection limit*	–	*500*	*1*	*1*	*0.1*	*0.5*	*0.1*	*0.5*	–	*1*	*0.5*	*0.1*	*1*
** Analysis methods*	–	*TD-ICP*	*FUS-ICP*	*FUS-ICP*	*FUS-MS*	*TD-ICP*	*INNA*	*INNA*	–	*FUS-MS*	*FUS-MS*	*FUS-MS*	*INNA*

Element	**In**	**Mo**	**Ni**	**Pb**	**Rb**	**Sc***	**Se**	**Sr**	**Th***	**U***	**Zn**	**Au**
Unit	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}	µ g g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}
Detection limit	0.02	0.01	0.1	0.01	0.1	0.1	0.1	0.5	0.1	0.01	0.1	0.001
Analyisis Method	Ultra ICP-MS	Ultra ICP-MS	Ultra ICP-MS	Ultra ICP-MS	Ultra ICP-MS	INNA	Ultra ICP-MS	Ultra ICP-MS	FUS-MS	FUS-MS	Ultra ICP-MS	Ultra ICP-MS
S-1 (Croatia)	<0.02	0.05	0.7	0.1	0.3	0.25	0.5	199.5	<0.05	<0.01	0.2	0.0049
S-2 (Austria)	<0.02	0.08	0.6	0.49	0.5	<0.01	0.2	155.8	<0.05	0.04	0.8	0.0019
S-3 (I taly)	<0.02	0.05	0.7	0.15	0.1	0.35	0.3	43.8	<0.05	<0.01	<0.1	0.001
S-4 (Portugal)	<0.02	0.04	0.9	0.13	0.6	<0.01	0.2	44.2	<0.05	<0.01	0.3	0.0005
S-5 (India)	<0.02	0.02	0.2	0.28	0.5	<0.01	<0.1	73.6	<0.05	<0.01	1.1	0.0034
S-6 (Pakistan)*	<0.1*	<2.0*	<1*	<5*	<1*	<0.01	<0.5*	22*	0.19	<0.01	5*	<0.0010*
PI – Piran salt	<0.02	0.03	0.4	0.35	0.6	<0.01	<0.1	100.5	<0.05	<0.01	1.3	0.0031
PI – Traditional salt	<0.02	0.18	0.4	0.26	1.9	<0.01	0.1	134.3	<0.05	<0.01	1.4	0.0032
PI – Flower of salt	<0.02	<0.01	0.1	<0.01	0.3	0.25	<0.1	28.6	<0.05	<0.01	<0.1	0.0016
PI – Natural bath salt	<0.02	<0.01	0.2	0.46	0.1	<0.01	<0.1	76.8	<0.05	<0.01	0.8	0.0034
PI –Seawater (powder)	<0.02	<0.01	0.2	0.34	0.1	0.19	<0.1	69.3	<0.05	0.07	1.3	0.0034
Relative error	*0 %*	*0 %*	*3 %*	*4 %*	*6 %*	*2 %*	*2 %*	*5 %*	*5 %*	*9 %*	*1 %*	*11 %*
** Detection limit*	*0.1*	*2*	*1*	*5*	*1*	–	*0.5*	*2*	–	–	*1*	*0.001*
** Analysis methods*	*FUS-MS*	*FUS-MS*	*TD-ICP*	*TD-ICP*	*FUS-MS*	–	*INNA*	*FUS-ICP*	–	–	*TD-ICP*	*INNA*

* Activations laboratories

key[37] was in the range of 0.87–1.24 μg g^{-1} and from Bahaia Brazil[38] 0.08 μg g^{-1}. The cadmium contents of the ten selected samples presented in this study were lower than or similar to the range of 0.01–0.03 μg g^{-1} reported for Brazil table salts[39] and also much lower than that observed in table salt from Nigeria[40] (i.e. 4.5 μg g^{-1}).

Salt composition depends on the origin of the salt and the salt production processes. In the case of the Sečovlje salina, marine and/or salina sediments are used for petola sanitation and cultivation processes contribute to petola composition and finally to salt composition. Marine mud is mainly composed of quartz, calcite, halite and clay minerals[41] and salina sediments from cristallization basins mostly contain quartz, carbonates and clay minerals.[42,43] Petola particles are mainly added to the salt during manual harvesting. These particles (containing microalgae) are also the major origin of organic matter in Sečovlje salt, in addition to that originating in seawater (brine) above the petola biomats. Additionally, diverse organic chemicals synthesized by the members of the microbial communities (such as osmotic stabilizers and different microbial metabolism products of those osmotic solutes...) influence the size and quality of the halite crystals in saltern evaporation and crystallization ponds[44] so future research should focus also on biological processes impacting the formation and quality of produced salt.

4. Conclusions

The elemental and mineralogical composition of various salt samples from the Sečovlje salina were compared with the quality of commercially available unrefined salts with different geographical origins. All studied samples are characterized by high quantities of halite, followed by gypsum, bischofite, langbeinite and, in some samples, also by dolomite, calcite, quartz and sylvine. Elemental analyses showed that Na, Mg, Ca, K, S, and Fe together with Cl (not included in this analysis) constitute the majority of selected salt samples. Minor concentrations of Si, Al, P, Mn and Ti were found in all salt samples. Comparison of salts from the Sečovlje salina showed that "*Piran salt*" has higher Mg values and "*Flower of Salt*" has a lower content of Ca. In the Piran samples the trace elements As, Au, Be, Bi, Co, Cr, Ga, Ge, Hf, Hg, In, Mo, Ni, Sc, Se, Th and U were lower than 0.5 μg g^{-1} whereas the average concentrations of Ag, Ba, Sr, Rb and Zn were 0.1–1.9 μg g^{-1}, 28.6–134.3 μg g^{-1}, <0.5–1.7 μg g^{-1}, <0.1–1.4 μg g^{-1} and <2 μg g^{-1}, respectively. This is comparable to the results from the commercially available unrefined salts. Analyzed samples were in the range of the values recommended by the Codex of legislation for the presence of toxic metals in salt and the quality of Piran (unrefined) salts is in accordance with national (Slovenian) regulations. Following the results of the presented research, a more detailed study of different Piran salts including the organic fraction, the impact of different seasonal weather characteristics as well as the marine mud and petola present in the crystallization basins is planned.

5. References

1. V. M. Sedivy, Solar Salt Ponds as a Clean Energy Bioreactors. in: Proceedings of the Second Salt Workshop on Ecology and Economy of Solar Salt Production, SIESAL, Sindicato da Industria da Extraçao do Sal no Ertado do Rio Grande do Norte, Mossoro, RN, Brazil between 23.-26. 11. 2010, http://salt-partners.com/pdf/Mossoro2010_PresentationSedivy.pdf (assessed: August 10, 2011).
2. R. Amdouni, *Global NEST J.* **2010**, *12*, 409–416.
3. R. H. Vreeland, W. D. Rosenzweig, D. W. Powers, 2000, *Nature* **2000**, *407*, 897–900.
4. C. L. Satterfield, T. K. Lowenstein, R. H. Vreeland, W. D. Rosenzweig, D. W. Powers, *Geology* **2005**, *33*, 265–268.
5. R. Amdouni, *Global NEST J.* **2009,** *11*, 96–105.
6. Z. Žagar, V soline so šli. In: Žagar, Z. (Ed.), Muzej solinarstva. Museo delle saline. Pomorski muzej »Sergej Mašera« Piran. 1992, No. 7.
7. Soline Pridelava soli, d.o.o. (Salt Production Co., Ltd), http://www.soline.si/ (assessed: September 2, 2011).
8. Krajinski park Sečoveljske soline (Sečovlje Salina Nature Park), http://www.kpss.si/ (assessed: September 2, 2011).
9. J. Faganeli, J. Pezdič, B. Ogorelec, T. Dolenec, B. Čermelj, *RMZ-mater. geoenviron.* **1999**, *46*, 491–499.
10. J. S. Davis, *Global NEST: the Int. J.* **2000**, *2*, 217–226.
11. J. *Global NEST J.* **2009,** *11,* 58–63.
12. N. Kovač, Ann. Ser. Hist. Nat. **2009**, *19*, 95–102.
13. J. Schneider, A. G. Herrmann, Saltworks natural laboratories for microbiological and geochemical investigation during the evaporation of seawater. In: 5th International Symposium on Salt-Northern Ohio Geological Society, **1980**, *2*, 371–380.
14. R. Tkavc, C. Gostinčar, M. Turk, P. T. Visscher, A. Oren, N. Gunde-Cimerman, *FEMS Microbial Ecol.* **2010**, 75, 48–62.
15. E. Roedder, *Am. Mineral.* **1984**, *69*, 413–439.
16. M. Dolenec, M. Poročilo o petrološko-mineraloških, RTG in XRF analiz. Ljubljana, ZVKD, RS, December 2010.
17. ACTLab Methods. http://www.actlabs.com/list.aspx?menu=64&app=226&cat1=549&tp=12&lk=no (assesed February 21, 2013).
18. AcmeLabs Methods. http://acmelab.com/services/method-descriptions/soil-till-and-sediment/ (assesed February 21, 2013).
19. Z. Šlejkovec, J. T. van Elteren, U. D. Woroniecka, *Anal. Chim. Acta* **2001**, *443,* 277–282.
20. H. Aral, B. D. Hill, G. J. Sparrow, G.J., 2004. CSIRO Minerals Report DMR-2378, Value Adding to Salts Recovered from Saline Waters in Disposal Basins in the Murray-Darling Basin, Proof of Concept Study, Appendix 2 – Production of Salts from Brines and Bitterns, MDBC Publication No. 80/04, Murray-Darling Basin Commission 2004, 37 p.,

http://www2.mdbc.gov.au/__data/page/334/Appendix2.pdf, (assessed: October 12, 2011).

21. Internal report (2002–2010), Soline Pridelava soli, d.o.o. /Salt Production Co., Ltd, Bassment archives.
22. T. B. Coplen, *Rapid Commun. Mass Spectrom.* **2011**, *25*, 2538–2560.
23. Pravilnik o kakovosti soli, Uradni list RS, št. 70/2003)/Rules on the quality of salt, OJ RS, No. 70/2003, pp. 10827, http://www.uradni-list.si/1/content?id=44331 (assessed: August 10, 2011).
24. D. C. Adriano, Trace elements in terrestial environments: biogeochemistry, bioavailability and risks of metals (2nd edition). New York, Springer-Verlag. **2001**, 867 p.
25. M. J. McLaughlin, D. R. Parker, J. M. Clarke, *Field. Crop. Res.* **1999**, *60*, 143–163.
26. C. Pruvot, F. Douay, F. Hervé, C. Waterlot, *J. Soil Sediment.* **2006,** *6*, 215–220.
27. P. Zhuang, M. B. McBride, H. Xia, N. Li, Z. Li, South China. *Sci. Tot. Environ.* **2009***, 407*, 1551–1561.
28. V. A. Lemos, A. S. dos Passos, G. S. Novaes, D. A., Santana, A. L. de Carvalho, D. G. da Silva, *React. Funct. Polym.* **2007**, *67*, 573–581.
29. M. Yaman, Y. Dilgin, N. Okumus, *J. Chem. Soc. Pakistan* **2004**, *26*, 17–22.
30. Y. Fu, B. Yang, *Spectrosc. Spect. Anal.* **2005**, *25*, 1518–1519.
31. M. Arabi, A. A. Mohammadpour, *Vet. Res. Commun.* **2006**, *30*, 943–951.
32. J. J. Rytuba, *Environ. Geol.* **2003***, 43*, 326–338.
33. Pravilnik o označbi geografskega porekla Piranska sol, Uradni list RS, / Rules on the geographical denomination of origin of "Piran salt" (Piran salt), OJ RS, No. 101/2003, pp. 14080, http://www.uradni-list.si/1/content?id=45551 (assessed: August 10, 2011).
34. *Codex Alimentarius Commission*, Codex Standard for Food Grade Salt**,** Codex Stan 150–1985, Rev. 1-1997, Amend. 1-1999, Amend. 2-2001, Amend. 3-2006, FAO/WHO Food Standards Program, Rome.
35. M. Soylak, D. S. K. Peker, O. Turkoglu, *Environ. Monit. Assess.* **2008**, *143*, 267–272.
36. M. Soylak, I. Narin, L. Elci, M. Dogan, *Kuwait J. Sci. Eng.* **2001**, *28,* 361–370.
37. M. Soylak, A. U. Karatepe, L. Elci, M. Dogan, *Turk. J. Chem.* **2003***, 27*, 235–242.
38. S. L. C. Ferreira, C. F. Brito, A. F. Dantas, A. C. S. Costa, **1999**, *48*, 1173–1177.
39. F. A. C. Amorim, S. L. C. Ferreira, *Talanta* **2005**, *65*, 960–964.
40. I. C. Nnorom, *Pakistan J. Nutr.* **2007**, *6*, 122–127.
41. B. Ogorelec, M. Misic, J. Faganeli, *Mar. Geol.* **1991**, *99*, 79–92.
42. B. Ogorelec, M. Mišič, A. Šercelj, F. Cimerman, J. Faganeli, P. Stegnar, *Geologija – razprave in poročila* **1981**, *24/2*, 179–216.
43. M. Zajc, Mineralogical characterization of sediments from the Sečovlje salina and Makirina bay in Croatia. Graduation thesis, Faculty of natural sciences and engineering, University of Ljubljana, Ljubljana, **2010,** *114 p.*
44. A. Oren, *Global NEST J.* **2010,** *4*, 417–425.

Povzetek

V različnih tipih naravne nerafinirane soli iz Sečovljskih solin (Slovenija) in v izbranih nerafiniranih soleh različnega geografskega porekla (Hrvaška, Austrija, Italija, Portugalska, Indija, Pakistan) smo določili in medseboj primerjali koncentracije glavnih in elementov v sledovih. V vseh analiziranih vzorcih smo določili podobne koncentracije glavnih elementov kot so natrij (Na), železo (Fe), aluminij (Al), mangan (Mn), titan (Ti) pri čemer je za vse tipe slovenske (Piranske soli) soli značilna nižja vsebnost silicija. Med slednjimi lahko označimo tip soli s trgovskim imenom *»Piranska sol«* z višjo vsebnostjo magnezija (Mg) oziroma sol *»Solni cvet«* z nižjo koncentracijo kalcija (Ca). Vrednosti koncentracij elementov v sledovih so bile nižje od 0,5 μg g^{-1} in so primerljive z rezultati drugih analiziranih vzorcev nerafiniranih soli. Raznolikost elementne sestave odraža specifične lastnosti, ki so posledica različnega geografskega porekla in procesov pridelave soli. Kvaliteta analiziranih vzorcev soli je v skladu s predpisanimi mednarodnimi standardi za živila (Komisija Codex Alimentarius), sestava soli iz Sečoveljskih solin pa ustreza tudi nacionalnim predpisom.