



Unlocking hidden mineral resources: Characterization and potential of bitterns as alternative sources of critical raw materials

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ABSTRACT

Mineral extraction from seawater brines has emerged as a viable solution to reduce Europe's reliance on imported Critical Raw Materials (CRM). However, the economic viability of this approach hinges on the local demand for sodium chloride, the primary product of such extraction processes. This study investigates the potential of residual brines, commonly known as "bitterns," generated during solar sea-salt extraction in traditional saltworks, as an alternative source of minerals. The Mediterranean region, encompassing South-European, North-African, Near East coasts, and parts of the Atlantic regions, is particularly conducive to exploring this prospect due to its extensive solar sea salt industry.

Saltworks in the region, adopting various operational strategies based on feed quality or local climate conditions, produce different types of bitterns, each holding a latent resource potential that has remained largely unexplored. Within the framework of the EU-funded SEArcularMINE project, it was conducted an extensive analytical campaign to characterize bitterns collected from a diverse saltworks network. The analysis revealed the presence of sodium, potassium, magnesium, chloride, sulfate, and bromide in concentrations ranging from g/kg, while boron, calcium, lithium, rubidium, and strontium were found in the mg/kg range. Additionally, trace elements (TEs) such as cobalt, cesium, gallium, and germanium were detected at concentrations in the order of µg/kg.

Detailed results on the composition of bitterns are presented, emphasizing the distinct characteristics observed at different sites. The estimated potential for mineral recovery from these bitterns is approximately 190 €/m³, considering the production capacity of about 9 Mm³ per year in the Mediterranean area. This finding underscores the significant contribution that mineral recovery from bitterns could make in securing access to CRMs for the European Union.

1. Introduction

Saltworks represent the most ancient and attractive route for table-salt production, the most important and widespread mineral recovered from seawater. A large number of these facilities is located in the

Mediterranean basin, including European, North-African and Near East coasts. A notable variety of saltworks are operating following different processes and under different operative conditions depending on the site. Indeed, the production process or the number of the adopted basins can be different according to the selected strategy for maximizing sea

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salt production. Even the type of feed can have different origins, varying from the sea to the ocean, rivers and salt lakes. This leads saltworks to produce at the end of the productive cycle very different type of exhausted brines, commonly called “bitterns”, that are typically diluted with rain or seawater during the non-productive season and eventually discharged periodically back to the sea. Such bitterns are extremely interesting to be characterized, due to the huge potential as source of valuable minerals including the so classified “Critical Raw Materials” (CRM) (European Union, 2023), thus potentially making them an important source to secure EU supply.

A map of several salt production facilities located in EU and Mediterranean basin is reported in Fig. 1. Advances in resource recovery processes and technologies over the last decade have made extraction of minerals and metals from seawater brines more cost-competitive in comparison to terrestrial mining (Diallo et al., 2015; Kumar et al., 2021).

Many studies have been carried out focusing on the potential recovery of the main elements from seawater and from brines including industrial brines such as produced waters (Campisi et al., 2023) and desalination brines (Ihsanullah et al., 2022), also studying the relevant energetic and economic sustainability. Relating to seawater, among the others, Bardi et al., assuming that energy requirements for extraction are directly linked to the element concentration, stated that the extraction from low concentration resources is expensive and not always economically and energetically sustainable (Bardi, 2010).

As a consequence, it was also derived that the economic gain increases with the increase of mineral concentration (Sharkh et al., 2022a) and the decrease of energy consumption during its extraction. For example, Loganathan et al. affirmed that mining of minerals such as B, Li, Rb and Sr from seawater could potentially be attractive if suitable methods of brine concentration and extraction were developed (Loganathan et al., 2017). In this context, the bitterns, containing ions concentrations even up to 40 times higher than in seawater, represent a natural source for recovering minerals with the lowest economic investment and the highest profit margin. The challenge is open and harvesting of some minerals will be more attractive if more robust processes for extraction are developed.

The metallic elements found in seawater at the highest concentrations are sodium, magnesium, calcium and potassium. They are the only ones commercially extracted today (Bardi, 2010). However, besides them, other elements contained in the bitterns at an affordable concentration are being considered more and more attractive for their growing market demand, as the case of Li, highly needed in batteries for electronics and electric cars, or Sr, mainly used as sulfate (celestite), employed in drilling fluids for oil and gas extraction. Rb is another

high-concentration mineral which, up to now, has shown a relatively small market, primarily used for specialty glasses (Sharkh et al., 2022a).

Recently, research and innovation focus has moved to the mining of metals and several compounds from the bitterns. For example, sodium sulfate (~97 wt% purity) can be recovered, as demonstrated by Sahu et al., by using an integrated process combining cooling crystallization, filtration, and drying as major unit operations from sulfate-rich bittern (140.8 g/L), generated in some specific saltworks in India (Sahu et al., 2021). Some authors also studied the recovery of potassium compounds used as fertilizers utilizing sea salt bitterns after removal of NaCl (Scherzberg and Schultheis, 2014; Trivedi et al., 2017) or from sea water using ion-exchange processes (Yuan, 2006; Korngold, 2020).

On the other hand, production of magnesium salts from desalination brines has been seen as attractive since desalination brines first became available in large volumes, but has not yet been commercialized (Abdel-Aal et al., 2017). Other studies have been focused on the recovery of magnesium compounds from real bitterns, such as magnesium chloride, by preferential salt evaporation reaching concentration 23 times higher than in seawater (Hussein et al., 2017) or also by using techniques of spray and thermal drying (Nalajala et al., 2022). Moreover, Cipollina et al. obtained $Mg(OH)_2(s)$ by using bitterns from Trapani saltworks (Sicily, Italy) with purity values ranging from 98 to 100% by using NaOH solutions (Cipollina et al., 2015). Bitterns with a Mg content of 58 g/L coming from an Egyptian saltwork were treated in a pilot scale to produce $Mg(OH)_2(s)$ via reactive precipitation by adding ammonia solution (el Rafie et al., 2019). In addition, Luong et al. produced magnesium citrate, nonahydrate and anhydrous, via crystallization and spray drying techniques, respectively, by using a waste bittern originating from a saltwork in Western Australia containing an initial Mg concentration of 44 g/L (Luong et al., 2022). Other authors studied even the recovery of high purity NaCl by evaporation method after precipitation of $Mg(OH)_2(s)$ and successive filtration, treating a bittern from Rembang (Indonesia) still containing high concentrations of Na^+ (18–20 g/L) (Jumaeri et al., 2021). Also untreated bittern has been used as a coagulant, due to the high Mg(II) content (Ayoub et al., 1999), to remove Pb(II) and turbidity from batik industry wastewater (Soedjono et al., 2021), or for the treatment of fish wastewater (Bagastyo et al., 2022). Lithium extraction has attracted a great interest due to the rapidly increasing market for Li-containing batteries for consumer electronics and electric vehicles. About 60% of current Li production comes from mineral deposits in Australia, and about 30% from brines in South America (Kramer, 2021). Although the concentrations of Li are at least to three orders of magnitude greater than seawater many efforts to evaluate the potential feasibility for its recovery are under development



Fig. 1. Representative map of salt production facilities in EU and Mediterranean basin (developed within the SearcularMINE project (SEArctularMINE, 2021)).

(Alsabbagh et al., 2021).

Within the activities of the EU funded project SEArcularMINE (Circular Processing of Seawater Brines from Saltworks for Recovery of Valuable Raw Materials), bitterns are considered as a preferential source to recover several valuable minerals, such as Mg, Li, B, Rb, Cs, Sr, Co, Ga, Ge, in a circular economy perspective (SEArcularMINE, 2021). Notably, for the first time also the recovery of trace elements (e.g. present at $\mu\text{g}/\text{kg}$) such as Cs, Co, Ga and Ge is taken in account in this project. Indeed, they are extremely valuable elements with a very attractive market price (U.S. Geological Survey, 2020).

Characterization of bitterns' ionic composition can be challenging. In fact, considering their very different concentrations range in the same matrix, it is necessary to use the most suitable analytical techniques. Baseggio used conventional standard methods to analyze the main elements on sea water samples such as the Volhard's titration for chlorides' detection, complexometric titration with EDTA for Mg and gravimetric analysis for sulfates (Baseggio, 1974). Kasedde et al. analyzed thirty brines samples collected from lake Katwe in Uganda using several analytical techniques, including Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), Inductively Coupled Plasma-Sector Field Mass Spectrometry (ICP-SFMS), ion chromatography (IC), and potentiometric titration, and results showed that the lake brines are highly alkaline and rich in Na^+ , Cl^- , CO_3^{2-} , SO_4^{2-} and HCO_3^- with lesser amounts of K^+ , Mg^{2+} , Ca^{2+} , Br^- , and F^- ions. Among the trace element B, I, Sr, Fe, Mo, Ba, and Mn were quantified (Kasedde et al., 2014). On the other hand, Cantlay et al. applied ICP-OES and ICP-MS for cation analysis in oil and gas well brines to determine the high concentrations of sodium, calcium, magnesium, potassium, iron, manganese, strontium and barium (Cantlay et al., 2020).

In this context, very few papers were published concerning the detection of trace elements in concentrated brines or bitterns due to the difficulty of characterizing elements at very low concentrations (e.g. $\mu\text{g}/\text{kg}$) in the presence of other main elements much more concentrated. Nayak et al. tried to detect the concentration of major, minor and trace elements in bitterns coming from Orissa in India. Ca and Mg were quantified by complexometric titration with EDTA, Na and K by flame photometer, sulfates by gravimetric analysis, chlorides by Volhard's titration and minor elements such as Fe, Mn, Ni, Cr, Co and Sb by Atomic Absorption Spectrometry (AAS) and Al, Ti, Si and B by ICP-OES (Nayak and Panda, 2014). In this study, the lowest concentrations found for trace elements vary from 0.4 $\mu\text{g}/\text{kg}$ for Sb to 4 mg/kg for B, while for Co was detected a concentration of 0.1 mg/kg.

In the present manuscript, a continent-wide bitterns library was generated by collecting and analyzing bittern samples from 18 sites in the Mediterranean region. Main results concern the evaluation of ions concentrations, for both main ions and trace elements. Furthermore, the huge potential of saltworks as source of valuable minerals is discussed by highlighting the possibility of contributing to secure the access of some of the Critical Raw Materials (CRM) within EU, estimating the possible gain derived from the treatment of 1 m^3 of bittern.

2. Sampling and characterization of bitterns

2.1. Description of bitterns origin

Samples of the bitterns were collected from 18 different saltworks sited in the Mediterranean basin and shipped to three different laboratories to be characterized, located at: i) University of Palermo, Italy (UNIPA); ii) Polytechnical University of Catalunya, Spain (UPC); iii) National School of Engineering of Gabes, Tunisia (ENIG). Samples were all collected from the crystallization basins in the period September-December 2020, after the harvesting season. Main information related to samples and the nature of saltworks from which they were collected are reported in Table 1. According to Non-Disclosure Agreements signed with the saltworks owners the name/location cannot be reported, nevertheless the table provides information on the type of

Table 1

Classification and description of saltworks from which bitterns samples were collected.

Site	Type of feed	Production process	Nature of the bittern	Basins
A	sea	NE	PTSL	TF
B	sea	NE	PTSL	TF
C	sea	NE	PTSL	TF
D	sea	NE	PTSL	TF
E	sea	Vacuum crystallization	PTSL	Mixed
F	sea	NE	Mg-Enriched liquor	Ultra-fractionation
G	sea	NE	PTSL	TF
H	salt-lake	NE	PTSL	SP
I	salt-lake	NE	PTSL	SP
J	ocean	NE	PTSL	TF
K	river	NE	PTSL	TF
L	sea	NE	PTSL	TF
M	sea	NE	PTSL	TF
N	subsoil	NE	PTSL	TF
O	subsoil	NE	PTSL	Mixed
P	sea	NE	PTSL	TF
Q	sea	NE	Mg-Enriched liquor	TF
R	sea	NE	PTSL	SP

NE: Natural Evaporation, PTSL; Post Table-Salt liquor TF: Traditional - Fractionated; SP: Single Pond.

feed, the production process, the nature of the bittern and the type of basins of the saltworks originated the samples. Most samples come from saltworks operating under natural evaporation process (NE), using seawater as feed and with a traditional, fractioned crystallization principle of operation (TF). As an example, a detailed explanation of their operation can be found in Vicari et al. (2022). In some cases saltworks operate under vacuum crystallization process (site E), or they are constituted of a single evaporating basin (SP) (sites H and I), rather than ultra-fractionated (site F) or mixed (sites E and O) systems. Besides seawater, also samples of bitterns produced from water from river (site K), ocean (site J), salt-lake (sites H and I) and subsoil (sites N and O) have been characterized. Most of the bitterns derived from the liquor withdrawn after table-salt harvesting (PTSL). However, in some cases the liquor has been intentionally further enriched in magnesium (sites F and Q).

2.2. Analytical methods and materials

Bittern samples have been characterized in three different laboratories at the University of Palermo (UNIPA), Polytechnical University of Catalunya (UPC) and National School of Engineering of Gabes (ENIG). In order to assess the reliability and consistency of measurements performed in the different laboratories, some samples were analyzed in the different labs and results compared (see section 2.3) in order to estimate the relative standard deviation and allow the final merging of results obtained from the different analytical laboratories.

2.2.1. pH, conductivity and density

Bitters samples were characterized by measuring pH, conductivity and density. At UPC pH measurement was done by using a combined pH-glass electrode (GLP 22, Crison) calibrated with standard reference solutions of pH 4.02 and 7.00 at low ionic strength; conductivity measurements were performed with a Crison GLP 31 EC; density was measured using hydrometers of different operating range, from 0.9 to 1.3 g/cm^3 , with a resolution of 0.001 g/cm^3 . At UNIPA, pH values of bitterns and conductivity were measured by using a pH-cond WTW 3320, previously calibrated with standard reference solutions of pH 4.02, 7.00 and 12.45 and of conductivity at 1413 and 111,800 $\mu\text{S}/\text{cm}$. A 10 cm^3 pycnometer (DIN ISO 3507) was used for density detection. At ENIG, pH values of bitterns of samples was measured by using a pH-

meter (AZ® pH meter, 86501, Accuracy ± 0.02) previously calibrated with certified buffer solutions at pH 4.00, 7.00, and 9.00 at low ionic strength (Ω METROHM Ltd. CH-9101 Herisau); conductivity was measured by using a Starter 3100C Conductivity Bench (OHAUS®, 00.0 $\mu\text{S}/\text{cm}$ to 199.9 mS/cm) and the density with a balance (SHIMADZU BW 320D, Accuracy $\pm 0.001\text{g}$) and an ASPIN precision fixed-volume pipettes (class A+, 5 mL, Accuracy $\pm 0.009\text{ mL}$). In all labs, measures were at least duplicated.

An accurate pH detection in bittrens can raise significant issues due to the very high ionic strength of samples that affect the junction potential of the potentiometric cell and the activity coefficient of H^+ ions (Dickson, 1993; Marion et al., 2011). Since there are no certified buffer solutions in the ionic strength range typical of bittrens, the correct calibration of the glass electrode requires a more accurate procedure considering the variability of bittren salinity, that must be repeated and adapted at each sample. For this reason, additional pH measurements were carried out at UNIPA labs, only with bittren samples A and B, with the aim of comparing the results with those previously obtained with the pH-meter calibrated with certified buffer solutions at low ionic strength (here named method *a*). More accurate pH measurements with the two selected bittrens samples have been carried out by using an Orion glass electrode Ross type 8102 previously calibrated through a strong acid – strong base titration (here named method *b*). A detailed description is provided in Supplementary Information (see Section S1).

2.2.2. Analytical methods for major elements concentration evaluation

Major anions in bittrens, namely Cl^- , SO_4^{2-} and Br^- , were analyzed by using IC at the three labs, whereas cations, namely Na^+ , K^+ , Mg^{2+} , were detected by IC at UPC and UNIPA and by ICP-OES at ENIG.

UPC lab used a Dionex ICS-1000 and ICS-1100 with the cation-exchange IONPAC® CS16 and anion-exchange IONPAC® AS23 columns. The mobile phases were a 0.03 mol/L $\text{CH}_3\text{SO}_3\text{H}$ solution for the cation-exchange column and a mixture of 4.5 mmol/L Na_2CO_3 and 0.8 mmol/L NaHCO_3 solution for the anion-exchange column.

A similar procedure was used at UNIPA by using a Metrohm 882 Compact IC equipped with the cation-exchange Metrosep® C4 and the anion-exchange Metrosep® A Supp 5 columns. In this case, the mobile phase for the cation-exchange column was a 5.5 mmol/L H_3PO_4 solution, whereas for the anionic one the same mobile phase used at UPC was adopted.

Finally, Na^+ , K^+ and Mg^{2+} were analysed at ENIG by ICP-AES (Activa-HORIBA JOBIN YVON). Samples were previously diluted (dilution factor of 400), acidified with 2% HNO_3 (Scharlau, Reagent grade, 65%) and filtered with 0.45 μm syringe filters. All the standard solutions used to obtain the calibration curves were prepared in ultrapure water (EVOQUA Water technologies) from single analytical standards of 1000 mg/L (Précis). Details on the method parameters for ICP-OES are reported in Table S2a. For the anions, a Metrohm 930 Compact IC Flex 1 was used, equipped with the anion-exchange Metrosep A Supp 7 columns. A Na_2CO_3 eluent of 3.6 mmol/L was used as mobile phase for the anion-exchange column.

2.2.3. Analytical methods for minor elements concentration (e.g. $\mu\text{g}/\text{kg}$) evaluation

ICP-OES (5100 ICP-OES from Agilent Technologies) and ICP-MS (7800 ICP-MS from Agilent Technologies) were used at UPC labs to determine the concentration of minor elements in solution (Ca^{2+} , B(III), Li^+ , Rb^+ and Sr^{2+}). Samples were preliminary diluted (dilution factor of 400), acidified with 2% HNO_3 (PanReac AppliChem, 65%) and filtered with 0.22 μm syringe filters. All the standard solutions used to obtain the calibration curves were prepared with ultrapure water (Merck Millipore) and single analytical standards of 1000 mg/L (Agilent). Details on the method parameters for ICP-OES and ICP-MS are reported in Table S2b and Table S2c. Instrumental operating conditions used in the case of minor elements detection at UPC labs including concentration range of the calibration curve are summarized in Table S2d and the

calibration curves are reported in Fig. S2a.

Different atomic spectroscopy techniques were used at UNIPA to determine minor elements. F-AES and F-AAS were used to determine Li/Rb and Ca/Sr, respectively, by using a PerkinElmer AAnalyst 200 spectrophotometer. Details of the analytical procedure and the obtained calibration curves are provided in Supplementary Information. For air/acetylene flame, air flow rate was set at 10 mL/min and acetylene flow rate at 2.5 mL/min. As reported in the relevant literature, calibration curves were prepared by adding an alkali metal chloride 0.1 % m/m, e.g. NaCl 1 g/L, in order to reduce/suppress the ionization of the metals, e.g. Li, Rb, increasing the method sensitivity (Fujinaga et al., 1980). With this respect, Riedel-de Haën $\geq 99.8\%$ NaCl was used, after drying at 110 °C in an oven for 2 h. Standards of 1000 mg/L in 2 % HNO_3 (CPAchem) for Li, Rb; AVS TITRINORM, VWR Chemicals for Sr and Ca (in 6.5 % HCl, Titrisol, Sigma-Aldrich) were used for calibration curves.

Boron concentration, and in some cases also calcium, were measured by ICP-OES (Perkin Elmer Optima 2100, equipped with an auto sampler model AS-90). Details on the method parameters and the adopted calibration curve are reported in Table S2e and Fig. S2b. In each case, samples were previously filtered with 0.45 μm syringe filters and suitably diluted (dilution factor of 200). For B detection, samples were also acidified with HNO_3 (Sigma-Aldrich, $\geq 65\%$) to have a pH of around 5. Calibration curves for B were performed by using 1000 mg/L standard solution in deionized water (CPAchem). Instrumental operating conditions used in the case of minor elements detection at UNIPA labs are summarized in Table S2f. All the solutions were prepared using freshly, CO_2 -free ultrapure water ($\rho \geq 18\text{ M}\Omega\text{ cm}^{-1}$) and grade A glassware.

2.2.4. Analytical methods for detection of trace elements

At UPC labs, ICP-MS (7800 from Agilent Technologies) was used to determine the concentration of trace elements in solution: Co, Ga, Cs and Ge. Samples were previously diluted (dilution factor of 400), acidified with 2% HNO_3 (PanReac AppliChem, 65%) and filtered with 0.22 μm syringe filters. All the standard solutions used to obtain the calibration curves were prepared in ultrapure water (Merck Millipore) from single analytical standards of 1000 mg/L (Agilent). Instrumental operating conditions used in the case of trace elements detection at UPC labs are summarized in Table S2g and the calibration curves are reported in Fig. S2c, while details on the method parameters are reported in Table S2c.

Co and Ga were also detected at UNIPA labs by using ICP-OES, Perkin Elmer model Optima 2100, equipped with an auto sampler model AS-90). When possible, Co detection was replicated by using F-AAS analysis for validation. Calibration curves for Co and Ga were performed with a 100 mg/L standard solution in 5 % HNO_3 (CPAchem) and they are reported in Fig. S2d. Instrumental operating conditions used in the case of trace elements detection at UNIPA labs are summarized in Table S2h, while details on the method parameters are reported in Table S2e. Due to the high salinity of the bittren samples, the quantitative analysis of trace elements was preceded by a pre-concentration/extraction process that is described in Supplementary Information (see Section S3).

2.3. Assessment of the replicability of analytical methods in the different labs

Analytical techniques performed at the three labs have been compared focusing on the analysis of four different samples in order to assess the replicability of analytical results in the three laboratories. In particular, the mathematical average value for each element was calculated and the dispersion respect to this value was evaluated as standard deviation and relative standard deviation to assess the precision of the analysis. As an example, the results obtained for the sample from site D, one of the 18 listed in Table 1, is reported in Fig. S4.

A very good reproducibility was obtained for major elements, especially for the cations, where relative standard deviation (RSD) less than 5% were found. Larger deviations were observed for minor elements,

especially in the case of Rb^+ and Sr^{2+} with values of about 40 %.

The charge balance was also evaluated (see Eq. (2)) in order to assess the reliability of the adopted analytical methods.

$$Charge\ balance\ (\%) = \frac{\sum_i c_i z_i}{\frac{1}{2} \sum_i c_i |z_i|} \quad (2)$$

where c_i and z_i represent the molar concentration and the charge of the ions of bittern sample. Only the main ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} and Br^-) were taken in account. An average value of 1.7% was obtained considering the analysis of all the samples, included those (A to D) characterized in the three labs.

3. Results and discussion

3.1. Bitterns composition

At first, samples were fully characterized in terms of pH, density and conductivity. The respective ionic strength was also calculated (see Table 2). For samples A, B, C and D, the provided values are average values from the three laboratories (UNIPA, ENIG, UPC). In this case, the standard error was estimated and reported in table. Instead, for the other samples, analyzed at UNIPA (from E to I), at UPC (from J to Q), and at ENIG (sample R), average values are reported with the related standard deviations. RSD was estimated for each sample and average values of 0.27%, 0.38% and 0.35% were obtained for pH, density and conductivity in the three labs.

For what concerns the pH, the values reported in the first raw were detected according to the method *a* and those reported in second raw were calculated according to the method *b* for samples A and B, whereas for the other bitterns they were extrapolated as described in section 2.2.1. As shown an average value of 8.28 was detected with a range of variation from 7.35 to 8.94.

As observed, the values of pH detected according to the method *b* are comparable to that of seawater (Marion et al., 2011). Moreover, these results reveal that the difference of the pH values detected according to the two different methods increases as the ionic strength of the solution increases, thus the greater the ionic strength of the bittern examined, the greater the error done by neglecting it. Indeed, discrepancies of 1.65 and ~1.20 units were observed for site A and B, respectively, thus errors of 20% and around 14% derive by using method *a* instead of method *b*. Then, a linear correlation was extrapolated to evaluate the theoretical pH, i.e. that which could be obtained by using method *b*, for all the 18 samples. As a result, average error of 16 % was then estimated, with a standard deviation of ±3%.

Regarding densities, more than 50% of bitterns show values of 1.22–1.23 kg/L, the rest has an average density of 1.26 kg/L. Only in one case, for site F, a very high density was observed, of 1.3 kg/L. This is the case of a Mg-enriched liquor bittern produced in a system of ultra-fractionated basins. Conductivities are in the range of 100–200 mS/cm, showing the lowest value for sample of site F. In Fig. S5 is possible to observe the relation between density and conductivity for the samples: the higher the density, the lower the conductivity. This is an interesting result which can be ascribed to the bitterns' composition, rather than to its salinity (that is very high in all cases), as emerges from further analyzed in the following sections.

For what concerns the relation between conductivity and ionic strength, it's possible to observe that the increase of the ionic strength led to a decrease of the conductivity. This can be explained considering that at the very high salinity of bitterns, the distance between anions and cations decreases resulting in the formation of nonconductive ion pairs which leads to a decrease of conductivity (Pavlikova et al., 2020; Zhang et al., 2020a,b).

The detailed composition of each sample of the bitterns is reported in Table 3. The elements analyzed for the 18 bitterns have been grouped as follows.

Table 2
General characterization of bittern samples (A to R) collected from 18 different saltworks sited in the Mediterranean basin.

	A ^d	B ^d	C ^d	D ^d	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
pH ^a	6.7 ±0.0	7.3 ±0.0	7.0 ±0.0	6.9 ±0.1	6.4 ±0.1	6.0 ±0.1	7.1 ±0.1	7.1 ±0.1	7.0 ±0.1	6.9 ±0.1	7.0 ±0.1	7.4 ±0.1	6.9 ±0.1	6.9 ±0.1	7.5 ±0.1	7.5 ±0.1	6.7 ±0.1	6.3 ±0.1
pH ^{b,c}	8.27 ±0.05	8.53 ±0.05	8.2 ±0.05	8.4 ±0.05	7.8 ±0.05	7.9 ±0.05	8.3 ±0.05	8.1 ±0.05	8.1 ±0.05	8.1 ±0.05	8.5 ±0.05	8.5 ±0.05	8.0 ±0.05	8.4 ±0.05	8.7 ±0.05	8.6 ±0.05	8.9 ±0.05	7.3 ±0.05
I (mol/L)	10.3	7.5	7.5	9.4	9.3	12.8	7.7	7.0	6.9	7.8	9.7	6.9	7.9	9.3	7.5	7.2	11.1	7.8
Density (kg/L)	1.273	1.226	1.234	1.259	1.261	1.304	1.232	1.224	1.223	1.235	1.259	1.218	1.224	1.262	1.231	1.226	1.270	1.2680
Conductivity (mS/cm)	±0.006	±0.006	±0.005	±0.003	±0.008	±0.008	±0.008	±0.008	±0.008	±0.004	±0.001	±0.001	±0.001	±0.001	±0.001	±0.001	±0.001	±0.001
	133.1	192	182	154	155.2	101.7	192.1	192.1	192.1	177	146	201.5	184.4	142.7	190.2	193.3	143.3	149.2
	±0.5	±4	±7	±4	±0.1	±0.1	±0.1	±0.1	±0.1	±2	±3	±0.7	±0.7	±0.5	±0.8	±0.3	±0.6	±0.4

^a pH values measured by pH meter calibrated with certified buffer solutions at low ionic strength.

^b pH values measured by e.m.f. of potentiometric cell calibrated at the same ionic strength of bittern (for samples A and B).

^c pH values extrapolated according to a linear correlation derived from results relieved for samples A and B.

^d Average values provided by the three labs and related standard errors.

Table 3
Complete overview of bitterns compositions from 18 different saltworks (A to R) sited in the Mediterranean basin.

Bittern sampling site		A ^a	B ^a	C ^a	D ^a	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	
Major elements (g/kg)	Na ⁺	34.7 ±0.6	68.4 ±0.2	68.9 ±0.6	44.6 ±0.0	38.0 ±0.3	5.27 ±0.05	68.3 ±0.6	78.7 ±0.7	80.7 ±0.7	65.6 ±0.2	40.61 ±0.03	73.0 ±0.2	65.1 ±0.3	40.3 ±0.2	74.20 ±0.05	74.80 ±0.01	20.0 ±0.2	38.7 ±1.2	
	K ⁺	10.1 ±1.2	6.05 ±0.17	5.32 ±0.10	10.05 ±0.03	11.5 ±0.1	6.61 ±0.05	6.01 ±0.05	6.00 ±0.05	5.38 ±0.05	4.87 ±0.05	11.39 ±0.04	4.84 ±0.11	6.83 ±0.06	11.9 ±0.2	7.10 ±0.03	5.08 ±0.02	18.5 ±0.1	12.80 ±0.16	
	Mg ²⁺	47.4 ±0.2	19.0 ±2.5	21.6 ±0.5	39.9 ±0.3	40.3 ±0.7	75.3 ±1.3	23.2 ±0.4	15.4 ±0.3	14.4 ±0.2	23.4 ±0.4	40.7 ±0.1	16.43 ±0.04	25.8 ±0.1	36.2 ±0.4	19.2 ±0.3	18.1 ±0.1	58.9 ±0.8	41.3 ±0.6	
	Cl ⁻	156 ±5	157 ±3	156 ±2	154 ±4	150 ±9	206 ±12	151 ±9	152 ±9	153 ±9	156 ±9	155 ±0.4	167 ±0.2	159.6 ±0.6	154 ±0.1	162 ±0.4	161 ±0.1	187 ±2	151.1 ± 1.2	
	SO ₄ ²⁻	65.7 ±1.9	28.6 ±0.6	29.5 ±1.0	46.8 ±1.5	47.1 ±2.3	24.6 ±1.2	31.4 ±1.5	23.7 ±1.2	22.8 ±1.1	34.1 ± 0.1	55.0 ±0.1	16.2 ±0.2	30.0 ±0.2	58.5 ±0.2	26.50 ±0.03	22.2 ±0.01	28.7 ±0.5	60.1 ±2.5	
	Br ⁻	2.01 ±0.1	1.07 ±0.13	0.85 ±0.07	1.58 ±0.04	2.23 ±0.17	5.00 ±0.37	1.21 ±0.09	0.45 ±0.03	0.38 ±0.02	0.84 ±0.01	1.69 ±0.01	0.84 ±0.01	1.03 ±0.00	1.73 ±0.00	0.83 ±0.00	0.75 ±0.01	2.92 ±0.02	n.d.	
	Minor elements (mg/kg)	Ca ²⁺	64.3 ±9.1	124 ± 65	173 ±1	100 ±1	95.2 ±3.2	37.3 ±0.0	192 ±32	230 ±3	247 ±3	170 ±3	99.5 ±1.6	269 ±4	167 ±6	97 ±10	195 ±12	221 ±1	19.0 ±0.4	100 ±11
		B(III)	147 ±3	71.8 ±22.9	61.1 ±6.6	92.1 ±2.1	132 ±3	397 ±9	66.6 ±3.2	173 ±6	150 ±6	46.3 ±0.4	118.3 ±0.2	58.1 ±0.4	67.4 ±1.6	141 ±6	76.8 ±6.2	68.4 ±1.1	200 ±5	n.d.
		Li ⁺	5.55 ±0.03	2.79 ±0.71	2.59 ±0.63	4.21 ±0.01	5.95 ±0.16	15.3 ±0.3	3.30 ±0.60	131 ± 1	119 ±1	2.24 ±0.11	4.90 ±0.31	1.80 ±0.14	2.24 ±0.08	5.24 ±0.14	5.92 ±0.25	2.27 ±0.04	6.00 ±0.03	n.d.
		Rb ⁺	4.68 ±0.95	2.14 ±0.84	2.15 ±0.93	3.86 ±0.02	6.09 ±0.03	4.28 ±0.12	3.34 ±0.02	9.17 ±0.12	7.66 ±0.12	1.38 ±0.04	3.30 ±0.06	5.02 ±0.07	1.82 ±0.31	3.19 ±0.13	2.20 ±0.06	1.23 ±0.02	4.7 ±0.1	n.d.
Sr ²⁺		13.2 ±4.7	21.5 ±4.7	15.0 ±7.5	10.2 ±0.1	4.36 ±0.16	<1	11.2 ±0.2	25.3 ±0.2	6.87 ±0.16	22.9 ±0.9	16.6 ±0.2	26.8 ±0.8	12.6 ±0.1	8.61 ±0.13	16.2 ±0.1	16.70 ±0.01	n.d.	n.d.	
Trace elements (µg/kg)		Co(II)	3.69 ±2.25	0.48	<4 ±0.39	1.86 ±0.11	2.22 ±0.11	2.46 ±0.11	<1	<1	<1	<57	40.0 ±15.9	<8 ±73.5	73.5	<8	<8	<8	<8	n.d.
	Ga(III)	36.8 ±6.4	0.40	16.2	3.92 ±1.13	<6	<6	<1	<6	<6	1.18 ± 0.16	50.0 ±7.9	3.28 ±0.08	40.8 ±32.7	103 ±8	1.86 ±0.26	4.77 ±0.70	<23	n.d.	
	Cs ⁺	2.23 ±0.10	1.53	0.61	4.64 ±2.37	n.d.	n.d.	n.d.	n.d.	n.d.	1.05	20.0 ±0.08	3.67 ±7.9	1.85 ±0.37	39.6 ±7.9	50.0 ±0.0	3.96 ±0.16	7.74 ±0.44	n.d.	
	Ge(IV)	0.63 ±0.03	0.87	0.92	0.34 ±0.04	n.d.	n.d.	n.d.	n.d.	n.d.	0.61 ±0.06	1.11 ±0.08	0.44 ±0.08	0.73 ±0.37	174 ±16	0.20 ±0.03	<0.33	<23	n.d.	

^a Average values provided by the three labs and related standard errors.

- major elements, namely Na^+ , K^+ , Mg^{2+} , as cations, and Cl^- , SO_4^{2-} , Br^- , as anions, with a concentration in the range of several grams per kilogram of bittern (g/kg);
- minor elements, namely B(III), Ca^{2+} , Li^+ , Rb^+ and Sr^{2+} , with a concentration in the range of a few milligrams per kilogram of bittern ($\mu\text{g}/\text{kg}$);
- trace elements, namely Co(II), Cs^+ , Ga(III) and Ge^{4+} , with a concentration in the range of micrograms per kilogram of bittern ($\mu\text{g}/\text{kg}$).

All the reported values are results of average measurements. As previously reported, for samples A, B, C and D, the provided values are average values from the three laboratories (UNIPA, ENIG, UPC) and, in this case, the standard error was estimated and reported in table. Instead, for the other samples, analyzed at UNIPA (from E to I), at UPC (from J to Q), and at ENIG (sample R), average values are reported with the related standard deviations. RSD was estimated for each element in the sample and values ranged in 0.62–3.89 %, 1.09–6.74 % and 7.96–30.48% for major, minor and trace elements, respectively (considering that values for samples A-D are averages provided from the three labs). As expected, detection of trace elements was more changing.

B (III), Ga(III), and Ge(IV) are present in the brines as oxoacids while Co(II) is complexed with Cl^- ions. Some trace elements were not detected (n.d.) in a few samples, whereas in other cases the limit of quantification LOQ was reported (<LOQ).

As expected, the alkaline and earth-alkaline elements found in the highest concentration are Na^+ , K^+ and Mg^{2+} , which could be commercially extracted as chlorides, sulfates and carbonates or in the form of hydroxide, for what concerns Mg^{2+} (Sharkh et al., 2022a). With respect to the seawater, where Na^+ is the most concentrated metal, bitterns present very high content of Mg^{2+} with a concentration similar or even higher than Na^+ . This fact represents one of the most important reasons

to consider bitterns as a primary source of Magnesium, which is also listed among the Critical Raw Materials.

For the case of anions, present as major component, Cl^- ions show the highest concentrations followed by SO_4^{2-} (see Table 3). Their concentration is around 160 g/kg in the most samples but in saltwork R (representing a single evaporative pond), where Cl^- concentration is below 120 g/kg, and in site Q and F, where the concentration reaches higher values (up to 200 g/kg in site F), representing a condition typical of saltworks where the bittern produced is a Mg-enriched liquor.

Among the minor elements, Ca^{2+} and B(III) show the highest concentrations, ranging between 40 and 400 mg/kg, whereas Li^+ , Rb^+ and Sr^{2+} are present below 25 mg/kg (except for Li in the case of bitterns collected from internal salt-lakes, site H and I, where it reaches a very high concentration of 120–130 mg/kg). These values are much higher (up to a factor of 50–100) than in seawater, where Li and Rb are present in the range of 0.1–0.2 mg/kg (Standard Sea Water composition, 2023). Sr^{2+} concentration, instead, remains close to seawater typical values, due to the precipitation of celestite (SrSO_4) along the evaporation basins in saltworks (Vicari et al., 2022), which prevent its accumulation in the bittern.

Finally, despite the high interest in terms of value and criticality, the remaining detected elements such as Co(II), Ga^{3+} , Cs^+ and Ge(IV) have been found only in traces (0.2–50 $\mu\text{g}/\text{kg}$).

Fig. 2 presents the results according to the different ranges of concentrations (from grams per kg, in Fig. 2a, to mg/kg, in Fig. 2b, to grams per kg, in Fig. 2c) by grouping the bitterns on the basis of the type of feed, e.g. sea, salt lake, ocean, river and subsoil (see Table 1).

It is worth noting that bitterns collected from sea-fed saltworks contain the highest values of Mg^{2+} and K^+ , whereas those from the salt-lakes show the lowest concentrations (see Fig. 2a). Moreover, among the anions, Cl^- and SO_4^{2-} concentration seems not to be affected by the type of feed, while Br^- is higher in bitterns derived from seawater. On the contrary, bitterns produced from salt-lakes show the highest

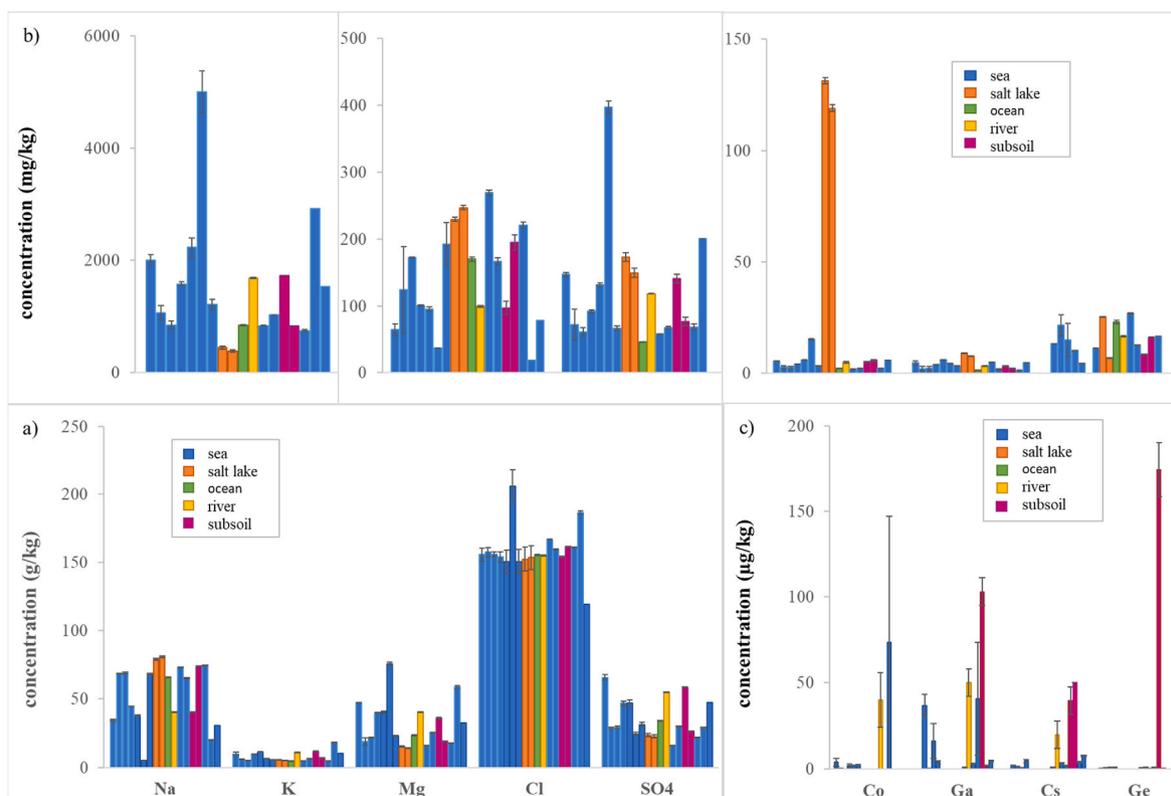


Fig. 2. Concentration of major (a), minor (b) and trace (c) elements detected in the bitterns classified according to the saltworks feed type. Standard deviations are reported in the form of error bars.

concentrations of Li^+ and Rb^+ , of 130 and 9 mg/kg, respectively, and they are very rich also of the other minor elements, such as Ca^{2+} , B(III) and Sr^{2+} (see Fig. 2b). In the other hand, the sample from saltworks fed by ocean water shows the lowest value of B(III) concentration.

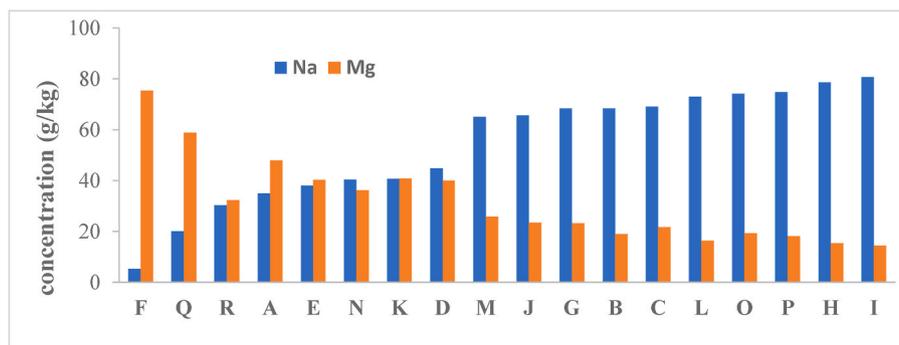
For what concerns the trace elements, although in some cases it was not easy to precisely determine the concentrations, the highest concentrations of Ga^{3+} , Cs^+ and Ge(IV) were found in the bittern from sites N and O, coming from the subsoil, with values of 170, 100 and 50 $\mu\text{g}/\text{kg}$, respectively.

The bittern from site K, fed by river water, shows quite high concentrations of Co(II), Ga(III) and Cs^+ with a concentration of 40, 50 and 20 $\mu\text{g}/\text{kg}$, respectively. Finally, most of the other samples from seawater show a concentration much lower than these already mentioned, especially in Ge(IV) cases where values from 0.2 to 0.9 $\mu\text{g}/\text{kg}$ are detected (see Fig. 2c).

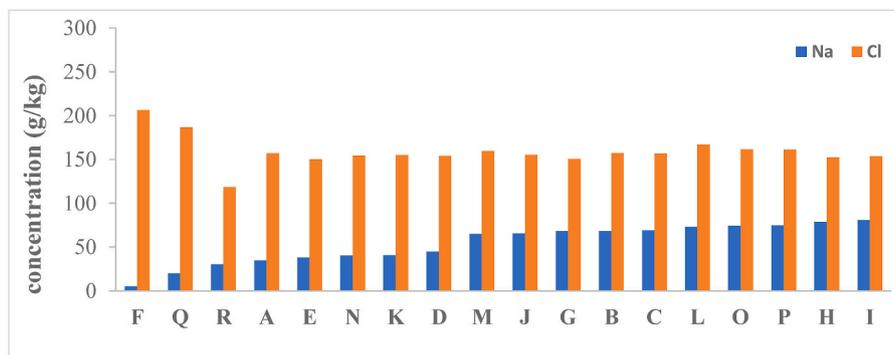
An interesting correlation between Na^+ and Mg^{2+} concentrations can be observed, as shown in Fig. 3a, indicating how the lower the Mg^{2+}

concentration the higher the Na^+ one. This fact can be ascribed to the different degrees of concentration of seawater, at which samples have been withdrawn from the sites. If Na^+ concentration is high, it means that the final evaporation stage was not achieved yet and, thus, there are still room for further concentrating Mg^{2+} . On the contrary, low Na^+ concentration likely indicates that a large amount of NaCl was recovered from the bittern by intensive evaporation of seawater and, thus, Mg^{2+} results in a much higher concentration.

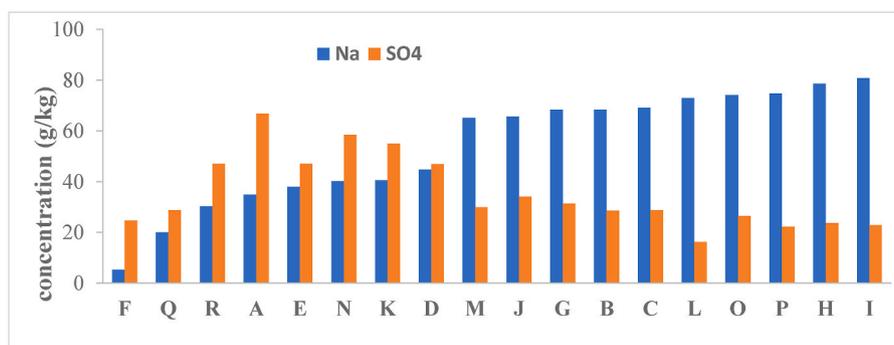
Focusing now on correlations between Na and the main anions, Fig. 3b and c presents the concentration trend of Na^+ compared to SO_4^{2-} and Cl^- , respectively. Although less directly correlated than in the $\text{Na}^+/\text{Mg}^{2+}$ case, Fig. 3b shows that at higher Na^+ concentration somehow lower sulfates concentration was detected. Looking at the trend for Cl^- ions, a fairly stable concentration was detected for most samples, independent from Na^+ increasing trend. An exception is observed for sites F and Q, where the lowest Na^+ concentration corresponds to the highest Cl^- one. In fact, in these sites the bitterns derive from Mg-enriched



(a)



(b)



(c)

Fig. 3. Comparison of trends of Na^+ concentration with Mg^{2+} (a), SO_4^{2-} (b) and Cl^- (c) concentration in all bitterns, ordered by increasing Na^+ concentration.

liquors, in which Cl^- ions, being conjugated with Mg^{2+} , reach a concentration up to 40 times that of Na^+ .

One last analysis of results has been performed focusing on the bittern density, probably the most relevant parameter adopted for the monitoring and control of the operation of traditional saltworks (Nayak and Panda, 2014; Vicari et al., 2022). In particular, results have been grouped per density ranges, leading to some interesting observations.

In Fig. 4, the concentration of all the elements detected in this work are reported for all samples analyzed. For each element the values are ordered according to the increasing values of sample density, starting from sample L (1.22 kg/L) to sample F (1.30 kg/L) (also see Table 2 and the inset of Fig. 4, where density values are reported as a function of the sites). Among the main and minor elements, Na^+ and Ca^{2+} concentration decreases as the density increases, with a trend which is more pronounced starting from densities above of 1.23 kg/L. On the contrary, the concentration of K^+ and Mg^{2+} (the two main cations competing with Na^+) increases, as well as for Br^- . For what concerns Cl^- ions, concentration is quite constant, but for the highest densities (1.27 and 1.30 kg/L) where it reaches values 20% higher. In analogy with the relation observed with Na^+ ions concentration, sulfates concentration increases at first as the density increases and then, starting from a value of 1.27 kg/L, it decreases. On the other hand, no clear trend is observed for the minor elements at lower concentrations, such a Li, Rb⁺ and Sr²⁺, neither for trace elements (not reported in Fig. 4).

3.2. Bitterns as potential source of strategic and critical raw materials

With reference to the list of elements of interest considered in the SEArCularMINE project (SEArCularMINE, 2021), the relevant minerals and compounds potentially producible from the treatment of bitterns are presented in Table 4.

Of course, the economic gain obtained by extracting minerals is proportional to both their market price and the obtainable amount (Sharkh et al., 2022b). Limiting our analyses to the sea-saltworks and their average concentration reported in the previous paragraphs (see Fig. 4, “sea” bars), the values for unit volume of bittern (1 m³) can be calculated, as reported in Fig. 5. It has to be clarified that the values reported in Fig. 5 refer to an ideal scenario in which the recovery of the ions in solution is 100% and the possible competition and mutual exclusion between the different minerals is resolved by distributing the ions in the different species according to their relative amount (e.g. sodium, is assumed to be extracted as chloride or sulfate in proportionally to the amount of the respective anions).

Roughly, if this competition is taken into account skipping sodium sulfate contribution, every cubic meter of average bittern contains about 190 € of valuable minerals. Thus, given the very high concentration of magnesium in the bittern, the most of this value might be given by the production of magnesium hydroxide.

On the other hand, even if found at a relatively low concentration,

Table 4

Minerals and compounds that can be extracted from saltworks bitterns and their value according to the Commodity Summary of United States geological survey 2022 (U.S. Geological Survey, 2022). Euro/dollar exchange 1.04 as for November 25, 2022.

Mineral	Specific value [€/kg]
NaCl(s)	0.23
Na ₂ SO ₄ (s)	0.17 ^a
KCl(s)	0.36
K ₂ SO ₄ (s)	0.55
Mg(OH) ₂	1.01 ^b
MgSO ₄ (s)	0.34 ^b
Br ₂ (g)	2.77
B ₂ O ₃ (s)	0.41
Li ₂ CO ₃ (s)	17.68
RbCl (s)	6520.80
SrSO ₄ (s)	93.60
Co(s)	50.44
GaAs/GaN (Ga pricing)	592.80
CsCl(s)	2329.60
Ge(s)	1248.00
HCl	0.07 ^b

^a Quotation from <https://www.chemanalyst.com/Pricing-data/sodium-sulfate-1480> (accessed the November 25, 2022).

^b Intra European trade value 2021 from Eurostat customs database using Harmonized System code 28.16.10, 28.33.21 and 28.06.10.

rubidium is an extremely valuable element with an attractive market price of about 6 k€ per kg of elemental rubidium (see Table 3). In fact (U.S. Geological Survey, 2020), in recent years the cost of this element has experienced and astonishing growth due to its application in quantum computing devices (Wang et al., 2021) whose potentially enormous market is still evolving. Other minerals such as gallium, germanium and cesium have similar quotations (see Table 3), but their concentration in bittern is so small that their value for unit volume of treated solution becomes negligible when compared to the others (see Fig. 5b).

However, considering that: i) the combined European and North African production of table salt is about 53 Mtons/year (Idoine et al., 2022), ii) Solar salt represents 10% of the salt produced in Europe (Eusalt, 2023), and iii) for every ton of salt produced by evaporation 1.7 m³ of bittern can be extracted (Basseggio, 1974), a total bittern production capacity of about 9 Mm³ per year can be calculated for the Mediterranean area. When combined with the average composition exposed above, the predictions for the Euro-Mediterranean production potential with respect to the SEArCularMINE targeted minor minerals and trace elements are reported in Table 5.

The corresponding values might appear as negligible amounts but they should be compared to the total global market figures. As an example, lithium production is estimated to be between 82 and 85 ktons/year (elemental lithium basis) (U.S. Geological Survey, 2022), a production of about 210 tons/year (corresponding to 1.12 ktons/years

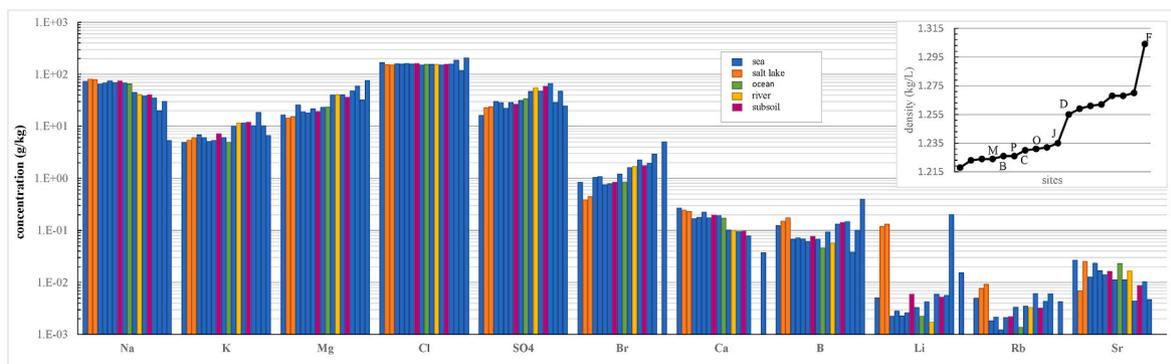
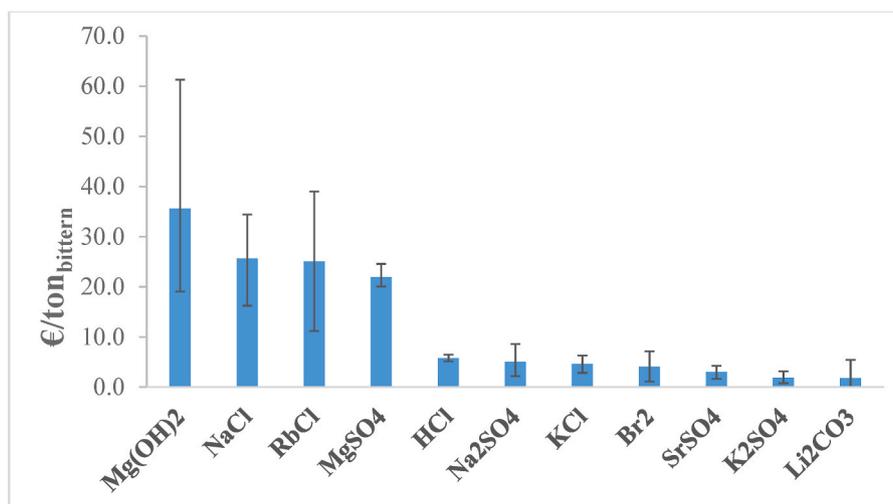
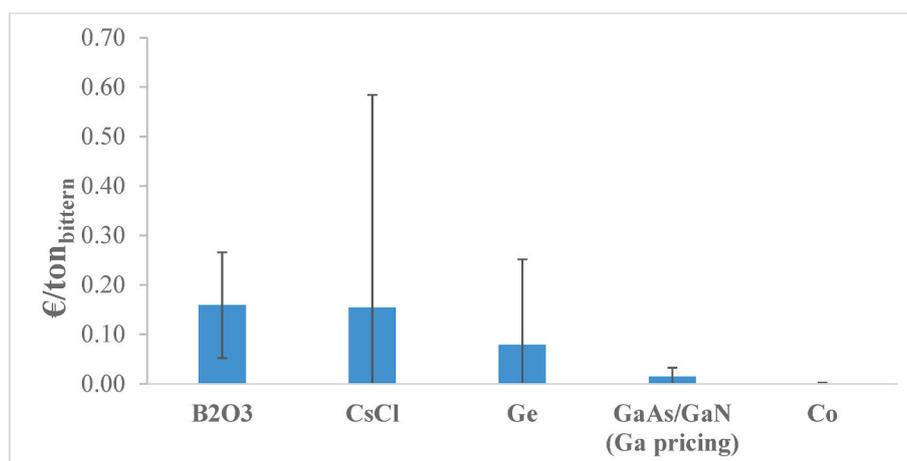


Fig. 4. Concentration of each element detected in the collected samples ordered according to the increasing values of sample density, starting from sample L (1.22 kg/L) until sample F (1.30 kg/L) (the inset reports density values measured for all sites).



(a)



(b)

Fig. 5. Minerals value in bittern according to the prices reported in Table 4 and the average composition of traditional seawater saltworks at major and minor minerals (a) and trace elements (b) along with standard deviation.

Table 5

Euro-Mediterranean potential related to minor minerals and trace elements annual production capacity from bitterns, calculated on the base of average composition of traditional seawater saltworks bitterns, European table salt production and a ratio of 10% between sea-salt and total salt.

Mineral	Production (tons/year)
B ₂ O ₃	4441
Li ₂ CO ₃	1116
SrSO ₄	354
RbCl	61
Co	0.25
Ga	0.28
Cs	0.96
Ge	0.70

of lithium carbonate, see Table 4) represents 0.3% of the total world production capacity and exceeds the entire Bolivian production for 2020 (Idoine et al., 2022).

Given the electrification pathway of the European Green Deal, the long-term wellness and stability of the Union is greatly dependent on

storage materials. For this reason, lithium was recently introduced in the EU list of Critical Raw Materials (European Commission, 2020).

Even cobalt, gallium and germanium belong to the list of CRMs for their use in enabling technologies which determines the competitiveness of the Union. Gallium is used to manufacture integrated circuits, lighting and CIGS solar cells (European Commission, 2020), more specifically it is essential for the construction of telecommunications devices for smartphones and military applications but also to manufacture Light Emitting Diodes, two markets that have pushed gallium annual demand growth over 17 % in 2019 (U.S. Geological Survey, 2020). Regardless of its strategic importance, a relatively small amount of gallium is consumed and produced annually in the world. Nowadays, about 300 tons are produced annually, mainly in China, followed by Russia (5 tons/year), Japan (3 tons/year) and Korea (2 tons/year) (U.S. Geological Survey, 2020). By comparing this information to the one reported in Table 4, gallium extraction from bittern in the Mediterranean area could represent 0.1 % of the global production of such element.

A larger contribution of about 0.5 % can be estimated for the case of germanium, where the total global production is around 140 tons/year, being produced 95 tons/year by China (U.S. Geological Survey, 2022). Germanium metal is a fundamental substrate for the construction of new generation multijunction photovoltaics capable of reaching

extraordinary energy conversion efficiency of more than 40 % (Guter et al., 2009), having lightweight and flexible structure such as the Roll-Out Solar Array (ROSA) already installed in the International Space Station (Spence et al., 2018). The adoption of this technology for space applications allows to foresee a relative short time for consumer version market possibly leading to an extraordinary increase in prices (over 21% in the first ten months of 2021) and trades (+24% exports from China) (U.S. Geological Survey, 2022).

Mutatis mutandi, similar considerations could be given for each element targeted by the SEArcularMINE project and the reader has already acquired the tool to provide this kind of calculation.

However, it is worth clarifying that a solution to the CRM issue goes well beyond the purpose of the present work and that rare elements extraction from bitterns alone cannot result in European independence from imports, but it can be regarded as a fundamental part of a complex answer to a complex problem.

4. Conclusions

Minerals extraction from bitterns, produced as a by-product of saltworks, can reduce Europe's dependency on imported Critical Raw Materials. The SEArcularMINE project analyzed 18 samples of bitterns from various Mediterranean regions, collected from saltworks that used different feed sources (sea, river, ocean, salt-lake, subsoil), process operations (natural evaporation and vacuum crystallization) and structures (single pond, traditional fractionated ponds, and even ultra-fractionated ponds).

Various analytical techniques (IC, ICP-OES, ICP-MS, F-AES and F-AAS) were used to determine physical-chemical parameters and ions concentrations. Different analytical techniques have been adopted depending on the nature and concentration of each element, requiring an initial elevate effort for a previous selection of the most suitable one.

Thanks to this variegated samples collection, it was possible to lay the foundations for the creation of a continent-wide brine library. The results showed that each type of feed source produced bitterns with unique characteristics. As an example, bitterns from the saltworks using salt-lakes' water had the highest concentrations of Li and Rb (130 and 9 mg/kg, respectively) and the lowest of Mg and K. On the contrary, seawater inlet leads to the highest concentration of Mg in the bittern (up to 60 g/kg), whereas the lowest value of B was detected in the sample produced using ocean as feed. Concerning the trace elements, higher concentration values, between 50 and 170 µg/kg, were observed when subsoil water was used as a feed to saltworks.

Finally, the economic potential of saltworks as source of valuable minerals was considered and a potential gain of about 190 € per m³ of produced bittern might be expected, considering an estimation of bittern production capacity of about 9 Mm³ per year for the Mediterranean area. Therefore, the use of residual brines from traditional saltworks could represent a promising solution to secure the access to some Critical Raw Materials for EU.

CRedit authorship contribution statement

S. Randazzo: Data curation, Methodology, Visualization, Writing – original draft. **F. Vicari:** Data curation, Formal analysis, Methodology, Software, Visualization, Writing – original draft. **J. López:** Data curation, Formal analysis, Investigation, Methodology, Software, Writing – original draft. **M. Salem:** Data curation. **R. Lo Brutto:** Data curation. **S. Azzouz:** Investigation. **S. Chamam:** Investigation. **S. Cataldo:** Investigation. **N. Muratore:** Investigation, Writing – review & editing. **M. Fernández de Labastida:** Data curation, Investigation, Methodology. **V. Vallès:** Investigation, Methodology. **A. Pettignano:** Methodology, Writing – review & editing. **G. D'Alì Staiti:** Resources, Validation. **S. Pawlowski:** Writing – review & editing. **A. Hannachi:** Writing – review & editing. **J.L. Cortina:** Methodology, Supervision, Visualization, Writing – review & editing, Validation. **A. Cipollina:** Methodology,

Project administration, Supervision, Validation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be available in Zenodo (<https://zenodo.org/communities/searcularmine-project/>)

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2023.140412>.

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