

# Hydrogeochemical Characteristics of Subsurface and Overland Runoff Indicating Seawater Intrusion into Deep Coastal Aquifers

Lalita Zakharikhina<sup>1,\*</sup>, Sergey Zakharikhin<sup>1</sup>, Polina Lesnikova<sup>1</sup>, Olga Bykhalova<sup>2</sup>

<sup>1</sup>Federal Research Centre the Subtropical Scientific Center of the Russian Academy of Sciences, Russian Federation

<sup>2</sup>Federal State Budgetary Organization, State Nature Reserve, Russian Federation

Received April 10, 2023; Revised July 2, 2023; Accepted August 15, 2023

## Cite This Paper in the Following Citation Styles

(a): [1] Lalita Zakharikhina, Sergey Zakharikhin, Polina Lesnikova, Olga Bykhalova, "Hydrogeochemical Characteristics of Subsurface and Overland Runoff Indicating Seawater Intrusion into Deep Coastal Aquifers," *Environment and Ecology Research*, Vol. 11, No. 6, pp. 979 - 992, 2023. DOI: 10.13189/eer.2023.110609.

(b): Lalita Zakharikhina, Sergey Zakharikhin, Polina Lesnikova, Olga Bykhalova (2023). *Hydrogeochemical Characteristics of Subsurface and Overland Runoff Indicating Seawater Intrusion into Deep Coastal Aquifers*. *Environment and Ecology Research*, 11(6), 979 - 992. DOI: 10.13189/eer.2023.110609.

Copyright©2023 by authors, all rights reserved. Authors agree that this article remains permanently open access under the terms of the Creative Commons Attribution License 4.0 International License

**Abstract** Seawater intrusion (SI) into deep freshwater aquifers is a serious problem in coastal areas around the globe that has been exacerbated in recent decades by climate change and rising sea levels. Pumping and seawater upcoming can intensify the mixing of groundwater and seawater within the aquifer to the point where fresh groundwater becomes unfit for drinking. Here, based on the study of subsurface and overland runoff (seepage, springs, and streams) conducted in the pristine Utrish Nature Reserve on the Russian Black Sea coast, several geochemical characteristics of the runoff indicating the occurrence of SI have been identified for the first time. We have termed the diffusion of highly diluted seawater from the seawater-freshwater mixing zone into deep aquifers and subsequently into subsurface and overland runoff the secondary contamination (SC) of subsurface and overland runoff. The identified characteristics are: positive correlation of excess trace elements with Cl and SO<sub>4</sub> anions predominant in seawater, consistently higher Br content (marine factor) in spring water compared to stream water, and, conversely, lower concentrations of Al, Cr, Zn, Cs, and all rare earth elements (REEs) (terrestrial factor). Furthermore, overland and subsurface runoff exhibited anomalous REE fractionation relative to rocks, channel sediments, and soils. The occurrence of europium (Eu/Eu\* = 3.96 in spring water and Eu/Eu\* = 1.44 in stream water) was a positive anomaly attributed to changes in redox

potential at the geochemical barrier at the seawater-freshwater interface. The impact of SI on stream water and springs fed by perched aquifers was linked to the topography of the area characterized by low hypsometry. The geochemical indicators described in this study will help establish the occurrence and magnitude of SI in groundwater aquifers in coastal areas without resorting to suboptimal sampling methods, such as drilling, which can damage aquifers. Furthermore, these indicators can serve as reference benchmarks for monitoring SI intensity in heavily used coastal aquifers to control pumping rates and reduce contamination by seawater due to upcoming and mixing for enhanced coastal water security.

**Keywords** Hydrogeochemical Parameters, Overland and Subsurface Runoff, Seawater Intrusion

---

## 1. Introduction

The incursion of a wedge of seawater far into confined and unconfined freshwater aquifers was first shown in European studies of coastal hydrogeology in the early 20th century [1]. There is now a large body of literature dedicated to this phenomenon, which has been described in many other regions [2-4].

Population growth in coastal areas has exacerbated the incidence of seawater intrusion (SI) due to more intense groundwater pumping, which results in lower water quality, limited groundwater withdrawal for industrial and agricultural uses, and deteriorating living standards [5]. Groundwater quality problems due to SI have been reported in coastal areas in California, the Cape Verde Islands, the US Gulf Coast, Italy, Israel, etc. [6].

The severity of SI is controlled by such factors as coastal morphology, land use patterns [7], and geological conditions, including aquifer lithology [8], which determines the hydraulic gradient (hydraulic pressure) in a coastal aquifer.

Simulations show that in low-gradient coastal landscapes susceptible to inundation, the freshwater-seawater interface migrates inland [9, 10]. Tidal motion has a direct effect on the freshwater-seawater mixing zone and inland displacement of the freshwater-seawater interface causes seawater to flow into pumping wells at high tide [11].

Climate change and rising sea levels are important factors exacerbating SI in coastal areas [12, 13]. Higher atmospheric temperatures due to global warming accelerate glacial melting, thereby supplying more water to the oceans and causing sea levels to rise. Rising sea levels increase seawater pressure at the continental margin, causing the freshwater-seawater mixing zone to migrate inland [1].

Overexploitation of groundwater resources is the most important anthropogenic factor that has an impact on coastal hydrology and SI. Excessive groundwater withdrawal has been found to intensify SI in Africa [14], Australia [15], China [16], Europe [17], India [18], America [19], Vietnam [20], etc.

Research of SI is based on the study of borehole hydraulic properties, hydrogeological cross-sectional modelling, laboratory analysis of groundwater chemistry, and shallow electrical sounding techniques (vertical electrical sounding, electrical tomography, and symmetric electrical profiling) [21]. Chemical methods that consider chloride and bicarbonate ratios have also been used to determine the spatial distribution, intensity, and controlling factors of SI [22].

The studies of SI also focus on establishing the spatial distribution of physicochemical properties of rocks and water, such as electrical conductivity, salinity, water type, total dissolved salts, and seawater mixing dynamics [23]. Both direct and indirect methods are used, such as physicochemical analysis of water samples (direct method) and interpretation of hydrologic properties based on measurements of volumetric conductivity and resistivity of aquifer materials (indirect method). The most typical direct methods of SI investigation are water table measurements and groundwater chemistry analyses [1].

Practical measures to halt the deterioration of SI conditions, such as brackish water pumping and aquifer recharge, have been discussed [24]. However, it has been

pointed out that in order to develop adequate and effective control and management methods, it is essential to fully understand the phenomenon of SI with all its inherent risks [25].

Although SI is a very complex issue with many potential lines of research, one area that has not been sufficiently elucidated is the effect of SI on the geochemistry of subsurface (seepage, springs) and overland (rivers) runoff.

When a deep aquifer is sandwiched between two dense bedrock formations, pressure can cause water to rise through natural fractures and pores [26]. If exposed to SI, such aquifers can, under certain conditions, become conduits of seawater into overland and subsurface runoff in a process that we refer to as secondary contamination (SC). The diffusion of SC from unconfined aquifers into overland and subsurface runoff may also proceed via perched aquifers under certain geomorphological conditions [26].

The potential SC of spring and river waters in susceptible coastal areas makes it imperative to study and monitor the elemental composition of subsurface and overland runoff.

Recent hydrogeological data from the Utrish Nature Reserve (Abrau Peninsula, the Black Sea coast of Russia) indicate that the area may be vulnerable to SI [21] and that there may be a risk of SC due to the local bedrock composition (fractured marl, limestone, and sandstone). For SI researchers, this pristine area is of particular interest because of the complete absence of anthropogenic pressures.

The study of SC is complicated by the fact that marine elements are greatly diluted during transport from the mixing zone and therefore occur in the subsurface and overland runoff at very low concentrations. Therefore, it is important to examine runoff chemistry for a large number of elements and determine not only absolute concentrations but also relative geochemical parameters, e.g., the ratios of elements of marine and terrestrial origin.

The aim of this study was, therefore, to establish hydrogeochemical indicators of SI in the subsurface and overland runoff in areas where deep aquifers are known to be affected by SI, and to investigate the elemental composition of runoff for a wide range of elements, including rare and dispersed species, to ascertain the occurrence of SI and explore the chemistry of SC.

## 2. Materials and Methods

### 2.1. Study Area

The topography of the study area in the Utrish Nature Reserve is characterized by a number of small uplands (up to 300-400 m above sea level) with steep slopes (between 20 and 35 degrees). They are divided by two narrow gorges called the Vodopadnaya Ravine and the Bazovaya Ravine (Figure 1); the Vodopadnaya Ravine has a year-round stream and the Bazovaya Ravine has a year-round spring

and a seasonal stream that flows only during spring flooding (they are filtered through beach sediments as they enter the sea). Due to the steep slopes of the study site, the soil cover is thin and stony. The diluvial gravel in the soil consists of fine-grained (2-5 mm) and some coarse-grained (5-10 mm) angular aggregates, often of surficial deposition. The sedimentary rock origin determines the lamellar structure of the lithic inclusions.

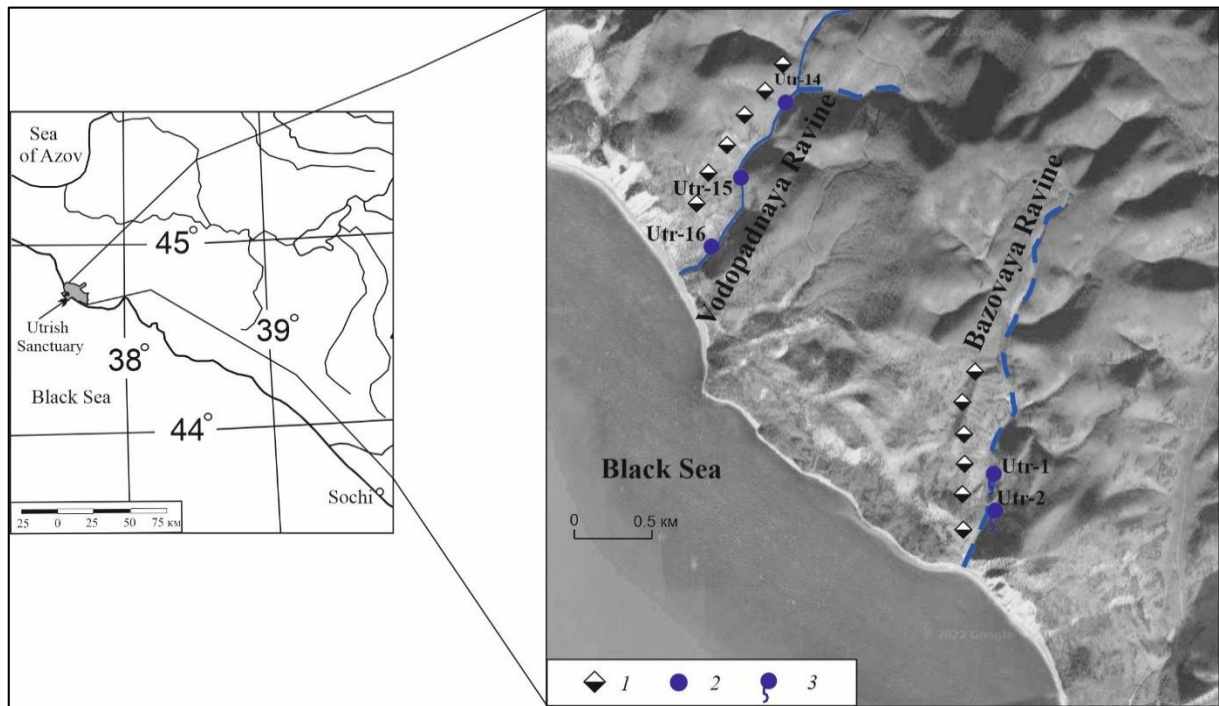
The bedrock consists of marl, siltstone, limestone, dolomite, clay, and sandstone of the Paleocene age (the Cretaceous age in the Vodopadnaya Ravine). There are Hg, Pb, and Cu mineralization zones to the northwest of the study area [27].

The climate is sub-Mediterranean, characterized by high mean annual temperatures. Mean annual precipitation ranges from 600-700 mm, most of which falls between November and March. Natural waters are formed under alternating wet, warm (winter, fall) and dry, hot (summer, spring) conditions, with a humidification coefficient of 0.50-0.85 [28]. Pistachio, hornbeam, oak, and juniper forests growing on brown soils are predominant in the study area. According to the Russian Soil Classification,

these are post-lithogenic, metamorphic, and typically brown soils [29], or Cambizol Fradic, according to the World Soil Resource Base [30].

To characterize the geochemical properties of overland runoff, water samples were collected at three sites along the Vodopadnaya Ravine stream from the headwaters to its mouth. Spring water was sampled from two springs in the Bazovaya Ravine (Fig. 1). Field work was performed between May and June 2022. Stream water sampling was conducted at a time when the stream was fed by both rainfall and groundwater seepage, within one day, at least 7 days after the last rainfall. Water samples were collected in sterile polystyrene tubes.

To determine the geologic factors that may influence water chemistry, samples of rock, channel sediment, and soil were also collected. Soils and rocks were sampled within the catchments of the two ravines. Channel sediments were collected at the stream water sampling sites from the fresh, fine-grained sediments, which were dried, sieved through a 1-mm sieve, and shipped for analysis (Figure 1).



**Figure 1.** Schematic map of sampling areas in the Utrish Nature Reserve. 1 – soil and rock sampling sites; 2 – river and channel sediment sampling sites; 3 – spring water and channel sediment sampling sites.

## 2.2. Sampling and Analysis

The cation-anion balance of macro-elements in water was determined by measuring the following parameters:

- hydrogen ion – by potentiometric method;
- dry residue – by gravimetric method;
- chlorine ion – by titration with silver nitrate solution in the presence of potassium chromate;
- sulfate ion – by specific turbidimetry with barium chloride;
- hydrogen carbonate ion – by titration with hydrochloric acid solution and methyl orange indicator;
- calcium and magnesium ions – by EDTA titrations.

Quantitative chemical analyses of waters, channel sediments, and soils were performed by mass spectrometry and inductively coupled plasma atomic emission spectroscopy (ICP-MS and ICP-AES): waters were analyzed for 60 chemical elements and channel sediments and soils for 71 elements. The margin of error between these methods and the measurement of chemical elements using external standards was  $\leq 6\%$  [31]. Limits of detection for these methods were: in water - up to nanogram per liter (ng/L) for microelements (REEs, U, Th, etc.) and below microgram per liter ( $\mu\text{g/L}$ ) for predominant elements; in channel sediments - hundredths of micrograms per gram ( $\mu\text{g/g}$ ) for microelements and hundredths of a % for macro-elements.

The assays were performed at the N.M. Fedorov Institute of Mineral Resources, Moscow, on an Elan-6100 mass spectrometer (Perkin Elmer, USA) and an Optima-4300 DV atomic emission spectrometer (Perkin Elmer, USA).

Element concentrations in rocks, sediments, and soils were determined according to a certified methodology (SCAM No. 499-AES/MS, 2015). Samples were digested with four acids: HF, HNO<sub>3</sub>, HCl, and HClO<sub>4</sub>. The decomposition stage of each sample was monitored using stable high-concentration isotopes (<sup>145</sup>Nd, <sup>161</sup>Dy, and <sup>174</sup>Yb).

The analytical method based on ICP-MS and ICP-AES consisted of three steps.

1. ICP-MS quantification of Li, B, Na, Mg, Al, P, S, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Sr, and Ba. This method can easily quantify many problematic elements (S, K, Ca, Fe).

2. MS-ISP quantification of Li, Be, B, Al, P, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Mo, Nb, Rh, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, REE, Hf, Ta, W, Re, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th, and U.

3. Comparison of results obtained by two independent methods. At this step, accuracy control between analytical methods for each sample was performed for elements such as Li, B, Al, P, Mn, Cu, Zn, Sr, and Ba, and corrections for matrix effects was made as needed.

The content of elements in aqueous solutions and extracts was determined by quantitative analysis using standard solutions. Certified Reference Material Trace Metals in Drinking Water (CRM TMDW) was used for water; Basalt, Hawaiian Volcanic Observatory BHVO-2 (US Geological Survey) for soils; and Trapp ST-2a (GSO 8671-2005) for sediments and rocks. Mass spectra were processed and elemental contents were calculated using mass spectrometer software.

Element concentrations ( $C_i$ ) in waters, rocks, and soils relative to their clarke numbers ( $C$ ) in river water [32], soil [33] and rocks [34] at all sampling points were computed using the formula  $C_c = C_i/C$  (where  $C_c$  is the clarke concentration). In this paper, we considered the entire range of values  $1 > C_c > 1$ , where  $C_c > 1$  indicates excess chemical elements and  $C_c < 1$  indicates deficient elements. Geochemical formulas for the studied waters were constructed by ranking and grouping chemical elements according to the  $C_c$  values.

Rare earth concentrations normalized to the North American Shale Composite (NASC) [35] were used to evaluate their department in the studied waters, rocks, channel sediments, and soils. The Eu anomaly was calculated by the formula  $E_{\text{an}} = E_{\text{un}} / (S_{\text{mn}} \cdot G_{\text{dn}})^{1/2}$ .

## 2.3. Statistical Analysis

The resulting data set consisted of the chemical composition of water, rock, channel sediment, and soil samples. Significant differences in the concentrations of chemical elements were tested using Student's test at  $p < 0.05$ . Statistical description and data analysis were made using the Microsoft Office 2010 software package (Microsoft, Inc., USA). Confidence intervals and least significant differences (LSD) were calculated and are given in Table 1.

**Table 1.** Average contents of elements in the river water of the continents (K) according to [36] and in the waters of the Utrish Reserve, mg/l.

Elements	Limits of detection (LOD)	K	Survey sites					LSD (p ≤ 0.05)
			Spring water		River water			
			Utr-1	Utr-2	Utr-14	Utr-15	Utr-16	
B	0.0009	0.02	0.056	0.054	0.054	0.055	0.061	0.0029
Na	0.0100	5	22.26	22.86	19.77	19.09	21.27	1.6022
Mg	0.0050	2.9	10.59	10.79	11.36	13.17	14.67	1.7530
Al	0.0008	0.16	0.02	0.02	0.01	0.02	0.09	0.0327
Si	0.0168	6	5.03	4.53	5.67	5.54	5.44	0.4645
S	0.0136	3.8	23.71	23.17	16.38	21.66	25.62	3.5014
K	0.0100	2	1.89	1.92	1.73	1.69	1.82	0.0992
Ca	0.0100	12	135.17	131.40	117.64	125.07	130.33	6.7875
V	0.0001	0.001	0.0004	0.00050	0.0005	0.0003	0.0002	0.0001
Cr	0.0008	0.001	0.0008	0.0008	0.0008	0.0013	0.0008	0.0002
Mn	0.0001	0.01	0.0001	0.00064	0.0029	0.0024	0.0020	0.0012
Zn	0.0005	0.02	0.0005	0.00053	0.0011	0.0007	0.0018	0.0005
Se	0.0005	0.0002	0.0050	0.00489	0.0033	0.0052	0.0066	0.0012
Br	0.0200	0.02	0.2376	0.23979	0.1995	0.1938	0.1980	0.0229
Sr	0.0001	0.05	0.6604	0.64168	0.7474	0.7741	0.8595	0.0887
Ba	0.0001	0.03	0.0455	0.04382	0.0460	0.0408	0.0404	0.0026
Pb	0.00002	0.001	0.00002	0.00002	0.00002	0.00002	0.00004	0.0000
Li	0.000006	0.0025	0.009976	0.010500	0.014509	0.015657	0.020130	0.0042
Rb	0.000020	0.002	0.000370	0.000401	0.000415	0.000362	0.000426	0.000028
Mo	0.000020	0.001	0.000268	0.000278	0.000241	0.000223	0.000315	0.000035
Sn	0.000020	0.00004	0.000020	0.000020	0.000040	0.000020	0.000040	0.000011
Sb	0.000007	0.001	0.000021	0.000020	0.000014	0.000016	0.000014	0.000003
Cs	0.000001	0.00003	0.000010	0.000010	0.000019	0.000018	0.000020	0.000005
La	0.000002	0.00005	0.000058	0.000069	0.000136	0.000187	0.000146	0.000005
Ce	0.000002	0.00008	0.000064	0.000129	0.0000514	0.0000618	0.0000502	0.000025
Pr	0.000001	0.000007	0.000013	0.000021	0.000045	0.000075	0.000056	0.000003
Nd	0.000002	0.00004	0.000038	0.000075	0.000219	0.000275	0.000219	0.000010
Sm	0.000001	0.000008	0.000010	0.000011	0.000043	0.000042	0.000043	0.000002
Eu	0.000001	0.000001	0.000010	0.000010	0.000012	0.000018	0.000010	0.000000
Gd	0.000001	0.000008	0.000014	0.000012	0.000031	0.000043	0.000038	0.000001
Dy	0.000001	0.000005	0.000010	0.000015	0.000026	0.000036	0.000036	0.000001
Er	0.000001	0.000004	0.000010	0.000010	0.000011	0.000017	0.000017	0.000004
Yb	0.000001	0.000004	0.000010	0.000010	0.000010	0.000013	0.000010	0.0000001
Re	0.000001	–	0.0000081	0.0000097	0.0000115	0.0000151	0.0000178	0.0000040
Tl	0.000001	0.001	0.000010	0.000010	0.000017	0.000016	0.000017	0.000004
Th	0.000001	0.0001	0.000010	0.000010	0.000020	0.000022	0.000016	0.000001
U	0.000001	0.0005	0.000510	0.000569	0.000683	0.000644	0.000651	0.0001

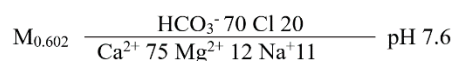
### 3. Results and Discussion

#### 3.1. Composition of Major Cations and Anions in Water

**Table 2.** Macro-element composition of river and spring waters in the Utrish Nature Reserve

Number of sampling points	Statistical characteristics	pH	Content, mg/L						
			Mtotal, mg/L	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>
<b>River water</b>									
6	Maximum	7.90	512	21.27	130.33	14.67	60.3	39.4	375.0
	Minimum	7.38	448	19.09	117.64	11.36	57.8	32.5	342.0
	Mean	7.64 ± 0.26	488 ± 35	10.04 ± 1.11	124.35 ± 6.37	13.07 ± 1.66	59.0 ± 1.26	34.9 ± 3.87	355 ± 17.59
	Equivalent %				11	76	13	21	9
<b>Spring water</b>									
4	Maximum	7.52	612	23.14	137.51	12.52	65.82	34.12	370.12
	Minimum	7.26	532	21.21	132.80	9.93	61.45	30.12	350.34
	Mean	7.34 ± 0.21	542 ± 29	22.26 ± 2.51	135.17 ± 7.2	10.56 ± 0.97	64.5 ± 1.78	31.9 ± 3.98	361.0 ± 16.4
	Equivalent %				12	78	10	22	8

The composition of major ions in the subsurface and overland runoff in the Utrish Nature Reserve is similar (Table 2). In general, the water can be characterized by the following chemical equation, where the corresponding percentages are indicated next to the ions, water salinity (g/L) is on the left, and pH is on the right.



The water is fresh, with salinity ranging from 0.448 to 0.504 g/L in stream water and 0.532 to 0.612 g/L in spring water. The pH is slightly alkaline and varies between 7.26 and 7.90. Major anions include chloride and hydrogen carbonate. Cations include calcium, magnesium, and sodium.

By comparison, the rivers of the nearby Mzymta and Sochi valleys in the Sochi area of the Black Sea coast have hydrocarbonate-sulfate calcium-magnesium composition [36, 37]. However, the only difference between them and the study site is that they are characterized by higher elevation above sea level. The characteristic differences in water chemistry between the study site and areas at higher elevations are: 1) the replacement of sulfate ions by chloride, 2) the presence of sodium in addition to the typical freshwater cations calcium and magnesium, and 3) a mineralization rate that is about five times higher. The predominance of chloride and sodium ions suggests a connection between the coastal aquifers with the sea.

The mixing of overland runoff with seawater in coastal areas due to tidal processes has been well studied [38, 39]. Seawater intrusion into coastal wetlands at the land-sea interface has also been thoroughly described [40-42].

Overland runoff in the study area (Abrau Peninsula) has no surface discharge into the sea but is entirely subsurface

at the mouths of streams, and filtered into the sea through coastal sediments. Therefore, the chemical characteristics of the runoff that indicate the connection to the sea are likely related to SI into deep coastal aquifers that feed the runoff.

Recent hydrogeological studies indicate that coastal areas near the Sukko village in the vicinity of the Reserve are vulnerable to SI [21]. In fact, SI is typical of deep groundwater aquifers along most of the Black Sea coast from Anapa to Sochi (Figure 2).

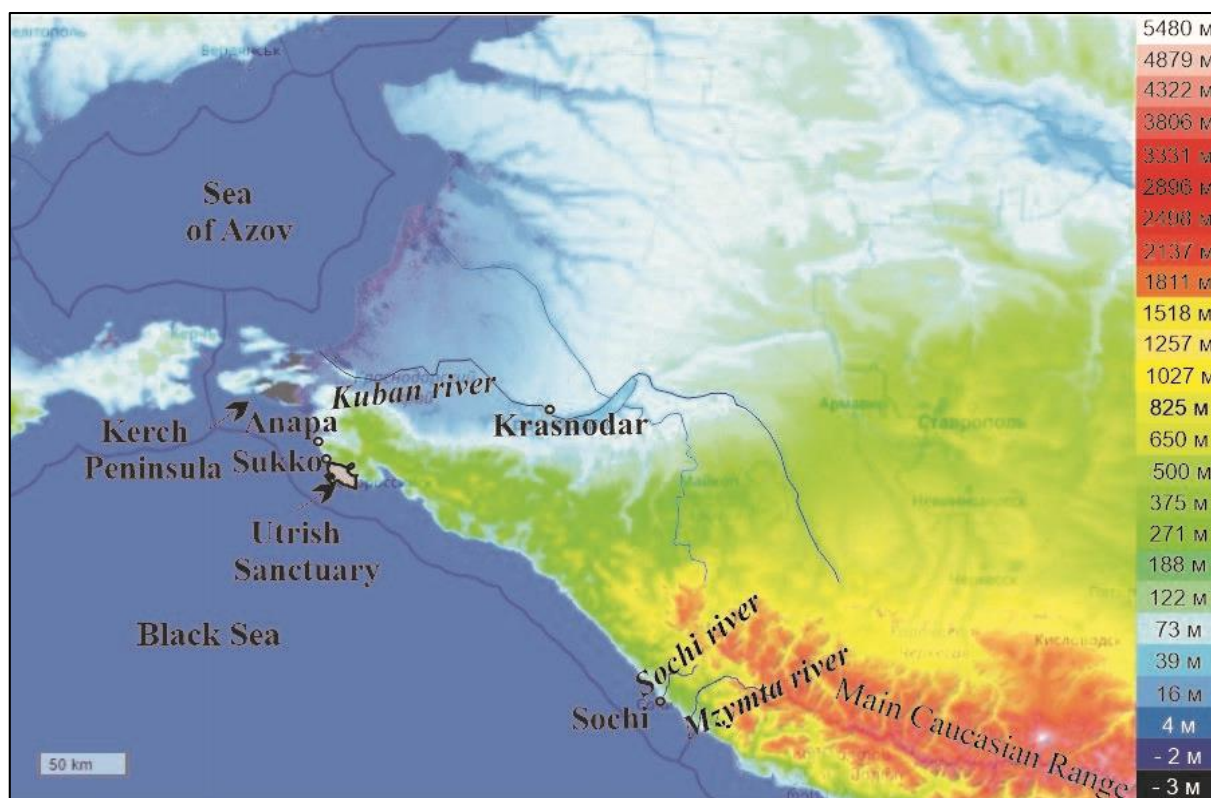
We refer to the effects of SI diffusion from the mixing zone to deep aquifers and subsequently to subsurface and overland runoff as secondary contamination (SC) of subsurface and overland runoff.

Secondary contamination of runoff is unequivocally related to the geomorphology of the coastal zone, as low-lying areas are clearly more susceptible to SC. Thus, in the coastal areas of the Mzymta and Sochi river valleys near the study area, there is no evidence of SC because of much higher elevations.

The Abrau Peninsula, where the Utrish Nature Reserve is located, is a coastal lowland with absolute elevations of about 100-400 m above sea level (asl). About 45 km north of the Abrau Peninsula is a vast depression of the Kuban River basin, where the relief varies from 20 to 70 m asl, and the central part of the Kerch Peninsula, 50 km northwest of the study site, is 1-2 m below sea level.

However, the Mzymta and Sochi river valleys are located at much higher elevations due to their proximity to the Caucasus Mountains. Even near the coast, elevations of about 1,000-1,200 m asl are common (<https://ru-ru.topographic-map.com/maps/e44u/Краснодарский-край/>) (Fig. 2).





**Figure 2.** Schematic map of the Black Sea coast of Russia

In SI-sensitive coastal aquifers, low topography likely contributes significantly to the SC of overland and subsurface runoff. However, the predominance of chloride and sodium ions and elevated runoff salinity in coastal areas may not be a definitive indicator of SI, because these characteristics may be controlled by many other factors, such as host rock composition (e.g., highly localized geochemical characteristics of the host rock), the presence of mineralized zones, and mineralized water seepage. Therefore, an in-depth runoff analysis of trace elements and the ratios of elements of marine and terrestrial origin is crucial to establish reliable SI indicators.

### 3.2. Microelemental Composition of Water

Despite the enriching effects of SI in the low-lying areas of the Black Sea coast, the elemental composition of runoff was poor. Thus, most of the 71 elements analyzed had Cc values below unity, which means they were deficient, while only 12 elements had Cc values above unity (Table 1). The lowest Cc values ( $Cc < 0.3$ ) were found for Mo, Al, Rb, Zn, Pb, Cs, and Th (Table 3).

Interestingly, some of the excess elements had fairly high Cc values: Se, Br, Sr, and Ca had Cc values above 10; S, Li, Na, and Mg  $\geq 3$ ; and B  $> 2$ .

The high Cc values of excess elements are clearly related to SI, given their correlation with the predominant seawater anions Cl and SO<sub>4</sub>. The correlation coefficients of Na, Ca, and Br with Cl anions were  $r=0.89, 0.91, \text{ and } 0.93$ ,

respectively, at  $r5\% \text{ crit.} = 0.33$ . The other group of excess elements had close correlations with SO<sub>4</sub> ions,  $r=0.77, 0.87, 0.87, \text{ and } 0.87$  for Se, Sr, Li, and Mg, respectively. Carbonate rocks abundant in the region and rich in Ca, Sr, and Mg also contribute to excess concentrations of these elements [34].

**Table 3.** Clarke values of elements in river and spring water (Cc values in parenthesis)

Water	Cc $\geq 1$	Cc $< 1$
River	Se(25.2)-Sr(15.9)-Ca(10.4)-Br(9.9)-Li(6.7)-S(5.6)-	Si,K(0.9)-Pr,Sn(0.8)-Ce,Dy(0.7)-Sm,Nd(0.6)-Gd(0.5)-Er,V(0.4)-La,Yb,Mo(0.3)-Mn,Al,Rb(0.2)-
Spring	Se(24.7)-Sr(13.0)-Br(11.9)-Ca(11.1)-S(6.2)-Na(4.5)-	K(0.9)-Cr,Si(0.8)-Sn(0.5)-V(0.4)-Mo,Er,Yb,Dy(0.3)-Pr,Rb,Gd(0.2)-

Consistently high Cc values of Se in all studied waters, ranging from 16 to 33 units, are associated with high Se content in rocks, channel sediments, and soils (Cc of 2.96, 4.89, and 2.10, respectively). Considering that Se has similar chemical properties to S [43]) (correlation coefficient  $r=0.94$  with  $r5\% \text{ crit.} = 0.33$ ), it is possible that another reason for high concentrations of this element in runoff is the effect of SI.

A steadily increasing concentration of excess elements from the source to the mouth of the Vodopadnaya Ravine also showed the effect of SI, and the increase was statistically significant: Se from 3.25 to 6.64 mg/L (NSR 1.21); Sr from 0.74 to 0.86 mg/L (NSR 0.09); Ca from 117

to 130 mg/L (NDS 6.7); S from 16.4 to 25.6 mg/L (NDS 3.5); Li from 14.5 to 20.1 µg/L (NDS 4.1); Na from 19 to 21 mg/L (NDS 1.6) and Mg from 11 to 15 mg/L (NDS 1.75). Thus, the content of typically marine elements in the stream water increased with proximity to the coast.

This means that the positive correlation between excess trace elements and the predominant seawater anions Cl and SO<sub>4</sub> can be considered as another hydrogeochemical indicator of SC in the coastal runoff. The presence of marine elements in surface runoff may not be related to the excess of these elements in seawater, but rather to chemical properties that promote or prevent the influx of marine elements into surface runoff. The occurrence of SC due to elemental chemistry needs to be evaluated in greater detail at more sites in coastal zones with different hydrogeological conditions.

### 3.3. Geochemical Indicators of Secondary Contamination

The lower mineralization of stream water compared to spring water (0.488 vs. 0.052 g/L, at HCP 0.04 g/L) was statistically significant and is attributed to the greater

influence of SI on groundwater seepage and springs than on overland flow. Of all the detected excess elements due to SI, the most consistently elevated concentration in spring water compared to stream water was noted for Br (higher by 0.04 mg/L, at an NSR of 0.02). In contrast, concentrations of Al, Cr, Zn, Cs and all REEs were consistently lower in spring water. These elements are characterized by fairly high C<sub>c</sub> values in rocks, sediments, and soils in the study area (Table 4).

Excess concentrations of Al, Cs, and REEs are particularly evident in comparison with their Clarke numbers for carbonate rocks (Table 5). The relatively high concentrations of Al, Cr, Zn, Cs and REEs in stream water can therefore be attributed to the migration of these elements from rocks and soil.

Given the differences between springs and streams, it is possible to establish a set of geochemical indicators of SI that covary with the mineralization of stream water. Thus, a decrease in mineralization of stream water relative to spring water coupled with a consistent increase in Al/Br, Cr/Br, Zn/Br, Cs/Br and  $\sum$  REE/Br may be a reasonably straightforward indicator of SI in deep coastal aquifers (Fig. 3).

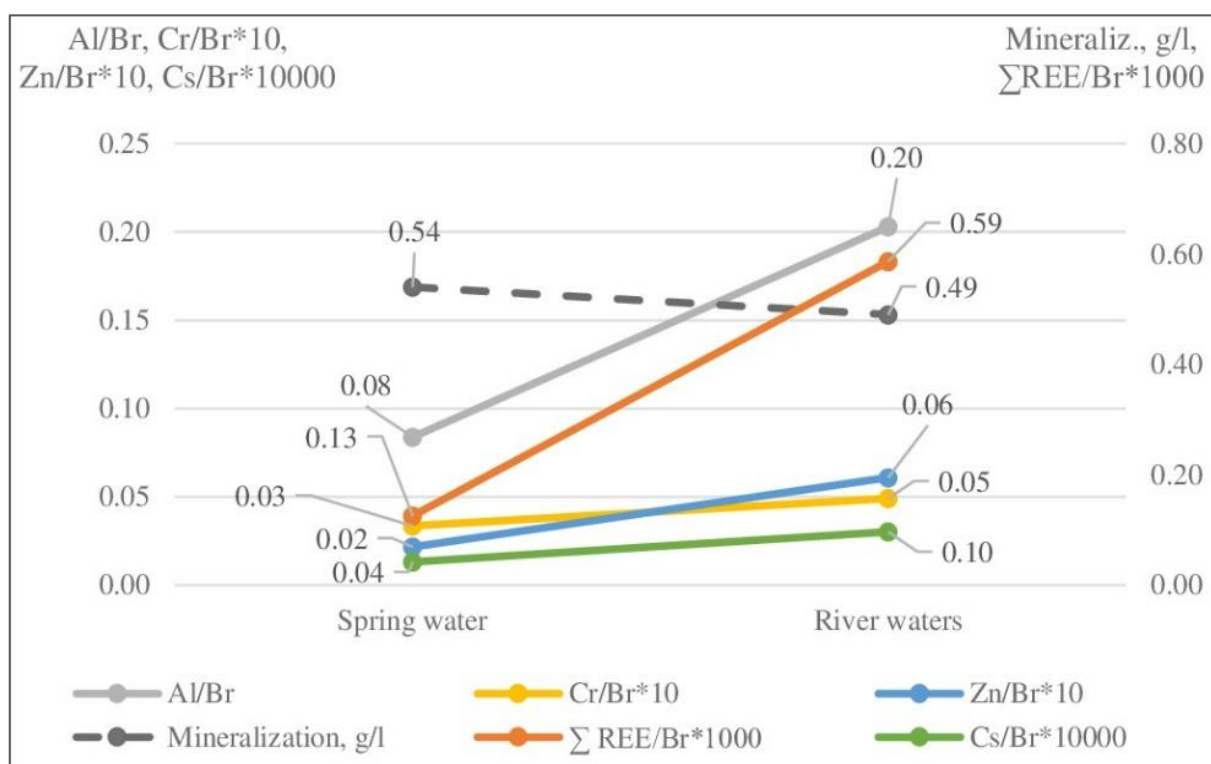
**Table 4.** Mean element concentrations, mg/kg (C - Clarkes), in sedimentary rocks (I) (Grigoriev, 2003) and continental soils (II) (Yaroshevsky, 2004), and mean Clarke numbers (C<sub>c</sub><sub>mean</sub>) for elements in rocks, channel sediments, and soils of the Utrish Nature Reserve

Elements	C		C <sub>c</sub> <sub>mean</sub>			Elements	C		C <sub>c</sub> <sub>mean</sub>		
	I	II	Rocks, n=8	Channel, n=12	Soil, n=24		I	II	Rocks, n=8	Channel, n=12	Soil, n=8
Na	13100	6300	0.10	0.10	0.22	Sb	1.2	0.9	0.24	0.38	0.58
Mg	18300	6300	0.22	0.28	1.05	Cs	7.7	3	0.35	0.49	1.7
Al	64100	71300	0.43	0.54	0.64	La	32	40	0.4	0.44	0.5
S	3600	850	0.05	0.12	0.41	Ce	52	50	0.53	0.57	0.88
K	19800	13600	0.57	0.68	1.3	Pr	6.8	7	0.44	0.44	0.62
Ca	72800	13700	0.67	0.6	1.1	Nd	24	33	0.48	0.46	0.51
V	91	90	0.7	0.94	1.21	Sm	5.5	5	0.41	0.39	0.66
Cr	58	60	1.68	2.59	2.17	Eu	0.94	1	0.47	0.44	0.63
Mn	830	500	0.24	0.56	0.81	Gd	4	4	0.45	0.41	0.62
Zn	43	60	1.09	1.56	1.27	Tb	0.69	0.7	0.39	0.35	0.51
Se	0.27	0.4	2.96	4.89	2.1	Dy	3.6	5	0.45	0.42	0.43
Sr	270	220	0.84	0.58	0.45	Ho	0.92	0.6	0.35	0.34	0.71
Ba	410	500	0.4	0.51	0.45	Er	1.7	2	0.54	0.54	0.62
Pb	12	20	0.59	0.94	0.79	Tm	0.78	0.4	0.17	0.17	0.46
Li	33	30	0.74	0.71	0.87	Yb	2	3	0.46	0.49	0.42
Rb	94	70	0.57	0.73	1.3	Lu	0.44	0.35	0.3	0.32	0.53
Mo	1.5	2	0.39	0.52	0.42	Tl	0.89	0.3	0.22	0.32	1.22
Sn	2.9	1.1	0.2	0.31	0.85	Th	7.7	6.5	0.55	0.6	1.04
						U	3.4	1.5	0.36	0.38	1.05



**Table 5.** Mean element concentrations, mg/kg (C - clarkes), in sedimentary carbonate rocks (Grigoriev, 2003), and mean clarke numbers ( $C_{c_{mean}}$ ) for elements in the rocks, channel sediments, and soils of the Utrish Nature Reserve

Elements	C	$C_{c_{mean}}$		Elements	C	$C_{c_{mean}}$	
		Rocks, n=8	Channel, n=12			Rocks, n=8	Channel, n=12
Al	11800	2.32	2.92	Eu	0.50	0.89	0.82
Cr	20	4.87	7.50	Gd	1.50	1.20	1.09
Zn	5	9.39	13.43	Tb	0.38	0.71	0.64
Cs	3.6	0.76	1.06	Dy	2.90	0.56	0.52
La	7.00	1.84	1.99	Ho	0.40	0.92	0.89
Ce	12.00	2.30	2.47	Er	0.75	1.23	1.22
Pr	2.60	1.14	1.14	Tm	0.14	0.94	0.97
Nd	6.60	1.73	1.69	Yb	0.90	1.03	1.09
Sm	1.90	1.20	1.14	Lu	0.11	1.21	1.28



**Figure 3.** Mineralization of spring and river water and marker elements (geochemical indicators) of marine (Br) and terrestrial (Al, Cr, Zn, Cs,  $\Sigma$  REE) origin

The characteristic department of the rare earth element lanthanum (La) and 14 lanthanides (Cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), and Ytterbium (Yb), and lutetium (Lu)) in water may be another such indicator.

Rare earth elements exhibit similar department in environmental and hypergene geochemical processes due to similar chemical properties. Under the conventional division of REEs into light REEs (LREE) (La, Ce, Pr, Nd), medium REEs (MREEs) (Sm, Eu, Gd, Tb, Dy) and heavy REEs (HREE) (Ho, Er, Tm, Yb, Lu), normalized to the North American Shale Composite (NASC) [44], a region-specific REE fractionation pattern attributable to rock properties has been observed. Rare earths are characterized by specific department in coastal areas. The study of this specificity enabled Chevis et al. [45] to distinguish REE fluxes with fractionation patterns indicative of the terrestrial REE origin from fluxes caused by marine effects associated with the reductive dissolution of Fe(III) in subsurface estuaries. In overland runoff and channel sediments, identical REE fractionation patterns have been observed [46].

Our earlier comprehensive study of natural environmental media (the Sochi coast of the Black Sea, the Mzymta River, and the Sochi River basin) under conditions similar to those in the Reserve demonstrated that REE fractionation patterns are identical in the related components of the natural environment, which was evidenced in the MREE enrichment. River waters exhibited the same REE fractionation patterns as rocks [47], soils, vegetation [48], and even bivalves in coastal waters [49]. The typical terrestrial REE fractionation pattern in bivalves faded only at a distance of ca. 1000 m offshore.

The rocks, soils, and channel sediments of the Reserve were characterized by a moderately high MREE content (Fig. 4), typical of the regional REE fractionation pattern. However, in-stream and spring waters, this pattern was disrupted due to SI; without the influence of SI, the fractionation pattern would have been consistent in all

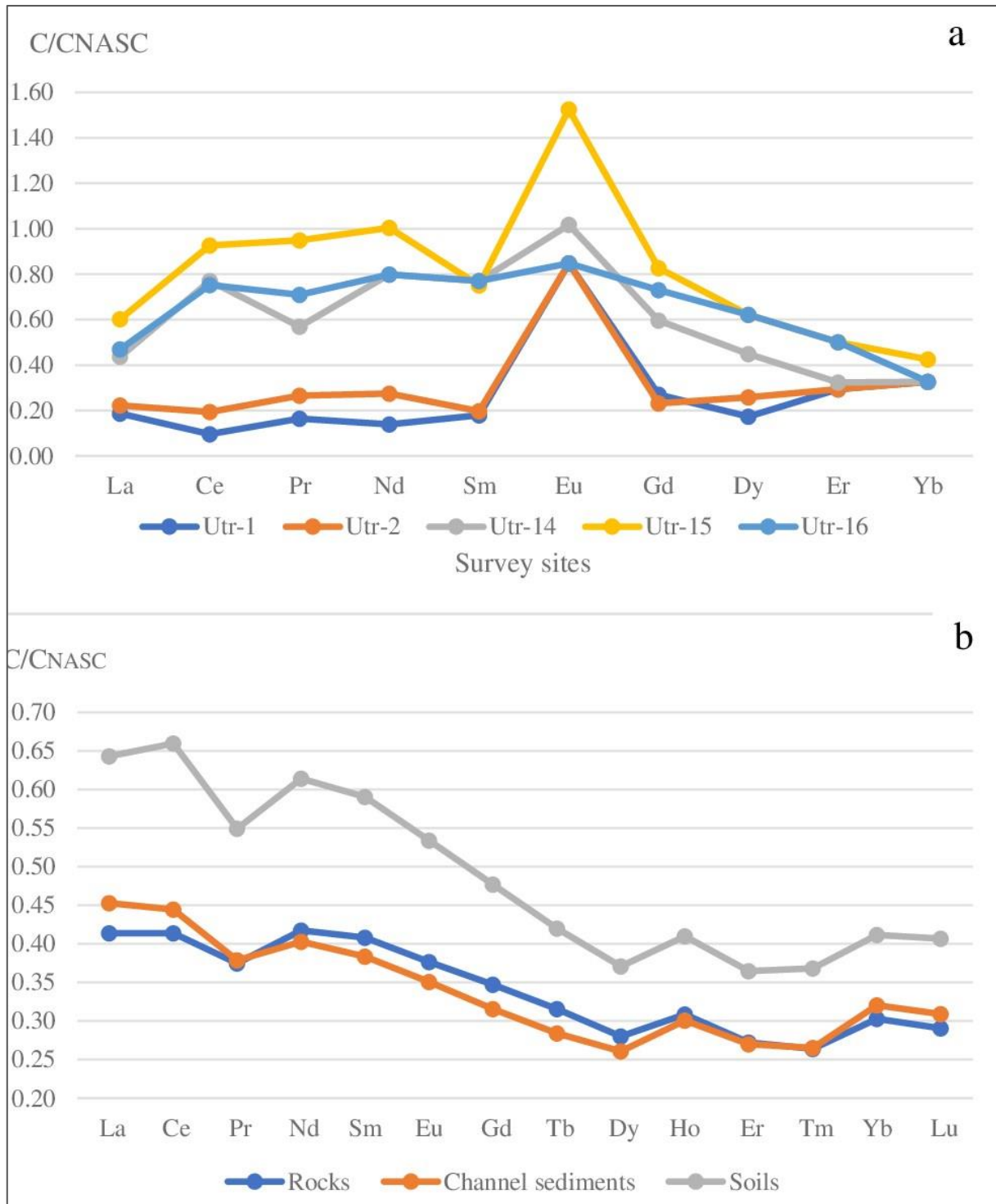
types of environmental media, as is the case in the Sochi area. Therefore, the anomalous REE fractionation pattern in stream and spring waters compared to rocks, channel sediments, and soils can be considered as another geochemical indicator of SI in coastal aquifers.

An even more striking indicator of SI was the europium anomaly observed in the spring ( $\text{Eu}/\text{Eu}^* = 3.96$ ) and stream waters of the Reserve ( $\text{Eu}/\text{Eu}^* = 1.44$ ). Previously, this phenomenon has been described mainly for rocks, and may occur as a deficit or excess of this element compared to other REEs, although some argue that this phenomenon is not typical of the hypergene zone.

There is no single generally accepted view of the cause of europium anomalies, and the issue remains controversial. One theory attributes them to the presence of europium-rich plagioclase and feldspar, but it may also be related to changes in redox conditions and Eu-specific acid-base properties [50].  $\text{Eu}^{2+}$ , an element with variable valence, has a strong reducing power and forms the strongly basic oxide  $\text{EuO}$ , while  $\text{Eu}^{3+}$  forms the acidic oxide  $\text{Eu}_2\text{O}_3$ .

Given that seawater has higher density, salinity, and redox potential than freshwater, positive Eu anomalies may be attributed to changes in redox potential within the geochemical barrier at the seawater/freshwater interface. The higher  $\text{Eu}/\text{Eu}^*$  ratio for spring water ( $\text{Eu}/\text{Eu}^*=3.96$ ) compared to stream water ( $\text{Eu}/\text{Eu}^*=1.44$ ) indicates seepage from deep groundwater aquifers that are typically more exposed to SI than stream water.

The geochemical indicators of SI in the subsurface and overland runoff identified here for the first time are important because they open up new avenues of SI and SC research. However, the small data sample size on which these geochemical indicators are based necessitates further corroborating research. New data from other locations and different regions would be useful to confirm the proposed indicators and may lead to the discovery of new ones. The presence of SI in coastal zones can be established by analyzing the geochemical indicators of subsurface and overland runoff without the need to drill boreholes to sample aquifers, given that drilling can exacerbate aquifer contamination by seawater.



**Figure 4.** REE concentrations in water (a), rocks, channel sediments, and soils (b) in the Utrish Nature Reserve normalized to the North American Shale Composite (NASC)

### 4. Conclusions

The stream and spring waters in the study area of the Utrish Nature Reserve were identified as hydrocarbonate-chloride calcium-magnesium-sodium. The predominance of chloride and sodium ions in the runoff suggests the occurrence of SI in deep coastal aquifers in the area. The

occurrence of SI in overland runoff and in perched aquifers feeding the springs is attributed to the low hypsometry of the terrain.

The trace element content of the sampled waters was generally negligible for most of the elements investigated. However, several elements were present in very high concentrations relative to their clarke numbers. These were

Se, Sr, Br, Ca, S, Li, Na, Mg and B. The high concentrations of these elements are attributed to SI, which is confirmed by the close correlations with the predominant seawater anions Cl and SO<sub>4</sub>.

The consistently high Br content in spring water relative to stream water, attributed to SI, and, conversely, decreased concentrations of Mn, Zn, Al, and all REEs, attributed to regional rock composition, enabled us to identify the following geochemical indicators of SI: (1) increasing ratios of Mn/Br, Zn/Br, Al/Br, and  $\sum$  REE/Br with decreasing mineralization of stream water relative to spring water; (2) positive correlation of excess trace elements with Cl and SO<sub>4</sub> anions predominant in seawater; (3) anomalous REE fractionation in water relative to rocks; and (4) positive europium anomaly due to redox shift at the geochemical barrier at the seawater-freshwater interface.

## Acknowledgements

The authors would like to express their gratitude to Andrei Tchourakov for the English translation of this paper and his valuable comments. The study was funded by the state assignment research of FRC SSC RAS FGRW-2021-0015, project No. 122032300363-3.

## REFERENCES

- [1] Abd-Elaty, I., Abd-Elhamid, H. F. and Negm, A. M. Investigation of Saltwater Intrusion in Coastal Aquifers. *Groundwater in the Nile Delta*. pp. 329-353. 2018. [https://doi.org/10.1007/698\\_2017\\_190](https://doi.org/10.1007/698_2017_190)
- [2] Capaccioni, B., Didero, M., Paletta, C. and Didero, L. Saline intrusion and refreshing in a multilayer coastal aquifer in the Catania Plain (Sicily, Southern Italy): dynamics of degradation processes according to the hydrochemical characteristics of groundwaters. *Journal of Hydrology Amsterdam* 307(1/4): 1-16. 2005. <https://doi.org/10.1016/j.jhydrol.2004.08.037>
- [3] Werner, A. D., Bakker, M., Post, V. E., Vandenbohede, A., Lu, C., Ataie-Ashtiani, B., Simmons, C. T. and Barry, D. A. Seawater intrusion processes, investigation and management: recent advances and future challenges. *Advances in water resources*. 51, pp. 3-26. 2013. <https://doi.org/10.1016/j.advwatres.2012.03.004>
- [4] Edwards, B. D. Saltwater intrusion in Los Angeles area coastal aquifers: the marine connection. US Department of the Interior, US Geological Survey. 2002. Available online: <http://pubs.usgs.gov/fs/2002/fs030-02/>
- [5] Demirel, Z. The history and evaluation of saltwater intrusion into a coastal aquifer in Mersin Turkey. *J. Environ. Manage.*, 70, 275-282. 2004. <https://doi.org/10.1016/j.jenvman.2003.12.007>
- [6] Khublaryan M. G., Frolov A. P., Yushmanov I. O. Seawater intrusion into coastal aquifers. *Water Resources*. T. 35. № 3, 274-286. 2008. <https://doi.org/10.1134/S0097807808030032>
- [7] Gupta G., Erram V. C., Maiti S., Kachate N. R., Patil S. N. Geoelectrical studies for delineating seawater intrusion in parts of Konkan coast Western Maharashtra. *International Journal of Environment and Earth Sciences*. 1, 62-79. 2010. <http://localhost:8080/xmlui/handle/123456789/668>
- [8] Ammar Ben S., Taupin J. D., Zouari K., Khouatmia M. Identifying recharge and salinization sources of groundwater in the Oussja Ghar el Melah plain (northeast Tunisia) using geochemical tools and environmental isotopes. *Environmental Earth Sciences*, 75, 606. 2016. <https://doi.org/10.1007/s12665-016-5431-x>
- [9] Hussain M. S., Javadi A. A. Assessing impacts of sea level rise on seawater intrusion in a coastal aquifer with sloped shoreline boundary. *Journal of Hydro-environment Research*, 11, 29-41. 2016. <https://doi.org/10.1016/j.jher.2016.01.003>
- [10] Ketabchi H., Mahmoodzadeh D., Ataie-Ashtiani B., Simmons C. T. Sea-level rise impacts on seawater intrusion in coastal aquifers: review and integration. *Journal of Hydrology*, 535, 235-255. 2016. <https://doi.org/10.1016/j.jhydrol.2016.01.083>
- [11] Wang J., Tsay T. Tidal effects on groundwater motions *Transp. Porous Media*, 43, 159-178. 2001. <https://doi.org/10.1023/A:1010634114160>
- [12] Werner A. D., Simmons C. T. Impact of Sea-Level Rise on Sea Water Intrusion in Coastal Aquifers. *Groundwater*, 47 (2), 197-204. 2009. <https://doi.org/10.1111/j.1745-6584.2008.00535.x>
- [13] Mardiha Mokhtar, Muhammad Azri Fikri B. Ariffin, Mohd Effendi Daud, Masiri Kaamin, Mohamad Azim Mohammad Azmi, Nor Baizura Hamid, "Sediment Properties of Eroded Coastal Area at Batu Pahat, Johor, Malaysia," *Environment and Ecology Research*, Vol. 10, No. 2, pp. 248-259, 2022. <https://doi.org/10.13189/eer.2022.100214>.
- [14] Van Camp M., Mtoni Y., Mjemah I. C., Bakundukize C., Walraevens K. Investigating seawater intrusion due to groundwater pumping with schematic model simulations: the example of the Dar es Salaam coastal aquifer in Tanzania. *Journal of African Earth Sciences*, 96 (14), 71-78. 2014. <https://doi.org/10.1016/j.jafrearsci.2014.02.012>
- [15] Narayan K. A., Schleeberger C., Bristow K. L. Modelling seawater intrusion in the Burdekin Delta Irrigation Area, North Queensland. Australia. *Agricultural Water Management*, 89 (3). 217-228. 2007. <https://doi.org/10.1016/j.agwat.2007.01.008>
- [16] Shi L., Jiao J. J. Seawater intrusion and coastal aquifer management in China: a review. *Environmental Earth Sciences*, 72, 2811-2819. 2014. <https://doi.org/10.1007/s12665-014-3186-9>
- [17] Einsiedl F. Sea-water/groundwater interactions along a small catchment of the European Atlantic coast. *Applied Geochemistry*, 27 (1), 73-80. 2012. <https://doi.org/10.1016/j.apgeochem.2011.09.004>
- [18] Kanagaraj G., Elango L., Sridhar S. G. D., Gowrisankar G. Hydrogeochemical processes and influence of seawater intrusion in coastal aquifers south of Chennai, Tamil Nadu India. *Environmental Science and Pollution Research*, 25 (9), 8989-9011. 2018. <https://doi.org/10.1007/s11356-017->

0910-5

- [19] Misut P. E., Voss C. I. Freshwater-saltwater transition zone movement during aquifer storage and recovery cycles in Brooklyn and Queens, New York City USA. *Journal of Hydrology*, 337, 87-103. 2007. <https://doi.org/10.1016/j.jhydrol.2007.01.035>
- [20] Ngo M. T., Lee J. M., Lee H. A., Woo N. C. The sustainability risk of Ho Chi Minh City, Vietnam, due to saltwater intrusion. *Geosciences Journal*, 19, 547-560. 2015. <https://doi.org/10.1007/s12303-014-0052-4>
- [21] Mironyuk S. G., Khlebnikova O. A. Signs and geological preconditions of seawater intrusion into coastal aquifers (on the example of the Black Sea) // *Geoecology. engineering geology. Hydrogeology. Geocryology*. 3, 24-37. 2022. <https://doi.org/10.31857/S0869780922030067>.
- [22] Panjaitan, D.; Tarigan, J.; Rauf, A., Nababan, E. S. M. Determining sea water intrusion in shallow aquifer using chloride bicarbonate ratio method. *Proceedings of the IOP Conference Series: Earth and Environmental Science (Banda Aceh, Indonesia)*. 205, 012029. 2018. <https://doi.org/10.1088/1755-1315/205/1/012029>
- [23] Cai, J.; Taute, T., and Schneider, M. Recommendations of controlling seawater intrusion in an inland aquifer for drinking-water supply at a certain water site in Berlin (Germany). *Water Resource Management*, 29 (7), 2221-2232. 2015. <https://doi.org/10.1007/s11269-015-0937-7>
- [24] Abd-Elaty I., Straface S., Kuriqi A. Sustainable saltwater intrusion management in coastal aquifers under climatic changes for humid and hyper-arid regions. *Ecological Engineering*. 171, 106382. 2021. <https://doi.org/10.1016/j.ecoleng.2021.106382>
- [25] Basack S., Loganathan M. K., Goswami G., Khabbaz H. Saltwater Intrusion into Coastal Aquifers and Associated Risk Management: Critical Review and Research Directives. *Journal of Coastal Research*. 38 (3). 654-672. 2022. <https://doi.org/10.2112/JCOASTRES-D-21-00116.1>
- [26] Mikhailov V. N., Dobrolyubov S. A. *Hydrology: a textbook for universities*. M.; Berlin: Direct-Media. 752 p. 2017. (In Russian).
- [27] Lavrishchev, V. A.; Prutsky, N. I.; Semenov, V. M. State Geological Map of the Russian Federation, Scale of 1: 200 000, Caucasus Series, Sheet K-37-V, 2nd ed.; Nauka: St. Petersburg, Russia. 2002. (In Russian).
- [28] Kazeev K. S., Kutrovskii M. A., Dadenko E. V., Vezdeneeva L. S., Kolesnikov S. I., Valkov V.F. The influence of carbonates in parent rocks on the biological properties of mountain soils of the northwest Caucasus region. *Eurasian Soil Science* 45(3): 282-289. 2012. <https://doi.org/10.1134/S1064229312030052>
- [29] Shishov L. L., Tonkonogov V. D., Lebedeva I. I., Gerasimova M. I. Classification of soils of Russia. V. V. Dokuchaev Russian Academy of Agricultural Sciences. 57-61. 2008. (In Russian).
- [30] Working Group WRB. World Reference Base for Soil Resources. International soil classification system for naming soils and creating legends for soil maps, World Soil Resources Reports. 106:181. 2014.
- [31] Karandashev, V. K.; Leikin, A. Y.; Khvostiko, V. A. et al. Water analysis by mass spectrometry method with inductively-coupled plasma. *Plant Laboratory. Mater. Diagn.* 81, 5–18. 2015. (In Russian).
- [32] Gordeev V. V. River flow into the ocean and features of its geochemistry. Moscow, Nauka, p. 152. 1983. (In Russian).
- [33] Yaroshevsky, A. A. Problems of Modern Geochemistry. Novosibirsk State University Publ, Novosibirsk. 2004. (In Russian).
- [34] Grigoriev, N. A. Average concentrations of chemical elements in rocks of the upper continental crust. *Geochemistry International*, 41, 711–718. 2003.
- [35] Gromet, L. P., Haskin, L. A., Korotev, R. L. and Dymek, R. F. The "North American shale composite": Its compilation, major and trace element characteristics. *Geochimica et cosmochimica acta*. 48(12), pp.2469-2482. 1984.
- [36] Litvinenko, Y. S., & Zakhariikhina, L. V. Geochemistry and Radioecology of Waters and Channel sediments of the Mzymta River, the Black Sea Coast. *Geochemistry International*, 60(4), 379-394. 2022. <https://doi.org/10.1134/S0016702922030041>
- [37] Zakhariikhina L., Litvinenko Y., Saburov R., Shevelev S., and Vareljyan G. Chemical typification, distribution patterns, and geochemistry of natural groundwater of the southern slope of the Caucasus Mountain Range. *Water*. 14(14), 2170. 2022a. <https://doi.org/10.3390/w14142170>
- [38] Kasai, A., Kurikawa, Y., Ueno, M., Robert, D., Yamashita, Y. Salt-wedge intrusion of seawater and its implication for phytoplankton dynamics in the Yura Estuary, Japan. *Estuarine, Coastal and Shelf Science*, 86(3), 408-414. 2010. <https://doi.org/10.1016/j.ecss.2009.06.001>.
- [39] Guerra-Chanis, G. E., Reyes-Merlo, M. Á., D éz-Minguito, M., Valle-Levinson, A. Saltwater intrusion in a subtropical estuary. *Estuarine, Coastal and Shelf Science*, 217, 28-36. 2019. <https://doi.org/10.1016/j.ecss.2018.10.016>.
- [40] Saha, K., Sanyal, P., Saha, S. Source assessment of tropical-marshland sediment for evaluating seawater intrusion in Chandipur, India: An integrated granulometric and stable isotope approach. *Estuarine, Coastal and Shelf Science*, 278, 108096. 2022. <https://doi.org/10.1016/j.ecss.2022.108096>.
- [41] Gong, W., Zhang, Z. Lipid biomarkers and organic matter carbon isotopes in estuarine sediments as proxies for evaluating seawater intrusion. *Estuarine, Coastal and Shelf Science*, 155, 38-46. 2015. <https://doi.org/10.1016/j.ecss.2015.01.016>.
- [42] Kumar Krishnan, Nadia A. S., Chong M. Y., "Ecological Risk Assessment of Heavy Metal Pollution in Mangrove Sediments of the Sepang Besar River, West Coast Peninsular Malaysia." *Environment and Ecology Research*, 10, 4, 497-507, 2022. <https://doi.org/10.13189/eer.2022.10.0408>.
- [43] Kurskov S. N., Rastegaev O. Yu. Selenium in natural water. Finding optimal concentrations // *Theoretical and applied ecology*. no. 3, 70-75. 2013. (In Russian).
- [44] Aubert, D., Stille, P., Probst, A., Gauthier-Lafaye, F. and Pourcelot, L. Characterization and migration of atmospheric REE in soils and surface waters. *Geochimica et Cosmochimica Acta*, 66(19), 3339-3350. 2002. [https://doi.org/10.1016/S0016-7037\(02\)00913-4](https://doi.org/10.1016/S0016-7037(02)00913-4)

- [45] Chevis D. A., Johannesson, K. H., Burdige, D. J., Cable, J. E., Martin, J.B., Roy, M. Rare earth element cycling in a sandy subterranean estuary in Florida, USA. *Marine Chemistry*, 176, 34-50. 2015. <https://doi.org/10.1016/j.marchem.2015.07.003>.
- [46] Chevis, D. A., Mohajerin, T. J., Yang, N., Cable, J. E., Rasbury, E. T., Hemming, S. R., Burdige, D. J., Martin, J. B., White, C.D. and Johannesson, K.H. Neodymium Isotope Geochemistry of a Subterranean Estuary. *Water. Sec. Water and Critical Zone*, 3, 1-21. 2021. <https://doi.org/10.3389/frwa.2021.778344>
- [47] Zakharikhina, L. V.; Sharafan, M. V. Behavior of rare earth elements in the soil and vegetation cover of the urban landscapes of Sochi. *Vestn. KRAUNTS. Nauki Zemle*, 50, 48–58. 2021. <https://doi.org/10.31431/1816-5524-2021-2-50-48-58>. (In Russian)
- [48] Zakharikhina, L. V., Malyukova, L. S., Ryndin, A. V. Genesis and geochemistry of the soils of urban landscapes of the Black Sea coast of Russia. *Catena*, 210, 105881. 2022b. <https://doi.org/10.1016/j.catena.2021.105881>
- [49] Zakharikhina, L. V.; Rudev, P. V.; Paltseva, A. V. Chemical composition and morphology of the Mediterranean mussel, Black Sea coast of Russia. *Marine Pollution Bulletin*, 179, 113692. 2022c. <https://doi.org/10.1016/j.marpolbul.2022.113692>.
- [50] Vodyanitskii Yu N. Geochemical fractionation of lanthanides in soils and rocks: A review of publications // *Eurasian Soil Science*. V. 45. № 1, 56–67. 2012. <https://doi.org/10.1134/S1064229312010164>