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SNOW COVER CHEMISTRY IN CRIMEAN FOREST ECOSYSTEMS: A CASE STUDY OF THE KARADAG NATURE RESERVE *

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Abstract: The aim of the study is to analyze the chemical composition of snow and the distribution of macroelements in the Karadag Nature Reserve in Crimea, where snowfall is rare. Snow samples were collected during the winter period from 2021 to 2024 at a background environmental monitoring station and analyzed for ion content and acidity. The results show that acidity varies from 6.00 to 7.46, with a predominance of sulfates, indicating anthropogenic influences. The chemical composition is determined by both natural and anthropogenic factors. The high ratio of cations to anions indicates buffering processes that reduce acidity, which may positively affect the ecosystem. The results emphasize the need for monitoring atmospheric precipitation to assess anthropogenic impacts.

Keywords: chemical composition, snow cover, forest ecosystems, Crimea, Karadag Nature Reserve

Introduction

Atmospheric deposition is a key driver of biogeochemical cycles, serving as a major transport mechanism for both natural and anthropogenic substances across terrestrial and aquatic ecosystems. Snow cover acts as a highly efficient natural archive of these inputs, integrating chemical signals from wet and dry deposition over time. Its composition provides critical insights into regional air pollution levels, making it a powerful tool for environmental monitoring [Vasilevich, Beznosikov, Kondratenok, 2011; Pristova, Vasilevich, 2011; Krnavek et al., 2012]. Unlike rainfall, which leads to immediate runoff, snow accumulates contaminants (including trace metals, sea salts, acids, and industrial emissions) and releases them abruptly during melt events, posing significant ecological risks [Krnavek et al., 2012].

The study of snow chemistry in Crimea offers a rare and scientifically valuable opportunity due to the region's unique climatic and geographical setting. While extensive research has been conducted in high-latitude, alpine, and heavily industrialized areas with persistent snow cover [Hunova et al., 2023; Kotova, Topchaya, Novikova, 2023; Makarov, Torgovkin, 2021; Aristarain, Delmas, 2002; Xue et al., 2020; Toom-Sauntry, Barrie, 2002; Domine et al., 2004; Nickus, 2003; de Caritat et al., 2005; Benassai et al., 2005; Yalcin et al., 2006; Dibb et al., 2010], Crimea's Southern Coast experiences snowfall only sporadically, for a few days per year. This infrequency results in highly concentrated deposition events, effectively capturing discrete "snapshots" of atmospheric chemistry.

Furthermore, Crimea's location exposes it to diverse pollution sources: marine aerosols from the Black Sea, long-range transport of industrial emissions from Europe, and localized anthropogenic activity. The combination of these factors makes Crimean snow a distinctive and understudied environmental record, offering insights into pollution dynamics in a Mediterranean coastal climate.

A key focus of this study is sulfate (SO_4^{2-}), a major component of snow chemistry with ambiguous origins. While natural sources such as sea spray and volcanic emissions contribute sulfates, elevated concentrations are often a definitive marker of anthropogenic pollution, particularly from fossil fuel combustion (e.g., power plants, industrial processes, and vehicle emissions) [Glazovsky, Zlobina, Uchvatov, 1983; Kurosaki et al., 2025; Karpachevskiy et al., 1998; Kulikova,

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1968; Hunova et al., 2023; Kotova, Topchaya, Novikova, 2023; Makarov, Torgovkin, 2021; Aristarain, Delmas, 2002; Xue et al., 2020; Toom-Sauntry, Barrie, 2002; Domine et al., 2004; Nickus, 2003; de Caritat et al., 2005; Benassai et al., 2005; Yalcin et al., 2006; Dibb et al., 2010; Pham et al., 2024]. Given sulfate's role in acid deposition and ecosystem degradation, accurately distinguishing natural from anthropogenic inputs is essential for assessing air quality and implementing effective pollution control measures.

Additionally, forest ecosystems can alter deposition patterns through canopy interception and chemical transformations [Karpachevskiy et al., 1998; Kulikova, 1968]. To minimize these confounding effects, this study centers on the Karadag Nature Reserve, a protected area where local vegetative interference is reduced, allowing for a clearer assessment of regional atmospheric deposition. By analyzing the chemical composition of Crimea's rare snow cover, this research aims to: (1) quantify the deposition of major ions (including sulfates) and trace elements, (2) rigorously evaluate the relative contributions of natural (marine, crustal) versus anthropogenic sources, and (3) leverage the unique context of Crimean snow to assess regional atmospheric pollution burdens impacting this sensitive coastal ecosystem. This study not only fills a critical gap in understanding pollution dynamics in a warming, low-snow region but also establishes a baseline for future environmental monitoring in the Black Sea basin.

Study Area

The study was conducted at the Background Environmental Monitoring Station (BEMS) within the State Nature Reserve "Karadag" (44°54′N, 35°12′E), a protected coastal steppe ecosystem in southeastern Crimea (Fig. 1).

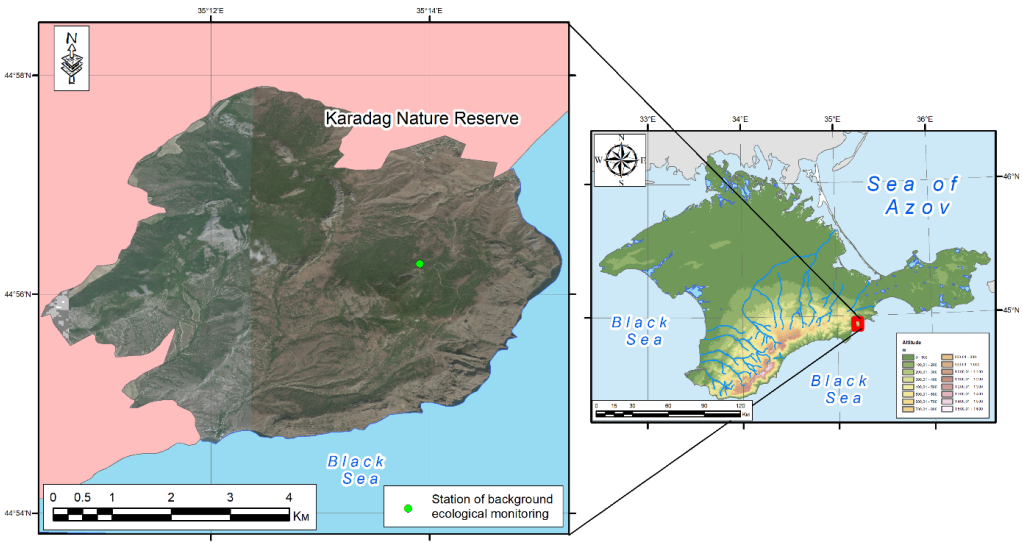

Fig. 1. Study area within the State Nature Reserve "Karadag"

Рис. 1. Исследуемая территория в Государственном природном заповеднике «Карадаг»

The site lies on the northeastern slope of Mount Svyataya, 1.5 km from the nearest settlement (Koktebel) and is shielded from direct marine influence by the Kok-Kaya Ridge (320 m elevation). The vegetation consists of steppe grasses with sparse tree undergrowth (canopy closure ≤ 60 %) [Pham et al., 2024].

The area receives an average annual rainfall of 450 mm (± 55 mm), with about 30 % of this precipitation occurring during winter months (December to February). Snowfall is episodic, featuring 3–5 significant snow events each season. Snow cover typically lasts between 5 and 15 days, supported by mean winter temperatures of 1.2 °C (± 2.1°C).

Materials and methods

Snow samples were collected during three winter seasons: January 15–20, 2021; February 1–5, 2023; and January 25–30, 2024. These periods represent peak snow accumulation events in Crimea, with each sampling campaign conducted 24–48 hours after snowfall cessation. The specific timing was selected to avoid melt periods, thus minimizing the impact on sample integrity and ensuring the capture of both wet and dry deposition. Surface snow from the top 0–5 cm was gathered using acid-washed Teflon tools into pre-cleaned HDPE containers, carefully avoiding ground contamination. Field blanks (n = 3 per season) and NIST 1640a reference materials were used for quality control, with recoveries ranging from 92 % to 107 %. Samples were immediately frozen at –20 °C and analyzed within 72 hours following RD 52.04.186-89 standards [RD 52.04.186-89]. All analyses were conducted at the A. O. Kovalevsky Institute of Biology of the Southern Seas (IBSS).

Nitrate (NO_3^-) and ammonium (NH_4^+) concentrations were measured via spectrophotometry using a KFK–ZOMZ photometer, with NH_4^+ determined by the Seji-Solorzano method. The nitrite ion was determined by the Bendschneider and Robinson method. Chloride (Cl^-) and sulfate (SO_4^{2-}) were analyzed using ion chromatography on the "STAYER A" system. The limits of the relative total error of the measurement result for the concentration of Cl^- and SO_4^{2-} at a confidence level of P = 0.95 did not exceed ± 13 % at mass concentrations from 0.10 mg/dm^3 to 1000 mg/dm^3. The detection limits for Cl^- and SO_4^{2-} were 0.001 and 0.002 mg/l, respectively. Major cations (Ca, Mg, Na, K) and trace metals (Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, Sr, I, Ba) [Lipatnikova et al., 2024] were quantified by ICP-MS (PlasmaQuant MS Elite). Detection limits for trace metals ranged from 0.01 to 0.1 μg L^{-1}. Results from quintuple analyses were averaged and reanalyzed when the relative standard deviation exceeded 10 %. Elemental recoveries and relative standard deviations (RSDs) for standardized reference standards were 96–105 % and < 10 %, respectively. Measured with a calibrated digital pH meter equipped with a KCl reference electrode and standardized using pH 4.0 and 9.2 buffer solutions.

To determine potential sources of dissolved ions in atmospheric precipitation and quantify their contributions, an enrichment factor (EF) analysis was performed. The EF was calculated for each ion relative to seawater and for each element relative to the Earth's crust, assessing the influence of marine and terrestrial sources on precipitation composition. The EF was calculated as follows [Katanayeva, Selyanin, 2011]:

$$EF_{sea} = [X/Na]_{samples}/[X/Na]_{sea}. \quad (1)$$

The enrichment factor (EF) relative to the average composition of the Earth's crust is calculated using the formula [Katanayeva, Selyanin, 2011; Vinogradov, 1967]:

$$EF_{crust} = [X/Al]_{samples}/[X/Al]_{crust}, \quad (2)$$

where X is the content of the element (μg L^{-1}) in both the sample and the upper part of the continental crust.

The clarke values of elements in seawater were taken from the data provided by Vinogradov [Vinogradov, 1967].

While all potentially toxic elements (PTEs) were analyzed, cadmium and zinc received particular attention due to: (1) their exceptionally high enrichment factors (EF > 10 000 for Cd) indicating strong anthropogenic influence; (2) known ecological risks associated with Cd bioaccumulation in Crimean ecosystems while Zn reflects widespread urban and industrial emissions; (3) their regulatory significance, as both exceed MPCs in regional environmental quality standards [GN 2.1.5.1315-03]. This prioritization aligns with recent Black Sea pollution studies [Gurov, Kotelyanets, 2022] highlighting these metals as key tracers of anthropogenic impact in coastal reserves.

Dominant winds during sampling periods come from the northeast, occurring 60 % of the time, according to hourly data from an OTT HydroMet WS 600 station.

Pearson correlation analyses were performed to explore relationships between ion and metal concentrations and meteorological factors such as wind direction. Data processing was conducted in R version 4.3.0, with statistical significance set at $p < 0.05$.

Results

The acidity of meltwater is crucial for understanding the chemical processes occurring during snowmelt. Acidic precipitation entering the soil enhances the migration and leaching of various elements from soil horizons. It is known that at an average atmospheric carbon dioxide (CO_2) concentration of 400 ppm (current global average) and a temperature of 20 °C, the pH of pure water in equilibrium with atmospheric CO_2 is approximately 5.6. If the pH of precipitation is above 5.6, it is considered alkalinized, whereas a pH below 5.6 indicates acidification.

The snowmelt water exhibited consistent alkaline conditions, with pH values ranging from 6.00 to 7.46 (mean: 6.49 ± 0.42), which were significantly higher than the expected atmospheric equilibrium pH of 5.6. The lowest pH recorded was 6.00 on 17 January 2021, while the highest reached 7.46 on 14 January 2021. In comparison, the natural pH of precipitation in equilibrium with atmospheric CO_2 is 5.6–5.7 [Trushkina, Trushkin, Demyanova, 2006], meaning values below this range suggest acidification, while higher values (as observed here) reflect alkalization.

Figure 2 presents the average concentrations of major components in snowmelt water, representing the chemical composition of the snow cover, along with the mean deposition fluxes of these components onto the underlying surface (expressed per unit area).

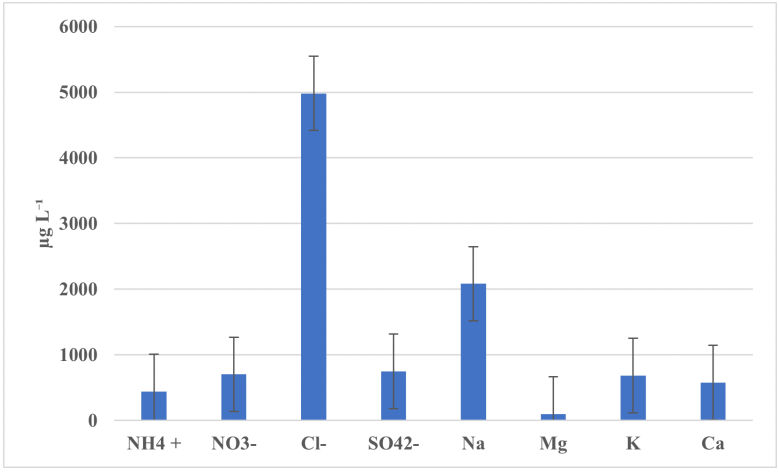

Fig. 2. Deposition of major chemical compounds in the study area (µg L^{-1})

Рис. 2. Содержание основных химических соединений в исследуемой зоне (мкг•$л^{-1}$)

Based on the molar concentration ratios of ions in snowmelt water during the study period (2021–2024), the following geochemical dominance series was established: $Ca^{2+} > Na^{+} > Cl^{-} > K^{+} > Mg^{2+} > SO_4^{2-} > NO_3^{-} > NH_4^{+}$. This ranking reflects the relative abundance of major ions, with calcium (Ca^{2+}) and sodium (Na^{+}) being the most dominant cations, followed by chloride (Cl^{-}) as the primary anion.

Chloride (Cl^{-}) was the predominant anion, with an average concentration of 4981.96 μg L^{-1} and a maximum of 8549.88 μg L^{-1}. Sulfate (SO_4^{2-}) averaged 749.33 μg L^{-1}, peaking at 1074.87 μg L^{-1}. Nitrate (NO_3^{-}) exhibited considerable variability, ranging from 290.00 to 1030.00 μg L^{-1}, with a mean value of 704.41 μg L^{-1}. Sodium (Na) averaged 2083.66 μg L^{-1} but showed a sharp decline during 2023–2024, dropping to values between 5.65 and 18.59 μg L^{-1}. Calcium (Ca) averaged 577.50 μg L^{-1}, reaching a peak of 1145.15 μg L^{-1}. Potassium (K) and magnesium (Mg) had mean concentrations of 684.72 μg L^{-1} and 99.61 μg L^{-1}, respectively. Ammonium concentrations varied widely, from 17.77 μg L^{-1} (21 January 2021) up to 1252.80 μg L^{-1}. Elevated NH_4^{+} levels suggest contributions from anthropogenic sources such as agriculture and transportation. The dominance of chloride and sodium suggests combined influences from marine aerosols and human activities. Elevated sulfate and nitrate levels point to contributions from industrial and vehicular emissions. Observed fluctuations in pH and ionic composition correlate with meteorological changes and shifting pollution sources over the study period. Overall, the pronounced spatial and temporal variability in snow chemistry highlights the need for continued source apportionment research and ongoing monitoring. These findings underscore the complex interplay between natural environmental processes and anthropogenic factors in determining the chemical characteristics of the snowpack.

The acid-neutralizing capacity of the snow cover was evaluated using the ratio of total an-ions ($A = [SO_4^{2-}] + [NO_3^{-}] + [Cl^{-}]$) to total cations ($K = [NH_4^{+}] + [Ca^{2+}] + [Mg^{2+}] + [Na^{+}] + [K^{+}]$) [Vasilevich, Beznosikov, Kondratenok, 2011; Zverev, Varvanina, Putilina, 1997]. This approach is well-founded, as cations in snowmelt water primarily originate from windborne mineral dust (e.g., carbonates, phosphates, and silicates) derived from soil and rock erosion. Upon dissolution, these minerals undergo hydrolysis, releasing hydroxide ions (OH^{-}) in quantities stoichiometrically linked to their cationic content. From the presented data (Table 1), it can be seen that the snowmelt water has K/A values > 1 (average value = 3.94). The high cation/anion ratio ($K/A = 3.94 \pm 1.2$), ranging from 2.8 to 5.1, indicates a strong carbonate buffering capacity, reflecting a significant influence of crustal cations on the alkalinity of the snowmelt water. Ratios > 1 confirm that all samples exhibited net alkaline conditions. This indicates a predominance of cations over anions in the snowmelt water, which may suggest the presence of sufficient neutralizing compounds that contribute to reducing acidity.

Table 1. Ratios of molar concentrations of the equivalent of major ions in snowmelt waters

Таблица 1. Соотношения молярных концентраций эквивалента основных ионов в талых водах

Indicator	Value
pH	6.49
$[SO_4^{2-}] / [NO_3^{-}]$	1.29
$[NH_4^{+}] + [Ca^{2+}] + [Mg^{2+}] + [Na^{+}] + [K^{+}] / [SO_4^{2-}] + [NO_3^{-}] + [Cl^{-}]$	3.94
$[Ca^{2+}] + [Mg^{2+}] / [SO_4^{2-}]$	16.36
$[Mg^{2+}] + [Na^{+}] / [Ca^{2+}] + [K^{+}]$	3.63
$[Na^{+}] / [Cl^{-}]$	1.59
$[Cl^{-}] / [Na^{+}]$	4.32
$[SO_4^{2-}] / [Cl^{-}]$	0.17

An excess of cations over anions may indicate the presence of compounds capable of neutralizing acids, which is associated with the hydrolysis processes of carbonate, phosphate, and silicate minerals. This may indicate a positive influence of natural processes on the acid-base state of the snow cover. If K/A values > 1 are recorded in conditions with a high level of anthropogenic impact (for example, near industrial zones), it may indicate the effectiveness of natural neutralization processes, despite potential pollution. High K/A values may also suggest that the snow cover in this area is less susceptible to acid precipitation, which can have positive consequences for the ecosystem, especially in conditions where acid rains can negatively affect flora and fauna. This highlights that, in this case, the snowmelt water is more balanced in terms of acid-base status, which may be related to differences in pollution sources and natural conditions. Thus, a K/A value > 1 may serve as an indicator of a more favorable acid-base state of the snow cover, which is important for assessing its impact on the environment.

The elements magnesium and sodium generally have a marine origin, while potassium is terrigenous. The ratio ($[Mg^{2+}] + [Na^{+}]$) / ($[Ca^{2+}] + [K^{+}]$) reflects the predominance of marine (> 1) or terrigenous (< 1) components. In the studied area, sodium and magnesium ions dominate over potassium and calcium ions, which is attributed to anthropogenic factors rather than the influence of marine aerosol. This assumption is supported by the $[Na^{+}]/[Cl^{-}]$, which is 1.59 indicates mixed sources. The ratio ($[Mg^{2+}] + [Na^{+}]$) / ($[Ca^{2+}] + [K^{+}]$) averages 3.63, indicating marine dominance in bulk cation balance. However, this alone is misleading: both Mg^{2+} and Na^{+} are also emitted from carbonate dust and anthropogenic sources (e.g., traffic, industry), so their abundance does not equate to marine origin. Crucially, the $[Na^{+}] / [Cl^{-}]$ ratio (1.59) is markedly higher than the seawater value (0.86), indicating excess Na^{+}, which is likely from terrigenous dust or anthropogenic inputs. Conversely, the $[Cl^{-}] / [Na^{+}]$ ratio averages 4.32 (range: 0.12–15.13), far exceeding seawater (1.16), signaling strong Cl^{-} enrichment. Thus, the elevated Cl^{-} is not marine in origin but anthropogenic. While Na^{+} and Mg^{2+} are present in marine proportions, their relative enrichment compared to Cl^{-} and K^{+}, combined with deviations in key ratios ($[Na^{+}] / [Cl^{-}]$, $[Cl^{-}] / [Na^{+}]$, $[Mg^{2+}] / [Cl^{-}]$) and co-variance with SO_4^{2-} and Cd, confirms that anthropogenic emissions have substantially altered the natural background.

The ratio of molar concentrations of the equivalent $[SO_4^{2-}] / [Cl^{-}]$ was used to determine the origin of the composition of atmospheric precipitation, as well as to assess atmospheric pollution from industrial emissions. The sulfate-to-chloride ratio ($[SO_4^{2-}] / [Cl^{-}]$) of 0.17 suggests a predominantly non-marine sulfate source. To evaluate the contribution of pollution sources to the atmosphere, the following ratios were calculated: $[SO_4^{2-}] / [NO_3^{-}]$, ($[Mg^{2+}] + [Na^{+}]$) / ($[Ca^{2+}] + [K^{+}]$), $[Na^{+}] / [Cl^{-}]$.

Table 1 demonstrates the relationship between NO_3^{-}, SO_4^{2-} и NH_4^{+}. The ratio of NH_4^{+} to NO_3^{-} in all samples is approximately 0.63. Nitrate and ammonium (NO_3^{-} and NH_4^{+}) are virtually absent in seawater and, therefore, do not correlate with sea salt, although there may be weak correlations between different classes of samples (r (NO_3^{-} / Na^{+}) = 0.39).

The content of macro and microelements in the filtrate of snowmelt water is presented in Fig.3. When compared to the maximum permissible concentrations (MPC) for water, only cadmium (Cd) was found to exceed the MPC. Thus, there are cadmium (Cd) pollutants in the snowmelt water in the studied area [GN 2.1.5.1315-03].

There is notable variability in element concentrations across different sampling dates, which may be attributed to seasonal changes, meteorological conditions, and pollution sources. In particular, the sample from 21 January 2021 stands out, with cobalt (27.79 µg/L), nickel (31.49 µg/L), and zinc (629.44 µg/L) concentrations significantly exceeding average levels, suggesting a possible short-term anthropogenic impact. Overall, the data indicate generally low levels of microelement and heavy metal contamination in the snowmelt water, with the exception of cadmium.

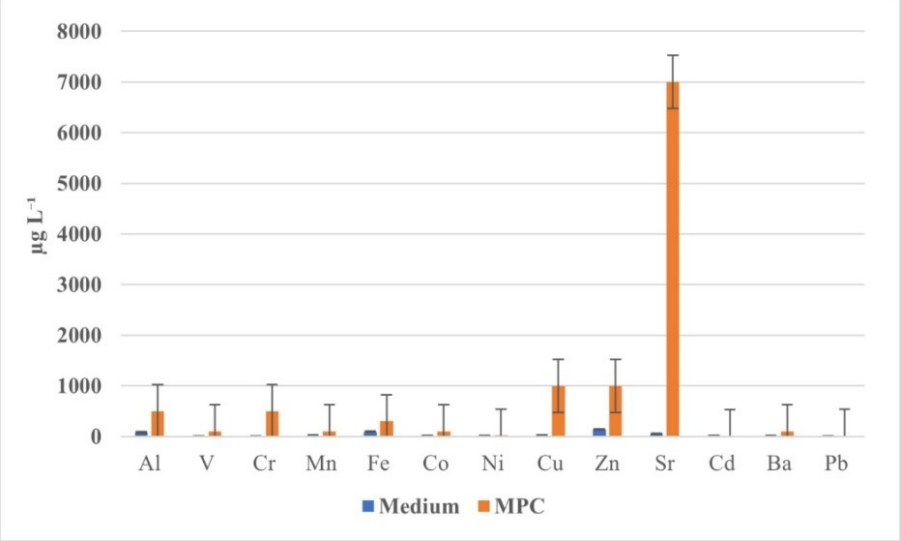

Fig. 3. Concentrations of microelements and heavy metals in snowmelt water (µg L^{-1})

Рис. 3. Концентрации микроэлементов и тяжёлых металлов в талой воде (мкг•$л^{-1}$)

The enrichment factor (EF) serves as a useful tool for estimating the relative abundance or deficiency of elements in atmospheric precipitation, distinguishing between marine and continental sources. This parameter also helps differentiate between anthropogenic and naturally occurring elements [Aničić et al., 2009]. To assess their origins, we calculated enrichment factors (EF) for selected elements (Table 2). Given the minor contribution of marine sources to overall elemental concentrations, only Na, mg, K, Ca, Sr, and Ba were considered in the analysis.

Table 2. Enrichment Factors (EF) in relation to sources of origin: Lithogenic and Marine

Таблица 2. Коэффициенты обогащения (EF) в зависимости от источников: литогенные и морские

Elements	Lithogenic	Marine
Na	86.62	1.00
Mg	5.54	0.40
Al	1.00	
K	28.46	8.85
Ca	20.28	7.25
V	4.39	
Cr	7.26	
Mn	18.70	
Fe	2.03	
Co	266.74	
Ni	157.14	
Cu	358.43	
Zn	1729.66	
Sr	152.40	32.32
Cd	32 696.28	
Ba	14.71	2617.28
Pb	96.13	

Metals with an EFcrust value close to 1 are typically derived from the natural weathering of the Earth's crust, whereas EFcrust values between 1 and 10 may reflect the influence of the local soil's chemical composition [Poissant, Schmit, Béron, 1994; Al-Momani, 2003]. Values ranging from 10 to 500 indicate moderate enrichment, while values exceeding 500 signify extreme enrichment, strongly suggesting significant pollution from anthropogenic sources [Poissant, Schmit, Béron, 1994].

According to Table 2, nearly all analyzed elements exhibit EF_{crust} values well above 10. Notably, Zn and Cd have EF_{crust} values greater than 500, classifying them as highly enriched ($EF_{crust} > 500$). Elements with moderate enrichment ($10 < EF_{crust} < 500$) include Na, K, Ca, Mn, Co, Ni, Cu, Sr, Ba, and Pb, with EF_{crust} values of 86.62, 28.46, 20.48, 18.70, 266.74, 157.14, 358.43, 152.40, 14.71, and 96.13, respectively. These values suggest enrichment from both lithogenic and anthropogenic sources, such as atmospheric pollution from industrial emissions and transportation, which are transported over long distances.

Trace metal contamination was particularly pronounced for cadmium: its concentration reached 1.8 µg/L, which was 4.2 times higher than the maximum permissible concentration (MPC), and the crustal enrichment factor (EF_{crust}) was exceptionally high at 32 696. Zinc (Zn) also showed significant enrichment (EF_{crust} = 1730), indicating industrial sources. Copper (Cu) presented a moderate enrichment (EF_{crust} = 358), suggesting mixed anthropogenic origins, while lead (Pb) exhibited enrichment (EF_{crust} = 96) primarily attributed to traffic emissions.

The EFsea value for Sr is 32.32, indicating other natural sources in addition to the sea. Additionally, Ba has EF_{sea} value of 2617.28, significantly greater than 500, reflecting a strong enrichment in snowmelt water and pointing to an anthropogenic origin. K and Ca have EF_{sea} values of 8.85 and 7.25, respectively, suggesting the influence of the chemical composition of local seawater. The EF_{sea} value for mg is 0.40, indicating dilution of this element in snowmelt water.

Wind data from 2021–2024 reveal dominant NW winds (37–86 % frequency in winter) averaging 1.8 m/s (gusts to 5.3 m/s). This pattern facilitates transport of industrial pollutants (e.g., Cd, SO_4^{2-}) from Sevastopol (85 km NW) and transboundary sources, while low speeds enhance local dust input (Ca^{2+}, Mg^{2+}).

Discussion

Snow in Crimea is characterized by a slightly alkaline pH range (6.00–7.46), indicating a neutral to moderately alkaline deposition environment. This has several ecological implications. As such snow melts, it can gradually increase soil pH, affecting the availability of nutrients. Although calcareous soils, which are widespread in Crimea, can partially buffer this effect, sensitive plant species may face certain challenges, such as: Reduced solubility of iron (Fe) and manganese (Mn), potentially leading to chlorosis in some species; Increased phosphorus (P) fixation, which may limit its availability to plants. Many tree species typical of Crimea (e.g., oak, beech, juniper) are generally tolerant of mildly alkaline conditions. However, prolonged exposure to such conditions may favor the spread of drought-resistant and calciphilous species at the expense of acid-sensitive vegetation. Snowmelt also influences the composition of streams and groundwater, where pH plays a key role in determining metal toxicity. Alkaline conditions reduce the bioavailability of toxic metals such as aluminum (Al) and lead (Pb), which benefits aquatic flora and fauna. While neutral pH is generally considered safe, fluctuations can cause stress in acid-sensitive species, including certain crustaceans and mollusks. In addition, alkaline conditions can alter soil microbial communities, slowing the decomposition of organic matter and affecting nutrient cycling. Unlike industrial regions, where snow pH often drops below 5.0 due to acid precipitation, Crimean snow is less acidic. This is likely due to the buffering effect of carbonate rich dust from local limestone and the neutralizing influence of marine sea salt aerosols. However, pH values above 7.0 may indicate the presence of anthropogenic dust (e.g., from construction or agricultural activities) or ammonia (NH_3) emissions from fertilizers or livestock operations.

The slightly alkaline pH of Crimean snow (6.00–7.46) is strongly influenced by the region's calcareous soils, which are rich in carbonates ($CaCO_3$, $MgCO_3$). These soils act as a natural buffer, neutralizing acidic deposition through the following mechanisms: (1) Carbonate Dissolution: Ca^{2+} and Mg^{2+} from limestone and dolomite dust dissolve in snowmelt, releasing bicarbonate (HCO_3^-) and hydroxyl (OH^-) ions that counteract acidity [Hunova et al., 2023]. (2) Cation Exchange: The high correlation between pH and Mg^{2+} ($r = 0.55$) confirms their dominant role in buffering, consistent with Crimea's widespread rendzina soils (shallow, carbonate-rich soils on limestone [Kotova, Topchaya, Novikova, 2023]. (3) Dust Input: Aeolian transport of alkaline dust from exposed limestone bedrock and agricultural areas further elevates snow pH, as seen in other arid/semi-arid regions (e.g., the Mediterranean, Central Asia). Unlike forested boreal zones (e.g., Siberia, Scandinavia), where soils lack carbonates and snow pH often falls below 5.0, Crimea's geology provides robust acid-neutralizing capacity. Compared to industrialized temperate regions (e.g., NE China, Eastern Europe), where anthropogenic SO_2 / NO_3 emissions dominate snow chemistry, Crimea's alkaline dust offsets acidity, yielding higher pH despite sulfate inputs.

A preliminary evaluation of natural water quality can be derived from key chemical parameters of atmospheric precipitation, specifically pH and total ion content (Σ_i). Our analysis reveals a significant positive correlation between these variables ($r = 0.67$), indicating that higher ion concentrations correspond to increased pH levels in precipitation.

The observed increase in snowmelt water acidity in the study area is principally attributed to sulfuric acid dissociation, as evidenced by the elevated sulfate-to-nitrate ratio ($[SO_4^{2-}] / [NO_3^-] = 1.29$). This sulfate predominance reflects more efficient atmospheric scavenging of sulfur dioxide compared to nitrogen oxides [Moody, Samson, 1989], consistent with established patterns of wet deposition chemistry.

The average monthly concentrations of sulfates in precipitation correlate well with their pH values ($r\ (pH/SO_4^{2-}) = 0.70$). The simultaneous occurrence of high sulfate concentrations and alkaline pH suggests a more complex mixed process rather than the mere presence of "sulfur compounds". Data from this study indicate that this correlation is most likely mediated by the co-deposition of aerosols and dust particles containing both sulfate anions and alkaline cations (particularly Ca^{2+} and Mg^{2+}). This hypothesis is strongly supported by the high correlation coefficients observed between pH and Ca^{2+} ($r = 0.65$) and Mg^{2+} ($r = 0.64$), as well as the extremely strong correlation between Ca^{2+} and Mg^{2+} themselves ($r = 0.99$). This points to a common erosional source for these cations, specifically carbonate dust particles from local soils. Therefore, the high pH is not a result of sulfate, but rather a consequence of the fact that both acidic and alkaline components are released simultaneously into the snow, with the predominance of the alkaline component (due to the abundance of carbonate dust) determining the neutral and alkaline pH values. This mechanism is consistent with studies from other regions with strong continental influence: for example, in industrial cities in Northeast China [Cao et al., 2013] and in Moscow [Eremina, Grigoriev, 2010], it was shown that suspended particles from construction sites and soil dust rich in calcium and magnesium bicarbonates effectively neutralize acidic components. Consequently, the mere interpretation of the pH–SO_4^{2-} correlation reflects the coexistence of industrial pollution sources (sulfur) and natural/anthropogenic buffers (dust). In contrast, nitrates did not have a significant impact on the acidity of the snow cover ($r\ (pH/NO_3^-) = 0.33$).

In studies conducted in northeastern China, it was shown that the calculated potential for acidification of atmospheric precipitation did not correspond to the values obtained during observations due to significant contributions from major cations (especially Ca^{2+}) present in soil dust and suspended substances of both anthropogenic and natural origin [Cao et al., 2013]. Eremina and co-authors explained the alkalinization of the snow cover in Moscow by the presence of aerosols and suspended particles from numerous construction sites in the urban agglomeration, which have an alkaline reaction (calcium and magnesium salts, bicarbonates), leading to the neutralization of acidic components in the snow [Eremina, Grigoriev, 2010]. Thus, the pH value of snowmelt water in the studied area was likely influenced by the buffering of snow cover acidity due to the increasing concentration of suspended substances in the atmospheric air, originating from both natural and anthropogenic sources.

There is a relationship between the acidity of meltwater and the concentration of calcium and magnesium ions: r (pH/Ca^{2+}) = 0.65, r (pH/Mg^{2+}) = 0.64. There is a relationship between the acidity of meltwater and the concentration of calcium and magnesium ions: r (pH/Ca^{2+}) = 0.65, r (pH/Mg^{2+}) = 0.64. The high correlation coefficients between the ions of alkali and alkaline earth metals: K^+ and Na^+ (r = 0.95), K^+ and Mg^{2+} (r = 0.99) and Ca^{2+} and Mg^{2+} (r = 0.99) indicate a common erosional source for the input of these components into the atmosphere.

Several studies attribute the increase in chloride (Cl^-) content in snow cover to its release into the atmosphere during coal combustion, as chlorine is a characteristic element of coal [Yudovich, Ketris, 2005]. In such cases, chloride concentrations would significantly exceed those of sodium, resulting in a [Cl^-] / [Na+] ratio much greater than 1. However, across most of the studied area, the [Cl^-] / [Na+] ratio ranges from 0.12 to 15.13, suggesting that chlorine is often not of marine origin.

Additionally, paired correlation analysis reveals a modest but notable relationship between chloride concentrations in snow water and magnesium (Mg^{2+}) (r = 0.26) and sodium (Na+) (r = 0.31), both elements typically associated with marine sources, which likely reflects a shared anthropogenic origin for these ions. Further supporting this, the average correlation coefficient between chloride and sulfate (SO_4^{2-}) concentrations is relatively strong (r = 0.58), indicating a common pollution source, such as coal burning during the winter season.

The molar ratio of sulfate to chloride ions ([SO_4^{2-}] / [Cl^-]) is commonly used to determine the origin of atmospheric precipitation composition and to assess atmospheric pollution from industrial emissions [Chudaeva, Chudaev, Yurchenko, 2008]. Most sulfate in the atmosphere is of non-marine origin. For example, in the background area of the Baikal Biosphere Reserve, the [SO_4^{2-}] / [Cl^-] ratio does not exceed 3 [Sanina, Sklyarova, Kostin, 2003].

In the present study, the [SO_4^{2-}] / [Cl^-] values in snow water range from 0.09 to 0.32, with an average of 0.17. These low ratios support the conclusion that the chloride ions observed in the study area primarily originate from fuel combustion emissions at thermal power plants during the winter season, rather than from marine sources.

The acidity of snow water, as described in the work, is due to the high content of sulfates, which is confirmed by the [SO_4^{2-}] / [NO_3^-] ratio equal to 22.1 [Gladun, Shelganova, Mayorova, 2024]. The effectiveness of acidity neutralization at the “Khabarovsk” station showed an excess of neutralizing compounds (K/A ranging from 2 to 5), with the main components being the cations Ca^{2+} and Mg^{2+}. The change in the ratio of [Mg^{2+} + Na^+] / [Ca^{2+} + K^+] from 1.8 to 0.8 indicates an increase in the emission of cations Ca^{2+} and K^+ into the atmosphere. The low value of [Cl^-] / [Na^+] (from 0.1 to 0.4) suggests a marine origin for the Cl^- ions, which is supported by the change in the [SO_4^{2-}] / [Cl^-] ratio from 4 to 6. For Blagoveshchensk, the average value of this ratio was 10.64 [Radomskaya, Yusupov, Pavlova, 2014].

The study [Vasilevich, Beznosikov, Kondratenok, 2011] showed that meltwater in the taiga zone has a K/A ratio of less than 1, in-creasing from south to north from 0.42 to 0.83 (with an average of 0.58). This indicates a deficiency of neutralizing compounds and a predominance of hydrogen ions, which corresponds to the overall situation in Russia, where cations account for about 30 % of the total ion content, excluding hydroxide ions and hydrogen ions.

In the study [Surkova, Eremina, Zorina, 2005], the authors showed that in the area of the Northeast coast of the Black Sea, the most evident sign of the predominance of continental influence on the chemical composition of precipitation is the high concentrations of SO_4^{2-} and NH_4^+. Calcium, on the other hand, is present in similar ratios in both marine and continental precipitation.

The presented ratios of major ions indicate a trend in the changing chemical composition of the snow cover across all meteorological stations, with Ca^{2+} becoming the dominant ion. It is known that the main sources of cations Ca^{2+} and Mg^{2+} entering the atmospheric air are aerosols from sea salt, dust

from aeolian deposits, industrial emissions, and suspended particles related to transportation. Sources of NO_x and SO_x emissions include energy and heating facilities, motor vehicles, industry, and municipal solid waste landfills. Sources of NH_3 emissions include agriculture, municipal solid waste landfills, the aftermath of forest fires, and industry [Duan et al., 2016; Vet et al., 2014]. Anions such as sulfates and nitrates typically form in the atmospheric air as a result of the oxidation of SO_2 and NO_2.

Mg^{2+} and K^+ are correlated with seawater and can enter snowmelt water either through dust deposition or precipitation, as well as via substitution in other minerals such as mirabilite. The low enrichment factor for Mg^{2+} (EF = 0.83) suggests minimal fractionation among its sources, indicating relatively uniform contributions. In contrast, the moderate enrichment of K^+ (EF = 13.41) points to an additional minor source unrelated to sea salt, likely dust. Fractionation of Mg^{2+} and K^+ sources may occur during precipitation processes, which become thermodynamically favorable at low temperatures [Weeks, Ackley, 1986]. While minerals formed from freezing seawater are typically pure stoichiometric phases, natural solid solutions and ionic substitutions can significantly alter the composition of precipitated minerals. For example, Mg^{2+} and K^+ can substitute for other ions in sea salt minerals, such as calcium (Ca^{2+}) in ikaite and sodium (Na^+) in mirabilite.

In seawater, the concentration of Mg^{2+} is roughly five times higher than that of Ca^{2+}, making it easier to detect Ca^{2+} enrichment against the relatively low sea salt baseline. Conversely, mineral dust typically contains more Ca^{2+} than Mg^{2+}. The observed enrichment of Ca^{2+} (EF = 28.95) from atmospheric deposition is attributed to the input of atmospheric dust, where the Ca^{2+} / Mg^{2+} ratio is substantially greater than 1.

The sources of NO_3^- and NH_4^+ in the snowpack exhibit greater stability compared to sea salt, and their transport patterns are consistent across all studied environments. Both nitrate and ammonium undergo biological transformations within the snowpack, leading to a more uniform distribution and weaker correlation with sea salt. Given that NO_3^- and SO_4^{2-} are primarily anthropogenic pollutants, a correlation between them is expected, as demonstrated in prior studies on aerosols and snow [Toom-Sauntry, Barrie, 2002]. However, the observed correlation in this dataset spans a wide range, reflecting high variability and distinct transport pathways across different environments.

For terrestrial snow, which is most comparable to the coastal/inland studies by Toom-Sauntry and Barrie [Toom-Sauntry, Barrie, 2002] and Yalcin et al. [Yalcin et al., 2006], the NO_3^- / SO_4^{2-} ratio ranges from 0.31 to 2.09. This range differs slightly but overlaps with Toom-Sauntry & Barrie's reported values (0.2–0.6) and aligns closely with Yalcin et al.'s ratio of 1.09, which is similar to our average (0.94). Nitrate levels in Barrow are higher than those in Alarte, likely due to the older snow sampled in Barrow compared to the freshly fallen snow analyzed in Alarte. Additionally, the elevated sea salt content in Barrow may promote a more alkaline snowpack pH, enhancing nitric acid absorption and further contributing to the observed nitrate enrichment.

The chemistry of snow nitrates, extensively examined in the literature [Yalcin et al., 2006; Honrath et al., 1999; Honrath et al., 2000], indicates that their relationships with other ions in snow are generally more complex than those of sulfates. This complexity arises because sulfuric acid and sulfate salts are non-volatile, whereas nitric acid is semi-volatile, although nitrate salts themselves are not volatile. As a result, older atmospheric particles can convert nitric acid into less volatile salt forms (e.g., $NaNO_3$) that become retained within the snowpack. Nitrate behavior is further complicated by the fact that their sources extend beyond sea salt aerosols and chemical losses, potentially involving in-snowpack processes as well. Therefore, the lack of correlation between nitrates and sea salt tracers observed in this study is not unexpected. To fully understand nitrate dynamics, more detailed analyses or additional research are needed, accounting for the temporal evolution of snow samples and variations in photochemical conditions.

Given the influence of snowmelt pH on trace element distribution, we evaluated Pearson correlation coefficients between snow water pH and elemental concentrations (Table 23). Mn, Co, Ni, Cd, and Pb showed negligible dependence on pH, with weak negative correlations (r = −0.14, −0.16, −0.13, −0.10, and −0.14, respectively). Several elements demonstrated moderate positive correlations with pH. Aluminum showed the most pronounced relationship (r = 0.61). Mg and Na had moderate associations Mg (r = 0.55), Na (r = 0.43). K, Fe and Ba showed weaker but significant relationships K (r = 0.31), Fe (r = 0.29), Ba (r = 0.22). This differential behavior suggests varying solubility controls and chemical interactions between these elements and the snow matrix as pH changes. The stronger positive correlations for Na, Mg, and Al may reflect their preferential release under less acidic conditions, while the pH-independent elements likely have solubility controlled by other factors.

We analyzed the relationship between pH and the alkali metals Na, Mg, and K separately. The results indicate a clear positive correlation between pH and these elements, whereas pH appears largely independent of Ca concentrations. This suggests that Na, Mg, and K contribute to neutralizing rainwater in the study area.

Variations in the pH of atmospheric precipitation significantly impact element solubility. According to [Grannas et al., 2007], the solubility of Cr, Ni, and Pb increases twofold or more at pH levels below 5.0. In contrast, highly soluble elements such as K, Ca, Cd, and V show no pH-dependent solubility changes. Given that trace element distribution is influenced by snow water pH, we calculated Pearson correlation coefficients between pH and the concentrations of the studied elements. The most significant positive correlation is observed with SO_4^{2-} (r = 0.70). As discussed in detail above, this coefficient should not be interpreted as a direct acidifying effect, but rather as an indication of the co-deposition of industrial pollutants (sulfates) and alkaline dust (rich in Ca^{2+}, Mg^{2+}) from both anthropogenic (e.g., construction) and natural (carbonate soils) sources, in which the cations effectively neutralize sulfuric acid. The correlation with Al (r = 0.61) and Mg (r = 0.55) also suggests that these elements may contribute to pH neutralization, making them important for assessing the acid-base balance. Na (r = 0.43) and Cl^- (r = 0.52) also show a positive relationship, which may indicate the influence of marine aerosols and other sources related to atmospheric precipitation. K (r = 0.31) and NO_3^- (r = 0.31) have moderate positive correlations, which may point to their relationship with changes in pH, possibly due to agricultural activities or other sources. Fe (r = 0.29) and Ba (r = 0.22) also exhibit weak positive correlations, which may indicate their presence in precipitation, possibly due to soil weathering or anthropogenic sources. The most pronounced negative correlation is observed with Cr (r = −0.34), which may indicate differences in sources and deposition processes. Other elements, such as Co (r = −0.16), Ni (r = −0.13), and Cd (r = −0.10), also show weak negative correlations with pH, suggesting that their concentrations are only slightly dependent on the acidity of snow water. For elements such as V (r = 0.07), Zn (r = 0.03), and Sr (r = −0.30), the correlation with pH is virtually absent, indicating their concentrations may be independent of acidity levels.

The correlation coefficients for major ions calculated for all snow samples indicate that Cl and Na are independent of each other, reflecting their different origins. Table 23 shows that Na has a positive correlation with Mg and K (r = 0.95 and 0.97, respectively), and Mg shows a positive correlation with Ca and Fe with Mn (r = 0.94 and 0.87, respectively). This may be related to common sources such as marine aerosol dust or geological processes. At the same time, Cd has a moderate negative correlation with Na and Ca (r = −0.66 and −0.80, respectively), indicating differences in sources or deposition processes. Other elements, including Co, Ni, Cu and Zn, exhibit weak correlations both among themselves and with other elements, suggesting a variety of sources or the influence of multiple factors such as anthropogenic activities or local geological conditions. It is also important to highlight that the primary sources of sodium (Na) are sea salt and atmospheric aerosols, particularly in coastal regions. Mg and Ca originate from mineral sources and dust and may also be related to agricultural activities. Meanwhile, Fe and Mn may come from soil and rocks as well as from industrial emissions. Heavy metals (Cd, Pb, Cu) often have anthropogenic origins related to industrial pollution, vehicular traffic, and other sources.

Table 3. Pearson correlation matrix of element concentrations and ions in atmospheric precipitation ($p < 0.05$)

Таблица 3. Матрица корреляции Пирсона концентраций элементов и ионов в атмосферных осадках ($p < 0,05$)

	Na	Mg	Al	K	Ca	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Sr	Cd	Ba	Pb	NH_4^+	NO_3^-	Cl^-	SO_4^{2-}	pH
Na	1.00	0.95	0.58	0.97	0.78	0.75	–0.31	0.49	0.96	0.23	0.22	0.59	0.37	–0.45	–0.56	0.91	0.17	–0.81	–0.25	–0.18	–0.02	0.43
Mg		1.00	0.73	0.94	0.78	0.76	–0.27	0.51	0.95	0.28	0.27	0.56	0.39	–0.42	–0.54	0.91	0.22	–0.74	–0.13	0.00	0.12	0.55
Al			1.00	0.52	0.31	0.73	–0.22	0.12	0.59	–0.19	–0.23	0.07	–0.15	–0.18	–0.22	0.50	–0.27	–0.25	0.25	0.15	0.25	0.61
K				1.00	0.80	0.79	–0.28	0.58	0.96	0.29	0.28	0.60	0.39	–0.46	–0.58	0.92	0.23	–0.83	–0.28	–0.20	–0.04	0.31
Ca					1.00	0.52	0.22	0.89	0.85	0.66	0.75	0.87	0.74	–0.02	–0.77	0.95	0.78	–0.80	–0.17	–0.31	–0.16	0.14
V						1.00	–0.28	0.40	0.82	0.03	–0.04	0.19	0.00	–0.32	–0.30	0.73	–0.14	–0.53	–0.16	–0.28	–0.26	0.07
Cr							1.00	0.52	–0.24	0.16	0.16	0.43	0.12	0.88	–0.49	–0.02	0.38	–0.04	0.34	–0.39	0.04	–0.34
Mn								1.00	0.59	0.61	0.66	0.87	0.61	0.32	–0.75	0.77	0.79	–0.59	0.06	–0.51	–0.21	–0.14
Fe									1.00	0.40	0.39	0.57	0.48	–0.42	–0.55	0.97	0.33	–0.81	–0.32	–0.18	–0.16	0.29
Co										1.00	0.99	0.48	0.96	–0.11	–0.21	0.51	0.95	–0.42	–0.43	0.08	–0.32	–0.16
Ni											1.00	0.59	0.98	–0.05	–0.41	0.54	0.99	–0.56	–0.33	0.03	–0.39	–0.13
Cu												1.00	0.62	0.25	–0.86	0.74	0.74	–0.64	0.11	–0.43	0.05	0.18
Zn													1.00	–0.16	–0.30	0.59	0.95	–0.52	–0.41	0.08	–0.21	0.03
Sr														1.00	–0.12	–0.22	0.02	0.33	0.65	–0.49	–0.05	–0.30
Cd															1.00	–0.69	–0.44	0.84	0.25	0.21	–0.32	–0.10
Ba																1.00	0.52	–0.82	–0.22	–0.29	–0.18	0.22
Pb																	1.00	–0.51	–0.50	0.14	–0.13	–0.14
NH_4^+																		1.00	0.54	0.16	–0.02	–0.12
NO_3^-																			1.00	–0.16	0.34	0.31
Cl^-																				1.00	0.58	0.52
SO_4^{2-}																					1.00	0.70
pH																						1.00

Due to the lack of data on the chemical composition of the snow cover in Crimea, we compared our findings with those from a study on elemental content in rainwater [Grannas et al., 2007], conducted on the Crimean Peninsula over a decade ago. Our enrichment values were found to be an order of magnitude higher. This discrepancy may be attributed to various factors, including increased anthropogenic activities such as rapid urbanization, population growth, and higher vehicle usage, as well as changing meteorological conditions, climate change, and shifts in biogeochemical processes within the ecosystem. Additionally, trace elements can be transported by winds. Studies [Kaya, Tuncel, 1997; Kayukova, 2011] have shown that winds originating from industrial regions play a primary role in carrying dust containing trace elements.

The EF analysis revealed the following element enrichment sequence: Fe < V < Mg < Cr < Ba < Mn < Ca < K < Na < Pb < Sr < Ni < Co < Cu < Zn < Cd. All macroelements, except Mg showed higher soil concentrations than Earth's crustal reference values. The decreasing order of enrichment coefficients for macroelements is: Na > K > Ca > Mg. Discrepancies arise because atmospheric aerosols do not perfectly mirror soil composition. Dust is enriched in Fe/Mn oxides and contains variable proportions of Si, Al_2O_3, carbonates, and calcite [Topchaya et al., 2020; Stachurski, Zimka, 2000].

As for trace elements, most exhibited EF > 500, with the sequence: Cd > Zn > Cu > Co > Ni > Sr > Pb > Mn > Cr > Ba > V > Fe. Notably, Cd has a very high EF of 32 696.28. The striking enrichment factor (EF) of cadmium (Cd) suggests significant anthropogenic contamination, as natural sources alone cannot account for such elevated levels. Several potential local and regional sources may contribute to this enrichment: Past industrial operations in Crimea, such as iron ore processing and coal combustion residues, may have left behind cadmium pollution in the environment; Vehicle-related emissions: Cadmium is released through tire wear, brake pad abrasion, and the combustion of lubricants, making road traffic a notable source of Cd in urban and roadside environments; Agricultural practices: Widely used in Crimean agriculture, phosphate fertilizers often contain cadmium as an impurity. Additionally, the use of sewage sludge and certain older pesticide formulations may introduce Cd into the environment; Industrial emissions from Eastern Europe: Air masses originating from heavily industrialized regions of Ukraine and Russia can transport cadmium-rich particles over long distances, contributing to atmospheric deposition in Crimea; Black Sea shipping: Marine traffic, including fuel combustion and cargo emissions, may also be a source of cadmium pollution in coastal areas.

Other heavy metals, including Zn, Co, Cu and Ni, also display high enrichment factors (EF), pointing to their anthropogenic origins. The EF values of the remaining elements indicate contributions from both natural and anthropogenic sources.

To evaluate how wind conditions affect the chemical composition of snow, we conducted a Pearson correlation analysis between wind speed (both average and gusts) and concentrations of major ions and trace metals in snowmelt water collected between 2021 and 2024. Cl^-, Na^+, Mg^{2+}, K^+, Ca^{2+} showed strong positive correlations (r > 0.6) with both average wind speed and gusts. This suggests that higher wind velocities enhance the atmospheric transport of sea salt aerosols (Cl^-, Na^+) and mineral dust particles (Mg^{2+}, K^+, Ca^{2+}) from local soils. The particularly strong association with chloride (r = 0.71) confirms the marine influence on snow chemistry in coastal Crimea. NH_4^+, NO_3^- exhibited weak negative correlations (r ≈ −0.4). This inverse relationship likely reflects their origin from local non-wind-dependent sources such as agricultural activities, vehicle emissions, and industrial processes. The lack of significant correlation of sulfate (SO_4^{2-}) (r = −0.25) indicates that sulfate deposition is primarily governed by stationary emission sources (e.g., fossil fuel combustion) rather than wind-driven transport mechanisms. Al, Fe, Mn, Sr, Ba) displayed moderate to strong positive correlations (r = 0.51–0.64), consistent with their derivation from wind-eroded soil particles. Aluminum (r = 0.62) and strontium (r = 0.64) showed particularly strong associations, highlighting the importance of local limestone dust in metal transport. Cd, Pb exhibited negative correlations (r ≈ −0.4), implying that their deposition

patterns are dominated by nearby emission sources (e.g., industrial facilities, urban traffic) rather than atmospheric circulation. V, Cr, Co, Ni, Cu, Zn showed no significant wind dependence ($|r| < 0.4$), suggesting complex deposition pathways involving both natural weathering and anthropogenic inputs. The robust correlations between wind speed and marine-derived elements (Na^+, Cl^-, Mg^{2+}) confirm that sea spray is a major source of ions in Crimean snow, particularly during high-wind periods. Strong associations between wind velocity and crustal elements (Al, Ca^{2+}, Fe, Sr) reflect the importance of local soil erosion, especially from carbonate-rich landscapes characteristic of Crimea. The lack of wind correlation for Cd, Pb, and nitrogen compounds suggests these pollutants originate from fixed emission sources with limited atmospheric dispersion.

This study demonstrates that wind speed plays a crucial role in governing the deposition of marine and terrestrial components in Crimean snow, while anthropogenic contaminants follow distinct deposition patterns. The carbonate geology of Crimea strongly influences snow chemistry through dust emissions.

Crimea's snow, though rare, provides a sensitive indicator of rising anthropogenic pressures (urbanization, agriculture, transport). The stark Cd EF increase compared to decade-old rainwater data [Yalcin et al., 2006] underscores accelerating contamination. Alkaline snowmelt may enhance soil carbon sequestration (via Ca^{2+}-organic matter binding), but Cd/Pb accumulation could disrupt microbial communities. Source apportionment (e.g., Pb isotopes for Cd tracing) is critical to mitigate emissions from coal combustion, fertilizers, and traffic.

Snow chemistry data from the Karadag Nature Reserve reveal two critical, synergistic threats to its unique biodiversity: alkaline snowmelt and extreme cadmium (Cd) contamination. Wind-blown carbonate dust from Crimea's limestone geology elevates snow pH, favoring calciphilous plants while suppressing calcifugous species and reducing bioavailability of Fe and Mn, thereby impairing growth of sensitive vegetation on nutrient-poor soils. More alarming is Cd enrichment (EF > 32 000), among the highest recorded globally. Despite low annual deposition, chronic Cd input leads to bioaccumulation in plants, entering food chains and biomagnifying in predators (insects → rodents → birds, reptiles, mammals), causing toxicity, reduced reproduction, and population declines. Alkaline conditions may stabilize Cd in organic matter, creating a long-term reservoir and potentially enhancing plant uptake, which represents a dangerous synergy. Though protected from direct land use, Karadag cannot escape atmospheric pollution. Snow, though rare, acts as a sensitive integrator of airborne contaminants, with Cd levels rising sharply since 2006 due to urbanization, phosphate fertilizers, and traffic emissions. While alkaline snowmelt may enhance soil carbon storage, Cd and Pb accumulation disrupt microbial function and nutrient cycling. Urgent action is needed: integrate long-term atmospheric monitoring into conservation planning and conduct isotopic source apportionment (e.g., Pb isotopes) to target emissions from coal, fertilizers, and vehicles. Without intervention, Karadag's biodiversity faces silent erosion, not from habitat loss, but from invisible, accumulating toxins.

Conclusions

The acidity of snowmelt in the studied area is buffered by sulfates and cations, which maintains a weakly alkaline reaction. This is influenced by both natural and anthropogenic sources. High values of the cation to anion ratio (K/A > 1) indicate a positive effect of natural processes on reducing acidity, which is beneficial for the ecosystem. However, anthropogenic factors, such as emissions from coal combustion, significantly impact the chemical composition of snowmelt, as evidenced by the high content of sulfates and chlorides. Comparisons with other regions show that the acid-base status of snowmelt depends on pollution sources and natural conditions, high-lighting the importance of regional studies. The concentration of Mg^{2+} in seawater exceeds that of Ca^{2+}, which explains the enrichment of the latter in snow,

likely from atmospheric dust. The ratio of NH_4^+ to NO_3^- is approximately 0.63, indicating constant sources of these ions in the snow cover. Contrary to expectations, the correlation between nitrates and sulfates shows high variability and different transport pathways. Further research is needed for a better understanding of the interactions affecting the chemical composition of snow.

The results showed that the only element exceeding the maximum allowable concentrations is Cd, indicating contamination. Correlation analysis revealed that the pH of snowmelt is almost uncorrelated with trace elements such as Mn and Pb, while a positive correlation is observed with Na, Mg, and Al, indicating their role in neutralizing rainwater. Changes in the pH of atmospheric precipitation affect the solubility of elements, increasing the bioavailability of elements such as Cr, Ni, and Pb at pH levels below 5.0. Anthropogenic sources of pollution, including industrial impacts, significantly influence the distribution of elements, as evidenced by high EF for Cd and Zn.

This study highlights the value of episodic snowfall as a critical archive of atmospheric pollution in the Mediterranean climates. Key findings include: (1) the first evidence of industrial cadmium contamination (EF > 32 000) within protected areas of Crimea; (2) identification of coal combustion and fertilizer use as priority targets for pollution control; (3) validation of snow-based monitoring as an effective tool in regions with infrequent precipitation. For future research we recommend: (1) implementing year-round aerosol sampling combined with on-site anemometry to track pollutant transport; (2) using Pb/Cd isotope ratios to differentiate between local and transboundary pollution sources; (3) assessing the role of forest canopy interception and quantify pollutant transfer from snow to soil.

Although constrained by the region's limited snowfall, this research shows that even rare snow events can provide disproportionately valuable insights into anthropogenic impacts on sensitive coastal ecosystems. Addressing these climatic limitations will help refine future monitoring efforts and inform effective pollution mitigation strategies.

Consequently, these findings underscore the importance of monitoring atmospheric precipitation quality and evaluating the effects of human activities on the ecosystem. This will be crucial for developing effective strategies to minimize pollution and safeguard the environment.

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ХИМИЧЕСКИЙ СОСТАВ СНЕЖНОГО ПОКРОВА В ЛЕСНЫХ ЭКОСИСТЕМАХ КРЫМА: НА ПРИМЕРЕ КАРАДАГСКОГО ПРИРОДНОГО ЗАПОВЕДНИКА

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Аннотация: Целью исследования является анализ химического состава снежного покрова и распределения макроэлементов в нём на территории Карадагского природного заповедника (Крым), где снегопады редки. Пробы снега, отобранные в зимний период с 2021 по 2024 год на фоновой станции экологического мониторинга, проанализированы на содержание ионов и кислотность. Выявлено, что кислотность варьирует от 6,00 до 7,46 с преобладанием сульфатов, что свидетельствует об антропогенном влиянии. Химический состав определяется как природными, так и антропогенными факторами. Высокое соотношение катионов к анионам указывает на буферные процессы, снижающие кислотность, что может положительно влиять на экосистему. Результаты подчёркивают необходимость мониторинга атмосферных осадков для оценки антропогенных воздействий.

Ключевые слова: химический состав, снежный покров, лесные экосистемы, Крым, Карадагский природный заповедник

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