forests

MDPI

Type of the Paper (Article)

Biogenic elements of atmospheric fallout and the impact of sub-Mediterranean forest communities of downy oaks on changes in the chemical composition of atmospheric precipitation

Cam Nhung Pham[1,*], Roman Gorbunov[1], Vladimir Lapchenko[2], Tatiana Gorbunova[1,3] and Vladimir Tabunshchik[1]

[1] A.O. Kovalevsky Institute of Biology of the Southern Seas of RAS, Sevastopol, Russia
[2] T.I. Vyazemsky Karadag Scientific Station – Nature Reserve of RAS – Branch of A.O. Kovalevsky Institute of Biology of the Southern Seas of RAS, Feodosia, Russia
[3] Peoples' Friendship University of Russia (RUDN University), Moscow, Russia

* Correspondence: nhung5782@gmail.com; Tel.: +79785291392

Abstract: In this work, studies of the biogenic composition of atmospheric precipitation and its change during the passage through the crowns of trees of a downy oak forest were carried out. First of all the content of rainwater-soluble compounds of all the considered elements in the rainwater under the forest canopy is higher than in the rainwater in the open area. It was revealed that the main forms of nitrogen in atmospheric fallout are nitrates and ammonium. Average concentrations of nitrogen anions in rainwater collected under the canopy are higher than in rainwater collected in an open area. The proportion of nitrite nitrogen in rainwater under the canopy is 6% higher than in rainwater collected in the open area. Simultaneously with the increase in the proportion of nitrite nitrogen, nitrate nitrogen decreased. For all considered biogenic substances, an increase in their content is observed in the warm period of the year. There is an inverse relationship between the concentration of inorganic nitrogen and phosphorus in precipitation and relative air humidity and wind speed. It has been established that the pH of precipitation falling under the crowns of trees is lower than the pH of precipitation in open areas. It was revealed that the increase in the concentration of biogenic elements in accordance with the phases of plant development during the growing season.

Keywords: atmospheric fallout, biogenic elements, chemical composition of precipitation, under the forest canopy, rainwater, downy oak forests.

Citation: To be added by editorial staff during production.

Academic Editor: Firstname Lastname

Received: date
Revised: date
Accepted: date
Published: date

Copyright: © 2023 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Atmospheric precipitation not only contributes to the removal of impurities from the atmosphere, but also leads to the entry of various chemical elements into the surface waters of land and the world ocean. The high efficiency of forest functioning is achieved due to the intensive and constant exchange of matter in the system atmosphere-forest canopy-soil. The chemical composition transformation of atmospheric water occurs after interaction with aboveground phytomass of forest stands. Precipitation is included in the biogeocenosis and actively affects the biological cycle. At the same time, the atmosphere is a significant source of biogenic elements, such as, for example, nitrogen, phosphorus, and silicon, which most often limit the development of the productivity of aquatic ecosystems [1,5,7].

Forest ecosystems have a significant impact on changes in the chemical composition and amount of precipitation. Passing through the crowns of woody plants, atmospheric

precipitation undergoes a number of transformations that lead to a change in its initial amount and chemical composition [4–7]. This leads to an increase in the content of most components of the under the forest canopy rainfall, in comparison with atmospheric precipitation, including biogenic elements [4, 7]. In particular, sodium and potassium are washed out directly from the leaves and tissues of plants [8]. Rainfall carries out the transfer of elements from the atmosphere to ecosystems and provides biogenic cycles in the plant-soil system. The authors of [5, 8] found that different woody vegetation has a different effect on the formation of rainwater acidity and the content of certain components in them. For all elements, there are both facies differences in their supply to the underlying surface, and intrafacial differences – under different trees and within their under the canopy space. This is a consequence of the biochemical features of the tree and the actual landscape-geochemical conditions of its growth [7–9, 10]. The effect of deciduous forest stands on the chemical composition of rainfall and surface waters, especially the microelement composition, is poorly understood.

The chemical composition of atmospheric precipitation and the content of biogenic elements in atmospheric precipitation on the territory of the Crimea were studied earlier [11–17]. These works were carried out in Sevastopol, Katseveli, Trudolyubovka, which are under technogenic influence. In environmentally friendly places and reserves, the content of biogenic and other chemical elements in precipitation, as well as the influence of the forest canopy on the chemical composition of precipitation on the territory of the Crimean Peninsula, has not been studied.

The purpose of this paper is to assess the content of biogenic substances (nitrogen, phosphorus) in precipitation and its change when passing through the crowns of trees of a downy oak forest on the Karadag State Nature Reserve territory.

2. Materials and Methods

The studies were carried out on the territory of the Karadag State Nature Reserve (Fig. 1). The Background Environmental Monitoring Station (BEMS) is located on the territory of the reserve, on the northeastern slope of mountain Svyataya on a site with steppe vegetation with isolated trees. The bordering forest area, in which precipitation was collected, is a downy oak-ash forest with dogwood in the undergrowth (crown density up to 60%). The distance to the nearest village Koktebel is about 1.5 km. The station is separated from the sea by the Kok-Kaya Ridge (320 m) [18].

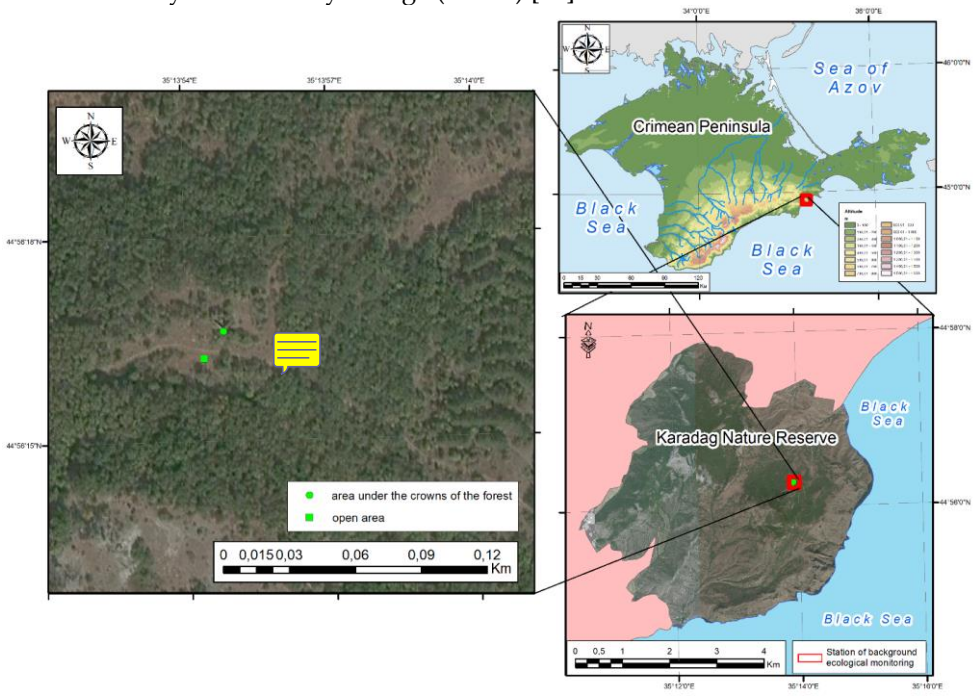


Figure 1. Study area map

Precipitation was collected monthly by sediment collectors with a height of 59 cm and a diameter of 26.5 cm. At the same time, accounting and analysis of atmospheric precipitation was carried out in an open area and under the forest canopy (Fig. 2). After each rain, the precipitation was poured into sterile containers. The resulting rainwater was delivered to the laboratory. Preparation of samples for analysis and laboratory analysis of the content of biogenic substances in the atmospheric precipitation of the selected samples were carried out in the scientific and educational collaborative center "Spectrometry and Chromatography" at the Research Center of IBSS (Sevastopol).



Open area	Under the forest canopy

Figure 2. Monitoring point for the content of biogenic elements in atmospheric fallout

All studied biogenic elements were determined by spectrophotometry, on a KFK-Z ZOMZ photometer. The method for determining the nitrate ion is based on the reduction of nitrates to nitrites. Copper-plated cadmium is used as a reducing agent, and EDTA Diatrium salt (Trilon B) is used as a complexing agent. The nitrite ion was determined by the Bendschneider and Robinson method. Ammonium nitrogen in precipitation was determined by the Seji-Solorzano method. Inorganic phosphate in the form of $H_2PO_4^-$ was determined by the Murphy-Riley method, which is based on the formation of a phosphomolybdenum complex and its subsequent reduction to a strongly colored blue compound [19].

Weather conditions data were recorded at the WS 600 weather station, which is installed on the territory of the BEMS. Climate data is recorded every hour.

For a detailed study of the relationship between factors (concentrations of nitrite ion, nitrate ion, ammonium ion, inorganic phosphorus, pH value, precipitation, relative humidity, wind speed), we calculated Pearson's correlation coefficients.

3. Results

3.1. Acidity

One of the most important indicators of the chemical composition of atmospheric precipitation is their acidity. Figure 3 shows the change in the pH of precipitation in the period from April 2021 to January 2022.

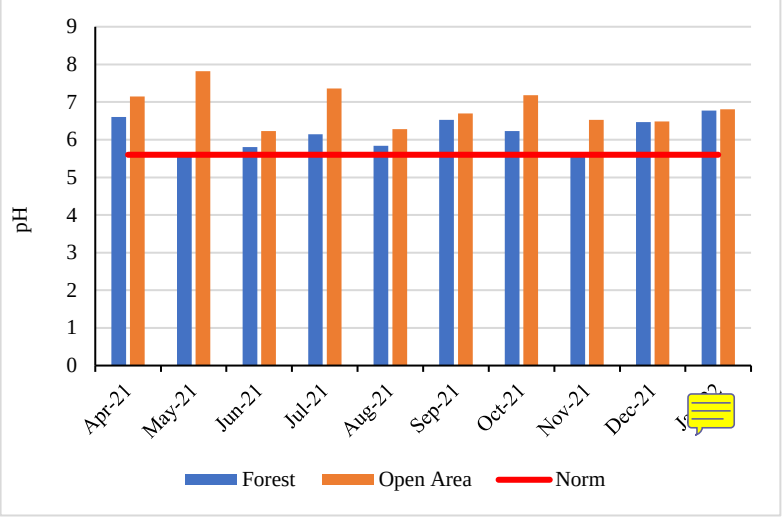


Figure 3. Changes in the pH of precipitation by months

The chart shows that during the research period in this area, pH = 6.23 ÷ 7.82 (average value 6.8). For rainwater that has passed through the canopy of trees, this indicator decreases pH = 5.55 - 6.77 (average value 6.1). However, in May 2021 the pH of rainwater collected in the open area had the highest value (pH = 7.82), and the pH of rainwater under the forest canopy had the lowest pH value of 5.55. Figure 3 shows the average contents of all considered elements for the entire period of the study. It shows that the content of rainwater-soluble compounds of all the considered elements in the rainwater under the forest canopy is higher than in the rainwater in the open area.

3.2. Inorganic nitrogen

Inorganic nitrogen compounds in natural water – ammonium ions, nitrous and nitric acids – appear mainly as a result of the final decomposition of protein origin substances. The relative contribution of nitrogen-containing ions to the composition of atmospheric precipitation is shown in Figure 4. Average concentrations of nitrogen anions in rainwater collected under the canopy are higher than in rainwater collected in an open area

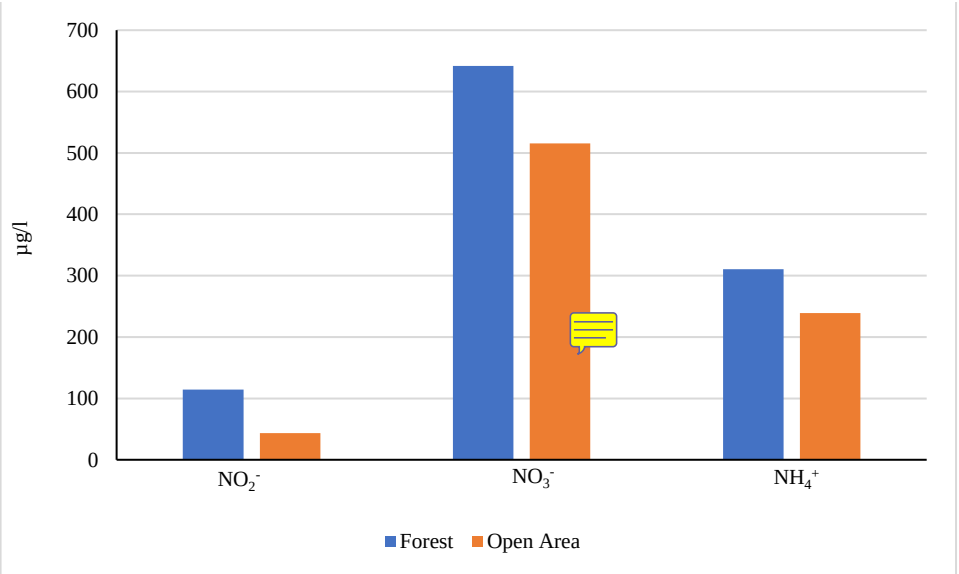


Figure 4. Average content of nitrogen in precipitation (µg/l) for the period 04.2021 – 01.2022

Priority forms of inorganic nitrogen are still nitrate and ammonium nitrogen (Fig. 5). The share of nitrate nitrogen in rainwater under the canopy and the share in rainwater collected in the open area was 65% and 60%, respectively. However, the proportion of nitrite nitrogen in rainwater under the canopy is 6% higher than in rainwater collected in the open area, which is 11% and 5%, respectively. Simultaneously with the increase in the proportion of nitrite nitrogen, nitrate nitrogen decreased from 65% in open areas to 60% under canopy, and ammonium nitrogen from 31% in open areas to 29% under canopy. Here it should be noted that the order of the relative contribution of nitrogen-containing ions in rainwater in the open area and under the forest canopy has not changed (NO_3^- >NH_4^+>NO_2^-).

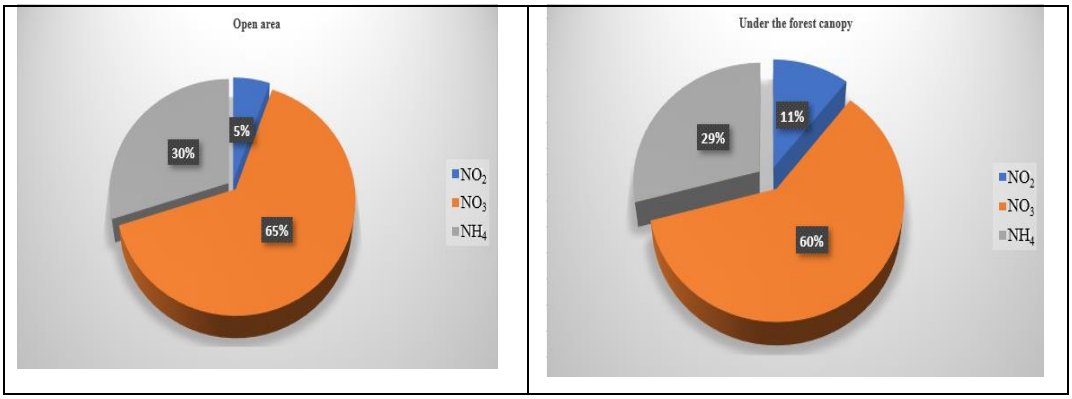


Figure 5. Relative contribution of nitrogen-containing ions

The acidity of rainwater in one area may differ from the acidity of rainwater in another area. This depends on the composition of gases contained in the atmosphere of a particular area, such as sulfur oxide and nitrogen oxides.

There was a sharp increase in nitrite in rainwater collected under the canopy in June. There is also a sharp increase in the content of the nitrate ion in May 2021 in the rainwater under the forest canopy and the ammonium ion in September 2021 (Fig. 6). This increase affects the total content of the resulting nitrogen ions. The average content of nitrogen ions in rainwater under the forest canopy is higher than in rainwater collected in an open area (Fig. 4). But in fact, all year round, the content of inorganic nitrogen under the forest canopy is less than in the open area. Often, in the rainwaters that passed through the forest canopy (in some months), only “traces” of nitrite and ammonium were found, which testifies in favor of their absorption by woody vegetation.

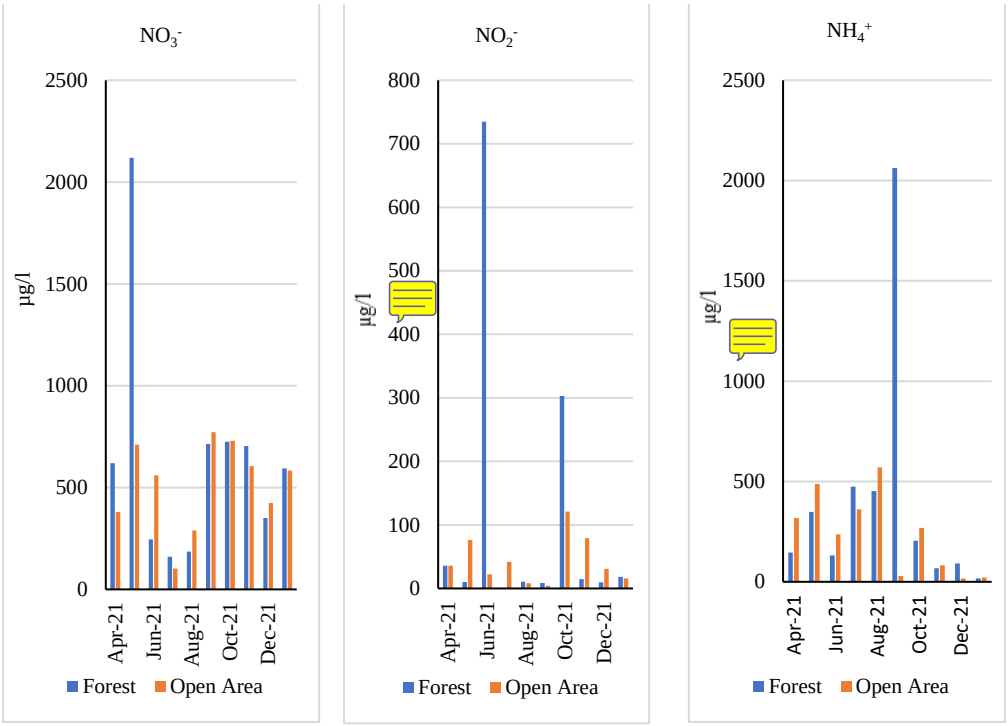


Figure 6. Change in the content of nitrogen ions by months (µg/l)

3.3. Inorganic phosphorus

Change in the concentration of inorganic phosphorus is shown in figure 7 (µg/l). The content of phosphorus in rainwater was characterized by an increase in the concentration of phosphorus in the summer. It can be seen from the figure that in June there was a sharp increase in the content of phosphorus up to 1157.67 µg/l. The content of phosphorus in the water collected under the forest canopy for all months is greater than its content in the open area. At the same time, the content of phosphorus in the rainwater under the forest canopy in June is higher than in July, and the content of phosphorus in the open area in June is lower than in July. The average concentration of inorganic phosphorus in atmospheric precipitation was 153.23 µg/l and 117.16 µg/l in rainwater collected under the canopy and in the open area, respectively. The average content of inorganic phosphorus in the rainwater under the forest canopy is not much higher than in the open area.

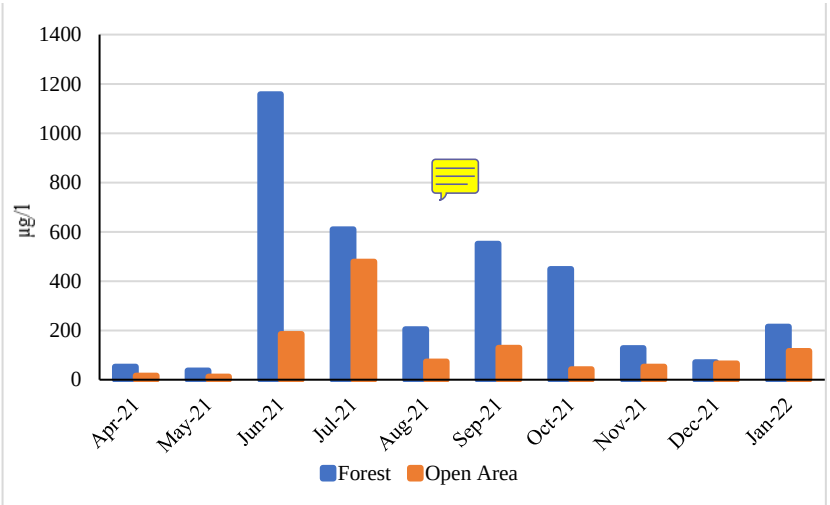


Figure 7. Change in the concentration of inorganic phosphorus in precipitation (µg/l)

3.3. Dependence of the biogenic elements content on weather conditions

Figure 8 shows the dependence of the concentration of inorganic nitrogen, phosphorus on the amount of precipitation, on the relative humidity of the air and on the wind speed during the study: from April 2021 to January 2022

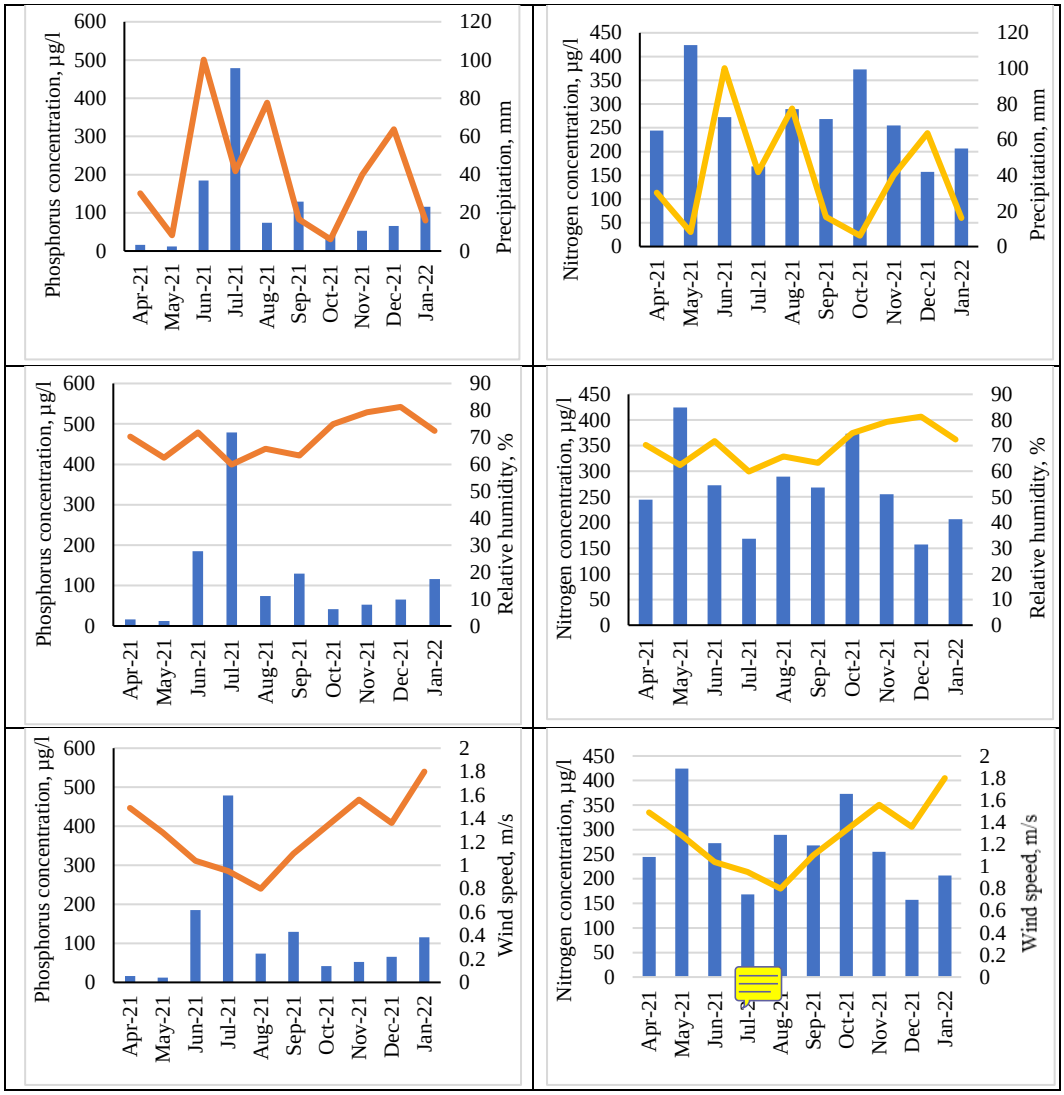


Figure 8. Dependence of the concentration of inorganic nitrogen, phosphorus on the amount of precipitation, on the relative humidity of the air and on the wind speed.

During the period under consideration, a decrease in the concentration of inorganic nitrogen is observed with an increase for precipitation. At the same time, no such dependence is observed for inorganic phosphorus. An inverse dependence of the concentration of inorganic nitrogen and phosphorus in atmospheric precipitation on the relative air humidity is observed (Fig. 8). The content of phosphorus increases with a decrease in wind speed, while such a dependence of the content of inorganic nitrogen on wind speed is not observed.

4. Discussion

4.1. Acidity

Usually, under normal conditions, rainwater has a pH = 5.6–5.7 [20]. During the study period, alkaline precipitation is observed in this area with an average pH value in the open area of 6.8, and the average pH value of rainwater under the forest canopy is 6.1.

The decrease in the pH value can be explained by the fact that rainwater, flowing down from the crowns of trees, washes away and dissolves dust particles, organic and mineral substances of an acidic nature. Thus, relatively "alkaline" precipitation, passing through the canopy of the studied forest, are acidified and become slightly acidic. Consequently, in the rainwater that has passed through the crowns of the forest, the content of rainwater-soluble compounds of all the considered elements in total increases significantly (Fig. 3). The analysis of sediment samples allows us to say that weakly alkaline precipitation falls mainly on the territory of the Karadag Reserve. This is explained by the fact that there are many limestone rocks on the territory of the peninsula, and the processes associated with the erosion and weathering of limestones lead to alkalinization of sediments ($CaCO_3 + H_2O + CO_2 = Ca^{2+} + 2HCO_3^-$). This result coincides with the results of [17].

4.2. Inorganic nitrogen

The decrease in the ammonium content can be explained by the fact that while rainwater flows through the forest canopy, the process of ammonium oxidation occurs due to contact with protein products and the presence of corresponding microorganisms accumulated on the surface of the leaves. The low content of nitrites, apparently, is explained by the fact that they are an intermediate product of the oxidation of ammonium to nitrates. These results are consistent with the available data on the ratio of nitrogen species in atmospheric precipitation samples [21–24].

In works [7, 19, 25] the order of contribution of nitrogen-containing ions is shown: $NH_4^+ > NO_3^- > NO_2^-$. In addition, in [11, 17], the contribution of nitrogen-containing ions looks like this: $NO_3^- > NH_4^+ > NO_2^-$. This order is identical to our result. Moreover, this can be explained by the difference in the characteristics of the study areas.

When compared between the open area and the area under the forest, it can be seen that the nitrogen content in the rainwater under the canopies is greater than in the rainwater collected in the open areas (Figure 4). These results correspond to the results obtained in [17].

The maximum values of nitrates were recorded both in the open area and under the forest canopy in May 2021, which amounted to 710 μg/l and 2120 μg/l, respectively. The maximum nitrite values were recorded in May and June 2021 for an open area (76 μg/l), and under the forest canopy, respectively (735 μg/l). At the same time, the maximum value of ammonium was recorded in August and July, respectively, for an open area (570 μg/l) and under the forest canopy (474 μg/l). No simultaneous high concentrations of all inorganic forms of nitrogen were observed in one sample. For a detailed study of the dependence between the concentrations of the nitrite ion, nitrate ion, ammonium ion and the pH value, we calculated the Pearson correlation coefficients (Table 1).

Table 1. Correlation coefficients between concentrations of nitrite ion, nitrate ion, ammonium ion and pH value (p = 0.05, n=10).

	NO_2^-	NO_3^-	NH_4^+	pH
NO_2^-	1			
NO_3^-	-0.22	1		
NH_4^+	-0.20	0.05	1	
pH	-0.24	-0.33	0.19	1

A. Under the forest canopy

	NO_2^-	NO_3^-	NH_4^+	pH
NO_2^-	1			
NO_3^-	0.34	1		
NH_4^+	0.14	-0,37	1	
pH	0.51	0.07	0.34	1

B. Open area

Table 1 shows that in the open area all components (except NH_4^+ - NO_3^-) have a proportional correlation (r>0). At the same time, pH strongly depends on the NO_2^- and NH_4^+ ions (r= 0.51 and 0.34, respectively) pH – NO_3^- almost independently of each other r = 0.07, almost equal to 0. NO_3^- – NO_2^- proportionally depends on each other (r = 0.34). A good

correlation of nitrate and nitrite nitrogen can be explained by similar sources of their entry into the atmosphere, as well as by the fact that they are elements of mutual transformation. At the same time, the difference in the sources of ammonium, nitrite, and nitrate nitrogen entering the atmosphere apparently explains the decrease in the correlation between these elements. At the same time, NH_4^+ – NO_3^- is inversely dependent on each other (r = -0.37). Under the forest canopy, on the contrary, almost all components are inversely correlated (r < 0), except for NH_4^+ – NO_3^- and pH – NH_4^+. At the same time, NH_4^+ – NO_3^- almost independently of each other r = 0.05, almost equal to 0. Here, unlike the open area, pH – NO_3^- has an inverse relationship to each other (r = - 0.33). This is logical, because the acidity of rainwater depends on the concentration of nitrate ions, the more NO_3^- in the rainwater, the lower the pH value of the rainwater.

4.3. Inorganic phosphorus

This result corresponds to the results obtained in [11] and [27] and is explained by the influx of phosphorus with the products of plant metabolism. In addition, this can be explained by the peculiarities of phosphorus migration in the biosphere, which is also associated with the influx of mineral forms of the element with dust particles formed during soil and rock erosion. pH – $H_2PO_4^-$ rainwater under the forest canopy has an inverse relationship to each other (r= - 0.18). At the same time, pH – $H_2PO_4^-$ rainwater in an open area is almost independent of each other (r = 0.08), almost equal to 0 (Fig. 9.).

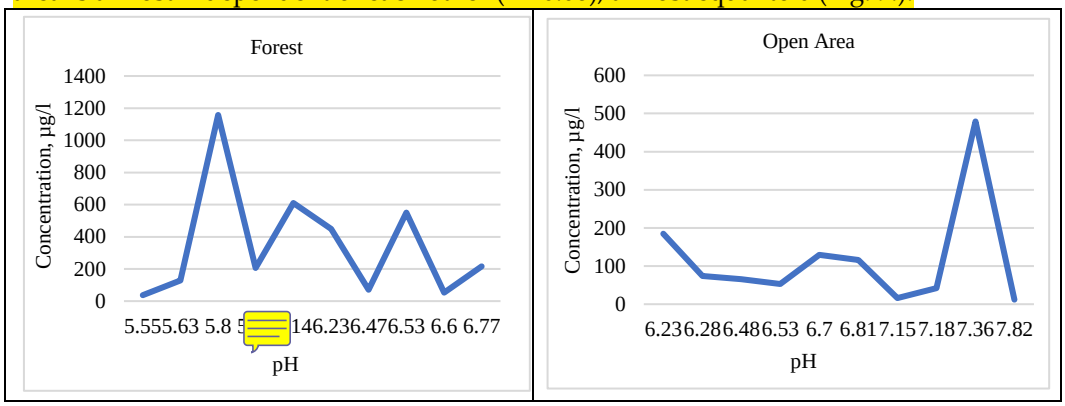


Figure 9. Relationship between pH and the concentration of inorganic phosphorus in precipitation.

4.4. Dependence of the biogenic elements content on weather conditions

The decrease in the concentration of inorganic nitrogen with an increase for precipitation is explained by the effect of sample dilution. In addition, the lack of dependence of inorganic phosphorus on the amount of precipitation can be explained by the strong spatiotemporal variability of phosphorus sources in the atmosphere [11]. With an increase in the relative humidity of the air, the amount of precipitation increases, and, consequently, the content of pollutants in them decreases, resulting in an inverse relationship between the concentration of inorganic nitrogen and phosphorus in precipitation and the relative humidity of the air [28, 29].

Table 2. Results of correlation analysis of time series of precipitation intensity and concentrations of nitrogen and $H_2PO_4^-$ them (p = 0.05, n=10).

	$H_2PO_4^-$	N	Amount of precipitation	Relative humidity	Wind speed
$H_2PO_4^-$	1				
N	-0.48	1			

Amount of precipitation	0.22	-0.34	1		
Relative humidity	-0.47	-0.22	0.18	1	
Wind speed	-0.44	-0.09	-0.50	0.57	1

As can be seen from Table 2, the values of the correlation coefficients between the series of concentrations of the considered substances in precipitation falling on the territory of the reserve during the study period and the amount of precipitation do not exceed the threshold of reliable correlation. This allows us to conclude that the intensity of precipitation is not a determining factor in the change in the concentration of inorganic nitrogen compounds in sediments. In general, it has a slight inverse effect on the change in nitrogen concentration. The amount of precipitation proportionally affects the change in the concentration of phosphorus in precipitation. Relative humidity has an inverse relationship with respect to the change in the concentration of components. Wind speed is also a determining factor in changing the concentration of phosphorus compounds, while nitrogen has almost no effect. Phosphorus is inversely correlated with inorganic nitrogen. So that as the concentration of phosphorus in rainwater increases, the concentration of nitrogen decreases, especially the concentration of nitrate.

In order to study the influence between the components in rainwater in more detail, we carried out a correlation analysis collected under the forest canopy and in an open area. The results of the correlation analysis are shown in Table 3.

Table 3. Results of correlation analysis (between forest and open area) (p = 0.05, n=10)

		Open area			
		$H_2PO_4^-$	NO_2^-	NO_3^-	NH_4^+
Forest	$H_2PO_4^-$	**0.56**	-0.18	0.01	-0.06
	NO_2^-	0.06	**0.09**	0.21	0.01
	NO_3^-	-0.52	0.44	**0.59**	0.20
	NH_4^+	0.15	-0.36	0.28	**-0.14**

Note: Bold indicates significant correlation coefficients among themselves

The table 3 shows that the combination of nitrogen and phosphorus in rainwater collected under the forest canopy and in the open area correlate well with each other. Phosphorus and nitrate proportionally affect each other. So that with an increase in the concentration in rainwater collected in an open area, an increase in their concentration in rainwater collected under the forest canopies is observed, except for NH_4^+. With an increase in the concentration of ammonium and nitrite in an open area, it leads to an increase in the concentration of nitrate in the rainwater under the forest canopy. This can be explained by the fact that all these substances are converted into the final form of nitrate. This means that while rainwater passes through the crowns of the forest, the reaction of oxidation of ammonium and nitrite to nitrate occurs. Nitrate in the open area is not a determining factor in changing the concentration of phosphorus under the trees. Similar results are also observed for ammonium in an open area with phosphorus under the forest canopy, and for phosphorus in an open area with nitrite under the canopy. At the same time, ammonium and phosphorus have a strong relationship with each other: phosphorus in rainwater in an open area proportionally affects the content of ammonium ion in rainwater under forest canopy, and ammonium in rainwater in an open area has feedback on the content of phosphorus in rainwater under forest canopy. An increase in the concentration of nitrate in rainwater in an open area leads to an increase in the concentration of nitrite under the forest canopy. This is because the reduction reaction of nitrate to nitrite has occurred.

Intensive processes can explain a more intensive supply of elements in the under-crown spaces on the surface of actively functioning trees, as well as by the washing off dust from the crown, which has a high sorption capacity.

5. Conclusions

The intake of biogenic substances (inorganic nitrogen, phosphorus) with atmospheric precipitation in the area of the Karadag State Nature Reserve has been determined since April 2021 to January 2022. It has been established that the main forms of nitrogen in atmospheric precipitation are nitrates and ammonium. For all considered biogenic substances, an increase in their content in the warm period of the year is observed, which is explained both by the inverse dependence of the concentration of elements on the amount of precipitation, and by the peculiarity of their migration and sources of income. There is an inverse relationship between the concentration of inorganic nitrogen and phosphorus in precipitation and relative air humidity and wind speed.

In this paper studies of the biogenic composition of atmospheric precipitation, under the forest canopy rainwaters on the territory of the Karadag State Nature Reserve were carried out. It has been established that the transformation of natural in the series atmospheric precipitation - under the forest canopy rainwaters for most of the determined components of the biogenic composition in increasing concentration. Studies have shown that the pH of precipitation falling under the forest canopy is significantly lower than the pH of precipitation in open areas. It is observed that rainwater pH under forest canopies is inversely related to almost all observed components except ammonium. At the same time, in an open field, it has a proportional relationship with nitrogen ions. The forest stand significantly increases the concentrations of NO_3^-, $H_2PO_4^-$, NH_4^+ ions and reduces the amount of NO_2^- in precipitation. It was found that nitrate in an open area is not a determining factor in changing the concentration of phosphorus under the forest canopy. At the same time, ammonium and phosphorus ions have a strong bond with each other. Nitrogen ions in the open field and under the forest canopy have a good relationship with each other. The edificatory plant determines the transformation of atmospheric precipitation penetrating through the vegetation cover. It was revealed that the increase in the concentration of biogenic elements in accordance with the phases of plant development during the growing season (from spring to summer and autumn).

Author Contributions: Conceptualization, R.G.; methodology, R.G. and C.N.F.; validation, V.T.; formal analysis, T.G., V.T. and V.L; investigation, C.N.F., R.G. and T.G.; resources, V.L.; data curation, V.T.; writing—original draft preparation, C.N.F.; writing—review and editing, R.G. and T.G.; visualization, V.T.; supervision, R.G.; project administration, R.G. All authors have read and agreed to the published version of the manuscript.

Funding: The research was conducted within the framework of the research topic of IBSS, registration number: 121040100327-3, of KSS – NR RAS – Branch of IBSS, registration number: 121032300023-7. The RUDN University Strategic Academic Leadership Program has supported this research.

Acknowledgments: The authors are grateful to Bovko N.I. (A.O Kovalevsky Institute of Biology of the Southern Seas of RAS) for support of the study.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

1. The 16th Baltic Sea Parliamentary Conference. – Berlin, Germany, 27 – 28 August **2007**. Available online: http://www.bspc.net/page/show/26 (accessed on 02.08.2022).
2. De Schrijver, A., Geudens, G., Augusto, L. et al. The effect of forest type on throughfall deposition and seepage flux: a review. *Oecologia*. **2007**, 153, 663–674. Available online: https://doi.org/10.1007/s00442-007-0776-1

3. Gong Zhang, Guang-Ming Zeng, Chun-Yan Du, Yi-Min Jiang, Xiao-Kang Su, Ren-Jun Xiang, Lu Huang, Min Xu, Chang Zhang, Deposition patterns in bulk precipitation and throughfall in a subtropical mixed forest in central-south China. *Forestry: An International Journal of Forest Research.* **2007**, 80, 211–221. Available online: https://doi.org/10.1093/forestry/cpm002
4. Pristova, T. A. Chemical composition of atmospheric precipitation, undercrown and surface waters in the middle taiga deciduous plantations of post-cutting origin. *Theoretical and applied ecology*. **2022**, 2, 63-69. – DOI 10.25750/1995-4301-2022-2-063-069
5. Marie-Claire Pierret, Daniel Viville, Etienne Dambrine, Solenn Cotel, Anne Probst. Twenty-five year record of chemicals in open field precipitation and throughfall from a medium-altitude forest catchment (Strengbach - NE France): An obvious response to atmospheric pollution trends. *Atmospheric Environment.* **2019**, 202, 296-314. Available online: https://doi.org/10.1016/j.atmosenv.2018.12.026
6. L. Gandois et al. Canopy influence on trace metal atmospheric inputs on forest ecosystems: Speciation in throughfall. *Atmospheric Environment.* **2010**, 44, 824-833. doi:10.1016/j.atmosenv.2009.11.028
7. G.V. Shiltsova, V.G. Lastochkina. Influence of the canopy of pine and birch forests on the chemical composition of precipitation in the Kivach Nature Reserve. *Proceedings of the Karal Scientific Center of the Russian Academy of Sciences*. **2006**,10, 180-184.
8. N. K. Kozhevnikova et al. Water migration of macroelements in coniferous-deciduous forests of Sikhote-Alin. *Siberian forest journal*. **2017**, 3, 60–73. DOI: 10.15372/SJFS20170306
9. Kravchenko I.Yu. Influence of the coniferous forest canopy on the chemical composition of atmospheric precipitation. In the collection: Geography: the development of science and education. Collective monograph based on the materials of the International Scientific and Practical Conference dedicated to the 155th anniversary of the birth of Vladimir Ivanovich Vernadsky. Managing editors V.P. Solomin, V.A. Rumyantsev, D.A. Subetto, N.V. Lovelius. Russia, **2018**. pp. 108-112.
10. Martynyuk A. A., Doronicheva E. V., Rykova T. V. Changes in the chemical composition of natural sediments under the canopy of pine plantations under conditions of technogenic pollution of the environment. *Lisoviy zhurnal*. **2011**. №. 1. P. 8-11.
11. A.V. Varenik, O.N. Kozlovskaya. Supply of biogenic elements with atmospheric precipitation to the surface of the Black Sea in 2010-2013. *Ecological safety of coastal and shelf zones and integrated use of shelf resources*: Sat. scientific tr. Issue 28. National Academy of Sciences of Ukraine, MGI, IGN, OF InBYuM. Editorial staff: Ivanov V.A. (chief editor) and others - Sevastopol, **2014.** P. 105-114.
12. Yu.P. Ilyin and others. The state of pollution of atmospheric precipitation in the city of Sevastopol in 1997 – 2006. *Science works of UkrNDGMI.* **2006**, Issue 255. P.166-184
13. M.A. Myslina, A.V. Varenik. Supply of inorganic nitrogen with atmospheric precipitation to the water area of the Sevastopol Bay in 2015-2016. *Ecological safety of the coastal and shelf zones of the sea.* **2019.** Issue 1. P.78-82/ doi: 10.22449/2413-5577-2019-1-78-82.
14. A.V. Varenik, S.K. Konovalov. Contribution of atmospheric precipitation to the supply of biogenic elements in the area of the Crimean coast. In Proceedings of the III International Scientific Conference in Memory of Corresponding Member of the Russian Academy of Sciences D.G. Matishov "Regularities of formation and impact of marine, atmospheric hazards and disasters on the coastal zone of the Russian Federation in the context of global climatic and industrial challenges." Rostov-on-Don, 15–19 June 2021. Rostov-on-Don. SSC RAS Publishing House **2021**. pp. 253-256.
15. A.V. Varenik et al. Quantitative assessment of the input of biochemical elements with atmospheric precipitation in the coastal regions of the Crimean Peninsula. In Proceedings of the II All-Russian Conference "Hydrometeorology and Ecology: Achievements and Development Prospects", St. Petersburg, Russia, 19 – 20 December **2018**, pp. 124-127.
16. Chaikina A.V., Kholoptsev A.V. Peculiarities of hydrochemical composition of atmospheric precipitation in summer 2004 near the village of Katsiveli (Southern coast of Crimea). *Ecological safety of coastal and shelf zones and integrated use of shelf resources.* **2005**. Issue 12. pp. 215-219.
17. E. P. Kayukova. Features of the chemical composition of precipitation of the Crimean training site of SPBSU. Vestnik SPbSU Series 7, Geology, Geography. **2011**. Issue 3. pp. 26-42.
18. V. V. Andreev, M. Yu. Arshinov, B. D. Belan *et al*. Surface ozone concentration over the Russian territory in the first half of 2020. *Optika Atmosfery i Okeana journal.* **2020**. V. 33. No. 9. P. 710-721. – DOI 10.15372/AOO20200908. – EDN VPUMVY.
19. V. V. Sapozhnikov *et al*. Methods of hydrochemical studies of the main biogenic elements. VNIRO, Moscow, USSR, 1988; 118 p.
20. Trushkina L.Yu., Trushkin A.G., Demyanova L.M. Hygiene and human ecology: textbook. 4th ed., revised and expanded. TK Velby, Prospekt Publishing House, Russia, **2006**; 528 p.
21. Guerzoni S., Chester R., Dulac F. et al. The role of atmospheric deposition in the biogeochemistry of the Mediterranean Sea. *Progr. Oceanogr.* **1999**, 44, 147 – 190. – doi: 10.1016/s0079-6611(99)00024-5;
22. Jickells T. Atmospheric inputs of metals and nutrients to the oceans: Their magnitude and effects. *Mar. Chem*. **1995**. pp. 199 – 214.;
23. Koçak, M., Kubilay, N., Tuğrul, S., and Mihalopoulos, N. Atmospheric nutrient inputs to the northern levantine basin from a long-term observation: sources and comparison with riverine inputs. *Biogeosciences*, **2010**, Issue 7, 4037–4050, https://doi.org/10.5194/bg-7-4037-2010
24. Medinets S., Medinets V. Investigations of atmospheric wet and dry nutrient deposition to marine surface in western part of the Black Sea. Turk. J. *Fish. Aquat. Sci.* **2012**, Issue 12, pp. 497 – 505.
25. N. A. Gashkina et al. Biogeochemical migration of elements in the "Atmospheric precipitation-crown water-soil water-lake" system in the background region (Valdai National Park). *Geochemistry*, **2020**, V.65, Issue. 7, pp. 693–710.

26. D.V. Kalinskaya, A.V. Varenik, A.S. Papkova. Phosphorus and silicon as markers of dust aerosol transport over the Black Sea region. *Modern problems of remote sensing of the Earth from space*. **2018**, V. 15, № 3, 217–225. DOI: 10.21046/2070-7401-2018-15-3-217-225 – EDN XSNFSP.
27. Savchenko V.S. Phosphorus in precipitation. *Water resources.* **1996.** Issue 185, pp. 11-17.
28. Salukvadze M. Study of the influence of meteorological, anthropogenic and terrigenous factors on the chemical composition of atmospheric precipitation in Eastern Georgia. Dissertation abstract, **2006**. Available online: http://www.nplg.gov.ge/dlibrary/collect/0002/000159/Avtoreferati%20rus.pdf (accessed on 02.08.2022).
29. Xingyu Jiang, Guang Gao, Jianming Deng, Guangwei Zhu, Xiangming Tang, Keqiang Shao, Yang Hu. Nitrogen concentration response to the decline in atmospheric nitrogen deposition in a hypereutrophic lake. Environmental Pollution. **2022**, 300, 118952. Available online: https://doi.org/10.1016/j.envpol.2022.118952 (accessed on 02.08.2022).