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Contribution of Atmospheric Depositions to Inventory of Nutrients in the Coastal Waters of Crimea

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Abstract: Coastal zones are extremely vulnerable and, at the same time, anthropogenically pressed. Excessive enrichment of marine waters with nutrients and organic matter can lead to "red tides", oxygen deficits, decreasing assimilation capacity, etc. The purpose of this work is to study atmospheric precipitations as a source of nutrients directly affecting waters of the coastal areas of Crimea and, ultimately, strengthening eutrophication consequences. In 2004–2008, and from 2015 to present, samples of atmospheric precipitations have been collected at the Marine Hydrometeorological Station in Sevastopol. They have been analyzed for the content of inorganic nitrogen, phosphorus, and silica. For 2009–2014, direct measurements are unavailable and a previously retrieved multiple nonlinear regression equation has been used to estimate the concentration of inorganic nitrogen in atmospheric precipitations depending on meteorological conditions, including the number of precipitations, number of days without precipitations, relative air humidity, wind direction vectors, and air temperature. Data obtained in this study have revealed that atmospheric precipitations are one of important inputs of nutrients for local areas. Their relative contribution increases on the time scale of days, while the role of rivers remains the most important on the annual scale. The contribution of atmospheric precipitations to the inventory of nutrients becomes more significant in the summer, when seasonal stratification in the water column prevents vertical mixing of waters, and the ambient concentration of nutrients in the upper layer of water is minimal.

Keywords: atmospheric precipitation; nutrients; inorganic nitrogen; inorganic phosphorus; silica; sea water; coastal areas of Crimea

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1. Introduction

Major inputs into the inventory of nutrients in the marine environment are from coastal sources, water exchanges, atmospheric precipitation, and organic matter recycling. Atmospheric input has been traditionally considered of minor importance, except for specific cases of oligotrophic offshore waters, when other sources and ambient concentrations of nutrients are limited [1–5]. Coastal zones have been considered well supported by nutrients from coast-based sources. The input of nutrients with atmospheric precipitations has been generally estimated by value of a few percent of the total annual input from all sources [6,7]. However, is it true for areas neighboring large industrial cities and/or on with heavy rain periods of hours to days?

Nutrients are important for primary production and productivity. Yet, excessive production of organic matter results in intensive consumption of oxygen resulting in "dead zones" with oxygen deprived conditions. This makes the question of sources of nutrients for marine systems crucially important. The number of "dead zones" increases exponentially, doubling about every 10 years since the 1960s [8]. Such zones have been already registered for more than 400 coastal sites worldwide with a total area over 245,000 km^2 [8]. The process of oxygen deprivation is most frequently registered for inland seas with limited or no water exchange with the ocean and high primary production and/or input of organic matter. The Black Sea is an inland and almost enclosed basin, which is particularly susceptible to the influence of riverine runoff [9]. The shelf and coastal area of this marine ecosystem is profoundly affected by increasing input of organic matter, nitrogen, and phosphorous compounds from the coast [10,11]. Although the load of main rivers is located in the north-western part of the sea, small rivers carry about 15% of the Danube's discharge into other coastal areas and may result in high local eutrophication. The level of pollution of the Black Sea coastal waters from mainland is quite acute, especially near large cities [12].

The Chernaya river is one of the largest rivers of Crimea (Figure 1). To make the effect more profound, it discharges water into the most-inland part of the 8 km long Sevastopol Bay with a highly restricted water exchange with the open sea.

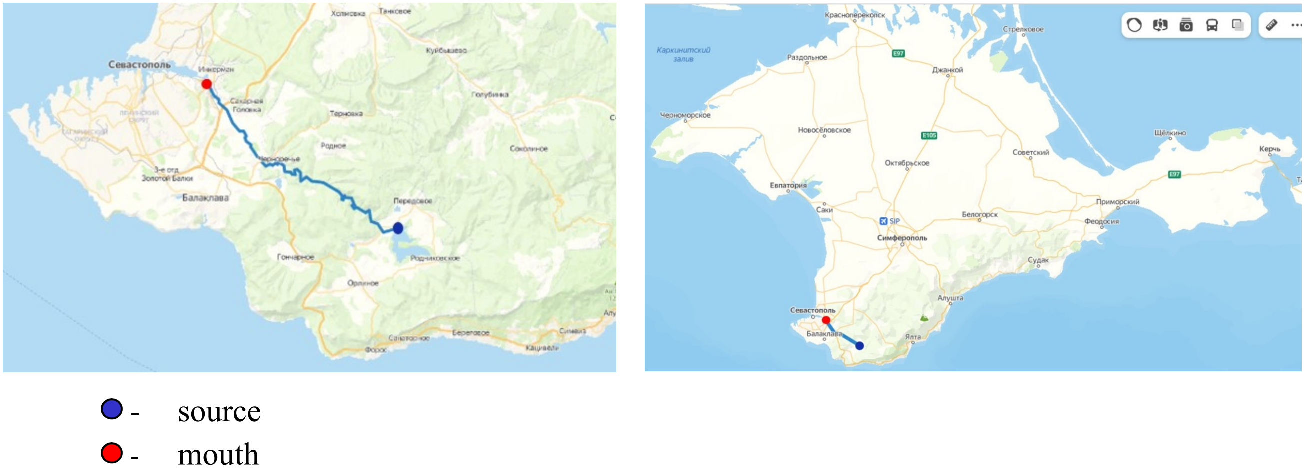


Figure 1. The Chernaya river near Sevastopol city (Images are from the Yandex map).

It discharges 1.73 m^3 s^{-1} of discharge on average [13], but it can be much higher in rainy periods. Estimates of the water balance of Sevastopol Bay have shown that the annual flow of the Chernaya River is about 70% of the volume of Sevastopol Bay [14]. Apart from fresh water, the Chernaya river delivers a lot of nutrients collected from farmlands up the river flow. It delivers 1000 tons of suspended matter on average, 52 tons of mineral nitrogen, and 6 tons of phosphorus annually [15]. This provides a significant impact on the state of coastal waters supporting high input of organic matter to the system due to primary production and resulting in seasonal hypoxia and anoxia in the bottom waters of the bay due to oxidation of produced and precipitated organic matter.

Another recognized source of pollution in the coastal area of Sevastopol [16] is wastewater. There are 35 outlets of wastewater on the coast of the Sevastopol region, providing about 56 million m^3 $year^{-1}$ (1775 m^3 s^{-1}) of wastewater of varying degrees of contamination. In addition to main outputs, there are 11 emergency wastewater outlets at the coast of Sevastopol. Storm water runoff in Sevastopol Bay contains up to 21.4–78.6 µM of nitrate, 4.28–1222 µM of ammonium, and up to 37.7–101 µM of phosphate [16]. The amount of nutrients discharged with wastewater into coastal waters of Sevastopol region can be up to 1600 t $year^{-1}$ for ammonium, 550 t $year^{-1}$ for nitrate, and up to 406 t $year^{-1}$ for phosphate [17].

The source of nutrients to marine ecosystems with atmospheric wet and dry depositions is far less accounted for. Yet, exhaust gases, fuel combustion products, and a continuous increase in the number of transport vehicles are the main sources of nitrogen oxide emissions to the local atmosphere [18]. About 90% of ammonium emissions are from agricultural activities [19]. The main natural sources of phosphorus to the atmosphere are due to the wind erosion of soil in arid areas, generation of biogenic aerosols by terrestrial vegetation (spores, pollen, plant residues, etc.), destruction of air bubbles on the surface of water bodies, and volcanic activity. Anthropogenic inputs of phosphorus are associated with the production and application of fertilizers, as well as with the metallurgical industry [20]. The presence of silica in atmospheric precipitations is primarily an indication of terrigenous particles. All these nutrients are removed from the atmosphere and deposited at the underlying surface with atmospheric precipitations [21].

Jickells (1995) [22] reviewed publications showing a dramatic increase in atmospheric nitrogen fluxes in the 20th century. The author of [22] argues that atmospheric depositions may support from 5 to 25% of nitrogen needed for new primary production under conditions of intense stratification in the water column in summer time. Im et al. [23] used the WRF/CMAQ modeling system to estimate dry and wet atmospheric nitrogen fluxes to be up to 0.36 Tg (N) year^{-1} (about 825 kg km^{-2} year^{-1}) for 2008.

Though nitrogen is often recognized as the limiting nutrient, phosphorus can also limit the rate of primary production. Mineral aerosols are the main source of phosphorus on the global scale (82%), with particles of biogenic origin (12%) and combustion products (5%) playing an important role with depositions far away from the site of dust generation [20]. The contribution of anthropogenic sources to the atmospheric input of total phosphorus and phosphate can reach 50% for oligotrophic marine ecosystems, in which productivity can be limited by phosphorus [20].

Unlike riverine inputs, atmospheric depositions affect surface waters directly and largely bypass marginal filters in river mouths [5]. The importance of atmospheric deposition for the nutrient budgets in coastal regions can vary greatly [5]. Thus, atmospheric N depositions contribute about 10% of total N inputs in Jiaozhou Bay, China [24]. It might account about 20% of nitrogen requirement in reefs of the Bahamas [25] and provide most of nitrogen inputs to the area off the central coast of Cuba, exceeding the estimated nitrogen fixation rates [26]. Finally, inorganic phosphorus and silica atmospheric fluxes and their importance for the ecosystems of coastal regions remain practically unknown.

This study is aimed to quantify the input of nutrients with atmospheric precipitations and to study its relative contribution to the coastal waters of Crimea on different time scales.

2. Materials and Methods

2.1. Precipitation Sampling

Atmospheric depositions were collected for every individual event of atmospheric precipitation at the Marine Hydrometeorological Station of Sevastopol (MGS) from 2004 to 2008 (only inorganic nitrogen, 228 samples), and, furthermore, they were collected from 2015 to 2021 (inorganic nitrogen, phosphorus, silica, 514 samples) (Figure 2).

Figure 2. Location of atmospheric precipitations sampling site (the image of the bay is taken from https://of-crimea.ru/dostoprimechatelnosti/buxty/sevastopolskaya-buxta.html (accessed on 27 February 2023); the image of Crimea is taken from https://education.nationalgeographic.org/resource/how-should-crimea-be-shown-national-geographic-maps (accessed on 27 February 2023)).

Samples were collected from the very beginning of every precipitation event including the initial, most concentrated portion of atmospheric precipitations. Meteorological data—the wind speed and direction, relative humidity, and air temperature—were registered at the start of precipitation. The amount of precipitation was also reported.

Atmospheric precipitations were collected with two samplers—a wet-only automatic precipitation sampler, which was open from the beginning of precipitation to its ending, and a permanently open sampler to collect the sum of wet and dry atmospheric precipitations. After sampling, material was quantitatively placed into plastic bottles. According to the Manual on Atmospheric Pollution Control [27], if precipitations fell within less than 1 h interval and with constant cloudiness, the sample was collected in one bottle. If the interval between individual precipitation events was longer than 1 h, atmospheric precipitations were collected as different individual samples. Additionally, sea surface water samples were collected in the area of atmospheric precipitation sampling (Figure 2, red point) for at least 5 days after precipitation took place. We had chosen the site for seawater sampling far enough from all local coastal sources of nutrients, including the river mouth and outlets. Moreover, the biogeochemical barrier (marginal filter) of the Chernaya River, Sevastopol Bay restricted the influence of the waters of the Chernaya River at the sampling area [14]. As many as 270 samples were collected in 2017–2019. Meteorological parameters such as wind speed and direction were also recorded for those days of seawater sampling.

2.2. Chemical Analysis

Atmospheric precipitation and seawater samples were analyzed in the laboratory of the Marine Hydrophysical Institute RAS (Sevastopol) for inorganic nitrogen, phosphorus, and silica concentrations using photometric analysis [28]. The ammonium concentration was determined photometrically with a spectrophotometer using a modified Sadgi–Solorzano method [29]. Sodium nitroprusside was used as a catalyst. In a phenol-hypochlorite reaction, the intensely colored blue compound indophenol was formed. In the laboratory, 10 mL of each sample was placed in plastic tubes. Then, 0.2 mL of phenol solution was added and (after mixing) 0.2 mL of hypochlorite solution was added. Samples and standards with added reagents were placed in a thermostat at 48–50 °C for 30 min. After cooling for 30 min in a dark place, the optical density of colored solutions was measured at a wavelength of 648 nm. Statistics of the results revealed that the minimum ammonia concentration determined by this method was 0.04 µmol L^{-1}. The method error was ±12%.

An automatic Skalar San^{++} flow analyzer was used to determine concentrations of nitrate and nitrite. The automated procedure was based on the cadmium reduction method [28]; samples were buffered to pH 8.2 and pumped through a column containing granulated copper–cadmium to reduce nitrate to nitrite. Nitrite (originally present and reduced from nitrate) was determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)ethylene diamine dihydrochloride to form a highly colored azo dye, and its optical density was measured at 540 nm. The minimum concentration determined by this method was 0.07 µmol L^{-1}. The method error was ±10%.

Inorganic phosphorus and silica concentrations were determined using a Unico spectrophotometer. The Murphy-Riley method was used to determine the inorganic phosphorus concentration [28]. The phosphorous–molybdenum complex was reduced by ascorbic acid in the presence of sulfuric acid and a catalyst, and its optical density was measured at 880 nm. The minimum concentration of phosphate determined by this method was 0.05 µmol L^{-1}. The method error was ±10%.

The silica analysis was based on formation of a blue silicomolybdenum complex [28]. Ascorbic acid was used as a reducing agent. To eliminate the interfering effect of orthophosphate, oxalic acid was added into the solution, preventing formation of a phosphorous–molybdenum complex. The minimum concentration of silica determined by this method was 0.05 µmol L^{-1}. The method error was ±10%.

2.3. Calculation of the Volume Weighted Mean Concentrations

The monthly and annual nutrients volume weighted mean (VWM) concentrations in rain were calculated using Equation (1) [30]:

$$C = \Sigma CiRi/\Sigma Ri \tag{1}$$

where

C is the VWM concentration, μmol L^{-1};
Ci is the nutrient concentration of each sample, μmol L^{-1};
Ri is the corresponding rainfall amount for each sample, mm.

When VWM is calculated, the effect of varying rainfall amounts is accounted for, and it makes a correct average of nutrient concentrations for rain events over the period of monitoring [30].

2.4. Calculation of Nitrogen Concentrations Using the Multiple Nonlinear Regression Equation

For the period of 2009–2014, when atmospheric precipitation sampling was not provided, the multiple nonlinear regression Equation (2) [31] was used to calculate nitrogen concentrations in atmospheric depositions. This equation accounted for variations in meteorological conditions.

$$\begin{aligned} \ln C = 4.55\cdot 1.0509\cdot \exp^{-0.065Ri}\cdot 0.96d^{0.0449}\cdot(0.0009f + 0.9282)\cdot(0.00006Vy^3 + 0.0015Vy^2 + 0.032Vy + 0.9963)\cdot \\ (-0.0004Vx^3 + 0.0003Vx^2 - 0.0009Vx + 0.9946)\cdot(0.0004Ta^2 - 0.0109Ta + 1.0518) \end{aligned} \tag{2}$$

where

Ri—number of precipitations, mm;
d—number of days without precipitations;
f—relative air humidity, %
Vy, Vx—wind direction vectors;
Ta—air temperature, °C.

The number of atmospheric precipitations is the most important meteorological parameter [32], and its variations determine 85% of variations in nitrogen concentrations [21]. This has allowed us to simplify calculations for this work and to limit accounted meteorological parameters to only number of precipitations. Precipitation data for the period of 2009–2014 have been retrieved from long-term observations at MGS. This equation of multiple nonlinear regression has also been used to estimate the inorganic nitrogen input with atmospheric precipitations in some other coastal cities of Crimea (Yevpatoria and Kerch). Meteorological parameters for these cities have been taken from www.rp5.ru. (accessed on 27 February 2023) by (LLC) "Schedule Weather".

Both measured in precipitations and calculated from data on meteorological parameters and precipitation from www.rp5.ru values of concentrations are available for Sevastopol. These data have been used to assess the consistency of the results of calculation with analytically determined values (for the open sampler). Our results have shown that the difference is about 14%. For example, the measured annual flux of inorganic nitrogen with atmospheric precipitation in 2019 was 23.43 mmol m^{-2} $year^{-1}$, and the calculated value using meteorological data from the archive www.rp5.ru was 26.60 mmol m^{-2} $year^{-1}$. The difference in these values is probably the result of the difference in the measured and reported amount of precipitation in Sevastopol in 2019: it is 333 mm according to the website and 308 mm for onsite monitoring. Therefore, data obtained using a multiple nonlinear regression equation can serve as a good approximation of nitrogen deposition to estimate the influence of atmospheric deposition on the input of nutrients to coastal waters with an error of under 15%.

3. Results and Discussion

Statistics for concentrations of nutrients in atmospheric precipitations and in seawater after precipitations have taken place are presented in Tables 1 and 2.

Table 1. Statistics for nutrients concentration in atmospheric depositions in Sevastopol.

	Nitrogen		Phosphorus		Silica	
	Wet-Only Sampler	Open Sampler	Wet-Only Sampler	Open Sampler	Wet-Only Sampler	Open Sampler
Max, μmol L^{-1}	465.76	799.58	18.17	45.65	34.46	36.79
Min, μmol L^{-1}	17.42	17.00	0	0	0	0
VWM, μmol L^{-1}	71.21	86.44	0.37	1.01	0.77	1.77
St. deviation, μmol L^{-1}	64.81	95.53	1.45	3.98	2.69	4.56

Table 2. Statistics for nutrients concentration in seawater after atmospheric precipitations in Sevastopol.

	Nitrogen	Phosphorus	Silica
Max, μmol L^{-1}	62.21	1.92	25.48
Min, μmol L^{-1}	0.47	0	0.51
Average, μmol L^{-1}	10.16	0.16	3.73
St. deviation, μmol L^{-1}	8.15	0.17	2.95

The average inorganic nitrogen flux with atmospheric precipitations in Sevastopol is 24.49 mmol m^{-2} $year^{-1}$ for wet-only depositions and 30.17 mmol m^{-2} $year^{-1}$ for the sum of wet and dry depositions. The phosphate average flux in Sevastopol is 0.14 and 0.38 mmol m^{-2} $year^{-1}$ for wet-only and the sum of wet and dry depositions, respectively. The difference is about two-fold between silica fluxes with wet-only and the sum of wet and dry depositions: 0.31 mmol m^{-2} $year^{-1}$ for the wet-only depositions, and 0.69 mmol m^{-2} $year^{-1}$ for the sum of wet and dry depositions. This large difference in wet and dry fluxes of phosphorus and silica may be due to deposition of terrigenous particles resulting from dust transportation from, for example, the deserts of Syria and the Sahara [33] and the spring and autumn plowing of agricultural fields in Crimea.

We carry out quarterly monitoring of the water quality of Sevastopol Bay. Concentrations of nutrients are routinely determined. We consider the average nutrients concentration obtained during monitoring in different seasons as ambient concentration in this work. The ambient concentrations of inorganic nitrogen, phosphates and silica in surface layer of the bay are presented in Table 3.

Table 3. The ambient concentrations of nutrients concentrations in surface layer of Sevastopol bay.

	Nitrogen, μmol L^{-1}	Phosphorus, μmol L^{-1}	Silica, μmol L^{-1}
Spring	3.88	0.03	1.85
Summer	3.54	0.06	2.25
Fall	6.27	0.08	3.80
Winter	7.53	0.04	2.03

The concentration of nutrients in the surface layer of Sevastopol Bay may significantly exceed the average ambient value after atmospheric precipitations. The maximum concentration of inorganic nitrogen in the surface water layer after atmospheric precipitation has exceeded the ambient value 17-fold in summer (62.21 μmol L^{-1}) and 3.5-fold in winter (26.51 μmol L^{-1}). This difference is 4- and 48-fold for inorganic phosphorus (0.24 μmol L^{-1} and 1.92 μmol L^{-1}) and is 11- and 9-fold for silica (25.48 μmol L^{-1} and 19.18 μmol L^{-1}) in summer and winter, respectively. The concentration of nutrients in surface waters of the bay usually decreases to ambient values in the next 4–5 days after precipitation. However, the content of nutrients in the surface layer of the bay may oscillate, decreasing and increasing again in case of repeated precipitations.

Such oscillations are most pronounced for the warm period of the year (Figure 3), when the stock of nutrients in the surface layer of the bay is low, and stratification limits the intensity of vertical mixing of waters and the inflow of nutrients from deeper layers.

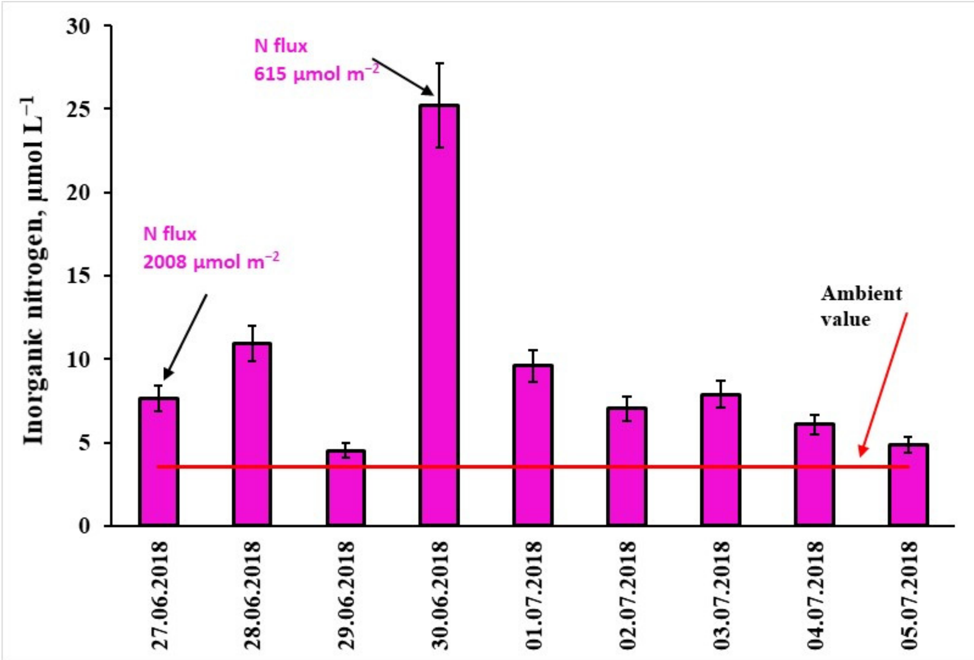


Figure 3. Variations in inorganic nitrogen concentrations in the surface layer of Sevastopol Bay after repeated precipitations in summer of 2018.

Similar to inorganic nitrogen, there have been traced oscillations in inorganic phosphorus and silica concentrations in the surface layer of the bay after repeated atmospheric precipitation in the next days (Figure 4).

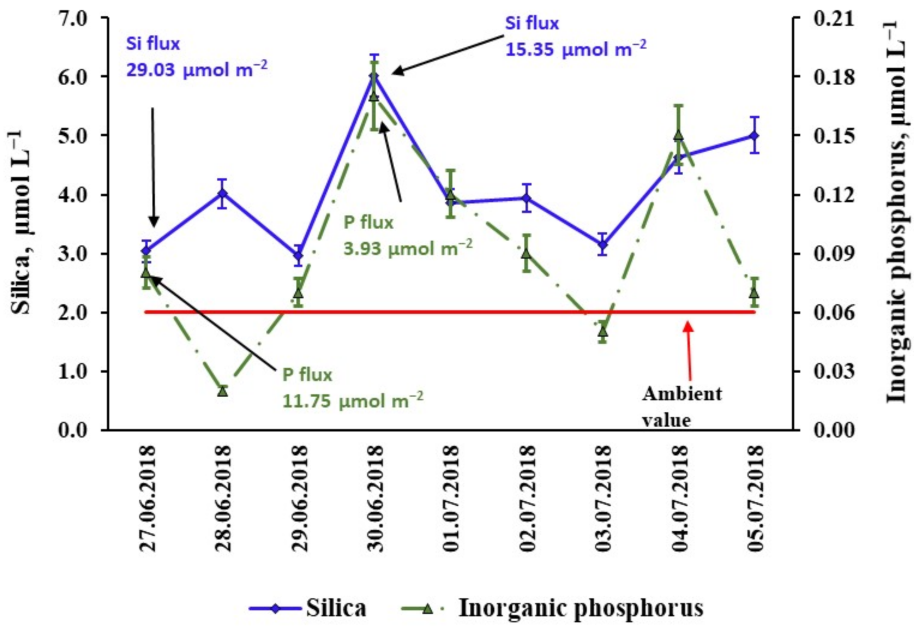


Figure 4. Variations in the inorganic phosphorus and silica concentrations in the surface layer of Sevastopol Bay after repeated precipitations in summer of 2018.

Yet, silica concentrations in sea water have been steadily above the ambient value of 2.25 µmol L^{-1}, while phosphate concentrations have oscillated from below the ambient value of 0.06 µmol L^{-1} on 28 June and 3 July to high above it on other days in summer of 2018. In a few days, the content of nutrients decreased. Data observed on July 4 might represent the advective transport of polluted waters to the observation area.

Opposite to the warm period of the year, the influence of atmospheric precipitations and oscillations in the nitrogen concentration after atmospheric precipitations are far less significant than in the cold period of the year (Figure 5).

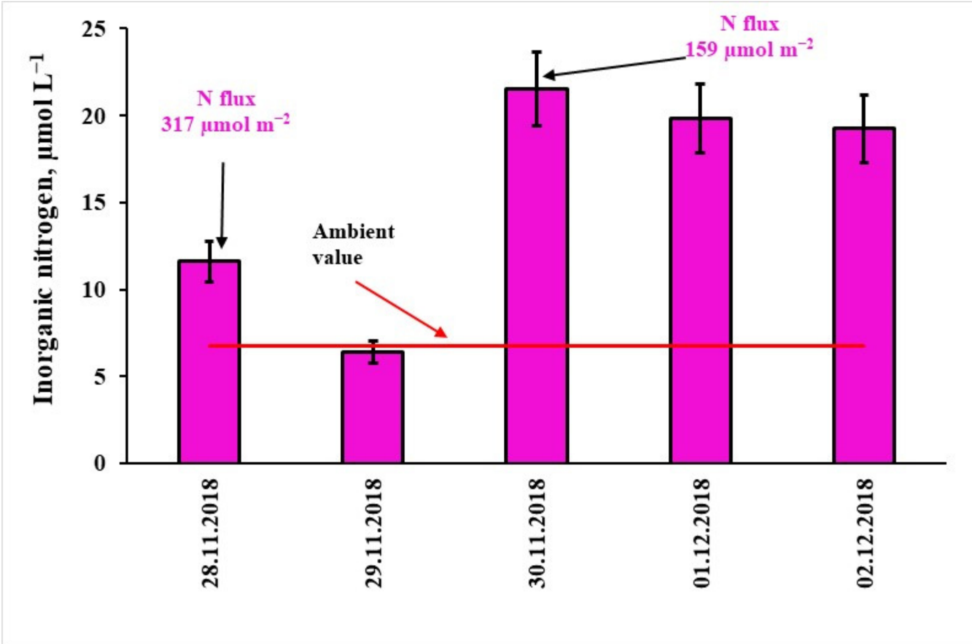


Figure 5. Variations in the inorganic nitrogen concentrations in the surface layer of Sevastopol Bay after atmospheric precipitations in winter of 2018.

The influence of atmospheric precipitation on the content of silica and phosphate in the surface layer of the bay is also insignificant in winter season (Figure 6). For example, there was a slight increase in inorganic phosphorus content in the seawater the next day after precipitation on November 28, while silica concentration, on the contrary, decreased. The opposite situation was observed after precipitation on 30 November. There was a traced increase in the silica concentration and decrease in the phosphorus concentration.

At the same time, the concentration of phosphate in the surface layer of the bay waters exceeded the ambient value (0.08 µmol L^{-1}) throughout the observation period (28 November 2018–2 December 2018), the silica concentration exceeded the ambient value (3.8 µmol L^{-1}) only after precipitation on 30 November 2018. Concentrations of nutrients in atmospheric precipitations on that day did not exceed the volume weighted mean value, suggesting that that change in the content of nitrogen, phosphorus, and silica in the surface layer of the bay could probably be explained by intensive vertical mixing.

There is no significant decrease in the concentration of inorganic nitrogen in the surface layer for several days after atmospheric precipitation in winter time. The content of nutrients may even increase in the case of wind engaged mixing of the bay waters. A weak or no stratification in the water column (Figure 7) supporting more intensive vertical exchange between the bottom and surface layers of water of the bay, which provides an input of nutrients to the surface layer, is the most obvious reason of these differences in the influence of atmospheric precipitations on the content and oscillations of the concentration of nutrients in surface waters.

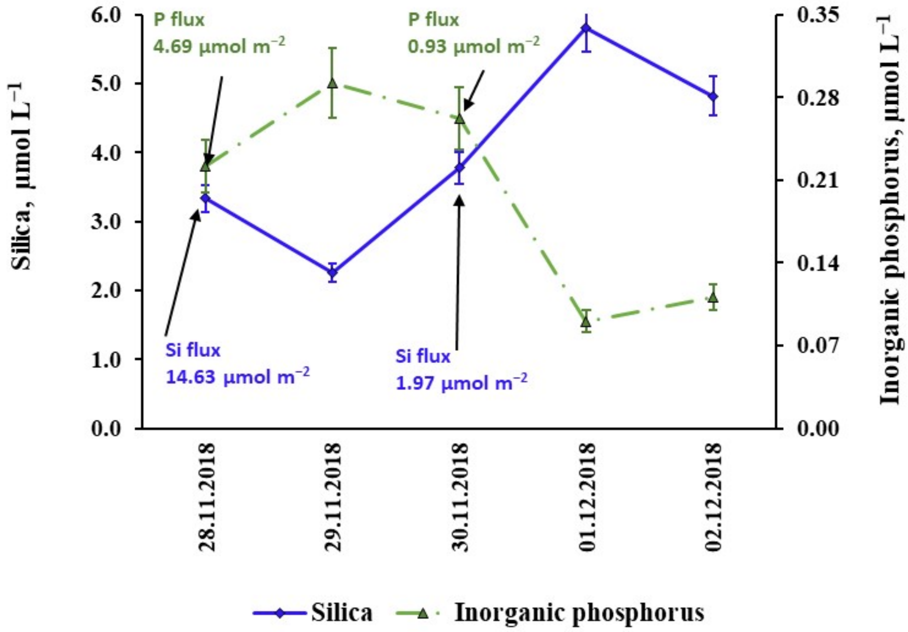


Figure 6. Variations in the inorganic phosphorus and silica concentrations in the surface layer of Sevastopol Bay after atmospheric precipitations in winter of 2018.

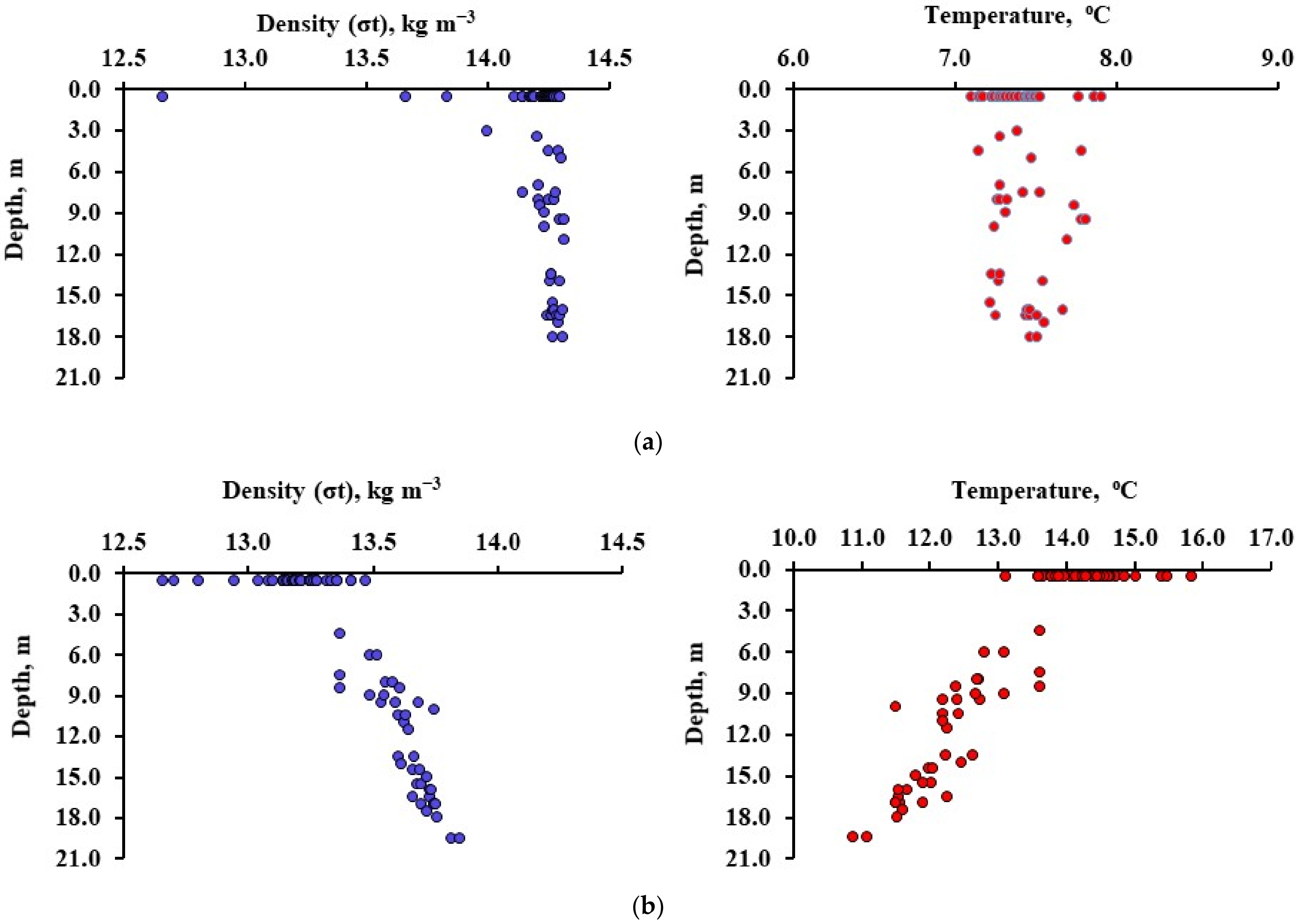


Figure 7. The vertical distribution of the density and temperature of seawater in Sevastopol Bay in February (**a**) and April (**b**).

Our results demonstrate that variations in VWM concentrations of inorganic nitrogen in atmospheric precipitations are inversely proportional to variations in the average annual number of atmospheric precipitations (Figure 8a). An assessment of this correlation using Student's *t*-test has revealed that the obtained dependence is statistically significant. This agrees with previous studies [34,35].

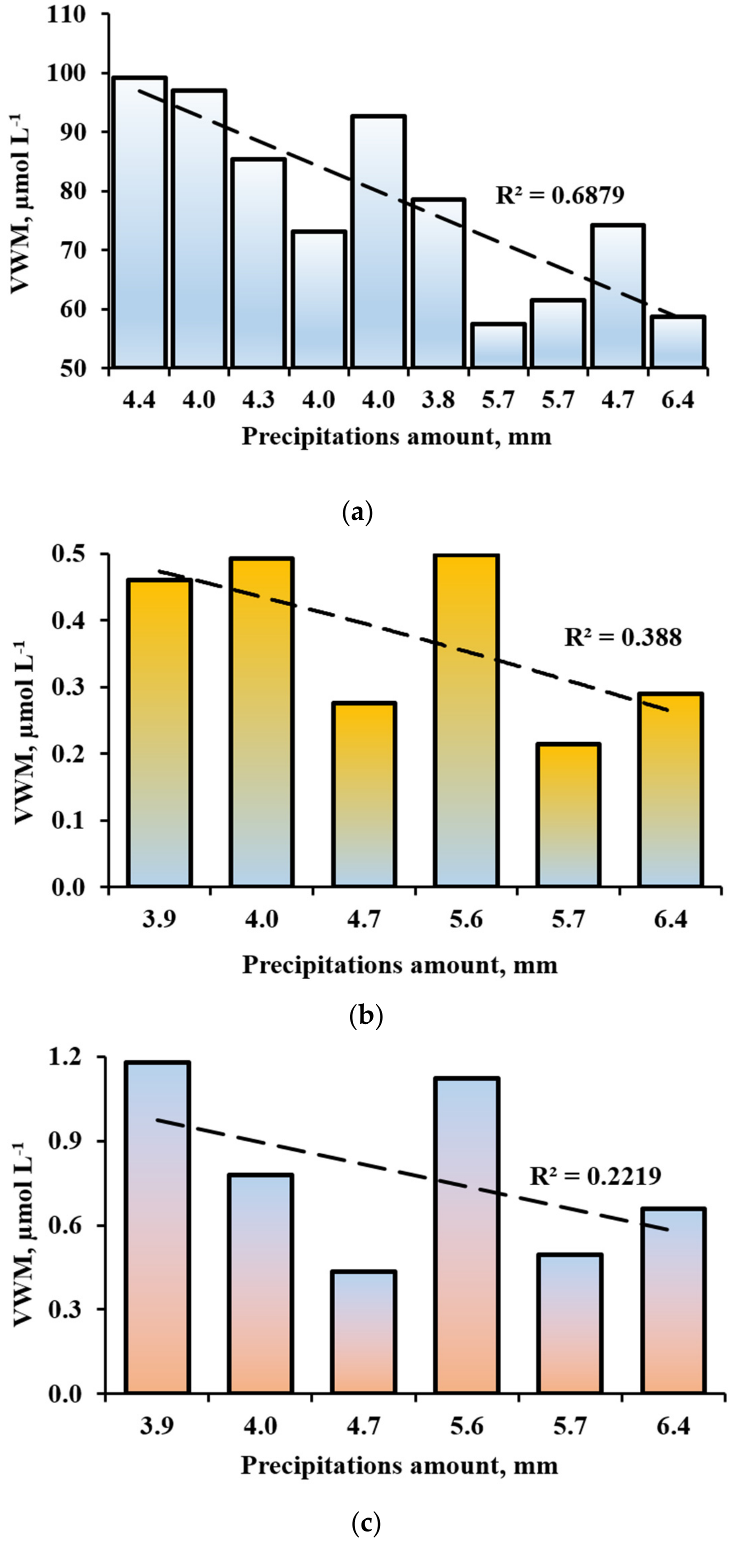
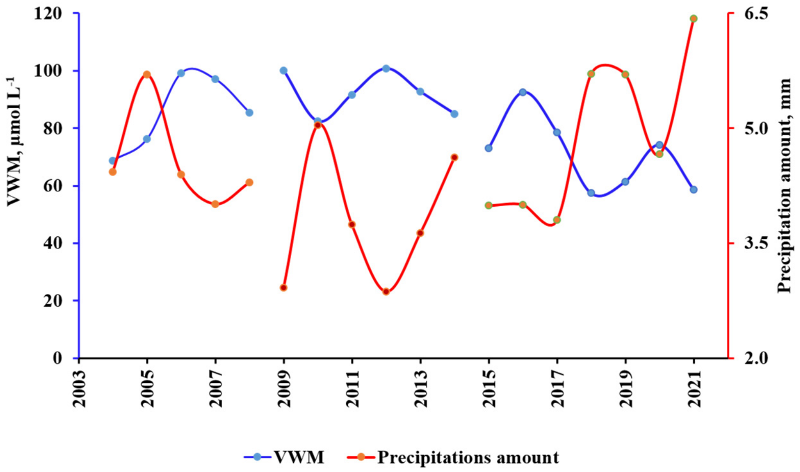


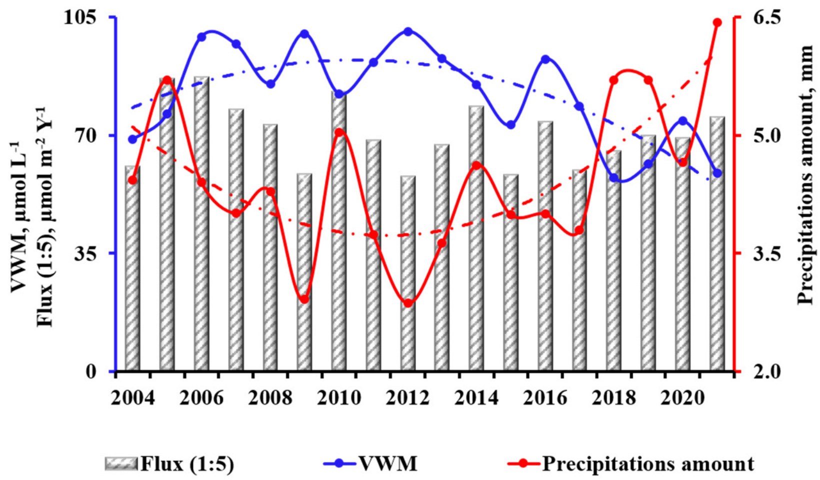
Figure 8. Relationship between the VWM concentration of inorganic nitrogen (**a**), inorganic phosphorus (**b**) and silica (**c**) concentrations in precipitations and number of precipitations.

Unlike nitrate, nitrite, and ammonium, which are well soluble in seawater, inorganic silica and phosphorus are typically in lithogenic forms, and they are less soluble in water. Therefore, the dependence of the VWM concentration of these elements on the amount of precipitation is less firm (Figure 8b,c).

Data on variations in VWM concentrations of inorganic nitrogen in atmospheric precipitations and the average amount of precipitations for the periods of sampling in 2004–2008 and 2015–2021 have been plotted to reveal an inverse dependence of these values: an increase in the VWM concentrations corresponds to a decreasing number of precipitations. At the same time, there are quasi-periodic oscillations in both concentrations and number of precipitations (Figure 9a).



(**a**)



(**b**)

Figure 9. Variations in VWM concentrations of inorganic nitrogen in atmospheric precipitations and the average amount of atmospheric precipitations (**a**—for three individual periods; **b**—as a combined plot for 2004–2021). The blue dotted line is the trend line for VWM concentration, and the red dotted line is the trend line for precipitation amount.

The values of inorganic nitrogen concentrations in atmospheric precipitations of Sevastopol in 2009–2014 have been calculated using Equation (2). The average amount of precipitations and the retrieved nitrogen concentrations reveal the same pattern of temporal variations as the periods of direct measurements in 2004–2008 and 2015–2021 (Figure 9a).

Variations in the concentration of inorganic nitrogen in precipitation and precipitation for the period from 2004 to 2021 are shown at Figure 9a, both for the periods of direct measurement of nitrogen concentration in precipitation in 2004–2008 and 2015–2021 (Figure 9a), and a combined plots with observational and calculated data for the entire study period of 2004–2021 is shown in Figure 9b.

The data reveal that the calculated concentrations of inorganic nitrogen in atmospheric precipitations fit well the trend and pattern of variations in observational data (Figure 9). When three individual periods are analyzed separately (Figure 9a), quasi-periodic opposite changes in the concentration of inorganic nitrogen and number of atmospheric precipitations are easily revealed. When all data are combined in one plot from 2004 to 2021 (Figure 9b), an inverse relationship between the concentration of inorganic nitrogen and the number of precipitations in Sevastopol can be seen on both the inter-annual and sub-decadal time scale (Figure 9b). Oscillations in the average amount of atmospheric precipitations at a sub-decadal time scale is the known feature of the water balance in the region of Crimea [36]. A shortage of fresh water periodically happens in the region every 5th to 7th year, raising the issue of additional sources of fresh water for portable and agricultural purposes. Yet, the flux of nutrients with atmospheric precipitations remains almost constant for an individual location, because changes in the concentrations of inorganic nitrogen and number of atmospheric precipitations are opposite to balance the result of their multiplication (Figure 9b).

Nutrients loaded from the coast and with atmospheric precipitations support additional production of organic matter, increasing pressure on coastal waters. An additional influx of nutrients with atmospheric precipitations can change the C:N:P:Si ratio in the surface waters of coastal marine ecosystems [33,37–39]. Atmospheric precipitations with extremely high concentrations of silica and phosphorus (even occasional events) can dramatically affect marine ecosystems, changing the structure of biological communities and the chlorophyll-a concentration. The input of dissolved nitrogen with heavy rainfall in summer may trigger phytoplankton blooms, resulting in high additional production of organic matter. Sinking detritus to bottom waters may result in seawater deoxygenation [40].

According to [16], the concentration of inorganic nitrogen in the river runoff of the Sevastopol region is 30,887 μg L^{-1}, and phosphates is 695 μg L^{-1}. This is mostly due to an influx of nutrients from the main regional rivers. The total runoff of these rivers is 245,858,106 m^3 $year^{-1}$ (https://nbcrs.org/regions/sevastopol/vodnye-resursy-nalichie-rek-ozer (accessed on 27 February 2023)). Based on these data, the annual load of nutrients into the coastal areas of Crimea is about 7594 t $year^{-1}$ for inorganic nitrogen and about 171 t $year^{-1}$ for inorganic phosphorus. The total load of nutrients with wastewaters to Sevastopol region bays [16] is about 1478 t $year^{-1}$ for inorganic nitrogen and 308 t $year^{-1}$ for phosphate. According to official data (http://www.depcxsev.ru/sevastopol_region.php), the area of the city's bays is 216 km^2. Then, the load of nutrients with atmospheric precipitations at the surface of the Sevastopol water area is about 94.11 t $year^{-1}$ for inorganic nitrogen and 1.27 t $year^{-1}$ for inorganic phosphorus (Table 4). The total input of inorganic nitrogen to the coastal waters of Sevastopol is provided for 82% by rivers, 16% by wastewater discharge, and 1% by atmospheric precipitations. For inorganic phosphorus, these values are 35.5%, 64%, and 0.5% by rivers, wastewater, and precipitation, respectively. These results suggest the very minor contribution of atmospheric depositions to the annual budget of nutrients in coastal waters. This leads to one general and widely accepted conclusion on the minor role of atmospheric deposition of nutrients in primary production of organic matter and an equally minor role of this contribution of nutrients to biogeochemical processes in coastal waters.

Table 4. Contribution of various sources of nutrients to their annual budget in coastal areas.

	River Input, t Year^{-1}	Wastewater, t Year^{-1}	With Atmospheric Precipitations, t Year^{-1}
Inorganic nitrogen	7594 (82%)	1478 (16%)	94.11 (1%)
Phosphates	171 (35.5%)	308 (64%)	1.27 (0.5%)

However, atmospheric precipitations do not fall uniformly throughout the year, and the river runoff also varies significantly between seasons. Atmospheric precipitations often happen in strong short-term events at the time scale of hours to days. Therefore, the contribution of different sources of nutrients to their annual budget varies at a shorter time scale from hours to seasons. The Crimean river's runoff accounts for about 35% of its annual value in winter, about 44% in the spring, about 12% in the summer, and about 9% in the fall [41]. The flux of nutrients with wastewater within the year is rather uniform. The flux of nutrients with atmospheric precipitations is 93.5 t season^{-1} for inorganic nitrogen and 1.41 t season^{-1} for inorganic phosphorus in summer. These nutrients' fluxes are 113.9 t season^{-1} and 2.14 t season^{-1}, respectively, in fall (Table 5).

Table 5. Contribution of various sources of nutrients to their seasonal budget in coastal areas.

	River Input, t Season^{-1} Summer/Fall	Wastewater Load, t Season^{-1}	With Atmospheric Precipitations, t Season^{-1} Summer/Fall
Inorganic nitrogen	911.3 (66%)/ 683.5 (58%)	369.5 (27%)/ (32%)	93.5 (7%)/ 113.9 (10%)
Phosphates	57.8 (42%)/ 43.3 (35%)	77 (57%)/ (63%)	1.41 (1%)/ 2.14 (2%)

Thus, the contribution of atmospheric precipitations in the summer–fall period increases many-fold and from 1 to 7% for inorganic nitrogen in summer and even to 10% in winter. For inorganic phosphorus, the contribution also increases several-fold from 0.5 to 1.2% in summer, and further to 1.8% in winter.

An assessment of possible contribution of a single event of atmospheric precipitations to the daily budget of nutrients has revealed that the maximum flux of both inorganic nitrogen and inorganic phosphorus with precipitations may reach 10.9 t day^{-1} and 1.34 t day^{-1}, respectively, in winter. Assuming that the flux of nutrients with wastewater within the year is rather stable, the daily load should be about 4 t day^{-1} for inorganic nitrogen and 0.8 t day^{-1} for phosphate (Table 6).

Table 6. Contribution of a single event of atmospheric precipitation to the budget of nutrients.

	River Input, t Day^{-1}	Wastewater Load, t Day^{-1}	With Atmospheric Precipitations, t Day^{-1}
Inorganic nitrogen	29.5 (66%)	4 (9%)	10.9 (25%)
Phosphates	1.9 (47%)	0.8 (20%)	1.34 (33%)

Based on the value of winter river runoff (35% of the annual value), the daily load of nutrients by the rivers is about 29.5 t day^{-1} for nitrogen and about 1.9 t day^{-1} for phosphorus. The contribution of atmospheric precipitation into the daily load of nutrients (especially with the observed dust transport from deserts) can reach 25% for inorganic nitrogen and 33% for phosphate during high water seasons. These values are in good agreement with other published data. Thus, Richon et al., (2018) [42] applied numerical modeling to reveal that atmospheric deposition may account, on average, for 10% of nitrate and for 5–30% of inorganic phosphorus external inputs into the Mediterranean Sea. Some researchers [43,44] indicated that direct deposition of nitrogen onto the water's surface (not including the contribution of nitrogen to the landscape and then exported to estuaries) contributes between 1% and 40% of the total nitrogen input to an estuary.

When different locations are compared, the calculated values of the inorganic nitrogen concentration in the atmospheric precipitation in the coastal cities of Crimea (Evpatoria and Kerch) for the registered amount of atmospheric precipitations resulted in different values of nitrogen fluxes. Data on the calculated fluxes of inorganic nitrogen (mmol m^{-2} $year^{-1}$) in Kerch and Yevpatoria, as well as measured fluxes in Sevastopol, in 2018–2020 are presented in Table 7.

Table 7. The input of inorganic nitrogen with atmospheric precipitation, mmol m^{-2} $year^{-1}$.

Year	Sevastopol (Measured)	Evpatoria (Calculated)	Kerch (Calculated)
2018	35.31	43.72	46.11
2019	23.43	35.68	27.61
2020	24.20	36.88	26.64

One of the reasons for the difference in these values can be the difference in the amount of precipitation between individual locations (Kerch vs. Sevastopol, for example). The effect of atmospheric load to the budget of nutrients in coastal waters can vary from at least 1.5-fold for other equal conditions. Yet, the river runoff is far less in Kerch as compared to Sevastopol, and the amount of municipal wastewaters are also far less in Kerch as compared to Sevastopol because the population of Sevastopol is about 5-fold of that in Kerch. This makes the atmospheric input of nutrients in the Kerch region far more important as compared to Sevastopol and Yevpatoria.

4. Conclusions

The concentration of nutrients in the surface layer of coastal areas, as we have demonstrated for Sevastopol Bay, may significantly exceed the ambient value after atmospheric precipitation. Atmospheric precipitations provide a significant input of nutrients into coastal waters. This is especially true and easily recognized on a shorter time scale of hours to days, while the role of the river load is important on the annual time scale. Thus, the input of nutrients with atmospheric precipitations on an annual basis does not exceed a few percent of their total input, but it can reach 25% for inorganic nitrogen and 33% for phosphate for the period of the rain events. The influence of atmospheric precipitations becomes more significant in summer when seasonal stratification in the water column prevents vertical mixing of waters, the concentration of nutrients in the upper layer of water is minimal, and the riverine input is also minimal.

It has to be taken into account that a substantial additional production and flux of organic matter may occur because the primary production processes also follow temporal variations in the content of available nutrients on the time scale of days. Another important issue related to the atmospheric input of nutrients is spatial and temporal variations in this input. This makes a long-term monitoring of atmospheric wet and dry precipitations to reconstruct regression equations for nutrients and to further study behavior of wet and dry forms nutrients from atmospheric precipitations important. Such regression equations are especially important for the analysis and modeling of the laterally resolved inputs of nutrients and their consequences.

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References

1. Michaels, A.F.; Siegel, D.A.; Johnson, R.J.; Knap, A.H.; Galloway, J. Episodic inputs of atmospheric nitrogen to the Sargasso Sea: Contributions to new production and phytoplankton blooms. *Glob. Biogeochem. Cycles* **1993**, *7*, 339–351. [CrossRef]
2. Spokes, L.J.; Yeatman, S.G.; Corneli, S.; Jickells, T.D. Nitrogen deposition to the eastern Atlantic Ocean: The importance of south-easterly flow. *Tellus Ser. B* **2000**, *52*, 37–49. [CrossRef]
3. Loye-Pilot, M.D.; Klein, C.; Martin, J.M. Major inorganic elements in north western Mediterranean aerosols: Concentrations and sources, Estimation of dry deposition of soluble inorganic nitrogen. In *Water Pollution Reports*; Martin, J.M., Barth, H., Eds.; European Union: Brussels, Belgium, 1993; Volume 20, pp. 271–277.
4. Troost, T.; Blaas, M.; Los, F. The role of atmospheric deposition in the eutrophication of the North Sea: A model analysis. *J. Mar. Syst.* **2013**, *125*, 101–112. [CrossRef]
5. Lønborg, C.; Müller, M.; Butler, E.C.; Jiang, S.; Ooi, S.K.; Trinh, D.H.; Wong, P.Y.; Ali, S.M.; Cui, C.; Siong, W.B.; et al. Nutrient cycling in tropical and temperate coastal waters: Is latitude making a difference? *Estuar. Coast. Shelf Sci.* **2021**, *262*, 107571. [CrossRef]
6. Jickells, T. The role of air-sea exchange in the marine nitrogen cycle. *Biogeosciences* **2006**, *3*, 271–280. [CrossRef]
7. Ngatia, L.; Grace, J.M., III; Moriasi, D.; Taylor, R. Nitrogen and phosphorus eutrophication in marine ecosystems. In *Monitoring of Marine Pollution*; Fouzia, H.B., Ed.; IntechOpen: London, UK, 2019. [CrossRef]
8. Diaz, R.J.; Rosenberg, R. Spreading dead zones and consequences for marine ecosystems. *Science* **2008**, *321*, 926–929. [CrossRef] [PubMed]
9. Zavialov, P.O.; Makkaveev, P.N.; Konovalov, B.V.; Osadchiev, A.; Khlebopashev, P.V.; Pelevin, V.; Grabovskiy, A.B.; Izhitskiy, A.S.; Goncharenko, I.V.; Soloviev, D.M.; et al. Hydrophysical and hydrochemical characteristics of the sea areas adjacent to the estuaries of small rivers of the Russian coast of the Black Sea. *Oceanology* **2014**, *54*, 265–280. [CrossRef]
10. Polyakova, T.V.; Polyakova, A.V. Variability Phytoplankton Community of North-Eastern Black Sea under the Influence of Natural and Anthropogenic Factors//Issues of Modern Algology. 2016. Available online: http://algology.ru/958 (accessed on 15 December 2022). (In Russian)
11. Polyakova, T.V.; Polyakova, A.V. Ecology of plankton in the northeastern Black Sea. *Pap. Mosc. Soc. Nat. Testers* **2016**, *62*, 36–61. (In Russian)
12. Kos'yan, R.; Podymov, I.; Pykhov, N. (Eds.) *Dynamical Processes in the Sea Nearshore Zone*; Scientific World: Moscow, Russia, 2003; 320p. (In Russian)
13. Report on the State and Protection of the Environment of Sevastopol. Available online: https://spn.sev.gov.ru/ekologicheskoe-sostoyanie-sevastopolya/doklad-o-sostoyanii-i-ob-okhrane-okruzhayushchey-sredy-goroda-sevastopolya/ (accessed on 15 December 2022). (In Russian)
14. Moiseenko, O.G.; Khoruzhiy, D.; Medvedev, E. Carbonate system of the Chernaya river and biogeochemical barrier zone of the Chernaya River—The Sevastopol bay (the Black Sea). *Phys. Oceanogr.* **2014**, *6*, 47–60. (In Russian)
15. Mezenceva, I.V.; Malchenko, Y.A. Integrated approach in the organization of marine pollution monitoring in coastal water areas in Sevastopol. In Proceedings of the N.N. Zubov State Oceanographic Institute; "Artifex" Publishing House: Obninsk, Russia, 2015; pp. 326–339. (In Russian)
16. Gruzinov, V.M.; Dyakov, N.N.; Mezenceva, I.V.; Malchenko, Y.A.; Zhohova, N.V.; Korshenko, A.N. Sources of Coastal Water Pollution near Sevastopol. *Oceanology* **2019**, *59*, 523–532. [CrossRef]
17. Verzhevskaia, L.V.; Minkovskaya, R.Y. Investigation of Human Impacton the Coastal Waters of Sevastopol Region. In Proceedings of the V.I. Vernadsky Crimean Federal University, Geoecology and Natural Management: Actual Issues of Science, Practice and Education: Materials of the Pan-Russian Scientific and Practical Conference, Simferopol, Russia, 17–20 October 2018; pp. 99–102. (In Russian)
18. Ferreira, J.; Andrade, D.I.; Fuziki, M.E.K.; de Almeida, L.N.B.; Colpini, L.M.S.; Lenzi, G.G.; Tusset, A.M. Catalytic Systems in the Reduction of Nitrogen Oxide Emissions in Diesel-Powered Trucks. *Sustainability* **2022**, *14*, 6662. [CrossRef]
19. Ma, R.; Li, K.; Guo, Y.; Zhang, B.; Zhao, X.; Linder, S.; Guan, C.; Chen, G.; Gan, Y.; Meng, J. Mitigation potential of global ammonia emissions and related health impacts in the trade network. *Nat. Commun.* **2021**, *12*, 6308. [CrossRef] [PubMed]

20. Mahowald, N.; Jickells, T.D.; Baker, A.R.; Artaxo, P.; Benitez-Nelson, C.R.; Bergametti, G.; Bond, T.C.; Chen, Y.; Cohen, D.D.; Herut, B.; et al. Global distribution of atmospheric phosphorus sources, concentrations and deposition rates, and anthropogenic impacts. *Glob. Biogeochem. Cycles* **2008**, *22*, GB4026. [CrossRef]
21. Minakova, E.A.; Shlychkov, A.P. Losses of Nutrients with Atmospheric Depositions in the Basin of the Moddle and Lower Volga//Regional Environmental Issues. 2018. Available online: https://cyberleninka.ru/article/n/vypadeniya-biogennyh-veschestv-s-atmosfernymi-osadkami-v-basseyne-sredney-i-nizhney-volgi (accessed on 15 December 2022). (In Russian)
22. Jickells, T. Atmospheric inputs of metals and nutrients to the oceans: Their magnitude and effects. *Mar. Chem.* **1995**, *48*, 199–214. [CrossRef]
23. Im, U.; Christodoulaki, S.; Violaki, K.; Zarmpas, P.; Kocak, M.; Daskalakis, N.; Mihalopoulos, N.; Kanakidou, M. Atmospheric deposition of nitrogen and sulfur over southern Europe with focus on the Mediterranean and the Black Sea. *Atmos. Environ.* **2013**, *81*, 660–670. [CrossRef]
24. Xing, J.; Song, J.; Yuan, H.; Li, X.; Li, N.; Duan, L.; Kang, X.; Wang, Q. Fluxes, seasonal patterns and sources of various nutrient species (nitrogen, phosphorus and silicon) in atmospheric wet deposition and their ecological effects on Jiaozhou Bay, North China. *Sci. Total Environ.* **2017**, *576*, 617–627. [CrossRef]
25. Barile, P.; Lapointe, B. Atmospheric nitrogen deposition from a remote source enriches macroalgae in coral reef ecosystems near Green Turtle Cay, Abacos, Bahamas. *Mar. Pollut. Bull.* **2005**, *50*, 1262–1272. [CrossRef]
26. Gonz'alez-De Zayas, R.; Merino-Ibarra, M.; Matos-Pupo, F.; Soto-Jim´enez, M.F. Atmospheric deposition of nitrogen to a caribbean coastal zone (Cayo coco, Cuba): Temporal trends and relative importance as a nitrogen source. *Water Air Soil Pollut.* **2011**, *223*, 1125–1136. [CrossRef]
27. Manual on Air Pollution Control, Moscow. 1991. Available online: https://docs.cntd.ru/document/1200036406 (accessed on 15 December 2022). (In Russian)
28. Bordovskiy, O.K.; Ivanenkov, V.N. (Eds.) *Metody Gidrokhimicheskikh Issledovaniy Okeana [Methods of Hydro-Chemical Ocean Studies]*; Nauka: Moscow, Russia, 1978; 271p. (In Russian)
29. Solorzano, L. Determination of ammonia in natural waters by phenolhypochlorite method. *Limnol. Oceanogr.* **1969**, *14*, 799–801.
30. Bhuyan, P.; Ahmed, S.; Hopke, P.K.; Hoque, R.R. Understanding the Chemistry and Sources of Precipitation Ions in the mid-Brahmaputra Valley of Northeastern India. *Aerosol Air Qual. Res.* **2020**, *20*, 2690–2704. [CrossRef]
31. Varenik, A.V. Applying the Brandon Method to Estimate the Concentration of Inorganic Nitrogen in Precipitation. *Russ. Meteorol. Hydrol.* **2019**, *44*, 326–330. [CrossRef]
32. Efimov, V.V.; Volodin, E.M.; Anisimov, A.E. Modeling of the Black Sea Region Climate Changes in the XXI Century. *Phys. Oceanogr.* **2015**, *2*, 3–13.
33. Varenik, A.; Kalinskaya, D. The Effect of Dust Transport on the Concentration of Chlorophyll-A in the Surface Layer of the Black Sea. *Appl. Sci.* **2021**, *11*, 4692. [CrossRef]
34. Schichtel, B.A.; Gebhart, K.A.; Morris, K.H.; Cheatham, J.R.; Vimont, J.; Larson, R.S.; Beachley, G. Long-term trends of wet inorganic nitrogen deposition in Rocky Mountain National Park: Influence of missing data imputation methods and associated uncertainty. *Sci. Total Environ.* **2019**, *687*, 817–826. [CrossRef]
35. Shou, C.-Y.; Tian, Y.; Zhou, B.; Fu, X.-J.; Zhu, Y.-J.; Yue, F.-J. The Effect of Rainfall on Aquatic Nitrogen and Phosphorus in a Semi-Humid Area Catchment, Northern China. *Int. J. Environ. Res. Public Health* **2022**, *19*, 10962. [CrossRef] [PubMed]
36. Tabunshchik, V.; Gorbunov, R.; Gorbunova, T. Anthropogenic Transformation of the River Basins of the Northwestern Slope of the Crimean Mountains (The Crimean Peninsula). *Land* **2022**, *11*, 2121. [CrossRef]
37. Varenik, A.V.; Konovalov, S.K. Variations in Concentrations and Ratio of Soluble Forms of Nutrients in Atmospheric Depositions and Effects for Marine Coastal Areas of Crimea, Black Sea. *Appl. Sci.* **2021**, *11*, 11509. [CrossRef]
38. Kumari, V.R.; Neeraja, B.; Rao, D.N.; Ghosh, V.R.D.; Rajula, G.R.; Sarma, V.V.S.S. Impact of atmospheric dry deposition of nutrients on phytoplankton pigment composition and primary production in the coastal Bay of Bengal. *Environ. Sci. Pollut. Res.* **2022**, *29*, 82218–82231. [CrossRef] [PubMed]
39. Ventura, A.; Simões, E.F.C.; Almeida, A.S.; Martins, R.; Duarte, A.C.; Loureiro, S.; Duarte, R.M.B.O. Deposition of Aerosols onto Upper Ocean and Their Impacts on Marine Biota. *Atmosphere* **2021**, *12*, 684. [CrossRef]
40. Xie, L.; Gao, X.; Liu, Y.; Yang, B.; Wang, B.; Zhao, J.; Xing, Q. Atmospheric wet deposition serves as an important nutrient supply for coastal ecosystems and fishery resources: Insights from a mariculture area in North China. *Mar. Pollut. Bull.* **2022**, *182*, 114036. [CrossRef]
41. Scheme of Complex Use and Protection of Water Bodies of the River Basins of the Republic of Crimea. Book 1 General Characteristics of River Basins Located in the Territory of the Republic of Crimea. Available online: https://gkvod.rk.gov.ru/uploads/gkvod/attachments//d4/1d/8c/d98f00b204e9800998ecf8427e/phpTxr9ug_2.pdf (accessed on 15 December 2022). (In Russian)
42. Richon, C.; Dutay, J.-C.; Dulac, F.; Wang, R.; Balkanski, Y.; Nabat, P.; Aumont, O.; Desboeufs, K.; Laurent, B.; Guieu, C.; et al. Modeling the impacts of atmospheric deposition of nitrogen and desert dust-derived phosphorus on nutrients and biological budgets of the Mediterranean Sea. *Prog. Oceanogr.* **2018**, *163*, 21–39. [CrossRef]

43. Nixon, S.W.; Ammerman, J.W.; Atkinson, L.P.; Berounsky, V.M.; Billen, G.; Boicourt, W.C.; Boynton, W.R.; Church, T.M.; Dioro, D.M.; Elmgren, R.; et al. The fate of nitrogen and phosphorus at the land-sea margin of the North Atlantic Ocean. *Biogeochemistry* **1996**, *35*, 141–180. [CrossRef]
44. Valigura, R.A.; Alexander, R.B.; Castro, M.S.; Meyers, T.P.; Paerl, H.W.; Stacey, P.E.; Turner, R.E. *Nitrogen Loading in Coastal Water Bodies: An Atmospheric Perspective*; American Geophysical Union: Washington, DC, USA, 2001. [CrossRef]