

Water Migration of Elements in Ornithogenic Ecosystems of the North Pacific Islands

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Abstract—Specific features of the chemical composition of surface water and water migration of elements in North Pacific islands with large population of marine colonial birds were analyzed. Ornithogenic factor was found to be determining in the composition of surface water in such ecosystems. The concentrations of nutrients (N, P, S, K) are informative hydrochemical parameters reflecting the effect of birds on the intensity of their migration in water. Spacious areas subjected to biogeochemical impact are formed around the islands populated by seabird colonies.

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INTRODUCTION

Specific nature of islands attracts attention of scientists in different fields. It was reflected most strikingly in the theory of island biogeography, which rationalized unusual properties of island flora and fauna [1]. On the other hand, many specific features of island flora and fauna still remain poorly studied. For instance, unusual ornithogenic landscapes, which cannot be found on the mainland, may appear in islands under certain conditions. High bioproductivity of the surrounding seawater areas, availability of appropriate habitat on the islands, and the absence of terrestrial predators and humans provide favorable conditions for birds to populate the whole island from beaches to top surface. The population of birds on such islands may reach millions, and rookeries exist over hundreds and thousands years. Large centuries-old bird colonies affect almost all natural components to produce a specific ornithogenic microrelief on most islands; they transform the land cover and chemical composition of surface and ground waters and act as the key factor for the entire island ecosystem [2]. The main components of the effect of birds on the island flora and fauna are zoomechanogenesis and the strongest geochemical impact. According to published data, only one pair of gulls with brood excretes from 85 [3] to 170 kg [4] over the nesting period. Marine colonial birds feed mainly on fish and marine

invertebrates. A general property of all marine foods is high concentrations of N, P, S, as well as of a number of microelements (Cu, Zn, Cd, Fe, etc.) [5]. One part of elements is retained by biogeochemical barriers at the phytal level and at the dry peat level [6, 7], while the other enters into the surrounding marine water with runoff, affecting species composition and productivity of subaqueous biocoenoses [8, 9]. Thus, a specific biogeochemical cycle connecting the subaerial and submarine parts of islands is generated in island ornithogenic ecosystems. Vital activity of seabirds plays the key role in this cycle, and its important part is migration of elements with surface and groundwater runoff.

Evaluation of the chemical composition of water and intensity of water migration of different elements and construction of a general model of biogeochemical cycle in ornithogenic ecosystems are problems that have not yet been solved. In the Russian science works of A.N. Golovkin are known (see, e.g., [8, 10]). He showed the existence of large areas exposed to biogeochemical impact around seabird rookeries in the Barents Sea. Some authors analyzed biogeochemical aspects of the behavior of ornithogenic ecosystems on coral islands in the tropical Pacific Ocean [7, 11], incorporation into trophic chains of nutrients entering into small rivers in New Zealand from petrel breeding colonies [12], heavy metal content in the gull nesting

areas [13], etc. The effect of colonial seabirds as landscape-forming factor in several North Pacific Islands was studied by us previously; a general model for structural–functional organization of ornithogenic ecosystems was proposed, bird impact on autotrophic biogenesis was analyzed, and some aspects of water migration of elements on particular islands were considered [9, 14, 15]. However, almost no summary reviews on this topic have been reported.

The goal of the present work was to reveal general trends in water migration of elements in ornithogenic ecosystems of the North Pacific Islands. The main problems were to compare the chemical compositions of surface waters and conditions determining them on different islands colonized by birds, reveal specific features of geographic location and landscape factors affecting the composition of geographic location, search for informative hydrochemical parameters reflecting contribution of the ornithogenic factor to the intensity of water migration of elements, and evaluate the effect of accumulations of large seabirds on the surrounding water areas.

SUBJECTS AND METHODS

Field studies including sampling of water, sediments, plants, and soils were performed on seven North Pacific Islands populated by large seabird colonies which occupied the entire island surface (see figure). Among the seven examined islands, three islands having surface water streams were studied in the present work, namely Matykil', Talan, and Starichkov.

Matykil' island is the largest one of the Yam Islands located in the northern Sea of Okhotsk (the surface area of the island is 8.7 km², and the maximal altitude is 697 m). The lithogenic base consists of granite intrusions, as well as of Jurassic sandstone and schist. From the landscape viewpoint, Matykil' island belongs to mainland low-mountain islands with a tundra–elfin wood–meadow phytome on dry peat soils. The island possesses a fairly thick water stream network which is active in summer and is characterized by a flow rate of 0.2–0.3 l/s. The island is a part of the Magadan Reserve, and the uniqueness of the island flora and fauna is related to the largest seabird colonies in the North Pacific, whose population is estimated at 7 to 11.4 million individuals [16].

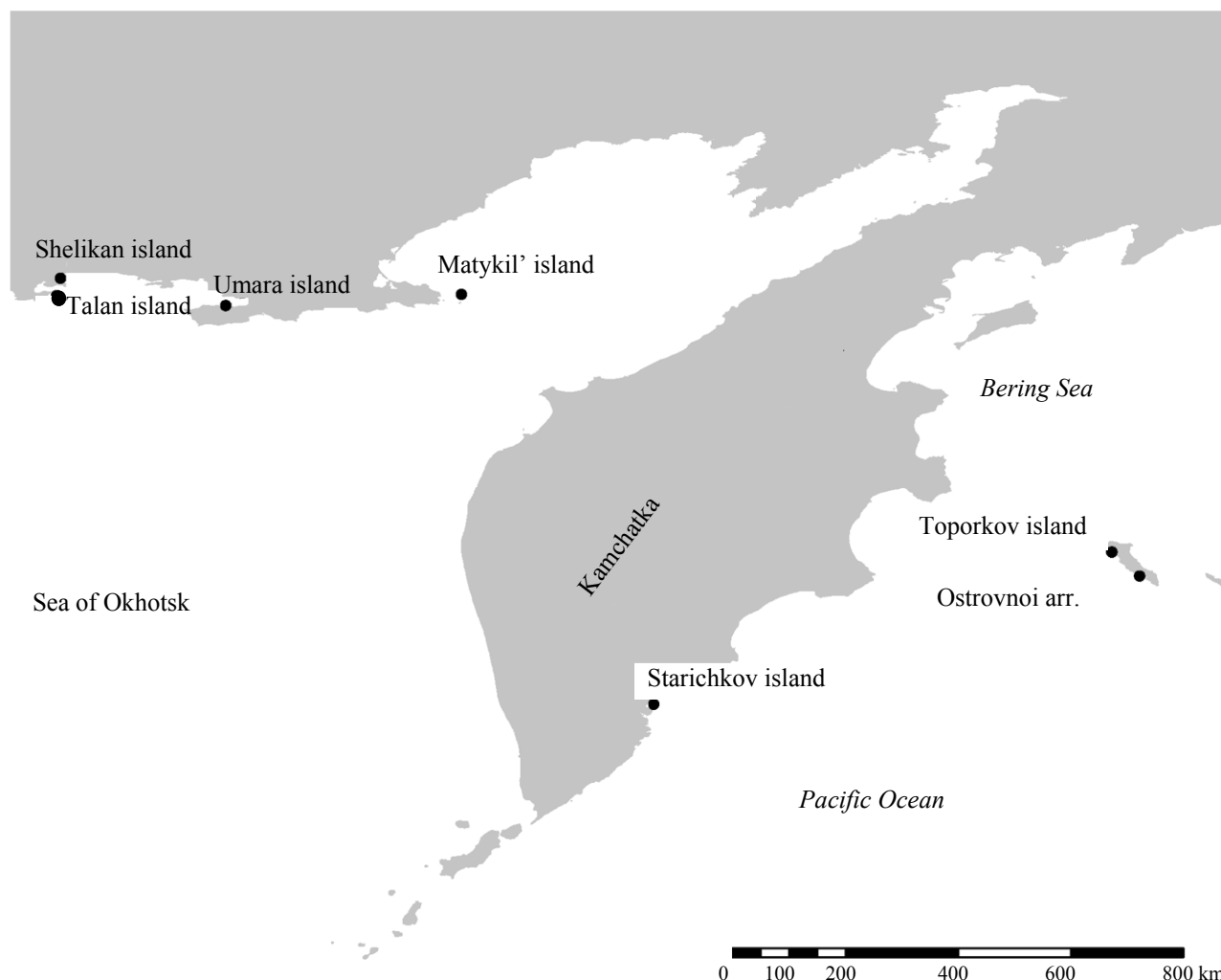
Talan island with an area of 1.6 km² and a maximum altitude of 219.5 m is located in the

Tauiskaya Bay of the Sea of Okhotsk. The island body is composed of Late Cretaceous quartz granodiorite intrusions. A marine terrace with a small thermokarst lake is attached at the northern side of the island at 3–5 m above sea level. The vegetation background is formed by thickets of mountain pines, reed grass meadows, and tundra shrubs on dry peat soils and podburs. The amount of precipitation and the area of the island give rise to a network of temporary streams with flow rates of 0.1–0.2 l/s. Brooks have mostly subsurface drainage under rubble blocks in the bottoms of valley-like lows and sometimes come out to the surface. Talan island is a natural monument of Federal value; it is populated by seabird colony which was estimated at 1–1.5 million individuals in the late 1980s; the bird population has now decreased to 600–700 thousand individuals [17].

Starichkov island is located in Avacha Bay of Pacific Ocean; it has an area of 0.4 km², and the maximum altitude is 147.5 m. The island is composed of volcanic-sedimentary rocks (andesites, basalts, tuffs, and sandstones). Its vegetable cover background is represented by mixed-grass and tall-grass meadows and alder thickets on volcanic ocher soil. Due to the small area the island has no permanent streams, but several brooks with a flow rate of 0.1 l/s appear in summer. Starichkov island has the status of a natural monument of regional importance; it houses a rookery mentioned even by H. Steller. The bird population is now estimated at 50 thousand [18] to 180 thousand individuals [19].

The examined islands may be divided into two groups with respect to their geographic location and landscape structure. Matykil' and Talan islands are located in a marginal sea and are composed of acidic rocks; their vegetation consists mainly of monodominant reed grass meadows that replaced the original shrub tundra and mountain pine thickets. Starichkov island belongs directly to Pacific Ocean and is composed mostly by basic volcanic rocks. Apart from reed grass meadows, vegetation of Starichkov island is largely contributed by tall-grass meadows like those occurring in Kamchatka, as well as by alder thickets. The common feature of all these islands is that colonial seabirds populate almost all island area, but the magnitude of their influence increases in going from the upper stratum to the coast.

The hydrochemical assessment included sample withdrawal from brooks, springs, and small lakes in



Geographic location of ornithogenic island ecosystems under study.

areas with different magnitudes of ornithogenic impact, as well from snowfield meltwater in apical parts of the island where the effect of birds is minimal. Meltwater was used as reference to detect variation of hydrochemical parameters in ornithogenic ecosystems. Determination of pH, salinity, ion composition, and total carbon and phosphorus in brooks on Matykil' island was performed at the Water Quality Analytical Center, *Rosa Ltd.* (Moscow), on Talan island, at the *VNNI-1* Analytical Laboratory (Magadan; in addition, the concentrations of nitrate and nitrite ions were determined), and on Starichkov island, at the Analytical Laboratory Kamchatka Research Institute of Fishery and Oceanography (Petropavlovsk Kamchatsky; in addition, different forms of nitrogen and silicon were determine). Apart from brook water, seawater

samples taken at different distances from Starichkov island were analyzed. The analyses were carried out according to standard procedures [20]. All the above laboratories have been approved by the National Accreditation.

Along with hydrochemical analysis, plants, soils, and sediments (by catenas typical of brook basins), as well as bird excrements, were analyzed. The ash content of plants and organogenic horizons was determined at the Analytical Laboratory, Physical Geography and Landscape Science Department, Faculty of Geography, Moscow State University. The concentrations of N, C, S, and H in soils, sediments, and bird excrements were characterized by the Dumas elemental compositions obtained using an Elementar

Table 1. Ionic composition and nutrient content of surface and ground waters in ornithogenic ecosystems

Location of water streams	pH	C _{org} , mg/l	Total ion concentration, mg/l	Ion concentration, mg/l									
				Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	NO ₃ ⁻	P	Si
Average for river water [7]	–	6.9	100.2	13	3.3	4.5	1.5	58.5	12.0	6.4	1.0	0.02	5.7
Coastal rivers of the Sea of Okhotsk in the Magadan region [21]	6.8–7.4	–	37.9–53.9	4.5–5.8	0.4–1.6	6.2–8.2 ^a	–	19.9–25.6	2.9–4.2	4.0–8.5	0.01–0.03	0–0.025	5.6–5.7
Brooks from snowfields on Matykil' and Talan Islands	4.3–5.9	2.2–4.6	35.0–45.1	2.7	1.3	5.7–8.2	1.0	18	2.8–2.9	11.1–11.3	4.0	0.07–0.4	–
Brooks, springs, and lakes on Matykil' and Talan Islands	3.4–5.8	3.4–12.4	80.0–298.4	18.0–70.0	4.4–22.0	7.1–31.0	1.5–13.0	6–14.0	2.5–47.1	22.3–94.3	1.5–50.5	0.2–3.2	–
Bol'shoi Vilyui river in Kamchatka [22]	–	–	73.97	7.4	2.1	10.9	0.61	26.8	9.16	17.0	–	–	5.2
Brooks on Starichkov Island	6.7–6.9	–	352.2–505.7	9.6–28.4	6.4–22.9	86.8–94.2	2.02–4.84	86.2–95.0	17.5–30.4	97.9–98.8	38.3–138.5	0.2–0.5	10.0–11.3

^a According to the data of Hydrological Annuals [21], the sum of alkali metal ion concentrations (Na⁺ + K⁺) is given.

Table 2. Concentrations of nutrients in bird excrements, soils, and sediments

Sample	Concentration, %			C/N
	N	C	S	
Bird excrements	12.22	26.34	0.97	2.1
Soils under stone runs with auk nests	8.88	43.64	0.98	4.9
Sediments in brooks	1.13	8.56	0.32	7.6

Vario ELIII analyzer at the Analytical Laboratory, Soil Geography and Landscape Geochemistry Department, Faculty of Geography, Moscow State University. The microelement compositions of ashes from plants, peats, and sediments was determined by approximate quantitative spectral analysis at the Analytical Center, Bronnitsy Geological and Geochemical Expedition, Institute of Mineralogy, Geochemistry, and Crystal Chemistry of Rare Elements.

CHEMICAL COMPOSITION OF SURFACE WATER IN THE ISLANDS AND FACTORS AFFECTING IT

The chemical compositions of river water in the islands of the Sea of Okhotsk and of Avacha Bay are presented in Table 1; these data were supplemented by average concentrations of ions and soluble forms of biogenic elements, calculated by V.V. Dobrovol'skii for river water [7], and by the data on rivers in the Magadan region taken from hydrology annuals [21] and Bol'shoi Vilyui river in Kamchatka [22]. It is seen that surface waters on the examined islands differ considerably from river waters in the eastern coasts of the Sea of Okhotsk and Kamchatka in salinity, ion ratio, and nutrient concentration. The island landscapes generally show high spatial variability of hydrochemical parameters, indicating change of the ratio and strength of factors and processes determining the composition of water. These factors include: aerial input of substances with precipitations, ornithogenic supply of bird metabolites, leaching from soils, and impulverization of marine salt.

The minimal values of most hydrochemical parameters were detected in the islands of the Sea of Okhotsk (Matykil' and Talan) in autonomous natural territorial complexes (NTC) on the apical plateaus developing under subaerial conditions. The main source of food in the upper reaches of brooks is ultrafresh meltwater which is characterized by weakly acidic reaction and a large fraction of thalassophile ions (Cl, Na). Despite insignificant effect of birds nesting in stone runs, the concentration of some nutrients (P, N) in the brook water is higher than in the rivers of Okhotsk coast where seabird colonies are absent.

The contribution of ornithogenic factor sharply increases in going to the middle and lower reaches of brooks that cross slopes with a high nesting density and diversity of bird population. Chemical elements are involved in water migration upon leaching from bird feces and from soils enriched in bird feces and

other products of their vital activity (pellets, eggshell, etc.), thus changing the composition of surface water. Their transformations are seen in several ways.

1. Change of the Conditions for Water Migration of Elements

Increase in the concentration of organic carbon (C_{org}), decomposition of uric acid salts excreted by birds, and formation of oxalic acid favor reduction of pH value down to 3.4 and generation of acidic medium not only in the brook water but also in the groundwater which comes to the surface in springs in the lower parts of slopes. Increased water aggressiveness stimulates acid leaching of soils. This is confirmed by the formation on Talan island of acid (pH 3.7–4.7) frost dry peat soils at slopes with very high density of nesting of various auk species [23]. Such trend may be reduced by washout of Ca from pellets and eggshell, which retains weakly acidic medium.

2. Increased Salinity and Nutrient Concentrations

Taking into account the composition of bird feces enriched in organic compounds and salts of uric and mineral acids (phosphates, ammonium urate and oxalate), they may be regarded as an important source of chemical elements in the formation of water streams. Increased salinity and concentration of ions in brook and spring water is related to leaching of sulfates, chlorides, readily soluble phosphorus compounds, nitrates, and other chemical substances from soils enriched in bird feces. The revealed trend is general for all islands occupied by seabird colonies, and lateral migration of nutrients occurs not only via surface water but also with ground water runoff.

Comparison of the analytical data on bird excrements with other natural components showed the following series of reduction in element concentrations: $C > N > S$ (Table 2), though the ratio between them does not remain constant. Accumulation of carbon in soils under stone runs where auklets nest results from not only bird excrements but also detritogenesis which increases its concentration by a factor of 1.6 as compared to excrements. Though the concentration of nitrogen in soils of ornithogenic landscapes is fairly high, it decreases as compared to excrements as a result of leaching. This changes the C/N ratio which is equal to 2.1 in bird excrements while reaches 4.9 in soils, indicating efficient involvement of nitrogen in the migration processes. The least concentration of the above elements was detected in sediments, for most of them is removed by water runoff.

Although North Okhotsk islands are characterized by fairly similar hydrochemical parameters of brooks maintained by meltwater, increase in the salinity (up to 79–88 mg/l) and concentrations of major ions in water on Talan island is expressed less contrastingly than on Matykil'. This may be due to lower bird population and groundwater migration of a considerable part of ingredients. Medium salinity water (223 mg/l) with increased concentration of C_{org} , nitrates (up to 50.5 mg/l), sulfates, and potassium ions was detected just in a spring on Talan island. Among surface waterstreams in lower catena levels, only thermokarst lakes in lower marine terraces that are free from bird nests may be distinguished by the ratio of ion concentrations in surface waterstreams. However, apart from input of elements from NTCs located at higher levels and splattering of bird excrements, the effect of marine salt impulverization on the composition of water increases. This follows from elevated content of thalassophile elements (Cl, Na). It should also be noted that the maximal pH value (5.3) was detected just in lake water on Talan Island (as compared to brooks and springs, pH 3.5–3.9). The reduced acidity indirectly indicates possible contact of the lake water and seawater, especially during high tide, as well as increase in the number of factors affecting water migration conditions. Transformation of the salt composition upon contact of river water and seawater and seasonality of these processes were shown for lakes in the Bol'shoi Vilyui estuary of Avacha Bay on the east coast of Kamchatka [22].

Enhanced ornithogenic impact on Matykil' Island makes downstream variation of hydrochemical parameters of brooks much more distinct, so that the overall concentration of ions increases by an order of magnitude as compared to meltwater. However, the magnitude of variation of these parameters changes in going from one region of the island to another, showing a relation to distribution of the bird population, landscape and ecological features of brook valleys, and conditions of generation of lateral streams [9]. The chemical composition of water changes most sharply in Ptichii Brook as a result of direct washoff to its canyon-like ravine of excrements and their decomposition products from rocks highly populated by nesting birds (guillemots, gulls, kittiwakes, horned puffins, etc.). The total ion concentration was found to reach 280–298 mg/l; water in the brook is brownish, and it contains increased amounts of C_{org} (10–12 mg/l), phosphorus (1.5–3.2 mg/l), potassium (8–13 mg/l), and

other ions; the pH value is reduced to 3.3–3.4. By contrast, weakly acidic medium (pH 5.0–5.7) and somewhat reduced concentrations of the above components (salinity 117–168 mg/l, C_{org} 7.1–7.8 mg/l, P 0.17–0.18 mg/l, K 1.0–2.6 mg/l) were observed in Pod'emnyi Brook having a broader bottom, where the belt of reedgrass bundles on dry peat soils in the bottom not only restricts contact of the slope runoff with the fluvial flow but also acts as lateral biogeochemical barrier that retains nutrients. Thus the effect of ornithogenic factor on the composition of water is controlled by the migratory landscape structure and biogenesis.

Brook waters on Starichkov Island located in Avacha Bay abeam estuary of Bol'shoi Vilyui differ from those typical of islands in the Sea of Okhotsk by acid–base properties (pH 6.7–6.9) and salinity (350–505 mg/l), the latter being contributed mainly by chloride and sodium ions, as well as by hydrogen carbonate ion. As applied to thalassophile elements, this may be related partly to the location of the island directly in the path of Pacific cyclones and enrichment of precipitation from the ocean, as well as to intense impulverization of sea salts in the coastal area; increased hydrogen carbonate concentration and reduced acidity may be determined by the base rocks which distinguishes the lithogenic base of Starichkov Island from Talan and Matykil' where granite intrusions predominate. On the other hand, increased salinity is favored by low water flow discharge of small streams, which may be crucial provided that water streams are continuously fed by mobile forms of elements leached from bird feces and soils saturated with excrements. This is especially true of nutrients. For example, the concentration of potassium and sulfates in brooks Starichkov Island is higher by an order of magnitude than in Bol'shoi Vilyui, while the concentration of Mg and Si is higher by a factor of 2 and more. It was just Starichkov Island where the maximal concentration of nitrates was detected. The largest values of all hydrochemical parameters were found for brooks in the southwest region of the island, where the largest bird colonies occur.

Regeneration of nutrients involves transformation of their organic forms into inorganic. This process is the fastest just for substances excreted by animals [24], including bird pellets and droppings. Different phases of the process under oxidizing conditions are reflected by the presence in brook water of different inorganic nitrogen species, such as ammonia ($N-NH_4$ 0.16–

Table 3. Intensity of aqueous migration of elements in surface water in summer^a

Location of water stream	Aqueous migration series with respect to K_x					
	1000n	100n	10n	n	0,n	0.0n
Average for river water [7]	–	Cl	S	Ca, Mg, Na	K, Si, Fe, P	–
Rivers in the Magadan region	–	Cl	S	Na, Ca, Mg, N	K, P, Si	Fe
Bol'shoi Vilyui river in the east of Kamchatka	Cl	–	S	Na, Ca, Mg	K, Si	–
Brooks on islands populated by seabird colonies	N, Cl	(S)	S, P	Na, Ca, Mg, (P), K	(K), Si	–

^a Elements whose rank in the aqueous migration series is different for different islands are enclosed in parentheses.

3.3 mg/l), nitrite (N–NO₂ 0.03–0.06 mg/l), and nitrate (N–NO₃ 8.6–31.3 mg/l). The concentration of unstable nitrite ions is generally the lowest, and different brooks are characterized by fairly similar nitrite ion concentrations.

INTENSITY OF WATER MIGRATION OF ELEMENTOV

The intensity of water migration of elements over island landscapes was estimated by calculating the coefficients of water migration (K_x). Insofar as the input of elements to water is controlled by a set of factors, including biological cycle, ornithogenic inflow, and air streams, K_x values were calculated with respect to the Clarke value rather than local rocks, which seemed methodologically more justified. Analysis of the water migration series (Table 3) showed that chlorine and nitrogen are the most mobile in ornithogenic landscapes and that nitrogen is even superior to chlorine. Increased ornithogenic influence, e.g., on Matykil' Island (Ptichii Brook), leads to addition of sulfur to the group of very mobile migrants. Unlike mainland landscapes on the east coasts of the Sea of Okhotsk and Kamchatka, where aqueous migration of potassium and phosphorus is limited to biological cycle, the behavior of these elements on the islands is strongly contrasting. Their migrating ability increases so that phosphorus becomes very mobile migrant, and potassium, readily mobile.

Taking into account high variability of hydrochemical parameters, it was interesting to estimate the degree of contrast in the behavior of chemical elements by the intensity of their aqueous migration. The calculation of the contrast coefficients (K_c) on the basis of K_x for particular elements in the lower and upper reaches of brooks revealed a general

relation for different islands: The migration ability of nutrients (N, P, S, K) leached from excrements and soils enriched with bird excrements changes most contrastingly (K_c ranges from 2 to 8). The same applies to groundwater which transfers a considerable part of elements. For example, the concentrations of nitrates, phosphates, and potassium in the groundwater on Talan Island are higher by factors of 12, 5, and 6, respectively, than in the upper reaches of brooks [15]. Efficient ingress of these elements into water streams indicates their elimination via surface and groundwater runoff, resulting in enrichment of sea water, especially in small bays.

According to the data of hydrochemical monitoring and analysis of nutrient distribution over the surface layer of sea water around Starichkov Island [25], the total inorganic nitrogen content (N–NH₄ + N–NO₂ + N–NO₃) of water in semiclosed bays on the west and south coasts of the island attains 3.7–10.8 μmol/l (0.05–0.15 mg/l), and the inorganic phosphorus content, 0.33–0.71 μmol/l (0.01–0.02 mg/l). These concentrations are within the limits reported for the most productive Pacific regions (2 to 30 μmol/l for inorganic nitrogen and 0.2 to 2.0 μmol/l for inorganic phosphorus) [26], but they drop down to background level as the distance from the island increases. It should be noted that just southwest and south parts of the island display increased concentrations of nutrients in brook water, high nesting density, and their persistently high location on the surrounding water [18]. The biogeochemical impact zone around Starichkov Island, defined by increase in nutrient concentration and bird population density, has an elliptical shape with an area of about 20 km². The affected zone around larger rookeries in the Barents Sea (hundreds thousand individuals) may reach 240 km² [10]. It is important that zones affected by

birds are not only hydrochemical but also biogeochemical. Bird excrements favor the primary productivity, productivity of diatoms and peridiniates, small flagellates, and other species constituting base food of zooplankton. Therefore, anomalously high occurrences of some zoobenthos and fish species (the latter being in turn seabird's food) are observed near bird colonies.

On the whole, the role of ornithogenic ecosystems in global cycle of matter and energy may appear more significant than it would follow from their relatively small size and limited occurrence. In particular, according to A.N. Golovkin, the amount of only inorganic phosphorus and nitrogen compounds entering into water from seabirds constitutes 3.9 and 19%, respectively, of the overall discharge of these elements into the World Ocean by rivers [8]. Chains of islands populated by seabird colonies also act as specific diffuse lateral biogeochemical barriers that restrict heavy metal input from migration cycles and their accumulation in deep-sea sediments [6].

CONCLUSIONS

(1) From the viewpoint of ecological geochemistry, study on the functioning of ornithogenic ecosystems is based on analysis of migration processes that are largely contributed by biogenic migration and runoff. Generation of the latter on islands populated by seabird colonies is determined by a set of abiotic and biotic factors, the main of which is ornithogenic. Geochemical impact produced by birds is responsible for variation of conditions for aqueous migration, mineralization of surface and ground waters, and their ionic composition and acid–base properties.

(2) Despite general factors determining the chemical composition of water under conditions of ornithogenic transfer of substances from the ocean and their subsequent involvement in biogenic and aqueous migration, the degrees of water transformation are different on different islands as compared to background levels. The reasons for these differences are related to the geographic position of the islands, their landscape structure, and population of bird colonies.

(3) It is advisable to use as indicators concentrations of nutrients (N, P, S, K) arising from bird excrements and their transformation products in island ecosystems to assess the effect of ornithogenic factor on the chemistry of surface and ground water. The

degree of water transformation is estimated by variation of its acid–base properties, contrast behavior of nutrients, and efficiency of their involvement in waterstreams.

(4) Islands populated by seabird colonies may be regarded as centers of nuclear systems possessing a high material and energy potentials. These systems give rise to extensive surrounding areas subjected to biogeochemical impact and favor increased biological productivity of subaqueous biocoenoses. Such ecosystems are characterized by considerable acceleration of matter and energy turnover compared to background parts of the World Ocean as a result of withdrawal of large amounts of fishes and invertebrates from the surrounding water areas, accumulation of bird excrements in nesting areas, and their transformation and transfer to the ocean.

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