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Changes in chemical composition of waters running off from the penguin rookeries in the Admiralty Bay region (King George Island, South Shetland Islands, Antarctica*)

ABSTRACT: Changes in chemical composition of the surface waters percolated through the soil and running off from the penguin rookeries are described. It was found, that the chemical composition of waters flowing from the breeding places depends on the size and rate of precipitation, and also on the location of rookeries. The longer and more complicated is the run off route of waters from the terrain of rookery, the more diluted are the solutions that reach the sea. In such case a significant part of phosphorus contained in the fecal materials may be retained on land, while most of ammonia volatilizes into the atmosphere.

Key words: Antarctic, pygoscelid penguins, penguin rookeries, decomposition, nutrients, chemical composition of waters

1. Introduction

Large sea-bird colonies, nesting on the limited site of the sea-shore give rise to an enormous fecal concentration. This natural organic fertilization is particularly important for the development and diversity of life on the narrow, ice-free coastal lowlands in the polar regions. Nutrients leached from excreta and spread by water and air enrich surrounding poor soils (Syroečkovskij 1959, Ugolini 1972, Eurola and Hakala 1977, Smith 1977, 1978, 1979), and fresh waters (Ganning and Wulff 1969, Grobelaar 1974, 1975, 1978a, 1978b, Krzyszowska in press, Heywood, Dornal and Priddle 1980, Priddle and Heywood 1980). Several authors have also reported that the solutions washed from the bird colonies

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down into the sea cause a remarkable increase in the nutrient level in the littoral waters (Golovkin and Gurevič 1973, Golovkin and Garkovaja 1975) and that could have important effects in the increase of their primary and secondary productivity. However, this phenomenon does not seem to be equally important everywhere in the polar regions (Bedard, Theriault and Berube 1980).

Up to now, the evolution of the chemical composition of waters during their downslope way has not been described, and, therefore, there is a lack of information concerned with this main soil-formation process of the ornithogenic soils. It is also difficult to find out in what form the nutrients reach the sea. Simple and quick experiments (Bedard, Theriault and Berube 1980, Galkina 1974) used in the examination of the water-soluble part of nutrients, ignore the process of intensive mineralization of guano (Pietr, Tatur and Myrcha 1983, Tatur and Myrcha in press).

2. Material and methods

Study Site

Investigations were carried out in the region of Admiralty Bay (62 09'S, 58 28'W) on King George Island, South Shetland Islands. In 1979, there were recorded about 45 000 pairs of penguins on the seven ice-free strips of the coastal line (Jabłoński in press). Three species of penguins, found in Admiralty Bay, nest at different sites (Jabłoński in press, Moczydłowski in prep. The Adelie penguins *Pygoscelis adeliae* (Hombron et Jacquinet) are more agile and reach further inland than any other penguin species do. Rookeries of the Adelie penguins (only Thomas Pt. and Llano Pt.) are usually situated far away from the sea and their nesting sites are localised on the permeable ground. Chemically aggressive solutions, washed down from the rookery, during their long and complicated way downslopes react with the weathered cover of the volcanic rock, and form a wide zone of alteration (Tatur and Myrcha in press).

Rookeries of the chinstrap penguins *P. antarctica* (Forster), found at Patelnia, Fur Seal Pt., Demay Pt., Shag Pt. and Chabrier Rock, are localised mainly on the steep, hard rocks near the sea. The waters washed down from these rookeries reach the sea faster and the zone of alteration, if it does exist at all, is small. Gentoo penguins *P. papua* (Forster) nest mainly in small rookeries on the stony beach. Their population is less significant here.

The best site for study was found to be on Llano Pt. During the summer 1979/1980, 18 335 pairs of penguins had been counted there, nesting in several rookeries on the area of about 15 hectares (Jabłoński in press). Nesting sites of the birds were situated mainly on the elevated

cliff, more than 100 m distant from the sea. About 82 per cent of the total penguin population on the Llano Pt. belonged to the Adelie penguins, but on the elevated cliff only this penguin species is nesting.

Since the way of the water running to the sea was longer here than in other places, surface water could be easily distinguished from that percolated through the soil, and the rate of its flow could be satisfactorily measured in the stream. The fate of solution washed down from other rookeries into the Admiralty Bay was less complicated and its way to the sea was shorter.

The way which guano was washed down from the main rookery localised on the elevated cliff is shown in Fig. 1. Following heavy rainfall, the solutions with guano suspension were displaced downslopes mainly on the surface of the soil. During small rainfall, or snow cover thawing, most of the solutions percolated through the soil. After a rain fall, the outflow of infiltrating water disappeared with a delay of few hours in pt. 2 (Fig. 1), after several days in pt. 3, and weeks in pt. 4. Beginning from pt. 4, as usually during a long way to the sea, a stream was formed. The stream flowed with short interruptions, in freezing periods, or prolonged spells of dry weather, during the entire austral summer.

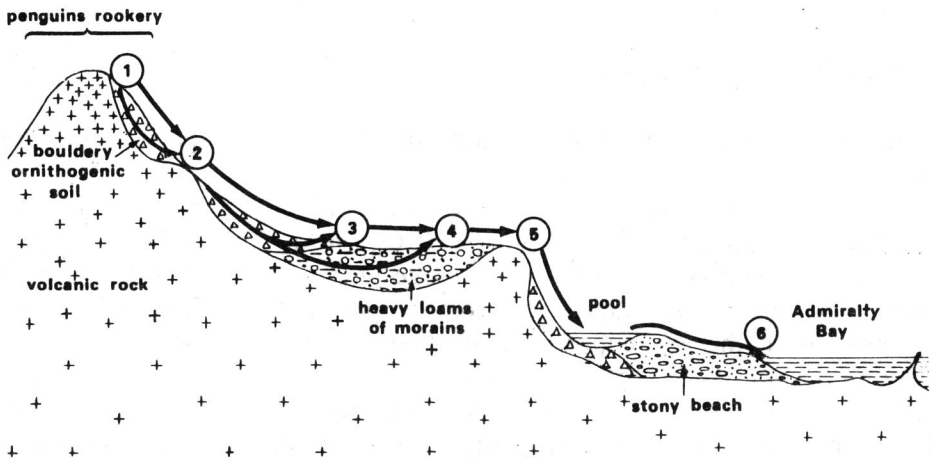


Fig. 1. The ways of water running off from the main rookery on Llano Pt. with schematically marked sampling points (1—6)

Methods

Water samples were collected nine times, under different meteorological conditions, at six sites marked in the diagram (Fig. 1), during the austral summer 1979/1980. Water was filtered (Whatman GF/C), and from that clear solution, after an appropriate dilution, the following determinations were performed:

— $\text{NH}_3\text{—N}$ by indophenol method according to Solorzano (1969),

— $\text{NO}_2\text{—N}$ and $\text{NO}_3\text{—N}$, after reduction on Cd, by naphthylethylene diamine method according to procedure recommended by the Smithsonian Institution (1978) in Laboratory guide for nutrient analysis of water, soil and plant material,

— *P*— colorimetrically, using the molybdenum blue method according to Strickland and Person (1968),

— Organic carbon by the method of wet oxidation with potassium dichromate according to Maciolek (1972),

— pH was tested colorimetrically, in the range 4.0–7.4.

The above mentioned analyses were carried out in the laboratory on the day of sampling.

To samples HNO_3 was added, and three months later, in these samples Ca, Mg, Al, Fe were determined by the atomic absorption spectrophotometry, as well as K and Na by the emission flame spectrophotometry, using Varian Techtron model 1200 instrument. To eliminate interfeerention during the Ca analysis, nitrous oxide-acetylene flame, an excess of Na, and a particular position of the burner were used (Ward and Biechler 1975). The analysis of the filter suspension was carried out in the same way as the analysis of guano samples (Pietr, Tatur and Myrcha 1983).

3. Results and discussion

Chemical composition of waters running off from, and by-passing penguin rookeries.

Fresh water in streams on King George Island usually belongs to a slightly mineralized water of the $\text{Cl-HCO}_3\text{-Ca-Mg}$ type, with a neutral reaction and slight conductivity in the range of 25–30 mS (Kozik, personal communication). Waters running off from the penguin rookeries leach several elements from the decomposed guano (Altschuler 1974, Tatur and Myrcha in press). The contrast between chemical composition of these waters and waters by-pasing penguin rookeries is therefore very sharp (Table I). Common ornithogenic origin of some determined elements in water results in a significant correlations between them, as well as with the main nutrient in this group, i.e. phosphorus (Table II). Thus, this given combination of data suggests that the avian manuring in some places can be the main factor controlling not only the level of nutrients N and P (Grobellaar 1974, 1978a, Priddle and Heywood 1980), but also other elements in water.

However, specific properties of the individual elements revealed during food assimilation by birds, guano decomposition, selective dissolution, reactions with rich substratum and volatilization of ammonia into the atmosphere, cause the existence of different proportions between elements in water, in comparison with the krill—the main food of penguins (Table III).

Table I

Changes of chemical composition of water in streams running off from catchment basin comprising the penguins rookeries and chemical composition of water in control stream. Data (mg/l) on the base of 18 measurements in point 5 and 6 (Fig. 1.) during the entire austral summer 1979/1980

Streams	N/NH ₃	N/NO ₃	P _{ortho}	Ca	Mg	K	Na	Al	Fe
biologically enriched stream	2-170	0-43	2-38	5-35	3-20	4-125	10-110	≤ 0.1-1.5	0.1-1.1
control stream (mean values)	0.2	0.8	0.03	1.2	0.8	1.1	13	≤ 0.1	0.1

Table II

Coefficients of correlation between phosphorus and other elements in water running off from catchment basin comprising penguin rookeries (n = 18)

	N	N/NH ₄	N/NO ₃	Al	K	Na	Fe	Ca	Mg
P	0.79	0.75	0.33	0.33	0.59	0.42	0.66	0.67	0.94

Table III

Comparison of ratios among elements in krill — the main food of the penguins and in waters carrying down products of the decomposition of penguins faeces. Comparison in relation to phosphorus

	P	N	Na	Ca	K	Mg
krill	100	605	176	56	40	22
water	100	274 (81—423)	320 (32—3000)	107 (21—148)	107 (31—260)	61 (22—370)

The decrease in nitrogen concentration in relation to phosphorus in water is mainly due to the intensive volatilization of ammonia into the atmosphere (Allen, Grimshaw and Holdgate 1967, Ganning and Wulff 1977, Pietr, Tatur and Myrcha 1983). A substantial increase in ratio of the metallic cations Ca, K, Mg to phosphorus is caused by the higher intensity of rock alteration due to the attack of chemically aggressive ornithogenic water, as well as by the decrease in phosphorus concentration resulting from the precipitation of aluminium-potassium and aluminium phosphates in the ornithogenic soils (Altschuler 1973, Tatur and Myrcha in press).

The concentration of mineral phosphorus in waters close to the rookery can be regarded, according to Stumm and Morgan (1970) as a saturated or, even, oversaturated solution; this is probably caused by chelating influence of soluble organic matter. In the soil surface layer, the chemical composition of water tends towards a physical and chemical balance, with precipitates of MG-NH₄ — and Ca — phosphates in neutral or alkaline reaction (higher solubility of mineral phosphorus). But in the deeper soil layers the balance is settled, with K-Al — and Al — phosphates in acid reaction (lower solubility of mineral phosphorus) (Tatur and Myrcha in press).

Influence of the meteorological conditions (rate and intensity of rainfall).

The selected data, presented in Table IV, V and VI, comprise the maximal recorded variation in chemical composition of the waters assayed. Apart from the effect of dilution during the prolonged flow, chemical composition of water running down from the rookeries depended mainly upon meteorological conditions that had determined whether the water was flowing on the soil surface, or percolating through the soil. Surface run-off follows a high rainfall, but usually does not follow the melting of snow cover.

Surface water washes down guano from the penguin rookeries. During

it way downslope, the guano suspension can be deposited among stones on the slope, or sedimented in the shallow pools on the beach. Because of sedimentation of suspension and rapid mineralization of guano (Pietr, Tatur and Myrcha 1983), nutrient in water were recorded mainly in mineral form, although a stormy rainfall and short transport could carry a great part of nutrients (especially phosphorus) in the undecomposed organic suspension (Table IV).

Table IV

Changes in chemical composition of waters running off on the surface of the soil from penguin rookery during period of heavy rain (mg/l)

Points of water sampling (according to Fig. 1)	Suspension			Mineral forms				pH	μS
	C_{org}	N_{org}	P_{org}	N/NH ₃	N/NO ₃	N/NO ₂	P_{orto}		
1	4800	1300	1490	7000	0.05	0.06	300	7.4	
2	1120	165	186	365	0.04	0.05	100	7.4	2820
5	374	102	115	170	0.05	0.18	38	7.4	686
6	209	58	65	90	0.06	0.02	25	7.4	366

Surface waters had a higher level of nutrients than waters percolated through the soil (Table IV, V and VI); their chemical composition was also essentially different. Mineral forms of nitrogen occurred almost exclusively as ammonia ions, thus resulting in neutral or alkaline reactions of these waters. An excess of ammonia in the soil surface layer inhibited the nitrification processes (Ganning and Wulff 1969), thus the nitrates were recorded only at the trace level.

The chemical composition of water running from the catchment basins, where the penguin rookeries were situated, changed immediately when the rainfall stopped. Organic suspension remained on the surface of the soil. The waters percolating through the weathered cover carried on nitrogen and phosphorus almost exclusively in the mineral forms, and carbon as soluble organic compounds (Table IV, V and VI). The proportions of mineral

Table V

Changes in chemical composition (mg/l) of water running off from the penguin rookery during dry period (wet surface of the soil on the rookery)

Points of water sampling (according to Fig. 1)	N/NH ₃	N/NO ₃	N/NO ₂	P_{orto}	$C_{dissol.}$	pH	μS
2	222	59	1.66	40	22	7.3	1280
3	88	56	0.2	37	9.3	5.1	855
4	7	36	0.05	9	3	4.0	
5	8	16	0.06	5	3	4.0	324
6	23	15	0.38	4	3	6.3	324

Table VI

Changes in chemical composition (mg/l) of water running off from the penguin rookery during extremely dry period (dry surface of the soil on the rookery)

Points of water sampling (according to Fig. 1)	N/NH ₃	N/NO ₃	N/NO ₂	P _{partic.}	C _{dissol.}	pH	µS
3	88	59	0.06	25	3.0	4.2	1090
4	4	22	0.0	2.0	3.1	4.0	
5	4	43	0.0	6.1	3.0	4.0	320
6	24	9	0.1	8.9	3.0	6.7	183

form of nitrogen were also different. In effect of nitrification, thanks to ammonia readily sorbed by the soil, there appeared gradually a higher level of nitrates, easily soluble and unadsorbed by the soil (Table V and VI, pts. 2, 3 and 4). The nitrification could only proceed in the deeper layer of the ornithogenic soils, where the richest population of nitrifying bacteria exists (Pietr, unpublished data). Decrease in ammonia concentration in percolated water was also supported by its enhanced volatilization into the atmosphere, resulting from the longer route. The highest value of the NO₃/NH₃ ratio was recorded during the dry period at the minimal rate of water flow (Table VI, pt. 5). However, a significant amount of nitrites was recorded only in the zone, where a still high level of ammonia had inhibited the second stage of nitrification (Table V, pt. 2).

Elimination of ammonia and production of nitrate was probably the main factors causing strongly acid reaction of water (Table V and VI, pts. 3, 4, 5). Higher level of the Al ion was recorded in strongly acid waters, due to intensified aggressivity of acid solutions in contact with easily altered silicate and aluminium-silicate of the soil. Neutralization of acid waters could take place during its run through shallow pools. Ammonia, the cause of an increase in pH in the pools, was produced as an effect of mineralization of the organic suspension, previously sedimented there during the high rainfall. The proportion of NH₃ and NO₃ could be also enhanced by the biological binding of nitrates (Ganning and Wulff 1969, Grobbelaar 1974, 1978b).

During heavy rainfalls, the chemical composition of the surface waters running off from the penguin rookeries varied widely. During dry periods, when water was only infiltrating through the soil, its chemical composition (pts. 5 and 6 in Fig. 1) is almost constant. Standard deviation of NH₄, NO₃ and P concentrations in these waters does not exceed $\pm 60\%$ during the entire summer.

Seasonal variations in the level of nutrients in water.

Limited sampling has not confirmed any relationship between the level of nutrients in run off waters from bird rookeries and the seasonal variation in intensity of bird manuring, though this fact has been men-

tioned in literature. That this relationship does probably exist, could be supposedly concluded from the paper by Ganning and Wulff (1969), but it has not been revealed under the conditions investigated. It is evident from the results reported in other paper (Tatur and Myrcha in press), that the return of matter that had been brought from sea to land in the penguin food, is delayed and does not close in annual cycle. Therefore it is likely, that the level of nutrients in water (Fig. 1, pts. 5 and 6) running down from rookeries, left by the penguins a month ago, was found to be almost the same as that during the maximal bird manuring.

In the area under investigation, plants have played a negligible role in the direct binding of nutrients from the biotically enriched waters. The penguin nesting site is often badly trampled, covered with liquid guano and devoid of plants. Nutrient-enriched water only occasionally penetrates large moss carpet on the periphery of rookeries (Thomas Pt., Llano Pt.). However, the process of accumulation of nutrients in the ornithogenic soils (Tatur and Myrcha in press) and volatilization of ammonia into atmosphere (Pietr, Tatur and Myrcha 1983), can play an important role in their elimination from water.

Influence of localization of penguin rookeries.

Present results may give some information elucidating the relation between the localization of penguin rookeries and the chemical composition of the waters reaching the sea.

In case of rookeries occupying hard rocks close to the sea (a typical nesting site of the Antarctic penguins), the route of water running down is the shortest, and the return of nutrients to the sea — the quickest. During a heavy rainfall, almost the whole guano deposit may be washed down. The waters reaching the sea are very concentrated and of chemical composition essentially typical for surface wash out ($\text{pH} > 7.4$; $\text{NH}_4 \gg \text{NO}_3$; high level of organic suspension).

Chemical composition of waters running down to the sea from the Antarctic penguin rookeries on Chabrier Rock, Shag Pt., Fur Seal Pt. may be compared with that of waters analysed in pts. 1 and 2 from Llano Pt., and those from Demay Pt. and Patelnia with waters in pts. 1, 2, 3 and 4 (Fig. 1, Table IV, V and VI).

When the nesting sites are distant from the sea and the way of the waters running down from rookery is longer and more complicated during percolation through permeable soils (such is a typical nesting place of the Adelie penguins), they reach the sea with a delay and are more diluted. The return of the nutrients to the sea is less complete because of the accumulation of phosphates in ornithogenic soils and raised ammonia volatilization into the atmosphere during such a longer route.

Except for short periods of surface flow during a heavy rainfall, waters

continuously reach the sea after having percolated through ornithogenic soils ($\text{pH} \leq 7.4$; $\text{NH}_4 \leq \text{NO}_3$; lack of organic suspension). Chemical composition of waters running down to the sea from Adelie penguin rookeries on Llano Pt. may be compared with that of waters analysed under pts. 5 and 6, and those on Thomas Pt. — with waters from pts. 2, 3, 4, 5 and 6 (Fig. 1, Table IV, V and VI).

4. Резюме

Исследования велись в период антарктического лета 1979/1980 в районе залива Адмиралти, на территории гнездовых колоний пингвинов рода *Pygoscelis*.

Исследования показали, что химический состав вод, стекающих с мест гнездования пингвинов резко отличается от состава вод типических потоков на острове Кинг Джордж (таблицы I и II).

В зависимости от величины и темпа осадков наблюдаются 2 разные дороги стока вод с территории гнездовых колоний (рис. 1). При обильных и интенсивных дождях воды стекают по поверхности грунта, тогда как при скурых осадках или в периоды между осадками воды проникают сквозь почву и дресвы. Воды, текущие по поверхности грунта, характеризуются несколько раз высшей концентрацией нутриентов, при чем их значительная часть, особенно вблизи колоний, может содержаться в еще не разложенной органической взвеси. Единственной важной формой азота является азот амонийный, а pH этих вод выше чем 7.4 (таблица IV). Воды, проникнувшие сквозь почву и дресвы, беднее нутриентами. Они не содержат органической взвеси, а желтокоричневую окраску придают прозрачным растворам растворимые органические соединения. Минеральный азот выступает главным образом в форме нитратов, а реакция вод сильно кислая (pH ок. 4.5). Эти воды могут стать нейтральными после протока через мелкие водоемы, возникающие часто на каменистых пляжах (таблицы V и VI).

Разный темп возвращения в море нутриентов, вынесенных с пищей пингвинами на сушу, зависит в значительной степени от расположения гнездовых колоний пингвинов, а это связано в свою очередь с типичной для отдельных видов селективностью по отношению к местам гнездования.

С колоний, расположенных на прибрежных скалах в непосредственном соседстве моря (типичные места гнездования антарктических пингвинов) сток мертвой органической материи и продуктов ее разложения является наиболее интенсивным и при том наиболее кратковременным, продолжающимся практически только во время дождя. Почти все экскременты могут стечь в море. Достигающие прибрежной зоны растворы сильно концентрированы; они происходят главным образом с поверхностных стоков ($\text{pH} > 7.4$, $\text{NH}_4 \gg \text{NO}_3$; значительное содержание органической взвеси). В случае когда дорога вод, стекающих с районов колоний длиннее и сложнее, а также когда места гнездования расположены далее от морского берега (типичная локализация колоний пингвинов Адели), тогда в прибрежные воды попадают более разведенные растворы. Время стока тогда значительно дольше.

Наряду с вольнами поверхностного стока, выступающими во время больших осадков, существует на исследуемой территории пости непрерывное, хотя менее интенсивное пополнение прибрежной зоны залива водами, происходящими главным образом с инфильтрации сквозь почву ($\text{pH} \leq 7.4$, $\text{NH}_4 \leq \text{NO}_3$, отсутствие органической взвеси). В этом случае значительная часть фосфора, содержащегося в экскрементах пингвинов может остаться на суше (фосфатация), а также больше аммиака может улечься в атмосферу.

5. Streszczenie

Badania prowadzono podczas lata antarktycznego 1979/1980 w rejonie Zatoki Admiralicji, na terenie kolonii lęgowych pingwinów z rodzaju *Pygoscelis*.

Stwierdzono, że skład chemiczny wód spływających z obszarów lęgowych różni się zasadniczo od składu chemicznego wód typowych strumieni wyspy Króla Jerzego (tabele I i II).

W zależności od wielkości i tempa opadów istnieją dwie różne drogi spływu wód z terenów kolonii lęgowych pingwinów (rys. 1). Przy wysokich i intensywnych opadach deszczu wody spływają po powierzchni gruntu, natomiast przy niskich opadach, lub w okresach pomiędzy opadami, wody infiltrują przez gleby i zwietrzeliny. Wody płynące po powierzchni gruntu posiadają kilkakrotnie wyższe koncentracje nutrientów, przy czym znaczna ich część, zwłaszcza w pobliżu kolonii, może być zawarta w nierozłożonej jeszcze zawieszinie organicznej. Jedyną ważną formą azotu mineralnego jest azot amonowy, a pH tych wód jest wyższe od 7.4 (tabela IV). Wody po infiltracji przez zwietrzelinę i gleby są znacznie uboższe w nutrieny. Nie zawierają one zawiesiny organicznej, a żółtobrazową barwę roztworom klarownym nadają rozpuszczalne związki organiczne. Azot mineralny występuje głównie w formie azotanowej, a odczyn wód jest silnie kwaśny (pH około 4.5). Wody te mogą zostać zneutralizowane w czasie przepływu przez płytkie zbiorniki wodne tworzące się często na kamienistych plażach za wyniesionymi wałami burzowymi (tabele V i VI).

Zróżnicowane tempo powrotu do morza nutrientów wyniesionych przez pingwiny na ląd wraz z pokarmem uzależnione jest w istotny sposób od lokalizacji kolonii lęgowych pingwinów. Fakt ten w znacznym stopniu wiąże się z charakterystyczną dla poszczególnych gatunków wybiórczością środowisk lęgowych.

Z terenów kolonii zlokalizowanych na przybrzeżnych skałach w bezpośrednim sąsiedztwie morza (typowe miejsce gniazdowania pingwinów antarktycznych) spływ martwej materii organicznej i produktów jej rozkładu jest najintensywniejszy i trwa najkrócej, bo praktycznie tylko w czasie trwania deszczu. Prawie wszystkie odchody mogą zostać zmyte do morza. Docierające do strefy przybrzeżnej roztwory są silnie stężone i pochodzą głównie ze spływów powierzchniowych (pH > 7.4, $\text{NH}_4 \gg \text{NO}_3$, znaczny udział zawiesiny organicznej). W przypadku, gdy droga wód spływających z terenu kolonii jest dłuższa i bardziej skomplikowana oraz gdy miejsca lęgowe położone są dalej od brzegu morskiego (najczęstsze usytuowanie kolonii pingwinów Adeli) do wód przybrzeżnych zatoki docierają znacznie bardziej rozcieńczone roztwory. Czas trwania spływu jest wtedy znacznie dłuższy.

Obok fal spływu powierzchniowego występujących w czasie trwania większych opadów, istnieje w badanym terenie prawie ciągłe, lecz mniej intensywne zasilanie strefy przybrzeżnej zatoki wodami pochodzącymi głównie z infiltracji przez gleby (pH \leq 7.4, $\text{NH}_4 \leq \text{NO}_3$, brak organicznej zawiesiny). W tym przypadku znaczniejsza część fosforu pochodzącego z mineralizacji materii organicznej zawartej w fekaljach pingwinów może zostać zatrzymana na lądzie (fosfatacja), a także więcej amoniaku może ulotnić się do atmosfery.

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