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**NATURAL AND ANTHROPOGENIC DISTRIBUTION OF CHEMICAL
ELEMENTS IN THE BOG AND LAKE DEPOSITS
OF THE KURTNA LANDSCAPE RESERVE
(NE ESTONIA)**

(Presented by U. Kirso)

Introduction

An objective estimation of the anthropogenic changes in the biogeochemical cycle is possible only with sufficient information on the geochemical background of the given area regarding corresponding components. To determine the latter it is not enough to know the clarks of elements or to operate with global means. Changing natural conditions lead to the essential changes in matter cycle processes, the intensity of migration varies, the change of energetic parameters gives rise to new associations, the formation or disappearance of geochemical barriers may lead to such changes in the concentration and structure of matter which can cause total reformation of landscapes and biocenoses. To secure scientific estimation of geochemical background values and of the tolerance limits of an ecosystem temporal surveillance of the components in the given location is needed. The best sources of information for geochemical reconstructions are lake and bog deposits preserving traces of the processes which have taken place in the Holocene, i. e. during the last 10 000 years. Combining geochemical data and the results of palaeoecological studies it is possible to find out correlations between changes in the absolute amounts of separate components and the development of communities. Correlative connections allow to pass on to prognoses as well as to determine the anthropotolerance limits of separate ecosystems and, thus, to regulate loads on natural systems or to use the latter in the tying up of industrial wastes and the regeneration of water.

Object and methods

The studies were performed in the Kurtna lake district. Samples were taken from the bogs of Kurtna, Niinsaare and Liivjärve, and the lakes of Konsu and Martiska. The profile of Kurtna bog deposits consists entirely of fen peat which started to form about 10 000 years ago. In the Niinsaare bog sand is covered by wood peat which is followed by fen peat, the formation of raised bog peat started around 4000 years ago. The peat core taken from the Liivjärve bog fully consists of raised bog peat. The bottom deposits of the Martiska and Konsu lakes consist of sapropels. Lake Martiska is a closed lake feeding mainly upon atmospheric precipitations, L. Konsu is a drainage lake into which presently is directed the water pumped out of mines. Thus, lakes of different feeding types, as well as bogs of various types and with different plant communities are represented.

The sampling was done with a hand-drill, the composition of the deposits was described on the spot, the surface of drill-cores was cleaned with a plastic knife and samples were taken for geochemical, lithological and botanical analyses. The thickness of samples was chosen so that each one would cover the time interval of 30—40 years. The chemical composition of the samples was determined by the neutron-activation method at the Institute of Physics, Acad. Sci. of the Latvian SSR.

The contents of 32 elements were determined: Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, As, Br, Sr, Rb, Sb, Cs, Ba, La, Ce, Eu, Tb, Yb, Hf, Ta, Th, U.

Different increment of deposits in different landscape elements does not allow comparison of geochemical information relying only upon the depth of deposits. For this reason, the age of the samples was determined using the radiocarbon and pollen analysis methods [1], and the depth-age charts were compiled for all the sections. Data comparison is given for the following time intervals: 8000 ± 500 ; 5000 ± 500 ; 3500 ± 500 and "the present", i. e. the last 30—40 years which witnessed considerable growth of human influence on biogeochemical cycle. These intervals were chosen proceeding from the development regularities of natural conditions: 8000 y. a. the present general formation of landscapes had taken shape, immigration of vegetation had come to the end, 5000 y. a. the s. c. Holocene Climatic Optimum was at its culmination, the water level of lakes had reached the current height, and the hydrothermal conditions about 3500 y. a. were rather similar to the present ones. So, 3500 ± 500 y. a. the geochemical parameters caused by the development of natural conditions should have been comparable with the current ones, differences result from anthropogenic influence on ecosystems.

A complex of geographical-geological methods was used to reconstruct the development of landscape elements, including the changes in hydrothermal conditions, water-level fluctuations in lakes, main features in vegetation development, etc. [2].

Results and their analysis

In dealing with the regularities of matter cycle the development of landscape elements and the prevailing migration type should be considered. This allows to divide the studied sections into 3 groups:

1) Aquatic migration is predominating. Concentrations of elements are mainly determined by groundwater and surface water input. The group is represented by the samples taken from the deposits of L. Martiska and L. Konsu. At this, in the case of L. Martiska the groundwater and catchment area matter flow is decisive; in L. Konsu, a drainage lake, the input with inflowing waters is added. Of course, the matter flow from the atmosphere is also added in both cases. Deposits of aquatic migration type are represented by 68 samples.

2) Subaquatic matter exchange process. The fen deposits from the Kurtna bog as well as the lower part of the Niinsaare section belong to this type. The water-level is approximately fixed by the level of the forming peat layer, the whole peat deposit is regularly overflowed. The matter flow consists of groundwater, surface water and atmospheric components. The number of samples describing this type of deposits is 45.

3) Aerial feeding type is characteristic of raised bogs where peat formation takes place in aerobic conditions, at which the level of waters is 5 to 50 cm below the forming sphagnum layer. So the input of matter into this layer takes place only from the atmosphere with wet or dry sedimentation. The sphagnum peat layer is characterized by samples taken from the

upper 5 meters of the Liivjärve bog and 3 m of the Niinsaare bog (67 samples all together).

In interpreting the results it is most important to know the regularities of the change of matter flow with concrete feeding types, as well as the change of the primary chemical composition of deposits in the course of their diagenesis. With aquatic type the determining factor is the change of groundwater level which is reflected in the change of the water-level in the lake. Water-level fluctuations influence the matter balance in the lake by the input of material from the littoral zone by erosion, as well as by the change of migration flow in connection with the change in the geochemical barrier. For this reason the basal deposits of the lakes, in which the lithophilic component dominates, have been excluded from analysis. In the already formed sediment complexes the in- and output of elements is of small importance as no relevant changes in the physico-chemical conditions take place. Changes, of course, occur in nutrients and in biophilic components, this especially in the course of biochemical and biological transformation of organic matter.

Subaquatic deposits (fen peat) acquire microelements either in biological process or in sorption. In lower layers, when the bog massif was smaller in area, a significant role was played by mechanical input, as a result of which the concentrations of lithophilic elements in lower samples are higher. The physico-chemical conditions of an already formed sediment complex are rather stable, so there is no reason to presume considerable postsedimentational migration. This is also confirmed by the concentration distribution curves of elements in time, where quite big variations in concentrations indicate that at least in the case of elements with small migrational ability the differences in concentrations from layer to layer are big, i. e. no levelling takes place.

The study of raised bog peat is of special interest as the corresponding samples reflect the changes in the amounts of only atmospherically transported matter. The problems are the biggest, however, with the preservation of primary information. The formation of primary chemical composition takes place under aerobic conditions, but along with the following accumulation of raised bog peat the water-level also rises and peat layers occur in anaerobic conditions. Such contrasting changes in conditions give rise to the geochemical barrier where the change of oxidizing conditions into reducing ones may lead to reformation of chemical composition. It should be mentioned, that we have not succeeded in finding practical confirmation to this hypothesis [3] as the current water-level in the majority of bogs coincides temporally with the accumulation of the peat layer formed in the beginning of intensive human activities. Thus, it cannot be definitely proved whether the increase of concentrations reflects human activities or is connected with changes in physico-chemical conditions.

The contents distribution curve of chemical elements in the Liivjärve raised bog clearly displays 2 sections: the lower one formed beginning about 8000 y. a. to 25—30 y. a., and the layer formed during the last 25—30 years where the concentrations of all elements are by tens of times higher (Fig. 1). Calculating the input of elements to cm^2 per year and comparing these values with the interval 3500 ± 500 y. a. we can see that due to the technogenic influence the input of some elements (Sb, Cs) has increased more than 1000 times, in case of the remaining elements 100 to 1000 times.

In the lower horizons the differences in the concentrations of elements are smaller fluctuating from 2 to 3 times. The values of atmospheric input were the smallest 4000—3500 and 400—100 y. a., bigger of the average 3000—1300 y. a. The chemical composition of the samples from the bog peat of the Niinsaare bog is comparable with that of the Liivjärve bog.

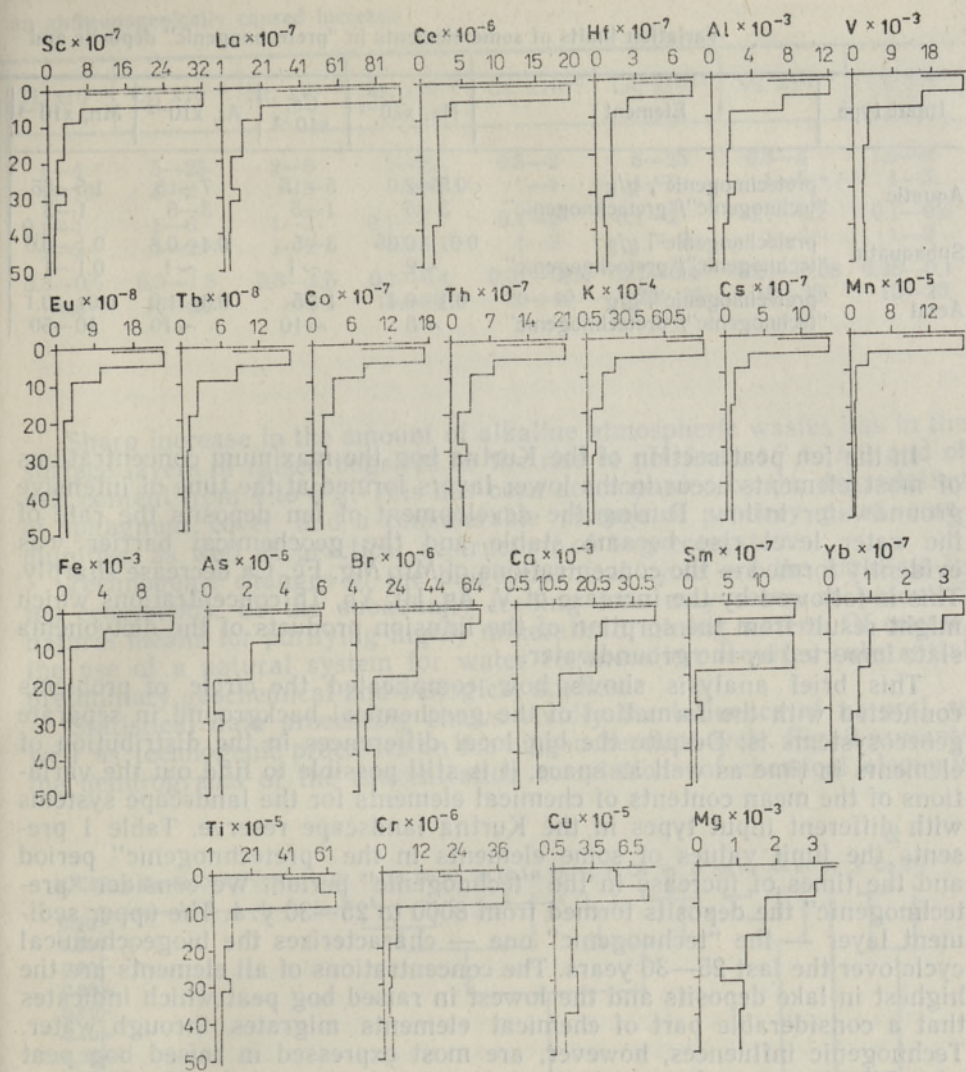


Fig. 1. The distribution of some chemical elements in the upper part of the Liivjärve bog section (g/g).

Big are the differences in the temporal distribution of elements in lake deposits. They result from the rather big differences in the feeding regimes of the lakes and in the development of physico-geographical conditions. The small size and the morphometric structure of L. Martiska have led to rather high concentrations of lithophilic elements connected with the wash-out of mineral matter from the coastal zone. The increase in the concentrations of most elements in the upper sediment layers is clearly expressed. In addition to the growth of atmospheric input a considerable part has been played by the fall of water-level connected with the exploitation of the Vasavere catchment. The fall of water-level by 2.5 m was accompanied by intensive erosion of sediments from the littoral zone. In the rather big L. Konsu the role of the input of elements from the catchment area is smaller, the matter transported with inflowing water is the most important. Though mining waters rich in microelements have been led into the lake during the last decades, the surface deposits show no considerable increase in the concentrations of these elements.

Variation limits of some elements in "pretechnogenic" deposits and

Input type	Element	Na, $\times 10^{-3}$	Ca, $\times 10^{-3}$	Al, $\times 10^{-3}$	Mn, $\times 10^{-4}$
Aquatic	"pretechnogenic", g/g	0.5—2.0	5—15	7—15	1.5—65
	"technogenic"/"pretechnogenic"	3—5	1—5	3—5	1—3
Subaquatic	"pretechnogenic", g/g	0.01—0.05	3—5	0.4—0.8	0.1—0.6
	"technogenic"/"pretechnogenic"	~2	~1	~1	0.1—1
Aeral	"pretechnogenic", g/g	0.1—0.4	1—5	0.3—1.0	0.01—0.1
	"technogenic"/"pretechnogenic"	~5	~10	~10	10—50

In the fen peat section of the Kurtna bog the maximum concentrations of most elements occur in the lower layers formed at the time of intensive groundwater inflow. During the development of fen deposits the rate of the water level rise became stable and the geochemical barrier was evidently formed — the concentrations of Mn, Mg, Fe, Ca decrease sharply. This is followed by the increase of V, As, Hf, Yb, Th concentrations which might result from the sorption of the infusion products of the dictyonema slate imported by the groundwater.

This brief analysis shows how complicated the circle of problems connected with the formation of the geochemical background in separate geoecosystems is. Despite the big local differences in the distribution of elements in time as well as space, it is still possible to find out the variations of the mean contents of chemical elements for the landscape systems with different input types in the Kurtna landscape reserve. Table 1 presents the limit values of some elements in the "pretechnogenic" period and the times of increase in the "technogenic" period. We consider "pretechnogenic" the deposits formed from 8000 to 25—30 y. a. The upper sediment layer — the "technogenic" one — characterizes the biogeochemical cycle over the last 25—30 years. The concentrations of all elements are the highest in lake deposits and the lowest in raised bog peat which indicates that a considerable part of chemical elements migrates through water. Technogenic influences, however, are most expressed in raised bog peat where the increase of concentrations in upper horizons is by 10—20 times. Practically no rise in the concentrations of elements occurs in the surface layer of fen peat, even in the case of such biophilic elements as Zn and Br. It follows from here, that in case of subaquatic input type partial aquatic outflow or infiltration of the atmospherically transported elements from the surface to the deeper deposit layers takes place. Big concentration increase coefficients in the upper horizon of lake deposits are partially connected with the fall of water-level and the input of mineral matter from the coastal zone.

Correlations between the concentrations of chemical elements and the state of the ecosystem were found. For this, changes of diatomic flora in lake deposits and plant communities in peat deposits were studied in dependence on the changes in the chemical composition. Although the concentration variations of separate elements in the "pretechnogenic" period are 2—3 times higher as compared with the means, this has not led to significant deviations in the state of the ecosystem. Likewise, the increase in the trophics of L. Martiska cannot be directly related to the rise in the concentrations of microelements, decisive here is the constant increase of the contents of macroelements and, first of all, of nutrients.

Yet, there is a direct connection between the input of elements and the state of the ecosystems of ombrotrophic bogs.

Ti, $\times 10^{-4}$	Cr, $\times 10^{-6}$	Br, $\times 10^{-5}$	As, $\times 10^{-6}$	Cs, $\times 10^{-6}$	La, $\times 10^{-6}$	Sb, $\times 10^{-6}$	Th, $\times 10^{-6}$
1—4	5—25	2—5	1—20	0.5—2	5—25	0.5—4	1.5—8
4—10	1—2	~3	~10	1—4	1—5	1—5	1—3
0.1—1	1—6	1—3	0.1—4	0.1—2	0.1—2	0.1—0.2	0.1—0.6
1—2	1—2	1—2	1—3	1—2	1—2	1—2	1—2
0.3—0.5	0.3—1.5	0.3—1.5	0.1—0.4	0.01—0.04	0.1—0.4	0.01—0.08	0.05—0.1
~8	10—20	~5	15—20	30—40	20—30	10—20	10—20

Sharp increase in the amount of alkaline atmospheric wastes has in the surface layers of raised bogs led to the rise of pH from 4.7 to 6.0 and of ash content from 4 to 6%. This has been accompanied by the degradation of sphagnum cover and a considerable change of primary plant communities, as well as practical destruction of bog ecosystems.

Technogenic changes of the biogeochemical cycle are the smallest in fen ecosystems. So the subaqually feeding fens may serve as potential natural means for purifying highly mineralized mining waters. Of course, the use of a natural system for water regeneration requires substantial preliminary geochemical and biological studies.

Statistical data processing shows vividly the influence of natural as well as technogenic processes on the biogeochemical cycle. Fig. 2 presents the dendrograms of the concentration correlations of chemical elements

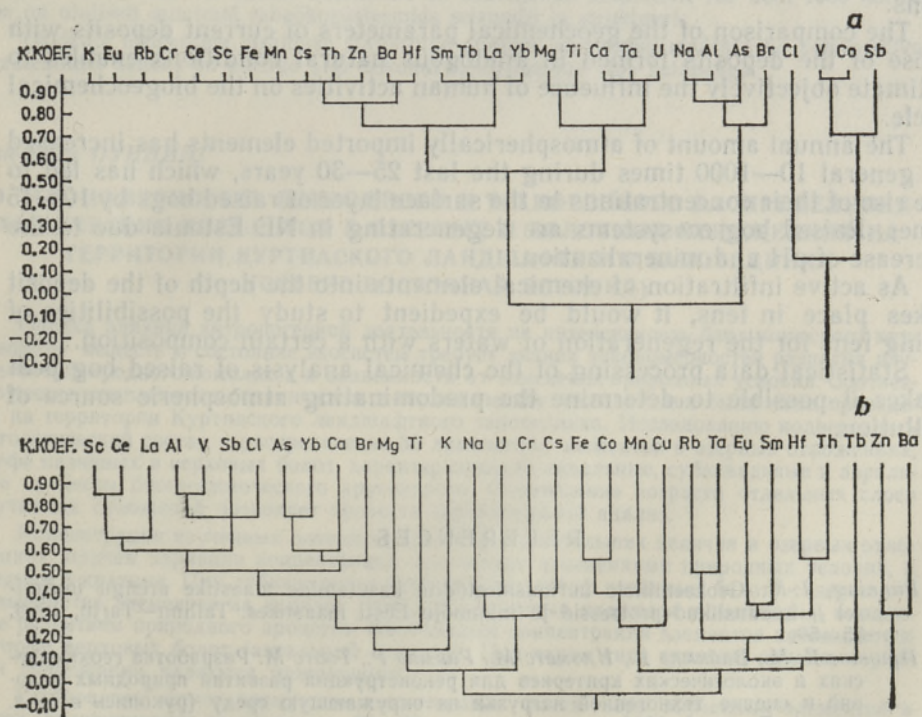


Fig. 2. Dendrograms of concentration correlations of chemical elements in the upper (0—8 cm) part (a — “technogenic”) and lower (8—372 cm) part (b — “pretechnogenic”) bog deposits in the Niinjärve bog section.

in the "pretechnogenic" and "technogenic" deposits of the Niinsaare bog compiled on the basis of correlation matrixes. Comparison of the dendrograms indicates considerable changes in the chemical composition of the atmosphere over the last 25—30 years. As the dendrograms based on the analyses of the Liivjärve raised bog deposits are also identical with those brought in Fig. 2 [4], there is no doubt about the sources of pollution — these are the electric power plants operating on oil-shale. Eu, Rb, Sc, K, Cs, Th characterized by high correlation coefficients have comparatively high concentrations in oil-shale. Such methodical approach allows to determine the predominating source of pollution in every concrete case. For this it is necessary to know the chemical composition of the wastes of the potential pollution sources, this especially concerning microelements. An increase of the correlations of respective indicator elements in raised bog peat refers to stronger influence of the pollution source in the given area. Biogeochemical studies are of special importance in ecology, they enable to describe and prognosticate the state of geoecosystems, and to carry out territorial planning. A new scientific approach — geochemical ecology — has lately been worked out to carry out these tasks [5]. However, it should be mentioned that an inverse task is also perspective — to reconstruct development of landscapes on the basis of geochemical data [1].

Conclusions

The most optimum way to determine the geochemical background is to study the distribution regularities of chemical compounds or elements in lake and bog deposits formed in different physico-geographical conditions.

The comparison of the geochemical parameters of current deposits with those of the deposits formed in analogous natural conditions enables to estimate objectively the influence of human activities on the biogeochemical cycle.

The annual amount of atmospherically imported elements has increased in general 10—1000 times during the last 25—30 years, which has led to the rise of their concentrations in the surface layer of raised bogs by 10—15 times. Raised bog ecosystems are degenerating in NE Estonia due to the increase of pH and mineralization.

As active infiltration of chemical elements into the depth of the deposit takes place in fens, it would be expedient to study the possibilities of using fens for the regeneration of waters with a certain composition.

Statistical data processing of the chemical analysis of raised bog peat makes it possible to determine the predominating atmospheric source of pollution.

REFERENCES

1. *Punning, J.-M.* Geokeemiliste uurimismeetodite kasutamise maastike arengu uurimisel // Looduslikud protsessid ja inimõju Eesti maastikes. Tallinn—Tartu, 1989, 55—59.
2. *Пуннинг Я.-М., Вайкмяэ Р., Иломес М., Раямяэ Р., Тоотс М.* Разработка геохимических и экологических критериев для реконструкции развития природных условий и оценка техногенной нагрузки на окружающую среду (рукопись в геол. фонде). Таллинн, 1988.
3. *Евдокимова А. К., Иломес М. А., Пуннинг Я.-М. К.* Возможности восстановления особенности атмосферного поступления тяжелых металлов в позднем голоцене // Изотопно-геохимические исследования в Прибалтике и Белоруссии. Таллинн, 1988, 34—48.

4. Punning, J.-M., Ilomets, M., Karofeld, E., Koff, T., Kozlova, M., Laugaste, R., Rajamäe, R., Taure, I., Varvas, M. Tehnogeensed muutused biogeokeemilises ainerings // Kurtna järvestiku looduslik seisund ja selle areng. Tallinn, 1989, 14—28.
5. Лукашев К. И., Вадковская И. Е. Эколого-геохимическое изучение биосферы. Минск, 1989.

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KEEMILISTE ELEMENTIDE LOODUSLIKU JA INIMMÖJUTUSLIKU JAOTUMISE SEADUSPÄRASUSTEST KURTNA MAASTIKUKAITSEALA (KIRDE-EESTI) SOO- JA JÄRVESETEDES

Inimmõjutusest tingitud biogeokeemilise aineriinge dünaamika ning geoökosüsteemide seisundi muutuste hindamine nõuab uuritava süsteemi loodusliku arengu seaduspärasuse tundmist. Kompleksed botaanilised ja geokeemilised uuringud tehti Kurtna maastikukaitsealal Kirde-Eestis. Akvaalse, subakvaalse ja aeraalse migratsiooniprotsessi seaduspärasuste hindamiseks määrati 32 keemilise elemendi sisalduse jaotus vastavalt järvesetetes, madalsoo- ja rabaturba lasundeis. Settekihtide vanuse määramine võimaldab võrdlevat analüüsi. Kõige suuremad on uuritud elementide kontsentratsioonid järvesetetes; tingituna loodusolude muutumisest erinevad kontsentratsioonid kihiti kuni 10 korda. Ligi suurusjärk väiksemad on enamiku elementide kontsentratsioonid subakvaalse toitumistüübi puhul (madalsooturvas), kusjuures loodustingimuste muutus ei ole tuntavalt mõjutanud kontsentratsioonide väärtusi. Väiksem on enamiku keemiliste elementide sisaldus aeraalse toitumistüübiga setetes (rabaturvas). Loodustingimuste ulatusliku muutusega on kaasnenu keemiliste elementide kontsentratsioonide varieerumine.

Selgesti on eristatav viimase 25—30 aasta jooksul moodustunud setete suure keemiliste elementide sisaldus rabaturbas, praktiliselt puuduvad muutused madalsooturbas. Aastane elementide õhu kaudu sissekanne on suurenenud keskmiselt 100 kuni 1000 korda. See on oluliselt muutnud rabaökosüsteemide seisundit ja struktuuri.

Üksikute elementide sisalduse statistiline analüüs võimaldab määrata ka domineeriva saasteallika. Selleks on uuritud alal esikohal elektrijaamad oma heidistega.

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О ЗАКОМЕРНОСТЯХ ПРИРОДНОГО И ТЕХНОГЕННОГО РАСПРЕДЕЛЕНИЯ ХИМИЧЕСКИХ ЭЛЕМЕНТОВ В ОЗЕРНЫХ И БОЛОТНЫХ ОТЛОЖЕНИЯХ НА ТЕРРИТОРИИ КУРТНАСКОГО ЛАНДШАФТНОГО ЗАПОВЕДНИКА (СЕВЕРО-ВОСТОЧНАЯ ЭСТОНИЯ)

Оценка влияния антропогенной деятельности на интенсивность биохимического круговорота веществ и состояний экосистем требует знания закономерностей развития изучаемого природного комплекса в зависимости от изменения природных условий. Соответствующие комплексные ботанические и геохимические исследования были нами проведены на территории Куртнаского ландшафтного заповедника. Исследованию подвергались литологический состав и распределение 32 химических элементов в озерных отложениях, торфе низинных и верховых болот, характеризующие аквальные, субаквальные и аэральные процессы биогеохимического круговорота. Определение возраста отдельных слоев изученных отложений позволяет провести сравнительный анализ.

Концентрации изученных элементов достигают наибольших величин в озерных отложениях, причем вариации концентраций, вызванные изменениями природных условий, в среднем 5-кратные. При субаквальном типе питания (торф низинных болот) содержание большинства элементов на порядок ниже, наименьшими являются и изменения, вызванные развитием природного процесса. Наименьшие концентрации элементов наблюдаются в торфе верховых болот (аэральное питание). При таком типе питания, однако, вариации содержания являются наивысшими.

Установлено четкое повышение концентрации почти всех изученных элементов в слоях, отложившихся за последние 25—30 лет на верховых болотах, в торфе же низинных болот изменения практически отсутствуют. За тот же период годичный атмосферный привнос большинства элементов повысился в 100—1000 раз, что уже вызвало ощутимую деградацию экосистем верховых болот.

Статистический анализ данных позволяет оценить доминирующий источник загрязнения. В данном случае таковым являются теплоэлектростанции.