CHAPTER 7

BOREAL AND SUB-BOREAL CLIMATIC ZONE

The Boreal and Sub-Boreal Forest ecosystems represent the forests of cold and temperate climate. These ecosystems occupy an extended zone in the northern part of the Northern Hemisphere. The total area is 16.8×10^6 km^2, or 11.2% from the whole World's territory.

The general scheme of biological and biogeochemical cycling in Forest ecosystems is shown in Figure 1.

1. BIOGEOCHEMICAL CYCLING OF ELEMENTS AND POLLUTANTS EXPOSURE IN FOREST ECOSYSTEMS

The plant species biomass of Boreal and Sub-Boreal Forest ecosystems accumulates a significant part of living matter of the whole planet. This value is about 700×10^6 tons of dry weight. The biomass per unit area of different Forest ecosystems varies from 100 to 300 ton/ha and even 400 ton/ha in the Eastern European Oak Forest ecosystems. The annual net primary productivity, NPP, varies from 4.5 to 9.0 ton/ha (Table 1).

The overall biomass accumulated in Forest ecosystems per unit area is 20–50 times higher than the annual productivity. This means that various chemical species are retained during long periods in plant biomass thus being excluded from biological or biogeochemical cycling. The duration of biological cycles may be from 1.5 to $>$25 years for Broad–Leaved Sub-Boreal Forest and Coniferous North Taiga Forest ecosystems, correspondingly. The slow turnover rates are connected with both a prevalence of aboveground biomass and slow mineralization of plant litterfall on the soil surface.

The microbial activity in forest soils is much more intense in comparison with Tundra ecosystems. Fungi, bacteria and actinomycetes play a significant role in degradation of carbohydrates of forest litterfall (Box 1).

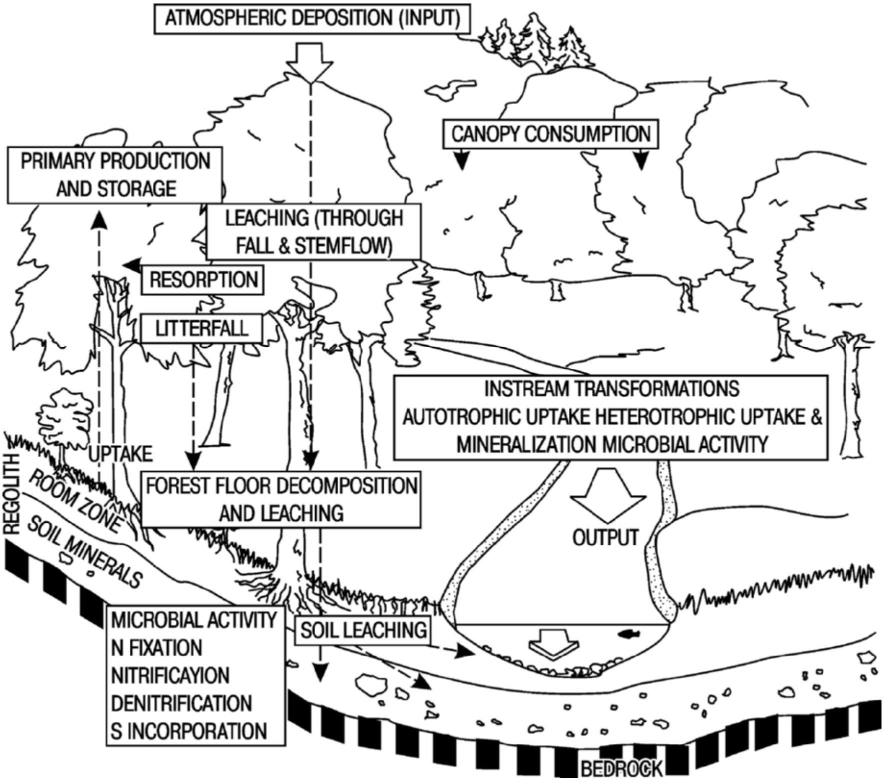

Figure 1. Schematic illustration of the biogeochemical cycling processes in Forest ecosystems (Nihlgard et al., 1994).

Box 1. Microbial regulation in Forest ecosystems (after Nihlgard et al., 1994; Fenchel et al., 1998)

The regulation of biogeochemical cycles by microbial populations is of most direct importance in the cycling of N, S, P, and C. Most of the ecosystem pool of these elements resides as organic forms in forest floor and mineral soil compartments. These organic complexes are subjected to microbial transformations, which regulate nitrate, sulfate and phosphate ions dynamics and availability. In turn, this influences indirectly

Table 1. Net primary productivity of Forest ecosystems, ton/ha.

Ecosystems	Coniferous north taiga forest	Coniferous and mixed south taiga forest	Broad–leaved sub-boreal forest
NPP	4.5	8.0	9.0

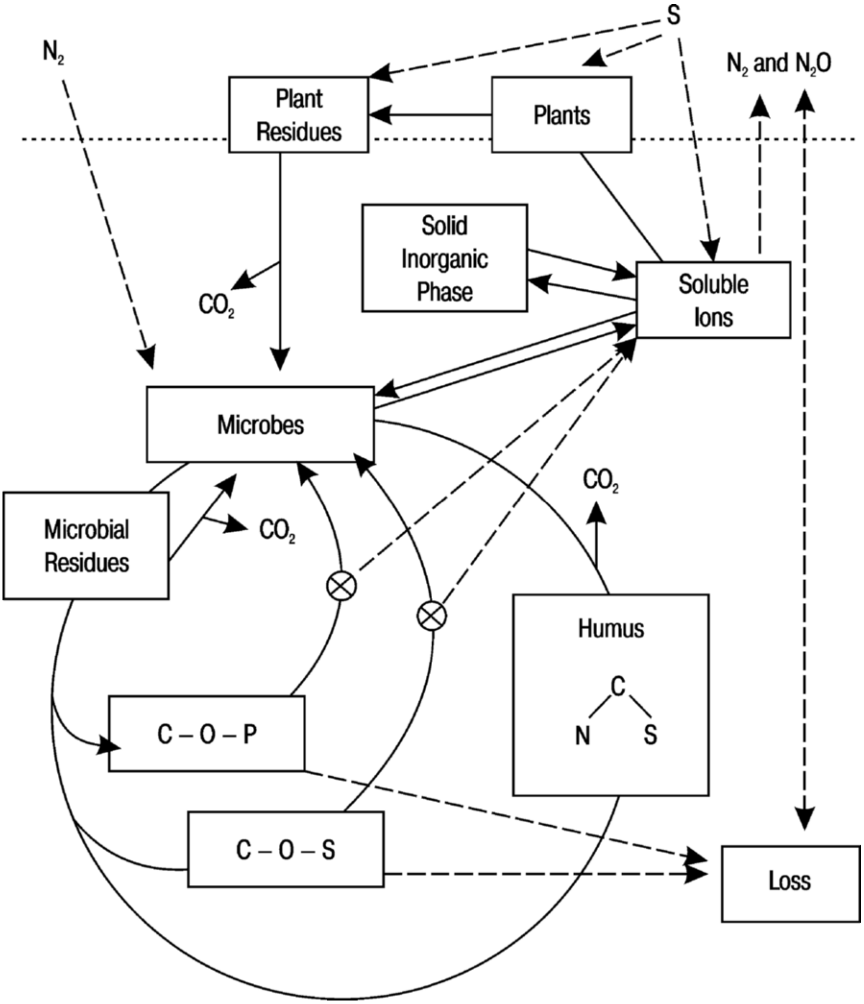

Figure 2. A tentative model illustrating decomposition interactions (Nihlgard et al., 1994).

the migration of other solutes though maintenance of ionic balances of solutions. For quantification of the role of microbes in forest biogeochemical processes, models like that shown in Figure 2 should be applied.

1.1. Nitrogen Cycle and Exposure Pathways

Since nitrogen is a nutrient, which limits the productivity of almost all Boreal and Sub-Boreal Forest ecosystems, its biogeochemical cycling is relatively well understood at present. The major N transformations and fluxes are shown in Figure 3.

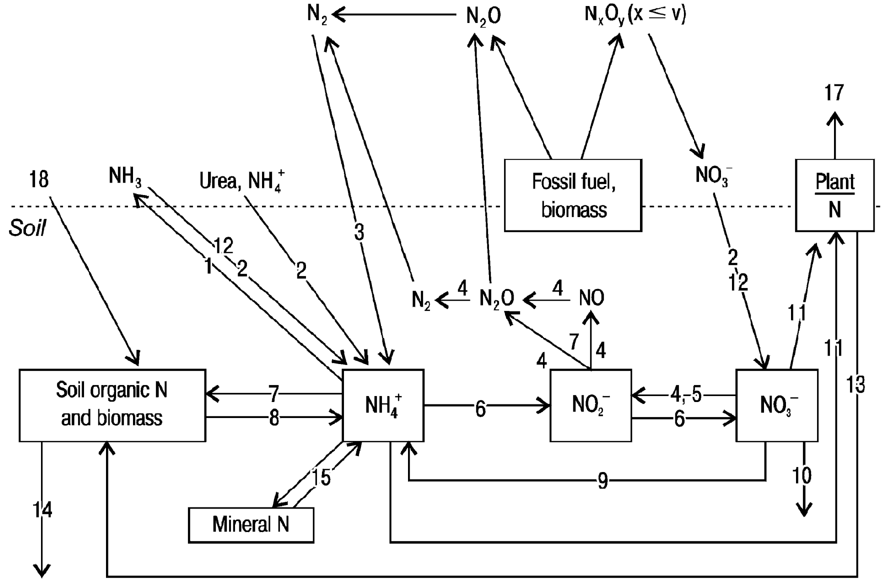

Figure 3. The general nitrogen model for illustrating the biogeochemical cycling in Forest ecosystems. Explanations for the fluxes: 1, ammonia volatilization; 2, forest fertilization; 3, N_2*-fixation; 4, denitrification; 5, nitrate respiration; 6, nitrification; 7, immobilization; 8, mineralization; 9, assimilatory and dissimilatory nitrate reduction to ammonium; 10, leaching; 11, plant uptake; 12, deposition N input; 13, residue composition, exudation; 14, soil erosion; 15, ammonium fixation and release by clay minerals; 16, biomass combustion; 17, forest harvesting; 18, litterfall (Bashkin, 2002).*

Processes of dinitrogen fixation, mineralization, immobilization, and nitrification have received the most attention, but there is a paucity of information on denitrification in forest ecosystems. The status and fluxes of nitrogen are strongly regulated by rates of N mineralization and immobilization. The rates of mineralization are greatly enhanced after clearcutting. The influence of clear cutting has been demonstrated in the experiments at Habbard Brook Experimental Forest and in Coweeta (see Likens et al., 1977). Over a three-year period after clearcutting a hardwood forest in Habbard Brook, forest floor organic matter decreased by 10.8 ton/ha, soil organic matter declined by 18.9 ton/ha and net N loss from the soil was estimated to be 472 kg/ha with an increased export of inorganic N in the stream waters of 337 kg/ha. Significant alterations of N fluxes have been monitored also at Coweeta. In the first 3 years after clear cut and logging, soil N mineralization increased by 25% and nitrification increased by 200%. However, only a small fraction of this mineralized nitrogen was exported from the ecosystem. The retention was owed partly to rapid revegetation and high rates of nitrogen uptake and partly due to microbial immobilization.

When nitrogen input owed to mineralization and atmospheric deposition exceeds the demand of both the vegetation and the microbes in undisturbed maturated forest ecosystems, the phenomenon of nitrogen saturation takes place (Gunderson and Bashkin, 1994). This phenomenon is accomplished by nitrogen leaching from the forest ecosystems. These nitrogen losses are highly variable, but generally sites in North America and Northern Scandinavia show N loss rates of <1.4 kg/ha/yr, whereas sites in southern Scandinavia and Central Europe exhibit loss rates often >7 kg/ha/yr. Generally, N leaching from undisturbed forest ecosystems starts when the N deposition rates are higher than 10 kg/ha/yr.

Fixation of molecular nitrogen, N_2, to ammonia in forest ecosystems can occur on and/or in a variety of forest substrates including plant canopy and stems, epiphitic plants compartments, wood, litter, soil and roots. A recent review of the magnitude of N inputs to forest ecosystems indicates that non-symbiotic fixation ranges from <1 to 5 kg/ha/yr and symbiotic fixation ranges from about 10 to 160 kg/ha/yr in early successional ecosystems where N_2-fixing species are present.

Denitrification, a dissimilatory pathway of nitrate reduction (see Section 3.3 also) into nitrogen oxides, N_2O, and dinitrogen, N_2, is performed by a wide variety of microorganisms in the forest ecosystems. Measurable rates of N_2O production have been observed in many forest soils. The values from 2.1 to 4.0 kg/ha/yr are typical for forest soils in various places of Boreal and Sub-Boreal Forest ecosystems. All *in situ* studies (field monitoring) of denitrification in forest soils have shown large spatial and temporal variability in response to varying soils characteristics such as acidity, temperature, moisture, oxygen, ambient nitrate and available carbon.

Thus, from the viewpoint of environmental risk assessment (critical loads) the most important exposure pathways are nitrate leaching and denitrification, which are both very sensitive to anthropogenic pollution. These links of biogeochemical nitrogen cycle should be firstly quantitatively parameterized to assessing environmental risk.

1.2. Sulfur Cycle and Exposure Pathways

Both inorganic and organic transformations are important in the sulfur cycle in Forest ecosystems. The major sulfur pools and transformation processes are shown in Figure 4.

Similarly to N, most S pools are found in organic form in forest floor and soil humus. However, unlike nitrogen, there are important abiotic processes, especially sulfate sorption processes, which play a critical role in regulating sulfate dynamics in forest ecosystems. An example of this type of exposure pathway was shown in the Habbard Brook whole-tree harvesting experiment, where the decrease in sulfate output from the watershed was attributed to sulfate adsorption, which was enhanced by soil acidification from nitrification (see above).

Biological exposure pathway of sulfur movement in soils of forest ecosystems is related to microbial transformation of sulfolipids. Back conversion of sulfate-S into organic matter immobilizes the anion and potentially reduces soil cation leaching. Processes of sulfur mineralization and incorporation proceed rapidly in response to several factors, including temperature, moisture, and exogenous sulfate availability in soils and water.

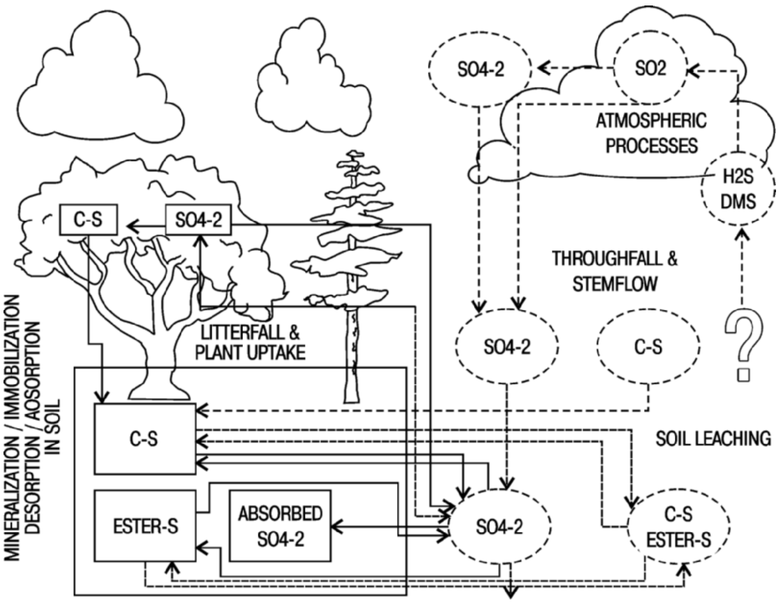

Figure 4. A model illustrating sulfur biogeochemical cycle in forest ecosystems (Bashkin, 2002).

1.3. Phosphorus Cycle and Exposure Pathways

The internal and external regulation of the phosphorus biogeochemical cycle in Forest ecosystems is tightly coupled to soil development and the change of phosphorus pools from the predominance of primary inorganic phosphorus (e.g., apatitte) to that of organic-P, secondary-P, mineral-P and occluded-P as is illustrated in Figure 5.

The organic phosphorus in forest soils is derived mainly by microbial synthesis and the accumulation of plant and animal residues plays a subordinate role. Much of the organic-P occurs in ester linkages (up to 60%) with lesser amounts in other forms. The leaching losses of P are ranged from as little as 7 g/ha/yr at Habbard Brook to up to 500 g/ha/yr for a glacier outwash in New Zealand. Loss rates generally are greatest in young, base-rich soils and lowest in acidic soils ($pH < 5.0$) with high content of sesquioxides, which may fix phosphates. Thus, soils at intermediate stages of development have the highest availability of phosphorus, which is partly regulated by microbial mineralization processes and open for pollutants' exposure.

1.4. Carbon Cycle and Exposure Pathways

The carbon biogeochemical cycle in Forest ecosystems is shown in Figure 6. This cycle is open and exposure to anthropogenic loading will definitely be accompanied by transformation of many cycle links. Global and regional climate change is the only example, the eutrophication of surface waters is the second one, however in the latest case the carbon cycle is coupled with those of nitrogen, phosphorus and

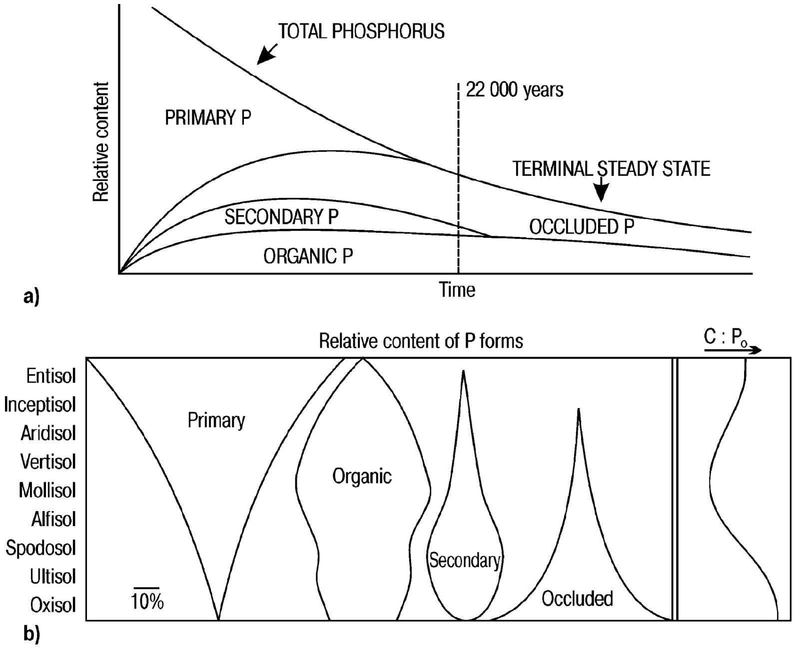

Figure 5. Biogeochemical transformations of phosphorus in forest soils: (a) the long-term relative development of different phosphate fractions in soils of the forest ecosystems; (b) the relative contents of P fractions in different soil types. Also, the idealized carbon to organic-P rates ($C{:}P_o$) are illustrated (Nihlgard et al., 1994).

some microelements like Fe and Mo. Accordingly, exposure to various anthropogenic pollutants is changing the carbon cycle and v/v the knowledge of the most sensitive links of C biogeochemical cycle will allow the regulation of the environmental risk assessment and risk management on a different scale.

Obviously the fates of N, S and P are tightly coupled not only with each other, but also with C dynamics of soils (Bashkin, 2002). For example, it has been suggested that the leaching of dissolved organic species of nitrogen sulfur and phosphorus contributes to the accumulation of these elements in mineral soils. This leaching of organics is an important component of soil formation of Spodosols, which are common especially in Northern Coniferous Forest ecosystems. The ratio between total nitrogen and total carbon, the C:N ratio, is widely applied to predict microbial mineralization–immobilization of nitrogen in soils (Figure 7).

Typically high C:N ratios (>60) for forest plant organic matter have a major impact on the nitrogen cycle. A number of empirical and theoretical analyses have established a strong linkage between nitrogen mineralization, assimilation and organic matter decomposition. In particular, C:N ratios >30 decrease mineralization and increase assimilation instead, with the balance between two processes dependent on the nitrogen content in microbial biomass. The latter parameter sets the minimum

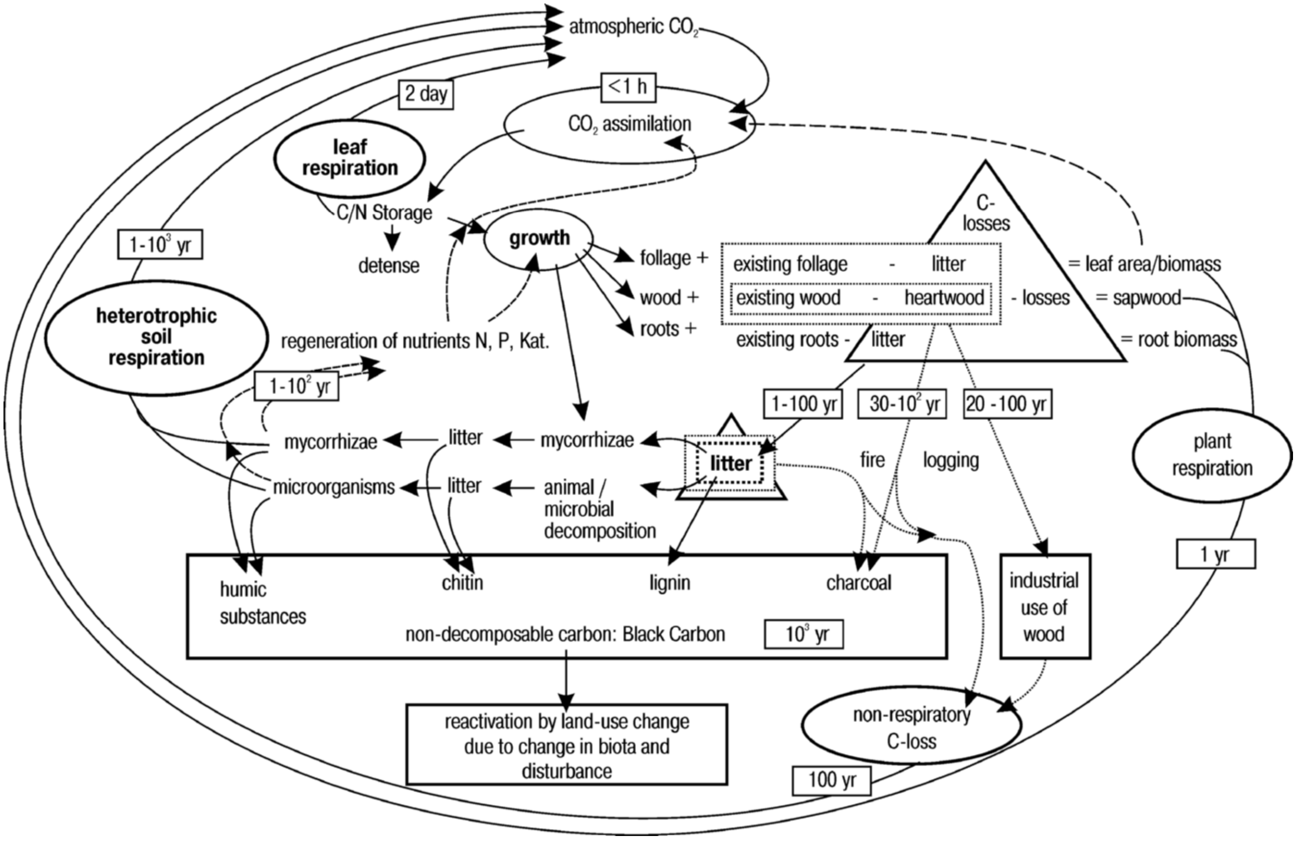

Figure 6. Carbon biogeochemical cycle in the hypothec forest ecosystem (Schulze, 2000).

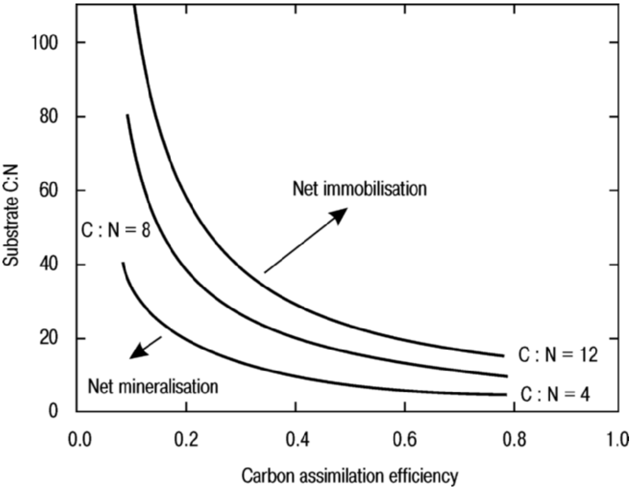

Figure 7. Relationship between net mineralization and immobilization of nitrogen as a function of substrate C:N ratio and microbial assimilation efficiency (F) for three different biomass nitrogen levels equivalent to C:N ratios of 4–8–12 (after Bashkin, 1987; Fenchel et al., 1998).

nitrogen requirement for biosynthesis per unit amount of substrate metabolized. Non-symbiotic nitrogen fixation can ameliorate nitrogen limitation, and to some extent high C:N ratios may be a determinant of soil microbial diversity.

However, the microbial activity is depressed during long and severe wintertime, and this leads to an accumulation of semi-mineralizable plant residues on the soil surface. With the increasing duration of cold season from south to north, the mass of these half-destroyed remains enlarges from 15 ton/ha of dry organic matter in Broad–Leaved Sub-Boreal Forest ecosystems to 80–85 ton/ha in Northern Taiga Forest ecosystems.

In the Northern Forest ecosystems, the relative content of chemical species in dead organic matter of forest litterfall is higher than that in living biomass. In Mixed and Deciduous Forest ecosystems, this is true for the total mass of chemical species, however some elements are more abundant in living biomass. Thus, the general biogeochemical feature of biological turnover in forest ecosystems is the prolonged retention of many chemical species in dead organic matter and exclusion from cycling (Table 2).

The data of Table 3 provide a general characteristic of trace element fluxes in Boreal and Sub-Boreal Forest ecosystems.

2. GEOGRAPHICAL PECULIARITIES OF BIOGEOCHEMICAL CYCLING AND POLLUTANT EXPOSURE

2.1. North American Forest Ecosystems

In the USA, two focal points for biogeochemical research have been the forest catchment ecosystems at Hubbard Brook Experimental forest in the White Mountains of

Table 2. Averaged fluxes and pools of biological cycling in Forest ecosystems (after Rodin and Bazilevich, 1965; Dobrovolsky, 1994).

	Ecosystems			
Fluxes and pools	Northern Taiga Spruce Forest	Southern Taiga Spruce Forest	Sub-Boreal Oak Forest	Southern Taiga Sphagnum Swamp
Pools, ton/ha				
Total biomass	100	330	400	37
Nitrogen	0.35	0.72	1.15	0.23
Dead organic matter	30	35	15	100
Annual fluxes, ton/ha/yr				
NPP	4.5	8.5	9.0	3.4
Litterfall	3.5	5.5	6.5	2.5
Nitrogen uptake	0.058	0.041	0.095	0.040
Nitrogen return	0.048	0.035	0.057	0.025

New Hampshire and Coweeta Hydrologic Laboratory, located in the southern Appalachians of North Carolina.

The nutrient cycles of the forest catchment ecosystems are to a large extent determined by biota, especially by the primary production of plants and by microbial decomposition. Severe losses from the ecosystem of important nutrients, e.g., Ca, Mg, K and P, are expected to lower the productivity when occurring in the root zone. Most nutrients available for circulation in the temperate forested ecosystems are found in the tree layer or in the accumulated organic mater of soil layer. This is especially true for the most important macronutrients (C, N, P, K, Ca, Mg and S). Nitrogen is almost completely bound to the organic matter and when it is mineralized it is either leached as nitrate or assimilated and immobilized by organisms in the soil. Including the humus horizon, the soil organic matter contains the largest pool of nitrogen in the Boreal Forest ecosystems (Figure 8).

For phosphorus and potassium this pool of organic matter is also of importance, but in the Boreal Forest ecosystems, a relatively higher amount is in the living biomass. The long-term soil development proceeds towards a lower rate of weathering in the root zone and relatively higher amounts in biogeochemical fluxes (Nihlgard et al., 1994).

Thus, one should mention that the quantitative estimates of various links of biogeochemical cycles of elements and their interactions are of crucial importance for environmental risk assessment for the given ecosystems under anthropogenic pressure.

Table 3. Averaged fluxes of trace elements in biological cycling of Boreal and Sub-Boreal Forest ecosystems (after Dobrovolsky, 1994).

	Forest ecosystems			
Ash/chemical species	Northern Taiga Coniferous Forest	Sub-Boreal Coniferous and Small–Leaved Forest	Sub-Boreal Broad–Leaved Forest	Sphagnum Forest Swamp
Average ash content, %	1.7	2.0	3.5	2.5
Total uptake of ash elements, kg/ha/yr	76	170	315	85
Trace element turnover, g/ha/yr				
Fe	304.0	680.0	1,260.0	1,500.0
Mn	364.0	816.0	1,512.0	75.1
Sr	53.0	119.0	221.0	68.0
Ti	49.4	111.0	205.0	401.2
Zn	45.6	102.0	189.0	62.6
Cu	12.2	27.2	50.4	12.2
Zr	11.4	25.5	47.2	14.3
Ni	3.0	6.8	12.6	13.6
Cr	2.6	5.9	11.0	10.9
V	2.3	5.1	9.4	10.2
Pb	1.9	4.2	7.9	12.0
Co	0.7	1.7	3.1	2.3
Mo	0.7	1.5	2.8	1.0
Sn	0.4	0.8	1.6	—
Ga	0.1	0.2	0.3	0.4
Cd	0.05	0.12	0.22	—

2.2. *Spruce Forest Ecosystem of Northwestern Eurasia*

Table 3 presents the averaged data for the whole forest area of Boreal and Sub-Boreal zone. However, there are definite peculiarities of biological and biogeochemical cycles in the individual ecosystems. We will consider the Spruce Forest ecosystem of the Karelia region, Russia. These ecosystems occur in the wide area of the Karelia, south from 63° N.

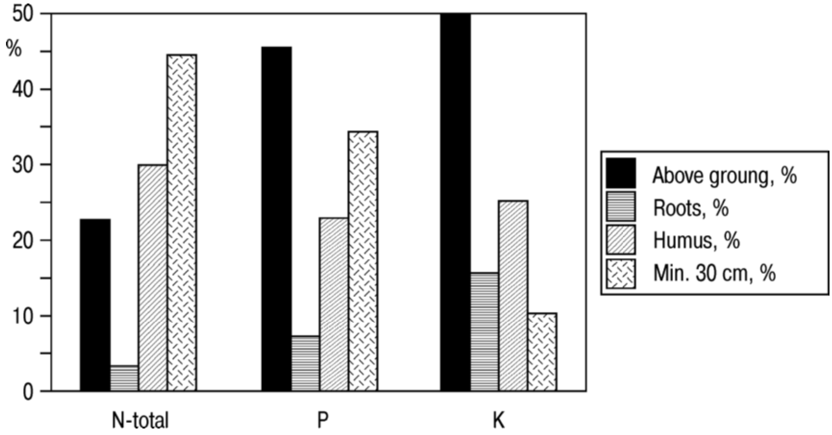

Figure 8. Relative distribution of N, P and K in the Boreal Forest ecosystem. Total amounts for the different fractions are given, expect for in the mineral soils down to 30 cm depth, where exchangeable amounts are given for P and K (Nihlgard et al., 1994).

The dominant species are the spruce (*Picea excelsa*), the birch (*Betula verrucosa, B. pubescens*), the aspen (*Populus tremula*), and the alder (*Alnus incana*). The moss and low bush layer is represented by the blueberry-bush (*Vaccinium myrtiilus*), hypnic mosses, separate species of cowberry (*Vaccinium uliginosum*) and flowering plants. The biomass of these Spruce Forest ecosystems reaches 10 ton/ha at the age of 100–150 years (Table 4).

We can see from Table 4 that most of the Spruce Forest ecosystem biomass is accumulated in trees, with trunk mass predominating. The values of annual Net Primary Production (NPP) and litterfall production are more connected with needles. In living matter, the mass of moss and bush species makes up to 2–3% of the tree biomass, whereas in dead matter (litterfall), it is up to 10%.

The distribution of trace metals in ash of living matter distinguishes from that in dead organic matter. About half of the total ash elements contained in the biomass is confined to the deciduous tree organs, whereas for the shedding, most ash elements are found in the needles. About 80% of ash elements are supplied from conifers to the soil in the shed needles, whereas their supply in the deciduous organs of mass and bush species is a mere 10%. The shedding trace metal losses from the living plant organs are accompanied by their redistribution into outer bark, where they may be retained during a long period. We can consider the retention of trace metals in bark of the conifers as one of the important sink in Spruce Forest ecosystems, which exclude these metals from biogeochemical cycles and regulate the exposure pathways.

The averaged fluxes and sinks of trace metals in biogeochemical turnover in Spruce Forest ecosystems are shown in Table 5.

There are significant differences in plant uptake of trace metals from soils. It is one of the most important pathways characterizing the exposure to various elements

Table 4. Biomass and total ash mass distribution in Spruce Forest ecosystems of the Karelia region, Russia (after Dobrovolsky, 1994).

Biomass components	Ecosystem parameters		
	Biomass	NPP	Litter production
Woody vegetation, ton/ha	40–100	4.0–9.0	2.0–5.5
Of this:			
Needles, %	10–15	36–38	56–60
Twigs, %	12–17	8–9	8–9
Trunks, %	50–60	41–43	22–25
Roots, %	17–19	12–13	9–10
Moss and low-bush vegetation, ton/ha	0.8–3.5	0.2–0.6	0.2–0.6
Total mass of ash elements (100%)			
Components of woody vegetation			
Needles, %	40–50	79–80	76–81
Twigs, %	13–18	4–5	2–3
Trunks, %	19–33	10–11	4
Roots, %	12–14	4–5	2–3
Moss and low-bush vegetation, %	3–8	5–9	7–10

Table 5. Averaged trace element mass budget for Spruce Forest ecosystems, Karelia, Russia (after Dobrovolsky, 1994).

Ecosystem biomass component and ash content, %	Annual NPP, kg/ha		Annual shedding, kg/ha	
	Dry organic matter	Total sum of ash trace metals	Dry organic matter	Total sum of ash trace metals
Conifer needles, 1.7%	1,440–3,420	24.5–58.1	1,120–3,300	19.0–56.1
Conifer bark, 1.3%	200–540	2.6–7.0	100–300	1.3–3.9
Moss and shrub species, 1.7%	200–600	3.4–10.2	200–600	3.4–10.2

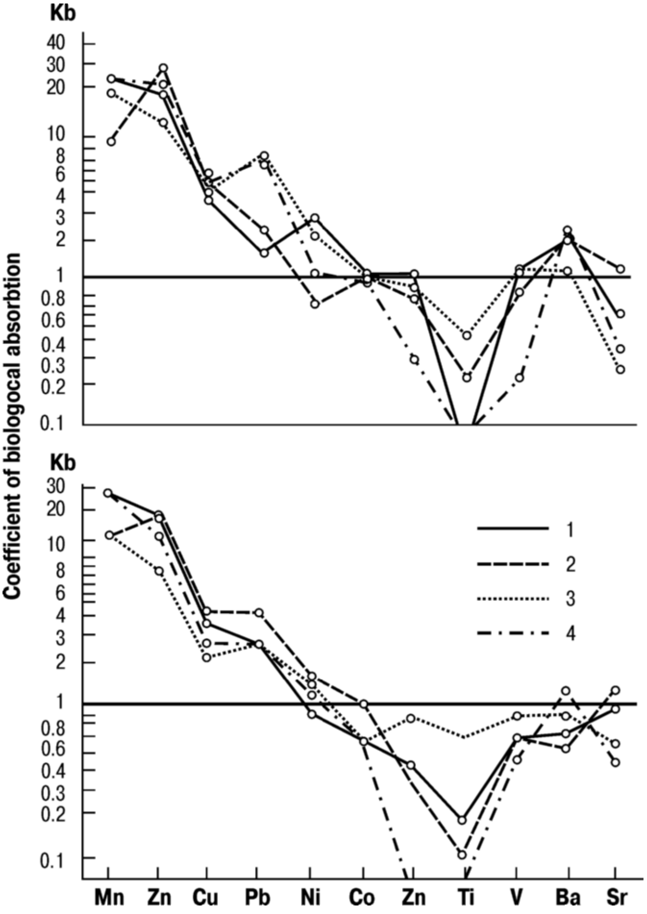

Figure 9. Exposure pathways based on the averaged coefficients of biogeochemical uptake, C_b, of trace metals in Spruce Forest ecosystems of the Karelia: top scheme represents the ecosystem with Podzols on diabase outcrops and bottom scheme represents the ecosystem with Podzols on gneiss outcrops. 1—spruce needles; 2—spruce bark; 3—hypnic mosses; 4—leaves and twigs of blueberry (based on Dobrovolsky, 1994).

accumulated in soil. The coefficient of biogeochemical uptake, C_b, presents the ratio between element content in plant species to its content in soil. Figure 9 shows the averaged values of these coefficients for the most plant species of Spruce Forest ecosystems, Karelia region, Russia.

We can see that the C_b values for lead, zinc, tin, nickel, and copper are an order of magnitude higher than those for zirconium, titanium, and vanadium. We can observe also that the curves follow a similar pattern independently of the composition of the bedrock, diabasis or gneissic, underlying the forest ecosystems. Simultaneously, various plants absorb the same elements at a different rate. For instance, mosses are

Table 6. Averaged major ash element mass budget for Spruce Forest ecosystems, Karelia, Russia (after Dobrovolsky, 1994).

Major ash element	Major ash element content, kg/ha					
	Ecosystem biomass		Annual NNP		Annual shedding	
	Mean	Limits	Mean	Limits	Mean	Limits
Ca	205	150–260	32	20–45	27	15–40
K	110	50–170	15.5	7–24	13	6–20
Si	52	40–65	14.5	10–19	13.5	9–18
Mg	32	25–40	5.5	4–7	4.5	3–6
P	30	15–45	4	2–6	3	1–5
Mn	20	15–25	3.3	2.2–4.5	2.9	1.9–3.9
S	8	6–10	1.6	1.2–2.1	1.5	1.2–1.9
Al	8.5	5–10	1.5	1–2	1.2	0.7–1.8
Fe	0.7	3.5–8.0	0.8	0.5–1.2	0.8	0.4–1.1
Na	1.5	0.5–2.5	0.3	0.1–0.5	0.2	0.1–0.3
Total	429	300–600	79	47–107	67.6	40–90

better accumulators of poorly absorbed metals, like Ti, Zr, V, than tree and small shrubs. The selective accumulation of metals by plants can be used in the exposure pathway characterization during environment risk assessment.

The quantitative parameterization of major ash elements involved in the biogeochemical turnover of Spruce Forest ecosystems is illustrated in Table 6.

One can see that for calcium, potassium, and silicon, biogeochemical turnover is within the limits of 10–30 kg/ha per year. The turnover for magnesium, phosphorus, manganese, sulfur, and aluminum is less than 10 kg/ha per year. These values are about 1 kg/ha per year for iron and sodium. These values can characterize the safety limits of exposure to the given species.

The heavy metal concentrations in spruce and blueberry species as the major components of Spruce Forest ecosystems are summarized in Table 7.

The statistical estimation of heavy metal concentrations in the Spruce Forest ecosystems of the Boreal climatic zone is the subject of wide variation, with coefficient of variation from 36 to 330%. However, we can note the clear trend in biogeochemical peculiarities and relevant exposure to heavy metal uptakes by dominant plant species.

First, the concentration of Sr, Ba, and Ti in spruce bark is relatively higher than in needles, while the latter are enriched by Ni and Zn. Second, the concentration of Zn, Ba, Cu, and Cr is higher in blueberry roots, than in the aerial parts. Third, the effect of zonal and local factors is remarkable. For instance, the Sr content in the needles

Table 7. The statistics of heavy metal contents in the major plant species of Spruce Forest ecosystems of Boreal zone, Karelia, Russia (after Dobrovolsky, 1994).

Heavy metals	Spruce species (*Picea excelsa*)				Blueberry (*Vaccinium myrtillus*)			
	Needles		Barks		Aerial parts		Roots	
	M, ppm	V, %	M, ppm	V, %	M, ppm	V, %	M, ppm	V, %
Zn	1,250	98	1,188	90	751	190	1,515	161
Ba	390	65	456	76	465	71	578	22
Ti	102	100	170	330	113	130	86	110
Cu	86	86	88	60	107	90	124	51
Pb	64	60	62	130	84	77	11	85
Sr	43	60	73	88	35	85	33	84
Zr	38	36	33	61	20	27	28	48
Cr	28	51	26	41	28	37	34	56
Ni	23	100	17	120	19	71	25	53
V	16	42	23	55	19	26	14	41
Co	12	80	13	61	13	70	14	70

Note: M is the arithmetic mean, ppm by dry ash weight, V is variation, %

and in the barks of the spruce is appreciably lower than the average content of this trace metal in the shedding of the World coniferous trees. This should be attributed to the effect of zonal factors influencing the active release of this metal. At the same time, the elevated content of Pb and Zn reflects the specificity of the bedrock since the dispersed sulfide mineralization is a characteristic feature of this Karelia region.

Using the results on biogeochemical uptake and content of trace metals in Spruce Forest ecosystems (Dobrovolsky, 1994), we can calculate the biogeochemical migration rates (Table 8).

We can see that the tree vegetation absorbs annually from soil tens of grams per hectare of Zn and Ba, units of grams of Ni, V, and Co. The absorption of trace metals by low bush species is smaller by an order of magnitude. Simultaneously, a similar amount of metals is released from the living biomass of the Spruce Forest ecosystems.

Of great interest is the calculation of a relative uptake of trace metals by forest species. The C_b values for each metal are similarly independent of the composition of crystalline bedrock and the depth of detrital deposits. For instance, the C_b values for Zn, Mn, Cu, and Pb are in a range from 2 to 30, they are considered as the elements of intense uptake. Poorly absorbed are Ni and Co, with C_b values about 1. The metals, such as Ti, Zr, and V, are very reluctant to be taken up and their C_b values are less than 1.

Table 8. Biogeochemical migration rates of heavy metals in the Spruce Forest ecosystems, Karelia, Russia.

Ecosystem plant components	Rates of biogeochemical migration of heavy metals, g/ha/yr						
	Zn	Ba	Sr	Cu	Pb	Ni	Co
Needles							
New grown	30–70	10–50	1–2	2–5	2–4	0.5–1.0	0.3–1.0
Lost in shedding	25–70	8–20	0.8–2.0	2–5	1–3	0.4–1.0	0.2–0.6
Bark							
New grown	4–8	2–4	0.2–0.4	0.3–0.6	0.2–0.4	0.1–0.2	0.03–0.04
Lost in shedding	2–5	0.7–2	0.1–0.3	0.1–0.4	0.1–0.2	0.1–0.3	0.02–0.04
Shrub vegetation							
New grown	3–8	2–5	0.2–0.5	0.3–10	0.3–0.8	0.08–0.2	0.04–0.1
Lost in shedding	3–8	2–5	0.2–0.5	0.3–10	0.3–0.8	0.08–0.2	0.04–0.1
Total plant uptake	37–86	14–59	1.4–2.9	2.6–6.6	2.5–5.2	0.68–1.4	0.37–1.1
Total shedding	30–83	10.7–27	1.1–2.8	2.4–6.4	1.4–4.0	0.51–1.3	0.26–0.74
Accumulation in tree bark	2–3	1.3–2.0	0.1	0.2	0.1–0.2	0.07–0.1	0.01

There is no doubts that these data are of the significance for pollutants' exposure assessment and environmental risk calculations.

2.3. Swampy Ecosystems of North Eurasia

The remarkable part of the forested area is swampy. In certain regions, like the vast West Siberian plain, swamp and waterlogged ecosystems occupy about 30% of the total area. The biogeochemical cycling in these ecosystems is very complex and specific. The slow rates of biogeochemical turnover, typical for all Boreal Forest ecosystems, are more depressed in Swamp ecosystems. For instance, in the *Sphagnum* Swamp ecosystem, the most widespread type of Swamp ecosystems, the annual NPP is only 10% or less from living plant biomass and less than 1% from the total mass of accumulated dead organic matter of peat. The rate of biogeochemical turnover in such an ecosystem is about 50 years.

There are significant differences between biogeochemical cycling in forest and swampy ecosystems of the Boreal climate zone. The annual growth (NPP) of moor vegetation is about 3.5 ton/ha, which is twice as small as that in a forest ecosystem. In the bog, the degradation of dead organic matter proceeds at a much smaller rate than in the forest. The mass of peat accumulated within a period of 100 years accounts for some 20% of the organic material formed in bog landscape. This is nearly 10 times higher than a relative mass of dead organic matter, preserved in forests.

In spite of small rates of organic matter degradation, the mineralized iron and heavy metals are permanently accumulating in stagnant bog waters. This leads to the larger uptake of these metals by swampy vegetation. In an area of 1 ha the annual uptake of Zn, Ba, Pb, and Ti amounts to tens of grams; of Cu, Zr, Cr, Ni and V to units of grams, Co to tenths of a gram, by moor plant species.

Taking into account the present and future oil and gas explorations extent in these areas the biogeochemical indices can greatly improve the exposure estimates and environmental risk assessment.

2.4. Broad-Leafed Deciduous Forest Ecosystems of Central Europe

Southward from the northern border of Boreal Forest ecosystems, the natural humidity gradually decreases simultaneously with the shortening of the cold winter season, which inhibits biogeochemical processes. Accordingly, the floral composition and geochemical conditions of ecosystems is altered also. The Coniferous Forest ecosystems grade into Mixed Forest ecosystems and then into Deciduous Forest ecosystems. Herbaceous plant species change the small shrubs and mosses. Biogeochemical processes become more active and annual NPP values are increasing as well. The litterfall amount is increasing but that of dead organic mater becomes decreasing. Consequently, changes occur in the chemical composition of plant species and in values of coefficients of biogeochemical uptake, C_b. In turn, it is related to the exposure pathway characterization.

The Broad–Leaved Forest ecosystems are widespread in regions of Sub-Boreal climate zone with a well balanced precipitation:evapotranspiration ratio. The southern periphery of the vast belt of Eurasian boreal and Sub-Boreal Forest ecosystems is represented by Oak Forest ecosystems. These ecosystems exhibit both the largest biomass and annual NPP rates in comparison with other forest ecosystems of this zone. However, the dead mass surface organic matter is 2–3 time less than that of coniferous forests.

The content of nitrogen in fallen leaves as a major shedding component is about twice as much as that in the needles of coniferous trees. The total sum of ash elements in the leaves accounts for 3–5%, average about 4% on dry weight basis. Accordingly, the concentration of calcium increases from 0.5 to 4.0%, potassium from 0.15 to 2.0% and silicon with a wide variation. The row of nutrient uptake is as the following:

$$\mathrm{C} > \mathrm{N} > \mathrm{K} > \mathrm{Si} \cong \mathrm{Mg} \cong \mathrm{P} \cong \mathrm{S} > \mathrm{Al} \cong \mathrm{Fe} \cong \mathrm{Mn}.$$

The amount of nitrogen in the biomass of the Oak Forest ecosystem reaches 900–1,200 kg/ha and the sum of ash elements is about 2,000–3,000 kg/ha, e.g., greatly in excess of nitrogen. The corresponding values for accumulation of nitrogen in annual growth are 80–100 and for ash elements, 200–250 kg/ha. An essential point is that the green leaves store 70–80% of the mass of uptaken elements, and the fallen leaves, 80–90% of the mass of elements eliminated from the biological cycle. Nitrogen as returned in the shedding products, amounts to 40–70 kg/ha, and the ash elements, to 180–200 kg/ha (see Box 2).

Box 2. Biogeochemical fluxes of elements in Oak Forest ecosystem (after Jakucs, 1985)

The distribution and mass budget of chemical species in the Oak Forest ecosystem have been studied in Hungary. The principal timber species is *Quercurs petraea*, accounting for 78% of the wood mass; *Quercus cerris* accounts for 22%. The shrubs are chiefly represented by *Acer campestre* and *Cornus max*, and the grass by the genera *Carex*, *Dactylis*, and *Poa*.

The mass of trees is 241.03; of shrubs, 6.54; of herbaceous grasses, 0.62, and the mosses, 0.0016 ton/ha. The distribution of chemical species in biomass and annual NPP is depicted in Figure 10 and summarized in Table 9.

Amongst the ash elements the most abundant in biomass is calcium, which is accumulated in leaves, in trunk wood, and in twigs. Potassium is dominant in annual NPP. The masses of trace metals in biogeochemical cycling of this Oak Forest ecosystem are roughly in correspondence to their respective average values for the

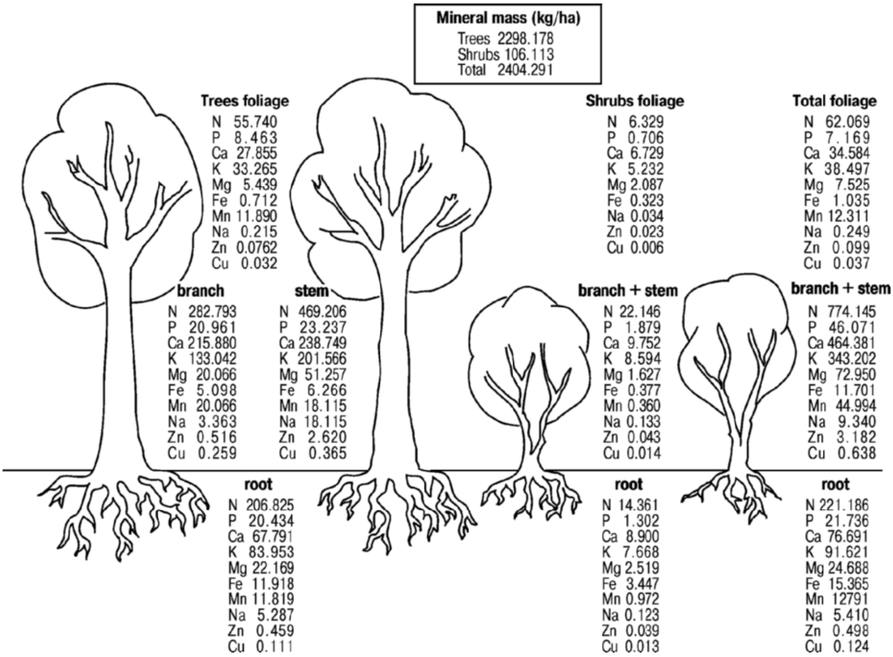

Figure 10. Mass distribution of chemical species in the Oak Forest ecosystem, Central Europe (Jakucs, 1985).

Table 9. The biogeochemical fluxes and pools in the Oak Forest ecosystem of Central Europe.

	Annual plant uptake, kg/ha			Pool in ecosystem, kg/ha		
Element	Trees	Shrubs	Total	Leaves	Stems, twigs	Roots
N	103.39	14.49	117.88	62.07	774.15	221.19
P	11.91	1.58	13.47	7.17	46.07	21.74
Ca	60.87	13.49	74.36	34.58	464.38	76.69
K	79.80	12.28	92.08	38.50	343.20	91.62
Mg	11.89	3.90	15.79	7.53	72.95	24.69
Fe	1.54	1.31	2.85	1.04	11.70	15.37
Mn	19.12	0.86	19.98	12.31	44.99	12.79
Na	1.01	0.14	1.15	0.25	9.34	5.41
Zn	0.28	0.04	0.32	0.10	3.18	0.50
Cu	0.06	0.01	0.07	0.04	0.64	0.12

other Oak Forest ecosystems of the Sub-Boreal climate. An exception to the rule is manganese, with its inordinately large fluxes in pool and annual NPP. Possibly, this phenomenon should be related with local landscape-geochemical peculiarities.

In may be of interest to compare the fluxes of elements in biogeochemical cycles of Oak Forest ecosystem with exposure to airborne deposition input. The latter were (in kg/ha/yr) for N, 17.7; for Ca, 14.7; for Mg, 1.8; for K, 4.2; for Na, 1.4; for P, 1.1; for Fe, 0.07; and for Zn, 0.14. The deposition input of these elements fall into a range of 20% (calcium) to 4.5% (potassium) relative to the respective biogeochemical fluxes (see Table 9). The airborne Fe input accounts for a mere 2.5%. Simultaneously, for some heavy metals, like zinc, the deposition input is commensurate with the fluxes of biogeochemical cycle.

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3. BIOGEOCHEMICAL FLUXES AND EXPOSURE PATHWAYS IN SOIL–WATER SYSTEM OF BOREAL AND SUB-BOREAL ZONES

3.1. Soil Compartment Features

The main soils of Forest Ecosystems are Podzols and Podzoluvisols. There are plenty of various soil subtypes, groups and families among these two main soil types. However, all forest soils have a number of common features originating in the similarity of processes occurring therein. The retarded biological cycle provides the organic materials for the build up of the covering layer on the soil surface. This layer consists

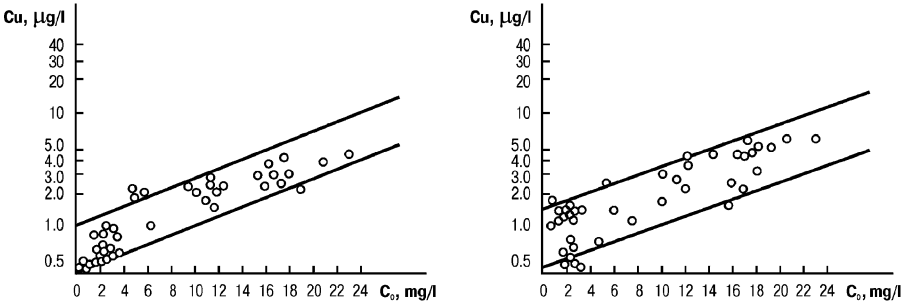

Figure 11. Relationships between organic matter concentration in permafrost soils of East Siberia Taiga Forest ecosystems and concentration of copper (left) and zinc (right) (Nikitina, 1973).

of partly decomposed plant residues and is called forest litter (A_0 horizon). The slow, but permanent, microbial decomposition of these materials leads to the formation of fulvic acids. The predominance of these mobile organic acids in humus structure and the predominance of precipitation over evapotranspiration are favorable to the formation of permeable, readily leached soils.

The second characteristic feature of Forest Ecosystem soils is the accumulation of macronutrients in the litter with sharp decreasing to the download horizon. However, the trace elements show the opposite trend and the concentration of micronutrients is gradually increasing up to the soil-forming rocks.

Two groups of chemical elements can be considered related to their distribution in soil profiles. The first group includes the essential nutrients actively absorbed by vegetation and relatively tightly bound in soil organic matter (Figure 11).

These elements are the main macronutrients, like nitrogen, phosphorus, potassium, and main micronutrients, like copper, zinc, and molybdenum. Their concentration in A_0 horizon is remarkably higher than in soil-forming rocks. For the second group representatives, the concentration in the A_0 horizon, although elevated in comparison with elluvial horizon, fails nevertheless to reach the rocks. The typical elements of the second groups are titanium, zirconium, vanadium, and chromium. The averaged distribution curves are shown in Figure 12.

Various forms of macro- and microelements differ in their ability to migrate and redistribute among the soil profile. The elements contained in clastic minerals are practically immobile. The elements, bound to finely dispersed clay minerals, are either co-transported with clay particles, or are involved in sorption–desorption processes. Part of the elements are found in concretions and also in very thin coating films of hydrated iron oxides; some elements make a part of specially edaphic organic compounds.

The determination of distribution pattern of various forms of both macroelements and heavy metals in soil profile is a very complicated task. We have to know the

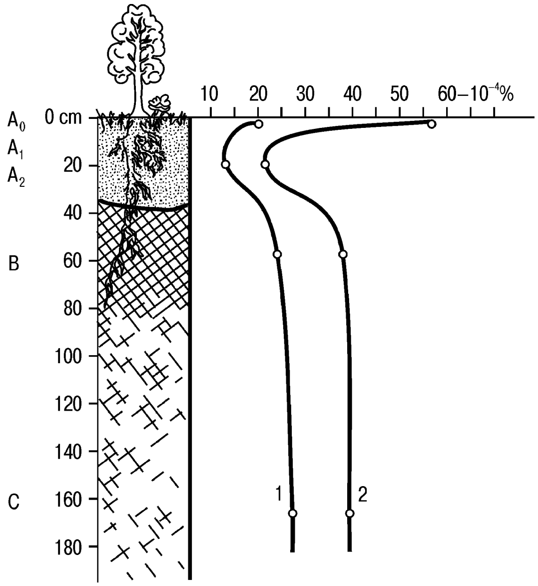

Figure 12. The profile distribution of vanadium (1) and copper (2) in typical Podzol of Boreal Forest ecosystems (ppm, 1 N HCl extraction) (Dobrovolsky, 1994).

distribution of organic matter, mineral particle, and microbes, the existence of different barriers, redox conditions, etc. (Box 3).

Box 3. Distribution of various forms of trace metals in podzols of boreal forest ecosystems (after Dobrovolsky, 1994)

In the Mixed Forest ecosystems a soil fraction less than 1 μm contains most of the elements previously confined in the forest litter and gradually involved in the biogeochemical cycle. In this fraction Cu and Mo forms account for 60–70% of the total soil content. The metals, poorly absorbable by plants, for example, Cr and V, occur in finely dispersed soil fraction in smaller amounts, about 20–30%.

Table 10 illustrates the variations of major forms of Cu and Co in typical Forest ecosystem Podzols of Moscow region, Russia.

We can see that the soluble and exchange forms of these metals are present in small amounts accounting merely for a few percent of the total metal content in soil. The content of organometal species is relatively high in the upper profile rich in humic species, whereas it drops sharply in the mineral horizons. Copper is extensively involved in the biogeochemical cycle in the Forest ecosystems and this is less profound for cobalt. It is noteworthy that a large part of metals (in particular, of copper) become bound to iron hydroxides. This is typical for various trace elements, including arsenic, zinc and other elements with variable valence.

Table 10. Distribution of copper and cobalt in Podzols of East European Boreal Forest ecosystems.

Soil horizon	Total metal content, ppm	Water-soluble and exchangeable	Metals bound with: Organic matter	Hydrated iron oxides	Mineral soil matter
		% of the total content of metal in soil			
		Copper			
A_1	7.4	3.1	32.4	51.3	13.2
A_1/A_2	7.4	3.6	24.3	45.9	26.2
A_2	6.0	3.2	26.7	55.0	15.1
A_2/B	16.8	2.7	3.6	10.5	53.2
B_1	20.6	3.8	4.4	43.2	48.6
B_2	19.4	3.9	4.6	54.1	37.4
BC	19.8	3.6	4.5	47.0	48.5
		Cobalt			
A_1	5.5	4.2	12.7	30.9	52.2
A_2	4.5	3.7	13.3	24.4	58.6
B_1	5.8	3.1	3.4	34.5	59.0
C	5.3	4.5	3.8	34.0	58.3

The excessive ground humidity is favorable to the formation of gley soils in Boreal forest ecosystems. Clay-podzolic soils with a massive forest litter layer provide the conditions for low water saturation. In high water-saturated conditions, a peat horizon is formed in the top layer of soil-forming boggy soils. In the forest litter of Podzols the concentration of fulvic acids is two or three times higher than that of humic acids; in contrast, humic acids are predominant in the peat horizon of Boggy soils. This is reflected in a lower pH of aqueous extraction from the forest litter of Podzols and in more active biogeochemical migration of elements in the corresponding ecosystems.

The concentration of many nutrients and heavy metals in Peat–Boggy soils is often higher than that in Podzols. In boggy soils the relative concentration of elements bound with humic acids is also significantly higher. For instance, in the Spruce Forest ecosystems of Karelia most of the mobile nickel forms are bound to humic acids, and those of copper to the fulvic acids. Consequently copper easily leaches from the soil upper layer with relevant accumulation in the download horizon. The concentrations of the organometal forms of trace elements in the soils of Swamp ecosystems compare with that of Podzols. However, the overall mass of organometal species in boggy soils is appreciably higher.

In the southern direction the Podzols are transferred into Podzoluvisols and Distric Phaerozems. These soils have less acidity and less pronounced migration of various elements. Accordingly, this determines the exposure pathways of pollutants, like heavy metals, in soil compartments of forest ecosystems.

3.2. Biogeochemical Exposure Processes in the Soil–Water System

Almost all biogeochemical exposure processes in Forest ecosystems are connected with aqueous migration in surface and ground water runoff. Low content of dissolved salts and organic species are the most characteristic features of surface runoff waters of Boreal climate forest ecosystems. This feature is particularly distinct in Taiga Forest ecosystems with permafrost soils where the zone of extensive water exchange in the river valleys is confined to supra-permafrost waters and to ice-thaw waters. A review of leaching processes is shown in Box 4.

Box 4. A brief review of soil leaching processes (after Johnson, 1992)

A concept of anion mobility may be considered a useful paradigm for explaining the net retention and loss of cations from soils, and thus exposure pathways. This paradigm relies on the simple fact that total cations must balance total anions in soil solution (or any other solution), and, therefore, total cation leaching can be thought of as a function of total anion leaching. The net production of anions within the soil (e.g., by oxidation or hydrolysis reactions) must result in the net production of cations (normally H^+), whereas the net retention of anions (by either absorption or biological uptake) must result in the net retention of cations.

The major anions in soil solutions are Cl^-, SO_4^{2-}, NO_3^-, HCO_3^-, and organic anions. Chloride may dominate soil solutions only in coastal areas. The four major anions often undergo oxidation–reduction and hydrolysis reactions that cause the net production or consumption of H^+, which in turn strongly affects the net retention or release of base cations from the ecosystem. Carbonic acid, which is formed by the dissolution and hydrolysis of CO_2 in water, is the major natural leaching agent in many temperate ecosystems. Carbonic acid concentrations in soil solution are many times greater than in precipitation or throughfall because of the high levels of CO_2 in the soil atmosphere. On dissociation, carbonic acid forms H^+ and HCO_3^-, H^+ exchanges for a base cation (or causes the dissolution of a mineral), and a bicarbonate salt leaches from the system. Because carbonic acid is a very weak acid, HCO_3^- becomes associated with H^+ to form carbonic acid at low soil pH. Thus, the carbonic acid leaching mechanism is self-limiting, and eventually becomes inoperable during the soil acidification process.

Organic acids are often the major cation leaching agents in extremely acid soils that occupy the boreal regions. These acids are stronger than carbonic acid and can produce low solution pH while providing organic counter-anions for cation leaching. Organic acids are also responsible for the chelation and transport of Fe and Al from surface (E or albic) to subsurface (Bs or spodic) horizons during the podzolization process. In theory, organic acid leaching, like carbonic acid leaching, is self-limiting because organic acids are typically weak acids. However, organic acids can provide very low soil and soil solution pH and still remain active in leaching processes.

Sulfate and nitrate are the anions of strong acids, and therefore leaching by sulfuric and nitric acids is not self-limiting because of solution pH alone. The deposition or other inputs of either S or N in excess of biological demands of these elements will ultimately cause an increase in SO_4^{2-} or NO_3^- availability within soil. In case of SO_4^{2-}, inorganic absorption processes may prevent increased leaching, but this is seldom true in the case of NO_3^-. In that soil SO_4^{2-} absorption is strongly pH dependent (increases with decreasing pH); there can be a negative feedback involved in sulfuric soil leaching that is at least partially self-limiting.

The input of chemical species from atmospheric deposition is the main source of feeding the supra-permafrost ground waters. The deposition contributes the significant amount of elements to natural waters of Boreal ecosystems. The concentration of trace metals in the ground waters of North Siberia Taiga Forest Cryogenic ecosystems is lower than their respective average values for the global riverine waters. In southern Boreal Forest ecosystems, the concentrations of trace metals in ground waters are merely several-fold higher than that in precipitation (Table 11).

The higher concentrations of some heavy metals, like Zn, Cu, Ni, and Pb, in snowmelt waters in comparison with rain waters is possibly related to the elevated content of solid particles in snow. Deposition fluxes are less important in the

Table 11. The concentration of trace metals in atmospheric deposition and ground waters of Siberian Taiga Forest ecosystems, μg/L (after Shvartsev, 1978; Dobrovolsky, 1994).

	Ecosystems				
	Tundra Forest of Middle Siberian High Plain			South Taiga Forest of West Siberia	
Trace metal	Rainwater	Snowmelt water	Ground water	Rainwater	Ground water
Mn	4.0	3.7	12.5	4.2	20.2
Zn	3.0	10.0	8.5	7.2	29.2
Cr	2.2	2.5	1.3	1.1	2.5
Cu	1.0	2.6	3.1	0.2	1.8
Ti	1.0	1.0	1.5	2.4	22.7
V	1.0	0.8	1.0	0.1	0.7
Pb	0.3	1.0	0.4	2.3	0.5
Ni	0.3	0.8	0.8	0.3	1.5

biogeochemical mass budget of elements in Southern ecosystems, than in northern Forest ecosystems.

The content of soluble salts increases in surface and ground water runoff of Forest ecosystems forwarding from north to south with a parallel decrease in soluble organic acids. To a certain extent, this may be related to the changes of soil-forming geological rocks. The biogeochemical processes in Podzols formed on sandy fluvioglacial and ancient alluvial deposits are favorable to a decreased solid salt content in waters and simultaneously to the relatively increased content of fulvic acids. Such a geochemical situation is common for the sandy lowlands of the East European plain, for instance, Meshchera and Belarussian Swamp Forest ecosystems. In contrast, the alteration of sandy deposits to clay rocks formed the clay soils and consequently this is accompanied with increase in both pH and solid salt content. This trend is clearly distinct in Table 12.

We can see the rise of heavy metal groundwater contents in the southward direction with increasing content of total soluble salts. However, this increase is not similar for various metals. For example, Zn is the most abundant metal in the waters of Tundra

Table 12. The average concentrations of trace metals in ground waters of Siberian Boreal and Sub-Boreal Forest ecosystems, μg/L (after Dobrovolsky, 1994).

	Forest ecosystems		
Trace metal	Tundra	Northern Taiga	Mixed
Zn	23.0	31.8	39.5
Sr	21.3	26.3	163.0
Mn	12.3	17.9	55.6
Ba	10.0	9.1	29.4
Li	3.97	6.09	19.0
Cr	2.52	2.16	4.02
Ti	2.34	4.64	21.9
Ni	1.91	1.63	5.29
Pb	1.88	1.16	2.88
Cu	1.70	2.98	5.11
As	0.73	0.99	4.15
Zr	0.68	1.28	2.27
Mo	0.64	0.92	1.28
V	0.50	0.88	1.45
Ga	0.35	0.49	0.63
Sr	0.22	0.50	0.77
Co	0.40	0.24	0.61
U	0.30	0.34	1.01
Ag	0.21	0.37	0.20
Be	0.02	0.04	0.18

and North Coniferous Forest ecosystems, whereas in Mixed Forest ecosystems it recedes to the third place after Sr and Mn.

An important role in the migration of trace metals in Forest ecosystems is connected with organic complexes and colloidal particles. For instance, the role of ionic forms of iron in water biogeochemical migration is of minor importance as compared with migration in metal–organic complexes, accounting for 80% of total content of metal in the soil waters. On average, about 50% of metals are subjected to biogeochemical migration as the metal–organic complexes (see Box 5).

Box 5. The role of metal–organic complexes in biogeochemical migration of trace elements (after Newman and McIntosh, 1991)

Of particular interest to biogeochemical migration of heavy metal is the effect of complexation on metal availability in the presence of natural dissolved organic matter. Humic and fulvic acids (symbolized here as Hum) are very distributed in soil solutions and surface waters, especially in surface waters with visible color. Hum is an important fraction of the dissolved organic matter, even in low color water. Other fractions of natural organic matter, including dissolved nitrogen organic compounds (oligo- and polypeptides) and synthetic organic compounds, such as polyaminocarboxylates (e.g., ethylenetetraacetic [EDTA], nitriloacetic acid [NTA]), may be important complexing agents for heavy metal ions in some waters thus determining their exposure to living organisms.

Metal ions complexed with natural macromolecular organic matter or strong synthetic chelating agents generally are considered not to be directly available to aquatic organisms, whereas inorganic complexes generally are. Aluminum fluoride complexes are important exceptions among inorganic complexes of interest in freshwaters. In addition, organometallic forms of several metals (e.g., methylmercury, triorganotin species), which are lipophilic, are bioaccumulated by aquatic organisms much more so than inorganic forms of the metals, and some organometallic complexes are toxic to aquatic biota.

For a variety of reasons, it is difficult to measure stability constants of metals with Hum, and the use of stability constants measured under a given set of solution conditions (so-called “conditional constants”) for a different set of conditions (e.g., at a different pH or different set of metals and Hum concentrations) must be done cautiously. Significant advances were made during the past decade in ways to model metal–Hum binding, and a sufficient variety of conditional binding constants are now available at least to approximate the metal-binding behavior of natural water and soil solutions containing Hum.

The example of calculated heavy metal speciation in Little Rock Lake, Wisconsin, USA is shown below (Table 13).

We can see that the most chelating properties are shown for Cu, in lesser degree for Cd and Pb, and a minimum for Mn and Zn.

Table 13. Calculated heavy metal speciation in Little Rock Lake, Wisconsin, USA.

	% of free ions		
Metal	pH 6.1	pH 4.7	Complexed ions, $>1\%$
Al	<1	18	$ALOH^{2+}$, $Al(OH)_2^+$, $AL(OH)_3^0$, $Al(OH)_4^-$, AlHum, AlF^{2+}, AlF_2^+
Mn	91	95	MnHum
Cd	73	75	CdHum, $CdSO_4^0$
Cu	22	25	CuHum, $Cu(OH)_2^0$
Pb	70	92	PbHum, $PbOH^+$, $PbSO_4^0$
Zn	93	94	ZnHum, $ZnSO_4^0$

During water migration the trace elements (heavy metals) undergo a systematic redistribution with the subsequent elementary landscapes in the catena from the watershed to relief depressions. The lowland swamps are typical subordinate ecosystems in the belt of boreal forests. Migration of metals associates mainly with soluble organic matter. More than 90% of Fe and similar percentage of other metals, like Mn, Cu, Zn, Ni, Cr and V, in lowland swamp waters migrate in the form of soluble metal–organic complexes.

Swamp ecosystems are placed both in watershed and subordinate relief positions. The elevated content of metals is monitored in the latter case (Table 14).

Table 14. The comparative estimation of average content of trace metals in surface waters of Swamp ecosystems, µg/L (after Shvartsev, 1999 and Dobrovolsky, 1994).

	Swamp ecosystem relief position	
Trace metals	Watershed	Subordinate
Mn	41.9	52.5
Ba	11.5	9.23
Zn	5.73	9.86
Cu	0.55	1.20
Ti	2.65	1.10
Pb	0.60	0.89
Ni	0.66	0.72
V	0.10	0.19

The elevated concentrations of trace elements in boggy waters lead to an elevated migration in biogeochemical cycles and finally to the increased accumulation in dead organic matter of peat. The metal content in the low peat lands of the Karelia is higher than that in watershed peat. For instance, for manganese it is higher by 2 times, for cobalt by 3–4 times, for molybdenum and copper by 56 times. In different Forest ecosystems of the World this proportion is similar. However, this is maximally distinguished in the Boreal Forest ecosystems and to a lesser degree in Sub-Boreal ecosystems, where the pH of natural waters tends to increase and the concentration of dissolved organic compounds, to decrease.

These quantitative values of exposure to heavy metals in the relevant pathway are of importance for environment risk assessment procedures in the forest ecosystems areas.