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Cycling and status of cobalt in some forest types

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Abstract

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The concentrations of Co were determined in the hydrological cycle (in maquis and fir forests), litterfall and soils in maquis, oak, beech and fir forests. The concentrations in the hydrological cycle were characterized by high variability. The concentrations in soil solution were much higher than those in the bulk deposition and throughfall. The contribution of the earth's' crust in the bulk deposition enrichment with Co was not high but some minor quantities of Co can be considered to be transported in long distances. The concentrations of Co in litterfall were high in the fraction composed of lichens, flowers and mosses, especially in the fir forest. The total content of Co was significantly higher in the soils derived from mica schist than those in the flysch. The residence time of Co in the forest floor was rather long. This is an indication that weathering in the mineral layers plays an important role in providing Co for plant uptake.

Keywords

cobalt, forests, soil, hydrology, litterfall

Introduction

Cobalt (Co) is a constituent of enzymes and proteins and has a specific role in plant metabolism. Hu et al. (2021) reviewed the role of Co in plants and concluded that Co can be considered as a micronutrient. Cobalt is an essential component of cobalamin (Vitamin B12), which is needed for activities of several enzymes and co-enzymes. Co affects the formation of leghaemoglobin involved in nitrogen (N) fixation in the nodules of leguminous plants (Mathur et al., 2006) as well as increasing the number of nodules and size per plant. Barket et al. (2010) found that plants of chickpea (*Cicer arietinum* L.) exposed to levels of Co less than 100 µM in nutrient solution significantly increased the number of nodules, their dry mass, the leghemoglobin concentration and activity of nitrogenase. The Co content affects not only the nitrogen fixation in nodules of leguminous plants but also the ability of free-living bacteria capable to fix N like *Azotobacter chroococcum* (Orji et al., 2018). Apart from the beneficial effects that Co has on mammals and plants, high concentrations of Co can bring about toxic effects. As the geogenic sources of cobalt are very limited and environmentally benign, its worldwide contamination is strictly considered anthropogenic (Klasson et al., 2016). Significant importance is attributed to Co compounds emitted to the air, mainly during the combustion of hard coal and petroleum, which are especially transferred to the soil environment during precip-

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itation (Biswas et al., 2013; Singh and Cameotra, 2013). Banerjee and Bhattacharya (2021) summarized the toxic effects that excessive quantities of Co can have on plants.

Remote forests are natural environments and for this reason, toxicity is a rare problem unless there is Co mining in the vicinity. Finding the content of Co in the various ecosystem components is a useful piece of information for the number of organisms living there and for the N fixing ability of the ecosystems. The aim of this work was to find the concentrations in the hydrological cycle, soil and vegetation of some remote forests in Greece having different vegetation. Three of them are mountainous forests and one is situated in the low Mediterranean zone (maquis vegetation).

Materials and methods

Sites description

The four sites from which the material was collected belong to the Intensive Monitoring Survey of the ICP Forests network (UN-ICP-*Forests*). They represent important forest ecosystems in Greece and this was the reason they were selected. The main forest vegetation for the three mountainous sites is Hungarian oak (*Quercus frainetto* Ten.), European beech (*Fagus sylvatica* L.), and Bulgarian fir (*Abies borisii-regis* Mattf.). The maquis vegetation consists of Holm oak (*Quercus ilex* L.), strawberry trees (*Arbutus unedo* L.) and green olive trees (*Phylirea latifolia* L.).

Further information about the plots is given in Table 1.

Samples from the hydrological cycle

Water samples analyzed for Co were collected weekly from the maquis and fir plots. More specifically, samples from the throughfall deposition were collected with 20 collectors placed randomly within the stand and bulk deposition with three collectors placed in a clearing about 100 m from the plot.

Soil solution was collected with zero tension lysimeters installed in two depths, 20 and 65 cm.

The periods of water samples collection for the two plots cover two hydrological years, i.e. October 2012 to October 2014. Details of the collection of the water samples can be found in Michopoulos et al. (2022).

Collection of litterfall

In all plots, litterfall was collected with 10 plastic cylinders systematically placed in a straight line at a distance of five m from each other with a surface area of 0.242 m^2 each. A composite litterfall sample of the 10 traps in total was transferred to the laboratory at each sampling. In the laboratory, the litterfall was separated into its fractions, foliar, woody (twigs, bark parts) and rest (flowers, lichens, mosses, insect frass) and weighed. Subsamples were ground in a ball mill for total analysis. The litterfall data (for Co) covers three years for the maquis plot (2012–2015), one year for the oak plot (2012–2013), one year for the beech plot (2012–2013) and two years for the fir plot (2012–2014).

Collection of needles and leaves

Needle and leaf samples were collected in 2013 in winter for the fir and maquis forests (dormant period) and summer for the beech and oak forests. The samples were collected from the upper part of the crown from five dominant trees and formed a pooled sample. From the maquis plot the leaves were collected from the holm oak trees, which was the dominant species. From the fir and holm oak trees the leaves collected were from the current year (2013) and rest years. Needles and leaves were dried at 80 °C for 48 h and then ground in a special mill and stored for analysis.

Collection of soil samples

Soil collection was carried out by systematic sampling in 2007. For each layer of the L, FH, 0–10 cm, 10–20 cm, 20–40 cm and 40–80 cm depths three replicates in space were formed. Details of the soil sampling can be found in Michopoulos et al. (2020).

The L and FH layers were weighed. The bulk density of mineral soils in all layers was measured by a cylinder having a volume of 129 cm^3. The samples of the FH and mineral layers passed through a 2 mm sieve.

Subsamples of the L, FH and mineral soils were pulverized in a ball mill for total elemental analysis.

Chemical analysis

The concentration of Co in water samples was determined with an ICP-MS instrument (Thermo iCAP Qc).

Litterfall and foliage samples were digested in a mixture of HNO_3–$HClO_4$ and their Co content was measured with the ICP-MS instrument mentioned above.

Exchangeable Ca^{2+}, Mg^{2+} and K^+ in the FH and mineral soil layers were extracted with a 0.1 M unbuffered $BaCl_2$ solution and their concentrations were determined with Flame Atomic Absorption spectroscopy (FAAS). The cation exchange capacity (CEC) was found by summing all the exchangeable cations including Al^{3+} and Mn^{2+} (the hydrogen ion concentrations were negligible). The concentrations of total N and organic C in soils were measured with a CN analyzer (Vario MAX). For the total Co in soils, soil samples were digested in a microwave oven with HF and aqua regia at a temperature range of 160–170 °C for 20 min. Concentrations of Co in the digests were determined with the ICP-MS instrument.

Data handling and calculations

The median concentrations of Co together with the ranges were calculated in the hydrological cycle, for bulk, throughfall, soil solution in the two depths for the fir and maquis plots in the two hydrological years mentioned above.

The averages and the ranges of Co concentrations were calculated for litterfall together with the litterfall mass-

Table 1. Characteristics of the areas from which the soil samples were selected

Area	Altitude (m)	Soil parent material (FAO, 1988)	Soil type	Vegetation
Amfilohia	360	Flysch	Eutric Cambisol	Holm oak, strawberry trees, green olive trees
Ossa Mountain	740	Mica schist	Dystric Cambisol	Hungarian oak
Ossa Mountain	890	Mica schist	Haplic Alisol	European beech
Karpenisi	1,170	Flysch	Cambisol	Bulgarian fir

es in order to estimate the mean residence time of Co in the forest floor. For the standing leaves and needles we had one value for current and the rest years because we had only one year of selection.

The effect of the earth's crust on the concentration of the three elements in bulk deposition was assessed as follows: The ratio value (xb/Alb) over (xc/Alc) shows the degree of influence of the earth's crust on the composition of rain. Where xb is the concentration (μg L^{-1}) of Co in bulk deposition, Alb is the concentration (μg L^{-1}) of Al in bulk deposition; xc is the concentration (μg g^{-1}) of Co in the earth's crust and Alc the concentration (μg g^{-1}) of Al also in the earth's crust. The higher the ratio the more important is the long-range transport of an element. This relationship has been used by several researchers to find the contribution of the earth's crust to metal concentrations in rain (Son and Gao, 2009; Zhou et al., 2012). The last mineral soil layer (40–80 cm) was taken to represent the concentration of Co in the earth crust. As both soils were developed on sedimentary rocks, the average Co concentration found in these soils was used. For Al the average concentration 8.8 mg g^{-1} in the earth crust was taken (Kabata-Pendias and Pendias, 2001).

For soils, the average concentrations and the coefficients of variations were calculated. In addition, the Co pools in the forest floor and minerals layers in the four forest types were calculated taking into account the Co concentrations and bulk densities. The Spearman correlation coefficients were estimated for Co, Ni and the rest of the soil properties. The Ni was included because of the high similarities it presented with Co. The total concentrations of Co in soils were classified in two groups, one in the soils developed on mica schists (beech and oak) and the other on sedimentary rocks (maquis and fir). The concentrations of Co for each depth between the two rock types were compared with a Mann-Whitney test.

The pools of Co in soils in both forest floor and mineral layers as well as the fluxes in litterfall together with the residence time (in years) of Co in the forest floor (L + FH) were also assessed. The residence time was calculated as the ratio of the pool of Co in the forest floor over the yearly average litterfall fluxes of Co (Gosz et al., 1976).

Results

There was high variability in the hydrological cycle of Co (coefficient of variation >100%) in the two forest types. For this reason, the median values were chosen to represent the central tendency of the concentrations (Table 2). For the rest of the parameters the average values were calculated. The concentrations of Co in the soil solution in both depths were found far higher than those in the bulk and throughfall deposition. Table 2 also contains the crustal enrichment median values of Co in the maquis and fir plots.

Table 2. Median concentrations and ranges (μg L^{-1}) of Co in the hydrological cycle of two forests as well as median values and ranges of crustal enrichment

	Maquis	Fir
Bulk	0.026	0.051
	0.004–0.325	0.014–0.356
Throughfall	0.061	0.049
	0.005–0.669	0.017–0.484
20 cm solution	0.383	0.271
	0.021–2.44	0.020–0.682
65 cm solution	0.451	0.257
	0.054–1.32	0.034–1.218
Crustal enrichment	11.0	16.0
	2.3–167	2.3–104

The concentrations of Co were appreciable in the non-foliar litterfall and woody (twigs) fraction of fir (Table 3). Beech leaves had the highest concentrations in the leaves fraction. With regard to Co concentrations in the standing leaves, it is worth mentioning that the holm oak plot had the highest concentrations of all forest types in both current and older leaves.

The soil properties and Co concentrations are showed in Tables 4 and 5. The Mann-Whitney test showed that the differences between the Co concentrations in the mineral soils derived from the two parent materials, schist and flysch, were significantly different for all the layers (Fig. 1). The highest concentrations were found in soils derived from schist parent material.

Table 6 shows the Spearman correlation coefficients between Co and Ni and the rest of soil parameters separately for the two rock types, flysch and schist. The Ni was also included in the coefficients matrix because of the similarities it showed with Co. Indeed, the vast majority of the correlations for the two elements was found almost identical.

Table 7 contains the pools of Co in soils as well as the residence times (in years) of Co in the forest floor. There is a great difference between the magnitudes of the Co stocks in the forest floor and mineral soils. In addition, the residence times in the forest floors of the four forest types are quite long (the maquis plot has the lowest value, almost half as the others).

Table 3. Average concentrations and ranges (mg kg^{-1}) of Co in the various fractions of litterfall and standing leaves in the 4 forest types

	Maquis	Oak	Beech	Fir
Foliar	0.223	0.344	0.440	0.315
	0.139–0.290	0.274–0.515	0.316–0.698	0.295–0.338
Non Foliar	0.492	0.275	0.586	1.103
	0.578–0.794	0.081–0.468	0.161–1.00	0.895–1.178
Twigs	0.275	0.120	0.186	0.610
	0.222–0.328	0.090–0.150	0.161–0.211	0.589–0.630
Leaves C[1]	0.233	0.157	0.189	0.058
R[2]	0.205			0.123

[1]C, current year; [2]R, rest years.

Table 4. Average concentrations and coefficients of variation of soil properties and total Co in the maquis and oak plots. Clay, sand, silt and C are expressed in percentages (%), N in g kg^{-1}, CEC in cmoles kg^{-1} and total Co in mg kg^{-1}.

Layer	pH	Clay	Sand	Silt	C	N	CEC	Co
				Maquis				
L					49.4	11.2		0.816
					(2.8)	(8.5)		(76.0)
FH	6.6				26.0	13.6	71.6	12.6
	(3.7)*				(7.1)	(8.2)	(8.2)	(6.8)
0–10 cm	6.26	23.6	20.3	56.1	5.0	3.3	24.6	23.7
	(2.0)	(6.2)	(8.9)	(2.4)	(14.0)	(13.0)	(12.0)	(3.2)
10–20 cm	6.18	24.2	21.6	54.2	2.73	1.89	15.9	25.7
	(6.6)	(14.0)	(15.0)	(0.6)	(17.0)	(14.0)	(20.0)	(1.4)
20–40 cm	6.12	26.0	21.2	52.8	1.44	1.15	12.9	27.0
	(2.3)	(19.0)	(22.0)	(1.5)	(17.0)	(14.0)	(11.0)	(0.8)
40–80 cm	6.53	29.3	20.1	50.6	0.86	0.83	13.8	28.2
	(5.7)	(15.0)	(22.0)	(4.9)	(14.0)	(11.0)	(13.0)	(3.6)
				Oak				
L					45.9	12.6		1.48
					(3.1)	(5.8)		(19.0)
FH	6.19				20.1	9.62	44.4	16.7
	(1.6)				(9.5)	(10.0)	(5.9)	(2.0)
0–10 cm	5.35	16.2	38.9	44.9	3.46	1.98	9.30	28.8
	(0.7)	(3.8)	(3.6)	(2.3)	(14.0)	(15.0)	(13.0)	(1.6)
10–20 cm	5.45	16.6	36.4	46.9	20.9	1.23	5.10	30.1
	(1.5)	(2.3)	(5.2)	(3.2)	(16.0)	(19.0)	(17.0)	(2.7)
20–40 cm	5.43	16.1	34.5	49.4	1.18	0.725	3.74	31.8
	(1.2)	(2.5)	(8.2)	(5.0)	(3.7)	(3.9)	(8.1)	(4.8)
40–80 cm	5.42	13.6	46.6	39.8	0.57	0.378	3.31	32.6
	(0.7)	(4.2)	(3.2)	(2.4)	(17.0)	(13.0)	(5.2)	(3.1)

*coefficient of variation. CEC, cation exchange capacity.

The concentrations of Co were appreciable in the non-foliar litterfall and woody (twigs) fraction of fir (Table 3). Beech leaves had the highest concentrations in the leaves fraction. With regard to Co concentrations in the standing leaves, it is worth mentioning that the holm oak plot had the highest concentrations of all forest types in both current and older leaves.

The soil properties and Co concentrations are showed in Tables 4 and 5. The Mann-Whitney test showed that the differences between the Co concentrations in the mineral soils derived from the two parent materials, schist and flysch, were significantly different for all the layers (Fig. 1). The highest concentrations were found in soils derived from schist parent material.

Table 6 shows the Spearman correlation coefficients between Co and Ni and the rest of soil parameters

Table 5. Average concentrations and coefficients of variation of soil properties and total Co in the beech and fir plots. Clay, sand silt and C are expressed in percentages (%), N in g kg^{-1}, CEC in cmoles kg^{-1} and total Co in mg kg^{-1}.

Layer	pH	Clay	Sand	Silt	C	N	CEC	Co
				Beech				
L					47.3	14.3		0.824
					(0.6)	(4.2)		(18)
FH	5.75				26.9	13.6	41.2	18.1
	(4.9)*				(3.5)	(1.1)	(12.3)	(8.4)
0–10 cm	4.83	20.0	26.4	53.6	4.32	2.09	6.92	35.6
	(2.4)	(5.5)	(10)	(3.5)	(4.5)	(8.2)	(2.0)	(4.2)
10–20 cm	5.08	21.8	22.8	55.4	2.95	1.54	4.69	37.3
	(2.1)	(2.1)	(0.8)	(0.9)	(8.7)	(11.0)	(5.2)	(5.5)
20–40 cm	5.24	21.5	21.3	57.1	2.09	1.20	3.61	42.7
	(0.6)	(0.3)	(4.3)	(1.7)	(12)	(8.6)	(9.2)	(5.6)
40–80 cm	5.27	15.0	30.4	54.6	0.908	0.582	2.67	38.8
	(1.1)	(4.1)	(6.7)	(3.5)	(3.2)	(2.2)	(8.5)	(8.2)
				Fir				
L					50.8	12.3		1.53
					(0.7)	(9.3)		(108)
FH	6.48				23.0	12.2	57.6	12.2
	(0.2)*				(14.0)	(13.0)	(9.5)	(12.0)
0–10 cm	6.07	27.2	29.5	43.1	5.12	3.31	18.2	19.8
	(2.0)	(2.0)	(1.2)	(0.9)	(20.0)	(16.0)	(15.0)	(5.0)
10–20 cm	5.77	31.2	24.7	44.1	3.36	2.45	11.7	18.7
	(3.1)	(2.1)	(8.1)	(3.4)	(10.0)	(9.4)	(12.0)	(12.0)
20–40 cm	5.54	33.0	21.0	45.9	2.75	2.12	8.98	19.7
	(1.2)	(6.7)	(6.0)	(5.4)	(3.5)	(4.4)	(4.9)	(9.3)
40–80 cm	5.32	34.9	23.2	41.9	1.53	1.35	6.63	17.9
	(1.5)	(14.0)	(11.0)	(5.6)	(19.0)	(15.0)	(4.0)	(23.0)

*coefficient of variation; CEC, cation exchange capacity.

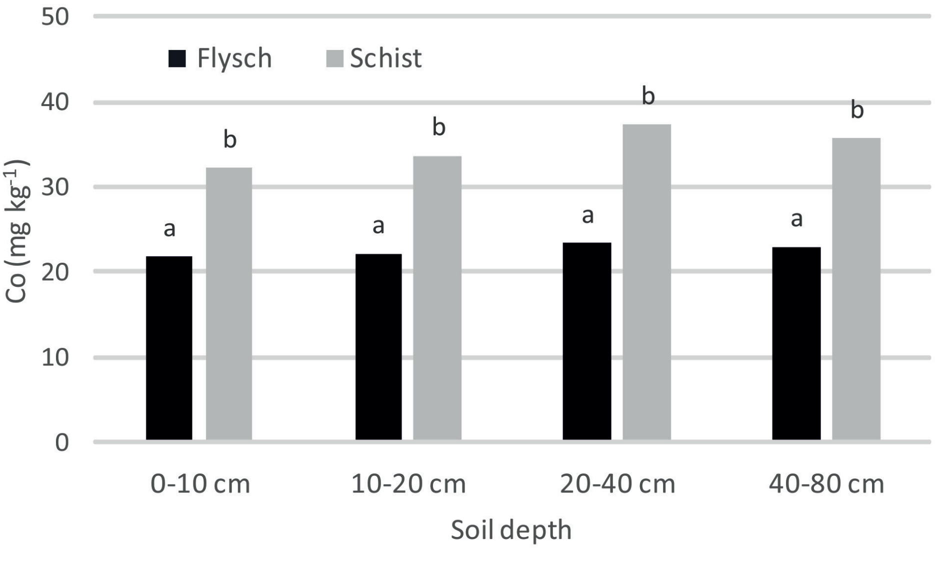

Fig. 1. Concentrations (mg kg^{-1}) of total Co in the various soil layers of the four forests (according to parent material). Different letters per layer and depth denote significant difference for at least 0.05-probability level.

Table 6. Spearman correlations for Co and Ni in the two rock types (Flysch and Schist). The bold denote significance level for at least the 0.05-probability level.

	Co	Ni	pH	C	N	Clay	Sand	Silt	CEC	Mn	Mg	Fe
Co (Flysch)	1	**0.94**	**0.67**	**–0.48**	**–0.54**	–0.38	**–0.50**	**0.60**	0.36	**–0.40**	0.35	0.21
Ni (Flysch)	**0.94**	1	**0.60**	**–0.56**	**–0.60**	–0.33	**–0.58**	**0.63**	0.27	**–0.47**	0.39	0.283
Co (Schist)	1	**0.95**	**–0.60**	–0.05	–0.11	**0.42**	**–0.79**	**0.78**	**–0.50**	**–0.55**	**–0.62**	0.13
Ni (Schist)	**0.95**	1	**–0.57**	–0.07	–0.15	0.34	**–0.78**	**0.82**	**–0.53**	**–0.58**	**–0.68**	0.17

CEC, cation exchange capacity.

Table 7. Pools of Co (kg ha^{-1}) in the forest floor and mineral soil, fluxes (g ha^{-1} yr^{-1}) of Co in litterfall and residence time (years) of Co in the forest floor in the four forest types

	Maquis	Oak	Beech	Fir
Forest floor	0.384	0.302	0.806	0.991
Mineral soil	105	225	227	89.3
Litterfall	1.17	2.1	2.52	2.54
Residence time	327	150	320	390

separately for the two rock types, flysch and schist. The Ni was also included in the coefficients matrix because of the similarities it showed with Co. Indeed, the vast majority of the correlations for the two elements was found almost identical.

Table 7 contains the pools of Co in soils as well as the residence times (in years) of Co in the forest floor. There is a great difference between the magnitudes of the Co stocks in the forest floor and mineral soils. In addition, the residence times in the forest floors of the four forest types are quite long (the maquis plot has the lowest value, almost half as the others).

Discussion

Hydrological cycle

There is not much information concerning the Co concentration in the whole hydrological cycle in forests. The existing data in literature refers mainly to precipitation in the open field. In this respect, the concentrations are close to the ones found in our work. Neal et al. (2010) found low concentrations (0.070 µg L^{-1}) and high variability of Co in the rain in the mid-Wales. In the rainwater close to a Meteorological Station near Dresden, Matschullat et al. (2000) found a concentration range of Co 0.005–2.09 µg L^{-1}, whereas Galloway et al. (1982) quoted a range of 0.75–1.00 µg L^{-1} in the wet deposition of USA. We cannot conclude if there is a systematic behavior of Co in throughfall as we had enrichment in the case of the maquis and absorption by the fir trees (Table 2). The first case implies dry deposition and the second one take up by plants. With regard to the soil solution, the only information we have was that of Gandois et al. (2010). They found 1.66 µg L^{-1} of Co in soil solution extracted with centrifugation from mineral forest soil samples collected in France. In our work, the soil solution was extracted with zero tension lysimeters. The different method explains the lower concentrations of Co found in the present work. In any case, the concentration of Co in soil solution in both soil depths was much higher than those in bulk and throughfall deposition. As will be seen later that difference is probably due to weathering and not to Co leaching from the forest floors.

Crustal enrichment of precipitation with Co

In this work, we found that the Co enrichment had some values higher than 10 and lower than 500 (Table 2). This means that some anthropogenic influence regarding the transfer of Co in the atmosphere is present. According to Poissant et al. (1994), ratios between 1 and 10 imply a large effect of the earth's crust on the composition of the elements in the rain, while values between 10 and 500 a moderate effect of the earth crust and the rest is complemented by anthropogenic influences. Steiness and Friedland (2005) classified Co in the first category (1–10) together with Cr, Fe and Mn. Indeed, the medians found 11.0 and 16, for the maquis and fir, respectively are very close to the limit of 10. However, there is great variability and some values exceed the 100 limit. Therefore, a definite conclusion for all the Co in rain cannot be drawn.

Standing leaves and litterfall

Maňkovská (1998) found 0.16 mg kg^{-1} and 0.17 mg kg^{-1} of Co in the second-year needles of Sitka spruce and beech leaves in Slovakia, very similar to our results for fir and beech. The reservation is that the leaves and needle sampling in the four forest types concern only one year. There is no information in literature with regard to Co content in litterfall. In our work, the concentrations of Co in litterfall were higher than those in standing leaves. Especially, the non-foliar fraction of maquis and fir forest types had high concentrations (Table 3). This is probably due to the exchange sites created by a variety of flora such as mosses, lichens and flowers. Cobalt contained in rain can stick to those exchange sites and enrich this litterfall fraction.

Soils

High Co contents have been observed in soils over serpentine rocks, up to 520 mg kg^{-1} and in soils around ore deposits, up to 85 mg kg^{-1}. In remote unpolluted soils, the range varies depending on the parent material. In soil samples of the United States the range was from 5.5 to 29.9 mg kg^{-1} and in Chinese soils, it was 5.5–97 mg kg^{-1} (Kabata-Pendias and Pendias, 2001). In order to compare the Co concentrations in soils of the four forest types with other soils, the method of extracting total Co should be quoted. In this work, the soils samples were digested with aqua regia and HF acid. This method dissolves soils completely and brings all Co in the digests. Other methods that do the same are fusion with lithium metaborate or carbonate salts and the X-ray fluorescence (XRF) method. Digestion with other inorganic acids such as nitric and sulfuric acids cannot dissolve the whole of a soil sample and consequently the Co concentration is lower than the real one. In a podzol soil in Sweden, TYLER (2005) using HNO_3 as a digest found 0.540 mg kg^{-1} of Co in the H layer of a beech forest. SUCHARA and SUCHAROVÁ (2002) analyzed the humus layer of 192 forest plots in the Czech Republic using nitric acid and hydrogen peroxide. They found an average of 5.2 mg kg^{-1} of Co with a range of 1.5 to 17.5 mg kg^{-1}. In an industrial area in India KRISHNA and GOVIL (2007) with the XRF method determined an average Co concentration of 46 mg kg^{-1} in surface soils. HERNANDEZ et al. (2003) determined the Co concentrations using HF/$HClO_4$ acid they found a range of 0.56 to 23 mg kg^{-1} of Co in some forest soils in France. They found that Co is generally mostly concentrated in deep horizons. The higher Co concentrations in deep horizons of forest soils could be associated to the clay contents in these soils, as argued by KRASNODEBSKA-OSTREGA et al. (2001).

Soil developed on schist had higher concentrations of Co (Fig.1) despite the lower pH of those soils. There are two possible explanations for this. The first could be a rather high oxide content in soils developed on schist. MCLAREN et al. (1986) found that Co sorption by mineral soils is strongly dependent on oxide contents and not on clay ones. In this work, the oxide content in soils has not been determined so it is a hypothesis to be verified for forest soils. The clay fraction can also absorb Co probably not in the same degree as the oxides. The second explanation could be a rather high concentration of Co in the biotite fraction of schist. This is another hypothesis to investigate.

The very good correlation of Co and Ni in both groups, schist and flysch with the other soil components (Table 6) imply a similar chemical behavior in soils. Table 6 shows that Co and Ni had a consistent negative dependence with Mn in both rock types and with Mg in soils derived from schist. Cobalt has a similarity with the ionic radii of Mg^{2+} (72 pm), Mn^{4+} (53 pm), Fe^{2+} (70 pm), Fe^{3+} (60 pm) and Ni^{2+} (70 pm). Cobalt [Co^{2+} (70 pm) and Co^{3+} (60 pm)] can easily substitute for these metals in soil minerals (BANERJEE and BHATTACHARYA, 2021). Negative correlation coefficients would imply a substitution effect. It can be concluded that this substitution takes place between Co, Ni and Mn in both types of rocks and between Co, Ni and Mg in schists.

The different correlation of Co in the two types of rocks with the pH is interesting. In the soil derived from schists the Co as well as the Ni concentrations, have a negative relation with pH and in the soils from flysch a positive one. Soils developed on schists are acidic and have a high content of aluminum (Al). It is probable that ionic Co and exchangeable Al^{3+} have an antagonistic relationship for exchange sites in the acidic soils. This process cannot take place in the soils derived from flysch where Al is relatively inert. In both rock types, the Co content had negative relation with the sand content. This was to be expected as sand is not effective in withholding ions. The Co concentrations in soils derived from schist did not have a significant relationship with either the organic C or total N, whereas there was a significant one in the case of flysch. The low pH in the soils derived from the schist rock brought about a destabilization of Co chelated compounds and lowered the correlation.

Residence time of Co in the forest floor

Table 7 contains the pools of Co in the forest floor and mineral soil as well the fluxes of Co in litterfall. There is a great difference with regard to the quantities in forest floor and litterfall fluxes. This is the reason that the residence time of Co in the forest floor is so long almost approaching the ones of heavy metals. We can conclude that the Co uptake does not take part from the forest floor pool but rather from the inorganic horizons. Weathering should play an important role in this respect taking into account the high stocks of Co in the mineral soil.

Conclusion

The Co from the atmosphere can be deposited in forest canopies and trapped and/or taken up by plants. Some of that Co can be derived from anthropogenic activities. Weathering enriches the soil solution relative to the rain or throughfall. Co and Ni have similar chemical behavior in soils. Both of them can be substituted by Mn and Mg in soil minerals. Soils derived from schist had higher concentrations of total Co probably because of higher concentrations of oxides. The correlations disclosed that the parent material played a crucial role in the chemical behavior of Co. High residence time of Co in the forest floors for all forest types were found. This emphasizes the role of weathering in providing Co for taking up by plants.

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