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Soil Buffering System Against Acid Deposition in Belgrad Forest Ecosystems

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Abstract

The paper presents a synthesis of a set of experiments, implemented towards understanding the acid buffering mechanism of Belgrad Forest soils. A long term ecological research, carried out in the region, pointed the exposure of Belgrad Forest ecosystems to acid deposition. Between 1999 and 2001 a set of supplementary studies was performed, focusing on this issue. The experiments included a lysimeter, a litter layer removal, and a cation retention study. Ceramic cup lysimeters were installed to various soil depths and the soil water ionic composition was monitored to determine the main buffering zones among the horizons. The upper 20 cm including the litter layer and Ah horizon had the main exchange mechanism, decreasing the hydrogen ion activity from $22.82 \mu\text{eq L}^{-1}$ to $0.56 \mu\text{eq L}^{-1}$. To identify the role of litter layer another experiment was employed which was basically a litter layer removal parcel study. Litter layer was removed from nine blocks and another nine blocks were remained as control. After the removal, soil samples were taken bimonthly from two depths (0-12 and 12-20) to determine the changes in soil properties. The pH and organic matter content was slightly higher in the upper 12 cm. Finally, the exchange capacities of single valance base cations, Na and K were compared -taking the soil horizons into account- with a totally controlled laboratory experiment. The cation retention capacities of the soil samples rich in organic matter were lower than the ones with less organic matter. The results of the three experiments revealed that, even though the upper soil horizons were responsible of hydrogen buffering in the region, the litter layer or humus layer did not have a particular role.

Keywords: Acid deposition, soil buffering system, soil water, cation exchange.

Introduction

The acid deposition phenomenon in Belgrad Forest region was documented by Serengil (2002). A significant amount of hydrogen, and acidic compounds including sulfur and nitrogen were detected in the precipitation water according to this study. The findings were also consistent with the records of a long term ecological and hydrological research carried out in the region.

This paper intends to address the buffering mechanism of these forest ecosystems giving the emphasis on the soil horizons. To do this, a set of experiments were added to the mentioned studies in 2000s particularly to find out the most effective buffering component of the ecosystem. The assessment of the acidic deposition and its effects on the ecosystem attributes are outside the scope of this paper.

Instead of identifying the soil system thoroughly, we utilized the basic systems approach, as explained by Müftüoğlu (1984, 1991). System analysis is a widely used approach in hydrology particularly in constructing black box models. It gives the advantage to focus on just the input and output, and literally eliminates dealing with complex system operations. The system operator, converting the input into output represents all complex processes with a single system behavior.

In this study a set of ceramic cup soil lysimeters was installed under the forest canopy to monitor the soil solution without changing forest floor structure. This experiment was coupled with a litter layer removal study and finally the base cations with single valance, Na^+ and K^+ were compared with a syringe procedure to investigate the relation between soil horizons and cation retention.

Site description and methods

Experimental sites

The experimental sites were located in Belgrad Forest (41° N, 28° E) an old-growth oak-beech natural forest near Istanbul (Figure 1). They were chosen in close proximity to keep parent material and soil homogeneity. The litter removal site was in Atatürk Arboretum while lysimeters were located on a gentle slope inside the forest, away from human interruption.

The climate of the watersheds and surrounding area according to Thornthwaite classification system is humid, mesothermal oceanic with a moderate soil-water deficit in summer. Long term annual precipitation and temperature are 1050 mm and 12.8 °C, respectively. A great portion of the precipitation falls from October to March.

Parent materials mainly consist of carboniferous clay schists and neogene loamy, gravelly deposits. The soils are usually shallow to deep, gravelly, loamy clay in texture, rich in organic matter with medium to good permeability rates. Soils have high erodibility potentials with no carbonate reaction. The mull type forest floor has an average depth of 5 cm (Özhan, 1977). Subsurface flow is the dominant flow component in the region (Balci et al., 1986).

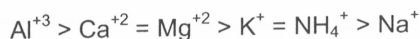
Topography is generally not steep, and mean elevation is around 140 m. Dominant vegetation includes oak (*Q. frainetto* Ten., *Q. cerris* L.) and beech (*F. orientalis* L.) tree species mixed with varying amounts of *Carpinus betulus* L., *Castanea sativa* Mill., *Populus tremula* L., *Alnus glutinosa* L., *Acer trautvetteri* Med., *Acer campestre*, *Ulmus campestris* L., and *Sorbus torminalis* Crantz. with a normal crown closure. The stands are mostly dominated by oak at the overstory and beech and hornbeam at the understory

Cation retention experiment

Most forest ecosystems exposed to acidic deposition shows a net output of base cations (i.e. Baumler and Zech, 1999; Ukonmaanaho and Starr, 2002). Introduction of H⁺ ions to the soil system both from atmospheric sources or inner dynamics (decomposition) can promote the mobilization and leaching of base cations. The base cation pool of the soil is simply provided by decomposition, mineralization and atmospheric deposition. However, the retention and leaching mechanism of the base cations in the various ecosystem compartments are specific and sparse.

Sodium is known as the least biologically relevant cation (Pierzynski et al., 2000). Plenty of Na⁺ was measured (660.4 eq ha⁻¹ yr⁻¹) around Belgrad Forest owing to its proximity to the sea both vertically, and horizontally. Potassium, on the other hand, is a significant nutrient and has slightly less deposition (529.96 eq ha⁻¹ yr⁻¹) (Serengil, 2002).

Cations are immobilized by negative charges of aluminum silica clay minerals and organic matter in the soil with changing degree of force related to the valance. If they are ranked according to the immobilization strength (liotrophic serie) (Pierzynski et al., 2000);



Aluminum is clearly the highest attracted cation by the negative surfaces in the soil matrix followed by Ca and Mg. We preferred to compare Na⁺ and K⁺ instead of Ca²⁺ and Mg²⁺ for 2 reasons; (1) They are single valance cations like H⁺, and (2) They have a totally different biologic relevance. Potassium is a significant nutrient whereas Na⁺ has the least biologic importance.

A mechanical vacuum extractor modified from Coweeta Hydrologic Laboratory Wetlab Manual (Deal et al., 1995) was used in cation retention experiment which is a simple equipment to extract exchangeable cations from soil samples.

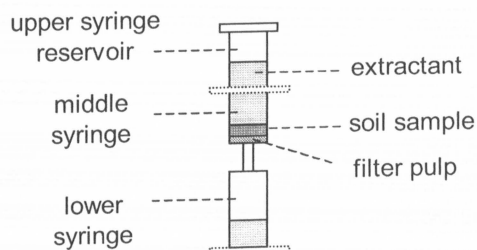


Figure 1. The centurion mechanical vacuum extractor.

Stepwise concentrations of Na⁺ and K⁺ solutions were prepared as extractants with a very sensitive Orion Ionmeter using ion selective electrodes. Vacuum is not applied during the experiment to maintain natural conditions.

Some properties of soils samples taken from humus (Ah), A, AB and B horizons to be used in this experiment are given below (Table 1).

Table 1. Basic properties of the soil samples used in the syringe experiment. Mean values of 3 samples from each horizon.

Soil property	Sampled horizon			
	Ah	A	AB	B
pH	5.66	5.06	5.23	5.35
El ($\mu\text{S}/\text{cm}$)	117.67	69.67	54.33	63.00
OM (%)	11.81	5.59	3.15	2.85

Lysimeter experiment

Ceramic cup lysimeters are simple but very useful gauges for monitoring the soil solution. The manufacturer of the lysimeters¹ we used provides the details and application principles. 9 lysimeters were installed at 3 soil depths; 20, 60 and 90 cm (also separates soil horizons). Soil solution was extracted with a vacuum pump and analyzed for the major ions in the laboratory of I.U. Watershed Management department after each precipitation event. 20 precipitation events were sampled in 8 months. Soil properties at the lysimeter site are given in Table 2.

Table 2. Soil properties at lysimeter site.

Soil depth (cm)	pH	EC ($\mu\text{S}/\text{cm}$)	Organic matter (%)	Particle fraction		Exchangeable equivalents (NH ₄ Cl extraction)				
				Sand	Clay	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	Al ³⁺
				(%)		meq L ⁻¹				
Litter	5.41	151								
O1	5.40	450				20.61	8.98	14.65	0.51	0.13
0-20	4.51	128	8.5	72.9	16.6	7.98	7.15	13.56	0.58	1.64
20-60	4.80	95	3.6	74.6	19.7	6.38	22.59	13.32	0.46	5.57
60-90	4.85	176	3.2	76.7	15.5	2.55	22.39	13.71	0.45	3.53

Litter layer removal experiment

The organic matter content of a forest soil -almost hundred percent- is provided by the decomposition of litter on the forest floor. The duration of the process is a function of driving climatic variables, mostly temperature and humidity (Pierzynski et al, 2000).

The objective of this experiment was to find out if upper soil horizons are capable of maintaining their basic properties during a period of one year without the litter layer organic matter recharge. It would also provide us to evaluate the role of litter layer in the ion exchange process during the penetration of rainwater into the soil. The expected scenario was an accelerated wash up of the base cations in the litter-removed sites to cause an increase in hydrogen activity to affect the soil properties in the mid term.

Square shaped 9 permanent plots adjacent to each other within 1-meter distance were determined and the litters over them were removed carefully not to damage Ah horizon. Another adjacent 9 plots in the same pattern were kept as the control. Soil samples were taken bimonthly from 2 depths (0-12 and 12-20 cm) and analyzed for pH, electrical conductance, organic matter and total nitrogen.

RESULTS AND DISCUSSION

Cation retention

¹ <http://www.soilmoisture.com>

The Figures 2,3, and 4 shows the retention curves of cations. To expose the role of organic matter we presented the results of the samples taken from Ah and B horizons in Figure 2. They had 11.81 % and 2.85 % organic matter contents, respectively, with a very similar, coarse textural composition (70-75 % sand). Besides its high mobility in the soil system, the retention potential of Na^+ is not influenced by organic matter content of the soil significantly, as seen on Figures 2, 3. . Further, the less organic matter content of the soil, the more Na^+ immobilization we determined. Apparently, organic matter in the soil did not provide an immobilization surface for Na^+ . Potassium, on the other hand, is strongly affected by the organic matter content of the soil but inversely. The outflux concentration pattern of the soil sample of Ah horizon is quite different from B horizon soil sample as seen in Figure 2. For the Ah soil sample the outflux Na^+ concentration increases with increasing influx concentration with a roughly linear and proportional trend, but the B horizon soil sample stores a considerable amount of the given K^+ and releases always a low steady concentration (Figure 4).

Even though K and Na are located pretty close in the lyotropic serie they look like had a totally different nature in cation exchange.

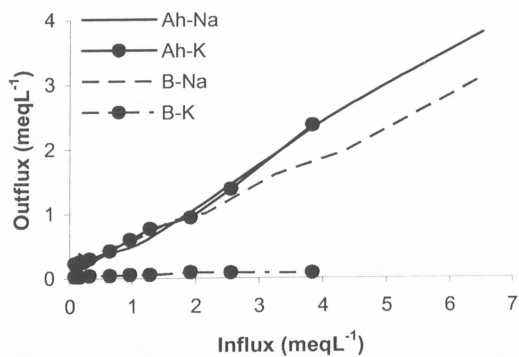


Figure 2. Influx and outflux Na and K concentrations of soil samples from Ah and B horizons.

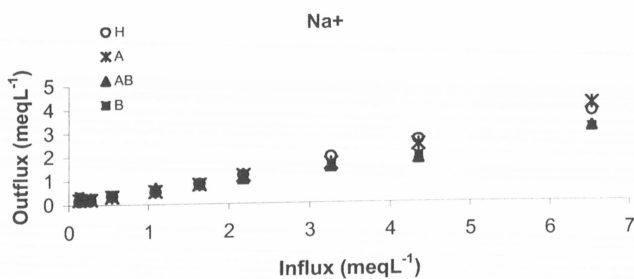


Figure 3. Influx and outflux Na concentrations of soil samples from all horizons under consideration.

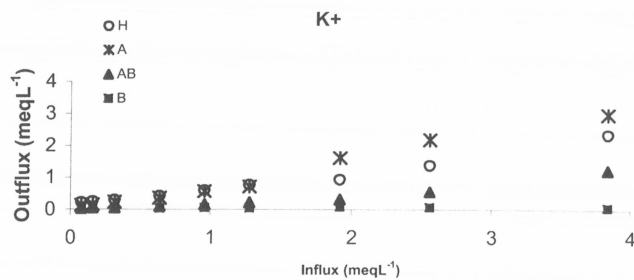


Figure 4. Influx and outflux K concentrations of soil samples from all horizons under consideration.

Lysimeters

The mean values of all measurements throughout the monitoring period are given below (Table 3). One can say at a glance that most ion exchange is occurring in the above 90cm of the soil profile. Electrical conductance an indicator of ionic activity increases shortly after infiltration and starts decreasing somewhere over 90 cm and immobilization starts over this depth. Hydrogen ion also decreases sharply at 20 cm depth which imply the fact that most H⁺ buffering activity has already been taken place in this relatively thin vertical soil column. However, we can still deduce a hydrogen activity below 20 cm looking at the mobilization of cations and slightly increasing soil pH parallel with depth (Table 2). The H⁺ flux also supports the statement that surface runoff does not constitute a significant portion of streamflow. We would measure a higher H⁺ activity in stream water if surface runoff was a significant flow type.

Table 3. Mean ion concentrations of precipitation, soil solution and stream water.

	EC μS cm ⁻¹	H ⁺	PO ₄ ⁻	Fe ²⁺	Fe ³⁺	SO ₄ ²⁻	Mg ²⁺	Al ³⁺	NO ₃ ⁻	K ⁺	Na ⁺
						μeqL ⁻¹					
Precip.	42.80	22.82	74.53	7.17	8.60	108.22	70.78	0.39	32.26	52.69	65.65
20 cm	119.75	0.56	168.24	14.46	12.28	164.48	268.79	69.91	23.23	172.89	231.59
60 cm	124.57	0.29	186.43	11.82	0.00	127.90	243.00	2.00	40.40	176.73	218.84
90 cm	91.78	0.19	84.88	14.29	0.61	206.29	227.17	1.60	30.69	92.07	180.72
Stream	221.17	0.08	109.26	19.35	25.27	155.46	284.77	0.53	43.55	57.54	760.87

Almost all mobilized 3 charged cations are attached again over 60 cm. Hence, it is likely to observe an accumulation layer for these ions above this depth. It is also verified that considerable hydrogen is introduced into the upper soil horizons to detach 3 charged cations. However, the portion of these acidic cations are still far below the basic ones. Other cations carrying one or two charges are more abundant and have more tendencies for leaching. Particularly, Na⁺ shows a huge, more than ten-fold increase in concentration from precipitation to the streamwater. The increase in Mg is also considerable, but K looks very conservative indeed, consistent with the results of syringe experiment. In interpreting above table (Table 3) the concentration effect should be kept in mind. The runoff ratio in the region is around 20 percent (Özyuvacı, 2004) and thus a five times increase in the concentration of an ion would likely be happened in case of no interaction in soil system. Therefore, if the stream concentration of a nutrient is roughly the same as the precipitation than we can definitely assume it as a conservative or biologically demanded ion.

The cation exchange process in the soil should be assessed together with anion activity, because equivalent amount of cation immobilization has actually the same neutralization effect with the equivalent amount of anion mobilization (Pierzyski et al., 2000). Additionally, sulfate and nitrate are known to be one of the main mechanisms of cation leaching. Johnson et al (1999) detected a considerable amount of decrease in cation mobilization due to 50 percent decrease in the exposure of these anions. Anions, particularly SO₄²⁻ is abundant in the upper soil because of higher organic matter content as expected but the sudden increase around 90 cm is a mystery. Nitrate is a more demanded anion biologically and does not seem like very related in cation exchange as SO₄²⁻.

Litter layer removal experiment

The H^+ activities of the soils tend to decrease with depth in the whole soil profile (Table 2), while this situation is reverse in the A horizon (Table 1). Litter layer and Ah horizons have lower H^+ activities. An explanation to this might be the introduction of dry deposited or mineralized (decomposition) base cations to the upper soil system.

0-12 cm represented the Ah while 12-20 cm the rest of the A soil horizon in the figures below (Figure 5, 6). All soil parameters looked similar in the early months of the experiment, while lower soil horizon had more consistent values. The difference between the treated (T) and control (C) plots in this zone was quite stable during the one-year post treatment period.

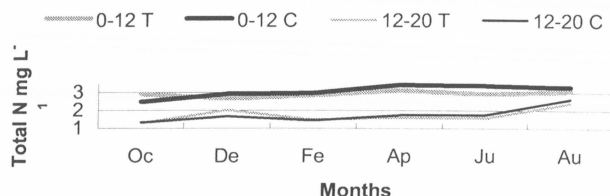


Figure 5. Temporal variation of N in litter removed and control parcels.

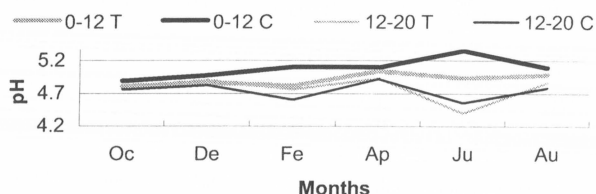


Figure 6. Temporal variation of pH in litter removed and control parcels.

The difference between the C and T plots varied particularly in the vegetation period, but was never statistically significant according to t test ($p > 0.05$). Hydrogen activity started to increase slightly at the upper soil (0-12 cm) possibly related with decreasing N content. The organic matter content of both plots T and C was almost same for the lower horizon (12-20 cm) but different for the above. However, the difference between the organic matter contents of the T and C plots was quite stable. It did not increase in time. EC values were almost similar throughout the experiment not affected from litter removal.

CONCLUSIONS

The soils of the Belgrad Forest neutralizing the acidity of precipitation water more than 100 folds were under investigation with 3 experiments based on system logic. The interpretations of input and output data provided information to some extent about this complicated structure.

The equivalent load of the H^+ entering the forest ecosystems of the region was quite variable in both seasonal and annual scale. It was $4.72 \text{ kmol ha}^{-1}$ in 1999-00 and $1.70 \text{ kmol ha}^{-1}$ in 2000-01 hydrologic years (Serengil, 2003). Considering the other driving mechanisms and factors in nutrient supply (annual precipitation, changes in origin of the pollution etc.), we can easily state that the nutrient input to the Belgrad deciduous forest ecosystems is unpredictable and strongly variable. The stream nutrient concentrations and loads –representing the output– on the other hand are stable and run in narrow up and down limits pointing. As an example pH always stays in 6.5-7.0 band throughout the year.

This regulating mechanism is a total ecosystem process, but the lysimeter study shows that there may still be outstanding compartments. The upper horizons of the soil profile are the responsible of the most

buffering and there is not much remaining to be neutralized below A horizon according to the results. It looks like, just after infiltration, the soil water rises to a higher pH than soil itself, and this goes on until the stream. The stream pH level might be lower if the main flow type was surface runoff. Some Al^+ is mobilized in the upper horizons but no evidence of harm was detected on the trees so far.

The Ah layer having the greatest organic matter content was a detachment horizon of cations. This statement was also verified with the cation retention experiment. The less organic matter the more cation immobilization. However, it can not be generalized to all cations, particularly to Na^+ . It is also proved that if the litter layer was removed for a duration of 1 year, the soil properties would not be affected significantly. Of course this statement might not be true for the erodable slopes.

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ABSTRACTS

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