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INFLUENCE OF ARTIFICIAL ACID RAINS ON THE SOILS OF DIFFERENT MECHANICAL COMPOSITION

Oksana Kovalchuk, Myroslav Malyovanyy, Olena Popovych, Nataliya Vronska

Lviv Polytechnic National University
12, S. Bandery Str., Lviv, 79013, Ukraine

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Abstract. Acid rain influence determination created on the basis of sulfuric, nitric acids and their mixture on the chemical properties of soil substrates of different mechanical composition

Key words: Acid rains, soils, mechanical composition of soil, chemical properties

1. Introduction

Emissions of pollutants into the atmospheric air before precipitation on the surface of the soil are exposed to atmospheric factors, as a result of which they undergo mechanical, physical and chemical transformation. Depending on the reaction of the discarded compounds on the environment activities, the substances as well as the individual components of the environment are exposed to changes.

Biotrophs (except phosphorus) can enter ecosystems, along with environmental pollution. Among the pollutants, the acid-forming substances predominate; first of all SO_2 and NO_x. The influx of these compounds from atmospheric air was initially evaluated solely as a toxic factor that limited the productivity of ecosystems and caused impoverishment of soils [1,2], however, recently researchers have focused on the fertilizing effect of emissions [3].

Soil is the environment that accumulates all components of emissions, which in turn initiate the direction of changes occurring in soil processes. At the same time, the soil is a reservoir of nutrients for plants and microorganisms, therefore, it is necessary to establish the effect of acidification on the quantity and stability of macronutrients in soils.

2. Material and methods

Practically the acid content in atmospheric precipitation is determined solely by strong acids (H_2SO_4 and HNO_3), The described phenomenon leads to the occurrence of acid rains [4]. Hence there is an assumption that by creating aqueous solutions based on strong acids and their mixtures with a certain pH and affecting them to the soils, we obtain an effect close to the acid rains action that occur in the natural environment in the atmospheric air.

The effect of artificial acid rains was studied (providing simultaneous pouring) on three types of soil substrates: sand, clay and peat.

Two-liter capacities with substrate placed under the cover were used for experiments. The aqueous solutions of acids for pouring were prepared in plastic cans by adding the calculated amount of sulfuric and nitric acids and their mixture in a volume ratio of 3: 1. Thus, three different solutions withthe pH value of 2.5, 3.0, 3.5, 4.0, 4.5 and 7.8 (control) were obtained.

The experiment lasted for 3 years. Soil watering was carried out for 10 months with a break for January and February. An assessment of acid rains effect was made by studying chemical changes in soils. Soil studies were performed according to generally accepted analytical methods [6].

Soil experiments are averages of two repetitions of samples, each of which is obtained by mixing the samples from 6 containers.

3. Results and discussion

Separate chemical properties of soils

The chemical composition and content of macroelements are the result of a number of factors, the most important of which are the mineralogical composition of the soil, the ingress of nutrients from the air and groundwater, as well as the intensity of processes in the ecosystem, driven by natural and man-made factors. The latter, first of all, include acid rains, which can significantly accelerate the weathering processes and significantly affect the washing of the upper layers of alkalis, thereby accelerating the process of soils degradation.

Reaction of soils pH

Saturation of substrates with artificial acid rains caused the acidification of soils, whereas in the containers taken for control, the pH was increased (water used for the experiment hadthe pH of 7.8). The results are presented in Table 1.

At the beginning of the experiment, the pH of the sandy soils was 5.9 in H_20 and about 5.0 in KC1, pH of clayey soils contained in the range from 5.5 to 7.5 in H_20 and from 4.6 to 6.9 in KC1; and pH of peat was in the range from 3.2 to 5.4 in water and 2.4 in KC1 to 4.7.

Watering the soil with acidic rains at pH 2.5 over three years resulted in a shift in the pH of the water on the sandy substrate from about 0.2 to 0.8 units, and the pH (KCl) – from 0.4 to 1.4, depending on the type of acidic water solutions made on the basis of sulfuric and nitric acids or their mixtures. This applies to a layer of soil to a depth of 15 cm. Deeper than 15 cm of soil pH is shifted to one unit under the influence of acidic factor on the basis of nitric acid. In soils at depths exceeding 20 cm, no pH changes were recorded regardless of the pH reaction of the aqueous solution.

Soils have undergone the greatest changes in pH under the influence of artificial acid rains, made on the basis of sulfuric and nitric acids mixture. Under the influence of acids solution with pH 2.5 in the soil layer with the thickness of 15 cm, the pH reaction in the aqueous solution was shifted from 0.5 to 1.5 units, while the pH in KC1 – within the range of 1.3 to 1.5 units. At pH 3.0 of acid deposition in a layer of soil up to 15 cm, the change in pH of water were from 0.3 to 1.5 and from 0.3 to 1.1 units in KC1.

At pH 3.5 of acidic aqueous solutions, the soil reaction was shifted by 0.3 units in water and 0.2 – pH (KCl). Acid rains with pH 4.0 caused acidification of sandy soil upper layers (5 cm) by about 0.2 units of pH. Acid solutions with pH 4.0 and 4.5 do not decrease the soil reaction, but in the control version (pH 7.8), on the contrary, pH was displaced to the alkaline side.

Table1

Reaction of pH substrates under the influence of artificial acid sands of various composition

pH of artificial acid rain	Profile depth	Nitric acid			Sulfuric acid			Mixture of sulfuric and nitric acids		
		sand	clay	peat	sand	clay	peat	sand	clay	peat
2.5	0-5	5.7	7.0	3.7	5.1	7.1	4.0	4.9	6.9	5.0
	6-10	5.6	6.7	3.9	5.1	7.0	4.0	4.6	6.0	4.2
	11-20	6.0	5.5	3.5	5.4	5.3	3.0	5.4	5.7	5.8
	21-35	6.2	5.7	3.4	6.1	5.2	2.9	6.1	7.0	5.7
3.0	0-5	6.3	7.3	3.1	6.3	7\.3	3.7	5.6	7.3	3.2
	6-10	6.0	7.5	3.1	6.5	7.2	3.5	4.4	7.2	3.3
	11-20	6.2	6.3	3.2	6.6	6.8	3.5	5.0	6.6	3.4
	21-35	6.8	5.6	3.1	6.9	5.4	3.1	6.6	7.2	5.7
3.5	0-5	6.5	7.4	4.4	6.2	7.3	4.0	6.0	7.5	3.3
	6-10	6.4	7.0	3.7	5.9	6.8	4.1	5.6	7.1	3.5
	11-20	6.7	5.7	3.3	6.0	5.5	3.0	5.6	7.0	3.4
	21-35	6.8	5.1	3.1	6.8	5.5	2.9	7.1	6.8	5.6
4.0	0-5	7.0	7.7	4.4	6.0	7.2	4.9	7.2	7.2	4.4
	6-10	7.0	7.5	4.9	5.7	7.0	4.2	6.1	7.3	3.7
	11-20	6.7	7.1	4.7	6.0	5.4	3.3	5.8	7.0	3.5
	21-35	6.3	5.6	3.5	6.4	5.4	3.1	7.3	6.1	5.5
4.5	0-5	6.5	7.7	4.5	5.3	7.5	4.5	6.5	7.4	4.1
	6-10	6.2	7.5	4.6	5.6	7.4	4.2	6.5	7.4	3.8
	11-20	6.3	6.7	4.5	5.7	5.9	3.4	6.0	7.1	4.3
	21-35	6.1	5.3	3.8	5.6	5.6	3.2	7.1	7.2	6.2
control	0-5	6.6	7.5	5.4	6.6	7.5	5.4	6.6	7.5	5.4
	6-10	6.2	7.5	5.6	6.2	7.5	5.6	6.2	7.5	5.6
	11-20	5.9	5.9	3.3	5.9	5.9	3.3	5.9	5.9	3.3
	21-35	5.9	5.5	3.2	5.9	5.5	3.2	5.9	5.5	3.2

Macro elements content in substrates

In the experiment, the content of individual chemical elements in the soils depended on their initial content and entering with water used for irrigation. The latter influence can be considered to be identical in all variants and insignificant (Table 2). It is accepted that the differences in the contents of the elements ions, present in individual capacities, were the result of the effect of simulated acid rain with different pH.

Table 2

The content of macro elements (%) in soils of different mechanical composition under the influence of artificial acid rains

Depositary type	Type of substrate	pH of artificial acid rain	Na	K	Ca	Mg	Fe	P_2O_5	$N_{\text{заг.}}$	C	C/N
Sulfuric acid solution	sand	2.5	0.025	0.170	0.062	0.054	0.407	7.3	0.129	1.16	8.99
		3.0	0.021	0.180	0.088	0.068	0.370	11.3	0.101	1.29	12.77
		3.5	0.021	0.149	0.094	0.061	0.422	9.3	0.090	0.89	9.67
		4.0	0.019	0.118	0.069	0.055	0.435	9.0	0.056	0.84	15.00
		4.5	0.023	0.099	0.064	0.048	0.344	9.1	0.062	0.82	13.22
		control	0.025	0.099	0.056	0.049	0.377	7.2	0.073	1.16	15.89
	clay	2.5	0.053	0.376	0.255	0.182	0.045	18.7	0.110	1.46	13.27
		3.0	0.047	0.348	0.275	0.167	0.947	22.5	0.112	1.40	12.51
		3.5	0.045	0.360	0.238	0.117	0.828	23.5	0.118	1.39	11.79
		4.0	0.048	0.350	0.218	0.180	1.002	12.2	0.118	1.38	11.69
		4.5	0.048	0.347	0.300	0.176	0.980	15.4	0.157	1.55	9.87
		control	0.044	0.360	0.250	0.172	0.954	14.1	0.134	1.49	11.12
	peat	2.5	0.075	0.052	0.660	0.068	0.216	15.4	1.036	49.89	47.97
		3.0	0.070	0.077	0.965	0.097	0.336	28.8	1.008	35.99	35.38
		3.5	0.080	0.059	0.813	0.091	0.350	19.7	0.966	34.32	35.38
		4.0	0.074	0.068	0.745	0.088	0.360	22.9	0.882	31.36	36.72
		4.5	0.095	0.067	0.808	0.085	0.308	22.8	0.854	32.68	36.27
		control	0.095	0.076	0.952	0.095	0.303	21.3	1.162	32.01	27.54
Nitric acid solution	sand	2.5	0.032	0.193	0.089	0.056	0.360	8.6	0.118	1.22	10.34
		3.0	0.026	0.171	0.078	0.055	0.360	7.6	0.095	1.25	13.15
		3.5	0.026	0.173	0.101	0.055	0.390	9.4	0.090	1.29	14.32
		4.0	0.022	0.117	0.093	0.056	0.420	11.9	0.090	1.17	13.0
		4.5	0.026	0.105	0.079	0.060	0.37	9.8	0.067	1.13	16.87
		control	0.025	0.099	0.056	0.049	0.370	7.2	0.073	1.16	15.89
	clay	2.5	0.050	0.364	0.238	0.182	1.045	15.1	0.118	1.34	11.36
		3.0	0.053	0.384	0.283	0.187	1.080	14.1	0.118	1.19	10.08
		3.5	0.046	0.347	0.228	0.169	0.934	23.6	0.123	1.20	9.76
		4.0	0.050	0.340	0.251	0.170	0.951	15.5	0.129	1.12	8.68
		4.5	0.050	0.347	0.266	0.185	1.007	11.0	0.112	1.01	9.02
		control	0.044	0.360	0.193	0.172	0.954	14.1	0.134	1.49	11.2
	Peat	2.5	0.075	0.054	0.739	0.076	0.248	19.0	1.09	49.78	45.3
		3.0	0.079	0.062	0.749	0.081	0.287	21.0	0.96	36.35	37.6
		3.5	0.097	0.051	0.598	0.075	0.295	18.4	0.74	37.85	51.0
		4.0	0.078	0.068	0.947	0.107	0.406	25.6	0.84	35.66	42.4
		4.5	0.083	0.077	1.129	0.099	0.318	25.3	1.24	31.06	24.9
		control	0.095	0.076	0.952	0.095	0.303	21.1	1.16	32.01	27.5
Solution of a mixture of sulfuric and nitric acids	sand	2.5	0.012	0.039	0.268	0.068	0.272	6.7	0.112	2.28	20.4
		3.0	0.016	0.051	0.273	0.064	0.273	23.1	0.084	1.46	17.4
		3.5	0.015	0.060	0.340	0.076	0.282	20.0	0.112	1.75	15.6
		4.0	0.023	0.067	0.301	0.083	0.320	21.0	0.123	1.47	11.9
		4.5	0.014	0.061	0.281	0.066	0.293	16.2	0.112	2.43	21.6
		control	0.016	0.041	0.385	0.083	0.305	6.2	0.101	2.28	22.6
	clay	2.5	0.027	0.222	0.189	0.186	1.052	8.4	0.112	1.58	14.1
		3.0	0.029	0.199	0.179	0.172	0.980	9.0	0.106	2.38	22.5
		3.5	0.032	0.198	0.153	0.179	1.005	6.9	0.106	1.86	17.5
		4.0	0.026	0.212	0.223	0.192	1.075	5.1	0.123	2.03	16.5
		4.5	0.025	0.195	0.231	0.185	1.038	5.8	0.146	1.93	13.2
		control	0.020	0.2058	0.176	0.181	0.994	9.0	0.118	1.72	14.6
	peat	2.5	0.076	0.033	1.043	0.190	0.408	21.9	0.980	68.73	70.1
		3.0	0.052	0.036	0.909	0.136	0.300	17.5	0.840	64.73	70.1
		3.5	0.053	0.029	0.915	0.306	0.291	18.9	0.896	65.75	76.7
		4.0	0.054	0.034	1.095	0.226	0.331	40.6	0.770	57.91	75.7
		4.5	0.067	0.036	0.804	0.246	0.359	25.0	0.952	72.23	75.9
		control	0.079	0.039	1.060	0.190	0.289	21.6	1.008	69.25	68.7

With the depth of the soil profile the *sodium* content slightly increases. This tendency is especially manifested in sand and peat and is somewhat disturbed by a more linked clay substrate. Of the three types of simulated acid rains, the greatest impact is observed with the application of acids H_2SO_4 and HNO_3 mixture. Differences in the content of Na in soils exposed to solutions of sulfuric and nitric acids are insignificant and significant under the influence of acids H_2S0_4 and $HN0_3$ mixture.

Potassium content decreases with the increase of soil depth under the influence of acid deposition irrespective of acids type. There is a clear correlation between the decrease in soil pH and the acidity of the rains. Under the influence of more acidic solutions, soils showed significantly higher potassium content with alkaline solutions (control). This phenomenon is not observed in clay formations.

Calcium content is formed differently depending on the type of soil and the type of acid deposit. In most cases, higher levels of Ca are found in the upper layers of the soil, which decreases to a depth of 25 cm and subsequently increases again. This phenomenon was most clearly manifested in peat soils, the largest deviations from the described tendency were observed on clay formations.

There was no clear tendency in the distribution of *magnesium* depending on the depth of soil and the influence of the acid factor. A slight increase of the iron content in the upper layers of the investigated soil profile was revealed, but this result is not unambiguous. Fe content in soils under the influence of sulfuric and nitric acid solutions is about 20 % lower than under the influence of their mixture.

The content of *phosphorus* in the soil does not change depending on the pH of the aqueous solutions and the type of acids, but a clear connection between its concentration and the depth of the soil profile is monitored. The smallest content of phosphorus is present in the surface layer of soil (other than treated with a mixture of acids) and the largest in the lowest layer, that is at a depth of about 35 cm. Distribution P_2O_5 in different levels of soil profile is very similar to the distribution of calcium.

As a result of the analysis slight differences are revealed in the content of total *nitrogen* in the soil, depending on the composition of artificial acid rains. The highest nitrogen content is observed in soils with the lowest pH under the influence of the acidic factor on the basis of sulfuric and nitric acids. A similar tendency is observed in soils treated with aqueous solutions based on a mixture of acids, taking into account that the absolute values are somewhat higher.

The *carbon* content is higher in soils treated with aqueous solutions with a lower pH value. This tendency is observed under the influence of acid rains on the basis of sulfuric acid, nitric acid and their mixtures. A more pronounced dynamics is observed for the influence of acids mixture.

Artificial acid rains, like natural sediments, have an effect on the soil. With excess of acid, cations in the soil (Ca, Mg, K, Na) are replaced by anions (protons of H + and cationic acids), which causes a decrease in the saturation with bases. According to the list of Hofmeister, monovalent cations (K, Na) are firstly released in this reaction, then divalent (Mg, Ca, etc.) followed by trivalent (eg. aluminum, etc.) [2]. Protons released during dissociation of acids lead to acidification, if not subjected to the influence of buffer systems [1].

The conducted studies on the level of acidity at 4 levels of depth showed the change in the pH reactions in the range of 0.5–1.0 unit on sand formations, which were sprinkled with acidic rains with the pH of 2.5 to 3.0. While acid rains with the pH higher than 3.5 not in all cases caused the change in the acidity of soils. Previously, similar results were obtained [4]. Soils pH indicators and number of macro elements indicate that during 3 years of the experiment, a clear acidification of soils and changes in the amount of the studied substances occurred only in the upper layers (from 0 to 10 cm) of sandy soils and peat and in a layer from 0 to 5 cm of clay.

The results of lysimetric studies [5] showed an increase in the washout of metal cations by acidic rains. The degree of washout increased significantly with a decrease in the pH of acid rains. This is especially true for calcium. As for the washout of other components, the results of the experiment did not give unambiguous indicators. From this work it appears that the majority of sulfur, which was added in the form of H_2S0_4, was left in the lysimeters. At the same time, the calcium washout increased by 25 %, the content of dissolved compounds significantly increased in water.

Slightly acid rains caused less leaking effects in very acidic soils than in weakly acidic or neutral soils. Changes in the amounts of Ca, Mg, K at different pH values may indicate that the bigger are the relative values for the washout, the smaller is the saturation of these soils and the lower the exchange capacity of cations. This phenomenon is observed in natural conditions (in forests), but the duration of the experiment was not enough to allow such significant changes in the investigated capacities.

The soil profile tends to reduce the amount of phosphorus. This is confirmed by the results of research [7]. In the soil profile, there was a declining tendency in the amount of calcium and zinc, increasing – as to the content of magnesium, manganese, iron and potassium, which coincides with the results of the studies [3, 4].

A small amount of NO_3 is detected in the infiltrate of sandy-clay soils [7]. The author emphasizes that along with mineralization the washout is very insignificant in the deeper and superficial layers of the soil profile. These processes are quite limited in acidic soils. In the presence of aluminum and heavy metals, the washout is limited even more [5]. Certain authors [3,4] note that nitrogen mineralization and NH4-N availability in soils with high nitrogen content are low.

4. Conclusion

• Irrespective of the type of acid rains during 3 years of research, the reaction of the pH of soils upper layers has shifted from 0.2 to 0.8 units in the acidic direction;

• The type of acidic effect is not essential for acidification increasing of soils;

• Significant acidification of soils is observed at depths of up to 20 cm during 3 years of research. No visible changes in the soil reaction are observed below this level;

• Nitrogen content in soils increases with the increase of artificial acid rains acidity, the carbon content increases with pH decrease;

• The content of sodium and calcium increases with depth, and especially – when applying mixture of sulfuric and nitric acids for pouring;

• There was no marked effect of the increasing acidification of soils on calcium content.

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