ATMOSPHERIC DEPOSITION EFFECTS ON AGRICULTURAL SOIL ACIDIFICATION STATE – KEY STUDY: KRUPANJ MUNICIPALITY

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Abstract: Acidification, as a form of soil degradation is a process that leads to permanent reduction in the quality of soil as the most important natural resource. The process of soil acidification, which in the first place implies a reduction in soil pH, can be caused by natural processes, but also considerably accelerated by the anthropogenic influence of excessive S and N emissions, uncontrolled deforestation, and intensive agricultural processes. Critical loads, i.e. the upper limit of harmful depositions (primarily of S and N) which will not cause damages to the ecosystem, were determined in Europe under the auspices of the Executive Committee of the CLRTAP in 1980. These values represent the basic indicators of ecosystem stability to the process of acidification. This paper defines the status of acidification for the period up to 2100 in relation to the long term critical and target loading of soil with S and N on the territory of Krupanj municipality by applying the VSD model. The Inverse Distance Weighting (IDW) geostatistic module was used as the interpolation method. Land management, particularly in areas susceptible to acidification, needs to be focused on well-balanced agriculture and use of crops/seedlings to achieve the optimum land use and sustainable productivity for the projected 100-year period.

INTRODUCTION

Soil acidification, as well as various degrees of soil sensitivity to acidification, depend on wet and dry sulphur, nitrogen, and carbon dioxide depositions [2], increased precipitation, geological base – parent rock [1], soil properties (current acidity, base saturation, cation-exchange capacity, soil texture, organic matter content), land use and vegetation [11]. Soil acidification as a form of soil degradation can cause major problems in environmental quality [9].

Convention on Long-range Transboundary Air Pollution has addressed some of the major environmental problems through scientific collaboration and policy negotiation. The LRTAP Convention uses critical loads of sulphur and nitrogen as indicators of natural ecosystem sensitivity to acidification and eutrophication [14]. These loads are used to define the limit values of S and N depositions at which terrestrial ecosystems remain stable in the long run. As such, these values represent the basis for planning, monitoring and reduction of acid pollutants.

Besides soil erosion, soil organic carbon (SOC) depletion, nutrient depletion and compaction, acidification is the main indicator of soil degradation [9]. Soil acidification is an important trigger for the release of iron, aluminium, calcium, magnesium and heavy metals to soil solutions. Soluble heavy metal compounds pose danger to plants and water [3]. The process of soil acidification can be considered as the main cause of reduced productivity of agricultural land. Soil acidification has recently been considerably accelerated by anthropogenic factors, primarily including increased emissions and depositions of acid pollutants, as well as the application of physiological acid fertilizers.

Therefore, reduced quality and productivity of agricultural soils represent one of the limiting factors to an increase in agricultural production in Krupanj municipality.

This paper uses a very simple dynamic soil acidification model (VSD) and the method of soil classification by soil sensitivity to acidification to show spatial distribution of various levels of sensitivity of the agricultural soil in Krupanj municipality to acidification. This spatial distribution was presented in correlation with soil properties, type of land use and acid deposition trends. The distribution of defined acidification statuses by chosen criteria will point to the areas and soil types with the highest risk of degradation and loss of productivity for the projected periods of 50 and 100 years.

Identification of the areas sensitive to acidification provides opportunities for land management by choosing the optimum land use method aimed at the achievement of sustainable productivity in the designed period.

STUDY AREA

Krupanj municipality covers an area of 366.75 km². The largest areas are covered by plough land used for corn and wheat production at lower altitudes, and oat and potato crops at higher altitudes. Large areas are covered by plum orchards, raspberry and blackberry fields and orchards of cherry and other fruit. Considerable areas are covered by established meadows and pastures. The highest income per unit area is achieved by farming and fruit growing.

Earlier researches conducted in the area of Krupanj municipality revealed the following percentages of soil categories: neutral and alkaline soil accounted for 16.7%; weak acid reaction in the soil was measured in 17.3 % of the samples, whereas acid reaction was measured in 15.7% of the samples. A highly acid reaction was found in 39.9% of the samples, whereas 18.6% of the samples had an extremely acid reaction. Hence, it can be concluded that the soils with an acid reaction dominate in the area of Krupanj municipality (Fig. 2).

Acid Deposition Sampling
The information on acid deposition inputs of SO_x, NO_x and NH_4 are collected in certain periods within the national network, and the data are available in the data base of the
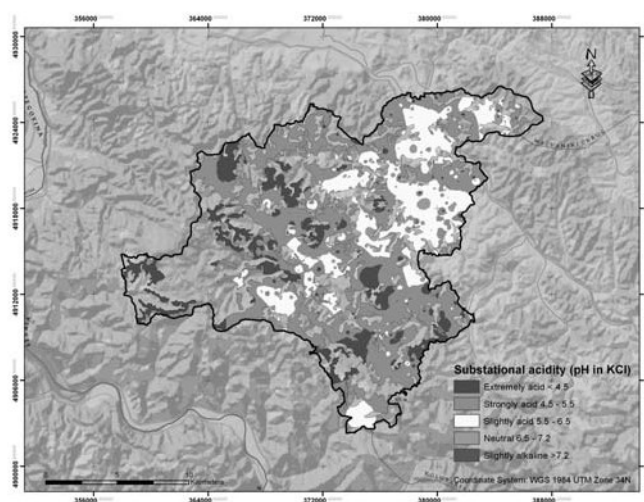
Fig. 1. Study Area

Fig. 2. Soil acidity ranking according pH in KCl

Republic Hydrometheorlogical Service of Serbia. Samples of depositions were obtained on a daily basis, by bulk method, using a collector and a polyethylen receiver located 1.5 m above the soil. The data measured for the period 1985–2007 in the Valjevo GMS station were used as reference data. Analytical procedures used for the analysis of bulk precipitation are: pH – value – potentiometry, conductivity – Conductimetry at 25°C, sulphate, nitrate, chloride – Ion chromatography, NH_4 – spectrophotometric method, as well as Na, K, Mg and Ca – AAS Flame method.

Soil Sampling and Analysis

Soil samples from the area of Krupanj municipality were taken during three years: 2006, 2007 and 2008 in the period from September to November. Soil sampling was performed at different depths ranging from 0 to 25 cm in 173 sites using exact coordinates. After sampling, the soil was air dried and ground to 2 mm.

Soil pH was determined with a glass electrode pH meter in a 1:2.5 water solution. Total N, and C in the soil were measured by an elemental CNS analyser, Vario model EL III [13].

Cation-exchange capacity (CEC) was determined by Kappen method.

Hydrolytic acidity values were determined by Kappen method, the alkali titration of 1:2.5 soil:Ca-acetate (pH=8.2) suspension after one hour shaking.

Base saturation (BS) was calculated using equation:

$$BS = S/CEC*100 \ [\%]$$

where: BS – base saturation, S – sum of base cations and CEC – cation-exchange capacity

Particle size distribution was determined by sieving and sedimentation [7].

Soil Sensitivity to Acidification (Kuylenstierna Method, 2001)

CEC and BS are key soil properties in the process of acidity neutralization according to the method of soil classification on the basis of sensitivity to the process of acidification [8]. Five classes of soil sensitivity to acidification from I (very sensitive) to V (poorly sensitive) were defined on the basis of 3 CEC categories and 5 BS categories (Table 1).

Table 1. Criteria for determining soil sensitivity to acidification (*Kuylenstierna,* 2001)

		CEC (cmol/kg) at field pH		
		< 10	10–25	> 25
Base Saturation (%)	0–20	I	I	II
	20–40	I	II	III
	40–60	II	III	IV
	60–80	III	IV	V
	80–100	V	V	V

Very Simple Dynamic model (VSDStudio 3.5., Alttera, 2001–2011, CCE)

The analysis of the process of acidification using the VSD model involves maximum critical loads of sulphur and nitrogen depositions in the ecosystem, the time of appearance of the first damages in relation to the chosen criterion during the process of deposition,

deposition reduction and ecosystem recovery time [15, 16, 18]. The VSD model is based on SMB equations, which is elaborated in detail in the literature [15]. The charge balance links all ions considered in the VSD model:

$$[H^+] + [Bc^{2+}] + [Na^+] + [Al^{3+}] = [SO_4^{2-}] + [NO_3^-] + [Cl^-] + [HCO_3^-] + [Org]$$
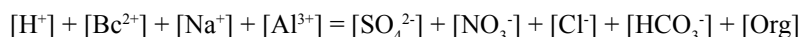
Where sum of Ca, Mg and K asumed as a single ion, Bc = Ca + Mg + K, and Na denotes sodium, SO_4 sulphate, NO_3 nitrate, Cl chloride and Org the sum of organic anions. All concentrations are expressed in moles of charge (equivalents), i.e. the ion molar concentration multiplied by its charge [15].

One of the main factors of future soil productivity and its sensitivity to the process of acidification are the quantities of acid depositions. The VSD model was used to estimate critical and target loads of S and N. These loads enable the lower limit of soil productivity for the existing agricultural crops, as well as the effects of current and future depositions to acidification status and soil productivity for the projected periods of 50 and 100 years.

Input data for the VSD model are obtained from the measurements taken at the soil depth of 20 cm. In this soil layer, the change of acidic depositions has the most prominent impact on the process of soil acidification.

The choice of a chemical criterion and its critical border values depend on the receptor/biological indicator (whether the root system of a certain plant species is sensitive to aluminium content or pH value for the particular land use) and the particular soil type for which the estimate is made.

Acidity-Soil pH is the mainly recommended criterion for organic soils, whereas the chemical criteria of $(Ca:Al)_{crit}$ or $(BC:Al)_{crit}$ [4] are recommended for mineral soils. Soil acidity (pH) is a multifunctional variable which influences the availability of nutritive elements (Ca^{2+}, Mg^{2+}, K^+, PO_4^{3-} i MoO^{2-}), toxicity (concentration) of certain metals (Al, Fe, Mn...) and the flow of biotic and abiotic processes in soil.

Hettelinig et al. [5] defined pH 4.0 as a representative point for maintaining the functions of forest ecosystem, whereas Sverdrup [10] points out that mechanisms of nutrient absorption by plants do not function below this pH level. The pH value of 4.2 was used as the critical value in order to protect both terrestrial ecosystems and surface and ground waters [4].

Mrvić et al. [12] argue that aluminium toxicity in the root system is manifested at pH 5.0, since large concentrations of exchangeable aluminium ion are suddenly released into the soil. The lower acidity limit of soil solution that enables the lower limit of the productivity of agricultural plantations for the majority of plants in the study area (potato, oath, berry fruit, cherries, pastures and meadows) is also at pH 5.0.

Geostatistical Analysis

On the basis of the CLC (CORINE Land Cover) database collected by Landsat 7 satellite monitoring, the municipality was divided into forest and non-forest areas. This means that only agricultural and potentially agricultural lands were taken into consideration in the data analysis.

The IDW (Inverse Distance Weighting) method was used for data interpolation. The IDW method is based on the assumption that values are more similar to each other in

closer areas than in the ones that are farther away. That way, by means of interpolation, the values are assigned to areas which were not sampled and they actually represent mere average values of the available sets of data.

RESULTS AND DISCUSSION

Soil Acidity Ranking in the Study Area

Areas of agricultural soil belonging to different acidity classes (Fig. 3) were defined on the basis of measured pH values of the sampled soils and their interpolation. Table 2 shows main VSD soil chemical input parameters by acidity classes that affects soil acidification process. The largest area is covered by strongly acidic soils – 45.95% of the total area and moderately acidic soils – 39.24 % of the total area, which accounts for 85.19% of the study area (Table 3). Soil acidity in these areas ranges from 5.0 to 6.0, which potentially makes these soils the most sensitive to acidification due to their low buffer capacity. This is especially true for the soils whose pH value ranges from 5.5 to 6.5 and whose cation exchange capacity is low (Table 2) [6]. Due to their carbonate – bicarbonate buffering system, soils with a 6.5 pH value and higher, as well as soils with 3.5–5.5 pH, tend to be well buffered as a result of the well-buffered hydrolysis reaction of aluminum [6]. Therefore, they are less sensitive to the process of acidification.

Table 2. Main VSD soil chemical input parameters according pH class

		pH ranges			
		< 5.0	**5.0–5.5**	**5.5–6.0**	**> 6.0**
number of samples		44	39	40	50
CEC (cmol/kg)	range	11.59–36.12	12.22–96.5	9.70–33.41	11.25–97.61
	x	22.93	24.31	20.88	30.02
	sd	5.33	12.84	5.11	15.55
BS (%)	range	9.81–91.90	13.87–98.48	20.87–94.32	21.63–99.15
	x	38.62	47.40	58.27	78.81
	sd	23.82	21.50	19.29	16.27
%C	range	0.05–0.62	2.91–3.19	3.21–3.47	3.49–4.64
	x	2.82	2.95	3.26	3.96
	sd	0.07	0.08	0.08	0.28
N	range	0.05–0.62	0.09–0.51	0.08–0.53	0.05–0.54
	x	0.24	0.24	0.24	0.28
	sd	0.11	0.11	0.13	0.14

x – mean value
sd – standard deviation
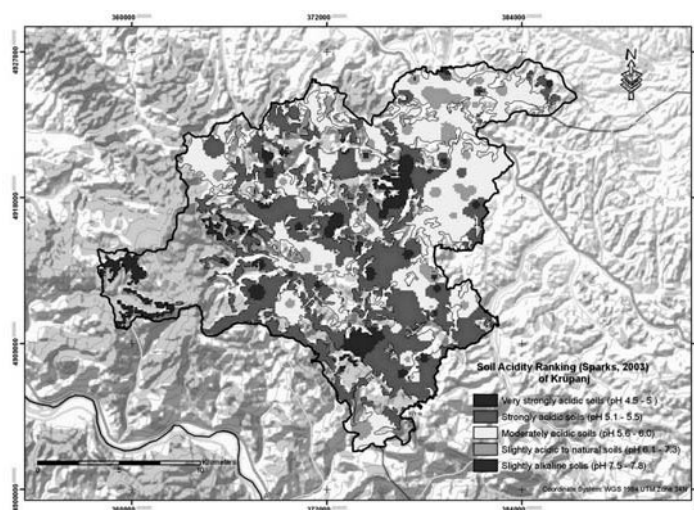CEC – cation-exchange capacity
BS – base saturation

Fig. 3. Soil acidity ranking

Table 3. Soil acidity classes

Soil Acidity Classes	Area (km²)	Area (%)
Very strongly acidic soil (II class)	19.93	9.02
Strongly acidic soil (III class)	101.45	45.95
Moderately acidic soil (IV class)	86.65	39.24
Slightly acidic to neutral soils (V class)	12.52	5.67
Slightly alkaline soils (VI class)	0.26	0.12
Total	220.80	100.00

Soil Sensitivity to Acid Deposition

Buffering capacity, i.e. acid-neutralizing capacity of soils, is primarily predetermined by CEC and BS. Classes of soil sensitivity to acidification are defined on the basis of three CEC classes and five BS classes (Table 4).

According to the obtained results, the most common soils are those with low sensitivity to acidification. These soils cover 58% of the agricultural area, whereas 17% of the area is covered by soils from the very low sensitivity class. On the basis of these data, it can be concluded that soils covering 73% of the area are not endangered by acidification. However, the soils with low pH values (pH <5.0) and low CEC values (9–15 cmol/kg[1] for the study area) are characterized by low productivity [6], even though they have a low level of sensitivity to acidification.
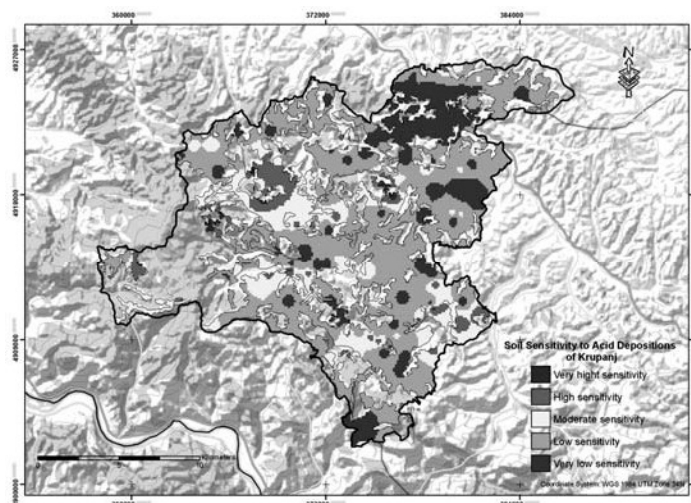
Fig 4. Soil sensitivity to acid depositions

Table 4. Soil sensitivity class to acid depositions

Soil Sensitivity Ranking	Area (km²)	Area (%)
Very high sensitivity (I class)	1.16	0.52
High sensitivity (II class)	12.10	5.48
Moderate sensitivity (III class)	41.20	18.66
Low sensitivity (IV class)	128.29	58.10
Very low sensitivity (V class)	38.05	17.23
Total	220.80	100.00

Soil Acidity Status – VSD Predictions

The highest values of S depositions were recorded in 1985, after which they started to decline (Fig. 5), and since 1990 acid depositions have not exceeded the critical values which enable the lower limit of productivity in agricultural soil. Apart from acid depositions, increased calcium depositions (average value of 0.15 eq/m²/year) were measured in these localities. These increased Ca depositions considerably boost buffer capacity of the soil and its tolerance to acid depositions and the very process of acidification.

Excessive acid depositions do not immediately disrupt the chemical criterion of the soil. The timing of the appearance of negative effects on the ecosystem caused by excessive acid depositions, i.e. a delayed reaction of soil to acid depositions (DDT) depends on the buffering capacity of the soil, and primarily on the cation exchange capacity (CEC). Negative effects can be manifested only after several decades. Also, the reduction in acid depositions to the level below the critical value does not imply safety of the ecosystem, and it sometimes takes decades for the soil to return to a stable state, which is called recovery delay time (RDT) [16].
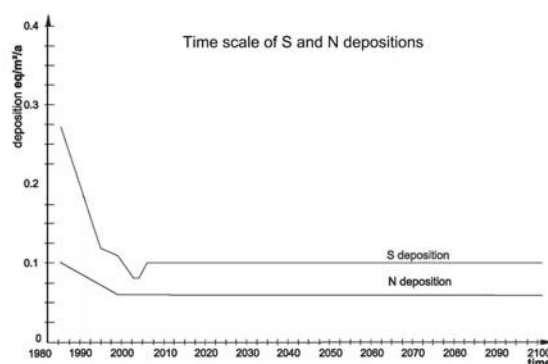
Fig. 5. Time scale of S and N depositions

Recovery Delay Time (RDT) implies that deposition is below the critical load but chemical and biological criteria are still violated. At this time recovery has not yet occurred. The time delay between achieving non-exceedance of critical loads and non-violation of criteria is referred to as the 'Recovery Delay Time' (RDT).

The first simulation was performed in order to determine whether the soils are capable of maintaining the measured pH values in the period from 2050 to 2100 with the current deposition trend and land use. We assumed that total (current and future) values of mineral and organic fertilizers added to the agricultural land would be absorbed by plants. Therefore, the measured pH value of the soil was used as a criterion, and its critical value (in the first case) for estimating the status of acidification.

The simulation of the process of acidification shows that the transgression of critical depositions is present in 38% of the localities with the measured pH values of the soil that exceed 5.6. Therefore, a further reduction in pH values is expected in these soils, according to the current trend of acid depositions. According to the above, stabilization of the pH value at a level above 5.6 cannot be expected in these soils in the period until 2100. This confirms that the soils with pH >5.5 are more sensitive to the loss of bases, because of the higher ability of acid ions to push out exchangeable bases [19], than in the case of soils characterized by pH values of 4.6<pH<5.5. Stabilization of soil pH in the interval from 4.6 to 5.5 could be expected on 46% of the localities until 2100 (RDT), i.e. on 14% of the localities until 2050, on 32% of the localities in the period from 2050 to 2100 and on 13% of the localities after 2100. Negative changes are not expected in only 3% of the samples.

The second simulation is concerned with the impact of current and expected depositions, according to the protocol on expected depositions, on the primary function of agricultural soils, i.e. its productivity. The critical pH value of 5.0 was defined as the key chemical criterion in the estimation of sensitivity to acidification and sustainable agricultural production in the area of Krupanj municipality.

The results obtained show that no transgression of the critical pH value of 5.0 is expected compared to the current trend of depositions, i.e. that the analysed agroecosystems are mainly in the recovery phase. In the period until 2100, stabilization of the pH value at 5 or higher is expected in these soils.

Productivity of the studied soils for the period until 2100 is expected on 99.9% (Table 5) of the areas as follows: in the period up to 2050 in 37.3% of the area, and in the period from 2050 to 2100 in 61.92% of the area. Only 0.72% of the area is already stable and only in this area recovery can be considered to have happened (Table 5).
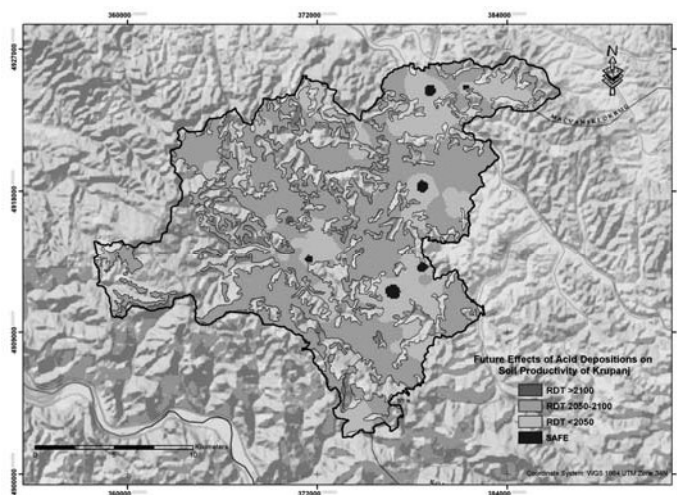

Fig. 6. Potential effects of acid depositions on soil productivity

Table 5. Potential Effects of Acid Depositions on Soil Productivity

	Area (km²)	Area (%)
Recovery Delay Time > 2100	0.15	0.07
Recovery Delay Time 2050–2100	136.71	61.92
Recovery Delay Time < 2050	82.36	37.3
SAFE	1.58	0.72
Total	220.8	100

CONCLUSION

Since the 1990s, acid depositions have not exceeded critical values, which means that all studied soils are going through the phase of recovery. If the current trend of acid depositions in the study area continues, it is estimated that:
- the soils with pH >6 and soils poorly sensitive to acidification will have stabilized by 2050,

- the soils with 5.0–6.0 pH values and the soils whose sensitivity to acidification is very low to moderate will have a longer recovery time period, i.e. from 2050 to 2100.

Even though stabilization of the pH value is expected in the study area on the basis of the current trend of depositions, it should be noted that the predicted period is very long on the one hand, and on the other that the increase in pH value is necessary for achieving the optimization of crop yield, especially in the case of crops such as wheat and corn (pH>5.5). Consequently, it can be concluded that it is necessary to carefully manage the agricultural land in Krupanj municipality for the purpose of sustainable production by applying amelioration in order to increase soil pH.

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