

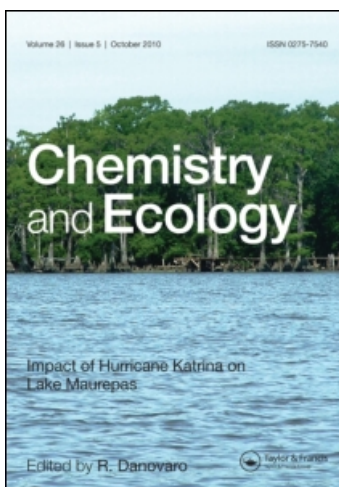
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## The effect of long-term fertilisation on arylsulphatase activity and sulphates (VI) content in a lessive soil

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The objective of this study was to evaluate effects of long-term mineral–organic fertilisation on the dynamics of arylsulphatase (EC 3.1.6.1) activity, the enzyme taking part in the mineralisation of sulphur compounds in soil. The soil under study was sampled in 2001–2004 three times over the vegetation period, at the beginning, in the middle and just before harvest. Plants were cultivated in the crop rotation: potato, winter wheat, spring barley and maize. The split-plot experiment was carried out as a two-factor one (fertilisation with cattle farmyard manure in five doses and fertilisation with mineral nitrogen in four doses). Samples were analysed for carbon of organic compounds, total nitrogen and pH in KCl, according to commonly used methods. Arylsulphatase activity was assayed according to Tabatabai and Bremner, and sulphates as described by Bardsley–Lancaster and modified by COMN-IUNG. Sulphur was abundant in this soil, and therefore the plants should be well supplied with this element. The highest arylsulphatase activity and sulphates (VI) content were found in the case of fertilisation with  $60 \text{ t} \cdot \text{ha}^{-1}$  farmyard manure. Significant correlations were noted between the parameters under study.

**Keywords:** arylsulphatase activity; fertilisation; organic carbon; pH; sulphates (VI); soil

### 1. Introduction

In soils, sulphur occurs mainly as organic compounds. Usually its total amount in the inorganic fraction (sulphates and sulphites) ranges from 6 to 14% [1]. A large part of the organic sulphur in soil (25.3–93.1%) is composed of esters containing sulphur [2]. It has been assumed that this is the most active and labile form of sulphur in soils. Hydrolysis of sulphate esters proceeds via cleavage of the O–S bond by the enzyme arylsulphatase [3,4]. Biochemical release of  $\text{S-SO}_4^{2-}$  from soluble and insoluble sulphate esters is controlled in soils by the content of organic sulphate esters, their amount adsorbed onto soil clay minerals, and the activity and persistence of extracellular sulphatases [5].

Sulphur deficits have been observed in the soils of western Europe since the 1980s [6]. Investigations carried out in Poland have also shown considerable sulphur deficits in soils and plants [7]. A growing number of studies reporting such a phenomenon in ecosystems in western and eastern Europe led to sulphur being treated as a nutrient crucial for plants. As a consequence, knowledge of sulphate (VI) concentrations, both in deficit and surplus, has become important,

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particularly due to the high dynamics of this form of sulphur in soils. For this reason, evaluation of seasonal changes in the content of this macroelement and the activity of arylsulphatase, the enzyme taking part in sulphur transformations in soils, especially over many years, has become increasingly interesting and important. The objective of this study was to evaluate the effects of long-term mineral–organic fertilisation on the dynamics of arylsulphatase (EC 3.1. 6.1) activity participating in the mineralisation of soil sulphur compounds.

## 2. Materials and methods

Soil samples were collected from a long-term static field experiment carried out from 1980 by the Department of Plant Nutrition of the Institute of Soil Science and Cultivation in Pulawy. The experiment is located at the Agricultural Experimental Station at Grabowo, Vistula. The geographical location of the site is 51°21'8" latitude and 21°40'8" longitude. It is characterised by a lowland mild climate with an average yearly temperature of 7.5 °C and average multiyear precipitation of 606 mm. According to the FAO classification, the soils of the Grabowo Agricultural Station are Albic Luvisols from sand. Crop rotation included potato, winter wheat, spring barley, maize. The split-plot experiment was carried out with two factors: factor I was fertilisation with cattle farmyard manure (FYM) at doses of 0, 20, 40, 60 and 80 t · ha<sup>-1</sup>; and factor II was fertilisation with mineral nitrogen as ammonium nitrate (34% N) at doses of N<sub>0</sub>, N<sub>1</sub>, N<sub>2</sub> and N<sub>3</sub>, where N<sub>2</sub> and N<sub>3</sub> are multiplications of dose N<sub>1</sub>. The doses N<sub>1</sub> in kg N · ha<sup>-1</sup> amounted 45 kg under potato and maize, and 40 kg under winter wheat and spring barley. Phosphorus and potassium fertilisers were used in the same way throughout the experiment (24 kg P · ha<sup>-1</sup> under potato and maize, 25 kg P · ha<sup>-1</sup> under spring barley and 21 kg P · ha<sup>-1</sup> under winter wheat; 70.5 kg K · ha<sup>-1</sup> under spring barley, 60 kg K · ha<sup>-1</sup> under winter wheat, 100 kg K · ha<sup>-1</sup> under potato and 133 K · ha<sup>-1</sup> kg under maize). The experiment was carried out in a split-plot system with four replications on the 8 × 5 m (40 m<sup>2</sup>) plots. The width of the paths between the plots was 1 m. All tillage measures were carried out according to commonly accepted methods.

Soil was sampled in four experimental years (2001–2004) three times over the plant vegetation period (beginning, middle and before harvest). Samples were prepared prior to measurement and then analysed for total organic carbon (TOC), total nitrogen (TN) and pH in 1 M KCl, according to commonly used methods. Arylsulphatase activity was assayed as described by Tabatabai and Bremner [8], and sulphates were assayed as described by Bardsley–Lancaster and modified by COMN-IUNG [9].

Multi-replication digital data from the analyses of soil material collected in 2001–2004 were evaluated by statistical procedures. Variation analysis suitable for multifold, tree-factorial experiments carried out in the split-plot system was undertaken. The analysis was carried out in the mixed model. FYM doses were assumed as the first factor, and the doses of mineral nitrogen and dates of soil sampling were treated as the second and third factors, respectively. The concentrations of carbon of organic compounds and total nitrogen collected every year were evaluated as a multifold two-factorial experiment with a randomised sub-blocks system (split-plot). Similarly, manure and mineral nitrogen doses were assumed as the first and second factors, respectively. Data were analysed for treatment effects by analysis of variance (ANOVA), then Tukey's test at  $p < 0.05$  was applied. The analysis was carried out using Statistica for Windows software.

## 3. Results and discussion

SOM, and the biological and biochemical products of its transformation, are crucial for the whole set of properties that identify the fertility and productivity of a soil. FYM plays an important role in

regulating the concentrations of soil solutions. It both protects germinating plants and developing hairy roots from the unfavourable influence of highly concentrated soil solutions and limits losses caused by the leaching of nutrients. Over the four years of the experiments, the concentration of organic carbon (TOC) in the soil under study ranged from 6.13 to 10.0 g · kg<sup>-1</sup>, depending upon the FYM dose and fertilisation with nitrogen (Table 1). The highest increase in TOC was found for objects with FYM doses of 60 and 80 t · ha<sup>-1</sup>. Samples collected from the treatment without FYM contained 23% less TOC than samples from the treatment with the highest FYM dose. Fertilisation with nitrogen affected TOC and TN. The concentration of carbon in the soil was highest at higher levels of nitrogen fertilisation (N<sub>2</sub> and N<sub>3</sub>). The results corroborated the findings of Böhme and Böhme [10], who reported a beneficial role for FYM in overall soil fertility and found that it is particularly active when applied jointly with mineral fertilisers. TOC and TN changed in particular years. The highest average concentration of both parameters in the brown podzolic soil under study was noted in 2002 (cultivation of winter wheat), whereas the lowest TOC was found in 2001 (cultivation of potato) and the lowest TN in 2004 (cultivation of maize) (Figure 1). pH values measured in 1 M KCl in the experimental years were in the ranges: 5.8–6.2, 6.3–6.8, 6.0–6.4 and 5.8–6.2, in 2001, 2002, 2003 and 2004, respectively. Reaction values of the analysed soil samples fitted exactly with the conditions considered optimum for arylsulphatase activity (5.5–6.2) [8].

The sulphates (VI) content in the soil samples over the four experimental years ranged from 9.20 to 38.76 mg · kg<sup>-1</sup> (Figure 2). A majority of Polish soil used for agricultural purposes contains sulphate concentrations of <25 mg · kg<sup>-1</sup> soil. The highest percentage of soils (~70% of the agricultural land) show concentrations fluctuating between 5.0 and 20.0 mg · kg<sup>-1</sup> soil [11]. The average S-SO<sub>4</sub><sup>2-</sup> content in soil samples taken from the Grabowo experiment over four years was 19.33 mg · kg<sup>-1</sup> (Table 1), according to the abundance of S-SO<sub>4</sub><sup>2-</sup> in soils, this is a high S content and secures a sufficient supply to plants [11]. An increase in sulphates was observed in the soil under study, along with increasing doses of FYM and ammonium nitrate (Table 1). The highest concentration of S-SO<sub>4</sub><sup>2-</sup> (22.17 mg · S-SO<sub>4</sub><sup>2-</sup> · kg<sup>-1</sup>) was recorded in soil samples collected from plots fertilised with the highest doses of FYM and mineral nitrogen. By contrast, the opposite tendency (15.29 mg · S-SO<sub>4</sub><sup>2-</sup> · kg<sup>-1</sup>) was noted in the case of a plot not fertilised with natural fertiliser and ammonium nitrate with the dose N<sub>2</sub> (Table 1). The highest concentration of S-SO<sub>4</sub><sup>2-</sup> was recorded in soil samples collected under winter wheat (Figure 2). No effect was seen for the time of sampling.

The activity of the enzyme under study in the period 2001–2004 in the analysed soil fluctuated between 0.004 and 0.386 μM pNP · g<sup>-1</sup> · h<sup>-1</sup> (Figure 2). Fertilisation with FYM affected the activity of this enzyme (Table 1). The highest value (0.337 μM pNP · g<sup>-1</sup> · h<sup>-1</sup>) was found for soil samples collected from the object fertilised with 60 t FYM · ha<sup>-1</sup>, but without nitrogen fertiliser. Dick et al. [12] also found a considerable increase in the activity of arylsulphatase and other enzymes after fertilisation of soil with FYM. No effect of nitrogen fertilisation or sampling time was detected. The use of nitrogen fertiliser caused a gradual decrease in arylsulphatase activity in the soil under study, compared with the non-fertilised plot. In the latter case, the enzyme was the most active (mean 0.265 μM pNP · g<sup>-1</sup> · h<sup>-1</sup>) (Table 1). These changes were clear, but still not statistically significant. The results indicated an inhibitory effect of ammonium nitrate on arylsulphatase activity. A negative influence of some ions (NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>) on soil enzymatic activity has been observed previously [4,5,12]. Whalen and Warman [13] were of the opinion that some of the ions inhibiting enzyme activity are removed from the soil by plants and microorganisms as components necessary for their growth and development.

The highest arylsulphatase activity was observed in soil samples collected under the cultivation of winter wheat (2002) (Figure 2). Decreases in arylsulphatase activity, and in sulphur, TOC and TN concentrations were noted in 2003 (Figure 1). It can be speculated that this situation was

Table 1. The content of total organic carbon, total nitrogen, sulphate sulphur (VI) and arylsulphatase activity in soil under study (mean of years and time of sampling).

FYM t · ha <sup>-1</sup> (I factor)	Total organic carbon g · kg <sup>-1</sup>					Total nitrogen g · kg <sup>-1</sup>					S-SO <sub>4</sub> <sup>2-</sup> mg · kg <sup>-1</sup>					Arylsulphatase μM pNP g · soil <sup>-1</sup> · h <sup>-1</sup>				
	Nitrogen fertilisation (II factor)																			
	N <sub>0</sub>	N <sub>1</sub>	N <sub>2</sub>	N <sub>3</sub>	Mean	N <sub>0</sub>	N <sub>1</sub>	N <sub>2</sub>	N <sub>3</sub>	Mean	N <sub>0</sub>	N <sub>1</sub>	N <sub>2</sub>	N <sub>3</sub>	Mean	N <sub>0</sub>	N <sub>1</sub>	N <sub>2</sub>	N <sub>3</sub>	Mean
0	6.13	6.75	7.53	7.40	6.95	0.738	0.774	0.802	0.813	0.782	15.75	15.34	15.29	16.81	15.80	0.175	0.153	0.194	0.182	0.176
20	6.89	7.56	8.35	8.60	7.85	0.578	0.606	0.602	0.628	0.604	17.95	18.35	18.50	19.00	18.45	0.243	0.249	0.205	0.214	0.228
40	7.36	8.06	8.97	8.81	8.31	0.845	0.880	0.876	0.907	0.877	18.87	19.07	19.36	20.32	19.40	0.262	0.212	0.211	0.198	0.220
60	8.07	8.34	9.16	8.74	8.58	0.879	0.912	0.941	0.940	0.918	21.03	21.67	21.88	21.52	21.52	0.337	0.314	0.298	0.282	0.307
80	7.85	8.57	10.0	9.16	8.90	0.886	0.922	0.955	0.984	0.937	21.24	20.22	22.17	22.29	21.48	0.308	0.278	0.283	0.281	0.287
Mean	7.27	7.85	8.81	8.54	8.12	0.785	0.819	0.835	0.854	0.823	18.97	18.93	19.44	19.99	19.33	0.265	0.241	0.238	0.231	0.244
HDS <sub>0.05</sub> I			0.690					n.s.					4.241					0.073		
II			0.683					0.026					0.931					n.s.		

Note: FYM, farmyard manure; n.s., not significant.

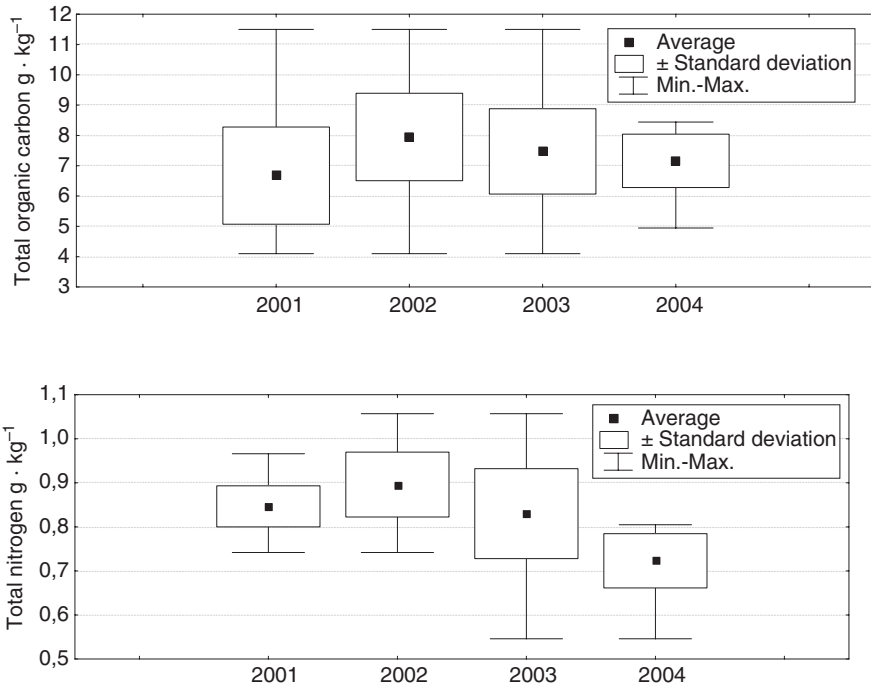


Figure 1. Total organic and total nitrogen content in soil under study (2001–2004).

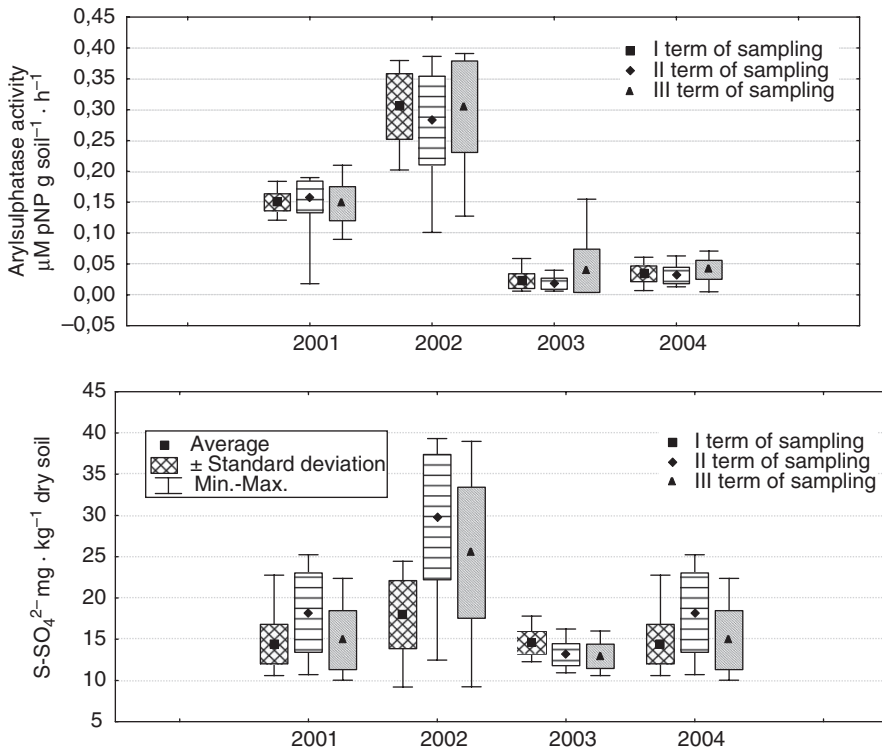


Figure 2. Arylsulphatase activity and sulphate content in the soil under study (2001–2004).

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caused by the cultivated plants reversing the direction of organic matter transformations. Average arylsulphatase activities were higher in fallow soil than in soils under barley and rape [14].

Significant correlations were found in the years of the study for the relationship between the activity of the investigated enzyme and concentrations of sulphates ( $r_{p=0.05} = 0.61$ ), organic carbon ( $r_{p=0.05} = 0.29$ ) and total nitrogen ( $r_{p=0.05} = 0.50$ ). Depending on the type of soil, some authors reported positive Pearson indexes for the activity of this enzyme and sulphur concentration in soil [15]. It has been also found that arylsulphatase is positively related to soil organic C content [16].

#### 4. Conclusions

The Albic soil under study revealed a high concentration of sulphur. Therefore, the experimental plants in the crop rotation should have enough of this bioelement for their growth and development.

The highest arylsulphatase activity and concentrations of sulphate sulphur (VI) were observed in the case of fertilisation with FYM at a dose of  $60 \text{ t} \cdot \text{ha}^{-1}$ .

The calculated correlation coefficients between arylsulphatase activity and concentrations of sulphate sulphur, as well as those found for the relationship between organic carbon and total nitrogen contents, confirmed a close inter-relationship among these parameters.

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