The humate preparations application were tested in the several field trials (A-introduction in soil, B-treatment of seeds before sowing, C-treatment of sowing)

In the laboratory experiment with Helrigel Mixture huminate promoted the benzoxazinones formation in the vegetative mass of the barley. It led to 20% decreasing of the atrazine content in the seedlings. The peat humates and the vermicompost products introduction into the soil took down the negative atrazine aftereffect on the barley growth and atrazine accumulation in the barley grain.

In particular the biohumus and preliminary processed poultry dung that had been incorporated into the soil provided the barley yield rising on the 12-27%. Atrazine content in barley grain decreased from 0.054mg/kg to the trace after fertilizers application. It was shown also biohumus took off atrazine oppression of soil biological activity and promoted the improving some enzymes activity

The humic substances impact on barley growth in the soil plots polluted with heavy metals was studied in the field trials. Combination of two trials (A+B) for humic substance application led to increasing of the barley bioproductivity as a rule.

Humates were studied also as antidotes in the field experiment on the joint herbicide 2.4D and heavy metals artificial pollution background.

In particular 2.4 D aftereffect led to reduction of barley productivity up to 35.6%. More positive impact on barley growth was fixed for B Humates trial. At the same time humate extracted from brown coal had highest protection effect from heavy metals pollution as huminate substance source for using in the B variant. The radionuclides accumulation in the barley grain has decreased due to humate application in the dose 0.25 $tonha^{-1}$.

The comparison of the obtained results shows that the introduction of the humic substances with other amendments provides an increasing for the soil buffer capacity in case of industrial inorganic pollutants. It was shown also that humic fertilizesrs and vermicompost are more available remediation amendments regarding to ordinary fertilizers. Thus model experiments showed distinct detoxication effectiveness of soil depending on dose, soil buffering, and kinds of humic amendments.

## Detoxifying effects of humic acids on acetochlor: structure-activity relationship

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Acetochlor is used on a large scale in USA and European countries as a weed-control agent. Being a persistence herbicide, acetochlor can be accumulated in soil resulting in pollution and damage of the environments. Humic substances as the major moiety of natural organic matter control detoxification of acetochlor in soil. That is why the use of preparations

of humic acids (HA) for detoxification of acetochlor is very promising in terms of soil remediation. HA can be obtained from different natural sources like soil, peat, coal etc. In this investigation the detoxifying activity of HA from soil, peat and coal on acetochlor has been compared.

HA (19 samples) were obtained from different soils (3 sod-podzolic soils (Umbric Podzols), 2 gray forest soils (Gray-Luvic Phaeozems), 2 chernozems (Chernic Chernozems)), peats (4 highland peat and 2 lowland peat samples) and 6 samples of charcoal. Detoxifying effects of HA were measured with the bioassay technique using the germination energy of barley seeds as a response. The experiments have been carried out under the following conditions: acetochlor concentration was 100 mg/L; HA concentration varied from 5 to 150 mg/L; exposure time was 24 h; duration of the experiment was 72 h. Barley seeds were exposed to the solution under study (distilled water as a control, solution of acetochlor, solution of HA of different concentrations and solutions containing constant concentration of acetochlor and different concentrations of HA) for 24-hour exposure time. Then the solutions were poured off; the seeds were put into the Petri dishes between wet layers of filter paper, and subjected to germination at the temperature of 20°C. The seeds germination energy was determined on the third day and estimated as the percent of germinated seeds. So, the herbicide effect of acetochlor, the stimulating activity of HA, and the detoxifying activity of HA have been evaluated. To estimate detoxifying effects of HA, the detoxifying constants of acetochlor binding to humic acids ($K_{OC}^{D}$) were calculated as described in Perminova et al [1]. The $K_{OC}^{D}$ is analogous to the binding constant $K_{OC}$ which is widely used to characterize interaction between natural organic matter and different ecotoxicants.

The obtained values $K_{OC}^{D}$ for the HA samples were in the range of $(11.6\text{-}117.2)\times10^{3}$ L/kg OC. HA samples used in the study could be put in the following ascending order according to $K_{OC}^{D}$ values: soil HA ≈ peat HA < coal HA. For the soil HA the following sequence was observed: Umbric Albeluvisols HA < Albic Luvisols HA < Chernozem HA.

The statistical data treatment for the sets of HA properties (elemental composition, molecular weight, and data of 13C NMR spectroscopy) and HA detoxifying effects has revealed the correlation between $K_{OC}^{D}$ values and HA properties such as H/C ratio ($r = -0.70$) and $C_{Ar}$ ($r = 0.81$). Thus, one can conclude that detoxifying ability of HA towards acetochlor increased along with on increasing aromaticity of HA.

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