IHSS, 3-8 July, 1994, St. Augustine, Trinidad. Ref. by S. M. Griffiths, M. B. Hayes, M. C. Thomas Ref. 2.

1024.

HUMIC SUBSTANCES AS NATURAL DETOXICANTS

Perminova, I.V., Lebedeva, G.F., Kovalevskiy, D.V., Kulikova, N.A, Philippova, O.I., Danchenko, N.N. and M.V. Lomonosov. *Moscow State University, Department of Chemistry, 119899, Moscow, RUSSIA.*

The role of humic acids - a major constituent of natural organic matter - in mediating biological activity (toxicity, bioaccumulation, uptake) of different chemicals released into the environment is still poorly understood. While they are usually prescribed by exposing mitigating impact on the biological activity both of heavy metals and organic chemicals, the opposite observations are reported as well: Given ubiquity and abundance of these substances in the environment, two main problems can be considered as follows: It is necessary to develop principles of quantitative estimation of the impact of humic acids on biological activity of main classes of harmful chemicals released into the environment (heavy metals, herbicides, petroleum and chlorinated hydrocarbons). The fact that biological activity of the chemicals change greatly in the natural surroundings and can be hardly be approximated by the forecasts of model experiments conducted in distilled water or pure sandy media, can not be skipped any longer. Expanded studies on interactions of the chemicals with natural organic matter - main factor altering biological activity of ecotoxicants in the environment - can improve the existing system of "maximum permissible levels" followed by much more realistic predictions of danger from the released chemicals. The other aspect of the problem under consideration, which can bring investigations on potential detoxifying properties of humic acids directly in the field of practical agricultural research is related to the existence of large natural resources of humic substances, such as peat and sapropel (lake bottom sediments) and a well developed industry of both humic fertilizers and biostimulators production. Under conditions of proved detoxifying impact of peat humic acids and, moreover, known specific activity to certain chemicals depending on the kind of peat they were extracted from, motivated the use of peat and other humics-enriched materials as detoxicants for soil media can be developed. Also information about "affinity" between characterized peat humic acid and certain kinds of chemicals can be used for the follow up research on directed synthesis of specific detoxifying agents on the basis of peat humics. The results presented below can serve as an initial step in approaching the discussed field. In the presented research different humics-containing materials were checked on their ability to mediate biological activity of such ecotoxicants as heavy metals and herbicides. Taking into consideration the priorities of these contaminants for natural environments, experiments with heavy metals were conducted in aqueous media and with herbicides in soil media. Purified isolated samples of riverine, marine, soils and peat humic acids were used for the experiments in aqueous media, where in natural conditions these substances comprise from 60 to 90% of the total dissolved organic matter. The toxicity of the three most dangerous heavy metals in water ecosystems - cadmium, copper and lead - was registered in the presence of humic acids of different origin as listed above. As a biotarget green algae *Chlorella vulgaris* was used as a test function, photosynthetic activity, determined by the fluorimetric method. For the soil media, different humic acid containing materials of natural (peat, sapropel) as well as artificial (hydrohumate and oxyhumate - peat hydrolysates, commercially available biostimulators) origin were used for the field experiments aimed to elucidate the impact of these materials on the toxicity of modern super herbicide - Glean - representative of sulfonyl-ureas. As a biotarget corn was chosen, and biological response was registered by comparing biomasses of the

plants grown on contaminated soil both in the presence and absence of humics-enriched materials. For the estimation of detoxifying ability of the tested humic substances we introduced a parameter "percentage of detoxification" which was calculated by the developed formula: $D = [1 - R_d/R_d \times (R_d - R_{d+t})/(R_o - R_t)] \times 100$, where D - per cent of detoxification; R - biological response for free algae - photosynthetic activity, for corn plants - dry biomass; R_o- biological response registered in the control experiments - tested medium without either toxicant (heavy metals or Glean) or detoxicant (humics materials); R_d - biological response in the presence of detoxicant; R_t - biological response in the presence of toxicant; R_{d+t} - biological response in the presence of both detoxicant and toxicant in the same tested medium. Use of the given formula allows us to evaluate a pure detoxification effect, the effect of additional fertilisation caused by inducing of humic materials, into the tested media is eliminated by the given technique of calculation. The results of the experiments conducted in aqueous media contaminated with heavy metals showed that in the presence of humic acids toxic impact on algae is greatly reduced. This general trend is valid for all four kinds of tested humic acids. However, while the detoxification efficiency of peat, soil and riverine humic acids are very close one to another, marine humic acids stands out, exposing much weaker detoxification impact on Cu, as well as Cd. This can be explained by the structural peculiarities of marine humic acids, which are characterised by the predominance of aliphatic, structural units followed by the reduction in the chelating ability of these substances, in comparison with such highly aromatic structures as peat, soil or fresh water humics. The conclusion which can be drawn from these results is that the marine environment can be considered as much more vulnerable to the toxic impact of heavy metal contamination than fresh water or soil ecosystems. It means that at the same level of pollution the ecological consequences for the marine environment can be much more severe. This fact demonstrates that the existence of the same maximum permissible levels of heavy metals for fresh water and marine eco-systems is illogical in terms of the real danger which these contaminants poses to the environment. Results of toxicological experiments in soil media also showed that all of the tested humic-enriched materials possessed detoxificating ability in relation to herbicide Glean, which was on the same level or higher than that of activated charcoal. However, the results are much more scattered than for the above discussed set of experiments, apparently reflecting the influence of not only humic components of these materials but of the other factors as well. Nonetheless, the conclusion can be made that humic-containing materials can be used as effective detoxicants for agricultural needs, but extensive research is needed on the selectivity and efficiency of their action on different groups of the contaminants.