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The Fate of Anthropogenic Organic Pollutants in Soil: Adsorption/Desorption of Pesticides Possessing Endocrine Disruptor Activity by Natural Organic Matter (Humic Substances)

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Introduction and Objectives

The purpose of this presentation is to firstly provide a general survey on the various phenomena that anthropogenic organic pollutants of various nature and origin are subjected in soils and on the specific role exerted by humic substances on these processes. The presentation will then focus on adsorption/desorption of two important classes of organic pollutants, that are some representative pesticides possessing endocrine disruptor activity and some properly active endocrine disruptor compounds (EDCs), onto soil humic acids (HAs) that are the most chemically and biochemically active fractions of humic substances and natural soil organic matter.

General Part

Organic pollutants can reach the soil either by purpose, such as pesticides and other agricultural chemicals, or incidentally through a variety of materials commonly used in agricultural practices, e.g., fertilizers and amendments. Once on the soil surface, the organic pollutant can be partially photodecomposed and/or volatilized, and partially enter the soil or be transported to surface aquatic bodies by runoff and/or erosion. When in the soil, the pollutant can be subjected to partial or total chemical decomposition and/or biodegradation. The original pollutant and, possibly, its breakdown products may be adsorbed to soil organic and inorganic constituents, uptaken by plant roots, and/or leached through the unsaturated zone eventually reaching the groundwater. All these processes are controlled by several factors including the physical and chemical properties of the pollutant and its breakdown products, the nature and thickness of the soil, the amount of water applied to the soil, and the type and extent of interactions between the pollutant and soil components.

EDCs are hormone-like substances that are able to interact with the development and functioning of endocrine systems in wildlife and humans by causing alteration, i.e., disruption, of their normal endocrine functions. Compounds proven or suspected to act as EDCs include natural and synthetic estrogens of human origin, several agricultural products such as pesticides, various industrial chemicals, and several products and byproducts of the paper, paint, plastic and pharmaceutical industries. These compounds may enter the soil through current agricultural practices and/or disposal of urban and industrial effluents, sludges and wastes. The response of soil to the estrogenic risk of endocrine disruptors is generally related to their distribution and speciation in the various soil phases, in which adsorption processes play a very important role. Depending on the strength and extent of interactions of EDCs with soil phases, they can either accumulate in the top soil layer or be

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moved down to deeper soil horizons and groundwater. Adsorption/desorption of EDCs onto soil HAs is generally considered one of the most important processes that controls EDCs behavior, performances, and fate in soil, including mobility, transport, accumulation, bioavailability and toxicity, and the assessment of the potential environmental hazard associated with EDCs. Thus, the evaluation of the kinetics and extent of adsorption/desorption processes of EDCs onto/from HAs in different soil horizons is very important to understanding EDCs behavior, performances, and fate in soil, and assessing the potential environmental hazard associated with them.

Experimental part

The pesticides possessing endocrine disruptor activity considered in this work are: atrazine, alachlor and *cis-* and *trans*-chlordane; and the proper EDCs are: bisphenol A (BPA), octylphenol (OP), 17-alpha-ethynilestradiol (EED) and 17-beta-estradiol (17ED). The HA samples used for experiments with pesticides and EDCs were isolated, according to conventional standard procedures: from the surface layer (0-30 cm) of five reference Eurosoils of the first generation (a Vertic Cambisol E1, an Orthic Rendzina E2, a Dystric Cambisol E3, an Orthic Luvisol E4, an Orthic Podzol E5), an alluvial soil (AS), two loamy carbonatic Terra Rossa soils (SO1, SO2) and two sandy soils (UK1, PO1), and the surface (depth 0-30 cm) and deep (depth 30-90 cm) horizons of two sandy soils (P30 and G30, and P90 and G90, respectively). Adsorption kinetics and adsorption/desorption isotherms and coefficients of each pesticide and EDC onto each HA sample were determined using the slurry-type (batch equilibrium) method and the HPLC technique with various detectors, with the exception of *cis-* and *trans*-chlordane that were analysed after preliminary solid phase extraction (SPE) and subsequent GC using an electron capture detector (ECD). Experimental data were fitted in linear and nonlinear, Freundlich and Langmuir equations. The distribution coefficient, K_d, was also calculated from available data.

Results and Discussion

Adsorption of EDCs onto all HAs examined occurs in two phases, a rapid one in the first few hours of contact, which corresponds to more than 90% of total adsorption, and a slow one that needs generally less than 24 h to be completed. Experimental adsorption data were best fitted in a linear isotherm for alachlor, Langmuir isotherm for BPA and 17ED, in a nonlinear Freundlich isotherm, S-shaped for *cis-* and *trans*-chlordane and L-shaped for EED, and either in a linear or a nonlinear, L-shaped Freundlich isotherm for atrazine and OP. Thus, no limiting adsorption is observed for all pesticides and EDCs onto HAs examined over the concentration range tested, with the exception of BPA and 17ED for which a maximum adsorption, i.e., saturation, is reached. In general, the values of the Freundlich constant, K, and of the distribution coefficient, K_d, calculated from the experimental isotherms do not follow the same trend for pesticides, but follow the same trend for EED and OP, which is: HA-G30 > HA-P30 > HA-P90 $\geq$ HA-G90. In general, the adsorption capacity of HAs for chlordane is much larger than that for atrazine and alachlor, which are adsorbed at almost the same extent by HAs. Further, the adsorption capacity for EDCs of HAs from surface horizon soils is much larger than that of HAs from deep horizon soils. The extent of adsorption of

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BPA onto HAs is generally smaller than that of the other three EDCs which are adsorbed at almost the same extent. Adsorption of EED and, especially, BPA onto HAs is generally reversible, and desorption occurs quickly and almost completely after few desorption steps. On the contrary, adsorption of OP is mostly irreversible, a partial desorption occurs slowly, and high amounts of OP are retained by most HAs at the end of the experiment.

Conclusions

In conclusion, the HAs examined in this work are able to adsorb variable amounts of pesticides possessing endocrine disruptor activity and EDCs that tend to accumulate in the soil surface horizon. The EDCs that are desorbed quickly and completely from HAs are expected to move easily down the soil profile, and possibly contaminate groundwater. On the contrary, the EDCs desorbed slowly and only partially are expected to remain mostly adsorbed by HAs, especially on the surface soil layer, with corresponding soil contamination but protection of groundwater. The carboxylic and phenolic hydroxyl group content, the organic free radical concentration, and the aromaticity and humification degrees appear to be the most important chemical properties of HAs affecting atrazine adsorption, whereas it is not clear which compositional, structural and functional features of HAs may affect adsorption of alachlor, chlordane and EDCs.

Keywords: Organic pollutants; pesticides; organic matter.