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# Contemporary Aspects of Soil Eco-Chemistry and Geochemistry in Bulgaria

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## Abstract

The paper focuses on the main aspects of contemporary soil eco-chemistry in Bulgaria. The issues tackled refer to: (i) analysis of chemical species, including contaminants; (ii) prediction of metal bioavailability and exposure to plants of chemical species in soil. A stress is made on pilot studies concerning organic geochemical markers, their analysis and quantification in soils (Fluvisols, Vertisols, Luvisols, Arenosols). A new aspect of soil eco-chemistry is related with analysis of compounds in water-soluble dissolved organic carbon in soil as molecular indicators of environmental change.

**Key words:** soil eco-chemistry, geochemistry, heavy metals, lipids, molecular markers

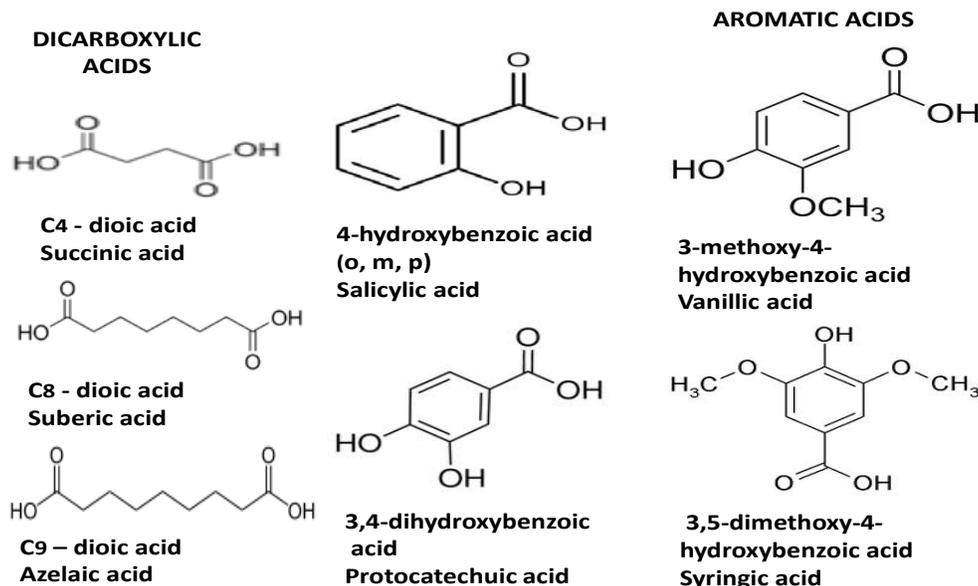
## Introduction

In the early years of soil science, soil chemistry was concerned with agricultural and pedogenetic aspects of soil science, and with chemical characteristics of soil as affected by the mineralogical composition, soil organic matter and environmental factors. With the growing urbanization and industrialization of society, soil chemistry evolved into soil eco-chemistry and “environmental soil chemistry” (Sparks, 2002). Soil eco-chemistry studies the origin, transport, behavior, fate and environmental risk of chemical species in soil and their interaction, including living organisms. It developed as emerging discipline at the intersection of ecology and chemistry of soils. The main aspects of soil eco-chemistry are related with (i) analysis of chemical species, including contaminants; (ii) transport and transformation depending on the soil environment; (iii) ecological and eco-toxicological effects and risk assessment of chemical species; (iv) monitoring of chemical pollutants in the soil-water-plants ecosystems; (v) prediction and modeling the fate and exposure to chemical pollutants; (vi) pollution control. When a contaminant (metallic or organic) is exposed to the soil environment it is subjected to abiotic chemical and/or physico-chemical, but also microbially mediated reactions which may increase or decrease the compound’s mobility and bioavailability. These are adsorption/desorption, precipitation, dissolution, complexation and oxidation/reduction reactions.

Assessing the active species of a contaminant in solution will make it possible to predict its fate and toxicity and develop scientifically sound and cost-effective remediation strategies.

### **State-of-the-art and recent advances**

Soil eco-chemistry in Bulgaria has been concerned with basic physico-chemical phenomena: ion-exchange in soils, clays and clay minerals (Arsova, 1998; Atanassova, 1995a,b; Atanassova & Ilieva 2003, Ganev, 1990; Taneva et al. 2010a,b), adsorption/desorption reactions of heavy metals and points of zero charge of soil adsorbents (Atanassova, 1995a; Atanassova 1999; Atanassova and Okazaki, 1997; Atanassova and Benkova, 2013; Atanassova & Simeonova, 2013; Ganev et al., 1993; Jokova, 2005; Jokova et al. 2011), “pools“ of metals in soils (Bacon and Dinev, 2005; Benkova et al., 2005; Chuljian and Hinov, 1976; Dinev, 2012; Faitondjiev and Hinov, 1980), mobility, bioavailability/complexation (Atanassova, 2003; Atanassova and Damyanova 2003a,b; Dinev et al. 2011; Dinev, 2012; Doichinova et al., 2014; Nenova et al., 2015; Raychev et al. 2001; Tsoleva et al. 2014). The chemistry of soil solution, the physico-chemical properties of the soil adsorbent, pH, ionic strength and metal speciation in solution affect the mobility, bioavailability and eco-toxicological effects of metals and their sorption to soil particles. Benkova & Atanassova (2015) investigated amelioration of soil acidity in Cu, Zn and Pb contaminated soils around metalliferous industrial plants in Bulgaria, using organo-mineral mixtures containing lime, phosphorite-glaucanite, peat, coal and Fe hydroxides. The organo-mineral amendments were effective in increasing the biomass yields and decreasing >70% (Zn) and > 90 % (Cu and Pb) metal solution concentration, as compared to the control variants. However, no significant differences in metals uptake among treated soils and control soils could be discerned, because the major species of Cu, Zn and Pb in the pH range of 5,7 – 7,4 were organic complexes with dissolved organic carbon (DOC) leading to a lack of correlation between solution/plant concentrations. The organic compounds present in the DOC fraction of soils are ligands for complex formation with metals in solution (Fig. 1). These low-molecular-weight organic acids have been identified in the total ion chromatograms of dichloromethane (DCM) fractions of hot-water-soluble extracts in soils (Atanassova et al. 2014, Atanassova & Doerr, 2014, 2015).



**Figure 1.** Low-molecular-weight organic compounds identified in hot-water-soluble extracts of soils (incl. water repellent).

The geochemical molecular markers are organic compounds *which preserve the signature of their sources and undergo insignificant structural changes during the process of their transport through the geosorbent*. These compounds possess different time of residence, stability, transportation and behavior in relation to their chemical properties and sources (Azevedo, et al., 2002; Yunker et al., 1999). Organic molecular markers are sensitive indicators of ecosystem properties and are related to specific sources of soil organic matter and type of anthropogenic contamination. Through organic marker analysis valuable information on sources in a complex multifunctional system of diverse anthropogenic influences, as well as implications on the transport and fate of these compounds, can be achieved. Molecular markers in organic geochemistry can be subdivided into three major groups as outlined by Eganhouse (1997), namely: (i) contemporary biogenic markers; (ii) fossil biomarkers, and (iii) anthropogenic markers. The first group of markers are compounds that are cellular constituents synthesized by microorganisms and/or vascular plants. Examples are phospholipids, aromatic acids and phospholipid ester bound fatty acids, alkanes, alcohols, chlorophyll and carotenoid containing pigments, high molecular weight terpenoids, etc. The second group consists of compounds detected in fossil fuels and coal deposits formed as a result of thermal alteration of biogenic compounds in a buried biomass deep into the Earth. Some of these compounds, e.g. alkanes, steranes, polycyclic aromatic hydrocarbons resemble in chemical structure the organic compounds synthesized by plants, bacteria and algae. The third group comprises compounds that result from human inputs, e.g. fecal sterols, coprostanol, synthetic surfactants and those directly

related to industrial activity, e.g. contaminant assemblages such as polychlorinated biphenyls, polycyclic aromatic hydrocarbons (PAH), chlorinated pesticides, etc. Some PAHs such as naphthalene, perylene and phenanthrene can be detected in tree species and termites (Wilcke, 2000). Thiele and Brummer (2002) find biosynthesis of 3-, 4- cyclic PAH following incubation of fresh plant residues with soil in a reducing environment under abiotic conditions. Other authors also report biogenesis of naphthalene, phenanthrene and benzo(g,h,i)perylene in oxygen-deficient soil environment (Atanassova & Bruemmer, 2004; Guggenberger et al., 1996; Wilcke et al., 1999). The fate and persistence of organic pollutants is a subject of numerous studies (Barracough et al., 2005, Gevaio et al., 2000, Pan et al., 2008). Although organic compounds are gradually degraded and their concentration decreases with time, there is hardly a situation of permanent soil clean-up, due to formation of “bound residues”, therefore the widely popular term “persistent organic pollutants” (POPs).

It has been found that only part of the organic compounds extracted by an organic solvent is bioavailable (Luthy et al., 1997). The transport and lability of organic compounds, including pollutants is governed by the following processes: (i) leaching with water flow; (ii) volatilization; (iii) chemical reactions, involving photolysis, hydrolysis, oxidation and reaction with soil organic and inorganic surfaces; (iv) biotic losses including mineralization by microbial action, and (v) soil adsorption. For hydrophobic organic compounds, many of which are classified as “persistent organic pollutants”, it has been found that labile forms diminish with time at the expense of tightly bound forms “bound residues” (Jones et al., 1996). According to Lanno (2003), “bioavailability” is a value of the potential of a chemical compound to enter into a biological receptor. The first stage has a physico-chemical trigger and includes adsorption/desorption and diffusion, controlled by the properties of the sorbent and the sorbate, i.e. specific soil parameters, e.g. hydrophobicity, solubility,  $pK_a$ , cation exchange capacity, pH, clay and organic matter content. The second stage is physiologically triggered and is controlled by the characteristics of the biological species.

Most of the hydrocarbons have biogenic origin and it's considered that anthropogenic activity actually does not “introduce” hydrocarbons as a new class of compounds into the environment, but has caused their accumulation, and therefore deleterious effects as, e.g. in the case of oil spills (Harayama et al., 1999). A range of organic compounds, some of which anthropogenic markers induce soil water repellency, e.g. in soils irrigated with treated sewage effluent (Wallach et al. 2005). The classes of organic compounds considered to relate to soil water repellency are alkanes, fatty acids, fatty acid esters, fatty alcohols, sterols and more complex organic compounds (Atanassova & Doerr, 2010; Morley et al., 2005). Recently Mataix-Solera et al. (2011) found that the use of low-quality wastewater for disposal purposes, followed by six years of ‘recovery’ with no irrigation, on a calcareous sandy soil (Xerofluent) under a *Populus alba* tree stand, led to soil water repellency development. Accelerated solvent extraction of these soils with dichloromethane revealed alkanolic acids ( $C_{16}$  -  $C_{20}$ ), n-alkanols ( $C_{22}$

- C<sub>28</sub>), steroids of plant and animal origin, and anthropogenic markers, alkylamines and quaternary alkyl ammonium salts (Fig. 2) exhibiting higher concentrations in the water repellent soils in the furrows, as compared to the control non-repellent soils (Fig. 3).

Water repellency appears to have developed where a specific threshold for compound concentration has been exceeded (e.g. n-alkanols ~C<sub>26</sub>; alkanolic acids C<sub>18-24</sub>) or for other specific waste water derived compounds, such as sterols ( $\beta$ -sitosterol), cholesterol derivatives, alkylammonium salts or fatty amines/or heterocyclic aromatic compounds (derivatives).

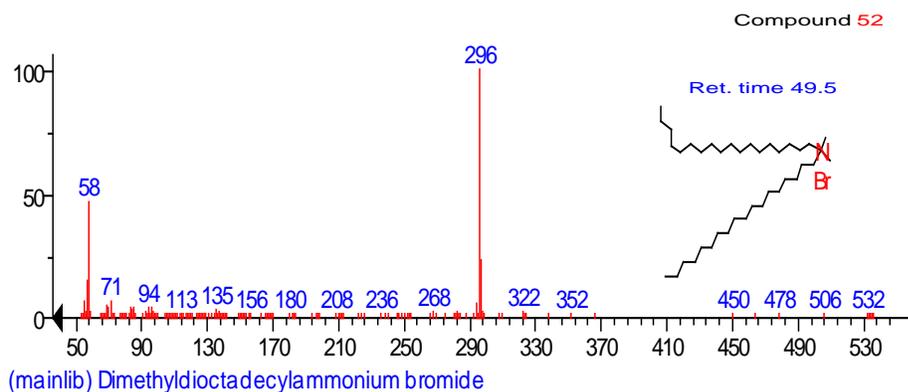
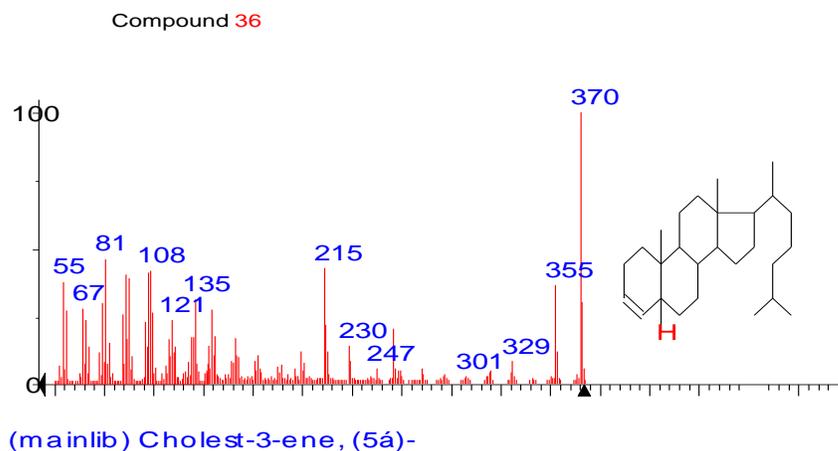
The necessity to make a quantitative assessment of the labile pool of organic carbon in soils arises from changes in the global carbon cycle in response to climate change (Schlesinger and Andrews, 2000), and is of major importance in determining the increase of carbon emissions as a result of anthropogenic activities and global warming. The degree of transformation and mineralization of soil organic matter is a function of climate, vegetation, soil mineral composition, land topography and time. It's considered that temperature is a major trigger determining the cycle of soil organic matter (SOM), especially the rapidly transforming organic fraction (Trumbore, 1997). The climate change effects on the labile fraction of SOM have not been studied in detail (Franzluebbers et al., 2001). Unravelling the feedback effect to climate change is particularly difficult, because of a range of diverse soil organic compounds exhibiting different decomposition kinetics and the presence of environmental constraints which obscure the intrinsic temperature sensitivity of substrate decomposition (Davidson and Janssens, 2006; Schmidt et al. (2011).

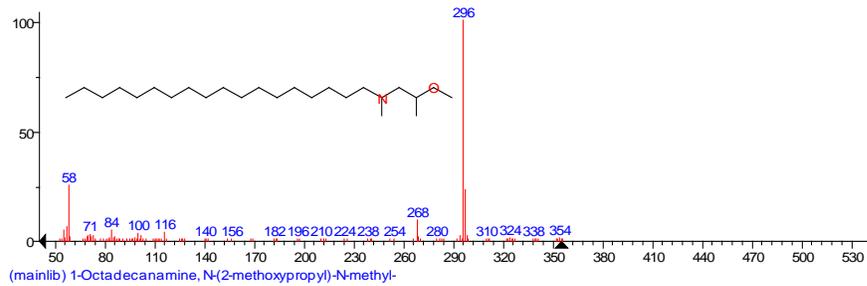
The labile and bound lipids and the lignin originating phenolic compounds are an important component of SOM (Dinel et al., 1990; Kögel-Knabner, 2000). The free lipids from plant waxes and the biopolymers cutin and suberin are representative of the aliphatic component of SOM (Kögel-Knabner et al., 1992; Kögel-Knabner, 2000). The content and composition of the free lipids of SOM depends on the specific vegetation and the soil physico-chemical properties (van Bergen et al., 1997; Dinel et al., 1990).

Organic geochemical studies with soils, clays and sediments in Bulgaria have been concerned with introducing innovative methods of analysis of organic compounds (geochemical markers) in natural and degraded soils (water repellent, anthropogenically and technogenically affected), (Atanassova and Doerr, 2010, 2011; Atanassova and Doerr, 2014, 2015; Atanassova and Teoharov, 2010; Atanassova et al. (2012); Atanassova et al. (2014). Organic contaminants, including persistent organic pollutants (POPs), their derivatives and emerging organic pollutants in soils, clays and sediments have received attention in the studies of Atanassova and Brümmer (2004); Atanassova and Teoharov (2010); Atanassova et al., (2014, 2015); Atanassova and Mills (2016).

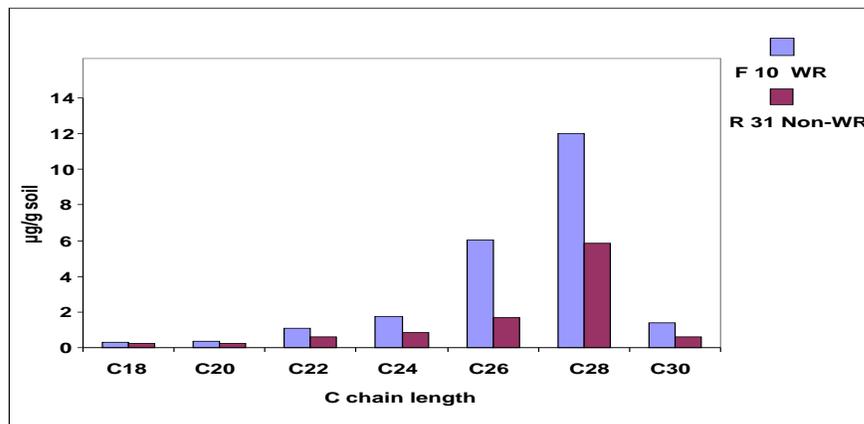
The advances in organic geochemical marker analysis are related to both methodological and fundamental aspects of identification, quantification and source apportionment. New methods of analysis have been elaborated and applied in various geosorbents: soils, sediments

and clays. Analysis has been carried out by making use of accelerated solvent extraction (ASE), Soxtec and sonication (Atanassova and Doerr, 2010, 2011, Atanassova et al., 2012, Atanassova and Teoharov, 2010, Atanassova et al. 2014). Recently, Atanassova and Doerr (2015) using alkaline saponification of dichloromethane (DCM) and dichloromethane/iso-propanol (DCM/IPA) fractions of hot-water-soluble extracts, have identified esterified aromatic acids contributing to soil water repellency in water repellent soils.

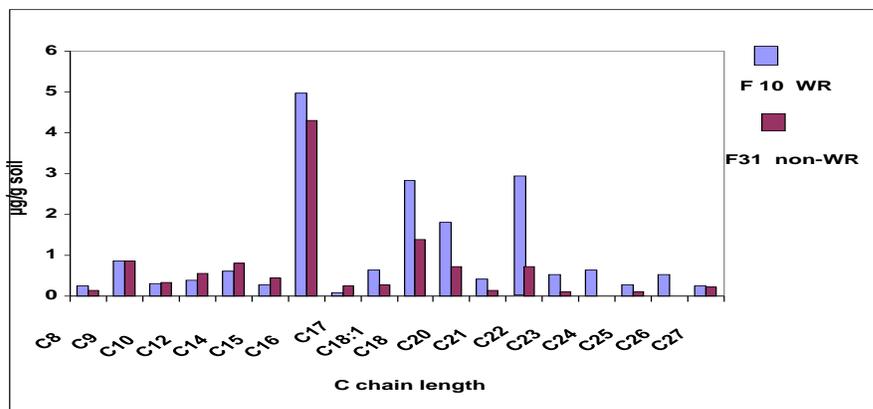




**Figure 2.** Detected anthropogenic markers in a waste water treated soil (Xerofluent) from Alicante, Spain.



(a)



(b)

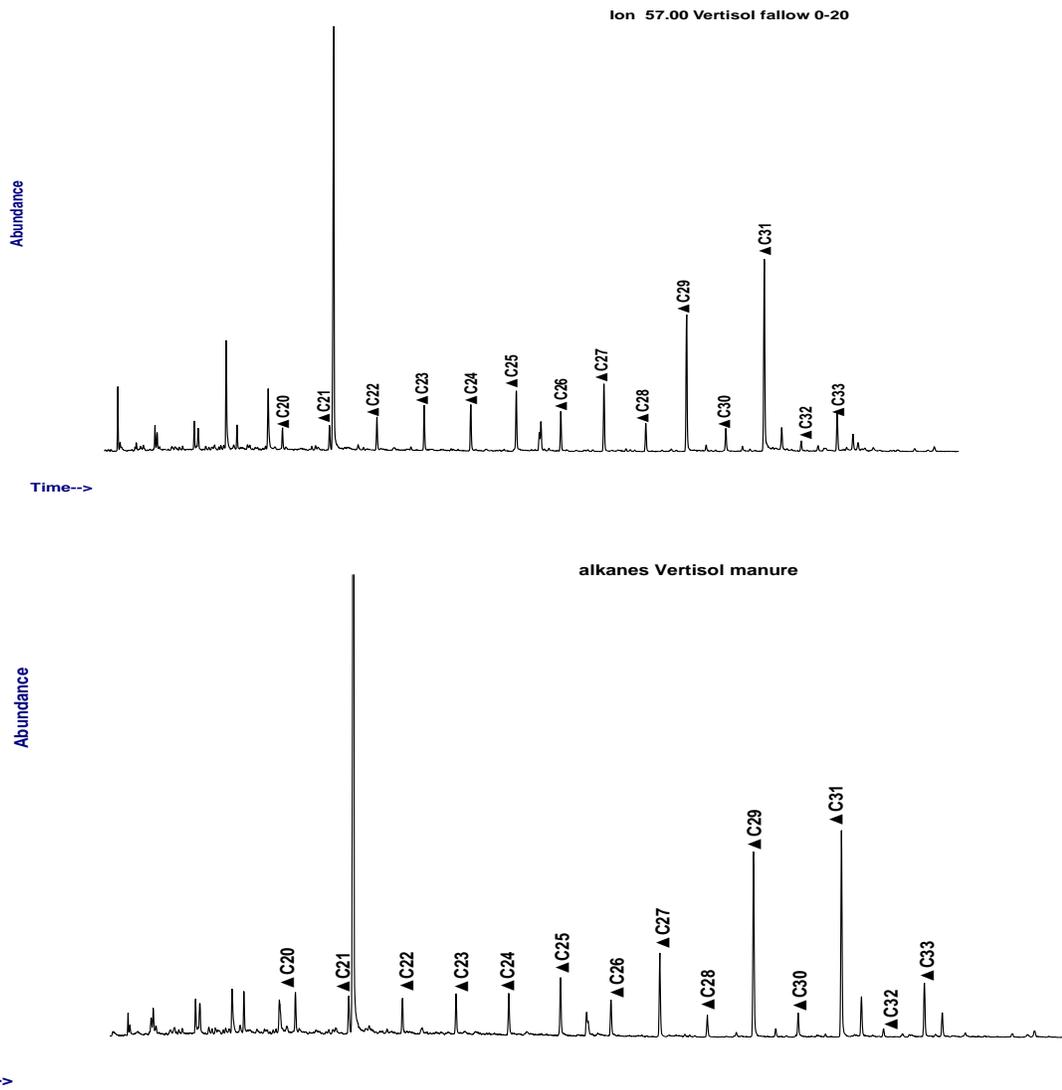
**Figure 3.** a) Absolute concentrations of n-alkanols in water repellent soils (furrows F10) and non-water repellent soils (ridge F31); b) Absolute concentrations of n-fatty acids in water repellent soils (furrows F10) and non-water repellent soils (ridge F31).

### Case studies

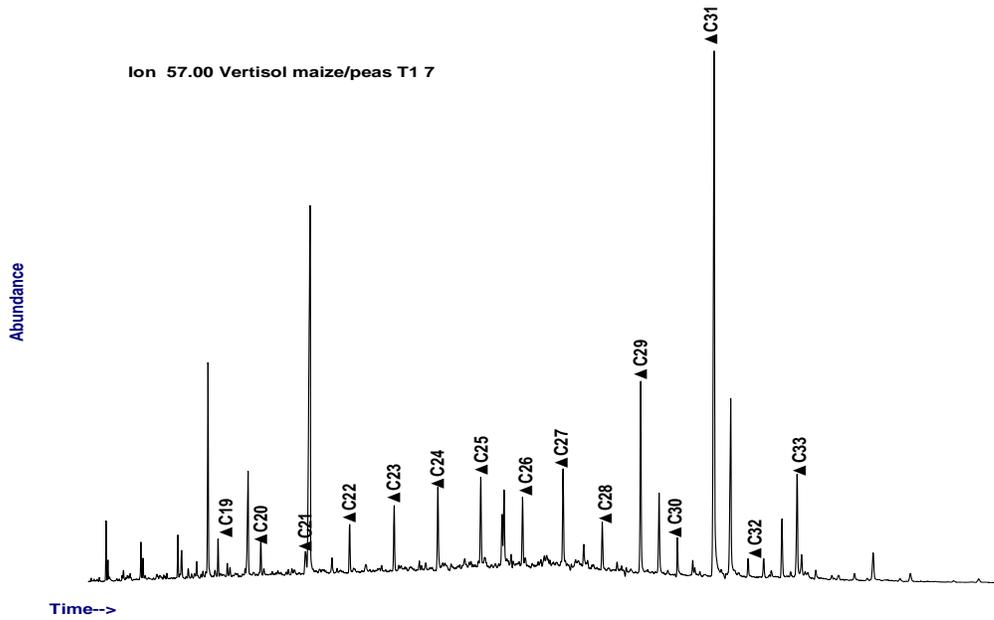
In a recent study, Atanassova and co-workers from the Institute of Soil Science, Agrotechnologies and Plant Protection (ISSAPP) in Sofia have investigated anthropogenically affected soils from the South-West of Kremikovtsi village. Analyzed were the signatures of lipid biomarkers in a Cinnamonic meadow soil (*Rhodic Gleyic Luvisol*) under the addition of 4,2 t/dka sludge from the Sofia Waste Water Treatment plant (WWTP) and from the experimental field at Bojurishte (*Vertisol*) under the effects of various conventional and organic farming, addition of green manure and withering of plant residues, as well as animal manure.

Long chain alkanes were detected with predominance of odd-over-even homologues maximizing at  $C_{31}$ , which shows a similar signature with that of genera *Hedera* (ivy), *Rubus* (blackberry, van Bergen et al. 1997), pine needles (Jambu et al. 1991), *Fraxinus*, grass species (van Bergen et al. 1997) and grass roots (Marseille et al. 1999). Alkane distribution (Fig. 4-5) shows dominance of vascular plants and a similar signature to that found in grazing fields and stubbles (van Bergen et al. 1997). The alkane distribution pattern is similar in the soils from Bojurishte following incorporation of maize/rye and maize/peas residues. The range of long chain alkanes with a maximum at  $C_{31}$  resembles that in soils with manure addition and follows unimodal distribution in the range  $C_{20}$  -  $C_{33}$  maximizing at  $C_{31}$ . Fatty alcohols distribution is also unimodal in the range of  $C_{22}$  -  $C_{32}$  maximizing at  $C_{28}$ . Relative amounts of the *n*-alkanols are the following:  $C_{22}$  – 13%,  $C_{26}$  – 11,2%,  $C_{28}$  – 24,3%,  $C_{30}$  – 13%,  $C_{28}$  – 24,3,  $C_{30}$  – 13%,  $C_{32}$  – 3,7. In the soils treated with farmyard manure  $C_{24}$ ,  $C_{27}$ ,  $C_{28}$ ,  $C_{29}$ , and  $C_{32}$  fatty alcohols were detected. The high proportion of the *n*-alkanols in the soils treated with farmyard manure (FYM) confirms the results of Bull et al. (1998). Very low intensities of fatty acids were obtained, most possibly due to a strong adsorption in the clay fraction of the Vertisol. Other identified compounds were plant sterols: stigmasterol,  $\beta$ -sitosterol, stigmast-4-en-3-one,  $C_{18}$  fatty acid, 2-[(1-oxotetradecyl)oxy]-1,3-propanediyl ester.

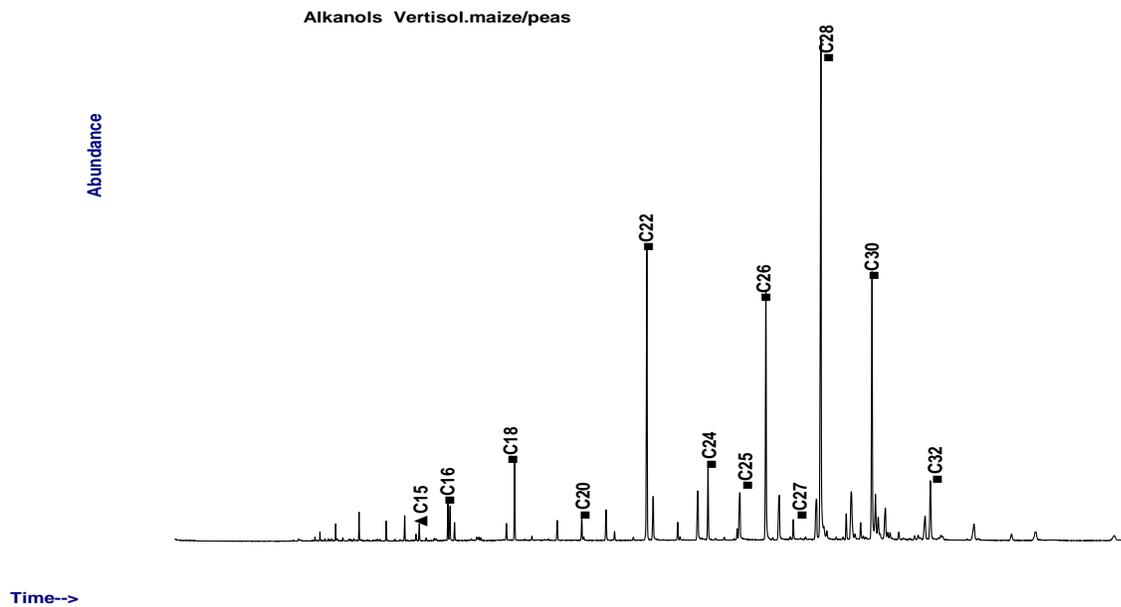
In the deeper soil horizons of the meadow Cinnamonic soil from the region of Kremikovtsi a different *n*-alkanes and *n*-alkanols distribution has been found with a maximum at  $C_{24}$  for *n*-alkanols instead of  $C_{28}$  in the range of  $C_{16}$ - $C_{30}$  (Fig. 6-9), showing the increasing role of the microbial source at the lower depth. The alkane distribution shows a CPI index  $\sim 1$ , which again implies a microbial source of soil organic matter.



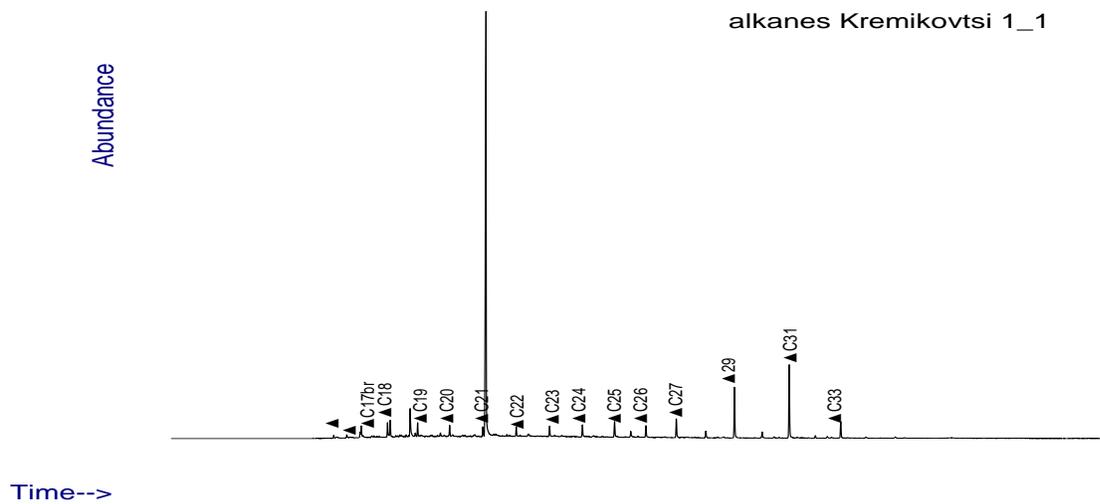
**Figure 4.** Distribution of alkanes, following addition of manure in a soil (Vertisol) from Bojurishte.



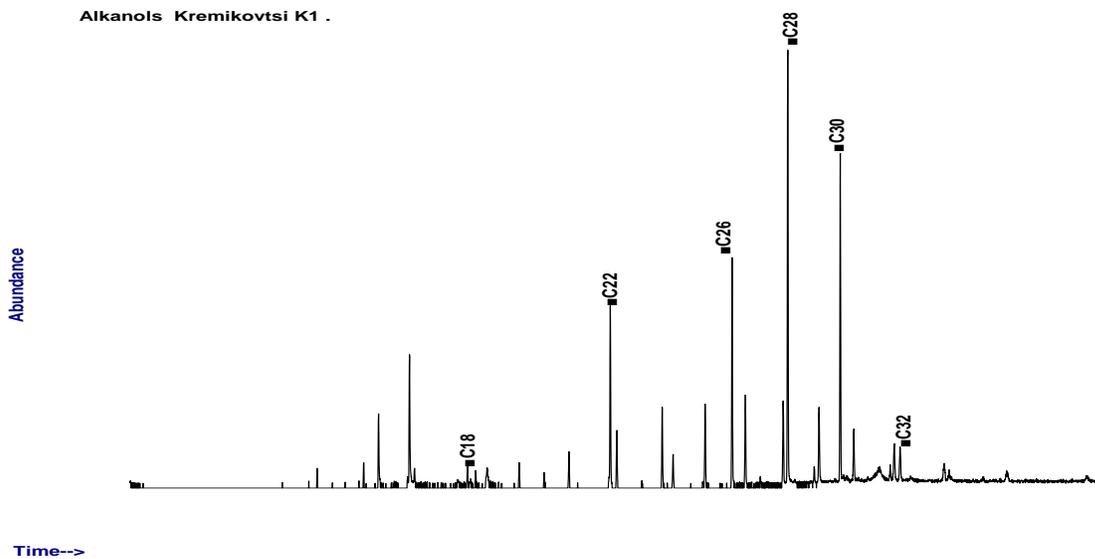
**Figure 5.** Distribution of *n*-alkanes ( $m/z$  57) in a Vertisol under green manure (maize/peas).



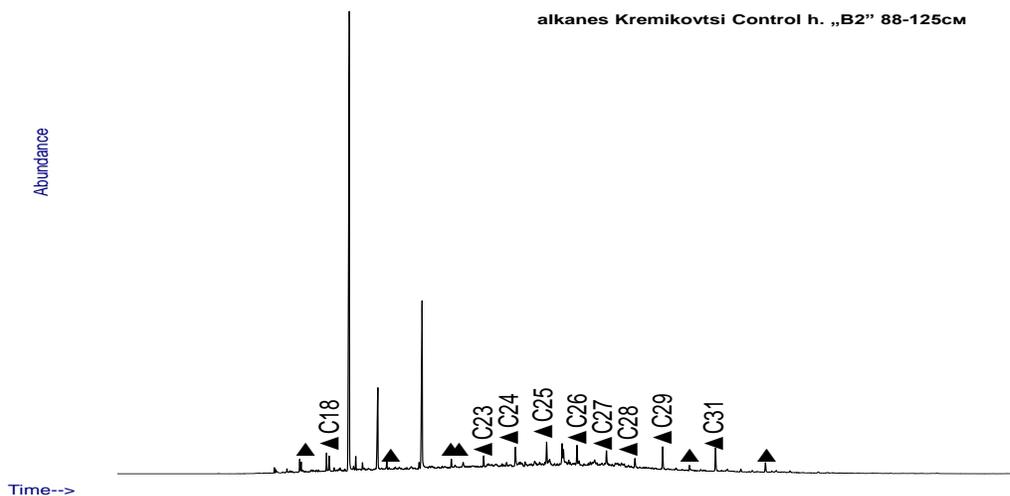
**Figure 6.** Distribution of *n*-alkanols (ion  $m/z$  75) in a Vertisol under green manure maize/peas.



**Figure 7.** Distribution of *n*-alkanes (ion  $m/z$  57) in a meadow Cinnamonic soil under sludge.



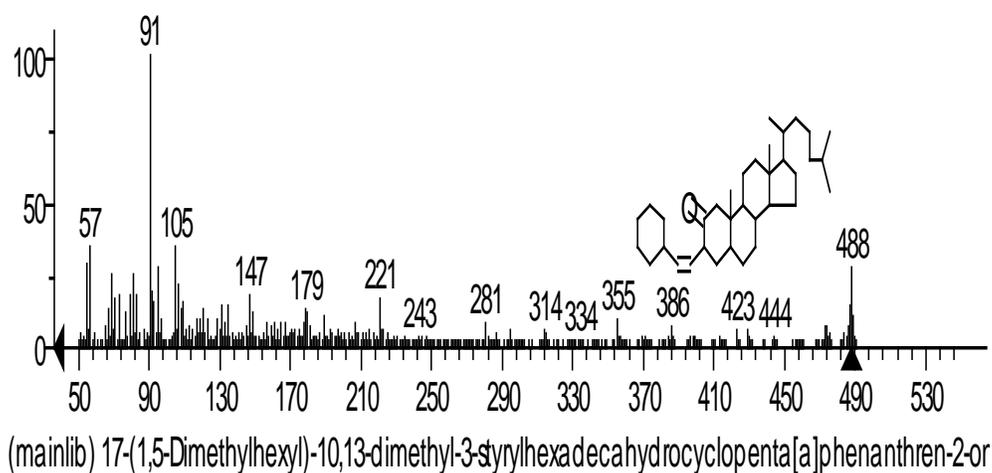
**Figure 8.** Distribution of *n*-alkanols ( $m/z$  75) in a meadow Cinnamonic soil under sludge from Sofia WWTP.

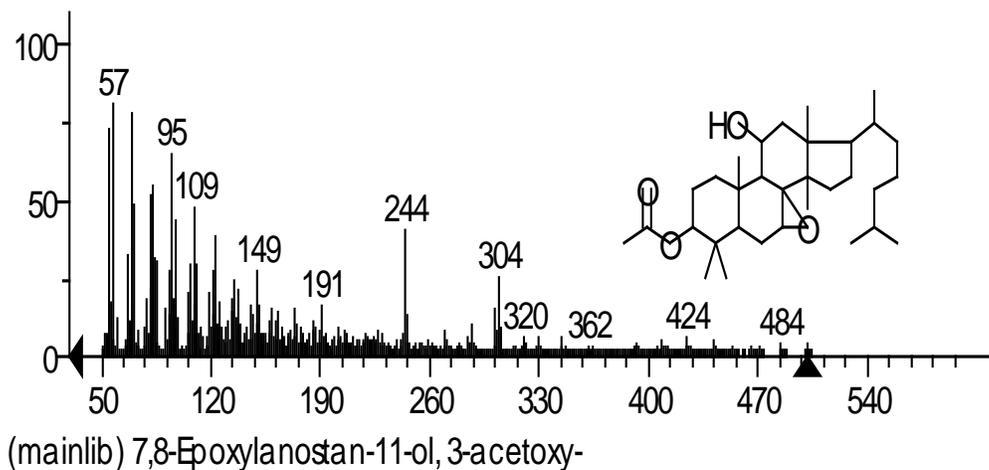


**Figure 9.** *n*-Alkane distribution in Kremikovtsi soil (untreated).

In a Meadow Cinnamonic soil (Urbic Garbic Mollic Technosols, Calcaric Humic Siltic) under deposited sludge from paint and print industry (Atanassova et al. 2011) some characteristic compounds in municipal sewage sludge were detected such as:

17-(1,5-Dimethylhexyl)-10,13-dimethyl-3styrylhexadecahydrocyclopenta[a]phenanthren-2-one; 3-acetoxy 7,8-epoxylanostan-11-ol (detected in oil spills), (Fig. 10 ); cholest-23-ene, (Z)- ; androstane.





**Figure 10.** Anthropogenic markers in sewage sludge from paint and print industry.

In the  $B_{u2}$ – $B_{gk}$  technogenically affected horizons, the following contaminants were detected: exo-tricyclo[5.2.1.0(2.6)]decane, a component in pulse-detonation engines is likely a contaminant compound. Another compound was 2-methyl-4-keto-2-hydroxy pentane released to the environment as a result of its use as a solvent, additive or synthetic intermediate for many materials.

In the gleyic  $G_{or}$  horizon, a suspected contaminant isopropyl myristate has been detected in the upper  $B_{gk}$  horizon. In addition, a compound with MF 62 similar to acenaphthylene, 1,2-dihydroxy with characteristic fragment ions  $m/z$  55, 73, 262, 328 was detected in  $B_2$  and  $B_{tg}$  horizons, but not in  $G_{or}$  horizon (Atanassova et al., 2015).

### Future challenges and trends in soil eco-chemistry

The future challenges and developments of soil eco-chemistry will have to answer the following critical questions: (i) What is the structure and chemical (physico-chemical) behavior of persistent organic pollutants and their derivatives (metabolites) in soil? How does compound's mobility and toxicity to organisms change in relation to soil environment? (ii) What is the fate of nanoparticles in soils depending on the size, shape, surface charge and soil characteristics, e.g., pH, ionic strength, organic matter, and clay content? (iii) What decision-support systems and remediation techniques should be elaborated to cope with mixed contamination in soils? (iv) Does metal toxicity stop the biodegradation of POPs? (v) What are the living receptors of toxic compounds in the environment?

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