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IDENTIFICATION OF ORGANIC POLLUTANTS IN AGRICULTURAL SOILS FROM TIANJIN, CHINA

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Summary: Organic pollutants in agricultural soils from suburbs of Tianjin were investigated. These included hydrocarbons (alkanes, fatty acids, steranes and triterpanes), phthalate esters, polycyclic aromatic hydrocarbons, and chlorinated pesticides. The pollutant composition directly points to strong contamination from fossil fuels derivatives.

Key words: Polycyclic aromatic hydrocarbons, chlorinated pesticides, fossil fuels

INTRODUCTION

Sewage irrigation on agricultural land has been common practice in the Tianjin area, as in other regions of northern China, due mainly to the shortage in water supply. Sludge and municipal refuse (made up mainly of household garbage and coal ash from heating systems) were applied as fertilizer and soil conditioner. The nature of these wastes are complex and heterogeneous, and contain a variety of organic and inorganic pollutants [1, 2].

Although some reports are available on the contents, distribution and ecological toxicities of heavy metals in the soils from the Tianjin area [3, 4], very limited information, if any, is currently available on organic pollutants in these soils.

The primary objective of this study was to identify the organic pollutants in soils from the Tianjin area, where sewage, sludge and municipal refuse have been extensively applied on agricultural land. Possible sources of these organic pollutants and the general pollution pattern were also discussed.

MATERIALS AND METHODS

Twenty surface soil samples were collected from agricultural fields in the Tianjin area where sewage and sludge had been applied. Sampling locations were selected to cover five rural counties and four suburban districts of the city. An uncultured soil from beneath pine trees was selected as control. Organic matter contents ranged from 0.86 till 15.95 %, and textures from sandy and silt, to clay. Vegetation was pine, corn, wheat, sorghum, rice, and vegetables. The irrigation/fertilization processes were as follows: none in the control, clean water irrigation, sewage, clean water/sewage, sewage/sludge, or sewage/sludge/refuse.

Organic pollutants were extracted by dichloromethane-methanol (2:1), under sonication. Ten grams of sample and 10 ml solvent was sonicated (3 x 30 min) and the extracts were separated by centrifugation. The combined extracts were dried by rotary vacuum evaporation, at room temperature, and then redissolved in 100 μl solvent.

The extracts were analysed in a Fisons GC-8000/MD 800. The separation was carried out on a 30 m x 0.25 mm i.d. fused silica SPB-5 capillary column (film thickness 25 μm), programmed isothermally for 3 minutes at 50 °C, from 50 °C to 100 °C at a rate of 30 °C/min, from 100 °C to 280 °C at a rate of 5 °C/min, and finally isothermally for 20 minutes at 280 °C. The carrier gas was helium.

RESULTS AND DISCUSSION

The major classes of organic compounds identified are listed in Table 1. These can be classified into the following categories: alkanes, fatty acids, phthalate esters, polycyclic aromatic hydrocarbons (PAH), chlorinated pesticides, triterpanes, and steranes.

Table 1. Major classes of organic pollutants in Tianjin soils

Class	Range[1]	Class	Range
n-Alkanes	C_{15}- C_{32}	Steranes	C_{28}
Isoprenoids	C_{19}, C_{20}	(Alkyl) PAH[2]	C_{10}- C_{22}
n-Fatty acids	C_{14}- C_{25}	Phthalate esters	C_{14}, C_{22}
Triterpanes	C_{29}, C_{30}	Chlorinated pesticides	C_{6}, C_{14}

[1] Range denotes number of carbon atoms.

[2] Alkyl substituents range from C_1 to C_5. The lower member, naphthalene, presents up to C_5 substituents. Higher members usually have methyl or dimethyl substituents.

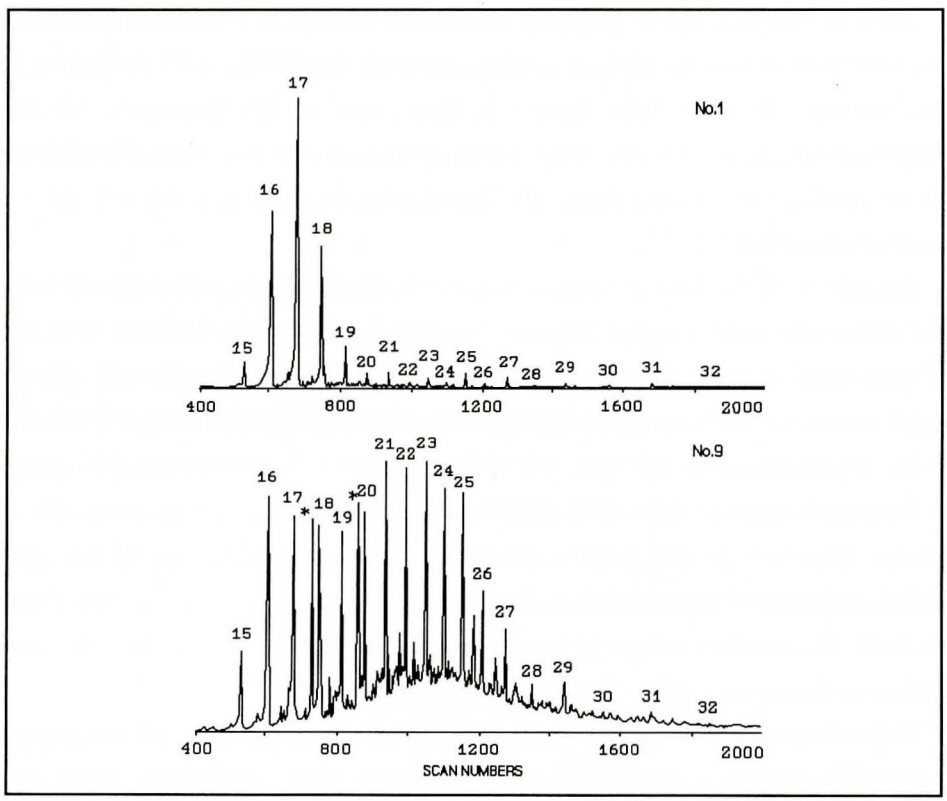
Chlorinated pesticides, namely lindane and DDT (as mixed isomers of DDT, DDE and DDD) were clearly identified in all soil samples except in those of rural counties and the control. The fact that none of these compounds was detectable in control and cultured fields irrigated by clean water alone indicates that sewage irrigation was the main source of these pollutants accumulated in the soil. The use of both lindane and DDT has been outlawed since 1982 in China. The residual amounts of the pesticides in the soil of Tianjin area remain high after a decade, primarily due to the persistence of these compounds which have been thoroughly investigated [5].

The most important organic pollutants found in the soil from the Tianjin area are perhaps the PAH. Around a quarter of the chromatographic peaks identified in most samples fall into this category. Of many PAH detected in these samples, benzoanthracene, chrysene, benzofluoranthene, benzopyrene, indenopyrene, and benzoperylene are typically considered to be possible human carcinogens [6]. Benzonaphtothiophene is a characteristic coal combustion product [7].

Even though the contents of organic compounds in these samples have not been measured, the relative amounts of them are believed to be related to peak areas. Referring to the ranks of peak areas of pyrene and benzofluoranthene it appears that the samples with relatively small amounts of PAH are the control soil, soils from rural counties (irrigated with clean water or sewage), and soil from the Northern District. To demonstrate the possible differences between samples from different areas, the 20 soils were classified into two groups: I) those from rural counties and from the Northern District, and II) others from suburban districts. A nonparametric test was performed, based on ranked total peak areas of all PAH. The calculated results of the test showed that the contents of PAH in the second group are significantly higher than those in the first ($f < 0.001$).

PAH are introduced into the environment via forest and prairies fires and anthropogenic combustion processes. Rural soils typically contain PAH, atmospheric fallout being considered the principal source of PAH [6]. Most soils in group I were from rural counties relatively far away from atmospheric pollution sources. The only exception in these groups is a soil located in the Northern District where the effect of atmospheric fallout is not as serious as in the other suburban district, as the dominant direction of the wind is from the North during winter when fossil fuels are used extensively for heating purposes in the city.

In addition to PAH, *n*-alkanes are also important pollutants from fossil fuel including coal and petroleum. *n*-Alkanes have been used as biological markers quite successfully as a result of their abundance and ease of detection [8]. The presence of *n*-alkanes ranging from C_{15} to C_{32} has been found extensively in all samples studied. Two types of distribution patterns were observed in the *n*-alkanes present in all extracts from soils. Examples of the typical *n*-alkane distribution of group I (control soil, No. 1), and group II (soil treated with sewage/sluge/refuse, No.9) are shown in Figure 1, where numbers indicate carbon atoms and * phthalate esters.



For all soil samples studied, the first parts of the diagrams from C_{15} to C_{18} are similar to each another, with the most abundant *n*-alkane appearing around C_{17}. As the application of sewage and other wastes has no significant influence on the amounts of these *n*-alkanes, they are probably derived from natural sources, e.g. microorganisms. In cyanobacteria and algae

normal hydrocarbon range is from C_{15} to C_{19}, C_{17} being predominant in most species [9].

The most striking difference in the *n*-alkane distribution pattern between the two groups, is the part of the chromatogram representing the alkanes from C_{19} to C_{32}. Group I soils show very small peaks and clear predominance of odd carbon number, which could be assigned to epicuticular waxes of vascular plants [10]. For group II, however, there is no marked odd/even predominance of *n*-alkanes in this range. The more or less uniform distribution of C_{19} to C_{32}, with almost no or low odd over even carbon predominance indicates a petroleum origin.

In addition to the *n*-alkane evidence, the anthropogenic input of fossil fuel pollutants in soils from the Tianjin area is also demonstrated by the presence of a considerably unresolved complex mixture of branched and cyclic hydrocarbons or "hump" in the soils from group II, (Figure 1, compare soils No. 1 and 9). Further evidence is provided in the identification of pristane and phytane, diagenetic products of phytol, triterpanes and steranes. The presence of the isoprenoidal markers in hydrocarbon fractions associated with the branched and cyclic hydrocarbon mixture confirms a petroleum origin for these compounds [8, 10]. Triterpanes and steranes are amongst the most important petroleum markers. Relatively low contents of triterpanes and steranes were found in soils from group I, compared to group II soils.

Fatty acids are some of the most widely distributed compounds in all living organisms, C_{16} and C_{18} being majoritary. This pattern is also reflected in the soil samples studied herein and in extracted humic materials [11]. The identification of methyl esters from fatty acids in the Tianjin soils can be attributed to the easy methylation of the acid group, in this case by the methanol used in the extraction process. Extraction with ethanol resulted in the identification of fatty acid ethyl esters [12].

Data have shown that a significant amount of phthalate esters was present in all samples including the control soil. Bidistilled solvents and glassware were used in the laboratory to avoid contamination by phthalates. Blanks for solvents were essentially free of phthalates. The highest amount of these compounds was found in soils from the East and West Districts, all of which were collected from horticultural fields where municipal refuse was applied on the land in addition to sewage and sludge. Phthalate esters are widely used in plastics, cosmetics, fragances, pesticides carriers, industrial oils and many other industrial products and have been detected in sewage, sewage sludge, and municipal refuse [1, 2].

CONCLUSIONS

Organic pollutants in soils from the Tianjin area have an anthropogenic origin and most likely come from combustion of fossil fuels. This points to considerable pollution of soils via atmospheric deposition, sewage, sludge and refuse applications.

PAH have been detected in all samples, which is in accordance with Laflamme and Hites [13] who found PAH in the most remote areas of the globe due to long-range transport and deposition of airborne carbonaceous particles formed by combustion. The contents of PAH in most suburban districts, however, were significantly higher than those in rural counties, indicating that the majority of the PAH were probably introduced into the soils via atmospheric fallout and agricultural practices (application of coal ash to soils). Municipal refuses causes significant increases in the amounts of phthalates in the soil, which are also widely distributed in all samples studied.

Considerable amounts of lindane and DDT isomers were found accumulated in soils treated with sewage and sludge, compared to the control soil and soils irrigated with clean water.

Organic pollution in the agricultural soils of the Tianjin area is considerable, and immediate actions, to control air pollution and improve waste water system, should be taken.

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