RESEARCH ARTICLE

STUDIES ON SOIL POLLUTION: ANALYSIS OF THE ORGANIC POLLUTANTS ISOLATED FROM SOIL SAMPLES

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Abstract

Environmental pollution due to the presence of Organic Polyaromatic hydrocarbons (PAHs) in the soil has been studied in the soil. In our current research study, Experiments are conducted to find the possible organic components present in the soil using appropriate extraction/isolation procedures with the help of organic solvents. The mixture of organic compounds isolated was analyzed initially by TLC, followed by GLC and 1HNMR Studies and the results are presented in this communication.

Keywords: Environmental Pollution, Soil Pollution, Polyaromatic hydrocarbons (PAHs), TLC, GLC, 1HNMR analysis.

Introduction

Environmental pollution namely air, water, soil became a major concern in recent times due to potential hazardous consequences. Several types of impurities constituents contribute to the soil pollution. Most of the time these constituents are added to the soil through improper solid waste disposal methods. The presence of organic Polyaromatic hydrocarbons (PAHs) in the soil makes it unusable for cultivation or for crop growth. This is resulted mainly because Polyaromatic hydrocarbons are highly toxic and presence of them cause several health disorders as reported in the recent literature, Polyaromatic hydrocarbons are a group of aromatic compounds having a benzene ring attached to several other aromatic rings. One of the very important Polyaromatic hydrocarbons is BaP (Benz pyrene) which is a major component of tobacco smoke and is highly carcinogenic. Apart from it there are several other PAHs such as anthracene, acenaphthene, pyrene, halogenated PAHs, Fluorene, Chrysene, Phenanthrene, etc (Adamczewska et al., 2000; Ahmad Gholamalizadeh Ahangar, 2010; Bellah et al., 2010; Guandiwang et al., 2004; Katikuosmanen et al., 2003; Leonard et al., 2010).

Polyaromatic hydrocarbons (PAHs) are found be highly toxic and pose serious health hazards according to several reports published in the literature (SenarO zean et al., 2009; Tahseen sayara et al., 2010; Wan et al., 2003; Weislo,1998; Marlene Rebola et al., 2008). Our present study aimed at finding the possible organic components present in the soil collected from different locations in and around Visakhapatnam of coastal Andhra Pradesh, India. We have presented the results of our studies as well as possible ways of converting more hazardous PAHs into less toxic and easily disposable derivatives such as sulphonic acid by sulphonation of PAHs.
Experimental details

Soil samples are collected from ten locations each one kg. 100 grams of each soil sample was digested with 500 ml of methanol at reflux temperature for 5 to 6 hours. Then the supernatant was filtered on a whattman filter paper followed by washing with methanol. The filtrate is distilled off to remove methanol and the crude substance was analyzed by using Thin layer chromatography (TLC). We have investigated the TLC in several mobile phases such as Hexane, Hexane+DCM(2:1) Hexane+Ethyl acetate(2:1) DCM+Methanol (3:1). The TLC plate of typical experiment is found to be shown Figure.1

From the study of the TLC we have observed that the crude mass contains mostly Polyaromatic hydrocarbons with less of either polyalkane or other polar organic substances. To support our observation we have recorded the Gas Chromatography (GC) for the crude mass which is found to be as shown Figure.1.

The data from the above GC clearly supports our observation that PAHs are the major components present in the crude mass. To continue our characterization of the constituents, we have recorded 1H NMR spectrum in deutriated chloroform solvent using tetra methyl saline as internal standard.

The crude mixture of organic compounds was submitted for recording 1HNMR spectrum. The mixture was dissolved in DMSO-D6 solvent and proton NMR was recorded from 1 to 14 delta. The 1HNMR thus obtained showed broad peaks in the aromatic region from 6.8 to 8 delta. Also a sharp singlet was found in the aromatic region indicating the presence of several aromatic protons typical of Polyaromatic hydrocarbons. Also found two peaks between 0.8 to 1.2 delta representing aliphatic protons. Hence it is concluded that the mixture contains essentially polyaromatic hydrocarbons and also alkylated polyaromatic hydrocarbons. The spectrum obtained is as shown figure.2.

As the consequences of the following above studies we have arrived at a conclusion that PAHs are only the constituents present in the product.

Suitable disposal methods

Having come to an understanding that PAHs are the chief constituents, we have decided to come up with a suitable and viable technique to convert more carcinogenic and toxic. PAHs into less toxic, easily disposable, easily drained with water source. We have conceived another chemical method that is sulphonation of PAHs using concentrated sulphuric acid. We have subjected the PAHs to sulphonation using molar equivalents of Conc.H2SO4 followed by moderate heating for approx. 2hours. The resulting reaction mixture was analyzed by TLC comparing with the starting PAHs and observed that no traces of PAHs were found in the TLC after the reaction which indicated that all PAHs are completely converted into their corresponding sulphonic acids which are found to be water soluble. A typical TLC is shown in figure.

Results and discussion

The samples collected from different locations are subjected to extraction procedure as detailed in the experimental section and subjected different methods of analysis. Initially Thin layer chromatographic technique was adapted to find the presence organic impurities present in the crude extracts. Various mixtures of organic solvents were used to optimize a proper mobile phase in order to observe the presence of organic impurities. Most suitable solvents systems were found to be pure hexane as mobile phase, mixture of hexane and ethyl acetate as mobile phase, a mixture of hexane and dichloromethane, and a mixture of dichloromethane and methanol as mobile phase and all the TLC plates were shown in the experimental section. From the study of the TLC we have observed that the crude mass contains mostly Polyaromatic hydrocarbons due to the nonpolar nature of the organic impurities with less of either polyalkane or other polar organic substances. To support our observation we have recorded the Gas Chromatography (GC). The data from the above GC clearly supports our observation that PAHs are the major components present in the crude mass. To continue our characterization of the constituents, we have recorded 1H NMR spectrum in deutriated chloroform solvent using tetra methyl saline as internal standard. The fact that the crude extract was easily soluble in chlorinated organic solvents such as dichloromethane, chloroform etc. indicate the presence of nonpolar organic compounds. The crude mixture of organic compounds was submitted for recording 1HNMR spectrum. The mixture was dissolved in DMSO-D6 solvent although the crude extract was easily soluble in deuterated chloroform to ruleout the presence of polar components and proton NMR was recorded from 1 to 14 delta.
The 1HNMR thus obtained showed broad peaks in the aromatic region from 6.8 to 8 delta. Also a sharp singlet was found in the aromatic region indicating the presence of several aromatic protons typical of Polyaromatic hydrocarbons. Also found two peaks between 0.8 to 1.2 delta representing aliphatic protons. Hence it is concluded that the mixture contains essentially polyaromatic hydrocarbons and also alkylated polyaromatic hydrocarbons. Our attempts to separate the mixture of organic compounds into individual pure compounds was not successful, however efforts to isolate the individual components is being attempted. Similarly the methodology was extended to the remaining samples collected from different locations and the results are tabulated (Table.1).

As it has been mentioned in the introduction that the presence of PAHs in the soil pose serious threat to the population around particularly with respect to the health and also the fertility of the soil is drastically affected. It is also mentioned that PAHs cause pollution through various means like through air, water and through the food sources. Hence a suitable dispersal method of solid waste containing a mixture of several PAHs is the need of the hour or is very essential in today's rapidly industrializing nations. We felt that sulfonation is one of the most suitable methods to toxic Polyaromatic hydrocarbons (PAHs) to sulfonic acid derivatives which are water soluble and can easily be drainedout. Also aromatic sulfonic acids in general act as surfactants hence can be removed easily.
Figure 2. The crude mixture of organic compounds was submitted for recording 1HNMR spectrum.
Table 1. Showing the different sampling areas

<table>
<thead>
<tr>
<th>S.No</th>
<th>Sampling station</th>
<th>Area</th>
<th>Presence of toxic compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S-1</td>
<td>2km from East</td>
<td>Present</td>
</tr>
<tr>
<td>2</td>
<td>S-2</td>
<td>5km from North</td>
<td>Absent</td>
</tr>
<tr>
<td>3</td>
<td>S-3</td>
<td>8km from West</td>
<td>Present</td>
</tr>
<tr>
<td>4</td>
<td>S-4</td>
<td>6km from South</td>
<td>Present</td>
</tr>
<tr>
<td>5</td>
<td>S-5</td>
<td>4km from North east</td>
<td>Absent</td>
</tr>
<tr>
<td>6</td>
<td>S-6</td>
<td>7km from North west</td>
<td>Present</td>
</tr>
<tr>
<td>7</td>
<td>S-7</td>
<td>1km from South east</td>
<td>Present</td>
</tr>
<tr>
<td>8</td>
<td>S-8</td>
<td>4km from South west</td>
<td>Absent</td>
</tr>
</tbody>
</table>

We have used concentrated sulfuric acid as sulfonating agent. The crude mixture containing organic compounds was heated to about 80 °C for approximately 3 hrs after which TLC was monitored against starting mixture and TLC results are also shown in figure 1. As the TLC clearly shows the complete disappearance of the starting mixture and presence of new polar compounds clearly indicates the conversion to sulfonic acid derivatives.

We believe that the technology adapted by us as mentioned above will become guidelines for analyzing the presence of solid contaminants. Also our approach to chemically modify more hazardous PAHs into less hazardous and easily disposable derivatives like sulphonic acids will be of much use for those who are adapting techniques for the safe disposal of the PAHs residues derived either from industries or otherwise.

Conclusions

We have attempted to identify the possible locations of the presence of PAHs and also attempted to develop suitable method of disposal. All our studies are supported by instrumental techniques. Further studies are in progress and results will be published in an appropriate journal.

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