Recent analytical study of affluent-petrochemicals on the environment and plausible effects of such chemicals on the human health around newly established oil refinery, Bina, Sagar district, M.P., India.

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ABSTRACT

The Bina town came up on the industrial map of India after the establishment of a new oil refinery in the year 2009. The environmental impact of the BORL, Bina, Sagar district, M.P. has been discussed in this paper, as the area was virgin before the establishment of this refinery in this area and also free from any pollution. A preliminary geochemical study of ‘soil and water’ samples analyzed for physico-chemical parameters reveals impact of the affluent petrochemicals on the environment released from the Oil Refinery. Gas chromatography and mass spectroscopy based results show presence of Polycyclic Aromatic Hydrocarbons like Pyridine-3 (1-methyl-2-pyrolidyl), Pyridine Indene Silane and Norvaline; higher range of petroleum hydrocarbons (benzene-1-methyl-hexadecyl, tetra-decanoic-acid, octa-decanoic-acid, 2-bromononane, hexadecanoic acid, dodecane-46-dimethy, n-alkenes); and unresolved complex mixtures of aliphatic compounds, which are causing ill effect on the environment, especially the ‘soil fertility’ and ‘water quality’, which in turn is likely to make impact on the ‘human health’.

Keyword: Central India, geo-environment, human health, oil refinery, petrochemicals, soil and water.

1. Introduction

The last decades of the twentieth century experienced a change as awareness towards the environment and importance of the soil as an environmental component and recognition of the need to maintain or improve its capacity to allow it to perform its various functions. At the same time there was a confirmation that the soil is not an inexhaustible resource and if used improperly or poorly managed, its characteristics can be lost in a short period of time with limited opportunities for regeneration (Nortcliff S, 2002).

However, the final disposal of potentially toxic residues in the soil has become a practical and inexpensive alternative and can cause altercation in the anthropological community, (Van strallen et al., 2004). Similarly, it will effect on the living organism of the study area.

The gathering of biological studies both laboratorial and field combined with chemical analysis of the contaminants, provides a real scenario of the effected system. The interaction between basic components of the environment, rock and groundwater is connected with material redistribution interaction of both reacting units and the system as a whole.
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A complete understanding of the processes of interaction between water and sediment requires not only the combination of theoretical studies, computational modeling and laboratory experiments (conducted under conditions similar and comparable to natural conditions), but also a necessary backward comparison with pollutant behavior in natural system. (Konecny F, et al., 2003) Petroleum and its products dominate as one of the important commodities consumed in the modern world (Lebland D, 2003).

It is expected that the production of 95 million barrels of petroleum per day in order to meet the growing worldwide demand of this resource over several decades, petroleum products have become very common pollutants in the environment as considerable amounts of petroleum compounds are discharged into environment through industrial effluents. Petroleum products are complex mixture of hydrocarbons composed mainly of carbon and hydrogen in different molecular arrangement. Large scale crude oil spills on soil, leakages from pipelines, underground and surface fuel storage tanks, indiscriminate spills and careless disposal and mismanagement of waste and other petroleum product by the society, constitute the major source of petroleum contamination in our environment. It has become a topic of interest and attracted increasing attention because of the carcinogenic, mutagenic and toxic effect. (Ribes A et al., 2003)

Generally, all the methods describe collection, preservation and storage of samples, procedures to concentrate, separate, identify and quantifying the contaminant in the sample, quality control criteria has a bearing on the analytical data and it should meet and the reporting of analytical data (Boxgep 1964). Many workers (Jacob J et al.,) have found that different methods give complementary information for the analysis of petroleum derived compound in the environment. The intention is to identify well established methods that are used as the standards methods approved by federal agencies and organizations such as EPA (Environmental Protection Agency) and ASTM (American Society for Testing and Material). There is no single method which gives a precise and accurate measurement of TPH (Total Petroleum Hydrocarbon).

The Bundelkhand area of Madhya Pradesh is an undeveloped region and this oil refinery is a step in the economic development of this area. The industrial development of this region was started by setting of this oil refinery and followed by a thermal power plant. The industrial development has brought a boom in economic scenario of the area vis a vis its impact on the environment. For the first time, authors attempted a study to assess the environmental impact of Bharat Oman Oil Refinery on its surrounding. It is the aim of this investigation to shed some light on those compounds that are present in the soil and water from surrounding refinery area, which affect the soil fertility and brought a change in water composition of this area due to this refinery. Primary analysis of sample collected from the surrounding of refinery by physico-chemical methods for Turbidity, Salinity, Conductivity, Alkalinity, pH, Total hardness, and carbon content have been carried out.

Analytical methods of petroleum content determination are of two basic types, i.e. spectroscopic and chromatographic. First type of method is IR absorption method which is fast for total petroleum hydrocarbon measurement because this method requires a short preparation and analytical time and is less expensive to use (EPA Draft Method 1664). Second type is gas chromatography with Mass spectroscopy must be used for identification of individual petroleum compound present in samples (U.S.EPA Method 3540C).
The present study shows the analytical results of several soil and water samples and preliminary characters of these investigations should be taken into account.

2. Material and method

2.1 Site selection

The sampling sites which covered about 5x5 km around BORL, Bina Refinery at Agasod Sagar district have been taken into account. Considering the suitability, according to the condition of Topography and drainage pattern, the study area has divided into grid to have a representative sample. Considering the drainage pattern, those streamlets and nallas were sampled which may carry the effluent from the refinery.

2.2 Sample collection and extraction

An initial survey was carried out on the contaminated site prior to sample collection of soil and water. Sampling of the area will be based on grid pattern covering refinery area and their nearby villages, which may get polluted from the effluent of the refinery. The soil samples were obtained from contaminated sites at depth of 30 cm from b horizon. Soil samples were collected into zip type plastic bags and placed in one liter wide mouth glass jars with Teflon lined cap and sealed.

These were put into appropriate containers and stored in the laboratory fridge at 40c. Water sample was also collected from tube well, hand pumps, drainage and other sources of contaminated sites near refinery area. The samples bottle with Teflon caps at a maximum temperature of 40c has stored. Before analysis, water sample were centrifuged. All samples were extracted using the soxhelate extraction procedure as outlined in U.S.EPA method 3540 (Annual Book of ASTM standards) and ASTM method D5369 (Draft International standard). Soxhelate technique is the most often used method for extraction of contaminant, a long time for GC-MS analysis. It has been proposed by many agencies (Berst J.D et al.,) as a method of choice for extraction of non polar organic contaminants. Dichloromethane (DCM) proved to be the most suitable solvent over hexane, acetone and toluene for their ability of not interfering with BTEX, C5-C9. The soil samples were analyze by GC-MS only. Physico-chemical study of soil samples was done for to determine the using pH, Nitrogen (N), phosphorus (P), Carbon percentage and electrical conductivity. pH was determined using the modified method of McLean (1982).

Preliminary water analysis methods are used for identification of TDS (Total dissolved solid), Turbidity, salinity, conductivity etc.

2.3 Instrumentation

Physico-chemical study of water and soil samples was done by using ALFA soil/ water analyzer kit model number S-2512, II B-1202. GC/MS study was carried out at SAIF, IIT Bombay. The determination of petroleum pollutant in soil and water samples by GC-MS was performed using an AGILENT model 7890 Head space injector, combipal auto sampler. Make of MS was JEOL model Accu TOFGCV specification EI/CI source and mass range was10-2000 amu. Mass resolution is 6000. The injectors’ volume was 1.5 micro liters. FT-IR
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study of soil samples was done by using Bruker Germany Model-3000 Hyperion Microscope with vertex 80 FTIR systems.

3. Result and discussion

The results of preliminary physicochemical study are shown in table (1) and (2), which is carried out for pH, Turbidity, alkalinity, total hardness and others parameters. The results clearly show that the composition of soil and water are slightly changed as compared to standard parameter given by EPA. The pH of water and soil samples are basic in some cases. The nitrogen content is less as obtain in the result of soil analysis (Table 1) which affects the fertility of soil.

Table 1: Physical and Chemical Characters of Soil.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Place Name</th>
<th>Longitude/ Latitude/ Elevation (m)</th>
<th>pH</th>
<th>Nitrogen %</th>
<th>Carbon %</th>
<th>Potassium (kg/hect.)</th>
<th>Phosphorus (milli mhos)</th>
<th>Soluble salts (milli mhos)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Crop Fields near area of Bina</td>
<td>N24°13'55&quot;/ E78°10'03.37&quot;/ 410</td>
<td>8.1±0.1</td>
<td>0.24</td>
<td>0.87</td>
<td>161.28</td>
<td>11.7</td>
<td>0.18</td>
</tr>
<tr>
<td>2</td>
<td>Near Kath village</td>
<td>N24°13'55&quot;/ E78°10'02&quot;/ 335</td>
<td>7.7±0.1</td>
<td>0.30</td>
<td>0.65</td>
<td>136.80</td>
<td>15.3</td>
<td>0.17</td>
</tr>
<tr>
<td>3</td>
<td>Dumping area of Refinery</td>
<td>N24°15'28&quot;/ E78°10'22&quot;/ 403</td>
<td>7.5±0.1</td>
<td>0.42</td>
<td>0.60</td>
<td>125.44</td>
<td>10.8</td>
<td>0.20</td>
</tr>
<tr>
<td>4</td>
<td>Near Agasod road Artifical Pond</td>
<td>N24°15'13.7&quot;/ E78°9'96&quot;/ 400</td>
<td>8.6±0.1</td>
<td>0.30</td>
<td>0.15</td>
<td>112.00</td>
<td>14.4</td>
<td>0.20</td>
</tr>
<tr>
<td>5</td>
<td>Shakti near Drainage</td>
<td>N24°15'58.7&quot;/ E78°08'72.9&quot;/ 391</td>
<td>8.2±0.1</td>
<td>0.35</td>
<td>0.75</td>
<td>120.56</td>
<td>10.8</td>
<td>0.16</td>
</tr>
<tr>
<td>6</td>
<td>Field area of Pateria village</td>
<td>N24°15'46&quot;/ E78°10'02&quot;/ 408</td>
<td>7.3±0.1</td>
<td>0.24</td>
<td>0.12</td>
<td>280.25</td>
<td>13.2</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Normal value: Nitrogen 280 Kg/hect., Potassium 108 Kg/hect. as per EPA.

FT-IR spectroscopy as a rapid screening tool for TPH (total petroleum hydrocarbon) in contaminated soil is used. The results of FT-IR TPH (Fourier transform infrared spectroscopy) are shown in Figure 1.

The IR absorbance is a measurement of the sum of the entire compound contributes to the total petroleum hydrocarbon result. IR base TPH method measures the absorbance of the C-H bond. Most IR based method in the United State typically measures the absorbance of a single frequency usually 2930cm-1 which corresponds to the stretching of aliphatic CH2 groups. During these studies a number of strong spectral peaks of TPH were detected in the IR spectra (shown in fig.1), which can be compared with standard samples. At a frequency of 2930 cm-1, IR spectrometer measure the energy absorbance of the C-H bonds. Peaks characteristics of alkyl –CH3 and –CH2 stretching vibrations were observed in the range 4500-4200/cm-1 and 3000-2700/cm-1. The results strongly show the presence of TPH in soil samples. IR based method to prove the presence of Total petroleum hydrocarbon but unable to show individual petroleum hydrocarbon because of its limitation and interferences of other organic groups that can affect data quality. GC-MS (Gas Chromatography-Mass Spectrometry) system is used to measure individual of target volatile and semi volatile petroleum constituents.
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Table 2: Analytical data of water sample

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Place name</th>
<th>Longitude/ Latitude/ Elevation (m)</th>
<th>pH</th>
<th>Turbidity</th>
<th>Alkalinity</th>
<th>Total Hardness (ppm)</th>
<th>Total Dissolved Solid</th>
<th>Residual Cl₂</th>
<th>Electrical Conductivity (μs/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hand pump of Kirode</td>
<td>N24°13’55’’/E78°10’32’’/410</td>
<td>7.2 ± 0.1</td>
<td>12.9 NTU</td>
<td>118 mg/L</td>
<td>180</td>
<td>400</td>
<td>nil</td>
<td>0.346</td>
</tr>
<tr>
<td>2</td>
<td>Bora wall of Kathai (Bora)</td>
<td>N24°13’55’’/E78°10’32’’/410</td>
<td>7.6 ± 0.1</td>
<td>16.2 NTU</td>
<td>100 mg/L</td>
<td>220</td>
<td>280</td>
<td>nil</td>
<td>0.589</td>
</tr>
<tr>
<td>3</td>
<td>Wall of Petharia village</td>
<td>N24°15’46’’/E78°10’46’’/408</td>
<td>7.4 ± 0.1</td>
<td>1.5 NTU</td>
<td>98 mg/L</td>
<td>240</td>
<td>360</td>
<td>nil</td>
<td>0.662</td>
</tr>
<tr>
<td>4</td>
<td>Hand pump of Petharia village</td>
<td>N24°15’46’’/E78°10’46’’/408</td>
<td>7.8 ± 0.1</td>
<td>1.6 NTU</td>
<td>200 mg/L</td>
<td>300</td>
<td>360</td>
<td>nil</td>
<td>0.634</td>
</tr>
<tr>
<td>5</td>
<td>Artificial pond near Gate (dump area)</td>
<td>N24°15’59’’/E78°10’35’’/409</td>
<td>8.1 ± 0.1</td>
<td>2.2 NTU</td>
<td>240 mg/L</td>
<td>320</td>
<td>230</td>
<td>nil</td>
<td>0.302</td>
</tr>
<tr>
<td>6</td>
<td>Hand pump of crop area Amrod</td>
<td>N24°16’24’’/E78°17’37’’/399</td>
<td>7.3 ± 0.1</td>
<td>2.6 NTU</td>
<td>110 mg/L</td>
<td>280</td>
<td>400</td>
<td>nil</td>
<td>0.724</td>
</tr>
<tr>
<td>7</td>
<td>Drainage of refinery, Bhurai</td>
<td>N24°15’67’’/E78°11’24’’/391</td>
<td>8.1 ± 0.1</td>
<td>1.2 NTU</td>
<td>125 mg/L</td>
<td>310</td>
<td>410</td>
<td>nil</td>
<td>1.104</td>
</tr>
</tbody>
</table>

Figure 1: FT-IR Spectra of Soil sample.
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Figure 2: GC-MS spectra of soil sample

In this study extractable soil and water samples was performed by comparison of the GC-retention time and the mass spectrometric fragmentation with reference substances. In this case, the identified compounds are Tetradecanoic acid (C14H28O2), 1,2Benzenedicarboxylic acid (C16H22O4) shown in Figure 2 and Figure 3.

The identification of compound is based on the mass spectral data using MS library of SAIF, IIT Bombay. The results from GC-MS analysis show the presence of the PAH (Polycyclic Aromatic Hydrocarbon) and other higher range of petroleum hydrocarbons. Results of GC-MS analysis confirm the presence of the Benzene-1-methyl-hexadecyl C23H40, Tetradecanoic acid, octadecanoic-acid, 2-bromononane, Hexadecanoic acid, Dodecane-46-dimethyl, n-alkenes, unresolved complex mixture of aliphatic originating from extractable sample, PAH (polycyclic aromatic hydrocarbon) such as Pyridine-3(1-methyl-2-pyrolidyl), pyridine, Indene Silane, Norvaline attach with oxygen containing compounds, it’s an acid form and others are present. Some spectra of GC-MS study were shown. The main advantage of the GC-MS method is that it gives more through information about the structure of compound obtains from samples as shown in Fig. 3. These investigations demonstrate that the approach used for the analysis of petroleum hydrocarbon and PAHs in soil and water sample obtain from surrounding areas is useful and accurate. All the methods applied on this investigation and the results obtained clearly show that soil and water are affected by petroleum hydrocarbons which affect the soil fertility and portability of water.

Figure 3: Result of GC-MS spectra
4. Conclusion

The qualitative study of data and results obtained using these methods are pointing that the petroleum hydrocarbon and PAHs are contaminating the surrounding environment. It is essential and important to monitor these natural resources regularly for sustainable and safe development.

Acknowledgments

The authors would like to thank the SAIF IIT Bombay for experimental work of this investigation and UGC for financial support.

5. References


5. EPA Draft Method (1664n), Hexane Extractable Material and silica Gel Treated (9SGT-HEM) by Extraction and gravimetry (oil and Grease and Total Petroleum Hydrocarbon).

6. EPA Draft Method 418.1 Total recoverable petroleum hydrocarbon by IR,Ground Water Analytical Inc. Buzzard.buy.M.A.


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