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Localization of polycyclic aromatic hydrocarbons and heavy metals in surface soil of Asia's oldest oil and gas drilling site in Assam, north-east India: Implications for the bio-economy

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ABSTRACT

The environmental influx of hazardous contaminants viz PAHs and HMs occurs due to oil and gas drilling, and processing of petroleum products in industrial facilities and refineries. This problem plagues crude oil drilling sites as PAHs are an essential component of and HMs coexist with crude oil. We analyzed the spatial distribution of 16 PAHs and 8 HMs in 10 contaminated sites of Assam, a state in India. These included Digboi, where crude oil was drilled in 1867 and the first oil well in Asia that was drilled. The Σ16 PAHs in soil were detected with a minimum of 13.48 and a maximum of 86.3 mgkg^{-1} and Σ 8 heavy metal concentrations in the soil ranged between 69.51 and 336.06 mgkg^{-1}. A negative correlation was detected between the relative concentrations of PAHs and HMs. The results confirmed that the non-biodegradable nature of HMs made them stay in the soil for longer periods of time. In our study, we found that the levels of lead, copper, nickel, and chromium (total) in soil were 73.62, 11.86, 58.97 and 158.66 mgkg^{-1}. The recovery percentage for PAHs and HMs were in the range of 67–97% and 90–95% respectively. Spatial distribution indices for Phenanthrene/Anthracene, Naphthalene/Acenapthhylene, Chyrsene/Benzo (*g*, *h*, *i*) perylene and Fluranthene/Pyrene) calculated for soil samples indicated that the spatial distribution of PAHs in soil is uneven which might be due to variations in contaminates disseminated in soil. Such regionalized concentration has serious implications on the bio-economy both in terms of health and economy, especially since the proximity of crude oil sites to paddy fields and/or tea plantations uniquely marks the landscape of upper Assam.

1. Introduction

Emerging contaminants came to occupy the center of environmentalism since the 1960s primarily due to the groundbreaking work of Rachel Carson who, in her landmark book *Silent Spring*, presented an apocalyptic vision of a world made barren by them [6]. The picture prophesied by Carson, while imaginary, is by no means irrelevant. It points to the bleak possibilities of the globe overridden with pollution that chokes its very life by entering into its soil, water, air; in effect every single one of its support systems. This is borne out by other case studies similar to Carson's but focusing on a range of other contaminants including polycyclic aromatic hydrocarbons (PAHs) and heavy metals (HMs). A case in point is South Central China, where 18 wild plant species were detected with simultaneous accumulation of PAHs and HMs from contaminated substrates, although disparities of PAHs and HMs in spatial distributions among sites was evident [40]. The concurrent accumulations of HMs and PAHs have gained substantial attention since soils impure with PAHs were often reported to contain high amounts of heavy metal [41,46]. A case of uptake of selected PAHs from contaminated soils by rice seedlings (*Oryza sativa*) in a rice ecosystem in Jinxing of Zhejiang Province, China, focused on the facts that PAHs were taken up by rice roots via passive processes

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and that their uptake was correlated with concentrations of PAH in rhizosphere [39]. Numerous studies have confirmed that the combination of these binary types of contaminants could present a great environmental threat to all biotic components of the ecosystem [23] and therefore the US Environment Protection Agency has ranked them (16 PAHs and Pb, As,Cr, Cd, Zn) among the top 12 contaminants of concern [43]. What emerges from this is the magnitude of the threat posed by these contaminants to the ecosystems around the world and the urgency with which this issue needs to be addressed.

The transport of polycyclic aromatic hydrocarbons (PAHs) and heavy metals (HMs) from point source to various components of the ecosystem is one of the major factors that jeopardize the well-being of the environment. PAH and HM co-exist with petroleum hydrocarbons and their infiltration into the environment causes contamination of soil and sediments which puts plants, animals and all living organisms at great risk [3]. PAHs are organic contaminants and are bound to suspended particles in the ecosystem due to their highly hydrophobic nature. However the most dominant PAHs in surface soil were those that had molecules with 2–3 rings [25]. These pollutants ultimately sink into the soil through wet deposition. The persistence of PAHs is therefore a serious environmental concern as they are actively carcinogenic, teratogenic and mutagenic, threatening the biota [9]. Previous research in this area has confirmed that 1, 2 and 3 fused benzenoid rings PAH are acutely toxic [36], while higher molecular weight PAHs are strongly suspected to be carcinogens [26].

The anthropogenic origin of PAHs is of great concern, especially in today's world. The point sources of PAHs have been briefly described by Ref. [47] and the refining and distillation of petroleum is one of the important causes of PAH contamination in the environment. The concentration of PAHs is approximately 2–10 times higher in urban areas (which are the usual centers of industries and refineries) than in rural areas [45]. This might be because oil drilling sites are a major source of PAH and heavy metal pollution but suffers from poor management and lack of environmental controls, which, in turn, may have a significant impact on the surrounding environment. PAHs are found in environmental samples almost always as complex mixtures. Drill Cuttings (DC), Water Base Mud (WBM), drilling fluids (DF),Oil Base Mud (OBM), consist of paraffins, cycloalkanes, alkenes, aromatics, sculpture compounds, nitrogen-oxygen compounds, and heavy metals, viz, Nickel, Chromium, zinc, manganese, cadmium, copper, and lead [5,10]. Crude oil is the most important and predominant energy resource for humans and the raw material of various petroleum products which are essential for daily life. However, during crude oil exploration, a vast amount of drilling mud/fluid is generated. Further, oil spills, leaks, and other releases of petroleum occur frequently during its transportation and result in the contamination of cultivated soil and groundwater, especially when associated with accidental spills [10]. This huge amount of toxic and persistent pollutants like PAHs, HMs, oil, grease, phenols, drilling fluid and mud affect organisms in the biosphere from genetic through molecular levels [44].

The effects of PAHs on mammalian health have been extensively studied [8] and findings have established that HMW-PAHs attack DNA to form covalent adducts with DNA. These PAHs and their primary metabolites cause chromosomal aberrations (hypodiploidy and hyperdiploidy, deletion and breaking) in mammalian systems after chronic exposure and can lead to mutations [15]. Moreover, due to their lipid solubility, PAHs are rapidly absorbed after entering the gastrointestinal tract [7], making this a major exposure route of PAHs.

PAHs are adsorbed and accumulated in the upper surface layer (humus) of soil and thus find their way into the ecosphere [17]. The soil matrix seems to act as the long-term storage area for PAHs as they are transported there, as stated above. Therefore spatial distribution indices of PAHs can be considered to be a reliable indicator of the state of environmental pollution in a given area. A significant percentage of PAHs released into the environment through anthropogenic sources disappear by photo-oxidation and biodegradation by plant microbes associations. However, a considerable amount is retained in soil surfaces from which living organisms come into contact with these PAHs. Furthermore, the incremental magnification of PAHs in the food chain damages the health of the ecosystem [13,27]. Although many plants have a range of potential cellular mechanisms to detoxify PAHs and HMs, they have certain limits beyond which even these plants cannot cope increased concentrations of these contaminants. It has also been observed that phytotoxicity increases in the presence of HMW-PAHs. In addition to soil environments, there is a significant concern of bio-accumulation of PAHs in aquatic environments too. Certain aquatic invertebrates bio-concentrate PAHs from the environment although only a limited number of such species have so far been identified. On the other hand phytoplanktons transport PAHs and play a vital role in their initial biotransformation [11].

There are a variety of mechanisms by which PAHs are degraded in the environment, including chemo-oxidation, photo-oxidation, and microbial degradation, which are considered to be the primary route of degradation of PAHs in soil [19]. In spite of such mechanisms PAHs still exist in soil in moderate to high concentrations. Many environmental regulatory agencies have established the critical limits for PAHs in soil in an attempt to reduce environment pollution and high risk of potential exposure to PAHs.

In this monitoring study, an attempt has been made to assess the spatial distribution of PAHs and HMs in the vicinity of Asia's oldest crude oil exploration site – Assam, a northeastern state of India (Fig. 1). Juxtaposition of crude oil exploration sites with rice fields or tea plantations is a predominant feature of the landscape, especially in the upper regions of the state. Therefore, accidental spillage during drilling and transportation and subsequent contamination of tea and rice field is a common feature in these regions. Moreover, it has been established that heavy metals enter into plant bodies in acidic soil [16]. By implication then, since tea plants normally grow in acidic soil, they become prone to accumulate heavy metals in their systems. This possibility necessitates a serious consideration of the impact of oil drilling sites on tea plantations near them, given the importance of tea in the state's (and by extension the country's) bioeconomy.

2. Materials and methods

2.1. Chemicals and reagents

For the purpose of our experiments on PAHs, Standard Pyrene, Anthracene, and Phenanthrene were procured from Spectrochem (Mumbai, India), and Acenaphthene, Acenaphthylene, Benzo(*a*) anthracene, Benzo(*a*)pyrene, Benzo(*b*)flouranthene, Benzo(*ghi*) pyrelene, Benzo(*k*)fluoranthene, Chrysene, Dibenzo(*a,h*) anthracene, Fluoranthene, Fluorene, Indeno (1,2,3,-*c,d*) pyrene, Naphthalene standards were procured from Sigma (St. Louis, MO, USA). The reference stock solutions were prepared by dissolving individual PAHs in analytical grade acetone (Merck Germany). The purity of each standard was ranged between 95 and 99%.

2.2. Soil sample collection sites

In this study soil samples were collected from 10 different crude oil drilling sites in Jorhat, Sivasagar, Dibrugarh and Tinsukia