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Role of black carbon in soil distribution of organochlorines in Lesser Himalayan Region of Pakistan☆

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ABSTRACT

Black carbon and total organic carbon (TOC) along with organochlorines (OCs) were analyzed in soils from four sampling zones of Lesser Himalayan Region based on source proximity/anthropogenic influences along the altitude. CTO-375 method was used for BC analysis while OCs were analyzed by GC-MS/MS system. BC and TOC ranged between 0.16–1.77 and 6.8–41.3 mg g^{-1} while those of OCPs and PCBs ranged between 0.69 and 5.77 and 0.12–2.55 ng g^{-1}, respectively. ∑DDTs were the dominant (87.9%) among OCPs while tri- and tetra- (65.5%) homologue groups among PCBs. Hexa-PCBs, however also showed higher contribution (20.4%) in the region. Source diagnostic ratios of DDE + DDD/DDT (0.1–1.53) indicated both fresh and old input while α-HCH/γ-HCH (0.19–2.49) showed presence of lindane in the region. Higher concentration of OCs were observed in Zone C at altitudinal range of 737–975 masl that are close to the human influences and potential sources of POPs. The results of linear regression analysis revealed potential input of BC in soil distribution of OC concentrations in the region.

1. Introduction

Persistent organic pollutants (POPs) such as organochlorine pesticides (OCPs) and industrial chemicals like polychlorinated biphenyls (PCBs) have been the focus of global concern in recent decades due to their persistence, bioaccumulation and omnipresence in the environment (Ali et al., 2014a; Chakraborty et al., 2013; Chakraborty et al., 2016; Li et al., 2015). Though, these chemicals have been banned or restricted in many countries, still their presence in environmental media, particularly far from areas of their application and production, is a matter of serious concern (Ali et al., 2014b; Muir et al., 1996; Rose et al., 2001). These chemicals migrated from warmer to colder regions where they undergo fractionation on altitudinal or latitudinal gradients (Zhang et al., 2002). Some of the selected POPs undergo preferential accumulation at high altitude mountain regions (Blais et al., 1998; Yang et al., 2013), a process termed “orographic” or “mountain cold trapping”. This orographic phenomena is different from “cold condensation” of high latitude regions in terms of closer proximity to emission sources (Tremolada et al., 2008), densely populated and industrialized regions (Kallenborn, 2006), local meteorological influences and changes in ecological gradients across short distances (Liu et al., 2014). The recent interest in studying the levels of POPs in mountain regions indicate the importance of high altitude environments (Ali et al., 2017a) in terms of ecotoxicity.

Refractory organic residues such as black carbon (BC) has received much interest due to its importance in many biogeochemical processes such as earth's radiative heat balance, global carbon cycle and as a pollutant carrier (Goldberg, 1985; Solomon, 2007). Though, there is no agreement on the definition of black carbon in the literature (Petzold et al., 2013) but generally this term refers to the carbonaceous particles formed during incomplete combustion of biomass or fossil fuels (Goldberg, 1985; Ni et al., 2014; Schmidt and Noack, 2000; Schmidt et al., 2001). BC has been reported to be ubiquitous in the environment, where it acts as a strong sorbent for POPs, thereby affecting the behavior of POPs in the soils (Cornelissen et al., 2005; Sun et al., 2008). Hydrophobic organic pollutants sorb with BC via occlusion into the carbon condensed structure, conditioning their transport to that of BC

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particles and limiting their bioavailability (Ahrens and Depree, 2004; Huang et al., 2003; Jonker and Koelmans, 2002; Koelmans et al., 2006).

The Greater Himalayas is a massive mountain range of 2400 km^2 in Asia that makes an arc from west to east and separates the Indian subcontinent from Tibetan Plateau. It has been divided into Higher Himalaya, Sub Himalaya and Lesser Himalaya, based on tectonics and structural data (Mughal et al., 2016). The Lesser Himalaya stretches along the main boundary thrust fault zone, with steep southern face and gentler northern slopes. In Pakistan, the Lesser Himalaya (north latitude: 33°-44′/35°-35′ and east longitude: 72°-33′/74°-05′) comprised of Azad Jammu & Kashmir (AJK), Rawalpindi-Islamabad districts and the entire Hazara division with an estimated area of 23,295 km^2 (Hussain and Ilahi, 1991). Hazara and Kalachitta are the two major geological zones of the Lesser Himalaya (Champion et al., 1965). The climate of Lesser Himalayas shows tremendous variations owing to altitude aspects, topography and vegetation cover of the region. Climatically, the region is categorized into subtropical continental lowland (foothills zone and plain) and subtropical continental highland (Murree, Siwalik, Hazara hills and outer and middle Himalayas). The average rainfall in the Lesser Himalayas varies between 70 and 90 mm in southern parts whereas 100–130 mm in northern parts. During winter, a large part of precipitation is in the form of snow. The vegetation of the region falls within subtropical, temperate, sub alpine and alpine zones (Abbasi et al., 2013). Studying the levels of POPs along with their relationship with carbon moieties in Lesser Himalayan Region is important due to its closer proximity to industrialized regions of Pakistan, India and China. Particularly, densely populated countries of South Asian region are situated in south of Himalayan range that are susceptible to high POPs emission (Ali et al., 2018). Therefore, this study was intended to investigate the levels of BC, TOC, OCPs and PCBs along with their relationship in soils of Lesser Himalayan Region. According to our knowledge, no study has been focused in depicting the detailed assessment of potential role of BC and TOC in distribution status of soil OCs in Lesser Himalayan Region. The specific objectives of this study were: (i) to assess the levels of OCs, BC and TOC in soils from Lesser Himalayan Region; (ii) to study the role and relationship of BC and TOC in distribution of OCs in Lesser Himalayan Region and (iii) to elucidate the composition profiles of OCs in Lesser Himalayan Region.

2. Materials and methods

2.1. Study area and soil sampling

For soil sampling, Azad Jammu & Kashmir (AJK) was selected from Lesser Himalayan Region that is located northeast of Pakistan (Fig. 1). The whole study region was divided into four zones from different altitudinal ranges i-e., Zone A (357–383 masl), Zone B (397–733 masl), Zone C (737–975 masl) and Zone D (1351–2324 masl). The assumed order to anthropogenic influence and POPs source proximity was as follows: Zone C > B > A > D. Eight soil samples from each zone were collected. Further details regarding sampling locations and zones of the sampling region can be found elsewhere (Ali et al., 2018, 2017b). SI Table 1 provide the details of all the sampling locations as well. Soil samples were collected at 0–10 cm depths. Schuster et al. (2011) collected surface (0–5 cm) and subsurface (5–10 cm) soil samples. This depth for soil sampling is important in terms of studying POPs biogeochemical processes. Prior to collection of the sample from each site, the debris and vegetation layer was removed. Soil samples were collected in composite of three from each sampling site. Corrosion free hand trowel was used for collection of all soil samples and kept in polyethylene bags. Soil sampling was done in accordance with procedure of USDA (Burt, 2009). They were then transported to the Department of Environmental Sciences, Quaid-i-Azam University where stored frozen at −4 °C until further analysis.

2.2. Extraction, clean-up, GC-MS analysis and QA/AC

Organochlorines were analyzed in soil samples according to the defined method (Ali et al., 2017b, 2014a, 2015c; Bajwa et al., 2016) which is provided in supporting information in detail. Briefly, 20 g of sample was taken from composite soil sample from each site and was subjected to Soxhlet extraction system using dichloromethane (DCM). Prior to start the Soxhlet extraction, surrogate recovery standards including PCB–30, –198, –209 and TC*m*X were added to each of the sample. Clean-up of the extracted samples was done by using column chromatography. GC–MS/MS Agilent 7890/7000 (column: VARIAN, CP–Sil 8 CB, 50 m, 0.25 mm, 0.25 μm capillary column) system was used for the analysis of OCPs and PCBs. This system was operated in multiple reaction monitoring mode with an EI source (−70 eV). Keeping in view the QA/QC procedures (supporting information), the resulting values were not blank and recovery corrected because there was no significant contamination observed for blanks and surrogate recoveries were greater than 75%. Following analytes of OCPs and PCBs were targeted in soil samples: α–HCH, β–HCH, γ–HCH, *o,p*′–DDD, *p,p*′–DDD, *o,p*′–DDE, *p,p*′–DDE, *o,p*′–DDT, *p,p*′–DDT, *cis*–chlordane (CC), *trans*–chlordane (TC), β–endosulfan, heptachlor, HCB, tri–PCBs (–28, –37), tetra–PCBs (–44, –49, –52, –60, –66, –70, –74, –77), penta–PCBs (–82, –87, –99, –101, –105, –114, –118, –126), hexa–PCBs (–128, –138, –153, –156, –158, –166, –169) and hepta–PCBs (–170, –179, –180, –183, –187, –189).

2.3. Physic–chemical parameters

The pH and EC (μS/cm) of all the soil samples were examined by Milwaukee (SM802) portable meter while the grain size composition i-e., percentage of sand, silt and clay was determined by Bouycous hydrometer method (Ali et al., 2015b). For total organic carbon analysis, soil samples were first treated with 1 M HCL in order to remove inorganic carbon (Sun et al., 2008) and then subjected to Vario EL III Elemental Analyser (Germany) for analysis. Black carbon analysis was done by employing chemo-thermal oxidation method (CTO–375), previously used by (Ali et al., 2014a, 2015a; Elmquist et al., 2008; Elmquist et al., 2007; Gustafsson et al., 2001). According to this method, dried soil samples (2–3 g) were first exposed to thermal oxidation at 375 °C for 18 h in a muffle furnace under constraint air flow and then digested with 1N HCL. The residual organic carbon was analyzed as black carbon using Vario EL III Elemental Analyser (Germany).

3. Results and discussion

Table 1 provides the summary of pH, EC and texture of all soil samples collected from different zones of the Lesser Himalayan Region. Generally, the pH was slightly acidic to basic (6.3–8.4) with average of 7.4 ± 0.5 in Lesser Himalayan Region. EC ranged between 110 and 310 μS/cm with average value of 198 ± 62 μS/cm. Sand fraction ranged between 43.5 and 73.8% followed by silt (3.8–41.8%) and clay (12.5–30%) with average values of 52.3 ± 7.1, 25.2 ± 8.3 and 22.5 ± 4.1%.

3.1. Total organic carbon and black carbon

The carbon content (TOC and BC) from Lesser Himalayan Region is shown in Table 2 and comparison with soils of mountainous and

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