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Occurrence and sources of natural and anthropogenic lipid tracers in surface soils from arid urban areas of Saudi Arabia

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ABSTRACT

Soil particles contain a variety of natural and anthropogenic organic components, and in urban areas can be considered as local collectors of pollutants. Surface soil samples were taken from ten urban areas in Riyadh during early winter of 2007. They were extracted with dichloromethane-methanol mixture and the extracts were analyzed by gas chromatography-mass spectrometry. The major compounds were unresolved complex mixture (UCM), plasticizers, n-alkanes, carbohydrates, n-alkanoic acids, hopanes, n-alkanols, and sterols. Vegetation detritus was the major natural source of organic compounds (24.0 ± 15.7%) in samples from areas with less human activities and included n-alkanes, n-alkanoic acids, n-alkanols, sterols and carbohydrates. Vehicular emission products and discarded plastics were the major anthropogenic sources in the soil particles (53.3 ± 21.3% and 22.7 ± 10.7%, respectively). The anthropogenic tracers were UCM, plasticizers, n-alkanes, hopanes and traces of steranes. Vegetation and human activities control the occurrence and distribution of natural and anthropogenic extractable organic matter in this arid urban area.

1. Introduction

Biogenic and anthropogenic organic matter (OM) is a major carbonaceous fraction in different ecosystems (e.g. Hansell and Carlson, 2014; Lischke et al., 2014; Schmidt et al., 2011). The occurrence and concentrations of OM in urban and rural/remote region soils vary spatially and seasonally (Fraser et al., 1998; Kononova, 2013; Oros et al., 2002; Trendel et al., 2010). One of the primary sources of OM in soil is material from plant litter. Other sources include anthropogenic organic chemicals such as pesticides and fossil fuel residues from vehicles (Al-Mutlaq et al., 2005, 2007; Rushdi et al., 2005, 2013; Yang et al., 2013). The composition, properties and distribution of this OM controls the formation of soil organic matter (SOM) and humification processes (Kononova, 2013; Scholes et al., 1997; Schmidt et al., 2011). Microbial activity and biomass are also important factors in SOM formation and alteration (Schmidt et al., 2011). Therefore, SOM varies in composition and properties. The major studies on soil OM have focused on bulk properties (Kögel-Knabner, 2000; Martin and Haider, 1986), whereas extractable organic matter (lipid) studies are relatively few (Otto and Simpson, 2005; Rogge et al., 2012; Rushdi et al., 2005, 2006). Less attention has been paid to the lower molecular weight OM (Kögel-Knabner, 2000).

Lipid compounds usually comprise 1–5% of the total SOM. They are derived from plants, fungi, bacteria and mesofauna, and generally consist of n-alkanes, n-alkanols, wax esters, fatty acids, steroids, terpenoids and acyl glycerols (Oros et al., 2002). These products are a result of decomposition and exudation of OM from various sources (Miller and Donahue, 1995). Lipids can be found

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either free in the soil matrix, chemically bound in humic and fulvic material, or absorbed to soil particles (Kononova, 2013; Schmidt et al., 2011).

Thus, characterization and identification of organic compounds and OM contents of surface soils are important for understanding the OM composition and compound sources that may be introduced to the different environmental compartments, such as for example: (1) absorption into the food chain, (2) advection into the atmosphere via dust resuspension, machinery and/or human activities, and (3) wash-in to water reservoirs. It will also aid to better understand the various effects on human health and environmental assessment processes.

The extractable organic matter (EOM) of surface soil has not been fully characterized for the Arabian Peninsula region. The preliminary results have shown that soil and sand dusts from Kuwait and Saudi Arabia contained a mixture of natural and anthropogenic OM (Al-Mutlaq et al., 2002, 2007; Rushdi et al., 2005, 2006). Based on aliphatic hydrocarbon contents of soil from Riyadh, the natural and anthropogenic sources ranged from 20 to 57% and from 30 to 55% of the total lipid tracers, respectively (Rushdi et al., 2005). Soil and sand samples from the vicinity of Kuwait City showed that the natural sources ranged from 15 to 78% and the anthropogenic sources ranged from 8 to 88% of the total lipid compounds (Rushdi et al., 2006).

The research hypotheses of this work are: (1) the EOM sources in soils of an urban arid region is mainly from traffic emissions; and (2) the sources of natural EOM are relatively low and are primarily from soil microbiota with lesser contributions from vegetation. Therefore, the main objectives of this work are to: (1) determine the chemical composition of the solvent EOM in soils from arid urban areas in Saudi Arabia, (2) identify the main sources of the EOM, and (3) examine the relative changes in the source abundances of the EOM. Consequently, surface soil samples were collected from various locations such as public parks, streets, and agricultural fields in the city of Riyadh to investigate the occurrence of natural biogenic and anthropogenic lipid compounds.

2. Experimental methods

2.1. Sampling and extraction procedure

Surface oil samples were collected in November 2007 from different metropolitan areas of the city of Riyadh in Saudi Arabia to characterize their solvent extractable lipid contents by gas chromatography-mass spectrometry (GC–MS) analysis. The samples were taken by scraping the uppermost layer (~1 cm) of the soil in a 30 cm^2 area of exposed surface. The locations of the samples were chosen to represent urban areas in and around Riyadh, ranging from highly populated, with different human activities such as public markets (OL), governmental site (NZ), industrial area (MN), rural areas with limited human impact (OG), and areas with agriculture (AQ, JZ, DR) (Fig. 1).

After air drying, each sample was sieved to obtain the fine particles (<125 μm) before extraction. The extraction was performed twice by adding a mixture of dichloromethane/methanol (40 mL 3:1 v/v) to about 5 g of the particles of each sample, ultrasonicating for 20 min, and then filtering through pre-extracted glass microfiber filters (*Whatman*®, GF/A filters). Each total extract was concentrated under nitrogen blow-down at room temperature to approximately 1.0–1.5 mL before GC–MS analysis. A 50 μL aliquot of each total extract was also derivatized with silylating reagent [N,O-bis(trimethylsilyl)trifluoroacetamide, BSTFA, *Pierce Chemical Co*] by the standard procedure before analysis by GC–MS. This derivatizing agent replaces the H in hydroxyl groups with a trimethylsilyl [$(CH_3)_3Si$, i.e., TMS] group for better GC resolution of polar compounds.

2.2. Instrumental analysis

The analyses of the total and silylated extracts were carried out by GC–MS, using an Agilent 6890 GC coupled to a 5973 Mass Selective Detector with a DB-5 (*Agilent*) fused silica capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) and helium as the

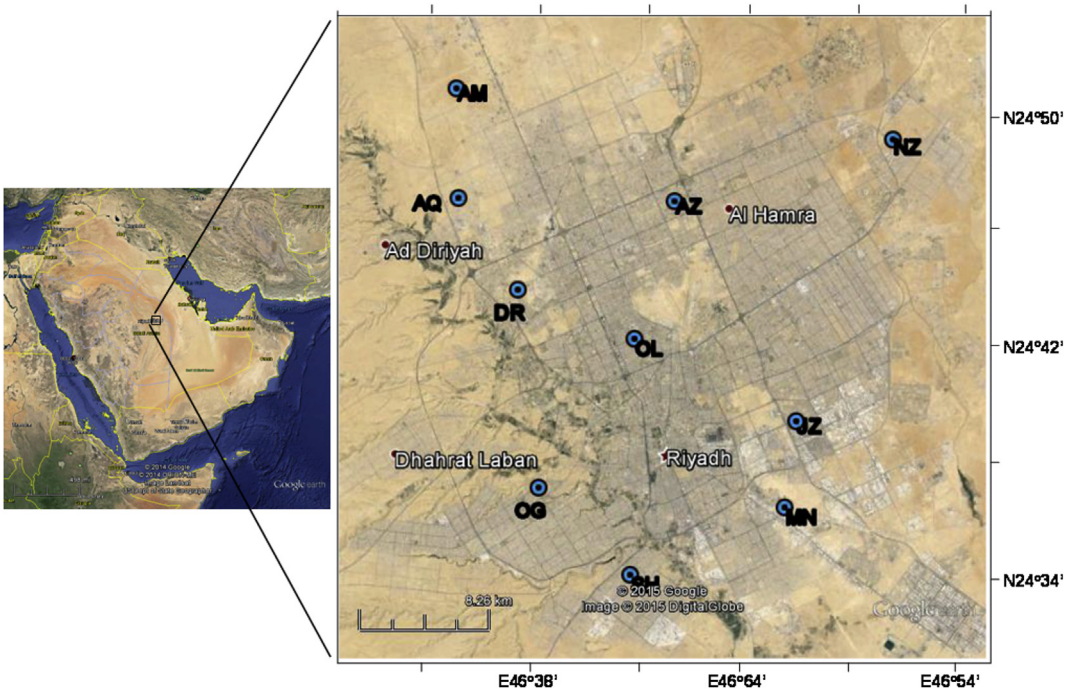

Fig. 1. Map showing the sampling sites and locations of the soil samples.