



One century of air deposition of hydrocarbons recorded in travertine in North Tibetan Plateau, China: Sources and evolution



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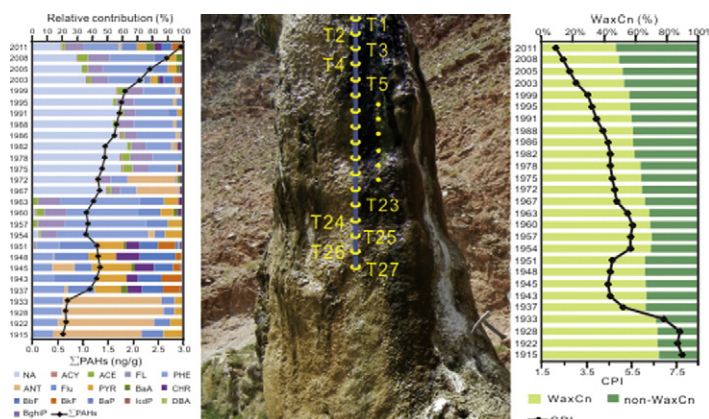
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HIGHLIGHTS

- Travertine was first used as a natural medium to study historical air deposition.
- One century of the air environment of hydrocarbons was reconstructed.
- The possible sources for hydrocarbons in NTP were identified.
- The evolution of NPT regionally and worldwide great events was reviewed.

GRAPHICAL ABSTRACT



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ABSTRACT

The characteristic distribution patterns of hydrocarbons have been used for fingerprinting to identify their sources. The historical air depositions of hydrocarbons recorded in natural media help to understand the evolution of the air environment. Travertine is a natural acceptor of air deposition that settles on the ground layer by layer. To reconstruct the historical air environment of hydrocarbons in the North Tibetan Plateau (NTP), a unique background region, twenty-seven travertine samples were collected systematically from a travertine column according to its precipitated year. For each sample, the precipitated year was dated while *n*-alkanes and polycyclic aromatic hydrocarbons (PAHs) were determined. Based on source identification, the air environment of hydrocarbons in the past century was studied for the region of NTP. Before World War II, the anthropogenic sources of hydrocarbons showed little influence on the air environment. During World War II and China's War of Liberation, hydrocarbons increased significantly, mainly from the use of fossil fuels. Between 1954 and 1963, hydrocarbons in the air decreased significantly because the sources of petroleum combustion decreased. From the mid-1960s through the end of the 1990s, air hydrocarbons, which mainly originated from biomass burning, increased gradually because agriculture and animal husbandry were developing steadily in Tibet and China. From the late 1990s, hydrocarbons in the atmosphere increased rapidly due to the rapid increase of tourism activities, which might increase hydrocarbon emissions from traffic. The reconstruction of the historical air hydrocarbons in NTP clearly reflects the evolution of the region and global development.

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1. Introduction

Aliphatic and polycyclic aromatic hydrocarbons (PAHs) play an important role in source identification because each source gives rise to characteristic distribution patterns of these compounds, known as hydrocarbon fingerprinting (Pietrogrande et al., 2010; Commendatore et al., 2012; Riccardi et al., 2013). PAHs are produced during fossil fuel combustion and biomass burning. *n*-Alkanes, which are straight-chain saturated hydrocarbons, are emitted from anthropogenic (fossil fuel combustion and biomass burning) and natural (plant wax and soil) sources (Miyake et al., 2006). Both PAHs and *n*-alkanes are highly resistant to degradation in the environment. Nevertheless, the majority of studies to elucidate hydrocarbon sources have focused on urban or populated areas and identified the sources as sediments, suspended matter, aerosols, and soils (Duan et al., 2010; Tobiszewski and Namiesnik, 2012; Riccardi et al., 2013; Bigus et al., 2014; Suneel et al., 2014). Recently, hydrocarbons in environmental background areas have garnered significant attention because the occurrence of hydrocarbons in background areas without point sources are more suitable to elucidate their regional or global cycling (Li et al., 2010; Yuan et al., 2014, 2015; Jautzy et al., 2015).

The atmosphere is a critical component in the global transport and cycling of hydrocarbons. Long-range atmospheric transport (LRAT) provides a mechanism to distribute hydrocarbons widely throughout the global environment (Dalla Valle et al., 2005). Due to LRAT, hydrocarbons can reach and affect remote ecosystems at high latitudes (Miyake et al., 2006; Friedman et al., 2014) and altitudes (Wania and Westgate, 2008). Therefore, the transported hydrocarbons can be preserved in sediments and glaciers in remote background areas where they were scavenged from air as dry or wet depositions, which are commonly used as tracers to reconstruct historical environmental changes at regional or global scales (Miyake et al., 2006).

The Tibetan Plateau (TP) is one of the most remote and isolated regions in the world and is often referred to as the “Roof of the World” or the “Third Pole” due to its high altitude (Yang et al., 2010). Hydrocarbons in sedimentary or glacial cores have received little attention for reconstructing the historical environmental changes in TP (Wang et al., 2008, 2010). Nevertheless, the previously studied areas focused either on the Himalaya region in southern TP, dominated by the Indian monsoon (Wang et al., 2008), or on the Qinghai Lake in eastern TP, dominated by the eastern Asian monsoon (Wang et al., 2010). Due to the difficulty of sampling, few reports on hydrocarbons in North TP (NTP), dominated by westerly wind, have been made. With the exception of altitude, the meteorological characteristics of NTP are completely different from those of southern and eastern TP, as NTP is a semi-arid region. Additionally, NTP is also the National Nature Reserve for Tibetan antelope. As NTP experiences very little human activity, anthropogenic hydrocarbons in the atmosphere should originate primarily by LRAT (Yuan et al., 2014, 2015). Therefore, identifying hydrocarbon concentrations and sources at different times is important for understanding the historical changes in the environment.

Travertine is a form of limestone deposited by mineral springs and is formed by a process of rapid precipitation of calcium carbonate (Török and Vásárhelyi, 2010). Similar to a glacier, travertine precipitates and consolidates upon the ground layer by layer. Due to these characteristics, travertine is a natural sampler for air deposition. The hydrocarbons deposited through both dry and wet air deposition are sealed and recorded in travertine at the corresponding layer. In comparison, glaciers primarily preserve only wet deposition, and hydrocarbons in sediments, particularly *n*-alkanes, are mixed with those from soils. Therefore, travertine is an ideal natural medium for recording historical air deposition and the air environment.

In this study, PAHs and *n*-alkanes in travertine cores were analyzed, and the primary goals were (1) to study the historical air deposition in NTP; (2) to identify the sources at different times using detailed hydrocarbon fingerprinting; and (3) to reveal the regional and global environmental evolutions in the past century.

2. Materials and methods

2.1. Sampling and dating

The sample site is proximate to Rongma Lake, which is located in Nima County of North Tibet (E86.5985°, N32.9625°, H4715 m), and the travertine column was growing vertically on the ground (Fig. 1). At the top, travertine was precipitated *in-situ* in 2011 with hot water at 40–50 °C. The samples were collected systematically layer by layer, starting at the top of the column, at an interval of 1.5–2 cm. Travertine samples were analyzed for ²¹⁰Pb, ²²⁶Ra and ¹³⁷Cs using a EURISYS Gamma Spectrometry at the Institute of Geology and Geophysics, Chinese Academy of Sciences. ¹³⁷Cs was measured at 662 keV, while ²¹⁰Pb was obtained via gamma-emission at 46.5 keV and ²²⁶Ra at 295 and 352 keV γ -rays emitted by its daughter isotope ²¹⁴Pb. The methods used were detailed in our previous study (Yuan et al., 2011).

2.2. Chemicals

The 16 US EPA priority PAHs and 21 *n*-alkanes (C₁₄–C₃₄) standard solutions (1000 μ g/mL) were products of Supelco (Bellefonte, PA, USA). The PAHs included naphthalene (NA), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FL), phenanthrene (PHE), anthracene (ANT), fluoranthene (Flu), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenzo[a,h]anthracene (DBA), and benzo[ghi]perylene (BghiP). In addition, 2-fluorobiphenyl (2-FBP) was used as a surrogate standard for the PAHs. Silica gel (100–200 mesh) (Qingdao Haiyang Chemical Co., Qindao, China) was activated in a drying oven at 550 °C for 6 h. Anhydrous sodium sulfate (Beijing Chemical Factory, China) was heated at 600 °C for 12 h to eliminate the remaining organic contamination. The solvents were all of analytical or pesticide grade.

2.3. Extraction and cleanup

Ten grams of each soil sample was ground with anhydrous sodium sulfate into a free-flowing powder. Each sample was extracted with 30 mL of hexane/dichloromethane (1:1, vol/vol) by ultrasonication for 4 min and subsequently centrifuged. This process was repeated three times, and the extracts were combined. The concentrated extracts were evaporated to 1 mL in a Kuderna–Danish concentrator under a gentle N₂ stream. Prior to extraction, 2-FBP was added as a surrogate standard. Extracts were cleaned with a chromatography column (30 cm \times 10 mm i.d.) containing 4 g of silica gel and 2 g of anhydrous sodium sulfate. The column was pre-eluted with 40 mL of hexane/dichloromethane (4:1, v/v) prior to loading the sample. The fraction containing the 16 PAHs and *n*-alkanes was eluted using 60 mL of hexane/dichloromethane (4:1, v/v). The solvent was evaporated for analysis to 30 μ L in a K–D concentrator under a gentle N₂ stream. Throughout the extraction, cleanup and analysis procedure, the analyses were protected from light by either wrapping the containers with aluminum foil or using amber glassware.

2.4. Analysis

The hydrocarbons were measured with an Agilent 6890 gas chromatograph (GC) coupled with an Agilent 5973 mass spectrometer using electron impact ionization in the SIM mode. The separation was performed on a fused silica capillary column (DB-5MS, 30 m \times 0.25 mm i.d., 0.25 μ m film thickness). The GC column was programmed as follows: an initial temperature of 100 °C for 2 min, an increase to 160 °C at a rate of 10 °C/min, an increase to 280 °C at a rate of 4 °C/min, and subsequently, a 10 °C/min increase to 300 °C, which was maintained for 10 min.

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