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Gas-particle distributions, sources and health effects of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs) in Venice aerosols

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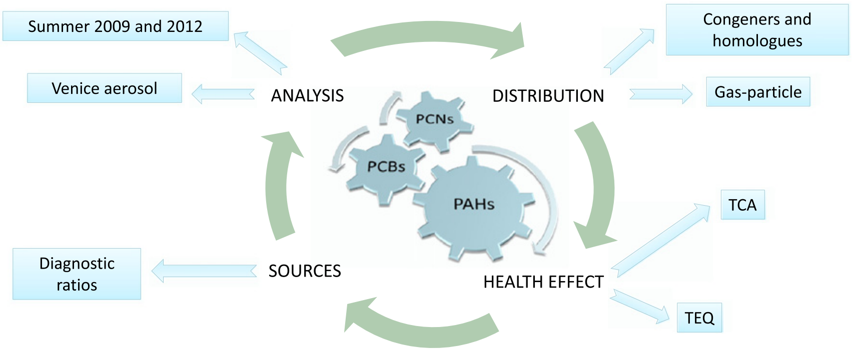
HIGHLIGHTS

- Gas-particle distribution of POPs in Venice is discussed.
- PCB-11 was found for the first time in aerosols in Venice and Europe.
- A high concentration of PCN-42 in 2009 samples was measured.
- Traffic was the major source of PAHs.
- A toxicological evaluation by TCA and TEQ methods was conducted.

GRAPHICAL ABSTRACT



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ABSTRACT

Air samples were collected in Venice during summer 2009 and 2012 to measure gas and particulate concentrations of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs). PCB-11, considered a marker for non-Aroclor contamination of the environment, was found for the first time in the Venetian lagoon and in Europe. An investigation on sources has been conducted, evidencing traffic as the major source of PAHs, whereas PCBs have a similar composition to Aroclor 1248 and 1254; in 2009 a release of PCN-42 has been hypothesized. Toxicological evaluation by TCA and TEQ methods, conducted for the first time in Venice air samples, identified BaP, PCB-126 and PCB-169 as the most important contributors to the total carcinogenic activity of PAHs and the total dioxin-like activity of PCBs and PCNs.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs) are semi-volatile organic compounds that are persistent and ubiquitous in the environment. PAHs can be produced by incomplete combustion from

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natural origins (e. g. volcanism, natural fires) or from anthropogenic origins (e. g. combustion of timber, waste, and fossil fuels). PCBs were first synthesized in 1929 and were widely used as dielectric fluids, hydraulic fluids and in many other applications until they were banned in the late 1970s (Desaules et al., 2008). PCNs were used in the electrical industry owing to their water-repellent, flame-retardant, dielectric and fungus-resistant properties. In addition, PCNs can be unintentionally generated by several industrial processes and by incomplete combustion from waste incinerators (Manodori et al., 2006a). Because of their toxicity and low reactivity PAHs, PCBs and PCNs are classified as POPs (Persistent Organic Pollutants) (Helm and Bidleman, 2003; UNECE, 1998).

POPs are affected by long-range atmospheric transport (LRAT) and their presence has been discovered in remote environments such as the Arctic (Hung et al., 2005; Polkowska et al., 2011) and Antarctica (Dickhut et al., 2012; Klanova et al., 2008; Negri et al., 2006). Bioaccumulation of these substances can cause adverse effects on human health including reproductive and immune effects, developmental anomalies and cancer (Desaules et al., 2008; Gambaro et al., 2004). Generally the atmospheric burden of POPs is relatively small compared to other environmental constituents but air is considered the most important pathway for their global redistribution (Piazza et al., 2013).

PAHs, PCBs and PCNs exist in the atmosphere as vapor phase chemicals and in a condensed form where they are adsorbed on atmospheric particles. Gas to particle partition of pollutants depends on molecular weight, atmospheric conditions (temperature, humidity and precipitation), the nature (origin and properties) of the aerosol, interactions between the compounds and the aerosol and the overall behavior of compounds in the atmosphere (Hassan and Khoder, 2012). The distribution between the gaseous and particle-bound phases is the most important factor determining removal mechanisms and residence time in the atmosphere (Gambaro et al., 2004). This distribution strongly influences POP transport and how pollutants enter the human body. Therefore, the evaluation of gas-particle distribution of pollutants in the atmosphere has received worldwide attention. Studies of POPs in the Venice lagoon have principally focused on sediments (Frignani et al., 2004, 2001; Moret et al., 2001) and surface waters (Manodori et al., 2006b; Moret et al., 2005) but very little is known about the role of aerosols in the transport of pollutants into the lagoon system and the gas-particle partition of POPs in this area.

The first objective of this work is to characterize the gas-particle distribution profile of atmospheric PAHs, PCBs and PCNs. Due to the importance of estimating the possible origin of pollutants in this area, we examined the sources of PAHs, using the diagnostic ratio method. This study presents the first Venetian lagoon samples that evaluate the toxicological activities of PAHs and the dioxin-like activity of PCBs while focusing on the differences between gas and particulate toxicological characteristics.

2. Material and methods

2.1. Reagents and materials

Pesticide-grade dichloromethane, n-hexane and toluene (Romil Ltd., Cambridge, UK) were used. All isotope-labeled standard solutions (EC-1434, EC-1426, EC-4187, EC-4188, EC-4189, CLM-2477, CLM-2722, CLM-3757 and CLM-2451) were acquired from CIL (Cambridge Isotope Laboratories Inc., USA); PAH native standard solutions (PAH Mix 9) were purchased from Dr. Ehrenstorfer GmbH (Germany); PCB native solutions (C-CS-01, -02, -03 and -05) were obtained from AccuStandard Inc. (USA); PCN native standard solution (ECN-5178) was acquired from CIL. All the tools and glassware were washed with an aqueous 5% (v/v) Contrad® solution (Decon Laboratories Limited, UK), dried and rinsed with dichloromethane and n-hexane.

2.2. Sample collection

Sixteen samples were collected on the Sacca San Biagio island (Lat. 45°25′40.14″ N; Long. 12°18′36.73″ E), which is located along the Giudecca Canal, southeast of the historical center. The island is not inhabited, permitting an evaluation of the sources of pollutants in Venice without the influence of an extremely local source. Venice and the surrounding areas are heavily affected by anthropogenic activities such as industrial emissions from the Porto Marghera industrial area and traffic pollution from the nearby Mestre motorway. The Sacca San Biagio island site is influenced by ship traffic (public transport, touristic and merchant shipping), aircraft flying to the Venice Airport and domestic heating (Stortini et al., 2009). Five samples were collected from August to September 2009 and eleven samples from July to October 2012. More details about the sampling dates and meteorological conditions during the sampling period are given in Table A.1.

Samples were collected using a high volume air sampler (AirFlowPUF, Analitica Strumenti, Italy; flow rate: 0.3 $m^3\ min^{-1}$), useful to keep gaseous and particulate phases separated. Air is first drawn through a quartz fiber filter (QFF, porosity 1 μm, size 102 mm, SKC Inc., USA) where particulate matter is entrapped and then through a polyurethane foam plug (PUF, height 75 mm, diameter 65 mm, SKC Inc., USA) to collect vapor phase compounds. PUFs and QFFs were replaced every 2–3 days. Before sampling, QFFs were furnace-treated at 400 °C for 4 h and PUFs were pre-cleaned by extracting with toluene using the Pressurized Liquid Extractor (PLE, Fluid Management Systems Inc., USA) under the following working conditions: 100 °C temperature, 1000 psi pressure, 7 min static duration, 2 cycles. The QFFs were then individually wrapped in a double aluminum foil. QFFs and PUFs were stored at −20 °C after sampling until extraction. Overall 8 field blanks were collected in order to determine any contamination during sample handling and preparation.

2.3. Analysis

A unique analytical method was used for PCBs, PCNs and PAHs (Piazza et al., 2013). Blanks and samples were spiked with a known amount of an isotopically labeled compound mixture containing 21 ^{13}C-labeled PCBs at 40 pg μL^{-1} and 3 ^{13}C-labeled PAHs at 1 ng μL^{-1} prior to extraction, PUFs and QFFs were extracted separately with a n-hexane/dichloromethane mixture (1:1, *v*/*v*) for three times using a Pressurized Liquid Extractor and the previously described conditions. Cleaning was performed by injecting the extracts onto a disposable neutral silica column using the automated PowerPrep system (Fluid Management Systems Inc.). Before the instrumental analysis each blank and sample was spiked with a known amount of the recovery standard solution containing ^{13}C-chrysene at 1 ng μL^{-1}, ^{13}C PCB-47 and ^{13}C PCB-141 at 40 pg μL^{-1}.

We determined fifteen of the US Environmental Protection Agency (EPA, 1981) priority PAHs: acenaphthylene (ACY), acenaphthene (ACE), fluorene (FL), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[*a*]anthracene (BaA), chrysene (CHR), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), benzo[*ghi*]perylene (BghiP), indeno[1,2,3-*c*,*d*]pyrene (IcdP) and dibenzo[*a*,*h*]anthracene (DahA). The determination of PAHs was conducted with a quadrupole mass spectrometer (Agilent 5975C, Agilent Technologies, USA), operating in electron impact mode (EI 70 eV), coupled with an Agilent 7890A (Agilent Technologies) gas chromatograph, equipped with a 60-m fused silica capillary column (0.25 mm I. D.; 0.25 μm; Agilent Technologies). Gas-chromatograph operating conditions are the following: injector temperature 290 °C; transfer line temperature 290 °C; oven temperature program 70 °C (1.5 min), 10 °C min^{-1} to 150 °C (10 min), 3 °C min^{-1} to 280 °C (28 min), 20 °C min^{-1} to 300 °C (0 min), 305° for 30 min (postrun); carrier gas (helium) 1 mL min^{-1} and splitless inject mode (split valve open after 1.5 min) with purge flow 50 mL min^{-1}.