Chemosphere 60 (2005) 1660–1666

CHEMOSPHERE

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Composition of torched crude oil organic particulate emitted by refinery and its similarity to atmospheric aerosol in the surrounding area

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Received 17 September 2004; received in revised form 1 February 2005; accepted 13 February 2005

Abstract

The absolute contents and relative distributions of organic aerosols [*n*-alkanes, *n*-alkanoic and *n*-alkenoic acids, *n*-alkan-2-ones and polycyclic aromatic hydrocarbons (PAH)] were determined in torched gases emitted during the crude oil extraction and in the free atmosphere of the Hassi-Messaoud city (Algeria). Monocarboxylic acids, both saturated and monounsaturated (from 9802 to 20 057 ng m^{-3}), accounted for the major fraction of the total particulate organic matter identified both in torch exhaust and atmospheric particulate. *n*-Alkanes were also abundant both in the direct emission (from 460 to 632 ng m^{-3}) and city atmosphere (462 ng m^{-3}) and displayed a peculiar fingerprint characterised by the presence of a set of branched congeners around even carbon-numbered homologues and a strong even-to-odd predominance along the whole carbon number range (C_{16}–C_{34}). Whilst *n*-alkan-2-ones were absent in the city and poor in smokes emitted from the torches (from 31 to 42 ng m^{-3}), PAH were present at low extents in all sites (from 18 to 65 ng m^{-3}). The incomplete thermal combustion of torched crude oil was very likely the main source of these particle-bound organic constituents in the city and its surrounding region.

Keywords: Particulate organic matter (POM); Crude oil; petrol oil extraction; Torches; Hassi-Messaoud

1. Introduction

The pollutants broadly emitted during crude oil extraction and petroleum refining processes are: sulphur oxides; carbon monoxide; nitrogen oxides; light hydrocarbons; hydrogen sulphide; mercaptans; particles (soot of torches and dust of catalysts). Depending on the type and quality of the crude oil and the intermediate products being processed as well as on the refined product demand, the types of processes employed in one refinery may be very different from the process operated at another. Due to this variability, emissions released from two petroleum refineries might be very different in their specific amounts (e.g. emissions per metric ton of crude oil processed) and in their compositions (McInnes, 1996).

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doi:10.1016/j.chemosphere.2005.02.041

Usually all refuse gases emitted during the petroleum refining are sent to the torches, where they are burned together with the liquids coming from emptying, canalisation cleaning, incidents or accidents of fabrication. Due to the variable qualitative and quantitative character of the burned material, it is very hard to reach the complete combustion of fuel without emission of black smokes. These smokes can be very dense and influence, at local and regional scale, chemical, optical and radiative characteristics of the atmosphere through direct (adsorption and scattering solar and terrestrial radiation) and indirect (modification of cloud processes) mechanisms (IPCC, 1990, 1992; Charlson et al., 1992).

During November 1999 a field investigation was performed to determine the contents of organic aerosols in Ouargla (Yassaa et al., 2001a). This town lies at a pipeline junction in the middle of the petroleum field region of Hassi-Messaoud and acts as an administrative centre of a well-watered oasis at the junction of several desert caravan routes. It was found that most particulate organics present in Ouargla air come from the crude oil extraction fields located not far from the city (Yassaa et al., 2001a). In order to evaluate at what extent the petrol oil industries contribute to the total budget of organic aerosols in the region surrounding Ouargla and to characterise organic composition of the smoke particulate matter emitted from the torches, we have conducted a monitoring campaign in the crude oil extraction fields of Hassi-Messaoud during June 2000. The Hassi-Messaoud region, which is located at ~80 km from Ouargla city and at ~900 km from Algiers, represents one of the largest petroleum industrial areas of Africa. Three sites were considered in this study. The first site was located nearby the torches of South Industrial Centre (SIC), the second one was nearby the torches of Naïli Abdelhalim North Industrial Centre (NAIC), and the last one was inside the urban agglomeration of Hassi-Messaoud (in Custody of Children Garden located at ~1 km from SIC). While the results obtained in the last site allowed to evaluate the impact induced by industrial emissions onto the air quality of surrounding cities, those obtained in the two former ones served to characterise the organic component of smoke particles emitted during the extraction and refining processes of petroleum.

2. Experimental

2.1. Airborne aerosols sampling

Samples of particulate were collected by enriching 24 m^3 of air onto PTFE inert membrane (*Teflo* R2PL047-type, provided by Gelman Sci., Ann Arbor, MI, USA, 47 mm o.d., 1 μm pore size) located at approximately 3 m diagonally above and to the side of the flames in the smoke plume. A medium-volume aspirating pump (1.0 m^3 min^{-1}) was used for this purpose. It was equipped with a size-selective inlet, suitable to collect only particles smaller than 10 μm, and a volume-counter for measuring the air passed through the filter. The particle-loaded filters were directly kept in dichloromethane solution to prevent any degradation and then stored at low temperature until chemical characterisation.

2.2. Sample extraction, clean-up and analysis

The chemical determination of organic aerosols was performed by using a procedure described extensively elsewhere (Ciccioli et al., 1996; Yassaa et al., 2001b). Briefly, samples were spiked with a solution containing internal reference compounds for the analysis, i.e. 1-bromotetradecane, 1-bromoeicosane, perdeuterated 1-nitropyrene, phenanthrene-d$_{10}$, pyrene-d$_{10}$, chrysene-d$_{12}$ and perylene-d$_{12}$; then the organic content of aerosols was extracted by refluxing enriched filters in Soxhlet, using a dichloromethane–acetone (4:1) mixture. The extract was evaporated and the residue was divided in two aliquots. Most of the extract (4/5 of the total) was fractionated through a column chromatography on neutral alumina (2 g, partly deactivated with 2.5% w:w of water). Non-polar aliphatic compounds were first recovered with *n*-hexane (6 ml), whilst the bulk of medium-polar organics were collected by passing dichloromethane (DCM, 6 ml) through the column; this fraction consisting of PAH, *n*-alkan-2-ones and more polar species.

The second aliquot of the sample extract (i.e. 1/5 of the total) was lead to react with boron trifluoride in excess of methanol to convert organic acids to their methyl ester analogues. A further elution through an alumina column of the reacted material, run by using DCM, allowed to clean alkanoic acid methyl esters from possible interferences. All sample fractions were stored in the dark at low temperature until the analysis.

n-Alkanes, esterified saturated and monounsaturated *n*-alkanoic acids, *n*-alkan-2-ones and PAH were determined by using a HP-5890-type gas chromatograph coupled with a HP-5970B mass spectrometric detector operating in SCAN mode, except for PAH where SIM mode was used. Both instruments were from Hewlett Packard Instruments, Palo Alto, CA, USA. Separations of analytes were obtained through a 25 m-long capillary column coated with a HP-5-type methylphenyl silicone stationary phase (i.d. = 0.2 mm, film thickness = 0.33 μm) provided by Hewlett Packard. The column temperature was maintained at 80 °C for 2 min, then programmed to 170 °C at 20 °C min^{-1} rate and held constant for 2 min; a second ramp (4 °C min^{-1} rate) heated column up to 280 °C and elution was completed isothermally within 15 min. The mass spectrometer