Contents lists available at ScienceDirect





Atmospheric Research

journal homepage: www.elsevier.com/locate/atmosres

Passive monitoring of particulate matter and gaseous pollutants in Fogo Island, Cape Verde



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ARTICLE INFO

Keywords: Dust deposition OC and EC Ions Morphology Acid gases SO₂ VOCs

ABSTRACT

An air quality monitoring campaign by passive sampling techniques was carried out, for the first time, between November 2016 and January 2017 on the Cape Verdean island of Fogo, whose volcanic mountain rises up to 2829 m. Levels of SO₂ and acid gases (HF, HCl, HNO₃, H₂SO₄ and H₃PO₄) were, in most cases, below the detection limits. Alkylpentanes, hexane, cycloalkanes and toluene were the dominant volatile organic compounds. The m,p-xylene/ethylbenzene ratios revealed that air masses arriving at Cape Verde have been subjected to significant aging processes. High toluene/benzene ratios suggested extra sources of toluene in addition to vehicle emissions. Deposition rates of total settleable dust ranged from 23 to $155 \text{ mg/m}^2/\text{day}$. On average, organic carbon accounted for 15.6% of the dust mass, whereas elemental carbon was generally undetected. Minerals comprised the dominant mass fraction. The dust levels were mostly affected by two main airflows: the westerlies and the Saharan Air Layer. These air masses contributed to the transport of mineral dust from desert regions, secondary inorganic constituents (SO₄²⁻, NO₃⁻ and NH₄⁺) and tracers of biomass burning emissions, such as potassium. Sea salt represented 12% of the mass of settleable dust. Scanning electron microscope observations of several particles with different compositions, shapes and sizes revealed high silica mass fractions in all samples, as well as variable contents of carbonates, sulphates, aluminosilicates, Fe, Ti, F and NaCl, suggesting that, in addition to the already mentioned sources, dust is likely linked to industrial emissions in the northern and north-western coast of the African continent. Although some atmospheric constituents presented higher concentrations near the crater, the small fumarolic activity still present after cessation of the eruption in February 2015 has a limited impact on air quality, which is most affected by long range transport and some local sources at specific locations.

1. Introduction

Fogo is the island of the Sotavento group of Cape Verde that reaches the highest altitude: nearly 3000 m above sea level at its summit, Pico do Fogo. The island has an area of 476 km^2 and approximately 40,000 inhabitants. The economy is essentially based on agriculture and fishing. The largest city, São Filipe, is located to the west. The island is a stratovolcano that has been intermittently active. The volcanic cone rises from a plateau about 8 km in diameter, called Chã das Caldeiras, and the walls on the western side reach almost 1000 m and end in a crater 500 m in diameter and 180 m deep. After 19 years of quiescence, Fogo volcano erupted in November 2014. The eruption produced fastmoving lava flows that travelled for several kilometres. Although the eruption of the volcano has ceased in February 2015, minor fumarolic activity is still present at the edge of the new crater. Moreover, the deposited ash is frequently remobilised by the wind causing significant health concerns. Fogo has a tropical savannah climate characterised by a relatively dry period and a wet period, the latter between August and October. Because of the altitude, temperatures are slightly lower than those of other islands of Cape Verde. The average annual temperature on the coast is roughly 23–25 °C, but decreases to values around 12–14 °C on the highest locations. There is an ever blowing, sometimes fierce sea wind on Fogo, which may temper temperatures. Nevertheless, when the dry and dusty Harmattan winds blow from the Sahara Desert

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https://doi.org/10.1016/j.atmosres.2018.08.002

Received 24 March 2018; Received in revised form 11 July 2018; Accepted 7 August 2018 Available online 09 August 2018

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over West Africa, which frequently occurs between the end of November and the middle of March, warm air is supplied to the island and temperatures rise.

The Cape Verde archipelago does not have an air quality monitoring network. Most of the studies have been carried out at the Cape Verde Atmospheric Observatory (CVAO), in the Barlavento island of São Vicente (Fomba et al., 2013, 2014; Jenkins et al., 2013; Müller et al., 2010; Niedermeier et al., 2014; Patey et al., 2015; Sander et al., 2013; Read et al., 2012). CVAO aims to advance understanding of climatically-significant interactions between the atmospheric remote background conditions and the ocean and to provide long-term data from field campaigns. Trace gas measurements began at the site in October 2006. Chemical characterisation of aerosol measurements and flask sampling of greenhouse gases began in November 2006, halocarbon measurements in May 2007, and physical measurements of aerosol in June 2008. On-line measurements of greenhouse gases began in October 2008. A study on the aerosol composition, sources and transport was also conducted between January 2011 and January 2012 at the former airport of Praia, in the south-eastern edge of the Sotavento island of Santiago, within the CV-Dust project (Almeida-Silva et al., 2013; Fialho et al., 2014; Gama et al., 2015; Gonçalves et al., 2014; Salvador et al., 2016). All these studies provide temporal discrimination, but are limited in what concerns the coverage of geographical patterns.

To our knowledge, no atmospheric monitoring study has been conducted so far in Fogo, an island with unique characteristics. As observed in other islands of the archipelago, it is expected that emissions from the ocean and the outflow of Saharan and Sahelian dust also affect Fogo. The long range transported air masses are mixed with freshly emitted pollutants from local sources, likely including volcanic ashes and fumaroles. The objective of the current study was to obtain, by passive methods, the distribution of dust and gaseous pollutants in this tropical Atlantic marine environment, in which the complex terrain and the absence of significant anthropogenic sources makes it appropriate for evaluating remote atmospheric conditions. This information is important not only to assess cumulative exposures, but also to better understand local and transboundary sources, circulation patterns and climate implications.

2. Methodologies

2.1. Sampling and analytical techniques

Due to the lack of electricity in many places and the complex topography, a baseline air quality screening based on passive sampling, starting on November 21, 2016, was carried out at 21 locations around the island (Fig. 1). This period is representative of the long dry season, since Cape Verde's climate is consistent through the year, with only a rainy season in the early autumn months, with September providing almost half of the annual average rainfall for the islands. Thus, in this study, atmospheric particulate matter settled by gravity involved only dry processes. Settleable particulate matter was collected on 47 mm diameter quartz fibre filters (Pallflex®), which were placed in uncovered petri dishes (Analyslide® from Pall) of the same internal size. These sampling devices were positioned at a height of approximately 120 to 150 cm height above floor level to represent the breathing zone. Filter pairs were exposed side by side to dust fall for 2 months. Before sampling, the filters were conditioned for at least 24 h in a room with constant humidity (50%) and temperature (20 °C) in accordance with the European Standard EN14907:2005. After sampling, the filters were reconditioned, reweighed and stored at -18 °C until chemical analyses. The gravimetric quantification was performed with a microbalance (RADWAG 5/2Y, accuracy of 1 µg). Filter weights were obtained from the average of six consecutive measurements with variations between them of < 0.02%.

Passive sampling tubes for volatile organic compounds (VOCs), acid gases (HF, HCl, HNO₃, HBr, H_3PO_4 and H_2SO_4) and SO_2 from Gradko International Ltd. (UK) were exposed at the same sites for 3 weeks,

starting on the same date as the settleable dust. These commercial polypropylene tubes, containing a paper filter impregnated with NaHCO₃ in glycerol or a tape treated with triethanolamine, were used for collecting acid gases and SO₂, respectively. After exposure, the filters or tapes were leached in water and analysed by ion chromatography (Dionex ICS1100 ICU10), following the Gradko in-house methods GLM3 (acid gases) and GLM1 (SO₂), which were certified by the United Kingdom Accreditation System (UKAS). VOCs were sampled in stainless steel tubes packed with Tenax and then determined by thermal desorption and gas chromatography coupled to mass spectrometry in accordance with ISO16000-6.

Each filter of a pair was analysed for its carbonaceous content by a thermal-optical technique and for water soluble ions by ion chromatography. The respective pairs were investigated by scanning electron microscopy to determine the type of minerals present, their size and shape.

For analysis of the carbonaceous material, two 9 mm diameter filter punches were used in each analytical run. Two replicate analyses for each sample were performed, one with acidification of the filter, the other without acidification. The difference between both determinations provides a rough estimate of the carbonate content. The filter punches were first heated in a non-oxidising atmosphere of N2 in order to volatilise the carbonaceous organic compounds (organic carbon, OC). After the first step of controlled heating, the remaining fraction was burnt in an oxidising atmosphere (mixture of N2 and O2) to evolve elemental carbon (EC). The CO₂ resulting from the thermal desorption/ oxidation of particulate carbon was quantified by a non-dispersive infrared (NDIR) analyser. During the anoxic heating, some OC is pyrolysed (PC), and for that reason, it is quantified as EC in the second stage of heating. The interference between PC and EC can be controlled by continuous monitoring of the blackening of the filter using a laser beam and a photodetector measuring light transmittance. Each one of the replicates was previously acidified in order to evaluate the influence of carbonates in the quantification of EC and OC. Punches of the filters were exposed to vapours of hydrochloric acid (HCl - 6 M) for approximately 4 h. After this period, the samples were transferred to a desiccator containing sodium hydroxide (NaOH), where they were kept overnight. The purpose of this process was to neutralise any excess of acid in the sample to protect de CO₂ analyser from corrosive HCl fumes.

Two other 9 mm diameter filter punches were subjected to extraction with 6 mL of Milli-Q ultrapure water under ultra-sonication for 15 min at room temperature. The liquid extracts were then filtered with a 0.45 μ m pore PTFE syringe filter to remove insoluble particles, and analysed for water-soluble ions. A Thermo ScientificTM DionexTM ICS-5000+ capillary high-performance ion chromatographic system with a dual pump was used. It enables the simultaneous determination of anions and cations in a single run.

The other filter of each pair was analysed with a HITACHI SU-70 high resolution scanning electron microscope (SEM) equipped with a Bruker energy dispersive spectroscopy (EDS) detector in order to detect the chemical elemental composition of the dust particles individually. The size and shape of each speck was also taken into consideration. The chemical analyses were interpreted in terms of particle classes (e.g. Si rich, S rich) and grossly comparable to mineralogical groups (e.g. quartz, volcanic glass, sulphates) (Scheuvens and Kandler, 2014). One of the aims of this study was to investigate the possible risk of the dust particles to the individuals living at each sampling site. For this reason, the highest concentration of each element was selected. Around 30 particles in each filter were analysed by SEM/EDS. The possible secondary emission influence of Si rich phases (fibres and basaltic glass) when this EDS spectra were examined was taken into account, as well as results from the standardless analysis.

2.2. Ancillary tools

A GPS (global positioning system) was used to record the coordinates of every sampling station for later data mapping. The Download English Version:

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