Journal of Hazardous Materials 324 (2017) 213–220

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Antimony speciation as geochemical tracer for anthropogenic emissions of atmospheric particulate matter

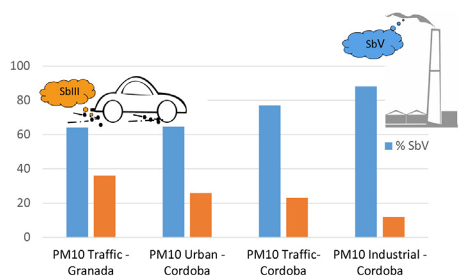
Daniel Sánchez-Rodas [a,b,*], Louay Alsioufi [a], Ana M. Sánchez de la Campa [a,c], Yolanda González-Castanedo [a]

[a] Center for Research in Sustainable Chemistry—CIQSO, Associate Unit CSIC-University of Huelva "Atmospheric Pollution", Huelva, Spain
[b] Department of Chemistry, Faculty of Experimental Sciences, University of Huelva, Huelva, Spain
[c] Department of Mining, Mechanics and Energetic Engineering, ETSI, University of Huelva, Spain

HIGHLIGHTS

- Geochemical anomalies of toxic elements in PM10 related to metallurgy have been identified in an urban ambient.
- Fugitive emissions from brass industries are an important source of metals and metalloids.
- Speciation of Sb(III) and Sb(V) in PM10 can be used as a geochemical tracer to identify the influence of industry and traffic on the air quality.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 4 August 2016
Received in revised form 5 October 2016
Accepted 22 October 2016
Available online 22 October 2016

Keywords:
Antimony
Speciation
PM10
Industry
Traffic

ABSTRACT

The chemical composition of atmospheric particulate matter (PM) has been studied at the cities of Cordoba and Granada (South of Spain) between 2007 and 2013, considering urban background, traffic and industrial monitoring stations. The results of Principal Component Analysis (PCA) indicated that geochemical anomalies observed in the ambient air of Cordoba (mainly Cu, Zn, Pb and Cd) are closely related to the geochemical profile obtained from fugitive metallurgy emissions of brass industries. These findings have been confirmed performing an Sb speciation analysis of PM10 samples, which allowed to distinguish between Sb(III) and Sb(V). The percentage of Sb(V) in PM10 found in the traffic station of Granada was 64–69%. At Cordoba, the percentage of Sb(V) was found to be higher (73–77%) at both urban background and traffic stations, indicating a possible second source of Sb in the PM of this city. The PM10 samples from the industrial station of Cordoba showed a 85–86% of Sb(V). A similar percentage (84–88%) of Sb(V) was found for the fugitive emissions of the brass industries, confirming this industrial source of Sb. These results show that Sb speciation can be a useful geochemical tracer to identify anthropogenic sources (traffic and industrial) emissions of PM.

1. Introduction

Sb is ubiquitously distributed in the environment due to natural processes and anthropogenic activities. It has no known biological function and it is considered an emerging element of environmental concern due to its potential toxicity for human health. Sb and its compounds are considered priority pollutants interest by the US Environmental Protection Agency and the European Union [1].

* Corresponding author at: Center for Research in Sustainable Chemistry—CIQSO, University of Huelva, 21071 Huelva, Spain.
E-mail address: rodas@uhu.es (D. Sánchez-Rodas).

http://dx.doi.org/10.1016/j.jhazmat.2016.10.051
0304-3894/

As the chemical properties of Sb resemble to the ones of arsenic, the toxicity and environmental risk of Sb depends on its oxidation state. Sb(III) is ten times more toxic than Sb(V), and inorganic Sb is more toxic than its organic compounds [2]. The International Agency for Research on Cancer (IARC) considers Sb(III) suspected of being carcinogenic in humans [3].

Sb can be found in atmospheric particulate matter (PM), a pollutant which represents a hazard both to the environment and the human health (e.g. climate change, air pollution and allergic respiratory diseases) [4]. The harmful effects of PM are associated to the size of the particles and their chemical composition [5]. The concentration of Sb in PM ranges from a few pg m^{-3} in remote areas to several ng m^{-3} in urban areas. The release of Sb to the atmosphere due to natural emissions (volcanoes) is less than a 5% in comparison to anthropogenic emissions, which are related mainly to traffic and to a minor extent to urban incineration [1,6,7]. The brake-pads of vehicles contain Sb_2S_3 as lubricant for friction material, which is emitted as particles during break wear. The heat generated during this process can oxide considerably Sb_2S_3 [8,9]. This emission produces road dust containing Sb [10]. Recently, traffic has been suggested as possible source to explain the atmospheric input of Sb in pregnant women from urban areas [11]. The other main emission source is the incineration of plastic wastes, which can generate fly ash containing Sb, as this metalloid is used as catalyst for the production of polyethylene terephthalate (PET) [12]. Smelters have been also reported as responsible for Sb emissions to the air, although there is limited information about this type of source [13]. Sporadic peaks of Sb in PM evidence sometimes a high industrial contribution in comparison to typical urban emissions [14].

There is abundant scientific works in relation to total Sb content in atmospheric samples (PM and fly ash) [15–19], whereas Sb speciation studies of individual Sb(III) and Sb(V) species are scarce [20–24]. The Sb speciation studies indicate that according to the particle size, Sb(III) is dominated by coarse particles, whereas Sb(V) is distributed in both fine and coarse fractions [21]. While Sb is present mainly as Sb(III) in the break-pads, the analysis of the dust from car braking systems and road dust has shown a significant conversion of Sb(III) to Sb(V) [22]. This is in agreement with other studies that have shown the presence of both Sb species in coarse particle samples (PM10) from urban sites, Sb(V) usually being at a similar or higher concentration than Sb(III) [23,24]. Also, Sb has been also found as Sb(V) in fly ash from waste incinerators [25]. On the contrary, the analysis of natural samples (e.g. volcanic ash) showed that Sb(III) was always the predominant species [20].

The main aim of the present study is to provide new insights about the distribution of Sb species in PM as a geochemical tracer for anthropogenic emissions (traffic and industrial). In this sense, a Sb speciation study has been performed with PM10 samples collected at an urban site (city of Cordoba, South of Spain), whose air quality is affected both by traffic and metallurgy emissions (brass industries). A detailed chemical characterization of the PM10 samples was performed at traffic, urban background and industrial monitoring stations, considering metals, metalloids and inorganic anions and cations. The metallurgy emissions of brass industries were also characterized in order to identify possible Sb emission sources. The results from Cordoba were compared to similar samples obtained from the near city of Granada, in which the Sb emission is related only to traffic.

2. Methodology

2.1. Study area

PM10 samples were collected from Cordoba, a major city of southern Spain with a population of ca. 330 000 inhabitants. Road traffic has been considered one of the main sources of air pollution in Cordoba [26,27]. The number of vehicles registered in 2014 is ca. 211 000 [28]. Moreover, a nearby industrial estate is located to the west of the city (Fig. 1), involved in brass metallurgy. The main final products are copper rod from electrolytic copper smelting, brass ingots, bars of Cu, Zn and Pb scrap, and shavings smelting.

In order to compare the results of Cordoba, PM10 samples were taken also at the city of Granada (population ca. 240 000) situated at a distance of 130 km. This city has also an import urban traffic (170 000 vehicles in 2014) [28], but no important metallurgic estates in its surroundings.

2.2. PM10 sampling strategies

A comprehensive PM10 sampling was designed to evaluate the industrial and urban atmospheric environments of Cordoba and

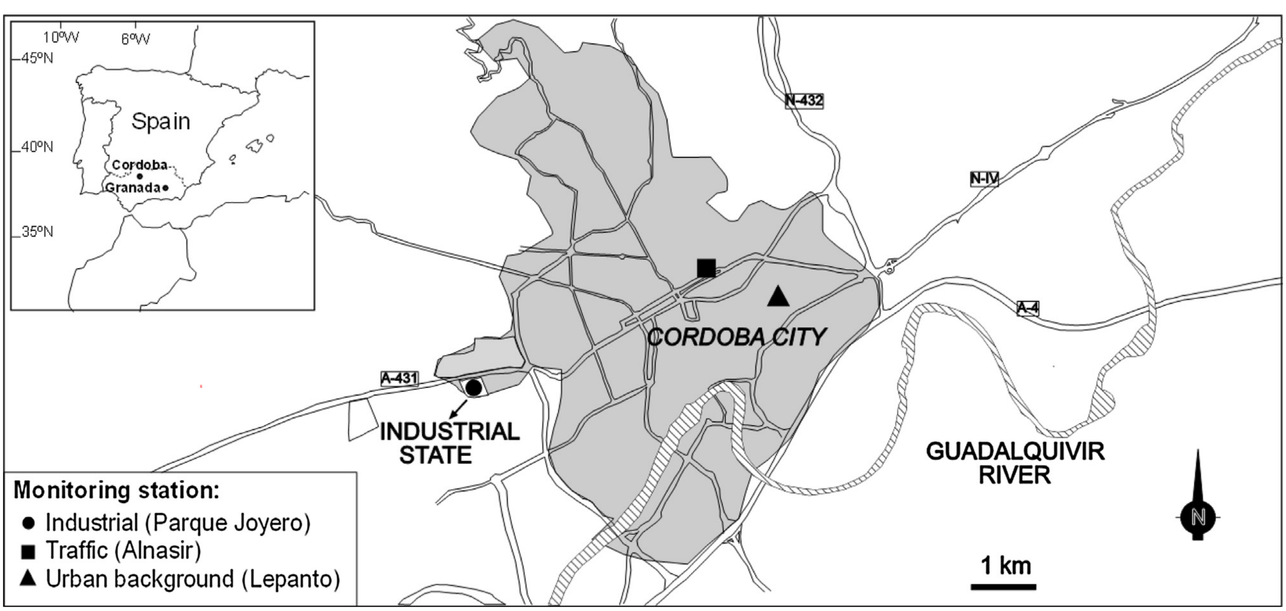


Fig. 1. Location map of monitoring stations in Cordoba.