Science of the Total Environment xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Science of the Total Environment

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

Chemical composition of Eastern Black Sea aerosol—Preliminary results

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HIGHLIGHTS

- We collected $PM_{2.5}$ and $PM_{2.5-10}$ at coastal region of the Black Sea region in Turkey.
- Samples analyzed for trace elements by EDXRF
- The source apportionment was carried out using PMF technique.
- PMF analysis identified four factors.

ARTICLE INFO

Article history:
Received 16 August 2013
Received in revised form 4 December 2013
Accepted 5 December 2013
Available online xxxx

Keywords:
Eastern Black Sea
Trace elements
Atmospheric transport
Aerosol

ABSTRACT

Trace element composition of atmospheric particles collected at a high altitude site on the Eastern Black Sea coast of Turkey was investigated to understand atmospheric transport of pollutants to this semi-closed basin. Aerosol samples were collected at a timber-storage area, which is operated by the General Directorate of Forestry. The site is situated at a rural area and is approximately 50 km to the Black Sea coast and 200 km to the Georgia border of Turkey. Coarse ($PM_{2.5-10}$) and fine ($PM_{2.5}$) aerosol samples were collected between 2011 and 2013 using a "stacked filter unit". Collected samples were shipped to the Middle East Technical University in Ankara, where Na, Mg, Al, Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Ba, Pb were measured by Energy dispersive x-ray fluorescence technique (EDXRF). Comparison of measured concentrations of elements with corresponding data generated at other parts of Turkey demonstrated that concentrations of pollution derived elements are higher at Eastern Black Sea than their corresponding concentrations measured at other parts of Turkey, which is attributed to frequent transport of pollutants from north wind sector. Positive matric factorization revealed four factors including three anthropogenic and a crustal factor. Southeastern parts of Turkey, Georgia and Black Sea coast of Ukraine were identified as source regions affecting composition of particles at our site, using trajectory statistics, namely "potential source contribution function" (PSCF).

1. Introduction

Atmospheric aerosol is composed of solid particles and liquid droplets suspended in the air. In last decades, atmospheric particles attracted attention due to variety of reasons. Aerosols are emitted into atmosphere both from natural sources and anthropogenic sources. The Earth energy balance and climate are affected by aerosol, as they interact both directly and indirectly through cloud formation with Earth's radiation budget (IPCC, 2001). They also have health effects (Hoek et al., 2002; Simkhovich et al., 2008) and cause visibility degradation (Lee and Sequeira, 2002).

The chemical and physical characteristics of Mediterranean and Eastern Mediterranean aerosol have been studied extensively and currently a broad database has been available for composition of eastern Mediterranean particles and implications of these compositions (e.g., Koçak et al., 2007; Koulouri et al., 2008; Koçak et al., 2012; Öztürk et al., 2012; Pey et al., 2013). Results of those studies illustrated that the Mediterranean aerosol is mainly a four component system, including crustal particles originating from arid regions at North Africa and Middle East (Koçak et al., 2012; Öztürk et al., 2012), an anthropogenic component originating from industrialized regions located at the north of the basin (Öztürk et al., 2012; Pey et al., 2013), a sea salt component and a biogenic component (Koçak et al., 2007; Koulouri et al., 2008). The anthropogenic component in the Mediterranean aerosol population was further investigated to understand types (Herut et al., 2001; Doğan et al., 2008) and locations of anthropogenic sources contributing to the aerosol composition in the Western and Eastern Mediterranean atmospheres (Koçak et al., 2004a; Güllü et al., 2005; Doğan et al., 2008). Physical and radiative characteristics of Eastern (Ichoku et al., 1999; Fotiadi et al., 2006) and Western (Mallet et al.,

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http://dx.doi.org/10.1016/j.scitotenv.2013.12.023

2011; Esteve et al., 2012) Mediterranean aerosols were also investigated through modeling studies (Barnaba and Gobbi, 2004; Spyridaki et al., 2006) and lidar network was established around the basin (Balis et al., 2003).

Studies to investigate chemical composition of Black Sea particles are not as abundant as the studies in the Mediterranean region. Few studies on particle composition in the Black Sea atmosphere demonstrated that the levels of particles and specific elements, particularly SO_4^{2-} are not significantly different from the levels of particles in the Eastern Mediterranean atmosphere (Hacısalihoğlu et al., 1992; Karakaş et al., 2004). However, particle composition at Eastern and Western Black Sea is not identical. Particle composition at the western parts of the Black Sea is influenced strongly from emissions in Balkan and central European countries and in that sense similar to the composition of particles sampled in the Eastern Mediterranean atmosphere (Hacısalihoğlu et al., 1992). Sources affecting Western Black Sea atmosphere originated from Central Russia (Dzubay et al., 1984; Karakaş et al., 2004) and countries surrounding the basin (Hacısalihoğlu et al., 1992; Tecer et al., 2008).

Studies targeted to understand types of particles in aerosol population and to understand where those sources are located are integral parts of aerosol studies in all basins, including the Mediterranean (Koçak et al., 2007; Doğan et al., 2008; Öztürk et al., 2012). Multivariate statistics, particularly factor analysis (Hopke et al., 1976) and positive matrix factorization (Paatero and Tapper, 1994) in recent years have been widely used for that purpose. Studies towards finding locations of source regions contributing to measured concentrations of pollutants in the Eastern Mediterranean and Black Sea basins are few (Doğan et al., 2010; Tecer et al., 2012). Trajectory statistics, which combines information on concentrations of pollutants with backtrajectory information to locate source regions, is a common tool which is applied not only in the Mediterranean region (Güllü et al., 1998, 2005), but also for other locations around the world (Chen et al., 2002; Abdalmogith and Harrison, 2005).

In this study multi-element data generated at a rural site on the Eastern Black Sea was investigated to understand (a) general characteristics of element concentrations, such as seasonality etc., (b) components of aerosol population at the eastern Black Sea and (c) locations of the sources of anthropogenic component in the aerosol mass. Statistical tools at all levels are extensively used to answer these questions. Positive matrix factorization was used to identify source types and potential source contribution (PSCF) approach, which is a widely used tool in trajectory statistics, was used to find potential source regions affecting chemical composition of Eastern Black Sea particles.

2. Materials and methods

2.1. Sampling location

Samples were collected at a station established in a timber-storage depot of the General Directorate of Forestry, on the Eastern Black Sea coast of Turkey (40°32′34″N 39°16′57″E). Location of the station is depicted in Fig. 1. Sampling point is approximately 50 km to the Black Sea coast and 200 km to the Georgian border of Turkey. The setting is typical rural with limited settlement around the station. There is also no significant industrial activity within a circle of 50 km radius around the station. Sampling was started in March 2011 and still continues; however, data from samples collected before January 2013 were used in this manuscript.

2.2. Sampling technique

Samples were collected with a Gent Stacked Filter Unit (SFU) (Hopke et al., 1997) on polycarbonate (Nuclepore) filters. The SFU consists of a pump, two cascade filters with pore sizes of 8.0 μm and 0.4 μm and a mass flow controller that fixes the air flow rate at 16.7 L min^{-1}. Filters were placed in a NILU, two-stage filter holder. When air is passed through such a system at a flow rate of 16.7 L min^{-1}, particles with diameters >2.5 μm are held in the top filter and particles with diameters <2.5 μm passes through the top filter and retained at the bottom filter. A pre-impactor, which has a cut-point at 10 μm are also included to the system. When SFU is operated at a flow-rate of 16.7 L min^{-1} particles with diameters >10 μm are held at the pre-impactor and are not allowed to reach to filters. Particles with diameters between 10 μm and 2.5 μm are held at the top filter

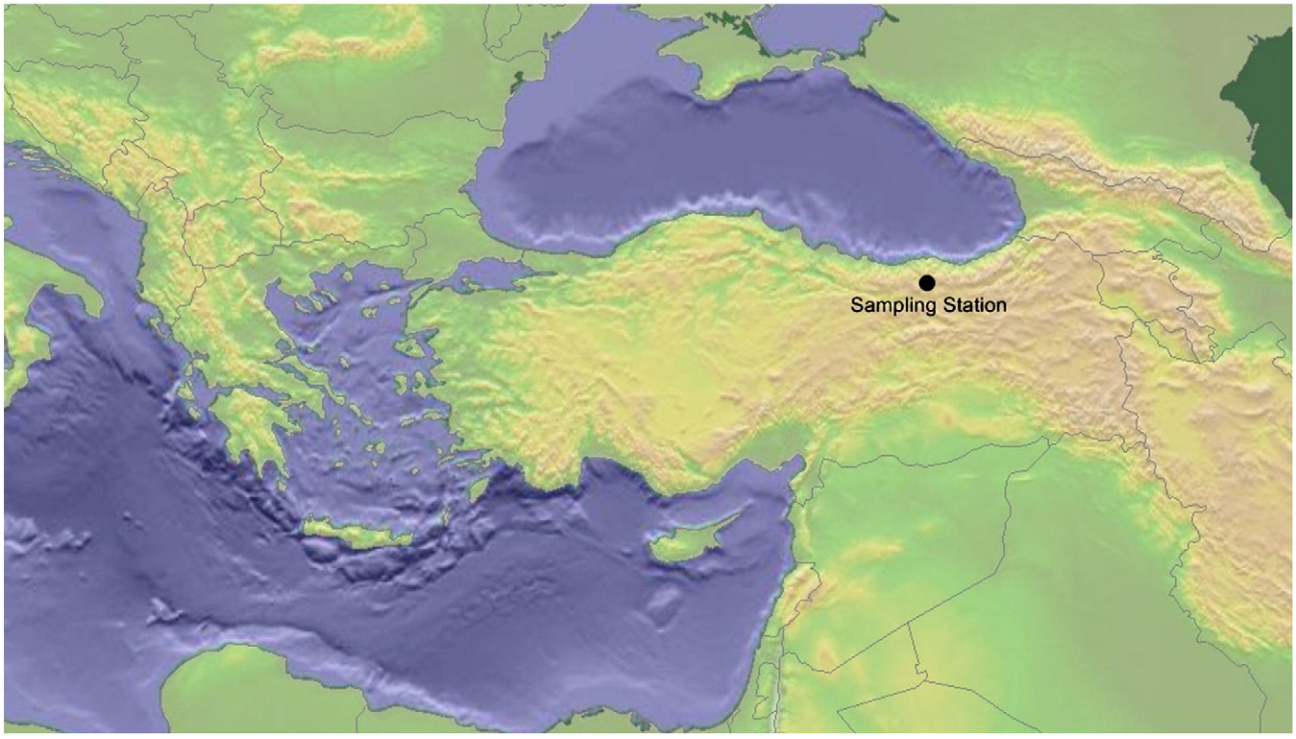

Fig. 1. Location of the sampling station.

Please cite this article as: Balcılar İ, et al, Chemical composition of Eastern Black Sea aerosol—Preliminary results, Sci Total Environ (2013), http://dx.doi.org/10.1016/j.scitotenv.2013.12.023