Atmospheric Environment 119 (2015) 262–272

Contents lists available at ScienceDirect

Atmospheric Environment

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

Mineralogy and geochemistry of atmospheric particulates in western Iran

Hesam Ahmady-Birgani[*, a, b], Hassan Mirnejad [c, d], Sadat Feiznia [b], Ken G. McQueen [e]

[a] Department of Range and Watershed Management, Faculty of Natural Resources, University of Urmia, Iran
[b] Faculty of Natural Resources, University of Tehran, Karaj, Iran
[c] Department of Geology, University of Tehran, Tehran, Iran
[d] Department of Geology and Environmental Earth Sciences, Miami University, Ohio, 45056, USA
[e] Faculty of Applied Science, University of Canberra, Canberra, ACT, 2601, Australia

HIGHLIGHTS

- Quartz and calcite are dominant minerals in the particulate samples collected in western Iran.
- Every dust event is characterized by varying assemblages of minerals, phases and chemical elements.
- Particulate minerals from ambient and dust event periods reflect diversity and number of source areas.

ARTICLE INFO

Article history:
Received 3 December 2014
Received in revised form
17 July 2015
Accepted 5 August 2015
Available online 8 August 2015

Keywords:
Atmospheric particulates
Physico-chemical properties
Mineralogy and geochemistry
Persian Gulf
Sea of Makran

ABSTRACT

This study investigates the mineralogy and physico-chemical properties of atmospheric particulates collected at Abadan (southwestern Iran) near the Persian Gulf coast and Urmia (northwestern Iran) during ambient and dust events over 6 months (winter 2011; spring 2012). Particle sizes collected were: TSP (total suspended particulates); PM_{10} (particulates <10 μm); and $PM_{2.5}$ (particulates <2.5 μm). Minerals were identified using X-ray diffraction (XRD); particle morphology and composition were examined by scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX). Major minerals detected are calcite, quartz, clay minerals and gypsum, with relative abundance related to sampling site, collection period, wind direction, sampling head, and total sample amount. The anomalously high calcite content appears a characteristic feature originated from calcareous soils of the region. SEM observations indicated a wide range of particle morphologies over the 1–50 μm size range, with spherical, platy, cubic, elongate and prismatic shapes and rounding from angular to rounded. Energy dispersive X-ray analysis of TSP samples from both sites for non-dusty periods indicated that the sampled mineral suite contained Al, Mg, Na, Cl, P, S, Ca, K, Fe, Ti, and Si, mostly reflecting calcite, quartz, aluminosilicates, clays, gypsum and halite. Additionally, As, Pb, Zn, Mn, Sc, Nd, W, Ce, La, Ba and Ni were detected in TSP, PM_{10} and $PM_{2.5}$ samples collected during dust events.

1. Introduction

Atmospheric particulates, particularly those displaced by dust storms, could significantly impact climate and environment globally (Buseck and Posfai, 1999; Prospero, 1999; Clarke et al., 2001; Bishop et al., 2002). Determination of physico-chemical properties and mineralogy of atmospheric particulates is of high importance in identification of their sources (Bergametti et al., 1989; Merrill et al., 1994; Davis and Guo, 2000; Ganor et al., 2000).

The mineralogy of solid particulates can be determined using X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) equipped with Energy Dispersive X-ray Spectroscopy (EDX), while their chemical compositions are commonly measured using X-ray Fluorescence (XRF) (e.g. Bergametti et al., 1989; Leinen et al., 1994; Merrill et al., 1994; Fan et al., 1996; Avila et al., 1997; Arnold et al., 1998; Mori et al., 1998; Moreno et al., 2003). The mineral composition and morphology of solid particulates in dust events are variable and depend on the exposed minerals in the source area

* Corresponding author. Department of Range and Watershed Management, Faculty of Natural Resources, University of Urmia, Iran.
E-mail address: h.ahmadybirgani@urmia.ac.ir (H. Ahmady-Birgani).

http://dx.doi.org/10.1016/j.atmosenv.2015.08.021
1352-2310/

(Singer et al., 2003), the geology and geomorphology of the location and type and direction of wind (Engelbrecht et al., 2009b; Zarasvandi et al., 2011). This information is crucial for understanding the nature and source of the dust.

Sokolik and Toon (1999) demonstrated that various mineral components including clays, quartz, carbonates, feldspars, sulfates and iron oxides should be included in dispersion models to estimate the properties of dusts. In the beginning hours of dispersion, dusts often consist of insoluble or low soluble components (Formenti et al., 2010). Others have demonstrated that newly dispersed dusts could act as cloud condensation nuclei or ice nuclei (Koehler et al., 2009; Connolly et al., 2009). Nucleation of cloud droplets generated by solid particulates is most likely influenced by mineralogical composition of the particulates. Calcite provides cloud condensation nuclei (Gibson et al., 2006), while clay minerals (kaolinite and illite) increase ice nuclei efficiency (Zimmermann et al., 2008). It is estimated that almost 50 percent of tropospheric particulates are minerals that originate from the deserts and their peripheral regions (Andreae, 1995).

Atmospheric particulates play a key role in removal, sedimentation and transportation of atmospheric pollutants (Sievering et al., 1989; Winchester and Wang, 1989; Dentener et al., 1996; Carmichael et al., 1996). Free silica in dusts (quartz, tridymite and cristobalite) can cause health problems in general and pulmonary diseases (silicosis) in particular (Yabuta and Ohta, 2003). The International Agency for Research on Cancer (IARC) indicated that silica, resulting in silicosis, has been categorized as a group 1 carcinogen since 1997 (Ferg et al., 2008). Whenever solid particulates in polluted air are inhaled, they are removed by the body defense mechanisms. However, these mechanisms are affected by particulate size, such that particles smaller than 5 microns can infiltrate into the alveolus and interfere with pulmonary functions (Cowie and Mabena, 1991; Filloon, 2001). Hence, determination of mineralogy of particulate components and their sizes are extremely important.

SEM provides information on type, size, shape and morphology of particulate matter, as well as the arrangement and textural features of particles (Tate et al., 2003). The particle size range, shape, roundness and angularity provide clues to the source and transport history of the materials (He et al., 2007). EDX provides information on the elements present and the chemical components and minerals making up the solid particulates. Dust events can also be chemically classified and the chemical components of individual particles, as determined by with EDX, are used to assess the minerals in the dust. For example, there is a high probability that mineral particles enriched in Ca, Ca–Mg, Si–Al and Si contain the major surficial minerals calcite, dolomite, clay minerals and quartz, respectively (Engelbrecht et al., 2009b). The ratios of key elements can also be utilized, as the elemental ratios of specific silicates commonly found in the Earth crust are fairly uniform (Queralt et al., 2001).

Combined observations of particle size distribution (by PSD), morphology (by SEM), mineralogy (by XRD) and element content (by XRF) can help identify the source of dust and its transport history (e.g. Tate et al., 2003). Physico-chemical properties of atmospheric particulates generally indicate a mixture of parent materials and changes due to their transportation (Queralt et al., 2001). Generally, chemical analyses of particulates are far more common than mineralogical analyses because they are easier to carry out on small amounts of sample (Leinen et al., 1994). However, mineral collection and identification in atmospheric dust may be more important for determining the source (Davis, 1984; Bergametti et al., 1989; Merrill et al., 1994; Avila et al., 1997). Pye (1987) showed that quartz-, carbonate- and feldspar-enriched dusts commonly have continental sources and originate from local areas within short to medium distances. In contrast, dusts enriched in fine-grained aluminosilicates and clay minerals typically indicate long distance transport and sources.

The main aims of this study are to examine airborne particulates at Urmia and Abadan, two meteorological sites in northwestern and southwestern Iran, respectively, and to assess their physico-chemical properties under non-dusty and dust event conditions. These observations should also provide information on the source materials of these atmospheric particulates.

2. Materials & methods

The samples from atmospheric particulates were collected at the Urmia and Abadan synoptic meteorological stations (Fig. 1-A) from December 2011 to May 2012:

1 Urmia synoptic meteorological station, 37° 53′ latitude, 45° longitude, 1332 m above mean sea level (AMSL), mean precipitation 256 mm, mean annual temperature 11.8 °C, temperate and cold climate.
2 Abadan synoptic meteorological station, 37° 27′ latitude, 48° 17′ longitude, 3 m AMSL, mean precipitation 146 mm, mean annual temperature 26 °C, arid and desert climate.

The dust samples at each site were collected over a six-month period using a Low Volume (LVS) Microcomputer Controlled Air Sampler, Micro PNS (Fig. 1-B). Each sample was collected within 168 h (one week) by 38 l/min suction volume (2.3 cubic meters per hr). Each month, three samples including TSP (Total Suspended Particulates), PM_{10} (Particulate matter less than 10 microns) and $PM_{2.5}$ (Particulate matter less than 2.5 microns) were approximately collected. The sample intakes on each instrument were 2 m high to prevent suctioning of suspended particles near to the ground surface during strong winds. To collect the samples, special filters were used that could both trap atmospheric particulates and continue to function during the suction process, including under very dusty conditions. Hence, quartz filters 47 mm in diameter filled with quartz interwoven amorphous fibers, were used. Fig. 2 shows representative examples of fresh and used quartz filters.

The particulate filled filters were removed from the sampler head and packed into zipper plastic bags to prevent contamination. Any small amount of dust dislodged from the filters during transport could also be preserved. The date, time, site and related information were recorded on the bags and samples were kept at 4 °C to prevent growth of microorganisms and chemical alteration. This conservative process was also continued during transportation of the samples. The mass of the samples were measured using a precision weighing balance. Before mounting the fresh filters into the sampler head, they were weighed precisely and after finishing the sampling period re-weighted and the weight of the fresh filters subtracted from the filters covered with atmospheric particulates (net weight).

First of all, the minerals in the samples were identified by XRD analysis, a non-destructive technique. Analyses were performed at the Research School of Earth Sciences, Australian National University (ANU) and at the laboratory of Sietronics Pty Ltd in Canberra, Australia, using Siemens D5005 X-ray Diffractometers, with CuKα radiation). Samples were scanned from 1° to 90° 2θ at 1° 2θ per minute on rotating sample holders. The data were analyzed using EVA software and each mineral peak was recorded. SIROQUANT software version 3.0 (developed by CSIRO in Australia) was used to quantify the minerals present in the samples. Since the volumes of collected particulates were small, the samples were placed directly on aluminum holding plates for insertion into the XRD machine.

Second, an SEM-EDX (HitachiS-4300SE/N) (Fig. 3) was used to