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Secondary inorganic aerosol evaluation: Application of a transport chemical model in the eastern part of the Po Valley

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HIGHLIGHTS

- A photochemical model has been used to study SIA distribution in the Po Valley.
- Good performance has been reached in spatial and temporal distribution.
- Concentrations were related to gaseous precursors and to the emission sources.
- Relation between model overestimation, input and boundary conditions was discussed.
- Specific ratios and a *no-boundary* simulation were used to assess SIA formation.

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ABSTRACT

Secondary inorganic aerosol (SIA) represents an important component of fine particulate matter in Europe. A photochemical model has been used to assess the distribution of secondary inorganic ions (sulfate, nitrate and ammonium) in the eastern part of the Po Valley, close to Venice. Specific meteorological and environmental conditions and very highly urbanized and industrialized areas make this domain one of the most polluted in Europe. Several studies have been conducted to assess particulate matter (PM_{10} and $PM_{2.5}$) areal distribution. However, SIA formation dynamics are still a research subject especially in the transition environments, where the changes in the orography and in the land-use can affect air mass movements and atmospheric composition. This paper is a first attempt to simulate SIA distribution by using a photochemical model in the sea/land Venice transition area. Moreover, a modeling approach with clean boundary conditions has been used to check local and regional influence on SIA levels in the domain. Results reveal that, despite the importance of regional influences, local formation processes are important in SIA distribution especially during warm periods. SO_4^{2-} and NH_4^+ are more linked to emission sources distribution than NO_3^- that tends to be more diffused in the study area. The use of a photochemical model, suitably tested in a such complex area, can improve air pollution knowledge and can help in air quality decision making.

1. Introduction

Particulate matter plays a key role in atmospheric processes affecting human health (Pope et al., 2009), visibility (Bäumer et al., 2008), air quality and climate change (IPCC, 2007). It also influences ecosystems and cultural heritage, being involved in acid deposition (Larssen et al., 2006; Nava et al., 2010). The chemical composition and the size of the particles are strongly linked to the emission sources and to the photochemical formation processes from gas-phase precursors (such as non-methanic volatile organic compounds – NMVOCs, NO_x, SO_2 and NH_3) (Seinfeld and Pandis, 2006). In order to reduce human exposure to PM, policies must focused not only on the reduction of primary particulate matter, but also on the reduction of gaseous precursor emissions involved in the formation of secondary particles (Renner and Wolke, 2010; Wu et al., 2008). Several experimental studies have been focused on PM levels, speciation and origin over Europe. Results show that both organic and inorganic fractions can contribute to PM_{10} and $PM_{2.5}$

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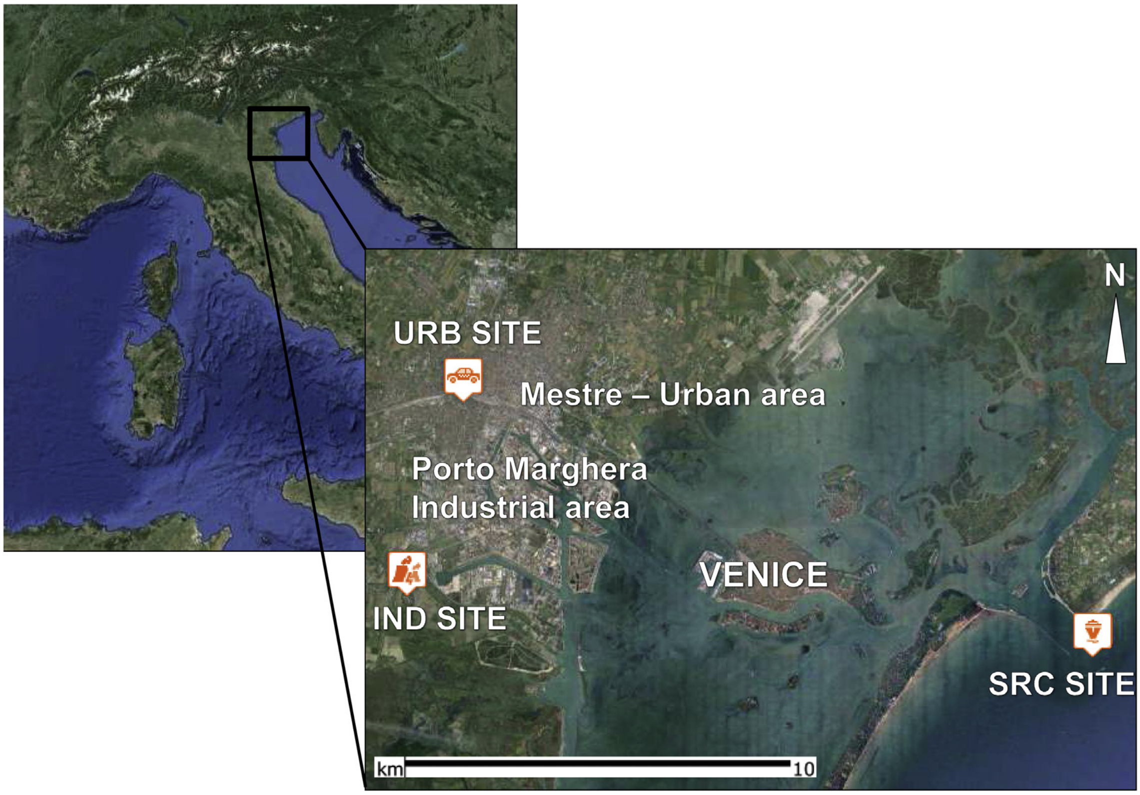

Fig. 1. Sampling sites location.

mass, strongly depending on the site considered (Putaud et al., 2010, 2004; Querol et al., 2004, 2009). SIAs have been defined as one of the major pollutants in air quality standards (EPA, 2008) and controlling precursor emissions can be considered an effective strategy to reduce their levels. However, recent studies show that the complexity of the intra-SIAs relationships provokes changes in nitrate levels that do not follow a linear dependence with changes in precursors emissions (Lei and Wuebbles, 2013; Liang et al., 2009). Moreover, SIA formation processes strongly depend on several other chemical and micro-meteorological factors, such as the concentrations of atmospheric oxidants, the characteristics of preexisting aerosols, the air temperature and humidity (Baek et al., 2004; Pathak et al., 2011).

In this scenario, photochemical models become important tools for air quality assessment and evaluation of control policies. Several European studies have shown a general model overestimation tendency for PM and SIA components (Matthias, 2008; Pay et al., 2012; Schaap et al., 2004; Vautard et al., 2009) and deep uncertainties in the estimation of meteorological input data and of PM sources. These studies also stressed the knowledge gap in the SIA formation processes in specific environment where land/sea transition could affect local circulation.

In this study, the considered domain represents a clear example of a land/sea transition area. The eastern part of the Po Valley is surrounded by mountains (Alps and Apennine mountains) and the sea (Adriatic Sea) and it is one of the most polluted areas in Europe. Some studies tried to explain SIA distribution in the north part of Italy (Andreani-Aksoyoglu et al., 2008, 2004; Landi et al., 2013) but no simulation has been done for this specific domain. By means of a photochemical model (FARM, Flexible Air quality Regional Model), this paper focuses on: (i) the model capacity to simulate SIA dispersion and transport; (ii) the characterization of SIA formation dynamics; (iii) the comprehension of the relation between secondary inorganic ions (SIIs) and gaseous precursors and (iv) the spatial SIA distribution. Moreover, a modeling approach with clean boundary conditions has been used to check local and regional influence on SIA levels in the domain as proposed in Pecorari et al. (2013).

2. Study area

The study area covers almost 2500 km^2 around the city of Venice that is located on the coast of the Adriatic Sea at the margin of the Po Valley. The main emission sources in the domain are: chemical and metallurgical works, oil refineries and coal power plants (Industrial area of Porto Marghera); busy roads and motorway; shipping and small boats traffic and the commercial and cruise dock operations; national and international flying traffic; artistic glass making factories (Rampazzo et al., 2008a, 2008b; Masiol et al., 2012). In this scenario, PM dynamics and formation processes are strongly influenced by atmospheric conditions. More specific information on meteorology and climatic conditions are reported in Pecorari et al. (2013).

3. Material and methods

3.1. Model description, setup and sampling

3.1.1. PM measurements and sampling

Three sites with different environmental conditions were selected in the Venice area: a semi-rural coastal site, Punta Sabbioni (SRC); an urban site in Mestre (URB) and an industrial site, near the Porto Marghera industrial area (IND) (Fig. 1). $PM_{2.5}$ samples were daily collected throughout one year (2009) according to EN 14907:2005 with a low-volume sampler (2.3 m^3 h^{-1}) on quartz fiber filters (Whatman QMA). $PM_{2.5}$ mass was measured by