Science of the Total Environment 407 (2009) 4312–4319

Contents lists available at ScienceDirect

Science of the Total Environment

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

Characterization of ozone precursor volatile organic compounds in urban atmospheres and around the petrochemical industry in the Tarragona region

Maria Rosa Ras, Rosa Maria Marcé *, Francesc Borrull

Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili, Campus Sescelades, Marcel·lí Domingo, s/n, 43007 Tarragona, Spain

ARTICLE INFO

Article history:
Received 29 October 2008
Received in revised form 27 March 2009
Accepted 1 April 2009
Available online 6 May 2009

Keywords:
Ozone precursors
Volatile organic compounds
Urban areas
Industrial areas
Petrochemical industry

ABSTRACT

This paper reports the results of an assessment of volatile organic compound (VOCs) levels in ambient air in samples collected at urban and industrial sites in southern Catalonia, which is home to one of the most important petrochemical complexes in southern Europe. This study contains data from a total of 192 samples collected in 2007, from May to October, at six air pollution measurement stations within the area of influence of several chemical and petrochemical industrial plants. The ambient air concentrations of a group of 65 VOCs, some of them ozone precursors, were determined by active sampling into sorbent tubes, thermal desorption and gas chromatography-mass spectrometry. At the same time, several meteorological parameters were also recorded, and levels of NO, NO_2 and O_3 measured by the automatic stations, have been included in the study as well. Ambient air profiles of the different areas were studied, and the ozone formation dependent on VOCs and NO_2 levels was also analysed, taking into account the photochemical ozone creation potential (POCP) for different groups of VOCs.

1. Introduction

The presence of photochemical smog in some urban and industrial regions is a problem of increasing concern. Photochemical smog is originated from the photochemical reaction of NO_x ($NO+NO_2$) and volatile organic compounds (VOCs) in the presence of sunlight. It is chemically characterized by a high level of oxidant compounds, mainly O_3. In urban areas, where NO_x and hydrocarbon emissions from traffic are high, O_3 tends to accumulate rapidly. The concentration of O_3 has a considerable effect on the oxidizing capacity of the troposphere, which affects human health by causing symptoms such as irritated eyes, cough, headache, chest pains and, in extreme cases, lung inflammation. O_3 is also toxic to plants, leading to a decrease in vegetation, and associated with the corrosion of urban structures. Moreover, it can be swept away by prevailing winds, thus leading to higher ozone concentrations in places far from the sources of emission of the ozone precursors. European legislation (Directive 2002/3/CE) regulates the standard levels of tropospheric ozone, and also recommends that a whole list of VOC ozone precursors be measured so that trends can be analysed, the efficiency of emission reduction strategies checked, and sources of emission determined.

VOCs may also represent a potential threat to human health. Although short-term exposure to particular concentrations of some VOCs present in air is not considered acutely harmful to human health, long-term exposure may result in mutagenic and carcinogenic effects. Exposure to VOCs can cause such acute and chronic effects as respiratory damage and can therefore increase, for example, the risk of asthma. They can also affect the nervous, immune and reproductive systems. Classic neurological symptoms associated with VOCs are feelings of fatigue, headaches, dizziness, nausea, lethargy and depression (ATSDR, 1995; Weschler and Shields, 1997; Rumchev et al., 2004; Baroja et al., 2005; Ulman and Chilmonczyk, 2007). Moreover, benzene and tetrachloroethene have been identified as powerful carcinogenic agents by the World Health Organization (WHO) (Srivastava et al., 2005). Today, European air quality standards regulate the maximum level of benzene, which was set at $10\ \mu g\ m^{-3}$ as of January 2005, but this limit is being progressively reduced by $1\ \mu g\ m^{-3}$ a year, to $5\ \mu g\ m^{-3}$ by January 2010 (Directive 2000/69/CE).

One of the main sources of ozone precursors are industrial processes such as those of the chemical and petrochemical industries. These industries are associated with the emission of sulphur compounds, nitrogen oxides, particulate matter and volatile organic compounds (VOCs), mainly hydrocarbons, originating in production processes, storage tanks, transport pipelines and waste areas (Kalabokas et al., 2001; Cetin et al., 2003; Rao et al., 2007; Ulman and Chilmonczyk, 2007). Furthermore, the main source of ozone precursors in urban areas is road traffic and other combustion processes, and fuel evaporation (Han and Naeher, 2006).

To properly understand the role of these compounds in urban photo-oxidation and the associated health hazards associated, detailed knowledge of their presence in ambient air is required (Kumar and Viden, 2007). For example, in the so-called 'titration effect' the NO reacts with O_3 to give NO_2 (The Royal Society, 2008).

* Corresponding author. Tel.: +34 977 55 81 70; fax: +34 977 55 84 46.
E-mail address: rosamaria.marce@urv.cat (R.M. Marcé).

0048-9697/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.scitotenv.2009.04.001

Simulations of photochemical models have been used to better understand the contribution of emission sources to ozone production (Jiménez and Baldasano, 2004; Lei et al., 2004; Jonson et al., 2006; Weinroth et al., 2006). Moreover, because individual VOCs have been shown to make different contributions to ozone, a variety of methods are used to rank VOCs depending on their ozone producing capacity. One of these methods is the photochemical ozone creation potential (POCP), which is defined as the change in the amount of ozone formed due to a change in emission of that particular compound (Andersson-Sköld and Holmberg, 2000).

To characterize ozone precursors accurately, appropriate analytical methods are required if individual VOCs are to be identified and quantified (Kumar and Viden, 2007). In recent years, adsorption in solid sorbents, subsequent thermal desorption (TD) with cryogenic enrichment and analysis by gas chromatography-mass spectrometry have become very useful for determining VOCs in air samples (Fastyn et al., 2005; Kuntasal et al., 2005; Volden et al., 2005; Palluau et al., 2007).

In the present study, we present an exhaustive monitoring campaign of six sampling sites in the Tarragona region, a highly industrialised area in southern Catalonia (Spain) which is home to one of the largest petrochemical centres in southern Europe. The ambient air profiles of several areas are studied by determining a group of 65 VOCs, 20 of which are recognized ozone precursors whose determination is recommended by the legislation on ozone in ambient air (Directive 2002/3/CE). VOCs were determined by active sampling in sorbent tubes and analysis by gas chromatography-mass spectrometry. A total of 192 samples were collected between May and October of 2007, at six air pollution measurement stations located in different urban and industrial areas. At the same time, various meteorological parameters were recorded, and levels of NO, NO_2, and O_3 measured by automatic stations were also included in the study. The influence of VOC and NO_x levels, and the meteorological parameters, were statistically analysed.

2. Materials and methods

2.1. Study area

Tarragona is a coastal area in southern Catalonia (Spain) where, because of its location and the advantages of its geographical characteristics, there has been extensive development in the chemical and petrochemical industries since the 1960s. Since then, new industrial factories have moved in to create various industrial areas throughout the region. Of these industrial areas, the North and South Complexes are the most significant and extensive and together account for most of the chemical and petrochemical plants in the region. The South Complex occupies an area of 717 ha and consists mainly of production centres. Some of the products manufactured at this complex are butane, propane, solvents, asphalt, naphtha and crude distillate. The North Complex occupies an area of 470 ha and, among other chemical factories, has an oil refinery. Some of the products manufactured at this complex are vinyl acetate, benzene, chloroform, methylene chloride, polyvinyl chloride, fuels, propane and kerosene. The production of both the North and South Complexes is about 18,000 Kt of chemical products per year (AEQT, 2003).

In recent years, there have been frequent occurrences of odour nuisance in the region, mainly in the inhabited areas surrounding the industrial complexes. As a result, the population has become increasingly concerned about the toxic effects of these emissions on human health and the environment. Tarragona is a coastal area surrounded by mountain ranges, where surface thermal inversion in atmospheric stability conditions is frequent, mainly during winter and autumn, hindering the dispersion of contaminants. However, some episodes of air pollution have resulted in high levels of ozone, especially in summertime, when more sunlight promotes the formation of O_3 from its precursors. Levels of VOCs in ambient air have been studied before in this region through a daily and annual monitoring campaign in urban and industrial areas (Ras-Mallorquí et al., 2007). Moreover, Jiménez et al. (2005) used a multiscale-nested air quality model to represent the chemistry and transport of tropospheric O_3 and its precursors NO_x and VOCs in a variety of hypothetical scenarios of emission controls, and to quantify the influence of several emission sources in the area. Fig. 1 shows a map of the Tarragona region indicating the location of the six sampling sites and the North and South complexes.

Sampling sites were located at six governmental automatic measurement stations at different areas in the Tarragona region. Samples were taken in these locations in order to compare the levels of VOCs with the parameters determined by the automatic stations (NO_2 and O_3 among others). The automatic stations selected were in Alcover (A), Bonavista (B), Constantí (C), the park in Tarragona City (T), Perafort (P) and Vila-seca (V) (see Fig. 1).

The city of Tarragona has about 130,000 inhabitants and about 82,000 vehicles. A short distance southwest of the urban area there is a large industrial port with a considerable volume of traffic consisting mainly of tankers transporting fuel and other petrochemical products. Moreover, the South Complex is less than 2 km from the city. The automatic station is located in a park which is outside the centre of the city near the two main access routes and surrounded by buildings.

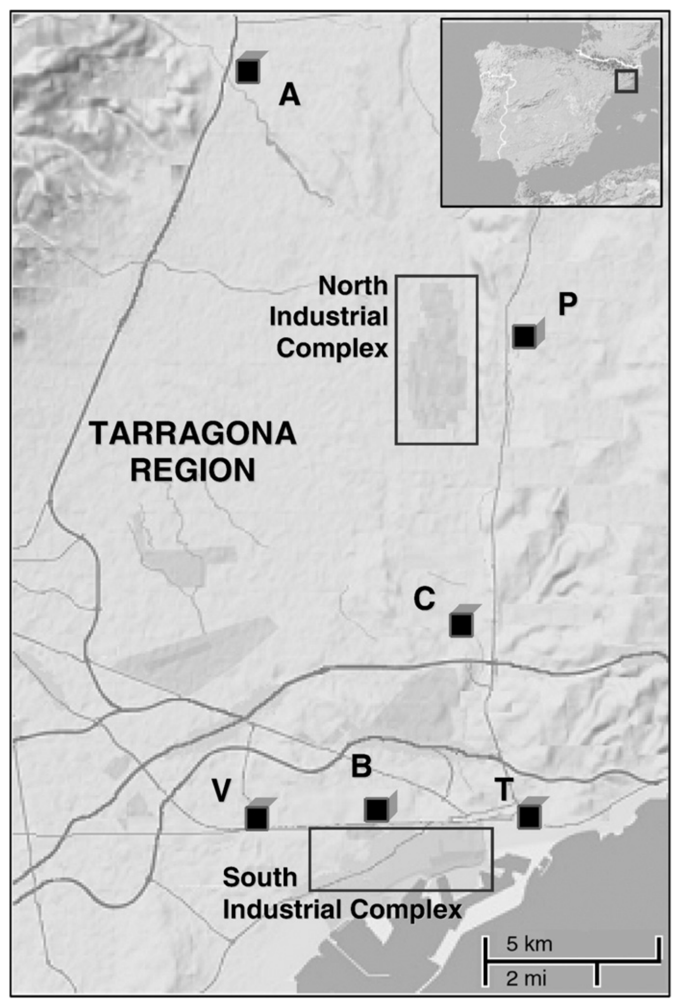

Fig. 1. Map of the Tarragona region showing the location of the North and South Complexes and the six sampling points: Alcover (A), Bonavista (B), Constantí (C), Perafort (P), Tarragona City (T) and Vila-seca (V).