



Biogenic and anthropogenic isoprene in the near-surface urban atmosphere – A case study in Essen, Germany



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ABSTRACT

Isoprene is emitted in large quantities by vegetation, exhaled by human beings and released in small quantities by road traffic. As a result of its high reactivity, isoprene is an important ozone precursor in the troposphere and can play a key role in atmospheric chemistry. Measurements of isoprene in urban areas in Central Europe are scarce. Thus, in Essen, Germany, the isoprene concentration was measured at various sites during different seasons using two compact online GC-PID systems. Isoprene concentrations were compared with those of benzene and toluene, which represent typical anthropogenic VOCs. In the summer, the diurnal variation in isoprene concentration was dependent on the biogenic emissions in the city. It was found that its maximum concentration occurred during the day, in contrast to the benzene and toluene concentrations. During the measurement period in the summer of 2012, the average hourly isoprene concentrations reached 0.13 to 0.17 ppb between 10 and 20 LST. At high air temperatures, the isoprene concentration exceeded the benzene and toluene concentrations at many of the sites. Isoprene became more important than toluene with regard to ozone formation in the city area during the afternoon hours of summer days with high air temperatures. This finding was demonstrated by the contributions to OH reactivity and ozone-forming potential. It contradicts the results of other studies, which were based on daily or seasonal average values. With an isoprene/benzene ratio of 0.02, the contribution of anthropogenic isoprene decreased substantially to a very low level during the last 20 years in Central Europe due to a strong reduction in road traffic emissions. In the vicinity of many people, isoprene concentrations of up to 0.54 ppb and isoprene/benzene ratios of up to 1.34 were found in the atmosphere due to isoprene exhaled by humans.

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1. Introduction

Isoprene (C₅H₈), a biogenic VOC (volatile organic compound), is an important ozone precursor, as it is highly reactive and is emitted in large quantities by vegetation. It has also been found that photo-oxidation of isoprene can lead to the formation of secondary organic aerosols (SOAs) (Claeys et al., 2004; Paulot et al., 2009). Global isoprene emissions from biogenic sources are estimated to be 440–600 TgC per year (Guenther et al., 2006). In contrast, the total global emissions of anthropogenic VOCs are only approximately 100 TgC per year (Kansal, 2009). Isoprene is primarily emitted by certain species of deciduous trees and shrubs (Guenther et al., 2006). The emission rate depends on temperature and light conditions (Guenther et al., 1991, 1993). Therefore, isoprene emissions are very high on hot, sunny days. Isoprene can be emitted in considerable amounts not only in rural, particularly wooded areas but also in urban areas where a large

number of isoprene-emitting trees are planted as urban vegetation (Taha, 1996; Benjamin and Winer, 1998).

Isoprene may also be of anthropogenic origin (Christensen et al., 1999; Reimann et al., 2000; Borbon et al., 2001). The anthropogenic contribution, which is primarily a result of road traffic emissions, can be determined via its ratio to the concentration of a typical traffic tracer outside the growing season and amounts to approximately 5% of the benzene concentration (Christensen et al., 1999; Borbon et al., 2001; Duane et al., 2002). Depending on the location and season, the urban isoprene concentration is dominated by biogenic or anthropogenic sources (Park et al., 2011; von Schneidmesser et al., 2011; Hellén et al., 2012). Human exhalation is another source of isoprene. Kinoyama et al. (2008) and Kushch et al. (2008) found average isoprene concentrations of 65 and 99 ppb, respectively, in the air exhaled by human test subjects. Isoprene is a by-product of metabolic cholesterol synthesis.

Although it has been known since the studies of Haagen-Smit et al. (1953) that VOCs and NO_x (nitrogen oxides) are major precursors of near-surface ozone formation, the importance of isoprene in ozone chemistry in urban areas is still being discussed (e.g., Wiedinmyer et al., 2001; von Schneidmesser et al., 2011). The photochemical relevance of isoprene in urban areas, where anthropogenic emissions

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dominate and concentrations of isoprene are often much lower than those of anthropogenic VOCs, is a subject of debate (Durana et al., 2006; Saito et al., 2009; Xie et al., 2008). However, not only is the concentration of a precursor important for ozone formation, but its ozone formation potential and reactivity are also important. In ozone formation, a VOC molecule (RH) initially reacts with OH radicals, producing a peroxy radical (RO₂). The peroxy radical is formed via H-atom abstraction in alkanes (R1a) and via addition of OH and O₂ to the double bond in alkenes (R1b). Both pathways of radical formation are possible in aromatic compounds, although addition of OH radicals to the aromatic ring is the primary reaction pathway (Seinfeld and Pandis, 2006). In a subsequent reaction, RO₂ oxidises nitrogen monoxide (NO), forming nitrogen dioxide (NO₂) (R2), which completes ozone formation by photolysis (R3).



Isoprene has both a high reactivity and a high ozone-forming potential and therefore can contribute to ozone formation quickly and efficiently (Carter, 1994; Atkinson, 2000). In addition, maximum isoprene emissions are reached around midday and in the afternoon of summer days with high air temperatures and high solar radiation and therefore occur during the time of day with the most favourable photochemical conditions and the highest ozone and OH concentrations (Lee and Wang, 2006). In contrast, anthropogenic emissions reach their maximum during rush hours in the morning and in the evening, with low OH concentrations and less intense solar radiation. When taking reactivity and seasonal and weather variations into account, isoprene is also among the most important ozone precursors in urban areas (Chameides et al., 1992; Xie et al., 2008; Saito et al., 2009; Ran et al., 2011; Hellén et al., 2012). Model studies have shown that biogenic VOCs, particularly isoprene, cause a significant increase in ozone concentrations in urban areas. It is not so much the average but the maximum ozone concentration that is boosted by biogenic VOCs (Bao et al., 2010; Im et al., 2011; Papiez et al., 2009). The contribution of individual tree species to this increase depends on whether more ozone is absorbed by deposition or more ozone is formed as a result of biogenic VOC emissions (Donovan et al., 2005; Nowak et al., 2000; Taha, 1996). The non-linearity of ozone chemistry must also be taken into consideration when assessing the relevance of biogenic VOCs (Lin et al., 1988; Sillman, 1999). Chameides et al. (1988) noted that the reduction in anthropogenic VOC emissions as an ozone reduction strategy will only lead to a slight decrease in ozone concentrations if biogenic VOCs are present in the urban atmosphere.

This study was motivated by the fact that only a few measurements of isoprene concentration have been conducted in urban areas in the central part of Europe (e.g., Derwent et al., 2000; Borbon et al., 2001; Langford et al., 2009; von Schneidemesser et al., 2011). The investigations of Derwent et al. (2000) and Borbon et al. (2001) were performed in the 1990s, but since that time, the concentrations of anthropogenic VOCs declined steeply due to reduced vehicular emissions (Stemmler et al., 2005; Dollard et al., 2007; von Schneidemesser et al., 2010). Thus, it can be assumed that the anthropogenic contribution to isoprene concentration also decreased greatly during the last twenty years, and biogenic emissions become more important in comparison to anthropogenic emissions in the summer (Dollard et al.,

2007). Another motivation was that average values were often considered when comparing isoprene to other precursors or when assessing the contribution of isoprene to ozone formation, e.g., mean annual concentrations (Derwent et al., 2000) and average diurnal variations in isoprene contribution to OH reactivity during summer and winter months (von Schneidemesser et al., 2011). However, due to the strong dependence of biogenic emissions on temperature and light conditions and their short atmospheric lifetime, isoprene is expected to be important in atmospheric chemistry, particularly on hot summer days.

The aim of this study was to investigate the temporal and spatial variations in isoprene concentrations in the urban area of Essen, Germany, to address the following questions: (i) What level does the isoprene concentration reach in the urban atmosphere of Essen, and what impact do meteorological conditions have on the concentrations? (ii) To what extent do anthropogenic isoprene emissions contribute to the current isoprene level? (iii) Should isoprene be considered an important ozone precursor in the near-surface urban atmosphere on summer days with high air temperatures?

The influence of various isoprene sources and meteorological conditions on isoprene concentrations was analysed by comparing the isoprene concentration with the concentrations of benzene and toluene, which represent typical anthropogenic VOCs. Benzene was chosen as a tracer of road traffic emissions. Toluene is one of the most abundant VOCs in the urban atmosphere and is emitted by road traffic and solvent use.

2. Experimental

2.1. Study area

The measurements were performed within the boundaries of the city of Essen. Essen is located in western Germany (51° 27' N, 7° 00' E) and is part of the Ruhr conurbation, which has a population of approximately 5.2 million (2011). Essen itself has approximately 566,000 residents (2013) and an area of 210 km².

There are only a few large wooded areas in the immediate vicinity of Essen (Fig. 1). The total area of woodland in the city is 32.39 km². Most of the woodlands are located in the less densely populated southern part of the city area and consist of mixed forest, with beeches and oaks as the most common tree species. However, it must be assumed that, in addition to the biogenic VOC emissions of the forests, urban vegetation has a non-negligible isoprene emission potential. Many trees, including a large number of isoprene high-emitters (Table 1), are located in urban green spaces (e.g., parks and cemeteries), gardens and backyards or on slag heaps and at the edges of railway facilities, water bodies, agricultural areas, playgrounds and sports facilities. As the photographs in Fig. 2 shows, there is a considerable amount of vegetation in the city centre of Essen. To a large extent, this urban vegetation is not included in land use data (Fig. 1) or tree registries. Finally, there are approximately 188,000 roadside trees in Essen. The most popular and common roadside tree is *Platanus × hybrida*, which is an isoprene high-emitter and accounts for approximately 9% of all roadside trees.

To investigate isoprene in the urban environment of Essen, measurements were carried out at various sites on selected days and during selected periods in 2011 and 2012 (Table 2). The air was sampled 4 m above ground level (agl), with the exception of the “car park” and “street canyon” (both 10 m agl) and “rooftop” (34 m agl) sites. Apart from the “park” site, all of the measurement sites are characterised by typical urban features (high degree of sealed surfaces and traffic areas in the immediate vicinity). At two sites (“rooftop” and “arterial road”), measurements were carried out over a period of several weeks to investigate the influence of various sources and meteorological conditions on the concentrations of isoprene, benzene and toluene at various times of day and during various seasons. Measurements were performed over several days during operations of the Christmas market in the city

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