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Ozone and its projection in regard to climate change

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HIGHLIGHTS

- Ozone dependence on NO_x and temperature at industrial and rural stations.
- Prediction of number of days with ozone exceedances in terms of climate change.
- Frequency of bad ozone days increases by 135% at the industrial station.
- Frequency of bad ozone days increases by 87% at the rural station.
- Ozone forming potential is significantly higher in rural areas than in urban ones.

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ABSTRACT

In this paper, the dependence of ozone-forming potential on temperature was analysed based on data from two stations (with an industrial and rural background, respectively) in North Rhine-Westphalia, Germany, for the period of 1983–2007. After examining the interrelations between ozone, NO_x and temperature, a projection of the days with ozone exceedance (over a limit value of a daily maximum 8-h average ≥ 120 μg m^{-3} for 25 days per year averaged for 3 years) in terms of global climate change was made using probability theory and an autoregression integrated moving average (ARIMA) model. The results show that with a temperature increase of 3 K, the frequency of days when ozone exceeds its limit value will increase by 135% at the industrial station and by 87% at the rural background station.

1. Introduction

Ozone is a secondary pollutant that is not emitted but is formed by photochemical reactions, especially during weather conditions with high solar radiation. It is vitally important to consider ozone as a pollutant not only because of its dangerous effects on the respiratory system but also because of its impact on forests and agricultural crops (Mücke et al., 2009; Booker et al., 2009). Ozone is one of the main components of photochemical smog, and ozone levels are driven by chemical reactions between oxides of nitrogen (NO_x), CO, methane and other volatile organic compounds (VOCs) in the presence of sunlight and high air temperatures (Emeis et al., 1997; Sillman, 2003; Jacob and Winner, 2009).

Motor vehicle exhaust, industrial emissions, gasoline vapours and chemical solvents as well as natural sources emit NO_x and VOC to help form ozone (Sillman, 1999; Guenther et al., 2000; Derwent et al., 2007; Saito et al., 2009). Anthropogenic emissions can form ozone even far away from the emission sources. If VOC and NO_x form peroxyacetylnitrate (PAN) in the vicinity of the sources, they can be transported over long distances to remote regions during cool weather conditions and can be released in these regions to form ozone when the temperature rises due to a change of weather

Abbreviations: NRW, North Rhine-Westphalia; NO, nitric oxide; NO_2, nitrogen dioxide; O_3, ozone; LANUV, Environmental State Agency for Nature, Environment and Consumer Protection; VOC, volatile organic compounds; NMVOC, non-methane volatile organic compounds; AVOC, anthropogenic volatile organic compounds; BVOC, biogenic volatile organic compounds; WALS, Duisburg–Walsum; EGGE, Horn-Bad Meinberg Egge; IPCC, Intergovernmental Panel on Climate Change; SRES, Special Report on Emission Scenarios.

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conditions because PAN breaks down quickly when the temperature is high (Sillman and Samson, 1995; Beine et al., 1997).

The relation between ozone and one of its main precursors, NO_x, can be simplified to only two reactions (Atkinson, 2000; Costabile and Allegrini, 2007):

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (R1)$$

$$NO_2 + O_2 + h\nu \rightarrow O_3 + NO, \quad (R2)$$

where $h\nu$ is the radiation energy with a frequency ν at wavelength $\lambda < 420$ nm, and h is the Planck constant, such that the reaction (R2) can only take place in daytime. The reactions come quickly into balance (after a few minutes), and the concentrations of NO_x and O_3 do not change further.

The other important reaction partner is a VOC molecule, which reacts with an OH radical to form a peroxide radical (RO_2) (R3). Especially under the influence of solar radiation, such reactive OH radicals are present at significant concentrations (Handisides et al., 2003).

In a subsequent reaction RO_2 oxidises NO to NO_2 (R4).

$$RH + OH + O_2 \rightarrow RO_2 + H_2O \quad (R3)$$

$$RO_2 + NO \rightarrow RO + NO_2 \quad (R4)$$

In reaction (R4) NO is oxidised to NO_2 without using O_3, and together with reaction (R2) a net production of ozone takes place. Subsequently, OH and NO_2 can react with each other (R5):

$$OH + NO_2 \rightarrow HNO_3 \quad (R5)$$

In this case, OH radicals and NO_2 are consumed to form nitric acid, and therefore, these compounds are no longer available to build up ozone by the reactions (R2)–(R4). Produced in the course of reaction (R5), nitric acid is water-dissolvable and can effectively be washed out of the atmosphere.

Which of the competing reactions (R3) and (R5) takes place depends on the NO_x concentration (Monks, 2004). Especially in urban atmosphere, many reactions determine the production and loss of OH radicals and thus ozone formation or loss (Handisides et al., 2003; Monks, 2004; Sadanaga et al., 2005; Yoshino et al., 2012).

VOCs contribute in different degrees to the formation of ozone due to their different reactivities and chemical constitutions (Carter, 1994; Atkinson, 2000; Saito et al., 2009). Since because biogenic VOCs (e.g., isoprene and monoterpenes) are quite reactive and their emission is temperature-dependent, they can form a substantial amount of ozone if the temperature is high (Fuentes et al., 2000; Lee and Wang, 2006; Narumi et al., 2009). Therefore, ozone formation seems to be temperature-dependent (Sillman and Samson, 1995; Narumi et al., 2009), although many of the reactions included in the ozone formation process are photochemical reactions and thus are light-dependent rather than temperature-dependent. Another aspect that causes the indirect dependence of ozone on temperature is the strong temperature dependence of the peroxyacetylnitrate (PAN) lifetime (Sillman and Samson, 1995; Barett et al., 1998; Kuttler, 2011). Barett et al. (1998) showed that the thermal decomposition of PAN and radiation are important factors for ozone formation. The relationship between high radiation and high temperature, especially in summer months, also results in a significant correlation between ozone and temperature. Accordingly, the registered ozone concentrations were extremely high over Europe during the heat waves in July and August 2003 (Bruckmann et al., 2003a,b) and in July 2006. In August 2003, measurements at 131 stations in 27 European countries showed that the maximum hourly ozone concentrations exceeded 220 $\mu g\ m^{-3}$ (the limit values of 1-h maximum ozone are 180 and 240 $\mu g\ m^{-3}$ for information and alarm, respectively; LANUV, 2010) over central Europe, covering a large region of Germany.

An exact investigation of the recent heat waves as a 'shape of things to come' can help both scientists in evaluating future climatic impacts and decision makers in developing appropriate response strategies. For that reason, it is absolutely necessary to model ozone behaviour in response to maximum daily temperature changes in the future.

The increase of average ozone concentrations during the last two decades at both industrial- and rural background stations was the main reason to analyse ozone behaviour patterns in detail (Melkonyan, 2011). Emphasis is given to the precursors of ozone (NO and NO_2 concentrations and their ratio; VOC data are not available) and maximum daily temperature.

On this basis, the events when ozone exceeded its limit value (daily maximum 8-h average) have been analysed to determine the probabilities of their occurrences in current and future climates at the industrial- and rural background stations in the western part of Germany.

2. Research area

The research area covers North Rhine-Westphalia state, which is the largest western Federal State of Germany in terms of population and economic output. The state has nearly 18 million inhabitants (Bezirksregierung Düsseldorf, 2010), contributes approximately 22% of Germany's gross domestic product and comprises a land area of 34.083 km^2. The region is characterised by a high population and traffic density as well as a high degree of industrialisation concentrated in the Rhine-Ruhr area. The negative impact of these conditions on the natural resources has led to intensive and successful efforts aimed at improving environmental conditions (air-pollution control, water-pollution control and soil protection). Concerning the reasons for environmental pollution, the proportion of non-point sources (traffic) has meanwhile considerably gained importance compared to point sources (industry).

In this paper, two stations (shown in the map: Fig. 1) with industrial (Duisburg Walsum, further named WALS) and rural backgrounds (Horn-Bad Meinberg Egge, named EGGE) have been chosen using the criteria of the longest dataset (running from 1983 to 2007) and the availability of data on both air-pollution and meteorological parameters.

The area where the industrial station (WALS) is located has an urban character, but the character of the station itself is an industrial one due to the existence of industrial production around it. Nearby, there are coking plants and mining, steel and paper-processing factories.

Horn-Bad Meinberg Egge (EGGE) is located in the forest area near Paderborn. Road L 826 passes by 1 km to the south. An access road runs approximately 100 m away from the station. Approximately 1.5 km to the east, there is a chip-processing factory. The remaining land is rural area.

3. Data and methods

Data on both ozone and one of its precursors (NO_x) as well as meteorology (air temperature, radiation, relative humidity, precipitation and wind speed) were provided by the North Rhine-Westphalia State Agency for Nature, Environment and Consumer Protection (LANUV, NRW, Essen) for the two stations (VOC data are