Airborne Ns (NO₂ and NH₃) in the Rijeka Bay Area (Croatia), 1980–1995

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The determination of ambient levels of nitrogen dioxide (NO₂) and ammonia (NH₃) in the Rijeka Bay area started in 1980, as a part of the air quality monitoring programme. The results of 15 years of surveying (1980/81–1994/95) on ambient levels of these pollutants at two sampling sites are given in this work. Site 1 is located in the city, opposite the eastern industrial zone. Annual means of NO₂ varied between 34 and 60 µg/m³ at Site 1 and between 14 and 26 µg/m³ at Site 2, but do not follow the 40% reduction in industrial emissions of this pollutant, probably due to the dominant impact of other minor sources, like traffic. Yearly averages of NH₃ were in the range of 13 to 26 µg/m³ at Site 1 and 7 to 16 µg/m³ at Site 2, and are practically constant during the period studied.

KEY WORDS: ambient levels, trend, emissions, nitrogen dioxide, ammonia

DOMAINS: atmospheric systems, environmental sciences, environmental chemistry, environmental toxicology, environmental management, environmental monitoring

INTRODUCTION

The products of SO₂, NO₂ (=NO + NO₃), and NH₃ emissions dominate the acidification of ecosystems. Dry and wet deposited NH₃ and NH₄ enter the soil layer as NH₄⁺ where nitrification occurs resulting in acid formation[1]. Furthermore, both nitrogen oxides (NOₓ) and NH₃ represent nitrogen inputs with eutrophying effects to sensitive ecosystems. While industrial combustion and transport processes are the main sources of SO₂ and NOₓ emissions, livestock agricultural activities are dominant sources of NH₃ emissions in Europe. Other anthropogenic sources of NH₃ emissions include industrial NH₃ and fertilizer production, human sweat and breath, pets, sewage, landfill, coal combustion, and biomass burning[2]. Recent evidence suggests that people and traffic may have a greater impact in the nonagricultural regions, as ambient levels of NH₃ were found to be higher in more densely populated areas as compared to less densely populated areas[3].

The anthropogenic emission of NOₓ for 1990 was estimated at 31 million t N/a, with the contribution of fossil fuel combustion accounting for 70% of the total, and biomass burning for another 20%. The emission from natural sources (lightning and soil processes) was calculated at an additional 19 million t N/a. On the other hand, the global emission of NH₃ was estimated at 54 million t N/a, 70% of which is attributed to food production[4].

Rijeka is an industrialized city with approximately 200,000 inhabitants situated at the head of Rijeka Bay. The first industrial plants were founded in the 19th century at the edge of the city (e.g., the paper mill and the old petroleum refinery); the plants are nowadays located in the city centre, thus causing serious air pollution problems. During the 1960s new facilities of the petroleum refinery were erected in the eastern suburban industrial zone (Urinj), while some of the refining processes remained at the old location. During the 1970s a new oil-fired power plant and a coke plant were founded in the vicinity of the new refinery. Due to high emissions from these major industrial sources, the city of Rijeka came to be one of the most polluted cities in Croatia during the 1980s.

An air quality monitoring programme that started in mid-1970s included determination of ambient levels of NO₂ and NH₃ in the vicinity of industrial plants. The results of 15 years of
surveying (1980/81–1994/95) of ambient NO₂ and NH₃ levels at two sampling sites within the Rijeka Bay area are presented in this work.

MATERIALS AND METHODS

The location of sampling sites is given in Fig. 1. Site 1 is situated within the city area, above the busy street that divides the old petroleum refinery from the residential area; the site is affected by emissions from this industrial plant. Site 2 is located in the settlement 25 km southeast of Rijeka, opposite the new petroleum refinery facilities, oil-fired power plant, and coke plant. (The latter closed down in 1994.)

Average daily concentrations of NO₂ were determined by the modification of the Saltzman method[5], while the daily NH₃ concentrations were determined spectrophotometrically[6]. The sampling year comprised the period from October 1 through the following September 30.

RESULTS AND DISCUSSION

NO₂ and NH₃ are involved in several chemical reactions in the troposphere. The gasses themselves, along with their chemical reaction products, are transported and deposited away from their sources. NO₂ is a short-lived gas with a lifetime of 1 to 10 days. Airborne NO₂ is involved in acidification and ozone production, but is also of great concern because of its toxicity to humans, animals, and plants. NH₃ has a lifetime of only a few hours to a few days. It is the primary acid neutralizing agent in the atmosphere, affecting the pH of aerosols, cloud water, and rainfall, but can be also an acidifying agent in nitrification processes[4].

Nitrogen Dioxide

While the first emission inventory on SO₂, based on 1989 data, was completed in 1992 for the Rijeka Bay area[7], the first emission inventory on NO₂ was completed only recently[8], although emissions of NO₂ from four major industrial plants (based on 1989 data) were estimated earlier[9].

In the only complete emission inventory, in 1995 the total emission of NO₂ was estimated to 3627 t/a (1104 t N/a). The contribution of three major industrial sources (the old and new petroleum refineries and the power plant) was 2727 t/a (830 t N/a), i.e., 75.2% of the total, while other industrial sources contributed 76 t/a (23 t N/a), i.e., 2.1%. The new petroleum refinery and the power plant remained the biggest sources of NO₂ emissions in the city and the eastern industrial area (traffic is

FIGURE 1. Location of sampling sites.
dominant in the rest of the region, and in the whole county area generally). Emission of NO\textsubscript{2} from traffic was estimated at 705 t/a (215 t N/a), forming 19.4% of the total, while the contribution of other sources was equal to 119 t/a (36 t N/a), i.e., 3.3%. According to 1989 data (4686 t/a = 1426 t N/a), emission of NO\textsubscript{2} from major industrial sources was reduced by 40%. Such a marked reduction in emission should result in a decrease in ambient levels of NO\textsubscript{2}. Annual means of NO\textsubscript{2} and NH\textsubscript{3}, together with corresponding trendlines, are given in Fig. 2 (for Site 1) and Fig. 3 (for Site 2). For comparative reasons, ambient levels of SO\textsubscript{2} are also presented.

While ambient levels of SO\textsubscript{2} show substantial decrease since 1989 at both sites (66% at Site 1 and 55% at Site 2), reflecting the 70% reduction in emissions from four major industrial sources[10], trends of NO\textsubscript{2} and NH\textsubscript{3} do not follow the reduced emissions of these pollutants. Annual means of NO\textsubscript{2} were in the range of 34 to 60 μg/m\textsuperscript{3} at Site 1 (often exceeding the national limit value of 40 μg/m\textsuperscript{3}) and 14 to 26 μg/m\textsuperscript{3} at Site 2. Maximum daily concentrations were mostly above 100 μg/m\textsuperscript{3} (maximum 169 μg/m\textsuperscript{3}) at Site 1, and between 40 and 90 μg/m\textsuperscript{3} at Site 2. Annual means of NO\textsubscript{2} at urban Site 1 were in the range of the corresponding values observed in 1987 in some U.K. cities (except London), while maximum daily concentrations were several times lower than the maxima observed in the U.K.[11]. The obtained yearly averages at both sites are in the range of the ambient levels of NO\textsubscript{2} observed in Denmark. While no difference in NO\textsubscript{2} for the summer and winter results were obtained in Denmark[12], the winter results were found to be higher in Great Britain[11]. During the last 5 years of survey (Table 1), seasonal variations are visible only once at Site 1, presumably due to dominant traffic emissions from the nearby busy street, and in 3 of 5 years at Site 2.

FIGURE 2. Annual means of SO\textsubscript{2}, NO\textsubscript{2}, and NH\textsubscript{3} at urban Site 1.

FIGURE 3. Annual means of SO\textsubscript{2}, NO\textsubscript{2}, and NH\textsubscript{3} at suburban Site 2.
TABLE 1
Seasonal NO$_2$ Concentrations (1990/91–1994/95)

| Year   | Site1 W | Site1 S | W/S   | Site2 W | Site2 S | W/S   |
|--------|---------|---------|-------|---------|---------|-------|
| 1990/91| 50      | 47      | 1.06  | 18      | 13      | 1.42  |
| 1991/92| 39      | 41      | 0.94  | 21      | 20      | 1.09  |
| 1992/93| 35      | 36      | 0.99  | 21      | 20      | 1.03  |
| 1993/94| 39      | 43      | 0.90  | 20      | 14      | 1.41  |
| 1994/95| 47      | 38      | 1.21  | 27      | 20      | 1.33  |

CONCLUSION

Industrial plants within the Rijeka Bay area represent the major air pollution sources regarding SO$_2$ (95% of total), NO$_2$ (77% of total), and NH$_3$. Reduction by 70% of SO$_2$ emissions since 1989 resulted in a decline in the ambient levels of this pollutant observed at both sites. In spite of reduction in industrial NO$_2$ emissions by 40%, the ambient levels of NO$_2$ do not follow the cited reduction. A possible reason for such behaviour is the dominant impact of minor NO$_2$ sources like traffic at these sampling sites. The same stands for ambient levels of NH$_3$, in spite of the fact that the coke plant ceased its production at the end of 1994. A possible involvement of nitrogen compounds in complex atmospheric chemistry could also be considered as a possible cause of a lack of downward trends in ambient levels of nitrogen gaseous pollutants.

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**This article should be referenced as follows:**

Alebić–Juretić, A. (2001) Airborne Ns (NO<sub>2</sub> and NH<sub>3</sub>) in the Rijeka Bay Area (Croatia), 1980–1995. In Optimizing Nitrogen Management in Food and Energy Production and Environmental Protection: Proceedings of the 2nd International Nitrogen Conference on Science and Policy. *TheScientificWorld* **1(S2)**, 343–347.

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**BIOSKETCH**

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