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SHORT COMMUNICATION

EMISSIONS AND AMBIENT LEVELS OF SULPHUR DIOXIDE IN THE RIJEKA BAY AREA

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During the eighties the city of Rijeka was one of the most polluted cities in Croatia with sulphur dioxide due to high emission of this pollutant from industrial plants. In mid-eighties, annual means of SO_2 exceeded 100 μg/m^3 in the city centre, in the Bakar Bay area varied between 70-80 μg/m^3, while in the suburban residential area they were up to 40 μg/m^3. In 1995 annual means were below the guideline value of 50 μg/m^3 in the whole Rijeka Bay area. Emission inventory based on 1989 data estimated total SO_2 emission to approximately 36,000 t a year, 95% of which from industrial sources. The update from 1995 data gave a new estimate of approximately 11,000 t a year, which is a 70.5% reduction of SO_2 emission. However, the contribution of emissions from industrial sources remained practically unchanged (95%). The emission reduction resulted in the decrease of ambient levels of SO_2. The paper presents trends in SO_2 annual mean concentrations in the period 1986-1995 for two urban sites, two sites situated in the industrial area east of the city, and a suburban residential site.

Key words:
air quality, air pollutants, emission inventory

The industrial development of the city of Rijeka began in the 18th century (rope manufacture, sugar refinery). Major industrial plants and air pollution sources were founded in the 19th century (paper mill, petroleum refinery). The facilities of the petroleum refinery, now situated practically in the city centre (Mlaka), were expanding until relocation to the new refinery that was built in the sixties in the eastern suburban part of Rijeka on the Kostrena peninsula (Urinj). Some refining processes, however, remained at the old location. The oil-fueled power plant was built in the vicinity of the

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new refinery during the seventies, while a new coke-plant was erected in the nearby Bakar Bay in the same period. The coke-plant was shut down in 1994. The extensive industrialization resulted in deterioration of air quality in the entire Rijeka Bay area, thrusting Rijeka to the top of the most polluted cities in Croatia during the eighties. This paper deals with the emissions and ambient levels of sulphur dioxide at five sampling sites within Rijeka Bay area for the period 1986-1995.

MATERIALS AND METHODS

The accumulation of air pollutants in the lower troposphere of the Rijeka bay area was facilitated by the complex orography of the city and its surroundings. Figure 1 shows the locations of industrial plants and settlements. The city is situated on hill sides reaching up to 200 m above sea level, while some settlements in the surrounding area are situated as high as 340 m (Fig. 1, Sites 4 and 5). This fact greatly reduces the possibility of pollutant dispersion, despite the high stacks of up to 250 m that are located at the sea shore (power plant and coke-plant), The complex orography makes the wind roses differ significantly, even within the city alone, although the dominant winds come from the north-northeast sections of the entire area.

The air quality monitoring programme for the Rijeka Bay area started in mid-seventies, before the beginning of the planned industrial activities. Due to high emissions from industrial sources and the use of high sulphur content fuel for residential heating and traffic, the annual means of sulphur dioxide exceeded 100 $\mu g/m^3$ at some sampling points within the city.

Emissions

The first emission inventory for the Kvarner Bay area was done in 1985 as a part of a study estimating the environmental impact of a planned coal-fueled power plant Plomin II (1). The emission inventory of big industrial sources located in Kostrena and the Bakar Bay was completed in 1991 (2). Based on data from 1989, a new emission inventory was done as a part of a study on environmental protection for the Rijeka municipality (3). All stationary sources such as industrial and power plants above 45 kW were included in the inventory. Sulphur dioxide emissions from traffic were excluded, since the highest traffic contribution (in the city centre) to the emission inventory was estimated to be less than 1% (4).

Ambient levels

Five sampling sites were chosen for the analysis of trends in the ambient sulphur dioxide levels for the period 1986-1995. (6,7). Two are located in the urban area. Site 1 is in Čandekova Street and is considerably affected by emissions from the petroleum refinery Mlaka. Site 2 is located in F.la Guardia Street, the very centre of the city which is characterized by dense traffic, numerous boilers and domestic heating facilities, and scarce possibility for ventilation. The Bakar Bay industrial zone has two

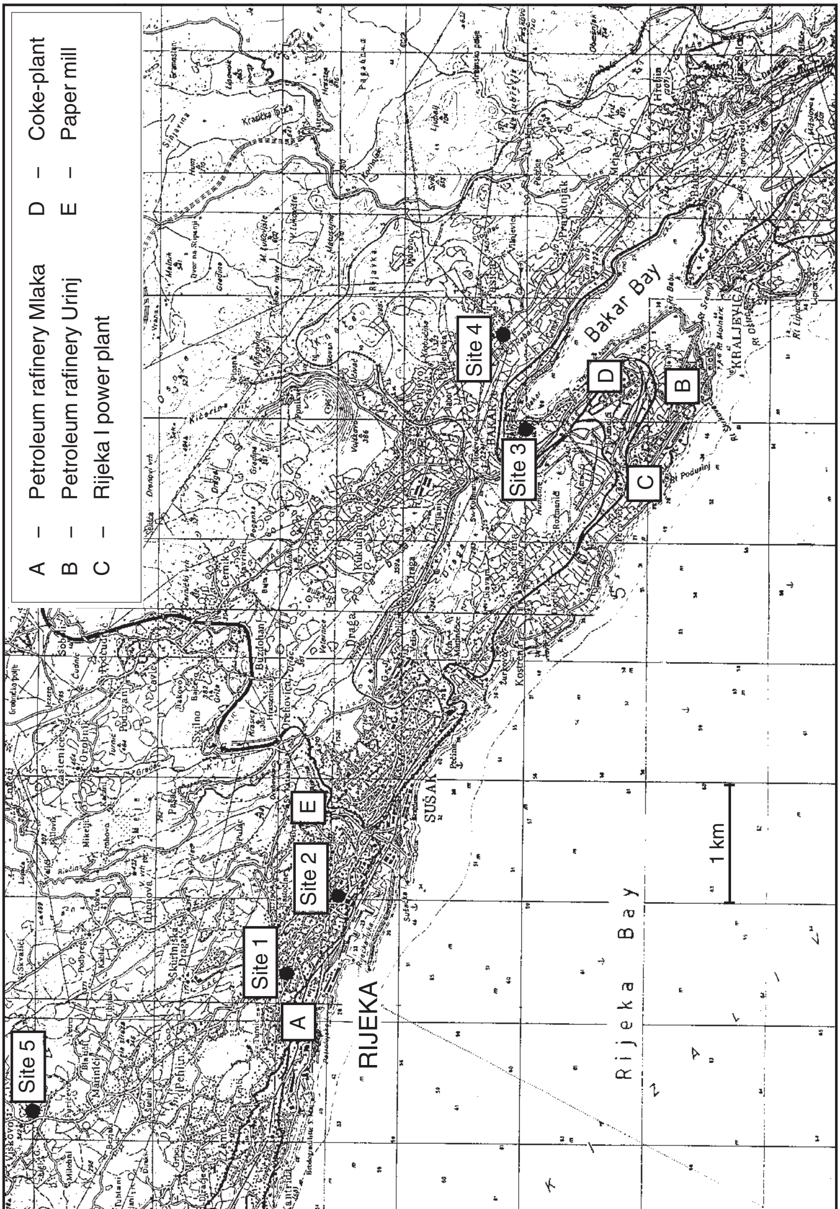

Figure 1 *Location of industrial sources and sampling sites*

sampling points. Site 3 is located in Bakar, a small town in the Bakar Bay with the coke-plant. Site 4 is situated in the suburban settlement Krasica, 250 m above the sea level, affected by emissions from the eastern industrial zone (petroleum refinery Urinj, Rijeka I power plant, and the coke-plant). At a considerable distance from the other sites, the control Site 5 is situated in Viškovo, a suburban settlement west from Rijeka, not directly affected by industrial emissions.

Air samples were collected in impinger bottles containing hydrogen peroxide solution on a daily basis throughout a year. The sampling was either manual (Sites 1, 2, 3 and 5) or semi-automatic (Site 4). At least 330 samples were collected over a year. Sulphur dioxide concentrations were determined by acidimetric method (8).

RESULTS AND DISCUSSION

In 1989 total sulphur dioxide emission was estimated to 36,320 t (Table 1). The contribution of four industrial sources, petroleum refineries Mlaka and Urinj, Rijeka I power plant, and the coke-plant in Bakar, was estimated to account for 91% of the total emission (32,935 t a year). With the inclusion of the paper-mill, the contribution reached up to 95%. The contribution of other sources was only 5%, including 13 municipal heating stations whose contribution was less than 2% and the remaining 210 boilers with less than 3% and domestic heating that participated with less than 1% of the total estimated emission (3).

Table 1 *Emission of sulphur dioxide in the Rijeka Bay area*

Source	Emission 1989		Emission 1995		Emission decrease	Relative difference
	t/y	%	t/y	%	%	Δ%
Petroleum refinery Mlaka (A)	3,557	9.82	1,036	9.69	70.50	–0.13
Petroleum refinery Urinj (B)	16,000	44.16	5,651	52.86	64.68	+8.70
Rijeka I power plant (C)	8,600	23.74	3,237	30.28	62.36	+6.54
Coke-plant (D)	4,778	13.19				
Paper mill (E)	1,260	3.48	279	2.61	77.86	–0.87
Municipal heating plants	690	1.90	202	1.89	70.72	–0.01
Boilers	985	2.72				
Domestic heating	360	0.99				
Total	**36,230**	100.00	**10,691**	100.00	70.49	

New emission inventory based on data from 1995 was done recently (5). The estimated emissions are given in Table 1. Due to a modification in data collection,

figures in rows 7 and 8 have been summed in order to make possible the comparison with 1989 data. The traffic emissions have been omitted from Table 1 for the same reason, despite the estimations of up to 171 t a year or 1.57% of the total sulphur dioxide emission in 1995 (5).

According to 1995 data, sulphur dioxide emissions dropped by 70.5%, compared to the 1989 data, but the contribution of major industrial sources remained practically unchanged. Although the coke-plant was shut down in 1994, the contribution to the total sulphur dioxide emission of the petroleum refineries Mlaka and Urinj and the Rijeka I power plant was 92.83% as compared to the 1989 estimation of 90.91%. Including the emission from the paper mill, the contribution of industrial sources remained the same, that is, approximately 95%. Despite the achieved reduction by more than 60%, the petroleum refinery Urinj and the Rijeka I power plant still remain the biggest sources of sulphur dioxide emission in the Rijeka Bay area. The contribution of the petroleum refinery Urinj to the total emission exceeds 50%, whereas the Rijeka I power plant contributes with 30%.

The reduction in emissions of sulphur dioxide came with the use of fuel with lower sulphur content, reduced production in the city, and a partial use of gas for energy supply in the petroleum refinery Mlaka and some municipal heating plants. The overall result was a drop in the ambient levels of sulphur dioxide in the entire Rijeka Bay area.

Annual mean concentrations

A common trend in annual mean SO_2 concentrations at chosen sampling sites (Fig. 2) was a slow decrease by the year 1991, except for Site 4 where the drop was observed as early as 1990. Then followed a trend of slight increase until the year 1993 with the exception of Site 1 that manifested nearly constant annual mean concentrations). Since 1993 all sampling sites manifested a sharp decrease in annual mean concentrations of sulphur dioxide. In 1995 they were below the national guideline value (GV) of 50 $\mu g/m^3$ (9), whereas at Sites 1 and 4 it occurred as early as 1994.

During the first five years of the studied period, annual means of sulphur dioxide were very high at urban sites, with values ranging from 93–124 $\mu g/m^3$. The highest annual means were registered in 1987 at sampling Site 1 (106 $\mu g/m^3$) and Site 2 (124 $\mu g/m^3$). Annual means of sulphur dioxide above 100 $\mu g/m^3$ have not been registered at these sampling sites ever since 1991.

Though affected by emissions of sulphur dioxide from major industrial sources, the annual means at sampling sites located in the Bakar Bay area were lower than the values observed at the urban sites. This could be explained by better circulation of air masses (sea breeze) and higher exposure to dominant winds (northeasterly bora and southern scirocco), which improved the ventilation of the whole area, although complex chemical reactions in the local atmosphere due to emissions from coke-plant are not to be neglected. The annual mean concentrations of sulphur dioxide varied between 50 and 76 $\mu g/m^3$ at Sites 3 and 4. The highest annual mean concentrations were obtained in 1986 and 1990 at Site 3 (74 $\mu g/m^3$) and in 1988 at Site 4 (76 $\mu g/m^3$). The distant Site 5 had manifested annual mean concentrations below the national guideline value for sulphur dioxide throughout the studied period.

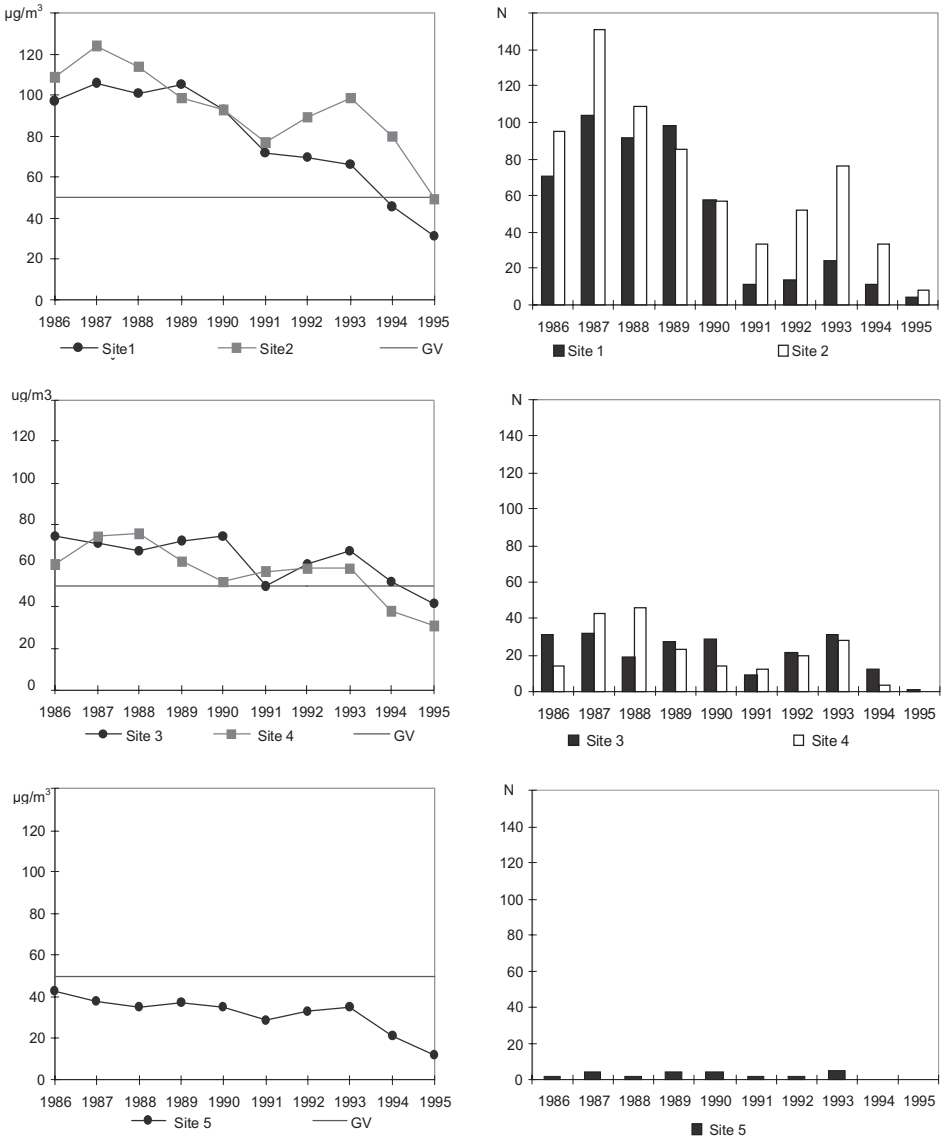

Figure 2 *Annual mean concentrations (µg/m³) and number of days (N) exceeding the national daily guideline value (GV) for sulphur dioxide in the period 1986–1995*

Maximum daily concentrations

Levels and frequencies of maximum daily sulphur dioxide concentrations observed at various sampling sites indicated different sources of this pollutant. In the first five years

of the studied period (1986-1990), maximum daily concentrations observed at Site 1 were in the range of 485-1084 $\mu g/m^3$, while in the latter five-year period (1991-1995) the corresponding range was 174-446 $\mu g/m^3$. That sampling site is strongly affected by emissions from industrial facilities and municipal heating plants. Maximum daily concentrations observed at Site 2 were lower in both five-year periods (298-383 $\mu g/m^3$ and 169-296 $\mu g/m^3$, respectively), although the annual mean sulphur dioxide concentrations were generally higher than at Site 1. This fact could be explained by a dominant impact of minor emission sources (boilers, traffic) constantly present in that area. Consequently, Site 2 had more days with average concentrations exceeding the national daily guideline value for sulphur dioxide of 125 $\mu g/m^3$ (9) in both five-year periods (497 and 202, respectively) than did Site 1 (248 and 64, respectively).

While urban sites had exhibited substantial decrease in daily maximum concentrations throughout the studied period, this trend was not as linear at sampling sites located in the Bakar Bay area. The maximum daily concentrations registered during the period 1986-1990 were in the range of 198-309 $\mu g/m^3$ at Site 3 and 166-308 $\mu g/m^3$ at Site 4, while in the latter five-year period these values varied between 131-339 $\mu g/m^3$ at Site 3 and 116-621 $\mu g/m^3$ at Site 4. The maximum daily concentration of 621 $\mu g/m^3$ was detected at Site 3 in 1993, during very unfavourable meteorological conditions. Similarly to the urban sites, number of days with mean concentrations exceeding the national daily guideline value was higher during the first five years of the studied period (138 $\mu g/m^3$ at Site 3 and 140 $\mu g/m^3$ at Site 4) than in the latter five-year period (74 $\mu g/m^3$ at Site 3 and 63 $\mu g/m^3$ at Site 4).

The drop in maximum daily concentrations, as well as the lower frequencies of higher daily means of sulphur dioxide are also visible at the remote Site 5. During the period 1986-1990, maximum daily concentrations were in the range of 167-332 $\mu g/m^3$, while in the latter five years their range was 80-202 $\mu g/m^3$. The number of days with average sulphur dioxide concentrations exceeding the national daily guideline value for sulphur dioxide was also higher in the first than in the last five-year period (16 vs. nine days).

Comparing the annual mean sulphur dioxide concentrations for the years during which the emission inventories were completed (1989 and 1995), we observed a substantial decrease in ambient sulphur dioxide concentrations at Site 1 (70.5%) and Site 5 (67.6%). These values are comparable with the amount of emission reduced at the petroleum refinery Mlaka, that is, with the general reduction in sulphur dioxide emission in the Rijeka Bay area. The decrease in ambient levels of sulphur dioxide registered at Site 2 was 49.5%, indicating a dominant impact of small and constant local sources such as traffic and boilers. In spite of the fact that the emissions of sulphur dioxide were reduced by 70% at the Bakar bay and Kostrena area, ambient levels of this pollutant show a decrease of only 41.7 % at Site 3 and 50% at Site 4.

CONCLUSION

With regard to sulphur dioxide ambient levels, the Rijeka Bay was one of the most polluted areas in Croatia during the eighties. Despite a reduction of almost 71% in

sulphur dioxide emission in 1995 as compared to 1989, the contribution of major industrial plants to the total emission had practically remained unchanged (95%). The emissions fell as a consequence of partial introduction of gas for energy supply in the petroleum refinery Mlaka and some municipal heating plants, of switching to the use of low sulphur content fuel, and of reduced production in some industrial plants. The substantially reduced emission caused the sulphur dioxide level drop by approximately 40-70% with regard to the levels observed in 1989. Despite the fact that the coke-plant ceased with production in 1994 and that the petroleum refinery Urinj and Rijeka I power plant reduced the SO_2 emission by approximately 60%, the lowest decrease in the ambient levels of sulphur dioxide was recorded in the industrial area (Sites 3 and 4). The reason for this could be the meteorological conditions allowing better ventilation by means of dominant winds, as well as the changed chemistry of the local atmosphere subsequent to the shutdown of the coke-plant.

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Sažetak

EMISIJA I IMISIJA SUMPOROVOG DIOKSIDA NA PODRUČJU RIJEČKOG ZALJEVA

Zbog visokih emisija iz industrijskih izvora, sredinom osamdesetih godina Rijeka je bila među gradovima s najvišom koncentracijom sumporovog dioksida u Hrvatskoj. Prosječne godišnje koncentracije sumporovog dioksida prelazile su 100 μg/m^3 u središtu grada, na području Bakarskog zaljeva godišnji prosjek kretao se od 70 do 80 μg/m^3, dok je

u prigrađu iznosio oko 40 μg/m^3. Od kraja osamdesetih godina započinje trend pada koncentracija sumporovog dioksida tako da su 1995. god. prosječne godišnje vrijednosti zadovoljavale preporučenu vrijednost kakvoće zraka na čitavom području Riječkog zaljeva. Razlog tomu je smanjenje emisija sumporovog dioksida u promatranom razdoblju. Katastrom emisija napravljenim na osnovi podataka za 1989. god. emisija sumporovog dioksida procijenjena je na oko 36.000 t/god., od čega je udio velikih industrijskih onečišćivača iznosio 95%. Novim katastrom na bazi podataka za 1995. god. emisija je procijenjena na oko 11.000 t/god., što je smanjenje za 70,5%. Unatoč tako velikom smanjenju emisije, udio industrijskih onečišćivača u ukupnoj emisiji sumporovog dioksida ostao je nepromijenjen (95%). Ovakvo smanjenje emisija odrazilo se na imisijske koncentracije sumporovog dioksida. U radu je dan prikaz kretanja koncentracija sumporovog dioksida u razdoblju 1986-1995. na dvije postaje na području grada Rijeke (Čandekova ul. i Ul. F. Ia Guardije) i Bakarskog zaljeva (Bakar, Krasica) te na jednoj u prigradskom naselju (Viškovo) na zapadnom dijelu Riječkog zaljeva.

Ključne riječi:
kakvoća zraka, katastar emisija, onečišćenja

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