

AIR POLLUTION IN ŠIBENIK BEFORE AND AFTER THE SHUTDOWN OF MAJOR LOCAL INDUSTRIES

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This study compares the values of the critical air pollution indicators (including sulphur dioxide, smoke, total deposited matter, gaseous fluorides, fluorides, and manganese in suspended particulates and deposited matter) measured in Šibenik for years 1989/90 when the industry was working with full capacity, and for years 1994/95 and 1995/96 when most plants were shut down due to Serbian aggression. The purpose of this study was to assess the influence of industrial air pollution sources on the air quality in Šibenik. The pollution indicators show that the air in Šibenik was excessively polluted until the major industries were shut down as a result of Serbian aggression in Croatia, while it is only slightly polluted today. These findings prove the dominant influence of industrial emissions on the air quality in Šibenik.

Key words:
air pollutants, follow-up, industrial sources

Before the Serbian aggression in Croatia, the main sources of air pollution in the Šibenik area were two plants (light metals and electrodes, and ferroalloys plants), the port for transshipment, and a warehouse of raw phosphate, asphalt base, and quarry. High emission of gases, particles and vapours were mainly the consequence of obsolete technology as well as of insufficient, inefficient and ill-maintained purification equipment.

The industry of Šibenik suffered significant damage from the Serbian aggression. The high voltage device of light metals plant was completely destroyed and all electrolytic furnaces became useless due to the aluminium congealment. The Croatian government decided to close the other plant as it also suffered significant damage. The port for transshipment was reactivated only in June 1996.

This paper compares the values of critical air pollution parameters measured in 1989/90 when the industry was working with full capacity and in 1994/95 and 1995/96 when most plants were shut down. The purpose of the study was to determine the degree to which these pollution sources affected the air quality in Šibenik.

METHODS

A network of sampling stations was established at selected locations (Table 1) to determine the degree of air pollution in the Šibenik area (1). Figure 1 shows the location of sampling stations and of the dominant pollution sources. Until 1990, the measurements were continuously performed and were reinstated in 1994, though to a slightly lower extent.

Table 1 Major pollutants measured at seven sampling stations in the Šibenik area

Location of sampling stations	Pollutant
1 Town centre	SO ₂ , smoke, gaseous F ⁻ , particulate F ⁻ and Mn, total deposited matter, F ⁻ in soluble part, Mn in soluble and insoluble part (Location 1)
2 Suburban area	Locations 2–7
3 West residential area	Total deposited matter, F ⁻ in soluble part, Mn in soluble and insoluble part
4 Highway	Since 1995. PO ₄ ³⁻ and NO ₃ ⁻ are also measured in the soluble part of deposited matter
5 East residential area	
6 Above light metals plant	
7 Above transshipment port	

(SO₂ and smoke being indicators of fuel combustion, fluorides of light metals plant, manganese of electrodes and ferroalloys plant, phosphates and nitrates of warehouse and transshipment emissions.)

Twenty four-hour samples of SO₂ were collected by sucking a measured volume of air through a 1% H₂O₂ solution (2) and the SO₂ was determined by the sulfate method (sensitivity 10–15 µg/m³) (3). Twenty four-hour samples of smoke were collected on Whatman No. 1 filter paper and the smoke was determined refractometrically (4). Twenty four-hour samples of gaseous fluorides were collected in a solution of 0.25 M NaOH, and particulate fluorides were collected on filter paper impregnated with a solution composed of 1% NaOH and 2% glycerol. Fluoride concentration was determined potentiometrically with a 2% reproducibility (ISE) (5). Twenty four-hour samples of suspended particulate matter were collected by sucking a measured volume of air (1000–1200 m³) through glass fiber filters (HV-sampler). The standard deviation was 10 µg/m³ at an average mass concentration of 112 µg/m³ of particulate matter in ambient air (6). The monthly samples of total deposited matter were collected by deposit gauges. (reproducibility 15%) (7). Deposited and particulate manganese was determined by the flameless AAS technique (8, 9). Nitrates and phosphates were determined spectrophotometrically (10).

RESULTS AND DISCUSSION

Figure 2 shows a summary of results for the station in the town centre concerning sulphur dioxide, smoke, fluorides and manganese concentrations (µg/m³).

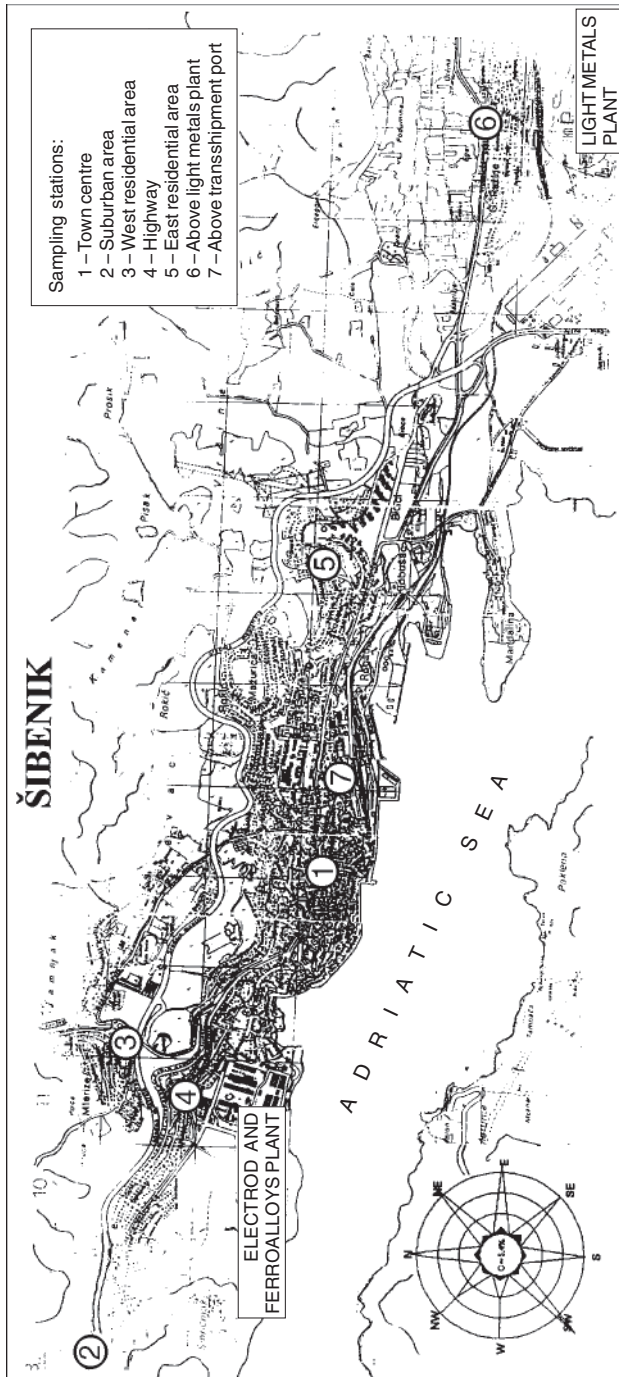


Figure 1 The location of sampling stations in the town of Šibenik

SO₂ and smoke

Mean annual concentrations of sulphur dioxide for years 1989/90, 1994/95, and 1995/96 ranged from 34.8 $\mu\text{g}/\text{m}^3$ to 42.8 $\mu\text{g}/\text{m}^3$ (98th percentile from 90.3 $\mu\text{g}/\text{m}^3$ to 110 $\mu\text{g}/\text{m}^3$). Mean annual concentrations of smoke for the same years ranged from 12 $\mu\text{g}/\text{m}^3$ to 22 $\mu\text{g}/\text{m}^3$ (98th percentile from 52 $\mu\text{g}/\text{m}^3$ to 105 $\mu\text{g}/\text{m}^3$) (Figure 2). The fact that concentration levels of SO₂ and smoke remained practically the same indicates that the main sources of these pollutants were domestic heating and traffic.

However, during the periods of measurement mean annual concentrations of SO₂ and smoke did not exceed the value recommended by the Croatian Ordinance (RV=50 $\mu\text{g}/\text{m}^3$) (12), which, according to the Law on Air Quality Protection (1), serves for categorization of areas by air quality into: 1. low pollution (below recommended value, RV), 2. medium pollution (between RV and limit value, LV), and 3. high pollution (above LV).

Fluorides

Mean annual concentration of gaseous fluorides in the town centre in 1989/90 was 4.13 $\mu\text{g}/\text{m}^3$ (98th percentile 60.31 $\mu\text{g}/\text{m}^3$) and of particulate fluorides 6.25 $\mu\text{g}/\text{m}^3$ (98th percentile 76.4 $\mu\text{g}/\text{m}^3$). In 1994/95 and 1995/96, gaseous fluorides dropped to about 0.12 $\mu\text{g}/\text{m}^3$ (about 30 times lower concentration) and particulate fluorides dropped to about 0.009 $\mu\text{g}/\text{m}^3$ (nearly 70 times lower concentration) (Figure 2). Thus Šibenik, which in 1989/90 was categorized as a high pollution area (above LV=1 $\mu\text{g}/\text{m}^3$), became a low pollution area (12) in 1994/95 and 1995/96 with regard to air pollution by fluorides. It is obvious that the source of fluoride air pollution in Šibenik was the producer of light metals.

Manganese

The town centre mean annual concentration of particulate manganese in 1989/90 was 0.759 $\mu\text{g}/\text{m}^3$ (98th percentile 3.297 $\mu\text{g}/\text{m}^3$). In 1994/95 and 1995/96, the annual means of manganese concentration decreased significantly (0.112 $\mu\text{g}/\text{m}^3$ and 0.033 $\mu\text{g}/\text{m}^3$ respectively). In all three periods of examination, the manganese mean annual concentrations were lower than the recommended value (RV=1 $\mu\text{g}/\text{m}^3$), but we should point out here that the concentrations were significantly lower during the last few years (12). Therefore, it is obvious that the source of manganese air pollution in Šibenik was light metals plant (Figure 2).

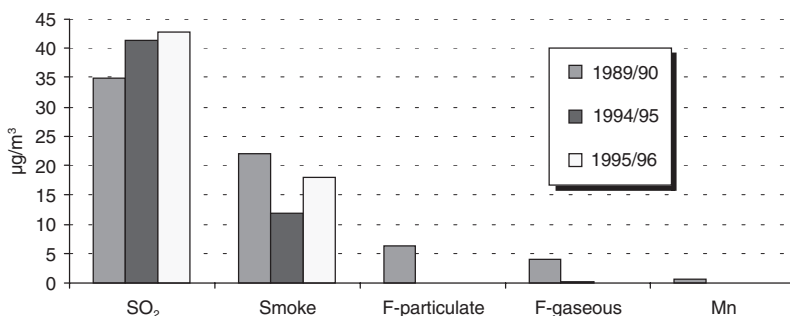


Figure 2 Mean annual concentrations of SO₂, smoke, fluoride and manganese
Measuring location no. 1 (town centre)

Total deposited matter

In 1989/90, the mean annual concentrations of total deposited matter by locations ranged from 379 mg/m²/day in measuring location no. 3 to 1032 mg/m²/day in measuring location no. 2. The highest monthly mean was 3600 mg/m²/day. The mean annual concentrations of total deposited matter exceeded the limit value (LV=350 mg/m²/day) (11) in all locations.

The decrease of concentrations occurred in all measuring locations during 1994/95. In the western part of the town, the mean annual concentrations (from 228 mg/m²/day to 239 mg/m²/day) were lower than limit value, but exceeded the recommended value (RV= 200 mg/m²/day), while in the eastern part they were below recommended value (11).

With the production resumed in 1995/96, total deposited matter manifested a slight increase. The highest increase was registered at the measuring location no. 2 above the quarry (410 mg/m²/day) where the mean annual concentration exceeded limit value (Figure 3).

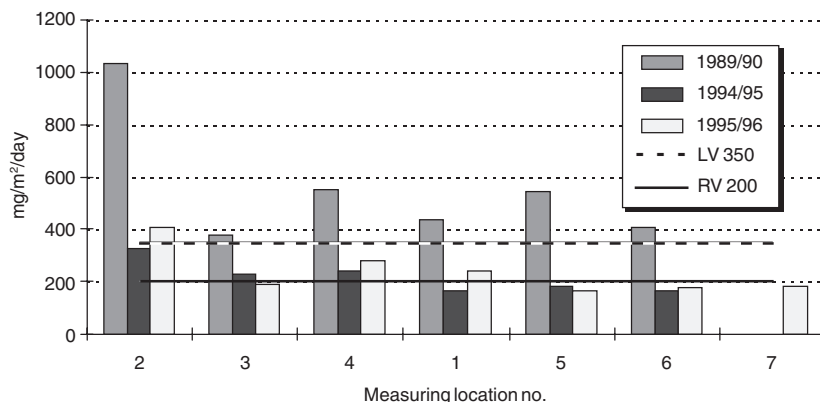


Figure 3 Mean annual concentrations of total deposited matter
LV – limit value; RV – recommended value

In regard to total deposited matter, the air in Šibenik was categorized in the 3rd category until 1990. In 1994/95, the air was slightly polluted (1st category) in the eastern parts, while in the western parts the pollution was moderate (2nd category). In the 1995/96 period, the air pollution was again significant (3rd category) (11) in the western parts.

Fluorides in deposited matter

Mean annual concentrations of fluorides in the soluble part of deposited matter during the 1989/90 period ranged from 6.96 mg/m²/day in the eastern part of the town and 0.864mg/m²/day in the town centre to 0.782 mg/m²/day in the western part.

Mean annual concentrations of fluorides in the soluble part of deposited matter for the years 1994/95 and 1995/96 were comparable throughout the town and ranged from 0.219 mg/m²/day to 0.290 mg/m²/day in 1994/95 and from 0.181 mg/m²/day to 0.245 mg/m²/day in 1995/96.

It is noteworthy that the fluoride concentrations in the air of the eastern part of the town were 30 times lower than in the 1989/90 period (Figure 4).

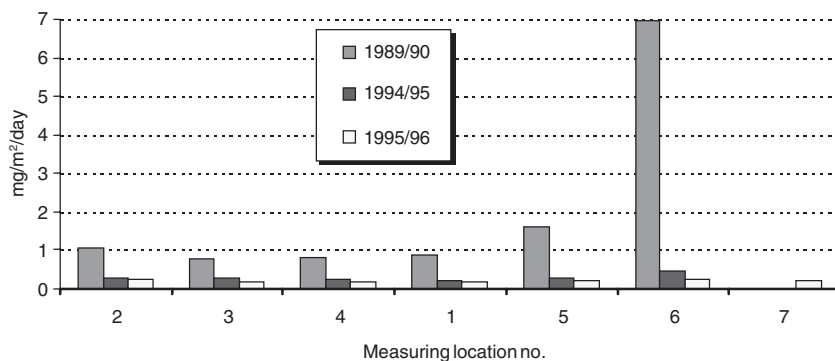


Figure 4 Mean annual concentrations of fluorides in the soluble part of deposited matter

Manganese in deposited matter

Mean annual concentrations of manganese in the soluble part of deposited matter in the 1989/90 period ranged by locations from 0.075 mg/m²/day to 0.216 mg/m²/day, while in the insoluble part they ranged from 0.513 mg/m²/day to 2.569 mg/m²/day. The highest concentrations were measured in the western part of the town (measuring location no. 3) (Figure 5).

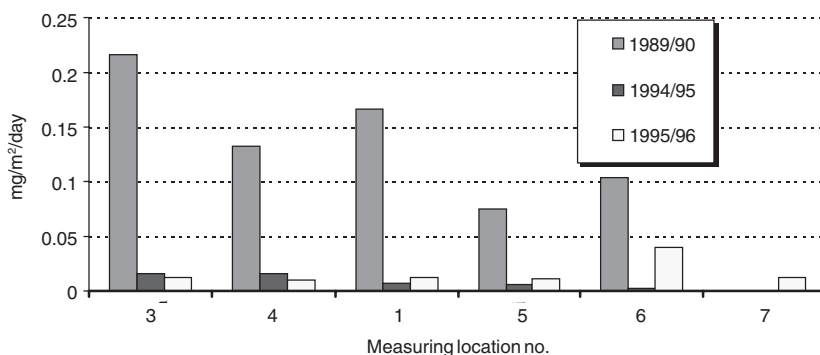


Figure 5 Mean annual concentrations of manganese in the soluble part of deposited matter

During 1994/95 the mean annual concentrations of manganese in the soluble part of total deposited matter ranged from 0.003 mg/m²/day to 0.012 mg/m²/day, while in the insoluble part they ranged from 0.027 mg/m²/day to 0.187 mg/m²/day. A further decreasing trend was registered during the 1995/96 period. It was observed that the concentrations of manganese in the western part of town decreased 35 times in comparison to the 1989/90 period. The pronounced differences in the concentrations of manganese and fluorides between the western and the eastern part of the town which existed in the previous years were seen to disappear (Figures 5 and 6).

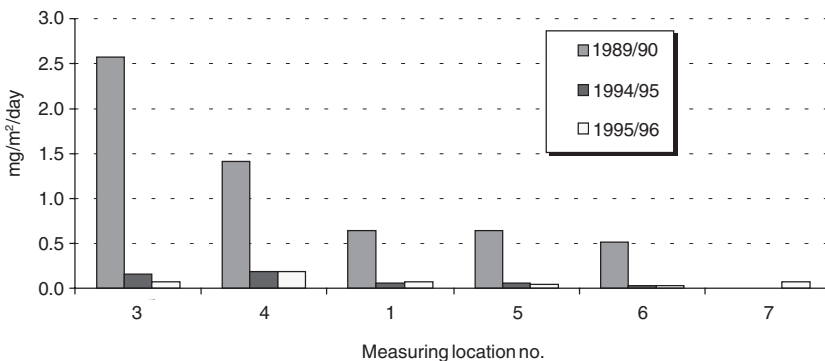


Figure 6 Mean annual concentration of manganese in the insoluble part of deposited matter

Nitrates and phosphates in deposited matter

In 1995/96, we began to examine nitrates and phosphates in the total deposited matter to determine the influence of the newly reactivated phosphate transshipment port (June 1996).

In the measuring period from November 1995 to August 1996, the monthly concentrations of nitrates were comparable with the mean concentration reaching 2.569 mg/m²/day. A slight increase in monthly concentrations was being registered ever since August 1996 as a consequence of the reactivation of the transshipment port. The mean annual concentrations of nitrates by measuring locations in Šibenik ranged from 3.49 mg/m²/day to 5.65 mg/m²/day (Figure 7). The concentrations of nitrates in total deposited matter did not significantly differ from those measured in other coastal towns (Rovinj 14 mg/m²/day, Rijeka 4–6 mg/m²/day, Pula 10–13 mg/m²/day) (12).

The phosphate content in total deposited matter was under detection limit (<0.01 mg/m²/day) in all measuring locations from November 1995 to June 1996. In June and July 1996 when transshipment port resumed operation, monthly concentrations manifested a sudden increase at the location above the port. After August 1996, the

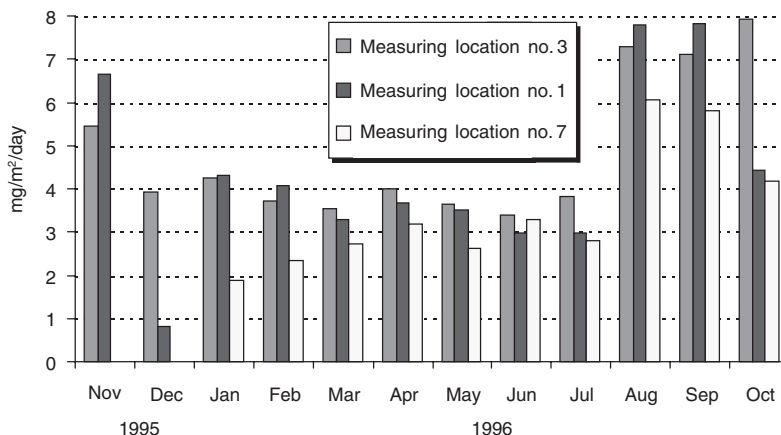


Figure 7 Monthly concentrations of nitrates

concentrations of phosphates stabilized and ranged from 0.103 mg/m²/day to 0.725 mg/m²/day (Figure 8).

Mean concentrations by measuring locations for the period June–November 1996 ranged from 0.159 mg/m²/day to 1.891 mg/m²/day. The concentrations of phosphates in total deposited matter in the Šibenik air were significantly lower than those measured in place with a fertilizer plant, where they ranged from 2.4 mg/m²/day to 10 mg/m²/day in 1995/96 (12).

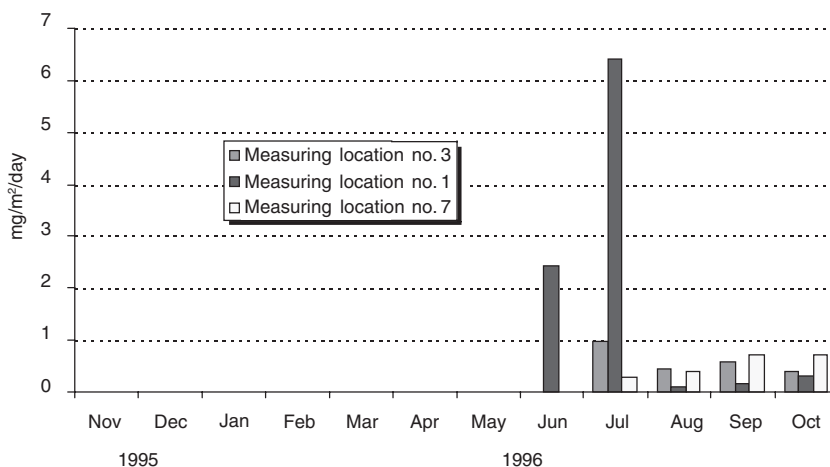


Figure 8 Monthly concentrations of phosphates

CONCLUSION

The comparison of the results obtained from the examination of critical parameters for the years 1989/90, 1994/95, and 1995/96 shows that the air in Šibenik was excessively polluted (3rd category) until the shutdown of major industries due to Serbian aggression in Croatia. With the considerably reduced industrial activity in the area today, the Šibenik air is only slightly polluted (1st category). This fact proves that the emissions from factory of light metals and factory of electrodes and ferroalloys had the highest influence on the air pollution in the Šibenik area.

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*Sažetak***ONEČIŠĆENJE ZRAKA U ŠIBENIKU PRIJE I POSLIJE PREKIDA RADA
NAJVEĆIH GRADSKIH INDUSTRIJA**

U ovome radu uspoređeni su rezultati ispitivanja koncentracija kritičkih pokazatelja onečišćenja zraka, i to plinovitih fluorida, fluorida i mangana u česticama, sumpor dioksida, dima, ukupne taložne tvari te istaloženih fluorida i mangana za mjerno razdoblje 1989/90., kada je industrija u Šibeniku radila punim kapacitetom i za razdoblja 1994./95., 1995./96., kada većina pogona nije bila u funkciji. Svrha je bila utvrditi utjecaj prije navedenih izvora onečišćenja na kakvoću zraka grada Šibenika. S obzirom na navedene pokazatelje kakvoće, utvrđeno je da je zrak u području grada Šibenika do agresije na Hrvatsku bio prekomjerno onečišćen (III. kategorija), a da je danas neznatno onečišćen (I. kategorija).

Ključne riječi:
industrijski izvori, onečišćenja zraka, praćenje

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