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OBSERVATION

AIRBORNE METAL CONCENTRATIONS IN SHIPYARD ENVIRONMENT

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Protection against corrosion in the shipyard is a source of airborne particles. From October 1996 to September 1997 samples of suspended particles (1 site) and dustfall (6 sites) were collected in the vicinity of a repairs shipyard situated in the Martinšćica Cove, east of the city of Rijeka, Croatia. Collected samples were analysed for lead, cadmium, iron, copper, and zinc content. Though annual mean concentrations of suspended particles, lead, and cadmium kept below the guideline values, the metal contents were generally higher than values measured in the city centre. The correlation between the quantity of abrasives used at the shipyard and monthly mean concentrations of all parameters except cadmium suggests that the shipyard was the main source of those pollutants. The annual mean, as well as maximum monthly amount of dustfall at the site next to the shipyard zone exceeded the national limit values, indicating considerable pollution of this area with coarse particles. The annual mean quantity of lead in dustfall exceeded the guideline values at the same site. The content of metals occasionally observed in dustfall at particular sites surrounding the shipyard depended on the location of corrosion protection activities and meteorological conditions within the Martinšćica Cove.

Key words:
air pollution, suspended particles, dustfall, metals, shipyard

Metal concentrations are routinely determined in either suspended particles or dustfall as a part of air pollution monitoring in the cities. Some airborne metals such as lead and cadmium are of great concern because of their toxicity. Others such as iron,

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manganese, and copper act as catalysts in some chemical reactions in the atmosphere (1). Human activities are the principal sources of airborne metals and the atmosphere is the principal carrier to other media such as water and soil. Sources of airborne metals in the urban atmosphere are power plants, industrial installations, heating, and traffic. Preparation of metal surfaces with abrasives (2) for protection against corrosion in shipyards is a significant source of airborne particles. The emissions consist of abrasives, old paint, coating, and other dirt.

This paper analyses the measurements of suspended particles and dustfall as well as their metal content (iron, copper, zinc, lead, and cadmium) from October 1996 to September 1997 in the surroundings of a repairs shipyard »Viktor Lenac« of Rijeka, Croatia. The shipyard is located somewhat to the east from the city proper, at the Martinšćica Cove, and occupies a part of the coastal area towards the Žurkovo Cove. The shipyard area is limited by the Rijeka-Split highway. The closest residences are only 30 m away from the shipyard. The landscape is very unfavourable for the nearby residents as they live on a hill just above the shipyard. Traffic is another significant source of airborne particles and metals. With the traffic density of 5,000 vehicles a day and the length of the highway surrounding the cove of about 1.5 km, the lead emission was estimated to 160 t/a. By contrast, the total lead emission from the shipyard was 272 t/a (3).

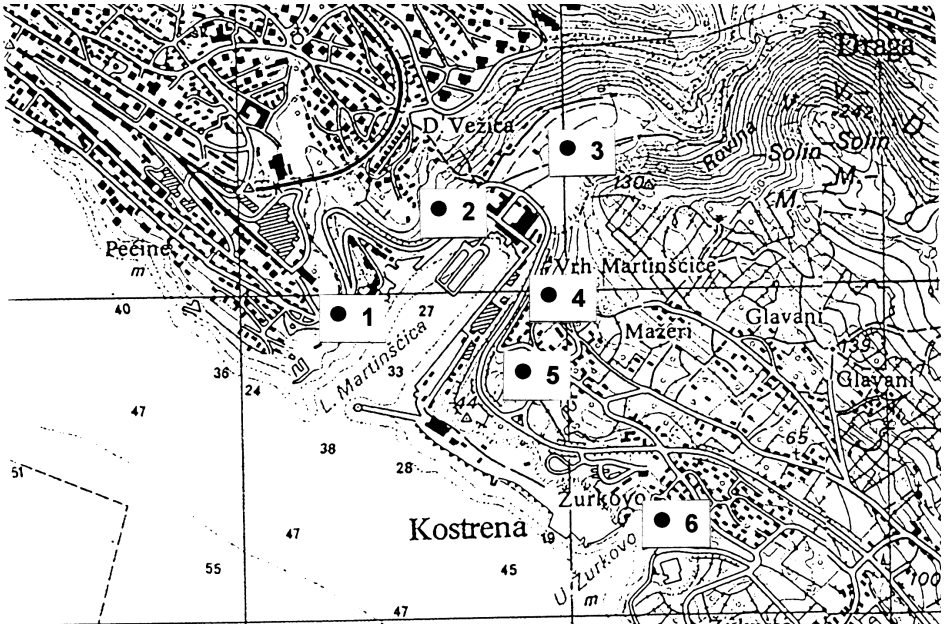

Figure 1 *Location of sampling sites for dustfall surrounding the repair shipyard »Viktor Lenac«: 1. Plumbum, 2. Martinšćica Curve, 3. Bunari, 4. Vrh Martinšćice I, 5. Vrh Martinšćice II, and 6. Žurkovo Cove*

MATERIALS AND METHODS

Samples of suspended particles were taken at Vrh Martinšćice I (Site 4, see Figure 1), located just above the shipyard. The particles were collected with a high-volume sampler on glass fibre filters. One hundred samples were collected between October 1996 and September 1997, of which 44 were analysed for the metal content. Concentrations of suspended particles were determined gravimetrically (4). The filters were extracted ultrasonically with the mixture of HCl and HNO_3, and the metals were determined by flame (iron, copper, and zinc) or graphite furnace (lead and cadmium) atomic absorption spectrometry (5).

Samples of dustfall were collected at six sampling sites surrounding the shipyard: 1. Plumbum, 2. Martinšćica Curve, 3. Bunari, 4. Vrh Martinšćice I, 5. Vrh Martinšćice II, and 6. Žurkovo Cove (see Figure 1). Twelve samples of dustfall were collected form each sampling site a month. The exceptions are Site 1 and Site 5 with one destroyed and one contaminated sample, respectively. Standard German gauges were used to collect dustfall (6). The metal content was determined by atomic absorption spectrometry after acid digestion (25% HCl) of the ash.

RESULTS AND DISCUSSION

Suspended particles

Table 1 shows concentrations of suspended particles and metals in the vicinity of the shipyard and includes measurements taken in the same period in the city centre of Rijeka for comparison (7, 8). The annual average of suspended particles at Site 4 (Vrh Martinšćice I) kept below the recommended value (RV=75 $\mu g/m^3$), while the 98th percentile (C_{98}) of 119 $\mu g/m^3$ was practically equal to the 98th percentile of the recommended value RV_{98}=120 $\mu g/m^3$. The annual mean concentrations of lead and cadmi-

Table 1 *Average (C), maximum daily (C_M), and C_{98} values of suspended particles and metals*

Location / Period	N	TSP(µg/m³) C	C_{98}	C_M	Metals N	Pb(µg/m³) C	C_M	Cd(ng/m³) C	C_M	Fe(µg/m³) Fe	C_M	Cu(µg/m³) C	C_M	Zn(µg/m³) C	C_M
Vrh Martinšćice															
1996/97	100	54	119	150	44	0.23	0.97	0.55	2.13	1.87	7.05	0.62	2.12	0.31	1.66
II-IX/1997															
with ABO	37	60		150	13	0.29	0.97	0.52	7.05	3.14	7.05	0.88	2.07	0.35	1.30
Without ABO	33	55		114	17	0.27	0.45	0.77	2.13	1.64	5.79	0.66	2.12	0.20	0.55
Rijeka															
1996/97	46	75	204	247	46	0.19	0.40	0.44	3.70	0.63	1.06	0.25	0.61	0.09	0.22

ABO – abrasive blasting operations

um also kept below the guideline values of 1 and 0.010 $\mu g/m^3$, respectively. Although the average concentration of suspended particles was approximately 25% lower, airborne metal concentrations were higher in the shipyard environment than in the city centre. The concentrations of iron, copper, and zinc were 3, 2.5, and 3.5 times higher, respectively, than the corresponding values in the city centre. The three metals were the major constituents of abrasives used in the shipyard (9) as well as of the coating, paint, and rust treated by abrasives. Concentrations of lead (approximately 20%) and cadmium (approximately 25%) were also higher in the shipyard environment.

Records on treatment with abrasives which included dates when these took place and quantities of abrasives are available from February 1997. Average airborne concentrations of suspended particles and lead were 9% and 7% higher respectively on treatment days than on »idle« days. Similarly, average airborne concentrations of iron almost doubled (91%), while zinc and copper increased 75% and 33%, respectively. The exception was cadmium with higher concentrations on »idle« days than on treatment days, which points to sources other than the shipyard.

The correlations between the average monthly concentrations of suspended particles/metals collected on treatment days and the monthly consumption of abrasives (February–September1997) point to the shipyard as the main source of these pollutants. For instance, the correlations between the consumption of abrasives and suspended particles and lead were r=0.513 and r=0.512, respectively (Figure 2). The correlations were even higher between the consumption of abrasives and the monthly averages for iron (r=0.815), copper (r=0.760), and zinc (r=0.911).

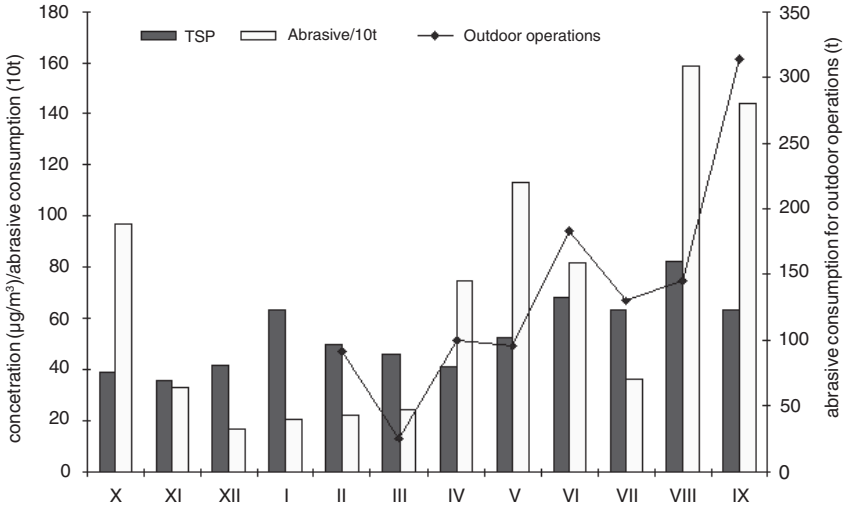

Figure 2 *Monthly average concentrations of suspended particles, total monthly consumption of abrasives, and the consumption of abrasives on days when suspended particles were sampled*

Dustfall

Table 2 shows the results of total dustfall measurements and quantity of metals found in the vicinity of the shipyard. The annual average of total dustfall at Site 4 (Vrh Martinšćice I) located just above the shipyard exceeded the national limit value (LV) of 350 mg/m^2 day. The monthly limit value of 650 mg/m^2 day was exceeded once in November 1996 and once in February 1997. The annual average of lead in dustfall exceeded the recommended value of 100 μg/m^2 day. Site 4 also recorded maximum concentrations of iron, copper, and zinc. By contrast, the annual means for total dustfall, lead, and cadmium kept within the recommended values on all other sampling sites. A higher content of iron, copper, zinc, and lead were observed in dustfall collected at Sites 1 and 2 (Plumbum and Martinšćica Curve), but the annual means of total dustfall were similar to other sampling sites.

Table 2 *Total dustfall (mg/m^2 day) and metal content (μg/m^2 day)*

Sampling site	N	Total dustfall C	Total dustfall C_M	Pb C	Cd C	Fe C	Cu C	Zn C
1. Plumbum	11	151	286	48	0.5	2592	99	206
2. Martinšćica Curve	12	142	266	41	0.5	2791	172	239
3. Bunari	12	91	177	14	1.0	1249	51	105
4. Vrh Martinšćice I	12	369	1607	220	0.5	28011	937	2608
5. Vrh Martinšćice II	11	121	235	11	0.7	1215	42	118
6. Žurkovo Cove	12	131	209	27	0.5	1216	52	93

Figure 3 shows the monthly totals for dustfall and metals at three sampling sites with the highest metal content: Sites 1, 2, and 4 (Plumbum, Martinšćica Curve, and Vrh Martinšćice I). There is no visible common trend in monthly totals for dustfall and metals at those sites. Extremely high total dustfall (1607 mg/m^2 day) and metal content (iron: 288 271 μg/m^2 day, zinc: 25 564 μg/m^2 day, copper: 8105 μg/m^2 day, and lead: 1248 μg/m^2 day) were measured in November 1996. Concurrently, higher total dustfall was recorded at the other two sampling sites, but the metal content was relatively low. The highest metal concentrations were measured at Site 1 (Plumbum) in September 1997 (iron: 5323 μg/m^2 day, zinc: 544 μg/m^2 day, copper: 219 μg/m^2 day, and lead: 156 μg/m^2 day). While the metal content in the sample of dustfall from September 1997 was low at Site 4 (Vrh Martinšćice I), Site 2 (Martinšćica) showed elevated iron, copper, and zinc. High concentrations of iron, copper, and zinc (8008 μg/m^2 day, 484 μg/m^2 day, and 519 μg/m^2 day, respectively) recorded in May 1997 at Site 2 (Martinšćica Curve) were followed by elevated concentrations of iron and zinc, but not copper at Site 1(Plumbum). Low metal content was found in a dustfall sample collected in the same month at Site 4 (Vrh Martinšćice I).

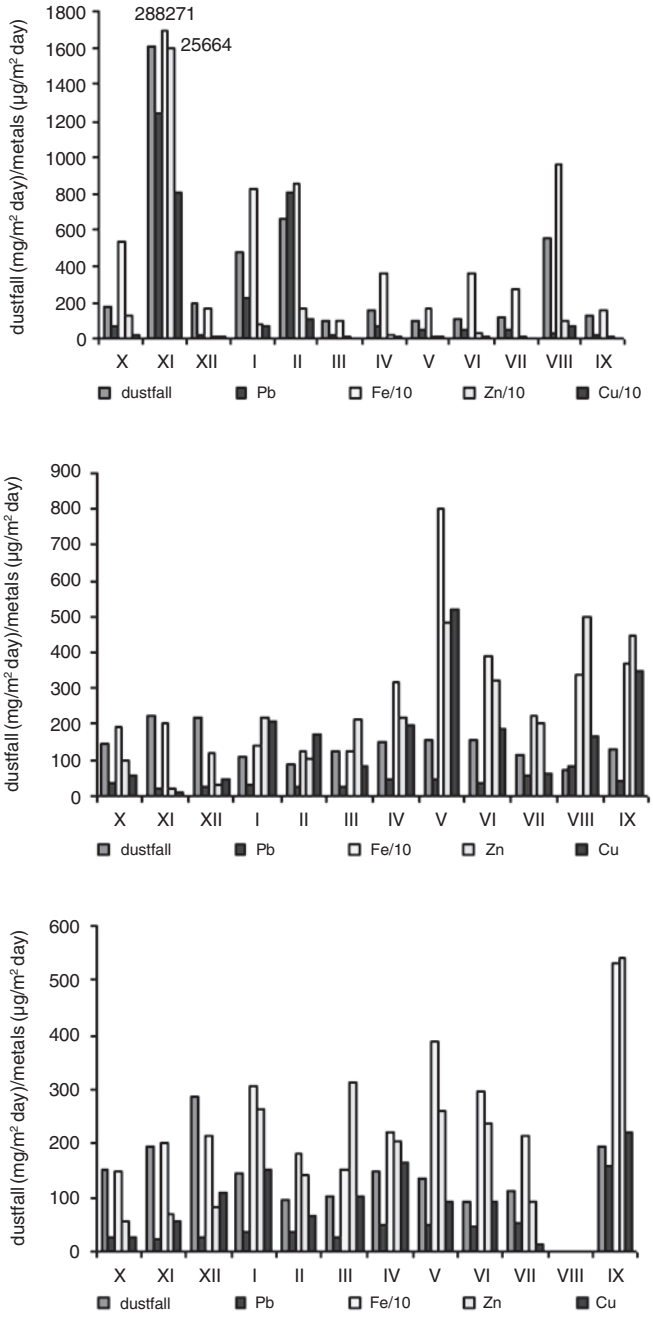

Figure 3 *Monthly amounts of total dustfall and metals at three sampling sites with the highest metal content*

CONCLUSION

Our measurements indicated that the treatment of metal surfaces with abrasives was a source of elevated concentrations of suspended particles and metals in the environment of the shipyard »Viktor Lenac«. This was confirmed by correlations between the monthly consumption of abrasives and of airborne concentrations of the recorded pollutants. Elevated quantities of dustfall and metals occasionally observed in the surroundings of the shipyard area depended on the location of treatment operations and on meteorological conditions in the Martinšćica Cove.

REFERENCES

1. Miller DL, Byrd YE, Perona MJ. Source of Pb, Cu and Zn in fogwater. Water, Air Soil Pollut 1987;32:329–40.
2. Conroy LM, Menezes RM, Sullivan PM. Lead, chromium and cadmium emission factors during abrasive blasting operations by bridge painters. Am Ind Hyg Assoc J 1995;56:226–71.
3. Croatian Institute for Urban Planning. Studija utjecaja na okoliš brodogradilišta »Viktor Lenac« [Environmental protection study of the »Viktor Lenac« shipyard, in Croatian]. Zagreb/Rijeka: Urbanistički institut Hrvatske; 1993.
4. World Health Organization (WHO). Selected Methods of Measuring Air Pollutants. WHO Offset Publication No. 24. Geneva: WHO; 1976.
5. Van Loon JC. Selected methods of trace analysis: biological and environmantal samples. New York (NY): John Wiley & Sons; 1985.
6. Određivanje taložne tvari [Dustfall measurements, in Croatian]. Direction SDČVJ 201 (Proposal). Sarajevo: Savez društava za čistoću vazduha Jugoslavije); 1987.
7. Institute of Public Health (Croatia). Izvještaj o praćenju onečišćenja zraka na području Županije primorsko-goranske [Air pollution in the Primorsko Goranska County, in Croatian]. Rijeka: Institute of Public Health; 1997. Annual Report.
8. Institute of Public Health (Croatia). Izvještaj o praćenju onečišćenja zraka na području Županije primorsko-goranske [Air pollution in the Primorsko Goranska County, in Croatian]. Rijeka: Institute of Public Health; 1998. Annual Report.
9. Institute of Public Health (Croatia). Preliminarna ispitivanja utjecaja brodogradilišta »Viktor Lenac« u Martinšćici na okoliš [Environmental impact of the »Viktor Lenac« shipyard, in Croatian]. Rijeka: Institute of Public Health; 1992. Preliminary Report.

Sažetak

SADRŽAJ METALA U ČESTICAMA U OKOLICI BRODOGRADILIŠTA

Poslovi antikorozivne zaštite u brodogradilištu (pjeskarenje, bojenje) izvor su emisija čestica u okoliš. U razdoblju listopad 1996. – rujan 1997. skupljani su uzorci lebdećih čestica (1 postaja) te taložne tvari (6 postaja) u okolici remontnog brodogradilišta »Viktor Lenac« u uvali Martinšćica. Iz skupljenih uzoraka određen je i sadržaj metala: željeza, bakra, cinka, olova i kadmija. Iako prosječne godišnje koncentracije lebdećih čestica te kadmija i olova zadovoljavaju preporučene vrijednosti, sadržaj metala je općenito viši (i do nekoliko puta) u odnosu na vrijednosti koje se dobivaju u središtu grada Rijeke. Na brodogradilište kao izvor emisija promatranih parametara upućuje korelacija ($P<0.05$) između potrošnje grita za vanjsko pjeskarenje po mjesecima te srednjih mjesečnih vrijednosti lebdećih čestica ($r=0.513$) i olova ($r=0.512$). Korelacija je još bolja ako se usporedi potrošnja grita s mjesečnim koncentracijama željeza ($r=0.815$), bakra ($r=0.760$) i cinka ($r=0.911$), karakterističnih za emisije prilikom pjeskarenja, dok korelacija s kadmijem nije statistički značajna te upućuje i na drugi izvor tog metala. Na postaji u neposrednoj blizini brodogradilišta, srednja godišnja i maksimalne mjesečne vrijednosti količina ukupne taložne tvari prelaze granične vrijednosti, a godišnja količina istaloženog olova viša je od preporučene vrijednosti, što upućuje na visoko onečišćenje zraka krupnim česticama. Na ostalim postajama ukupne količine taložne tvari zadovoljavaju preporučene vrijednosti i na razini su količina koje se evidentiraju na drugim postajama županije, dok je sadržaj metala mnogo viši. Povremeno pojavljivanje visokih vrijednosti metala u taložnoj tvari na pojedinim postajama oko brodogradilišta ovisi kako o lokaciji vršenja radova unutar radnog prostora tako i o meteorološkoj situaciji u zaljevu Martinšćica.

Ključne riječi:
brodogradilište, lebdeće čestice, metali, onečišćenje zraka, taložna tvar

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