14

Air Pollution and Its Impacts – The City of Rijeka Case Study

Ana Alebić-Juretić
Teaching Institute of Public Health/ School of Medicine, University of Rijeka
Croatia

1. Introduction

During the late sixties and seventies the city of Rijeka underwent second rapid industrialization. Few huge plants (new petroleum refinery facilities, power plant, coke plant) were erected in the industrial zone eastwards from the city. As a consequence, high emission levels resulted in elevated ambient air pollution so that the city was one of the most polluted in Croatia during the mid-eighties. Thus the annual means of sulphur dioxide exceeded double the WHO guideline at some urban sites. The beginning of air pollution monitoring programme dates back to early seventies with first measurements of sulphur dioxide (SO_2), black smoke (BS) and fallout within the city. Due to air pollution from the newly built industrial plants, the programme was extended to more parameters at the beginning of eighties, thus including: nitrogen dioxide (NO_2), ammonia (NH_3), hydrogen sulphide (H_2S), total suspended particulates (TSP), metals and polynuclear aromatic hydrocarbons (PAHs). All these parameters were measured by chemical methods, while first automatic network with only three analyzers (SO_2, O_3 and TSP) was established only in 2000, as the first automatic network in Croatia.
As the ambient levels of air pollutants diminished considerably since mid-nineties, a synthesis of the work done in the last 25 years dealing with long-term air pollution and its effects on materials, plants and humans is presented.

2. Long-term trends of air pollutants

2.1 Emissions

The elevated air pollution since the beginning of eighties was the reason to undertake first steps towards its abatement. Therefore, the first emission inventory including major big sources was done as early as 1989 (MEISA, 1991).
This inventory attributed major emissions of SO_2 and NO_2 to industrial point sources. Reduced production in war/post-war period resulted in approx. 70% lower emissions of SO_2 and 35% of NO_2 in 1995 (Ekonerg, 1997). The recuperation of economic activity and use of cleaner fuel led to their increase in 2001 (Regional Centre, 2002) and 2006 (County, 2009). Contrary to SO_2 , whose total emission remained bellow 50% of that in 1989, the total NO_2 emission is approaching that on 1989, but due to increase of contribution from traffic. In

fact, the number of vehicles increased by 60% between 1995 and 2001, with additional increase of 20% in the period 2001-2006. In all these inventories emissions from harbour were missing. The first emission inventory for harbour activities estimated for 2008 SO_2 emission to 425 t year^{-1} and NO_2 to 849 t year^{-1} (ARCADIS, 2011) that is < 5% for SO_2 and approx 20% for NO_x of the total emission in 2006.

	SO_2				NO_2			
Sources	1989	1995	2001	2006	1989	1995	2001	2006
Petroleum refinery Urinj	16000	5651	7795	7127	2019	1501	1918	1552
Rijeka I power plant	8600	3237	7179	6672	1240	943	1172	1335
Petroleum refinery Mlaka	3557	1036	1639	1761	472	283	128	208
Coke plant	4778				955			
Subtotal:	32935	9924	16613	15560	4686	2727	3218	3095
Other industry	1260	411	470	185		76	159	29
Traffic	200	171	163	147	864	705	1100	1400
Other	2035	356	635	422		119	118	200
Total:	36430	10862	17881	16314	5550	3627	4595	4724

Table 1. Emissions of sulphur dioxide and nitrogen oxides (as $NO_{2)}$ in t year^{-1} in the Rijeka Bay Area

2.2 Ambient levels of some pollutants

Maen daily concentrations of various pollutants were determined by the following methods:

a. sulphur dioxide – standard British acidimetric method (WHO, 1976); since 2000 automatic analyzer Monitorlab 8850 (Monitorlab, USA)
b. black smoke – reflectometry (Perry & Jung, 1977)
c. nitrogen dioxide – modification of Saltzman method (Perry & Jung, 1977); since 2003 analyzer API M 200 (Advanced Pollution Instrumentation, USA)
d. ammonia – spectrophotometrically with Nessler reagent (WHO, 1976)
e. hydrogen sulphide - modification of molibden blue method (Vadic, 1982)
f. ozone – analyzer API M 400 (API, USA)
g. total suspended particulates (TSP) and since 2006 PM_{10} – gravimetrically (WHO, 1976)
h. suspended particulates PM_{10} – since 2003 analyzer TEOM 1400a (Rupprecht &Pataschnik, USA)
i. metals – atomic absorption spectroscopy (van Loon, 1985)
j. polycyclic aromatic hydrocarbons – HPLC with UV detector (Alebic-Juretic, 1994)

Comparing the results of chemical methods with those obtained by analyzers of SO_2 and NO_2, it turned out that there is no significant difference between either methods for SO_2, while NO_x analyzer gave approx 20% higher concentrations relative to chemical method. As the PM_{10} concentrations obtained by analyzer are systematically lower, the corresponding correction factor was employed (EC, 2002). Since 2000 the sulphur dioxide and ozone analyzer from the Institute site together with TSP analyzer in the suburban site above shipyard formed a first automatic Air Quality Network in Croatia with automatic collection and elaboration of the data. Three years later the network was extended to six more

automatic sites, with possibility for display of the hourly data in real time on the Institute web-site (www. zzjzpgz.hr). That was also the first such a web site established in Croatia.

2.2.1 Sulphur dioxide and black smoke

Sulphur dioxide (SO_2) is generated by combustion of fossil fuel. Its emission depends on sulphur fuel content. Annual mean concentrations of SO_2 in four urban sites (Fig 1) follow

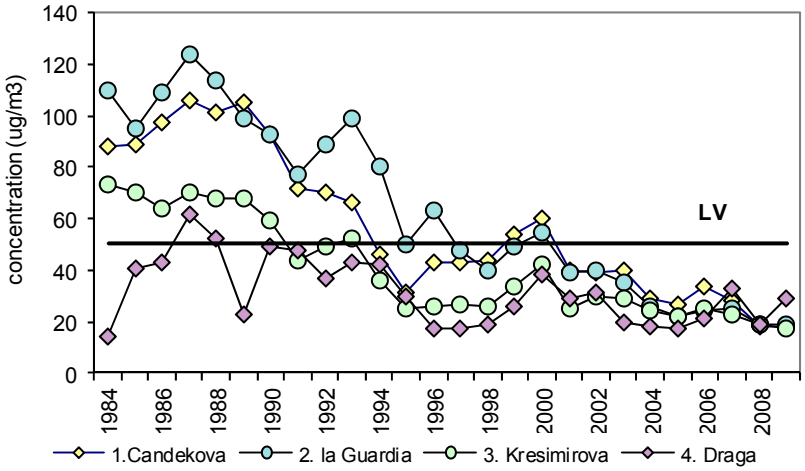


Fig. 1. Annual mean concentrations of sulphur dioxide (limit value LV=50 μg m^{-3})

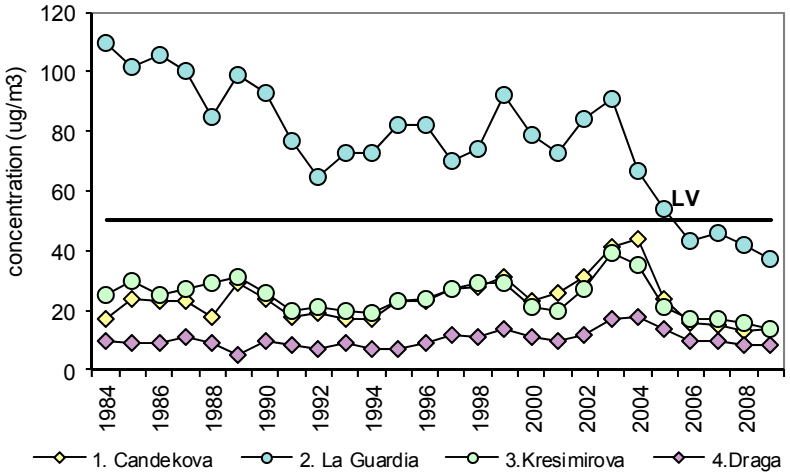


Fig. 2. Annual mean concentrations of black smoke (limit value LV=50 μg m^{-3})

the emission patterns. Sulphur dioxide and black smoke (BS) were blamed for several smog episodes during fifties and sixties in Europe and America that caused increased mortality among exposed population. Because of switch to cleaner fuel, the SO_2 concentrations diminished considerably during early eighties in Europe, with annual means < 100 μg m^{-3} (WHO, 2000) that are presently even lower (20-30 μg m^{-3}). Similar behaviour is observed in Rijeka. Thus, 70% in SO_2 emission reduction resulted in the equivalent decrease in ambient air SO_2 concentrations between 1989 and 1995 (Matkovic & Alebic-Juretic, 1998). Subsequent increase in SO_2 emissions in 2001 followed by slow decrease towards 2006 are reflected proportionally in ambient air concentrations. Since 2001 the limit value for SO_2 is observed at all four urban sites.

Except for urban F. la Guardia street with heavy traffic, the black smoke did not represent critical pollutant. In spite of a slight increase in annual concentrations from 2000 to 2004, the BS at three urban sites obeyed the limit value since the beginning of monitoring. Sharp decrease in BS concentration in 2004 (except at suburban site Draga) is due to introduction of natural gas in the city center for heating, that finally enabled drop of annual BS concentrations bellow limit value in F. la Guardia street in 2006 (Fig. 2).

2.2.2 Nitrogen dioxide

Nitrogen oxides NOx are generated mostly from air by combustion of fossil fuels. Therefore it is more difficult to diminish their emissions and consequently ambient levels. The principal source of NOx is traffic. NO_2 is precursor of photochemical smog. As irritant, NO_2 might affect respiratory system. Urban levels of NO_2 are in the range 20-90 μg m^{-3}, while background level is 10 μg m^{-3} (WHO, 2000). Time trends in annual NO_2 concentrations in Rijeka show a decreasing trend at industrial site (Mlaka) and no significant trend at urban traffic site (Krešimirova St), in spite of the increased emission of NO_2 in the period 2001-2006 (Fig 3).

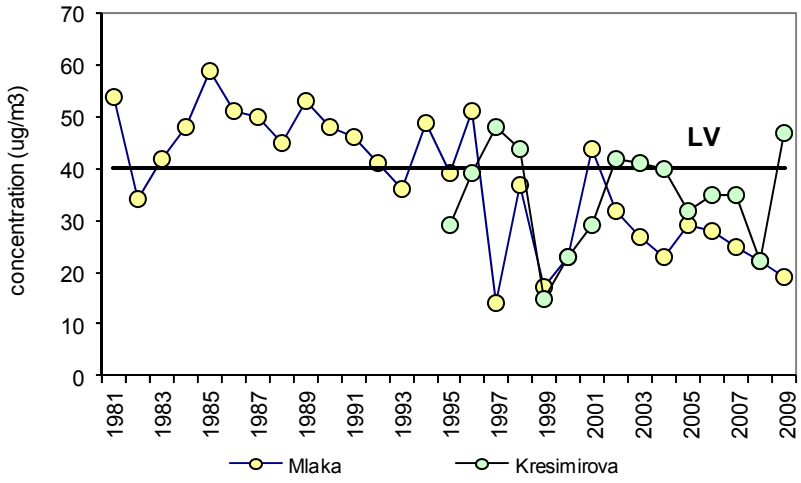


Fig. 3. Annual mean concentrations of nitrogen dioxide (limit value LV=50 μg m^{-3})

2.2.3 Ammonia

Ammonia ambient levels also show a slight decline (Fig. 4). It is interesting to notice that closing up the coke plant in 1994, a major source of ammonia in the area (993-1323 t/year estimated by emission inventory from 1989), did not affect significantly the time trend, not even at the neighbouring site Kraljevica. It is well known that ambient levels of ammonia do not follow its emission. Such a behaviour is explained by high reactivity and/or volatility of airborne ammonia.

Agriculture is generally considered as the main source of airborne ammonia, but it is scarcely present in this karst area. The urban and suburban levels of ammonia are rather high, but they are diminishing in the remote areas, with distance from the city (Alebic-Juretic , 2008). Therefore, urban and industrial sources should be responsible for the observed ammonia levels.

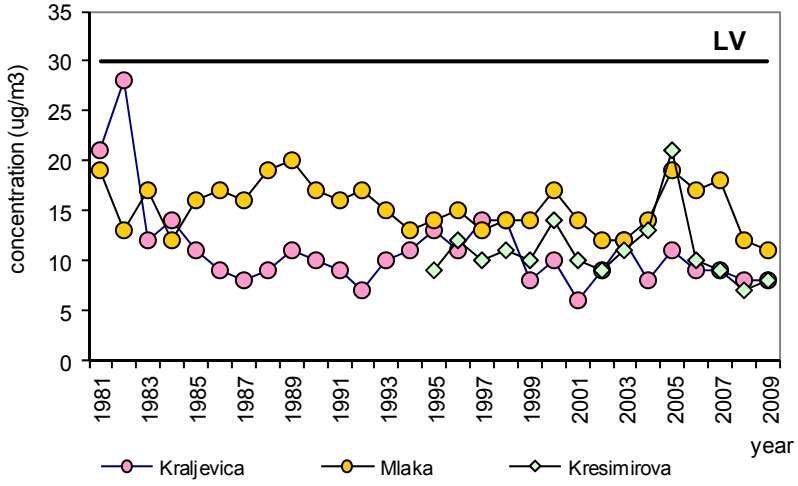


Fig. 4. Annual mean concentrations of ammonia (limit value LV=30 μg m^{-3})

2.2.4 Hydrogen sulphide

Hydrogen sulphide is a gas of unpleasant smell. It is generated from elementary sulphur or sulphur compounds and organic material exposed to elevated temperature. There is no trend in hydrogen sulphide regarding the annual means at the site opposing petroleum refinery, in spite of temporarily high annual values (Fig 5). Such a curve shape reflects the (un)success in control of production processes. In 2008 the production ceased at this location, but in spite of that, the area resulted to be excessively polluted by H_2S due to hourly tolerant limit values (TV=7.6 μg m^{-3} in 2009) exceedances at automatic monitoring station (Trogirska St) during heating season, thus indicating boilers as the H_2S sources (Alebic-Juretic et al, 2009).

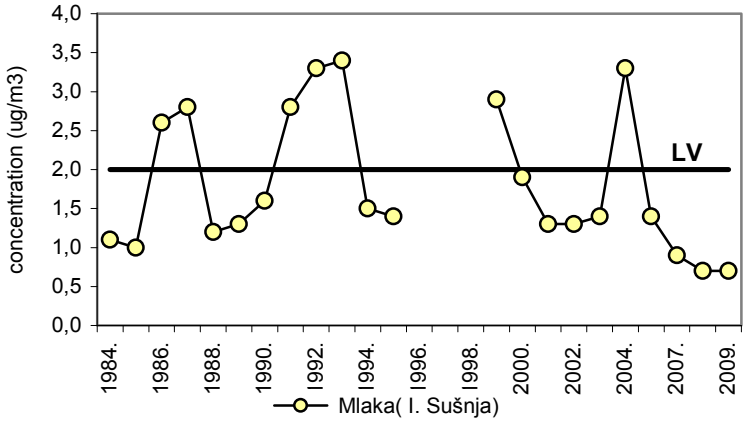


Fig. 5. Annual mean concentrations of hydrogen sulphides (limit value LV=2 μg m^{-3})

2.2.5 Ozone

Tropospheric ozone is secondary pollutant generated from NOx and reactive hydrocarbons under conditions of high insolation and elevated temperature. Therefore elevated concentrations of tropospheric ozone are registered during summer. Ground levels of ozone are the result of several processes taking place in the boundary layer like local photochemical production, horizontal transport on regional and/or synoptic scale, vertical transport from the stratosphere and ozone sinks like photochemical destruction with NO and deposition on surfaces. Ground level ozone is irritant and might have harmful effects on human health.

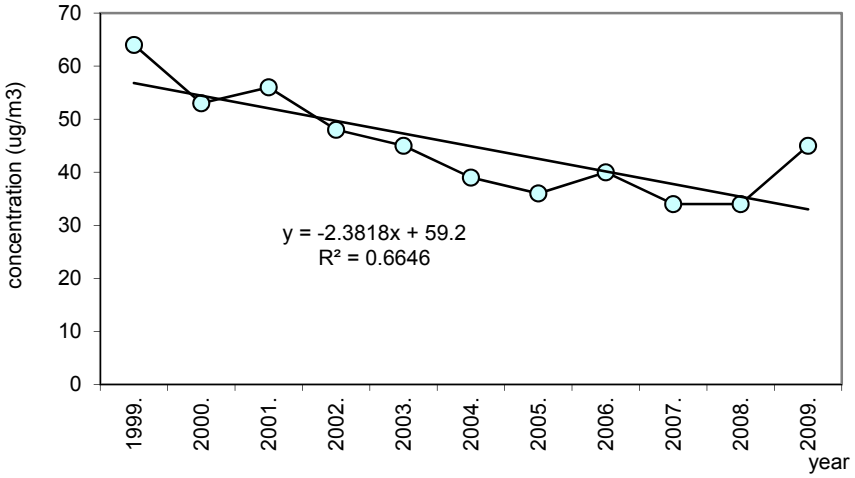


Fig. 6. Annual mean concentrations of ozone

Contrary to some other parts of Europe, the ambient concentrations of ozone show a declining trend in Rijeka since the beginning of measurements in 1999. As the same trend is observed at elevated remote location (Puntjarka) since 1990, this seems to be regional phenomena (Alebic-Juretic, 2008a).
Declining trend of ozone is preserved in spite of higher annual concentration in 2009 relative to several preceding years.Such a high concentration is obtained because an exceptionally high summer temperature and ozone levels in August, with registered hourly means above 200 μg m^{-3}. Similar condition has appeared only in August 2000, and was only recently explained by combination of local ozone production and regional transport.

2.2.6 Suspended particulate matter (TSP and PM_{10})

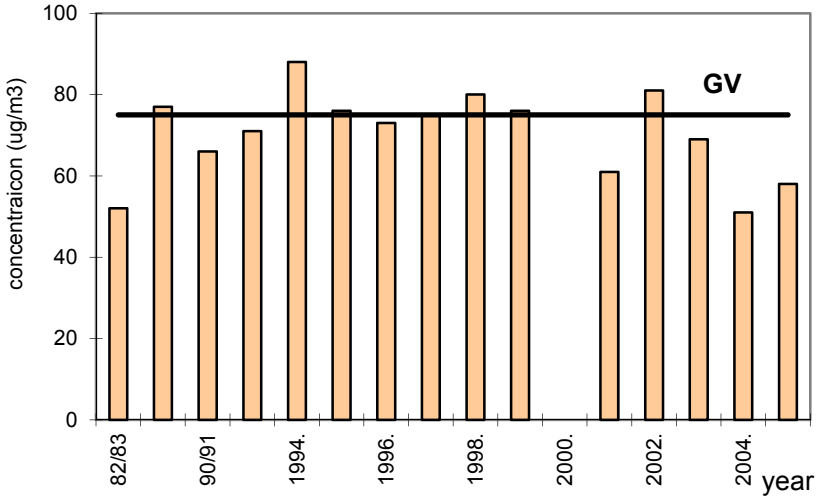
Suspended particulates are formed of complex mixture of organic and inorganic compounds. According to their dimensions, the suspended particulates are grouped into fine with aerodynamic diameter d<2.5 μm, and coarse particulates with d>2.5 μm. Fine fraction of particulates contains secondary generated aerosols (from gas-solid conversion), particulates formed by combustion and secondary adsorbed metals and organics. Coarse fraction usually contains soil particles, fugative dust from streets and industrial sources. Suspended particulates are usually divided into: total suspended particulates (TSP), particulate matter with aerodynamic diameter <10 μm (PM_{10}) and particulate matter with aerodynamic diameter <2.5 μm ($PM_{2.5}$). Particulate matter that can reach human respiratory system (PM_{10}) are emitted from various sources: natural (volcanoes or dust storms) or anthropogenic (industry, domestic heating, traffic). The latter sources are more important regarding air pollution (WHO, 2000).
First systematic monitoring of particulates started with discontinuous TSP measurements in Rijeka in 1991. Due to change in legislation, these measurements are switched to PM_{10} in 2006. These are not the first measurements of PM_{10} ever, since three years earlier a continuous monitoring with analyzer started.

2.2.6.1 Discontinous measurements

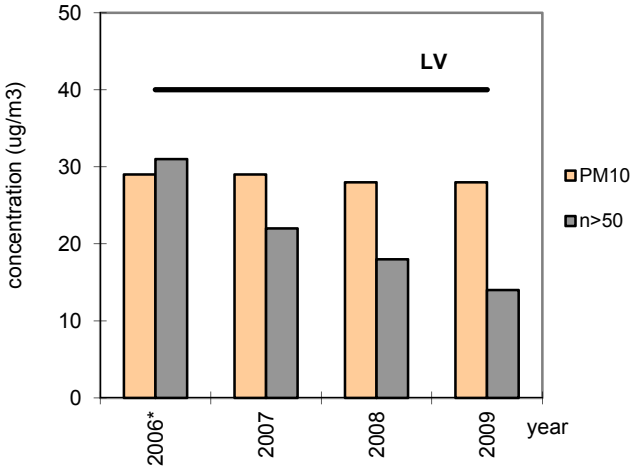
The grain silo in the harbour was a big source of suspended particulates. Thus, the annual concentrations of total suspended particulates (TSP) were always close to the limit value (Fig.7a), but the daily values were often exceeded (Alebic-Juretic, 2005). Only after installation of the new dust suppression system in the silo in mid 2003, the limit value was finally obeyed. Results of PM_{10}, that replaced TSP measurements in 2006 (Fig 7b), also fulfilled the limit value. The number of exceedances was bellow allowed 35 days per year. This limit was approached only in 2006 (6 month).

2.2.6.2 Continous measurements

Continous measurements of PM_{10} with analyzers started in 2003 in the city of Rijeka. The results are given in Fig.8. The analyzer is a part of a traffic station on the busy street level, thus the results are different from discontinous sampler located on the roof of the Institute, in the same street. Though the annual means were around limit value LV, the number of exceedances was 2-3 times higher than allowed per year (35 times). This number diminished only in 2007, presumably due to introduction of natural gas in the city center.



a.



b. * six months data

Fig. 7. Annual means of a. TSP (guideline value GV = 75 μg m^{-3}) and b.: PM_{10} (limit value LV = 40 μg m^{-3}) in the city of Rijeka (n>50 – number of average daily concentrations exceeding daily limit value LV_d = 50 μg m^{-3})

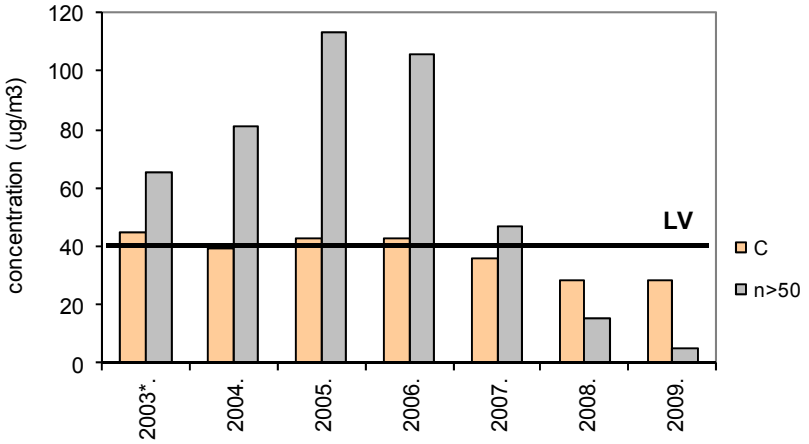


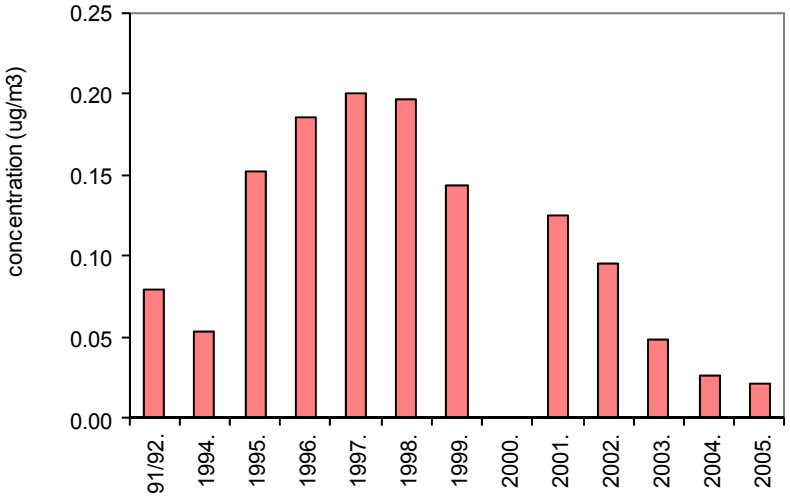
Fig. 8. Annual means (C) of PM_{10} measured with analyzer (n>50- number of exceedances of LV_d =50 μg m^{-3})

2.2.7 Lead in suspended particulate matter (TSP and PM_{10})

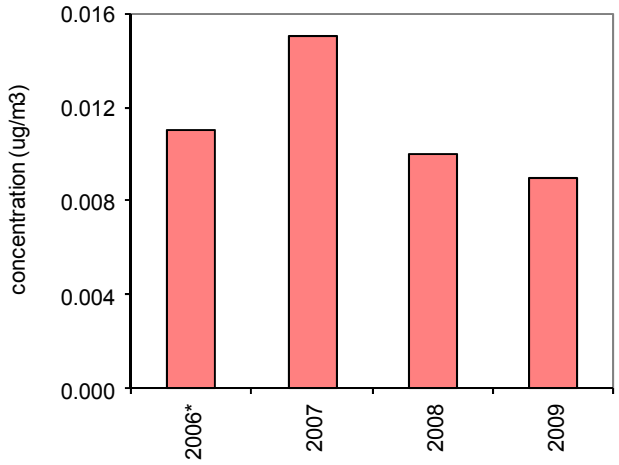
Samples of TSP and PM_{10} were analyzed on lead and cadmium content since the beginning of PM measurements. These analyses were extended to iron, zinc and copper, as typical for metal and shipyard industry. The biggest differences in metal concentration over time is found with lead, since traffic was the main source of this metal, and switch to unleaded petrol diminished the airborne lead considerably. Concentrations of lead in TSP were always bellow respective limit value since the beginning of measurements in early nineties. As the traffic was the main source of lead, its airborne concentrations show increase to the end of nineties due to increase in number of vehicles. The subsequent decreasing trend is due to major use of unleaded petrol (Alebic-Juretic, 2005), up to 2006 when the leaded petrol disappeared from the market (Fig 9). Lead content in PM_{10} is also low and bellow the respective limit value.

2.2.8 Polycyclic aromatic hydrocarbons in suspended particulate matter (TSP and PM_{10})

Polycyclic aromatic hydrocarbons (PAHs) are generated by incomplete combustion of organic material (fossil fuel). The main sources of PAHs are coke plants, petroleum refineries, traffic and domestic heating. The most studied PAHs is benzo(a)pyrene , a known carcinogen representing potential threat to public health. Occasional determination of PAHs in TSP dates back to mid eighties, while systematic measurements started only in 2001. Since 2006 PAHs are analysed in the PM_{10} fraction. The highest concentrations of BaP and PaHs were obtained at the beginning of nineties, at the time with the highest pollution with combustion products (SO_2, black smoke). The concentration of BaP was up to 5 ng m^{-3}, while the concentrations of total PAHs were 10-12 times higher. The declining trend of BaP and PAHs started by the end of nineties (Alebic-Juretic, 2005), while in 2005 the concentrations of BaP fell bellow 1 ng m^{-3}. In the PM_{10} fraction of suspended particulates the concentrations of BaP are even lower.

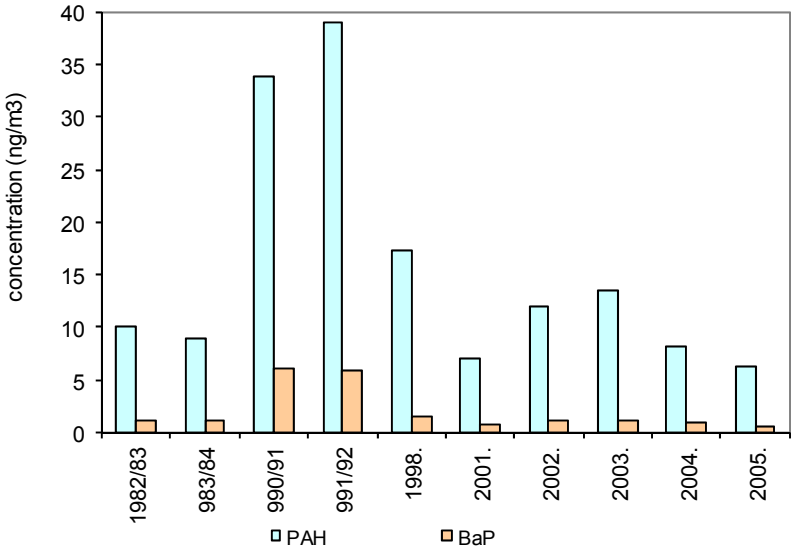


a.

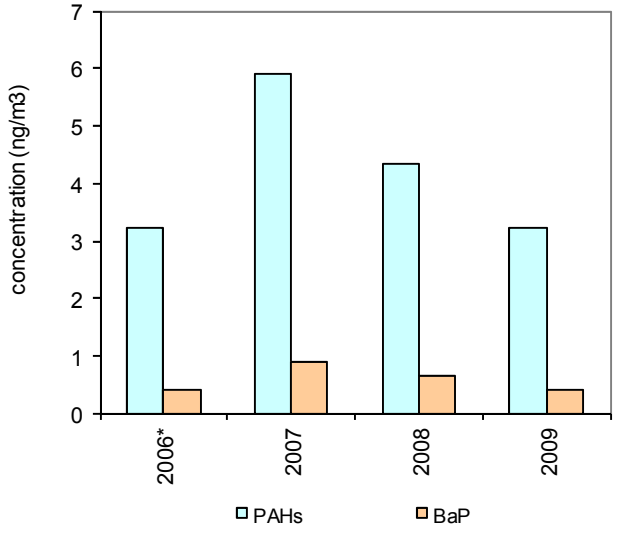


b.

Fig. 9. Lead in suspended particulates in Rijeka, a. TSP (LV=1 μg m^{-3}) and b. PM_{10} (LV=0.5 μg m^{-3}) (* six month value)



a.



b.

Fig. 10. Concentrations of total PAHs in a. TSP and b. PM_{10} (* six months value)

2.3 Air pollution effects on materials - paintings

High ambient concentrations of SO_2 might deteriorate the buildings and sculptures made of calcite. As a consequence the edges loose their sharpness and the surface is covered by a layer of dirt formed from gypsum (derived from airborne H_2SO_4 and calcite) and soot. Similar process occurs in indoor environment, i.e. interior walls covered with plaster. Therefore, the most abundant aerosol in indoor environment is gypsum, $CaSO_4 \times 2\ H_2O$. Indoor gaseous and particulate pollution in museums is often correlated to pollutants outdoor concentrations leading to different conclusions: indicating outdoor pollution as a source for the observed indoor concentrations (Ligocki et al, 1993), pointing out some (un)known indoor sources (Mouratidou & Samara, 2004) or taking as a proof of effectiveness of the installed HVAC system (Salmon et al, 2005).

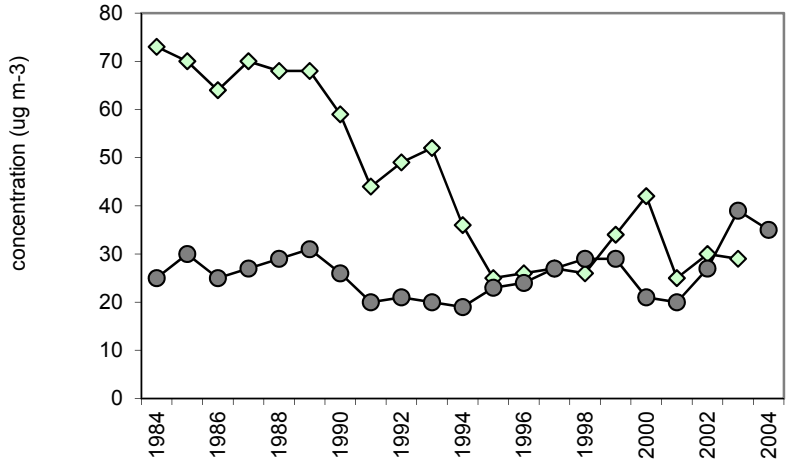
The Museum of Modern and Contemporary Art (MMCA) in Rijeka is situated on the second floor of a building located in the very center of the city, between two busy city roads. The Museum will move into the new location, also in the city centre, facing another busy city road and apparently worse considering air pollution. Since air pollution is found to be one of the risk factors for preventive conservation of artworks, the aim of the work was to evaluate possible effects of air pollution on paintings already kept in the central depot located within the Museum area. The paintings analyzed were randomly chosen from those that were subjected to restoration prior to be exposed in the exhibition area. Two of the paintings were kept in the central depot, while the other two were stored in the auxiliary depot, and were taken for comparative purposes. The characteristics of the selected paintings are given in Table 2.

No	Author	Title	Year	Technique	Dimension/ cm	Depot/ since	Remark
1.	Butozan M.	Man in the interior	1942	oil/ canvas	138x100	Central/1980	thick paint layers, varnish, mostly smooth surface
2.	Seferov V.	The nude	1933	oil/ canvas	117x170	Central/1974	visible canvas fiber, mostly rough surface
3.	Lusic T.	Imbarco a ferro	1989	acrylic/ canvas	151x249.5	Cent/1993 Auxil/1994	completely smooth surface
4.	Grozdanic Ž.	Kiefer-Knifer	1991	combined	159.5x224	Cent/1991 Auxil/1994	rough structured, uneven wax coated surface

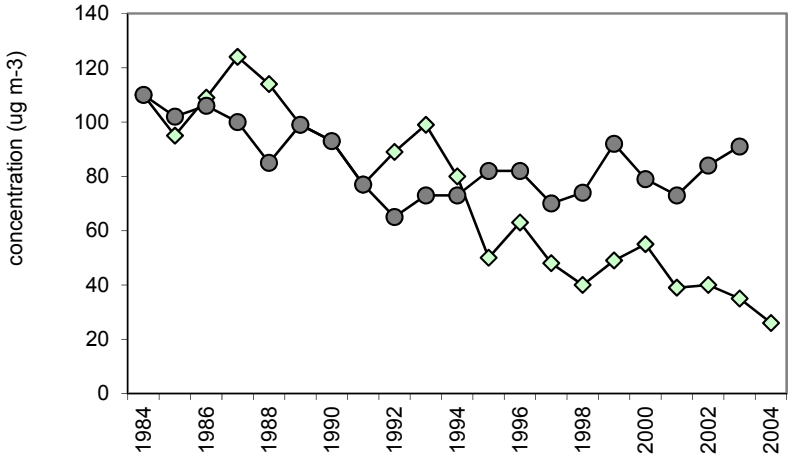
Table 2. The characteristics of the paintings selected for analyses (Alebic-Juretic & Sekulic-Cikovic, 2009)

The central depot is located on the second floor of the Museum's building, in the very centre of the city. The storage rooms were ventilated occasionally just by opening the windows, thus enhancing penetration of the outdoor pollution. Furthermore, the paintings were exposed to considerable seasonal temperature oscillations. The auxiliary depot was located in the basement flat of the building situated on the busy city road. The paintings remained locked in this location until restoration. No exact measurements of air pollution are available for the depots' locations. Due to environmental conditions (sampling point heights approx 15 m above street level, location between two busy roads) the results of such measurements obtained at the Institute building (Site 1) may approximate the outdoor air pollution at the

central depot, characterized by higher pollution with SO_2 relative to that of black smoke. The air pollution at the auxiliary depot is very likely to be similar to that of another, poorly ventilated busy street (Site 2) in the city center that is characterized by high black smoke concentrations, exceeding SO_2 since mid-nineties.



a.



b.

Fig. 11. Annual means of SO_2 (green) and black smoke (grey) at: a. Site 1 representing central depot, and b. Site 2 representing auxiliary depot (from Alebic-Juretic & Cikovic-Sekulic, 2009)

Instead of measuring a set of gaseous and particulate pollutants indoor and outdoor, dirt removed from paintings during restoration works was analysed. Dirt is deposited on the paintings surfaces as the result of soiling process during decades of storage in the depots. The surface dirt was removed from the first painting (No 1: Butozan) by pieces of cotton wool soaked in demineralized water, while subsequently cotton wool was replaced by a synthetic fiber cloth .The parameters determined were those used for ambient air pollution monitoring: total "dirt", soot, lead, individual polynuclear aromatic hydrocarbons (PAHs) and water extract ionic content.

The amount of dirt was determined gravimetrically, as the weight gain of cotton wool/synthetic cloth after cleaning the paintings. To enable the comparison between the obtained results, the total amount of dirt was normalized against the paintings surface area giving the results in mg m^{-2}.The amount of soot is also determined gravimetrically, as the ignition loss at 800^{o}C of ashes obtained by burning the cotton wool/synthetic cloth samples. The lead content was measured by graphite furnace AAS (Perkin-Elmer Z 4001) after dissolving ashes in acidic mixture HNO_3/HCl (van Loon, 1985). The ionic content of the dirt was determined from the water extract obtained by extraction of "dirt" in ultrasonic bath for 60 min. The ionic content was determined by modular Methrom ion chromatography system. The operating conditions are described elsevere (Alebic-Juretic & Sekulic-Cikovic, 2009). The PAHs were extracted from cotton wool/cloth by cyclohexane (100 ml) in ultrasonic bath (60 min). The individual PAHs were determined from the purified cyclohexane extract using HPLC (Helwett Packard 1050) with UV-VIS detector, according to the previously described procedure (Alebic-Juretic, 1994).

The highest amount of total "dirt", soot, lead and total PAHs (Figure 12) are obtained from painting No1 (Butozan). Since this is the second oldest painting in this study, the unknown previous history of keeping, as well as the nature of thick oily paint might be responsible for this result. In the oldest painting No 2 (Seferov) lower values of total "dirt", soot and particularly lead and total PAHs are found, thus indicating better keeping conditions, e.g. more distant from combustion sources, prior to arrival in the Museum's depot. The lowest amount of total "dirt" and total PAHs are found in painting No3 (Lusic), possibly due to incorporation of dust and dirt onto the acrylic film. The (non-polar) wax coated surface of painting No 4 (Grozdanic) collected more total "dirt", soot and total PAHs than painting No 3, that was contemporary kept in the auxiliary depot. Unexpectedly low lead content in water extract from the same painting was found. The possible reasons for were: either the low possibility of sticking the mineral particles onto non-polar wax surface, or the mineral particles were embedded into the wax layers that prevented their efficient extraction. The interesting feature is that the percent content of soot obtained from paintings kept in the auxiliary depot is relatively high (approx. 0,65%) compared to those found on paintings kept in the central depot, in spite of 2-3 times longer exposure times to possible air pollutants. The plausible reason for this finding is the impact of soot emission from heavy traffic, as the auxiliary depot was located beneath the street level. (Alebic-Juretic & Sekulic-Cikovic, 2009).

The individual PAH profile (Fig 13) also indicate the possible air pollution impact. The more complete profile is found in paintings kept in the auxiliary depot (No 3 and 4), i.e. in the vicinity of the busy street – the source of PAHs. Lack of some individual PAHs in paintings from the central depot (No1 and 2) suggest their earlier date exposure to exhaust gases containing PAHs and subsequent degradation.

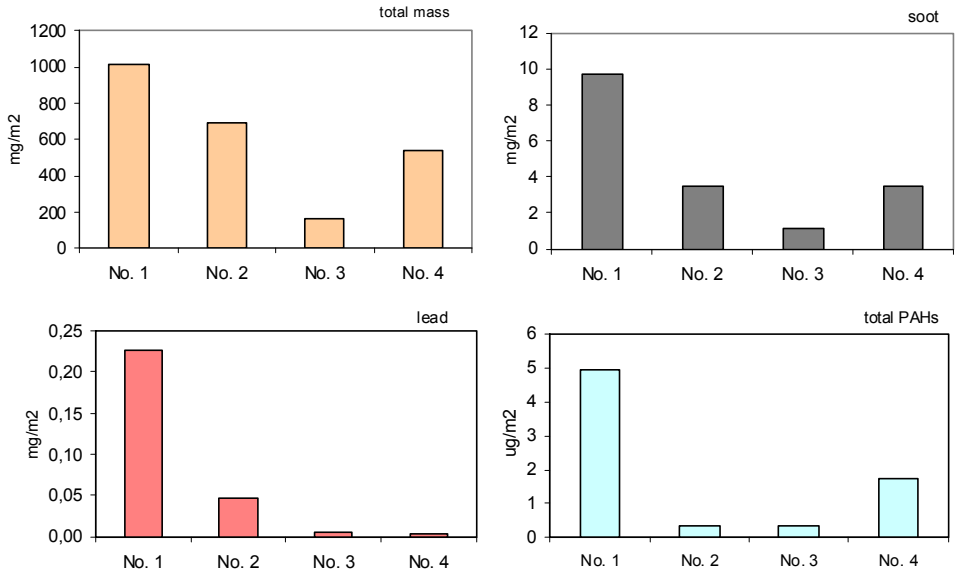


Fig. 12. Total mass, soot, lead and total PAHs deposited on paintings: No1: Butozan, No2: Seferov, No3: Lusic and No4: Grozdanic

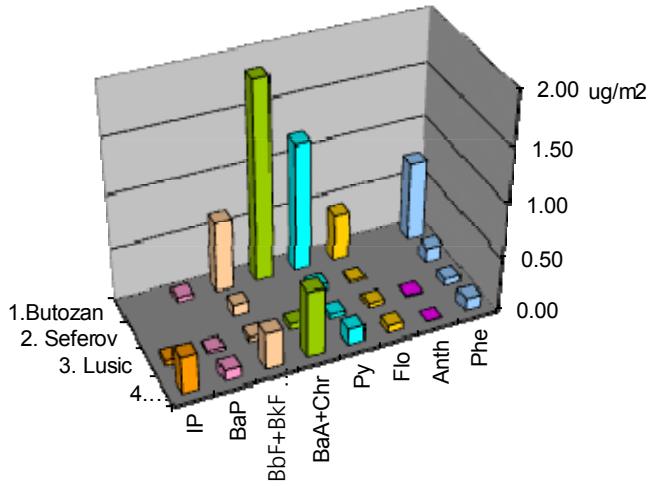
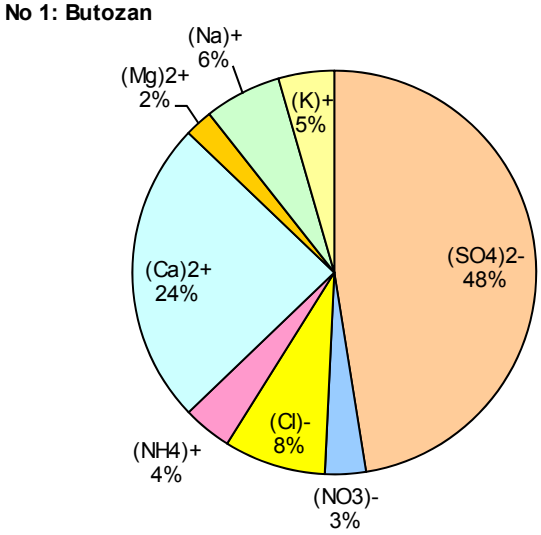
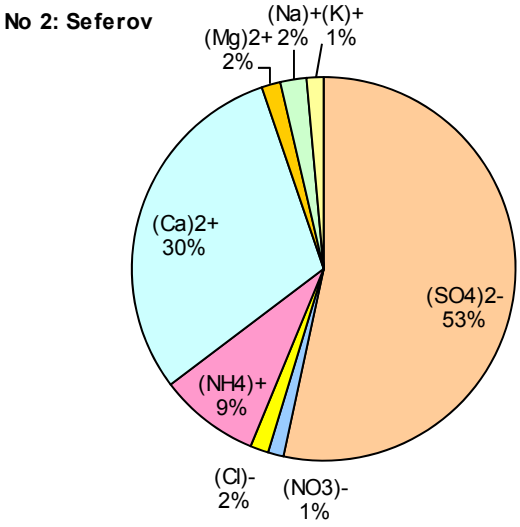
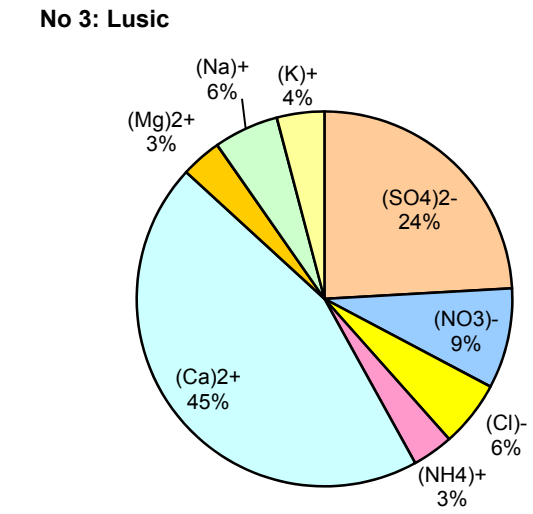


Fig. 13. Individual PAH profile obtained from surface dirt analyses (Phe-phenanthrene, Anth-anthracene, Flo-fluoranthene, Py-pyrene, BaA- benzo(a)anthracene, Chr-chrysene, BbF-benzo(b)fluoranthene, BkF-benzo(k)fluoranthene, BaP-benzo(a)pyrene, IP-indeno(1,2,3-c,d)pyrene)

A common feature of the analysed fractions is the predominance of sulphate and calcium in all paintings (though with different percentage). This is in agreement with findings that Ca rich particles are the most abundant in the indoor museums atmosphere (Camuffo et al., 2001). Higher values of analysed ions are found in older paintings (No 1 and 2) kept in the central depot indicating thus the cumulative effect. Comparing the ionic content expressed in meq m^{-2}, a clear difference between paintings kept in the central and auxiliary depot is evident (Fig 14). The excess of sulphate in paintings from the central depot may indicate the







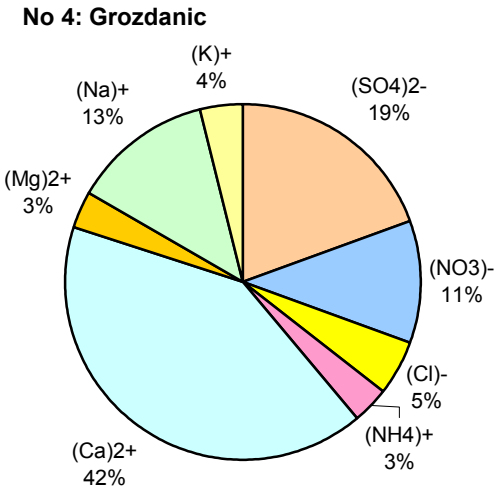


Fig. 14. Percent content of ionic components of dirt on painting analysed given as meq m^{-2} (Alebic-Juretic & Sekulic-Cikovic, 2009).

impact of air pollution by sulphur dioxide during decades of storage, including the eighties with highest air pollution with SO_2 within the city. The excess of sulphate may originate either from the reaction of SO_2 with already deposited calcite on the paintings, or as the result of H_2SO_4 formation via catalitic reaction on the surface of the paintings thus causing damages. Traces of reduced sulphur compounds (sulphides, mercaptans, disulphides), either gaseous or as constituent of pigment (e.g. cinober) might also be the source of SO_2 and sulphates on painting surfaces (Van Grieken et al., 1998). On the contrary, excess of calcium was found on paintings from the auxiliary depot, and could be attributed to dominant pollution by soil and/or plaster wall particles. It is worth to notice that meq m^{-2} amounts of ions are similar in paintings that were contemporary kept in the auxiliary depot (No 3 and 4), thus indicating the cumulative effect of soiling. Higher quantity of nitrate found in the latter paintings might also be in favour of some traffic impact, though bias are due to the fact that some pigments and coatings contain nitrate (Alebic-Juretic & Sekulic-Cikovic, 2009).

In conclusion: the excess of sulfates on a dirt film on paintings kept in depots during the period of highest air pollution indicated ambient SO_2 as the possible source. The nature of pigments, varnish and paints is also crucial for the aerosol deposition and/or surface gas reactions on artworks. Therefore it is hard to quantify their deposition/reaction rates. Since the ambient SO_2 concentrations decreased considerably, the traffic originated pollutants: NOx and particulates will be critical for the artworks to be stored in the new museum building. In spite of the fact that higher museum standard will be achieved, considering the air pollution and high financial cost regarding implementation of HVAC, further efforts for preventive measures are needed. These may include: identification and measuring indoor and outdoor air pollutants, space planning of the storage area, target cleaning, adequate protection of artwork and proper maintenance of the exhibition and storage areas (Alebic-Juretic & Sekulic-Cikovic, 2009).

2.4 Air pollution effects on vegetation – lichens

Lichens are an association of fungi (mycobionts) and green algae or cyanobacteria (photobiont). As they have no cuticle or protective wax layer and no stomata to regulate uptake of gaseous molecules, the exchange of nutrients occurs directly on the lichens surface. Therefore lichens are very sensitive to air pollution and have been used as bioindicators for over a century. Absence of cuticle favours accumulation of toxic metals in thallus and lichens can be used to map the pollution over wide areas (Minganti et al., 2003; Pinho et. al., 2004).

For many years sulphur dioxide was the main pollutant in urban and industrial areas. Elevated concentrations of SO_2 induced deterioration of lichen flora within such areas. Depending on air pollution levels, urban centers were often classified as "lichen desert", surrounded by so called "struggle zone" where some kinds of lichens can survive, though with some morphological changes. It is succeeded by so called "normal zone" with least air pollution and normal abundances of lichens. Though the first study of lichen flora in Rijeka was published already in 1902 (Schuler, 1902), the first classification on zones was done only in 1986 (Figure 15), at the time of highest air pollution within the city (Alebic-Juretic & Arko-Pijavac, 1989).

Except in the city center, two small lichen deserts were found at the elevated areas (>100 m a.s.l) under impact of plumes from paper mill (No 15: Kozala) and new built plant facilities in the east industrial zone (G. Vezica).

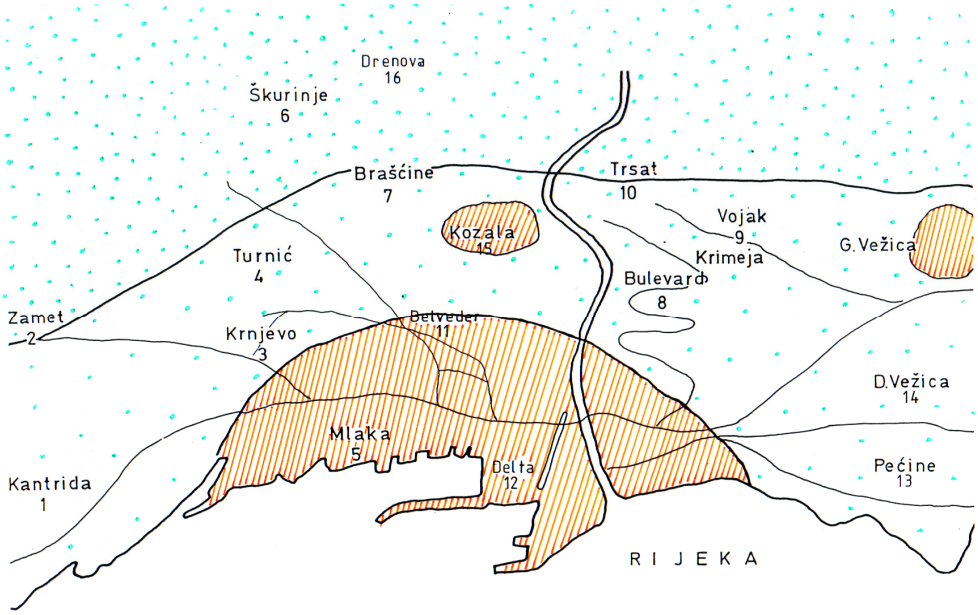
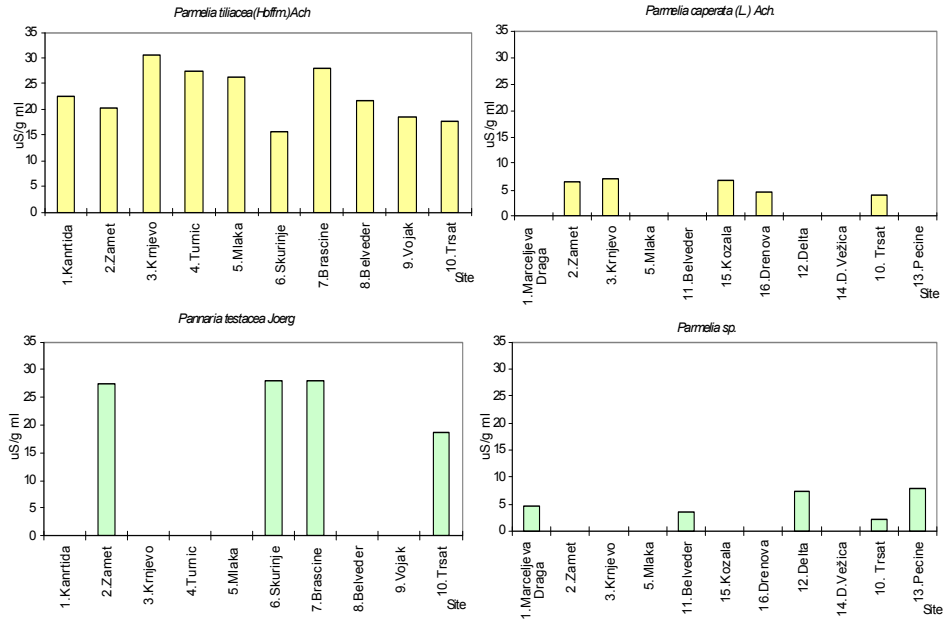


Fig. 15. Lichen zones in the city of Rijeka in 1986: lichen desert- yellow lines; struggle zone- rare green dots; normal zone- green dots (Alebic-Juretic & Arko-Pijavac, 1989)

Samples of two lichen species collected in winter 1985/86 *Parmelia tiliacea* (Hoffm) Ach and *Pannaria testacea* Jørg were used to perform simple biological test sensitive to early stages of membrane damage (Pearson, 1985). After preconditioning in humidity chamber for 2 hours (water temperature 35^{o}C), and rinsing with deionized water for few seconds, pieces of lichen thalli (approx 50 mg weight) were immersed in deionized water (conductivity 1.5-2,.0 μS) for 5 min. The increased conductivity of the solution, caused by electrolyte leakage (mainly K ions) from the tissue, was measured by a conductometer. The lichens were desiccated for 48 h and weighted, and conductivity per mass of lichen and volume of solution were calculated (.μS mL^{-1} g^{-1}). The same solution was used to check the leakage of potassium ions in deionized water by flame photometry and calculate the amount of K per mass of lichen (mg g^{-1}). Measurements were done in triplicate, except in the case when mass of lichen was insufficient for the third measurements. Correlations between K (mg g^{-1}) and conductivity (.μS mL^{-1} g^{-1}) confirmed ($r>0.9$) leakage of potassium to be the principal cause of the increased conductivity (Alebic-Juretic & Arko-Pijavac, 1989). The results of the Pearson test are given in Fig 16.



a. winter 1985/86. b. winter 1995/96.

Fig. 16. Results of Pearson biological test applied to lichen specimens collected in a. winter 1985/86 and b. 1995/96 (Alebic-Juretic & Arko-Pijavac, 2005)

In the *Parmelia tiliacea* experiment the largest specific conductivity was found in samples from sites 3, 4, and 5 (above the petroleum refinery facilities) thus indicating that these zones were exposed to higher air pollution levels, with winter concentrations > *70 μg m*$^{-3}$ that were indeed measured in the city centre (Fig. 17). *Panaria testacea* (more susceptible to SO_2 concentrations) collected at Sites 2,6,7 and 10 – where the same test applied to *Parmelia tiliacea* had its lowest values (except site 7) also showed increased specific conductivity implying that these zones had experienced winter average concentrations above 30 μg m^{-3}. There are no data on SO_2 concentrations in these areas, but it is assumed to be the cleanest within the urban area, because of largest distance from the city centre and industrial zones and, being on the elevated terrain, more exposed to dominant winds (mainly from NE directions). The unexpected result obtained with *P. tiliacea* at Site 7 could be explained by the fact that this complex hilly area is on the boundary between the struggle zone and the normal zone, but in the proximity of a small lichen desert (Fig. 15), where *P. testacea* can still be found (Alebic-Juretic & Arko-Pijavac, 1989).

The test on membrane integrity was repeated to specimens of lichens collected randomly within the city area after ten years, in winter 1995/96 (Alebic-Juretic & Arko-Pijevac, 2005). In the meantime, the sulphur dioxide emission within the wider city area was reduced by 70%, due to the switch to lower sulphur content oil, reduced production and/or cessation of activity of some industrial plants, e.g. coke plant. Consequently, the ambient levels of SO_2 were diminished by 50-70%. As a result, the annual means of SO_2 at the most polluted city center dropped from 100-110 to less than 50 μg m^{-3} (Matkovic & Alebic-Juretic, 1998), while the winter means decreased from approx. 80-140 to 30-60 μg/m^3 (Fig. 17).

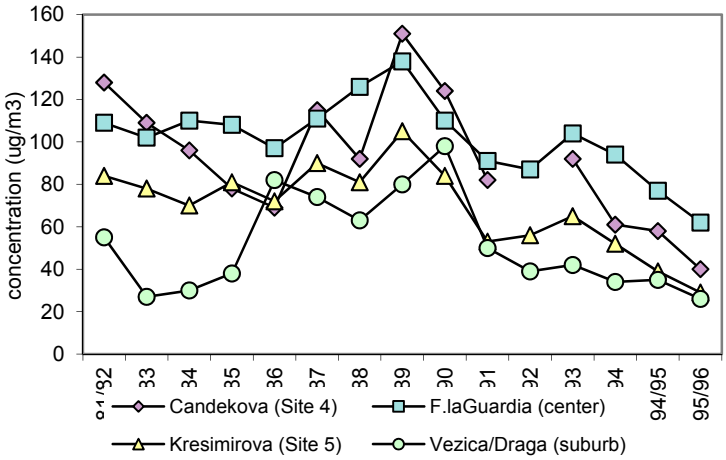


Fig. 17. Winter average (December- February) concentrations of SO_2 in the city of Rijeka (Alebic-Juretic & Arko-Pijevac, 2005).

The lichens collected during this second campaign were: *Parmelia spp., Parmelia caperata (L.) Ach., Parmelia conspensa* and *Physcia sp*. Generally, the values of specific conductivity (Fig. 16 b) are 2-4 times lower compared to the values obtained in the first campaign (Fig.16 a). The maximum values of specific conductivity in *P. caperata* specimens were obtained from samples collected at the same sites (3-Krnjevo) or in their proximity (15-Kozala) where the maximum values were obtained during the 1985/86. study. The same stands for the minimum values obtained in two strains of lichens collected within the park area at Site 10 (Trsat) during the both campaign undertaken. *P. caperata* strain is more sensitive among *Parmelia* species and is known to tolerate ambient SO_2 concentrations up to 40-50 $\mu g/m^3$ (Ferry, 1973).The highest specific conductivity in *Parmelia sp.* strains were found in samples collected at Site 12 (Delta), a former lichen desert zone, and Site 13 (Pecine) area (Fig 16.b). The largest specific conductivity was obtained in specimens of *P. conspensa* (18.6 $\mu S\ g^{-1}\ ml^{-1}$) collected at Site 14 (Donja Vežica), situated close to the former small lichen desert. Another species that gave high specific conductivity was *Physcia spp.* (8.6 $\mu S\ g^{-1}\ ml^{-1}$) collected within the park area at Site 5 (Mlaka), but close to the petroleum refinery (Alebic-Juretic & Arko-Pijevac, 2005).
In conclusion, the lower specific conductivity, the predominance of more sensitive *P. caperata* among the collected samples and reappearing of lichens in the areas classified earlier as lichen desert (city center and a small lichen desert zone in the upper part of the city) indicated recovering of their natural habitat due to decrease of SO_2. Similar situation with new lichen species found and disappearance of "lichen desert" subsequent to reduction in SO_2 emission was observed in central Italy during mid-nineties. Even earlier, during the eighties, the decrease of SO_2 levels in Paris caused the reappearance of lichen species from the previous century in the Luxemburg Gardens (Conti & Cecchetti, 2001).

2.5 Air pollution effects on human health

2.5.1 Respiratory system

Air pollution affects primarily human respiratory and cardiovascular, and indirectly reproductive system. During the period of high air pollution in the eighties several studies

were conducted to estimate the air pollution effect on human health. The first of this study dates back in early eighties (September 1981-August 1982) and investigated occurrence of respiratory disease among preschool children (n=1299) in the city of Rijeka and its suburban communities affected by air pollution from SO_2 and black smoke. The level of air pollution varied significantly between selected six locations, except for SO_2 in summer. The city centre suffered the highest air pollution with annual means twice as much as WHO guideline values for SO_2 and black smoke. Maximum levels of both pollutants were found in winter at all sites. Spearman rank correlation indicated that incidence of overall acute respiratory diseases, acute diseases of lower respiratory system and acute non-obstructive bronchitis were in correlation to black smoke ($p<0.05$). The incidence of non-obstructive bronchitis correlated also with ambient SO_2 concentrations ($p<0.05$). Other correlations were not statistically significant. In spite of the good correlations between air pollution and respiratory diseases in preschool children, the authors could not eliminate infectious diseases as a possible cofounding factor, since there was no significant difference in incidence of respiratory diseases in six communities with different level of air pollution (Bartonicek-Brgic and Matkovic, 1989).

The second investigation was carried out during late eighties regarding ventilatory functions in non-smoking woman (n=176) living in two settlements in/or close to the industrial zone (Bakar, Krasica) with higher level of air pollution comparative to women (control group, n=58) living in the community on the west side of the city of Rijeka (Viškovo) without direct impacts from the industrial plants. Relative values of forced vital capacity (FVC), forced respiratory volume in one second (FVC_1), and values of FEV_1/FVC ratio, i.e. Tiffeneau index (TT) as absolute and relative in relation to normal population according to CECA norms were analysed. During the period 1986-1990 annual SO_2 concentrations exceeded WHO guideline of 50 μg m^{-3} at Bakar and Krasica. While the annual concentrations were in the narrow range (67-74 μg m^{-3}) in Bakar, after initial increase up to 78 μg m^{-3} in 1988, the annual values in Krasica decreased approaching the WHO guideline in 1990. The annual means of SO_2 remained approx. 40 μg m^{-3} during the whole 5 year period. In the first measurements in 1986, women from Bakar and Krasica showed considerably lower values of all ventilatory functions, except for the Tiffeneau index, than did the controls from Viškovo. In the repeated measurements five years later, the values of all pulmonary functions, except for Tiffeneau index were again lower in Bakar, but not in Krasica, where no statistical difference regarding control group (Viškovo) was found. These observed effects might indicate the long-term exposure to air pollution (Matkovic et al, 1998).

2.5.2 Reproduction

The adverse effects of environmental exposure to air pollution on reproductive events are less investigated. There are several studies regarding associations between air pollution by and low birth weight. Air pollution with SO_2 and TSP, or more complex mixture of these pollutants were associated to excess risk for low birth (Wang et al., 1997) and preterm delivery (Xu et al., 1995). In the Czech study both, low birth weight and prematurity were associated to SO_2, and to less extent to TSP pollution, while there was no such an association for IUGR (Bobak, 2000). Since the town of Rijeka suffered from high air pollution during the eighties, a retrospective control study was performed in order to evaluate possible impact on the outcome of pregnancies.

Sulphur dioxide was chosen as an indicator of air pollution because of the most abundant data available, i.e. the longest time series and the largest number of monitoring stations. Maternal residence during pregnancy was taken as the exposure variable: the city of Rijeka

being the high exposure and the rest of the region forming the low exposure zone (≤ 40 μg/m^3. Based on the birth records from the Clinic, a retrospective cohort study was carried out. The "preterm cohort" comprised all preterm births (gestational age <37 weeks) registered during 1987-1996. IUGR newborns, defined as those having birth weights bellow 10th percentile, formed "IUGR cohort" (not shown here). A common "reference cohort" comprised eutrophic term newborns. An increase in preterm incidence since 1993, in spite air pollution decline (Fig. 18), was the reason to analyze the periods 1987-1992 and 1993-1996 separately (Alebic-Juretic et al., 2001).

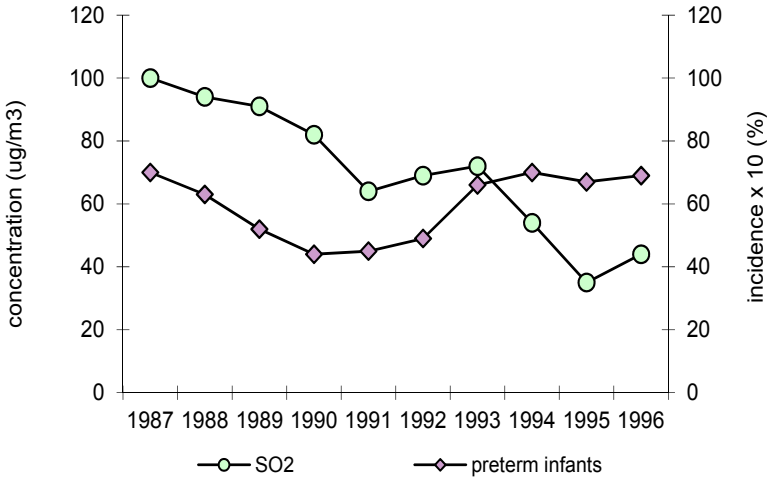


Fig. 18. Annual means of SO_2 concentrations within the city with incidence of preterm deliveries among mothers-city residents

For the overall period we found an increase of 11% in risk of preterm delivery among mothers-city residents (Table 3).

Zone	Preterm cohort	Reference cohort	OR	95% CI
1987-1996				
Region	714	11591	1	
City	1110	16188	1.11	1.01-1.23
1987-1992				
Region	352	7253	1	
City	662	11016	1.24	1.08-1.41
1993-1996				
Region	362	4338	1	
City	448	5172	1.04	0.90-1.20

Table 3. Risks of preterm birth within the city area relative to the rest of the region (Alebic-Juretic et al., 2001)

During the years of higher pollution this risk is even higher, while in the subsequent period a slightly elevated, but not statistically significant risk is observed. The calculated Mantel-

Haenszel estimator of the common odds ratio (OR), controlled for two periods studied, was OR_{MH}= 1.14 (95%CI=1.03-1.25) suggesting a 14% higher relative risk for preterm deliveries within the city. The Breslow-Day test for the homogeneity of the ORs was boundary significant (p=0.055), suggesting the possible difference in ORs between analyzed periods. Considering each socio-demographic parameter (maternal age, education, martial status, smoking habits and newborns sex) and two periods, an increase from 12 to 16% in relative risks is observed within the city (Table 4). Ambient concentrations of SO_2 were taken as an index of air quality. Breslow-Day tests for homogeniety of the ORs were insignificant in all cases for the two periods and levels of socio-demographic factors, these factors could not account for the elevated relative risks for preterm births observed in Rijeka vs. the region. Thus, elevated ambient air pollution may be considered as a possible cause. No association regarding IUGR births was found in this study (Alebic-Juretic et al., 2001).

	Preterm births		IUGR births	
Parameter	OR	95% CI	OR	95%CI
Mothers' age	1.12	1.02-1.24	1.08	0.97-1.20
Education	1.15	1.04-1.27	1.07	0.96-1.19
Martial status	1.13	1.03-1.25	1.06	0.95-1.01
Smoking habits	1.14	1.03-1.25	1.06	0.95-1.18
Newborns' sex	1.16	1.05-1.27	1.08	0.97-1.20

Table 4. Estimate of common relative risk adjusted for two periods considered and each of the listed parameters

3. Conclusion

This work gave synthesis of air pollution problem in the city of Rijeka. Due to early identification, a lot of work has been done for its abatement. Therefore, Rijeka had a leading role in many aspects regarding air pollution monitoring and management. Thus, Rijeka is the only town in Croatia with 25 year experience in providing emission inventories, one of the few places with long term data of nitrogen pollutants (NH_3 and NO_2), and the first town to establish automatic network for air quality monitoring and providing information to public of real time data on the web site. All these actions resulted in significant reduction of air pollution due to combustion processes (SO_2, black smoke, lead, PAHs, H_2S, fallout, TSP). Though, there is still to work on air pollution by traffic (NO_2, VOC, particulates), traffic related secondary pollutants (O_3, nitrate, sulphates), and long range transport (wet and dry deposition, PM_1, ozone).

4. Acknowledgment

Financial contribution from the University of Rijeka Foundation (Contract No: SN-IZ 1/2001) was used for open-access publishing. Opinions given within this chapter are solely the author's and do not express neccessarily the statements from the University of Rijeka Foundation.

5. References

Alebic-Juretic, A. Matković, N., Crvelin, G. Zubak, *V* (2009) New Regulations on Air Quality – The Case of the Petroleum Refinery Mlaka. *Proceedings of 6th Croatian Meeting Air*

Protection '09, pp. 376-382, ISBN 978-953-6609-06-2, Zadar, Croatia, September 14-19, 2009 (in Croatian)

Alebic-Juretic, A. (2008) Airborne Ammonia and Ammonium within the Northern Adriatic Area, Croatia. *Environmental Polution*, Vol. 154, n.d., pp. 439-447, ISSN 0269-7491

Alebic-Juretic, A. (2008a) Ozone levels in the Rijeka Bay Area, Northern Adriatic, Croatia. Proceedings of HARMO12 Conference, *Hrvatski meteorološki časopis (Croatian meteorological Journal)*, Vol. 43, n.d., pp.397-400, ISSN 1330-0083

Alebic-Juretic, A. (2005) Polycyclic Aromatic Hydrocarbons and Metals in Total Suspended Particulates Collected in Rijeka, 1982-2004. *Proceedings of 4th Croatian meeting Air Protection '05*, pp.184-189, ISBN 953-6609-04-05, Zadar, Croatia, September 12-16, 2005

Alebic-Juretic, A. (1994) Polycyclic Aromatic Hydrocarbons in the Urban Atmosphere of Rijeka (Croatia), *Fresenius Environmental Bulletin*, Vol.3, n.d. ,pp. 89-94., ISSN 1018- 4619

Alebic-Juretic, A. & Arko-Pijevac, M. (2005) Lichens as Indicators of Air Pollution in the City of Rijeka, Croatia. *Fresenius Environmental Bulletin*, Vol. 14, No. 1, pp. 40-43, ISSN 1018-4619

Alebic-Juretic, A. & Arko-Pijevac, M. (1989) Air Pollution Damage to cell Membranes in Lichens- result of Simple Biological test Applied in Rijeka, Yugoslavia. *Water, Air and Soil Pollution*, Vol. 47, n.d., pp. 25-33, ISSN 0049-6979

Alebic.Juretic, A., Frkovic, A. & Simic,D. (2001) The Effects of Air Pollution on the Outcome of Pregnancies. *International Journal of Gynecology&Obstetrics*, Vol.75, n.d., pp. 315-316. ISSN 0020-7292

Alebic-Juretic & Sekulic-Cikovic (2009) The Impact of air Pollution on the Paintings in Storage at the Museum of Modern and Contemporary Art, Rijeka, Croatia. *Studies in Conservation*, Vol. 54, No. 1 , (March 2009), pp. 49-57., ISSN 0039-3630

ARCADIS (2011) *Technical Assistance on the Development of Cost-Efficient Emission Reduction Measures for the Port of Rijeka*, Project Report (draft final) , ARCADIS, Project number- 11-004750/Version B/24-01-2011, Antwerp (Belgium), pp. 66/141

Bartonicek-Brgic, V. & Matkovic, N.(1989) Sulphur Dioxide and Black Smoke Air Pollution Impact on Incidence of Respiratoryy Diseases among Preschool Children in Rijeka. Proceedings of the First Yugoslav Clean Air Congress, Book II, pp.734-747, ISBN Zenica, Yugoslavia, June 14-16., 1989 (in Croatian)

Bobak, M. (2000) Outdoor Air Pollution, Low Birth Weight, and Prematurity. *Environmental Health Perspective*, Vol. 108, No. 2, (February), pp. 173-176, doi:10.1289/ehp.00108173

Camuffo, D., Brimblecombe, P., Van Grieken, R., Busse, H-J., Sturaro, G., Valentino, A., Bernardi, A., Blades, N., Shooter, D., De Bock, L., Gysels, G., Wieser, M. & Kim, O. (1999) Indoor Air Quality at the Correr Museum, Venice, Italy. *The Science of the Total Environment*, Vol. 236, n.d., pp. 135-152, ISSN 0048 9697

Conti, M.E. & Cecchetti, G. (2001) Biological Monitoring: Lichens as Bioindicators of Air Pollutin Assessment- A Review. *Environmental Pollution*, Vol.114, n.d., pp. 471-492, ISSN 0269-7491

County (2009) *Programme for Air Quality Protection and Improvement in the Littoral-Highlands County in the Period 2009-2012*, Littoral-highlands County, ISBN 978-953-7221-33-1, Rijeka, pp. 23-28.

EC (2002) Guidance to Member States on PM_{10} Monitoring and Intercomparisons with the Reference Method, EC Working Group on Particulate Matter, January 2002

EKONERG (1997) *Air Quality menagement- Basis for spatial planning of the Littoral-highlands County*, Ekonerg, Zagreb, pp. 10/43-21/43 (in Croatian)

Ferry, B.W., Baddeley, M.S. & Hawksworth, D.L., Eds (1973) *Air Polution and Lichens*, The Althone Press, London, UK

Ligocki, M. P., Salmon, L. G., Fall, T., Jones, M.C., Nazaroff, W.W. and Cass G.R. (1993) Characteristics of airborne particles inside southern California museums, *Atmospheric Environment*, Vol. 27, n.d., pp. 697-711, ISSN 1352-2310

Matkovic, N. & Alebic-Juretic, A. (1998) Emissions and Ambient levels of Sulphur Dioxide in the Rijeka bay Area, *Arhiv za higijenu rada i toksikologiju*, Vol. 49, No.2, pp. 155-1263, ISSN 0004-1254

Matkovic, V., Matkovic, N., Kontosic, I., Jonjic, A. & Matkovic, V. (1998) The Effect of air Pollution on ventilatory Function in Nonsmoking Women. *Arhiv za higijenu rada i toksikologiju*, Vol. 49, No.1, pp. 19-25, ISSN 0004-1254

MEISA (1991) Project *Proposal of Monitoring Air Pollutants and Odours Emitted by Petroleum refinery Rijeka, Iron works Sisak-Coke plant Bakar and TPP Rijeka I* , Environmental Protection Centre, Maribor, pp. 3-11 , 3-63, 3-90, 3-100, 3-108 (in Croatian)

Mingati, V., Capelli, R., Drava, G., de Pellegrini, D., Brunialti, G., Giordani, G. & Modenesi, P. (2003) Biomonitoring of Trace Metals by Different Species of Lichens (Parmelia) in North-West Italy. *Journal of Atmospheric Chemistry*, Vol. 45, n.d., pp. 219-229, ISSN 1573-0662

Mouratidou, Th. & Samara, C. (2004) $PM_{2.5}$ and Associated Ionic Component Concentrations Inside the Archeological Museum of Thessaloniki, N. Greece. *Atmospheric Environment*, Vol. 38, n.d., pp. 4593-4598, ISSN 1352-2310

Pearson, L.C. (1985) Air Pollution Damage to Cell Membranes in Lichens. I Development of a Simple Monitoring Test. *Atmospheric Environment*, Vol. 19, n.d. ,209-212, ISSN 1352-2310

Perry, R. & Young, R.J. Eds. (1977) *Handbook of Air Pollution Analysis*", Chapmam and Hall, ISBN 0 412 12660 5, London

Pinho, P., Augusto, S., Branquinho, C., Bio, A., Pereira, M.J., Soares, A. & Catarino, F.(2004) Mapping Lichen Diversity as a First Step for Air Quality Assessment, *Journal of Atmospheric Chemistry*, Vol. 49 , n.d., pp. 377-389, ISSN 1573-0662

Regional Centre (2002) *Report on Environmental Conditions within the Littoral-highlands County*, Regional Centre for Sustainable Development and Environmental Protection, Rijeka, pp. 43-47 (in Croatian)

Salmon, L.G., Mayo, P.R., Cass, G.R. and Christoforou, C.S. (2005) Airborne particles in new museum facilities. *Journal of Environmental Engineering*, Vol. 131, n.d., pp. 1453-1461, ISSN 1573-0662

Schuler, J. (1902) *Zur Flechtenflora von Fiume*. Separat-Abdruck aus Mittheilungen des Naturwissenschaftlichen Clubs in Fiume., 1901, Jahrgang VI, Buchdrukerei P. Battara, Fiume (Rijeka)

Vadic , V. (1982) Method for Hydrogen Sulphide Measurements in the Atmosphere, *Zaštita atmosfere*, Vol.10, No. 3, 116-118. YU ISSN 0350-1973

van Loon J.E.: *Selected Methods of Trace Analysis: Biological and Environmental Samples*, John Wiley& Son, New York, 1985. ISBN 0-471-89634-9

Wang, X., Ding, H., Ryan, L. & Xu, X. (1997) Association between Air Polution and Low Birth Weight: A Community based Study. *Environmental Health Perspective*, Vol. 105, No.5., (May), pp.514-520, doi:10.1289/ehp.97105514

WHO (1976) *Selected Methods for Measuring Air Pollutants*, WHO offest Publication No 24, ISBN 92 4 170024 6I, Geneva , Switzerland

WHO (2000) *Air Quality Guidelines for Europe*, 2nd Ed., WHO Regional Publications, European series, No. 91, ISBN 13583, Copenhagen, Denmark

Xu, X., Ding, H. & Wang, X. (1995) Acute Effects of Total Suspended Particulates and Sulphur Dioxides on Preterm Delivery: A Community Based Cohort Study. *Archive of Environmental Health*, Vol. 50, No.6 , pp. 407-415 ISSN 0003-9896