

MERCURY IN ATMOSPHERE OVER RURAL, URBAN AND INDUSTRIAL PARTS OF ZAGREB CITY

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In recent years Zagreb city encounters severe pollution problems in aquatic, terrestrial and atmospheric environment. A random or permanent monitoring of some inorganic gaseous pollutants in atmosphere has already been organized and published elsewhere. By means of a sophisticated mercury vapor analyser with a Zeeman effect background corrector, however, continuous registration along two traverses (monitoring routes) over rural, urban and industrial parts of Zagreb has been elaborated for the first time. Data show strong anthropogenic influence in the Žitnjak industrial area. The anomaly high 105 ngm Hg, on the 21 October moved slightly to downtown by change of wind direction on the 31 October. Intensity raised as much as 155 ngm Hg, 15 times augmented in comparison to a background value on the Medvednica mountain. Explanation should be sought in denser public traffic, change of wind direction and lowering of atmospheric pressure.

Introduction

Permanent increase of inorganic solid and gaseous pollution in atmosphere over inhabited areas, caused by uncontrolled growth of cities and unplanned urbanization in strictly industrial regions with still »dirty« industry, makes serious ecological problems. Mercury is also one of the most dangerous pollutants in modern human environment and study of its concentration, distribution and environmental cycles is of primary importance. Zagreb city encounters similar troubles, but Hg-pollution monitoring in atmosphere has not been elaborated till now.

Recent development in construction of sensitive and selective mercury vapor analysers enables measurements of background values and pollution control in rural and urban areas. Continuous registration of mercury in ambient air in the research has been performed by a Zeeman atomic absorption analyser with attached circulating cell in the compartment between the light source and mirror and by air pumping at a rate of 4 lmin.

Expecting strong anthropogenic mercury emission, there were two monitoring traverses across rural, urban and industrial part of Zagreb laid on October 21 and 31, in a long period of stable, sunny

Ključne riječi: Živa, Atmosfera, Zagađenje zraka u Zagrebu, Zeemanov atomski apsorber.

Posljednjih godina grad Zagreb se susreće sa značajnim ekološkim problemima zagađenja svih medija; vode, zraka i tla. Povremena i stalna praćenja koncentracije određenih anorganskih zagađivača u atmosferi izvode se već duže vrijeme, a rezultati su publicirani u znanstvenim časopisima. Međutim, prvi put u našem gradu je korišten model suvremenog živinog analizatora s korektorom analitičkih šumova, baziranom na Zeemanovon efektu, koji omogućava kontinuirano registriranje vrijednosti koncentracija žive u zraku. Mjerenja su izvedena uzduž dviju trasa koje prolaze kroz ruralne, urbane i industrijske predjele grada Zagreba. Rezultati mjerenja su omogućili izradu grube geokemijske karte distribucije žive i lokaciju anomalnih koncentracija u najugroženijim područjima. Anomalija od 105 ngm Hg, registrirana 21. listopada (subota), vidljivo se pomakla u smjeru prema centru grada 31. listopada (utorak). Njezin intenzitet je porastao na 155 ngm Hg, 15 puta više od prosječnih vrijednosti na Medvednici, a položaj ukazuje na značajan antropogeni utjecaj u području industrijske zone Žitnjaka. Objašnjenje ove pojave treba tražiti u pojačanom utjecaju gradskog prometa, promjeni smjera vjetrova i sniženju atmosferskog pritiska kao predznaka pogoršanja vremenskih uvjeta.

mid–autumn weather. The carbone instrument was registering mercury at 1.5 m above ground level along the routes continuously.

The presented research is an attempt to record possible anthropogenic influence, background values and rough distribution of mercury. Future measurements will be taken more comprehensively regarding length and direction of monitoring routes and different wether conditions for better understanding of pollution processes, sources and construction of pollution maps.

Some notes on geochemistry of mercury

Mercury in nature exists in a large number of chemical and physical forms with a wide range of properties important for its environmental behavior. The three most frequent chemical forms observed are: elemental mercury (Hg^0), with high vapor pressure and low solubility in water, divalent inorganic (Hg^{2+}) with strong affinity to many inorganic and organic ligands, particularly those containing sulfur, and methyl mercury ($(CH_3)Hg^+$). The last one is resistant to environmental degradation, enriched by living organisms and capable of passing through important biological barriers such as the blood/brain

and placenta, upsetting metabolism of nervous system. The volatile mercury compounds present in air are those having relatively high Henry's law constant like Hg^0 and dimethyl mercury.

Separation of different compounds of gaseous atmospheric mercury is difficult and methods are still being developed. It is assumed that elemental mercury is the main volatile form, but dimethyl mercury may also occur. Slemr et al. (1981) claim that dimethyl mercury makes up 30% of the total gaseous mercury over European continent although in some recent works they are less convinced in that statement. Particulate mercury in air is normally collected on filters but chemical forms are still unknown. It does not make, however, a large proportion of the total air-borne mercury (1–10%).

Mercury participates in a number of complex environmental cycles that involve conversion among different chemical forms. Two of the cycles play the most important role, the atmospheric and aquatic-biological one.

The atmospheric cycle consists of conversion of divalent inorganic mercury to gaseous elemental mercury and/or $(\text{CH}_3)_2\text{Hg}^+$, and subsequent reoxidation of elemental mercury to water-soluble forms, which are then scavenged by precipitation or dry deposition at the surface. The oxidation process, is not known, but photochemical oxidants, including ozone are likely to be important. The atmospheric residence time of the volatile, elemental mercury is few months, maybe even one or two years (Lindquist, 1985).

The aquatic-biological cycle is characterized by formation of methyl mercury, its enrichment in organisms and nutritional chains and finally its destruction (demethylation). Methyl mercury is the dominant form of mercury in higher organisms. It represents, however, a very small amount of the total mercury in aquatic ecosystem.

Fluxes of mercury and its compounds to atmosphere are formed by following natural processes: volcanic emissions, windblown dust from dry continental areas, emission of gaseous mercury from the ocean and other water bodies, degassing of sulfide deposits and the upper-mantle through deep-seated tectonic structures.

The volcanic emissions are negligible according to Mackenzie and Wollast (1977). Flux associated with dust particles has been estimated by Lanzy and Mackenzie (1979) to be about 25 ton per year, also negligible amount. Some attempts have been made to measure soil degassing rates.

Increase of natural background values might be also affected by presence of outcropping or blind sulfide ore bodies or degassing of the earth mantle through deep tectonic fractures, which serve as a conduit.

Mashyanov (1980) compiled data over certain ore deposits: Au-polymetallic $(3-12) \cdot 10^{-7} \text{ mg l}^{-1}$, Q-Au metamorphic $(2-6) \cdot 10^{-7} \text{ mg l}^{-1}$, Hg-cinnabar $(6-11) \cdot 10^{-7} \text{ mg l}^{-1}$, Sb-deposits $(2-4) \cdot 10^{-7} \text{ mg l}^{-1}$, $(10^{-7} \text{ mg l}^{-1} = 100 \text{ ng m}^{-3})$. Over some oil deposits maximum concentration reached $10 \cdot 10^{-7} \text{ mg l}^{-1}$. Palinkaš et al. (1989) determined Hg

anomalies over bauxite-ore bodies in Istria 2–5 times higher than the local background value.

Results of direct continuous measurements of mercury content in near ground atmosphere over aquatorium of the Lake Baikal revealed connection of active tectonic elements and stability of mercury anomalies in space and time (Ilyin et al., 1987). Deeply seated active tectonic zones under a cover of the sea water, thick several thousand meter, were efficiently recognized in air along the shelf of Kamchatka and Chukotka (Ganeev et al., 1984).

The estimates of global »pre-industrial« emission range between 2500 ton and 30000 ton per year and are considered to be extremely uncertain. They are based on ice-core data from Greenland, that are likely to be rather incorrect (Lindquist, 1985).

Mercury as a pollutant in atmospheric environment

Mercury is highly volatile element: air in equilibrium with liquid mercury will contain 14 mg m^{-3} at 20°C . Threshold limit value (TLV) or maximum allowable concentration (MAC) for mercury vapor in air is set at $0,05 \text{ mg m}^{-3}$ as established by Inter. Symp. in Stockholm, 1968 (Report of an International Committee, 1969), and all mercury spills are very dangerous. Even mercury compounds are very volatile, f.e. cinnabar, HgS , gives 10 ng m^{-3} in dry air (O'Neil, 1985).

Its concentration originates both from natural sources (mercury and sulfide ore deposits, and active volcanism) and anthropogenic activity. For the global atmosphere, current anthropogenic emission corresponds in magnitude to natural processes (pre-industrial) and present background fluxes are probably augmented significantly by man's activity during industrial era (Lindquist, 1985).

Present-day technogenic pollution give rise to mercury mobilization and transfer between land, water and air. An estimate of global emission by Mackenzie and Wollast (1977) gives value of 10000 ton per year. Chase and Weich, 1973 (cited in: Ozerova, 1986) claim that 1/2 of the total emitted mercury in USA originates from fossil-fuel combustion and 1/3 from smelters. The other contamination sources are chlor-alkali plants, oil and gas industry, cement factories and public traffic. Use of fungicides, pesticides, waste incineration should be mentioned as well.

All of the above estimates refer to the total mercury. Very little is known about chemical forms of mercury in anthropogenic emissions. It has been generally assumed that much of the emitted mercury is in elemental state. Most of mercury releases to water are in inorganic form and to land in any or several of these forms.

Data on mercury concentration in air are scattered all over publications. Since analytical techniques have been developing gradually, early data should be taken prudently, although obtained values do not differ significantly. As early as 1934 Stock and Cucuel (1934), recorded 8 ng m^{-3} Hg in unpolluted air, Johnson and Braman (1974) reported values between $3-300 \text{ ng m}^{-3}$ in rural Floridian areas. An ambient background level in clean

air masses was determined by Slemr et al. (1979) at values of $1.0\text{--}4.0\text{ ngm}^{-3}$. Concentration in coastal air, not greatly contaminated by local industry, recommended by Fitzgerald and Gill (1979), are about $2\text{--}10\text{ ngm}^{-3}$. Williston (1968), for example, found $0.5\text{--}50\text{ ngm}^{-3}$ for the San Franciscan Bay area. Ferrara et al. (1982) obtained values for different surroundings in Italy: rural $1.2\text{--}4.1$, urban $2.2\text{--}31.5$, industrial $12.1\text{--}35.5$ and mineralized $8.2\text{--}86.3\text{ ngm}^{-3}$. Schroeder (1982) recently reviewed atmospheric mercury determinations as follows: air (clean) $0.5\text{--}5\text{ ngm}^{-3}$, with maximum 30% for $(\text{CH}_3)_2\text{Hg}$, air (urban) $0.5\text{--}50\text{ ngm}^{-3}$, with 0–5% $(\text{CH}_3)_2\text{Hg}$, and air (polluted, industrial) $20\text{--}50\text{ ngm}^{-3}$, with 5% $(\text{CH}_3)_2\text{Hg}$. Slemr et al. (1985) gave values for mercury in surface air over the Atlantic ocean at a background level of about 2 ngm^{-3} and 1 ngm^{-3} for southern hemisphere oceanic area, and finally we shall mention values accepted by World health organization (1978) cited in Kupchella and Hyland (1984) as a background of 50 ngm^{-3} and 20 ngm^{-3} as an average.

Analytcs, monitoring routes and weather conditions

Techniques for determination of low mercury concentration ($<1\text{ ngm}^{-3}$), normally occurring in ambient air and natural waters, are available only recently and are still under development. There are several techniques frequently applied for that purpose: cold-vapor atomic absorption (CVAA), plasma-atomic emission (with detection limit better than $0,005\text{ ng!}$) and different portable atomic absorption techniques using Zeeman's or spectral phase effects in high selectivity background correctors (Sveshnikov et al., 1980. Ganeev and Turkin, 1989).

With low background concentration of gaseous mercury in ambient air ($0,5\text{--}5\text{ ngm}^{-3}$) accumulative sampling, involving particle filtration and acidic oxidative dissolution or adsorption on gold or silver has been necessary. Due to recent improvement in sensitivity of portable mercury spectroscopic instruments (2 ngm^{-3} , the lower detection limit) there is a possibility of direct recording of background fluctuation in unpolluted, natural surrounding and in urban and industrial areas for pollution control.

The presented measurements have been done by a Zeeman atomic absorption mercury vapor analyzer. A prototype of the instrument, used in field work, was constructed in the Institute of the Earth crust, Leningrad State University by Sveshnikov et al. (1980). It operates on a basis of differential absorption method, using Zeeman's effect and isotope splitting effect of the mercury spectral line at $253,7\text{ nm}$ wavelength. A light source is a mercury lamp filled by isotope 204, situated in a stable magnetic field. The compartment between the light source and mirror accomodates a plastic circulation cell with two quartz-windows, provided for continuous registration of mercury by pumping ambient air through it with flow of 4 lmin (block-scheme of the instrument and the cell during injection calibration is displayed on Fig.1).

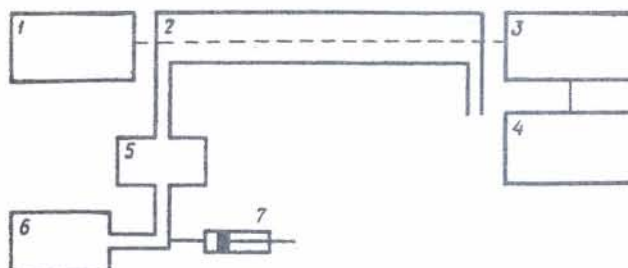


Fig. 1 Block-scheme of the instrument assemblage during dynamic way of calibration (after Sholupov et al., 1988)
1—light source, 2—circulation cell, 3—light receiver, 4—printer, 5—ballast volume 6—compressor, 7—injection.

Sl. 1 Blok-shema instrumentacije u toku dinamičnog načina kalibriranja (po Šolupovu i dr., 1989).
1—izvor svjetla, 2—protočna ćelija, 3—elektronski pojačivač signala, 4—šampač, 5—balastni volumen, 6—kompresor, 7—injekcija.

Calibration of the instrument may be done by two operations: comparison of equivalent optical density and dynamic manner. By the former, standards are thin hermetically sealed cuvettes, filled with air under normal atmospheric pressure, supplied with a droplet of metallic mercury, and with different thickness of the compartment between window glasses. Practical problem arises during measurements of very low concentrations, what requests an especially thin cuvette, less than $0,05\text{ mm}$ or its cooling, very inconvenient during field work. Dynamic manner consists of exhausting of 1 cm^3 saturated mercury vapor from a container into an injection, then dilution in the injection $10\text{--}50$ times and again extrusion into circulating cell with integer time of 5 sec. . The base-line control is done by filtration of ambient air flowing through the analytical cuvette. Efficiency of absorption filter is more than 99% . Both methods give reliable standard values, testified under working condition (Sholupov et al., 1988). The instruments enables detection limit of 10 ngm^{-3} , enough efficient to determine fluctuation bellow a background level in rural and urban areas in Zagreb.

Continuous monitoring of mercury concentration in air was done along two routes. The first one began in the downtown (Mining-geology-oil engineering faculty), along Savska cesta — street, passing over the Sava river into the rural area on the foothills of Samoborska gora, then back following Ljubljanska-Beogradska avenues, through the Žitnjak, industrial part of the city, returning over Sesvete to the downtown, Ribnjak Moša Pijade street, up to the Medvednica mountain and again back in the downtown, at the Britanski trg-square (Fig.2). The second route is almost the same with slight differences presented on Fig. 3.

The routes obviously comprise rural, urban and industrial parts of Zagreb and had been chosen to register mercury concentration of »the natural« background level (if such, at all, in the region exists) and anthropogenic influence across the city.

The measurements were being performed by the car-borne instrument with continuous recording, but only instantaneous registration was executed every

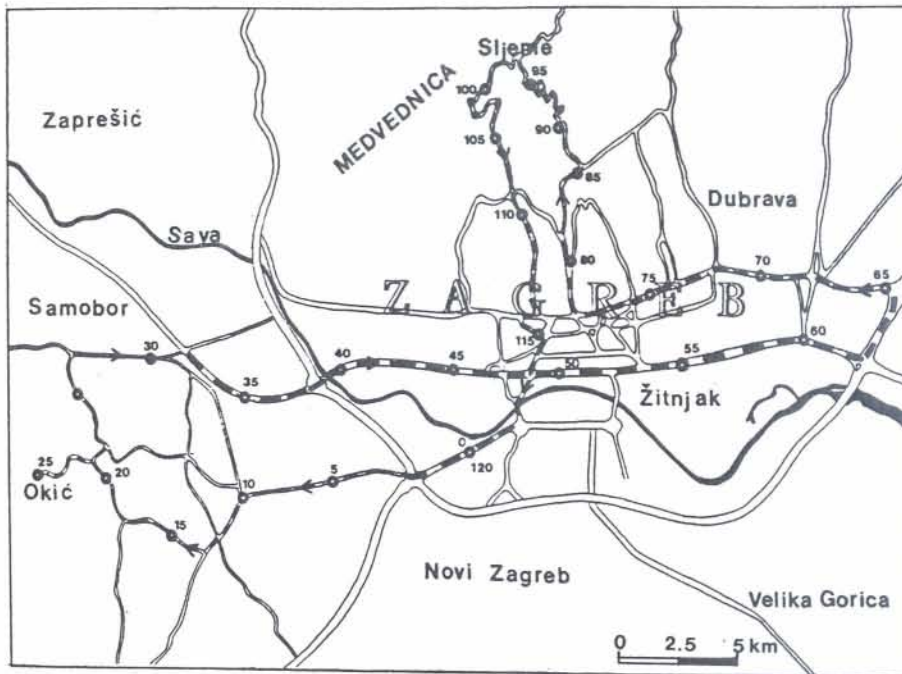


Fig. 2 Monitoring route I, on the 21 October.

Legende: 1. Monitoring route 2. Important monitoring points and distance in km.

Sl. 2 Mjerni profili na ruti I, dana 21. listopada.

Legenda: 1. Mjerna trasa 2. Važnije mjerne točke i razdaljina u km.

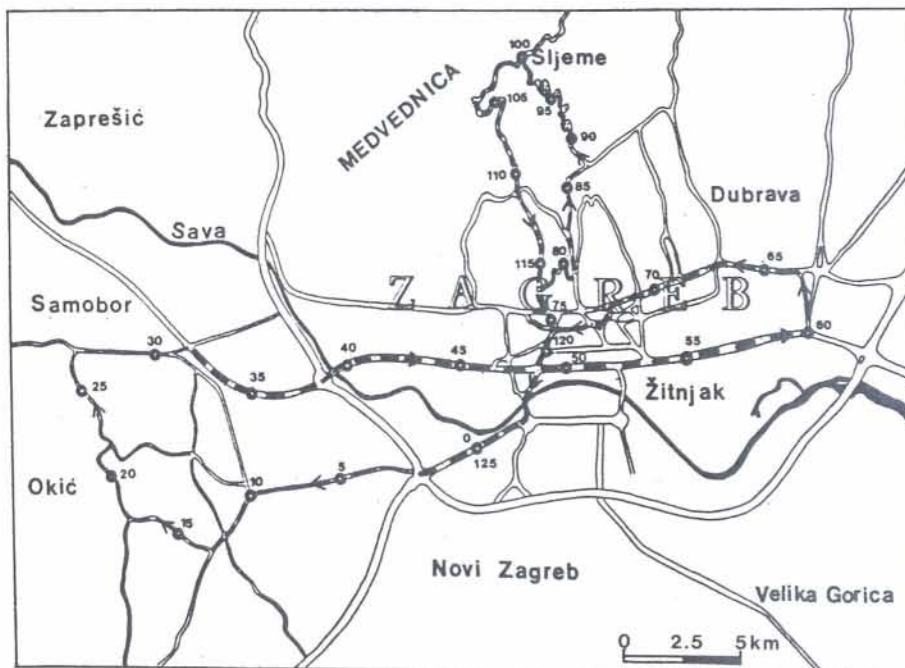
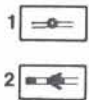


Fig. 3 Monitoring route II, on the 31 October.

Legende: 1. Monitoring route 2. Important monitoring points and distance in km.

Sl. 3 Mjerni profili na ruti II, dana 31. listopada.

Legenda: 1. Mjerna trasa 2. važnije mjerne točke i razdaljina u km.



kilometer along the route I and II on the October 21 and 31, 1989, between 11 and 15 hours.

Weather conditions were stable, sunny, over the whole period, without precipitation and almost the same temperature range between 15–21 °C. The only factor, which changed significantly is direction of weak, 1.4 msec⁻¹ WSW wind, on the October 21 to 0.4 msec⁻¹ ESE wind on the October 31.

Slight decrease of atmospheric pressure, temperature and increase of humidity on the October 31 was a first sign of weather spoiling which might have affected mercury distribution pattern. Weather conditions, registered by Center for meteorological research (Republic Hydrometeorological Institute of SR Croatia), are presented in Table III.

Table I

Concentration of mercury in air along the route I, on the 21 October, 1989.
Koncentracija žive u zraku uzduž mjernog profila I, dana 21. listopada, 1989.

Registration points (5 km distance)	Hg (ngm ⁻³)	Registration points (5 km distance)	Hg (ngm ⁻³)
0 University hosp.	50	40 the Sava river	70
5 Lučko	25	45 Prečko	95
10 Rakov potok	30	50 TV center	90
15 Galgovo	35	55 Žitnjak	97
20 Konjščica	45	60 Sesvete	105
25 Okić	15	65 Sesvete	57
30 Sv. Nedelja	45	70 Dubrava	65
35 Rakitje	45	75 Maksimir	70
80 Zvijezda	65		
85 Gračani	50		
90 Adolfovac	50		
95 Brestovac	20		
100 Grafičar	20		
110 Kraljičin zdenac	26		
115 Pantovčak	35		
120 RGN faculty	37		
125 University hosp.	52		

Table II

Concentration of mercury in air along the route II, on the 31 October, 1989.
Koncentracija žive u zraku uzduž mjernog profila II, dana 31. listopada, 1989.

Registration points (5 km distance)	Hg (ngm ⁻³)	Registration points (5 km distance)	Hg (ngm ⁻³)
0 University hosp.	60	55 Žitnjak	100
5 Lučko	50	60 Sesvete	100
10 Rakov potok	33	65 Dubrava	110
15 Galgovo	60	70 Maksimir	113
20 Konjščica	45	75 Meduličev street	120
25 Rakovica	45	80 Ksaver	110
30 Sv. Nedelja	35	85 Gračani	98
35 Rakitje	58	90 Road to Sljeme	58
40 The Sava river	95	95 Runolist	25
45 Prečko	90	100 Željezničar	6
50 TV centar	110	105 Grafičar	15
110 Šestine	65		
115 Pantovčak	80		
120 Zagrepčanka	75		
125 University hosp.	63		

Results and discussion

Monitoring results along the routes I and II listed in Table I and II and drawn in Fig. 4 and 5. Distribution of concentrations, without doubt, shows serious anthropogenic influence, clearly expressed by a contrast anomaly spreading over the eastern urban and industrial part of the city. The lowest registered values around 10 ngm⁻³ were over the rural area in Samoborska gora and in the forested region on the top of Medvednica mountain. The highest values, approaching 105 ngm⁻³ were recorded in the industrial part of the city in Žitnjak on the October 21 (Saturday). On the October 31 (Tuesday), a normal working day, concentration increased over 155 ngm⁻³ and the center of anomaly moved to the downtown, probably due to intensive city traffic, but the change of wind and atmospheric pressure could also be another reason (Fig. 6 and 7).

Table III

Meteorological data on the 21 and 31 October, 1989. Determined by the Center for meteorological research, Republic Hydrometeorological Institute of Croatia
Meteorološki podaci dana 21. listopada 1989. Mjerenja izvršio Centar za meteorološka istraživanja, Republičkog hidrometeorološkog Zavoda Hrvatske

The 21 October					
Time (hour)	Temperature (°C)				
	11	12	13	14	15
Zagreb–Grič	15.0	16.2	17.6	18.7	19.1
Zagreb–Maksimir	15.9	17.8	18.8	19.9	20.4
Puntijarka	13.2	14.3	14.8	14.6	14.6
Wind speed and direction (m/sec)					
Zagreb–Grič	SSE 1.7	SSW 1.5	SSW 2.0	SSW 2.6	SSW 2.1
Zagreb–Maksimir	SSE 0.8	SSW 0.6	SSW 1.3	WSW 1.4	WSW 1.7
Puntijarka	SSW 1.1	S 1.0	SSW 1.3	W 0.8	WSW 1.2
Humidity (%)					
Zagreb–Grič	74	69	64	63	–
Zagreb–Maksimir	72	61	58	59	55
Puntijarka	65	65	59	62	62
Air pressure (hPa)					
Zagreb–Grič	1007.6	1007.7	1007.4	1007.0	–
Zagreb–Maksimir	1012.3	1011.9	1011.5	1011.3	1011.3
Puntijarka	913.1	913.6	913.4	913.6	913.4
The 31 October					
Time (hour)	Temperature (°C)				
	11	12	13	14	15
Zagreb–Grič	15.2	16.1	17.0	17.9	17.9
Zagreb–Maksimir	14.5	15.9	17.4	18.0	18.1
Puntijarka	13.4	14.6	15.0	15.1	14.7
Wind speed and direction (m/sec)					
Zagreb–Grič	–	–	–	–	–
Zagreb–Maksimir	SSW 0.4	quiet	ESE 0.4	ESE 0.4	ESE 0.4
Puntijarka	SSW 2.3	SSW 2.6	SW 2.0	WSW 2.3	WSW 2.3
Humidity (%)					
Zagreb–Grič	91	82	75	75	–
Zagreb–Maksimir	82	75	73	72	68
Puntijarka	56	54	51	50	50
Air pressure (hPa)					
Zagreb–Grič	1002.6	1001.9	1001.1	1000.6	–
Zagreb–Maksimir	1004.9	1004.7	1004.1	1003.7	1003.4
Puntijarka	907.4	907.3	906.9	906.7	906.6

The shape and intensity of anthropogenic anomaly strongly depends on technogenic effects, which in urban surrounding overcome natural factors like soil porosity and thermal conductivity, soil moisture, pH and Eh conditions, temperature of soil and near-surface atmosphere, thickness of snow cover, atmospheric pressure, precipitations (rain, snow) etc. (Altman et al., 1986). The general pattern of mercury distribution may be significantly reshaped by wind, especially in the case of point sources, situated at certain distance from the ground level what is not a case with subsurface, natural emission

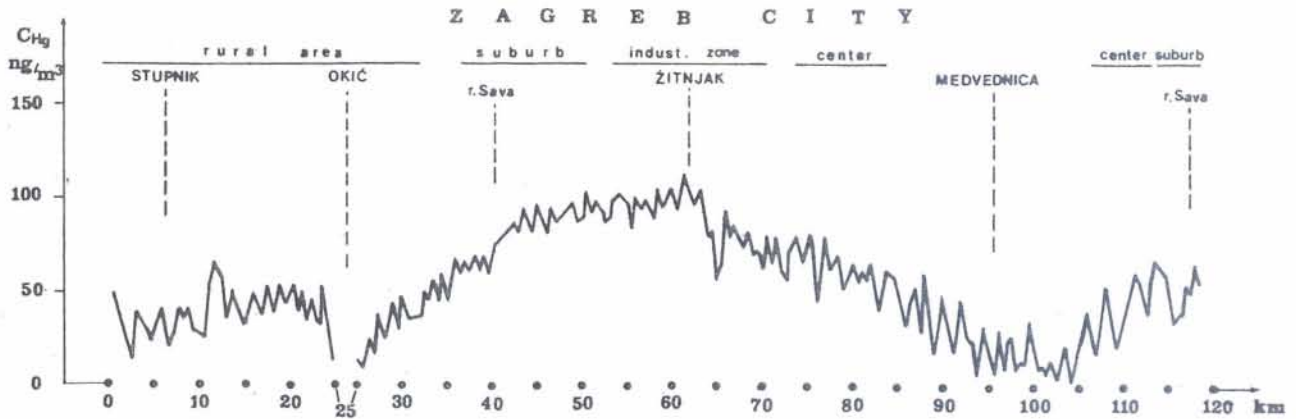


Fig. 4 Concentration of Hg in air (ngm^{-3}) along the route I
 Sl. 4 Koncentracija žive u zraku (ngm^{-3}) uzduž rute I

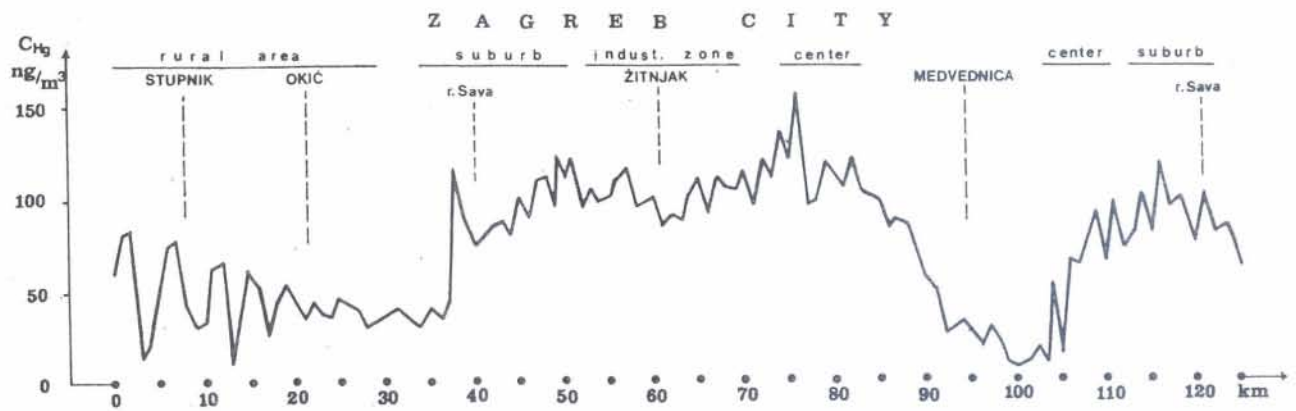


Fig. 5 Concentration of Hg in air (ngm^{-3}) along the route II
 SL. 5 Koncentracija žive u zraku (ngm^{-3}) uzduž rute II

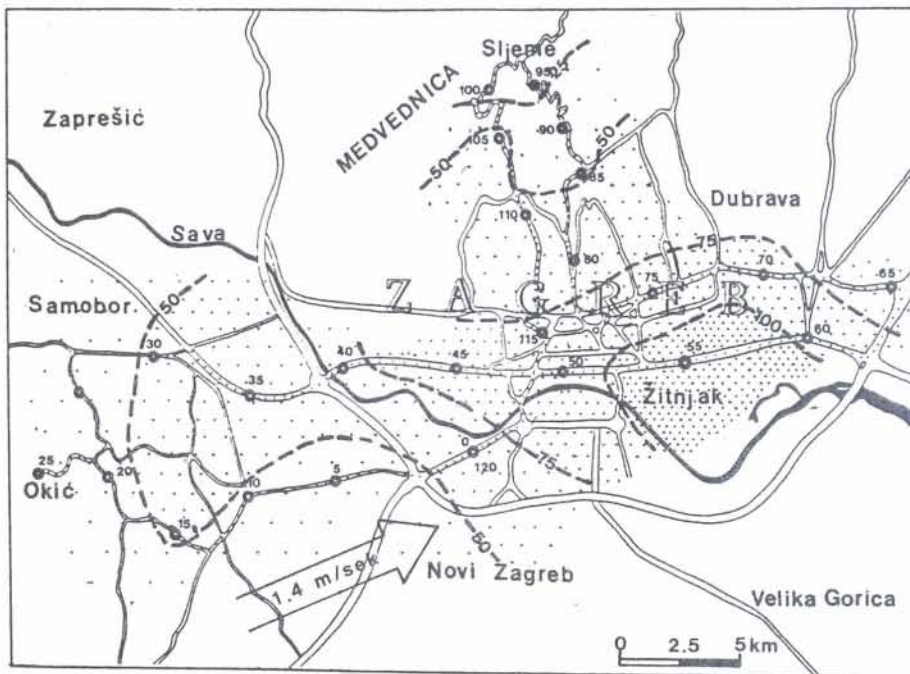


Fig. 6 Mercury distribution on the 21 October, 1989.
 Sl. 6 Distribucija žive dana 21. listopada, 1989.

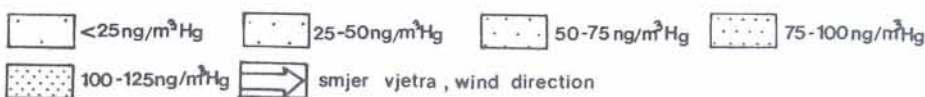
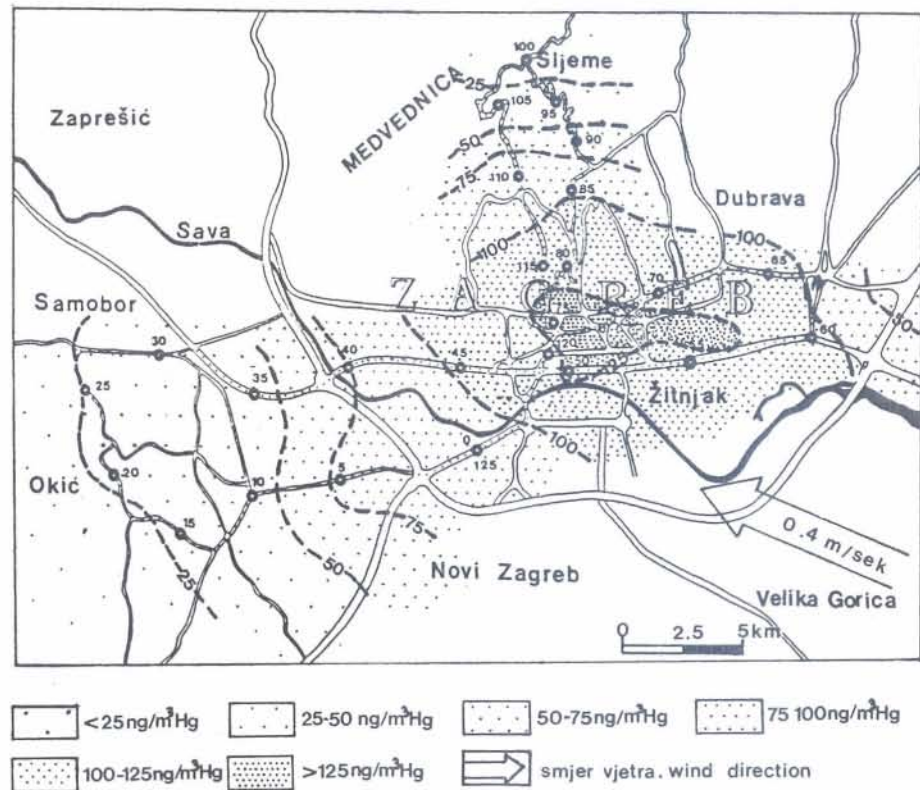


Fig. 7 Mercury distribution on the 31 October, 1989.

Sl. 7 Distribucija žive dana 31. listopada, 1989.



or pollution. Mashynov (personal communication) determined mercury anomaly 12 km from the shale-oil plant (Estonia) on the counter windward side of the source, although smoke was not observable. In Middle Asia, he observed an extensive halo of about 100 km² and higher than 700 m around a metallurgical plant.

Mercury content in American coals varies greatly between 100–33000 ppb. Accepting an average Hg-value of 1000 ppb, coal production of 3×10^9 ton would release an enormous quantity of 3000 ton Hg in atmosphere. It points out on a serious problem of fossil/fuel combustion in power plants and household heating. In the plum of a coal-fired plant Lindberg (1980) measured concentration of total gaseous mercury in excess of 100 ngm⁻³ within a few km from the source (5–10 ngm⁻³ are normal concentration in (flue) gas). It should be mentioned, however, that a dominant fraction of the mercury emitted from a point source is dispersed regionally or globally and a small fraction is deposited locally (10%).

Some gas and oil deposits are fairly enriched in mercury, particularly if affiliated to deep regional tectonic structures—lineaments, a phenomena explained by Ozerova (1981) as a mantle degassing process. Gas deposit Groningen in Netherland (Achterberg and Zaanen, 1972) with colossal reserves of several trillions m³, contains about 2×10^{-4} gm⁻³ or in total 3 000 ton of mercury. Yearly gas production yields 15 ton of mercury by separation procedure, but 5 ton of mercury is lost, however, due to imperfection in separation technology (Tischendorf et al., 1973).

The authors measured concentration in gas from some Croatian gas and oil fields, obtaining values of 100–200 ngm⁻³.

Lack of data on mercury content in crude oil, gas and their refinements, and coal as well, does not enable calculation of a reliable budget on mercury emission in Zagreb atmosphere.

Modern portable instruments, with high sensitivity, selectivity and ability of continuous monitoring would be efficient assistance in detection of contamination sources and pollution level during extremely bad weather conditions. On a basis of two-days measurements, limited length of the monitoring routes and uniform weather condition the paper does not pretend to give the complete description of mercury distribution, source positions, and other influencing factors, but rather to show on possible pollution hazard in certain areas of the city, especially during bad atmospheric conditions and extensive use of coal/fired heating and public traffic.

Conclusion

Monitoring results along traverses I and II without doubt show serious anthropogenic influence. The contrast anomalies, caused by industrial activity, over the eastern urban and industrial part of Zagreb are augmented 15 times above the background value in rural parts of the city. Public traffic contributes to the general distribution pattern, although weather condition and wind direction may not be neglected.

Without knowing mercury content in fossil-fuels or their refinements it is impossible to calculate reliable mercury emission budget. The task of future investigation will be directed in two ways. Measurements of mercury in different kinds of common fuels, and further monitoring under different weather conditions, which will result in construction of pollution maps, and precise determination of pollution sources in the city.

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REFERENCES

- Achterberger, A., Zaanen, J. J. (1972): Sparen kwik in het Groningen aardgas. – *Chemich Weekblad*, v. 68, 8, 59–110 (cited in: Ozerova, 1981).
- Altman, E. L., Mashyanov, N. R., Sveshnikov, G. B. (1986): O vliyanii meteoroglogicheskikh uslovii na gazovye oreoli rtuti v atmosfernom vazduhe. – *Fizika atmosfery*, 11, 81–91, Vilnius.
- Craig, P. J., (1986): Organometallic compounds in the environment (principles and reactions). – Longman, 368 p.
- Ferrara, R., Petrosino, A., Maserti, E., Seritti, A., Barghigiani, C. (1982): The biogeochemical cycle of mercury in the Mediterranean, Part 2: Mercury in the atmosphere, aerosol and in rainwater of a northern Tyrrhenian area. – *Environ. Technol. Lett.*, 3, 449–456 (cited in: Lindquist, 1985).
- Fitzgerald, W. F., Gill, G. A. (1979): Subnanogram Determination of Mercury by Two Stage Gold amalgamation and Gas Phase Detection Applied to Atmospheric Analysis. – *Analyt. Chem.*, 51, 1714–1720.
- Ganeev, A. A., Mashyanov, N. R., Sveshnikov, G. B., Sholupov, S. E. (1984): O vozmozhnosti kartirovaniya aktivnykh tektonicheskikh struktur po gazovim areolam rtuti and morskoi poverkhnostyu. – *Dokladi Akademii nauk SSSR*, y. 275, 5, 1162–1164, Moskva.
- Ganeev, A. A., Turkin, J. I. (1989): *Spektralno-fazovye effekti i ikh analiticheskoe primenenie*. – *Zhur. Analit. Khimii*, XLIV, Moskva.
- Ilyin, T. J., Mashyanov, N. R., Sveshnikov, G. B., Taliev, S. D., Sholupov, S. E. (1987): O pit primeneniya gazortutnoi syemki na akvatorii ozera Baikal. – *Vestnik LGU*, V. 7, 7, 78–82, Leningrad.
- Johnson, D. L., Braman, R. S. (1974): Distribution of atmospheric species near ground. – *Envir. sci. Technol.*, 8, 1003–1009 (cited in: Lindquist, 1985).
- Lantzy, R. J., Mackenzie, F. I. (1979): Atmospheric trace metals: global cycles and assessment of man's impact. – *Geochim. Cosmochim. Acta*, 43, 511–525.
- Lindberg, S. E. (1980): Mercury partitioning in an power plant plum and its influence on atmospheric removal mechanisms. – *Atmos. Environ.*, 14, 227–231, (cited in: Lindquist, 1985).
- Lindquist, O. (1985): Atmospheric mercury – review. – *Tellus*, 37 B, 136–159.
- Mackenzie, F. T., Wollast, R. (1977): Sedimentary cycling models of global processes. – In the sea (ed. Goldberg et al.) J. Wiley and Sons, New York (cited in: Lindquist, 1985).
- Mackenzie, F. T., Wollast, R. (1977): Sedimentary cycling models of global processes. – In the sea (ed. Goldberg et al.) J. Wiley and Sons, New York (cited in: Lindquist, 1985).
- Mashyanov, N. R. (1980): O pit eksperimentalnoi razrabotki metoda poiskov mestorozhdenii poleznikh iskopaenikh po gazovim areolam rtuti v atmosfer. – *Vestnik LGU*, 12, 47–54, Leningrad.
- O'Neil, P. (1985): Environmental Chemistry. – George Allen & Unwin, 232 p., London.
- Ozerova, N. A. (1981): Novii rtutnii rudnii pojas v zapadnoi Evrope. – *Geol. rud. mestorozhdenii*, 6, 49–56.
- Ozerova, N. A. (1986): Rtut i endogennoe rudoobrazovanie. – Nauka, 231 p., Moskva.
- Palinkaš, L. A., Sholupov, S. E., Šinkovec, B., Miko, S., Sesvečan, T. (1989): Mercury in soil and atmosphere as a pathfinder element for Istrian bauxite deposits – a tentative exploration model. – *Rud. geol. naftni zbornik*, 1, 47–62, Zagreb.
- Report of an International Committee (1969): Maximum allowable concentration of mercury compounds. – *Arch. Environm. Health*, 19, 891 p., 1969 (cited in: Wimmer, 1974).
- Sholupov, S. E., Drevaly, T. B., Mashyanov, N. P., Platonova, N. M. (1988): O sposobakh graduirovki rtutnih gazoanalizatorov. – *Vestnik LGU*, v. 7, 14, 3 – 7, Leningrad.
- Schroeder, W. H. (1982): – *Environ. Sci. Technol.*, 16, 394A–400A (cited in: Craig, 1986).
- Slemr, F., Seiler, W., Eberling, C., Roggendorf, P. (1979): The determination of total gaseous mercury in air at background levels. – *Anal. Chim. Acta*, 110 35–47.
- Slemr, F., Seiler, W., Schuster, G. (1981): Latitudinal distribution of mercury over the Atlantic ocean. – *J. Geophys. Res.*, 86, 1159–116 (cited in: Lindquist, 1985).
- Stock, A., Cucuel, F. (1934): Die Verbreitung des Quecksilbers. – *Naturwissenschaften*, H, 22, 24, 390–393 (cited in: Wedepohl, ed., 1978).
- Sveshnikov, G. B., Turkin, J. I., Altman, E. L., Mashyanov, N. R., Sholupov, S. E. (1980): Aparatura dlya distancionnogo atomno-absorbicionnogo spektralnogo analiza parov rtuti v atmosfere. – In: *Geokhimicheskii metodi poiskov glubokozalegayushchikh rudnikh mestorozhdenii* (Fursov, V. Z., ed., 1980), Nauka, Novosibirsk.
- Tischendorf, G., Paelchen, W., Ungethuem, H. (1973): Zum Sistem der Faktoren und Indikatoren bei der Prognose und Such von Quecksilberlagerstätten. – *Zeitschrift Angew. Geol.*, B 19, 8 385–397 (cited in: Ozerova, 1981).
- Wedepohl, K. H., ed. (1978): Handbook of geochemistry. – Vol. II/5, Springer Verlag.
- Williston, S. H. (1968): – *J. Geophys. Res.*, 73, 7051 (cited in: Fitzgerald and Bill, 1979).
- Wimmer, J. (1974): Quecksilber in der Umwelt (Ein Literaturuebersicht). – *Die Bodenkultur*, 25, 3, 272–290.

Živa u zraku iznad ruralnih, urbanih i industrijskih dijelova grada Zagreba

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Stalno povećavanje zagađenja atmosfere krutim anorganskim česticama i plinovima iznad nastanjenih krajeva uzrokovano je nekontroliranim rastom gradova te neplanskom stambenom izgradnjom u izrazito industrijskim područjima i predstavlja teški ekološki problem. Živa je jedan od najopasnijih zagađivača suvremenog ljudskog okoliša i studij njezine distribucije i kružnih tokova je od primarne važnosti. Zagreb se susreće sa sličnim problemima ali kontrola koncentracija žive u zraku, uzduž mjer-nih trasa, do sada nije obavljena.

Razvoj modernih, osjetljivih i selektivnih analizatora žive u zraku omogućuje mjerenja na nivou fonskih vrijednosti u prigradskim područjima. Kontinuirano mjerenje žive u ovom radu izve-deno je pomoću Zeemanovog atomskog apsorbera s pridodanom cirkulacijskom ćelijom, u prostoru između izvora svijetla i zrcala, uz protok zraka od 4 l min^{-1} .

Očekujući izražen antropogeni utjecaj postavljene su dvije trase mjerenja kroz ruralna, urbana i industrijska područja grada Zagreba. Prva trasa započinje u centru grada kod Rudarsko-geo-loško-naftnog fakulteta, zatim ide Savskom cestom, prelazi rijeku Savu, prolazi kroz ruralna područja na obroncima Samo-borske gore, vraća se u grad uzduž Ljubljanske i Beogradske avenije, kroz Žitnjak, do Sesveta, ponovo u centar grada, kraj Ribnjaka, ulicom Moša Pijade, penje se na Medvednicu, nazad u centar grada na Britanski trg. Druga trasa je gotovo identična

uz neke male izmjene u centru grada uzrokovane komunalnim radovima (Sl. 1 i 2).

Mjerenja su izvedena 21. i 31. listopada, između 11 i 15 sati, u periodu stabilnog, sunčanog jesenskog vremena. Instrument, transportiran terenskim vozilom, registrirao je sadržaj žive $1,5 \text{ m}$ iznad nivoa tla, kontinuirano uzduž rute.

Najniže vrijednosti su registrirane na ruralnom području, na obroncima Samoborske gore i u šumovitom predjelu na vrhu Medvednice (10 ng m^{-3}). Najviše vrijednosti, 105 ng m^{-3} , zabilje-žene su na Žitnjaku 21. listopada (subota). 31. listopada (utorak), tokom uobičajenog radnog dana, koncentracija se povećala na 155 ng m^{-3} , a anomalija se pomakla prema centru grada, vjero-jatno zbog utjecaja gradskog prometa, promjene vjetra i pada atmosferskog pritiska, kao znaka pogoršanja vremena.

Distribucija žive, bez svake dvojbe, pokazuje snažan antropo-geni utjecaj, izražen s kontrastnom anomalijom u istočnom, indu-strijskom dijelu grada. Tehnogeni emisija prekriva prirodnu i istraživanje isplinjavanja žive uzduž nekih važnih tektonskih linija na ispitivanom području je nemoguće. Na bazi dvodnevnog mje-renja ovaj rad ne pretendira da da potpunu sliku distribucije žive, izvore zagađenja, specifikaciju živinih kemijskih oblika, već da ukaže na moguću opasnost od zagađenja u određenim područ-jima grada, naročito u vrijeme izuzetno loših vremenskih uvjeta (nizak atmosferski pritisak) i povećanog korištenja krutih goriva za grijanje domaćinstava. Nastavak istraživanja će posvetiti ovim problemima više pažnje.