Impact of phase out of leaded gasoline on the air quality in Budapest

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Abstract

As part of an air pollution study in Budapest, size-fractionated aerosol samples were collected by stacked filter units and cascade impactors, and some criteria pollutants and meteorological parameters were recorded in 1996, 1998 and 1999. The samplings were performed at three urban locations including an urban background site, a downtown site, and a tunnel. Elemental composition of the aerosol samples was measured by instrumental neutron activation analysis and/or particle-induced X-ray emission spectrometry; and black carbon (BC) was determined by a light reflectance technique. Since leaded gasoline was completely phased out in Hungary on 1 April 1999, the atmospheric concentrations of some typical transportation-related air pollutants (i.e. Pb, Br, BC and CO) were used for overviewing the actual impact of the phase out on the air quality and on the aerosol characteristics. For the background site, mean concentration of Pb and Br was not changed significantly. In the downtown site, the phase out resulted in a concentration decrease by a factor of 3–4 for Pb and Br. For the tunnel, concentrations of Pb and Br were decreased by a factor up to 9 and 28, respectively. Correlation between the pollutants, their crustal enrichment factors, and average elemental mass size distributions are also presented and discussed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Lead is a hazardous heavy metal that has a damaging impact on human health, in particular on children and pregnant women. The negative effects of Pb pollution are well documented [1]. The main symptoms include difficulties in mental development (e.g. reading and learning disabilities) and in concentration, adverse effects on kidney function, blood chemistry and cardiovascular system, and hearing degradation. Direct inhalation of airborne Pb or ingestion of Pb-contaminated food (e.g. from Pb-soldered food cans), dust, soil, water or Pb-based paint can all contribute to the Pb exposure. Nevertheless, it is the airborne Pb that causes the primary exposure under ordinary conditions. The key indicator of the Pb exposure is the blood lead level (BLL). Before measures were taken to reduce the Pb emissions by vehicles, exhaust fume from internal combustion engines using leaded gasoline was the main source of the atmospheric Pb emissions in urban areas in industrialized countries. It accounted typically for approximately 90% of the atmospheric Pb in big cities [2]. A strong linear correlation between the average concentration of Pb in gasoline and the population BLL was observed for many locations [1]. Coherently, Pb concentrations reaching the percent level in the urban roadway dust were sometimes reported. By phasing out leaded gasoline in many countries, the relative significance of the automotive Pb emission is rapidly decreasing. At the same time, the other emission sources like industrial works, such as lead smelters, production and destruction of lead batteries, and waste incinerators, etc., are gaining in importance.

Lead is (or used to be) added to petrol in the form of an organic tetraalkyl lead (tetramethyl lead or tetraethyl lead) as anti-knock agent. To a lesser extent, Pb is said to be required for its lubricant properties by soft exhaust valve seats of older internal combustion engines. The highest concentration of Pb in gasoline in the world is basically approximately 0.84 g/l, because at higher concentrations the Pb additives provide little additional benefit to the octane rating of the gasoline [1]. During the combustion, the Pb compounds react with the ethylene dihalides (ethylene dibromide and ethylene dichloride) also added to the petrol as scavengers. Lead is emitted by the exhaust stream in inorganic particulate forms, predominantly as $PbClBr$ and $2PbClBr \cdot NH_4Cl$ [3]. Other possible components [e.g. PbO, $PbSO_4$, $3Pb_3(PO_4)_2 \cdot PbClBr$, HBr] have only been recorded as minor or trace constituents [4]. Chlorine is emitted from several other anthropogenic and natural sources, but Br has only a few other industrial sources and a low natural background. Therefore, the association of Pb with Br allows their use as traditional marker elements for automotive emissions. Since the mole ratio of Br and Pb in the principal components mentioned above is 1, their mass ratio (often referred as ethyl ratio) should be 0.386. Unfortunately, the lead dihalide is not stable in the atmosphere and the halogens are progressively lost in a volatile form from aged automotive exhaust. Hence, reported values of Br/Pb ratios measured in the absence of obvious industrial Pb contributions vary considerably [3]. Direct usage of the Br/Pb ratio for determining the vehicular contribution to the atmospheric lead burden may not, therefore, be possible, and the ratios need to be approached with a certain amount of caution.

Hungary decreased the concentration of Pb in the leaded gasoline gradually from 0.6 g/l to 0.4 g/l in 1985, and from the later level to 0.15 g/l in 1992 for octane numbers (ONs) 92 and 98 [5]. Unleaded gasoline was introduced to the market in 1989. Its share increased from 6% in 1991 to 71% in 1997 [6]. The measures taken have led to a constant and significant reduction of vehicle-related Pb emissions; its amount relative to the total Pb emission was estimated at 66% in 1998. Within the harmonization process of the regulatory framework in the environmental policy of Hungary with that of the European Union, leaded gasoline was completely phased out on 1 April 1999. For the unleaded gasoline ON 91, 95 and 98, the EU lead limit, i.e. maximum permissible Pb concentration of 0.013 g/l (Directives 85/210/EEC) has been adopted. Since the number of diesel-driven light duty vehicles, heavy-duty vehicles and buses was approximately 11% of the total vehicles, and the diesel-driven passenger

cars made up approximately 9% of all passenger cars in 1998, the phase out affected the majority of the vehicle fleet [6]. Hence, atmospheric concentrations of Pb and Br were expected to drop after April 1999.

The main objectives of the present work are to overview the atmospheric concentrations and characteristics of the main transportation-related aerosol pollutants in coarse and fine size fractions before and after the phase out of leaded gasoline, to discuss their relationship and their elemental mass size distributions, and to determine the importance and extent of the actual changes in the air quality. Lead, Br, and black carbon (BC) in the size-fractionated aerosol samples collected at an urban background site, at a downtown location, and within a tunnel, all in Budapest, in 1996, 1998 and 1999 are considered for our present purposes.

2. Collection of samples

As part of a comprehensive air pollution study in Budapest, aerosol samples were collected by different sampling devices. Gent-type stacked filter units (SFUs) were used to separate the aerosol into two size fractions by sequential filtration through two Nuclepore polycarbonate membrane filters of different (8 and 0.4 μm) pore size [7]. The sampler is also equipped with an impaction stage having an inlet cut-off point of 10 μm equivalent aerodynamic diameter (EAD) at a given (15–16 l/min) air flow rate. As a consequence, the aerosol particles are separated into a coarse (approx. 10–2 μm EAD) and a fine (< 2 μm EAD) size fraction on the filters. Another type of sampler used was a single-orifice Battelle-type PIXE International cascade impactor (CI) with seven impaction stages and a backup filter stage. The impaction stages have effective cut-off EADs of 16, 8, 4, 2, 1, 0.5 and 0.25 μm, and the backup filter collects particles < 0.25 μm EAD. The impaction stages consist of polycarbonate film coated with a thin layer of either vaseline (first six stages) or paraffin (last stage); the backup filter is a Nuclepore polycarbonate membrane filter with a pore size of 0.4 μm.

The nominal air flow rate for the impactor is 1 l/min.

The SFU aerosol samples were collected at three urban sites in Budapest [8,9]. With regard to the first two sites, one of them was chosen on the western border of Budapest within the wooded campus of the Central Research Institute for Physics (KFKI). Since the prevailing wind direction in Budapest is northwest, this site was considered as the 'urban background'. The second sampling site was located in the downtown in a small park at Széna Square at the automated monitoring station of the Municipal Institute of the State Public Health Officer Service (ÁNTSz FI). This site is affected by heavy traffic nearby. Daily aerosol samples were taken with planned and regular interruptions at both sites. The typical sampled volume was approximately 19 m^3. The sampling was always performed in April and May. In 1996, a total of 33 sample pairs were collected at both sites on semi-consecutive days, while in 1999, three sample pairs were collected at both sites on consecutive days. The third sampling site was downtown in the Castle District Tunnel (CD Tunnel), which is 350 m long, approximately 9 m wide, and varies from 8 to 11 m in height. It comprises two-lane traffic of passenger cars, light-duty vehicles, and buses. Traffic through the tunnel during the sampling was recorded on videotapes for traffic characterization. The typical total vehicle circulation in both directions was 1780 h^{-1}, and the vehicle fleet comprised 86% passenger cars, 8% light-duty trucks, vans and jeeps, 2% buses and heavy-duty trucks, 2% two-stroke engines and 2% of other vehicles (mainly motorcycles). The vehicle composition approximates to the national ratios. In May 1998, two samples were collected within the tunnel at approximately the halfway point from approximately 09.00 h to 15.00 h on two consecutive days. In June 1999, two samples were collected within the tunnel from approximately 08.30 h to 12.00 h, and two samples were taken outside the tunnel from approximately 12.30 h to 17.00 h on two consecutive days. The typical sampled volume was 3–5 m^3. Several field blank filters were also collected in each sampling campaign. All filters were placed into plastic Petri dishes and were

stored in a refrigerator at a temperature of approximately 4°C.

The cascade impactor samples were collected at all sampling sites in April–June 1999 in order to determine the detailed elemental mass size distributions of many elements. Six daily CI samples were collected at the KFKI campus on six consecutive days, and five CI samples were taken within the tunnel from approximately 08.30 to 17.00 h on two consecutive days. At Széna Square, separate daylight (from approximately 07.30 to 21.30 h, 10 samples) and night (from approximately 21.30 to 07.30 h, 11 samples) CI samples were obtained on semi-consecutive days.

Collection of aerosol samples performed at Széna Square was complemented with simultaneous measurement of some criteria pollutants (i.e. NO, NO_2, SO_2, CO, and total suspended particulates) in cooperation with the ÁNTSz FI by commercial equipment [9]. All samplings were also completed with meteorological observations including ambient temperature, pressure, horizontal wind speed and direction, and relative humidity measurements.

3. Analytical methods

Approximately a half section of each filter was analyzed by instrumental neutron activation analysis (INAA) for up to 49 elements at Budapest Research Reactor. Atmospheric concentration data for Br were obtained as part of the panoramic analysis procedure. A quarter section of each filter was analyzed by a light reflectance method (by a commercial smoke stain reflectometer) for BC, and by particle-induced X-ray emission spectrometry (PIXE) for up to 29 elements at the University of Gent. Atmospheric concentrations for Pb were measured by PIXE. Particulars concerning the experimental setups and procedures have already been described [8–10]. The analyses were performed without any sample treatment. The quality of the analytical values for each series was continuously controlled by concentration ratios for those elements that were measured by both INAA and PIXE, and was

found within approximately 5–10% for elements that were determined with good precision by both methods [11]. Atmospheric concentrations were converted to that at standard temperature and pressure (STP, 273 K and 1013 hPa). The cascade impactor samples were analyzed by PIXE only, for up to 29 elements.

4. Results and discussion

Mean atmospheric concentrations and standard deviations of Pb, Br, and BC, their correlation coefficients (Corr), mean Br/Pb concentration ratios, and mean crustal enrichment factors (EFs) for Br and Pb in the coarse and fine aerosol size fractions collected at the KFKI campus, Széna Square, and within the CD Tunnel before and after the phase out of leaded gasoline in Hungary are shown in Tables 1–3. The EFs were calculated relative to Mason's average crustal rock composition with Al as reference element [12]; the correlation data are only given when they are meaningful. It is worth mentioning that both the 30-min and 24-h concentration limits for Pb valid for Budapest are 300 ng/m³. The mean concentrations for coarse Pb in downtown in 1996, and that in the tunnel in 1998 were a factor of approximately 10 and 280 higher, respectively than that at the KFKI campus (the urban background site). For fine Pb, differences of a factor of 3 and 17 were observed when intercomparing the same sampling sites. In 1999, atmospheric concentrations of coarse Pb at the downtown site and within the tunnel were three times and 75 times higher, respectively, than at the urban background site. For fine Pb, comparison of the sampling sites resulted in differences of a factor of 3 and 4, respectively. The standard deviations of Pb and Br indicate that the daily concentrations exhibit considerable variability in general and that they can change by a factor up to approximately 3 over time [9]. Hence, change in the concentration values or time trends can only be considered to be significant when its magnitude exceeds this extent. At the KFKI campus, the changes in the concentration of fine Pb and Br are not signifi-

Table 1
Mean atmospheric concentrations and standard deviations of Pb, Br, and BC in ng/m^3 STP, their correlation coefficients (Corr), mean Br/Pb concentration ratios, and mean enrichment factors (EF) calculated relative to average crustal rock composition with Al as reference element in the coarse and fine aerosol size fractions collected at the KFKI campus (urban background) in 1996 and 1999

Aerosol variable	1996		1999	
	Coarse size fraction	Fine size fraction	Coarse size fraction	Fine size fraction
Pb	4 ± 2	18 ± 8	4.8 ± 0.5	9 ± 3
Br	3.4 ± 0.6	6 ± 2	< 3	3.6 ± 1.6
BC	350 ± 190	2200 ± 1000	150 ± 70	1200 ± 300
Corr(Pb, Br)	0.28	0.52	−	−
Corr(Pb, BC)	0.80	0.56	−	−
Br/Pb	0.68	0.38	−	0.26
EF(Pb)	65 ± 35	1214 ± 620	176 ± 29	1158 ± 920
EF(Br)	298 ± 230	2322 ± 1680	> 624	2586 ± 997

cant; at Széna Square, concentrations of both Br and Pb in both size fractions exhibit a significant decrease by a factor of 3–4. The largest change is observed for the samples collected within the tunnel, as expected. While Pb and Br decreased in the coarse size fraction by a factor of approximately 3 and 17, respectively, they were changed by a factor of approximately 9 and at least 28, respectively, in the fine size fraction. Atmospheric concentrations of Pb and Br in the coarse size fraction are still significantly higher than that outside the tunnel in the ambient air, but the fine Pb and Br values agree practically with those obtained outside. In contrast to Pb and Br, the atmospheric concentration of BC did not change significantly over time at any of the sampling

sites, which is evidence that there was no significant alteration in the average intensity of the automotive emissions over the time investigated. As a consequence, the concentration changes for Pb and Br are to be attributed to the phase out of leaded gasoline.

The relation of Pb and Br to the vehicular emission is often inferred from a high correlation between their concentrations. There is practically no linear correlation between Pb and Br for the coarse size fraction from the KFKI campus in 1996, suggesting that contribution of the automotive emissions to the urban background is negligible. In contrast, the correlation is fairly high for the samples taken in the downtown in 1996. It means that both elements originate from a com-

Table 2
Mean atmospheric concentrations and standard deviations of Pb, Br, and BC in ng/m^3 STP, their correlation coefficients, mean Br/Pb concentration ratios, and mean enrichment factors (EF) calculated relative to average crustal rock composition with Al as reference element in the coarse and fine aerosol size fractions collected at Széna Square (downtown) in 1996 and 1999

Aerosol variable	1996		1999	
	Coarse size fraction	Fine size fraction	Coarse size fraction	Fine size fraction
Pb	50 ± 25	54 ± 17	13 ± 5	16 ± 5
Br	14 ± 7	16 ± 4	4.3 ± 0.5	4.1 ± 1.0
BC	2200 ± 700	7800 ± 1800	1300 ± 300	6400 ± 1100
Corr(Pb, Br)	0.87	0.81	−	−
Corr(Pb, BC)	0.93	0.83	−	−
Corr(Pb, CO)	0.70	0.70	−	−
Br/Pb	0.31	0.32	0.45	0.32
EF(Pb)	231 ± 63	2900 ± 1300	99 ± 27	1483 ± 633
EF(Br)	352 ± 132	4500 ± 2100	194 ± 6	2300 ± 560

Table 3
Mean atmospheric concentrations and standard deviations of Br, Pb, and BC in ng/m^3 STP, mean Br/Pb concentration ratios, and mean enrichment factors (EF) calculated relative to average crustal rock composition with Al as reference element in the coarse and fine aerosol size fractions collected within the Castle District Tunnel in 1998 and 1999

Aerosol variable	1998		1999	
	Coarse size fraction	Fine size fraction	Coarse size fraction	Fine size fraction
Pb	1065 ± 43	298 ± 12	359 ± 47	34 ± 7
Br	510 ± 130	141 ± 30	30 ± 2	< 5
BC	21000 ± 1000	42000 ± 1000	32000 ± 4000	47000 ± 4000
Br/Pb	0.39	0.54	0.08	–
EF(Pb)	2012 ± 400	14272 ± 2800	150 ± 30	524 ± 100
EF(Br)	3590 ± 700	36452 ± 5400	64 ± 13	> 418

mon source that is automotive emission. However, the regression lines for Pb and Br for the Széna Square do not have zero intercept, which may imply that at least one of the elements has additional significant emission sources. The correlation is further reinforced by high correlations between Pb and BC, and Pb and CO. (BC and CO are being emitted largely but not exclusively by automobiles.) The Br/Pb ratio for the samples from Széna Square in 1996 was somewhat smaller than the ethyl ratio, but of the same order as the Br/Pb ratios typically observed in urban areas [3].

Lead and Br are highly enriched in both size fractions and at all sampling sites. Interestingly, EFs for the KFKI campus (in particular for the fine size fraction) were not really changed by the phase out suggesting again that there is another principal source for atmospheric Pb in the urban background. The EFs decreased by a factor of approximately 2 for Széna Square, and they were changed by 1–2 orders for the samples collected within the tunnel in 1998 and 1999 as a consequence of the phase out of leaded gasoline.

Figs. 1 and 2 show average elemental mass size distributions for Pb and Br, respectively, for samples collected at the KFKI campus, Széna Square, and within the tunnel in 1999 after phasing out leaded gasoline. For the filter stage, the cut-off diameter (more precisely the d_{50} value) was set at 0.125 μm EAD. At the background site, the elements have practically unimodal size distribution with a pronounced fine mode. The mass median aerodynamic diameters (MMADs) of Pb and Br

are at approximately 0.6 μm EAD. In the downtown, the elements have essentially bimodal size distributions but their mass is mainly in the fine size fraction. Their MMAD is, therefore, below 1 μm as well. The fine mode points to the importance of high-temperature emission sources. The size distributions for the tunnel are completely different from the ones at the two other sites. The elements have unimodal size distribution here, but most of their mass is present in supermicrometer particles. The MMAD for Pb and Br are 5.2 and 6.0 μm EAD, respectively. Most likely, they have to be attributed to road dust resuspension and dispersion processes, and the contribution of automotive emission can already be considered to be not significant.
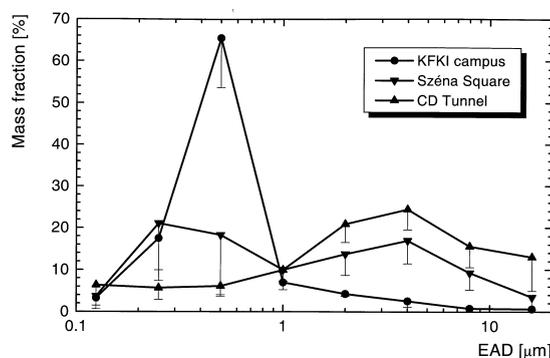

Fig. 1. Average elemental mass size distributions of Pb for the KFKI campus, Széna Square, and Castle District Tunnel in Budapest in 1999 after phasing out leaded gasoline. The data are plotted vs. the cut-off points of the impaction stages.
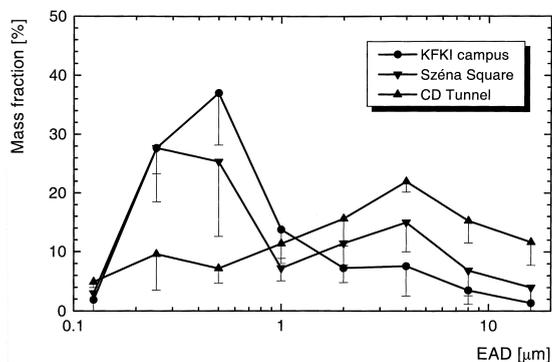
Fig. 2. Average elemental mass size distributions of Br for the KFKI campus, Széna Square, and Castle District Tunnel in Budapest in 1999 after phasing out leaded gasoline. The data are plotted vs. the cut-off points of the impaction stages.

Acknowledgements

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