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GENERATED IN THE BOSTON SUMNER TUNNEL
AND ENVIRONS

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INTRODUCTION

This study of air particulates in the Sumner Tunnel was designed to better define the chemical composition of inorganic constituents generated by automotive activity. The tunnel was chosen for study because of anticipated higher than normal concentrations of automobile products inside relative to those outside.

The long term objective is to develop a procedure for resolving a mixture of air particulates into its individual source components in a realistic way. To do this adequately requires detailed information on individual sources among the more important of which are gasoline combustion products and other substances generated by automotive activity.

EXPERIMENTAL

The Sumner Tunnel runs approximately WNW from its entrance portal in East Boston to its exit portal in downtown Boston. Portal-to-portal distance is 2061 meters or 1.07 miles. Two Staplex model TFLA and one Bendix model 550 high-volume air samplers stationed on the walkway inside the tunnel at approximately 330 meters, 450 meters, and 575 meters respectively from the exit portal.

A second Bendix instrument was positioned 40 meters from the exit portal at sidewalk level next to the guard station on the plaza into which tunnel traffic empties.

Four sets of particulate samples were collected on 10 cm diam Whatman #41 filters for approximately 4 hour periods on 30 and 31 August 1973. Air volume passed per sample averaged 115 cubic meters. Data on the number of vehicles which passed through the tunnel during the sampling periods was provided by tunnel authorities and averaged 2144 vehicles per hour. (Table 1).

Whatman #41 was chosen for use as a collection matrix due to its relatively low blank values for most elements (Dams, et. al., 1972). Filters were dried, desiccated and weighed before and after

exposure and total particulate weights were determined. One half of each filter was ashed at 450°C in a muffle furnace; the ash was weighed to the nearest microgram on a Cahn Electrobalance and sealed in 1 cm outside diameter polyethylene capsules. The capsules were packed into a "rabbit" and irradiated at the MIT Reactor for 8 hours in a flux of 2×10^{13} neutrons per square centimeter per second.

Individual elements were assayed by High-resolution gamma-ray spectroscopy using a 30 cc Ge(Li) detector. Spectra were stored on magnetic tape and reduced by computer. Data were obtained for 18 elements.

Two-thirds of each remaining filter was ashed at room temperature using RF generated atomic oxygen in a Tracerlab model LTA600 low temperature asher. The ash was weighed and decomposed in hot concentrated HCl and HNO₃, then made up to 10 ml volume with distilled H₂O. The resulting solution was approximately 1 N in HNO₃. Eight elements were assayed by Atomic Absorption Spectroscopy including six in common with the neutron activation analysis, for comparison purposes.

One-sixth of each sample remains unprocessed to date and will be used to check on some inconsistent results, as discussed later.

RESULTS

Results of these analyses are summarized in Tables 2 and 3.

The composition of the samples taken within the tunnel differs in major respects from that outside only in the concentrations of Pb and Br, both of which are contributed directly by automotive exhausts (Middleton, 1971).

However, lead and bromine concentrations in the outside air were also substantial and indicate that air within the tunnel is being efficiently exchanged. In Table 2 is given the composition of the tunnel samples and of the outside air, expressed as parts per million in mineral ash, averaged for three sets of samples. Table 3 contains the averaged concentrations of elements in air in units

of nanograms per cubic meter. The Pb data were obtained by Atomic Absorption Spectroscopy, all other elements were obtained by Neutron Activation Analysis using the U.S. Geological Rock Standard W-1 as reference. Standard deviations are presented to indicate the variations among samples. Also included in each table is a t-test of the means "plaza" vs "tunnel", at the 95% confidence level for each element. A "YES" signifies that the means are statistically different at this confidence level; a "NO" signifies that they are not.

DISCUSSION

Pb and Br

The low concentrations of Br in both the tunnel and plaza samples is clearly anomalous. The Pb/Br ratio is about 40:1, whereas one expects about 25:1 based on the composition of "PbBrCl". As noted elsewhere, this ratio is rarely found (Robbins and Snitz 1972), since Br is known to be lost by photolytic decomposition (Pierrard, 1969), diffusion processes, or both. We conclude that in our method of sample preparation by muffle furnace ashing at 450°C the majority of the Br was lost by diffusion and vaporization. However, we note that the ratio of Na to Br is about 14, which suggests that the Br is from sources in addition to sea water, for which the value is about 165.

The concentration and gaseous fraction of bromine in Cambridge air was examined (Moyers, et.al., 1972). They found .12-.45 $\mu\text{g}/\text{M}^3$ compared to .12-.94 $\mu\text{g}/\text{m}^3$ in the particulate form. Particulate V was .08-1.32 $\mu\text{g}/\text{m}^3$ and Pb varied from .4-3.7 $\mu\text{g}/\text{m}^3$. The ratio of total Br to Pb varied with wind direction being typically .32 with the wind from a Westerly direction, and as high as .62 with the wind from an Easterly direction. The authors attribute this to free Bromine from a maritime source.

This accords with the results of the University of Maryland Group who observed that Br and Cl distributions with particle size.

in the Baltimore Harbor Tunnel are bi-modal with a small-particle component resulting from combustion of leaded gasoline and a large-particle component consisting of particles present in intake air, possibly enriched in Br and Cl by gas-phase surface attachment (Gordon, et. al., 1973). We intend to check our results by running a second neutron activation analysis on the remaining sample sections prepared by low-temperature ashing methods.

Zn

The Pb/Zn ratio is of some interest. In this study it is quite variable (6.8 in the plaza and 25 in the tunnel). In a series of particulate samples taken on the roof of the chemistry building at Boston College, (February-March 1970), the ratio averaged 4.9. The Pb and Zn were almost perfectly correlated for this 40-day period suggesting an automotive related source.

It is possible that many of the variations noted in elemental ratios in polluted air are due to particle size effects. The B.C. rooftop samples, with an enrichment of Zn with respect to Pb may indicate that a greater fraction of the Zn is more easily suspended than Pb.

The Possible Significance of Resuspension

The high concentrations of particulates found outside the tunnel during this particular sampling episode were undoubtedly related in part to the stable atmospheric conditions which prevailed. It is probable that much of the particulate found near ground level is material resuspended by moving vehicles. We note that the composition of the material both outside and inside the tunnel has the chemical composition of a polluted soil, i.e., the typical concentrations of substances found in the soil augmented by Sb, Zn, Pb and Br. Of these, only Pb makes any significant contribution to the total weight of the sample.

In the B.C. study we noted an inverse correlation between the concentrations of the "soil" elements typified by Fe, Sc and Ce and the automotive exhaust elements typified by Br, on a day to day basis. On days characterized by brisk winds, generally from the west, the concentrations of Zn, Pb, Sb and Br were usually somewhat decreased relative to those of the Fe, Ce, Sc group; the reverse situation obtained when the winds were light and from a northerly or easterly direction. Since the sampling station was elevated (4th floor level) apparently the earth crustal elements were found in high concentrations only when the wind could loft larger resuspended particles to greater altitudes. The increased atmospheric turbulence associated with stronger winds also effected a dilution of the automotive products.

If this view is correct, the automotive pollution term should include these "indirect" contributions to the particulate burden as well as direct ones.

It is of interest to compare our results with those of an earlier, more detailed study of air quality in the Sumner Tunnel in July and September 1961 (Larsen and Konopinski, 1962). We report eight elements in common: Sb, Cr, Co, Cu, Fe, Pb, Mn, Zn. The authors of the earlier study present their results for individual elements as indices defined as concentration ratios:

$$\frac{[\text{outlet}]}{[\text{inlet}]} - 1.$$
 Selected data are given in Table 4.

Table 4 indicates that the concentrations of the elements found in common are always somewhat higher in the outlet air of the earlier study (a factor of 2.5 to 4 for most elements). We further note that the concentrations of the inlet air in the 1961 study for Pb is significantly lower than that in the 1974 study. This combination of circumstances certainly renders the earlier study more appropriate for discerning the contributions due to automotive activity.

The average concentration of Pb in the tunnel is $11 \mu\text{g}/\text{m}^3$ compared to $4 \mu\text{g}/\text{m}^3$ of air in the plaza. Thus, the net Pb expelled from the tunnel each minute is $(11-4) Q$ where Q is the intake and outlet rate in cubic meters per minute. A traffic count during our study gave an average of 2144 vehicles per hour or 35.7 vehicles per minute. The Boston half of the tunnel is 0.55 mile long, therefore the number of vehicle miles accumulated per minute is 19.6. Using an estimate of $35,000 \mu\text{g}^{\text{Pb}}/\text{vehicle-mile}$ derived in the earlier study (Larsen and Konopinski, 1962) leads to $3500 \times 19.6 = 6.86 \times 10^5 \mu\text{g}^{\text{Pb}}/\text{min}$ introduced into the tunnel. Since we are dealing with a closed system (if any piston effect is ignored) and a steady-state situation in which the amount of Pb generated by automotive activity is being removed at the same rate it is introduced, $(11-4) Q = 6.86 \times 10^5$ and $Q = 9.8 \times 10^4 \text{ m}^3/\text{min}$. The total volume of the Boston half of the tunnel is $4.93 \times 10^4 \text{ m}^3$. Therefore Q/V is of the order of 2 min^{-1} which is about 4 times higher than the 1962 value of 0.5.

We are informed by tunnel authorities that the maximum flow rate is presently $2.79 \times 10^4 \text{ m}^3/\text{min}$. (see Table 5) compared to $1.73 \times 10^4 \text{ m}^3/\text{min}$. in 1962. This factor of 1.6 along with other differences between Larsen and Konopinski's study and ours (such as different traffic flow, sampler locations, and atmospheric conditions) can in part account for the factor of 4 difference Q/V values obtained. However the unaccounted for factor of 2.5 difference is troublesome.

SUMMARY

A series of air particulate samples was collected in the 1.1 mile long Boston Sumner Tunnel on 31 August 1973. Analysis of the samples by neutron activation and atomic absorption yielded data for 18 elements.

Those found to be definitely correlated with automotive activity are Pb and Br. Cu, Co and Mn show a negative correlation.

Data from an earlier study in our laboratory showed Zn and Sb correlated well with Br suggesting an automotive source for these elements. No confirmation of this was obtained in this study. Resuspension is postulated as an important consequence. The concentrations of earth crustal elements were in general slightly less in tunnel air. A possible reason for this is that the higher concentration of Pb necessarily causes concentrations of other constituents to decrease (even at the atom-for-atom level) to maintain a mass balance.

A comparison of our Pb data with that of Larsen and Konopinski, 1962 led to a supposition that ventilation capacity had been somewhat increased since 1962. This was confirmed by tunnel authorities.

We quote from Ter Haar (1972) with respect to the overall problem of automotive pollution: "A review of the available published information on particulate emission gives some idea of automotive contribution to total man-made atmospheric particulate. The contribution of the automobile varies with particulate load from values as low as 3% in a "heavy particulate" city (St. Louis) to 37% in a basically clean area (Los Angeles) with the average for the United States being about 1.8%. NASN data for the lead content of total suspended atmospheric particulate shows, for 27 cities where data are available that only 0.51% of the particulate is lead. Thus, it seems we are being asked to control, at a large cost, a very small portion of the total atmospheric particulates." (underlined added).

This statement, by a representative of the Ethyl Corporation, ignores several important factors. His choice of Los Angeles as a "basically clean area" is somewhat ironic considering the bad name Los Angeles has given the automobile. As the Sumner Tunnel study by Larsen and Konopinski shows, the contribution of carcinogenic constituents of the particulate product (benzopyrene) is not insignificant. Thus Ter Haar chooses to ignore the quality factor. As to lead, only epidemiological studies in the future will reveal the true impact of this substance, present in concentrations of 1-5 $\mu\text{g}/\text{m}^3$ in our city air. But more importantly,

in the context of particulate loading, in city streets. it is probable that the automobile is responsible indirectly because of its dynamic resuspension action for a much higher percentage of the total particulate burden than noted by Ter Haar on the basis of direct automotive emissions.

We wish to express sincere appreciation to Mr. Theodore H. Rider of Weston Observatory and the New England Consortium on Environmental Protection for his support of this study and to the officials of the Massachusetts Turnpike Authority, especially Mr. William P. Driscoll, Superintendent of Tunnels, Mr. John J. Downing and Mr. William Olzewski, staff engineers, for their courtesy and invaluable assistance during the sampling phase. This work was supported in part by the U.S. Atomic Energy Commission under contract number AT(11-1) 3015

TABLE 1
SAMPLING PERIOD
SUMNER TUNNEL TRAFFIC FLOW
31 AUGUST 1973

<u>HOUR (EASTERN DAYLIGHT TIME)</u>	<u>NUMBER OF VEHICLES PASSED</u>
0600 to 0700	1980
0700 to 0800	2760
0800 to 0900	2568
0900 to 1000	1936
1000 to 1100	2168
1100 to 1200	1894
1200 to 1300	1934
1300 to 1400	2290
1400 to 1500	2104
1500 to 1600	2301
1600 to 1700	2013
1700 to 1800	1699
1800 to 1900	2156

TABLE 2
PARTS PER MILLION IN MINERAL ASH

ELEMENTS	PLAZA		TUNNEL		t-TEST OF MEANS	EARTH CRUSTAL	SEAWATER
	MEAN PPM	S	MEAN PPM	S			
Au	0.031	0.019	0.026	0.019	NO	0.005	TRACE
Br*	2400	1300	5800	3100	NO	1.6	65
Ce	29	6.1	26	13	NO	46	0.0004
Co	48	8.7	21	2.7	YES	23	0.0001
Cr	240	21	250	65	NO	200	TRACE
Cu	52000	51000	4600	2700	YES	70	0.05
Eu	1.5	0.25	1.2	0.11	NO	1.1	0
Fe	49000	3500	52000	7100	NO	50000	0.01
Hf	0.45	0.046	0.31	0.060	YES	4.5	0
La	14	1.8	13	6.1	NO	18	0.0003
Mn*	7600	7300	1900	510	YES	1000	0.005
Na	35000	18000	26000	3000	YES	28300	10,561
Nd	103	61	189	81	NO	24	0
Pb*	67000	27000	130000	47000	YES	16	0.0045
Sb*	88	12	94	24	NO	12	TRACE
Sc	7.7	1.7	6.9	0.92	NO	5	TRACE
Th	9.4	0.56	7.8	1.4	NO	12	< 0.0005
W	341	241	294	192	NO	69	TRACE
Zn*	14000	9600	9300	2400	NO	132	0.01

*Suspected to be indices of automotive activity

TABLE 3
ng/m³

ELEMENT	PLAZA		TUNNEL		t-TEST
	MEAN ng/m ³	σ	MEAN ng/m ³	σ	
Au	0.0017	0.00092	0.0019	0.0010	NO
Br	130	65	440	220	NO
Ce	1.6	0.29	2.1	2.7	NO
Co	0.27	0.053	0.68	0.95	NO
Cr	14.	36	19.	6.5	NO
Cu	2800	2500	360	110	YES
Eu	0.082	0.0059	0.088	0.026	NO
Fe	2800	460	3900	1200	NO
Hf	0.022	0.0022	0.025	0.0074	NO
La	0.79	0.21	1.0	0.62	NO
Mn	400	350	160	50	YES
Na	1900	750	1800	370	NO
Nd	5.6	2.6	14.	11.	NO
Pb	4000	2400	11000	1700	YES
Sb	5.0	1.2	6.9	1.8	NO
Sc	0.43	0.017	0.51	0.15	NO
Th	0.53	0.071	0.60	0.22	NO
W	19.	11.	25.	14.	NO
Zn	870.	700.	670.	230.	NO

TABLE 4
COMPARISON OF SUMNER TUNNEL AIR QUALITY
1962 vs 1973

ELEMENT	INDEX 1962 Larsen & Konopinski	ng/m ³ (outlet)	INDEX 1973 This Study	ng/m ³ Tunnel
Co	0.10	22	1.5	0.68
Cr	0.47	128	0.36	19.
Cu	3.15	278	-0.87	360
Fe	9.33	23400	0.39	3900
Mn	1.66	133	-0.60	160
Pb	39.5	44500	1.8	11000
Sb	0.11	170	0.38	6.9
Zn	0.48	2248	-0.23	670

TABLE 5
SUMNER TUNNEL VENTILATION SYSTEM
FLOW RATES, 31 AUGUST 1973

	BOSTON	E. BOSTON
6-7 A.M.	71,250 cfm EXHAUST 70,000 cfm INTAKE	45,750 cfm EXHAUST 44,750 cfm INTAKE
7-10 A.M.	855,000 cfm EXHAUST 840,000 cfm INTAKE	457,500 cfm EXHAUST 447,500 cfm INTAKE
10-11 A.M.	285,000 cfm EXHAUST 280,000 cfm INTAKE	183,000 cfm EXHAUST 179,000 cfm INTAKE
11 A.M.-6 P.M.	855,000 cfm EXHAUST 840,000 cfm INTAKE	549,000 cfm EXHAUST 537,000 cfm INTAKE
6-7 P.M.	427,500 cfm EXHAUST 420,000 cfm INTAKE	274,500 cfm EXHAUST 268,500 cfm INTAKE

BOSTON	E. BOSTON
EACH EXHAUST FAN:	
LOW-71,250 cfm	LOW-45,750 cfm
HIGH-142,500 cfm	HIGH-91,500 cfm
EACH INTAKE BLOWER:	
LOW-70,000	LOW-44,750
HIGH-140,000	HIGH-89,500

PRIOR TO 1963, THE BOSTON VENTILATION CAPACITY EQUALED THE
EAST BOSTON CAPACITY.

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