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To: D. R. Diggs
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From: E. S. Jacobs

AIR QUALITY CRITERIA REPORT ON LEAD

Attached are my comments on the November, 1976 EPA draft of the "Air Quality Criteria for Atmospheric Lead" document. While I have reviewed the entire document, I have concentrated my efforts on those sections dealing with the analytical methods and environmental chemistry.

In summary I find the section on analytical methods is very inadequate. It lacks discrimination of good and bad air lead methods, does not discuss air sample siting, and does not provide a suitable evaluation of existing air lead data. It does not comment on the suitability of methods used to measure blood lead levels. The sections on environmental chemistry of lead, such as emissions, source, particle size, and composition are satisfactory, except for a few isolated items which I have noted in my attached comments.

ESJ/eaa
Attach.

TEH 0470222

COMMENTS ON EPA
"AIR QUALITY CRITERIA FOR ATMOSPHERIC LEAD"

ABSTRACT

page xix, line 10 - The significance of coarse and fine particle size is needed.

page xix, line 13 - This statement on vapor phase lead is too strong for an abstract based on the minimum amount of data available on this subject.

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

page 1-2, line 5 - These statements on organic lead emitted to the atmosphere can be confusing. "Organic lead -- emissions from storage and transfer is small. Inorganic lead emissions -- account for over 90 per cent of total lead emitted." This could be interpreted as 10 per cent of lead emissions are due to organic lead emissions. This is incorrect, since the best data suggest a maximum of about 1 per cent may be organic lead even near service stations (page 5-56 to 5-59).

page 1-3, line 7 - This may be correct for some fine particles, but the average residence time for atmospheric lead is of the order of 7 to 30 days and is highly dependent on the weather conditions.

page 1-4, line 21 - Only two reported laboratory studies have shown chemical transformation of lead halide to lead oxides and carbonates. Only one is referenced on pages 3-3 to 3-5. Both suggest the chemical transformation is not significant in terms of lead effects.

page 1-5, line 1 - What does "--- short-lived peaks have been found." mean?

page 1-5, line 3 - No data are referenced in the report to support this statement. However, there are several recent studies published in the literature which report laboratory bioconversion of the alkyl lead salts to tetraalkyl compounds. Other prominent workers in this field have been unsuccessful in alkylation of lead in biological systems. These data are all based on lab studies and this statement is much too positive for general state of this work. (See page 5-90.)

page 1-5, line 10 - The capability to obtain accurate and precise lead measurement exists today, but the data, both air lead and blood lead data, reported in the literature are of poor quality. This needs to be emphasized. Examples of this problem related to air lead data collected by NASN are mentioned on page 4-8, but the data from an inaccurate procedure and the corrected procedure are used together without regard for analytical differences. More significant problems are related to the data reported for blood lead. In most of the data prior to 1970, the results were obtained with the dithizone method which was primarily designed to determine if a blood lead level was above or below 40-60 μg Pb/100 ml of blood. The precision of the dithizone method is at best ± 10 per cent for blood lead levels of 40 μg/100 ml. While the precision and accuracy generally improve for higher levels, at lower levels the deviation becomes much worse and replicate analysis for blood containing 20 μg Pb/100 ml show a standard deviation of 50 per cent. (USPHS method for Determining Lead in Air and Biologic Materials).

page 1-6, line 12 - This is the only underlined sentence in the Summary. The significance is not discussed in the report. What is important is the particle size and air lead concentration at breathing level.

page 1-8, line 4 - This is a speculative statement not supported by data.

page 1-8, line 5 - This statement discusses some of the importance of the underlined statement on page 1-6, line 12.

page 1-11, line 9 - What is the origin and rationale for this suggested screening level of 30 μg/100 ml? We should object to use of this, since it can easily be transposed in the future to a maximum level.

page 1-10 to page 1-12 - This section is weak and needs to be beefed-up and made stronger to support the air lead standard of 5 $\mu g/M^3$.

page 1-16, Conclusion 2 - Data to support this are not given in the report. This is a speculative argument.

page 1-17, Conclusion 5 - Again support for this is weak.

page 1-20, Recommendation 5 - Support for this standard is weak. Suggest other recommendations should be included:

7. Analytical methods for air lead and biological lead should be standardized and extensive precision and accuracy data obtained to indicate limit of data use.

8. Trends in airborne and biologic lead should be documented. (EPA has done very little work in this area and this was Recommendation No. 1 in the 1971 NAS report on Lead.)

SECTION 3, CHEMICAL AND PHYSICAL PROPERTIES

page 3-5, line 1 - J. M. Pierrard data on transformation of air lead and exhaust lead not included. This was cited in NAS report on Lead. Should we send this in for inclusion in our response to this report? (Copy of information attached.)

page 3-5, line 19 - Table 3-1 does not show data on lead in soil. Table apparently left out.

SECTION 4, SAMPLING, PREPARATION AND ANALYSIS

In general this section is weak and too superficial in coverage of analytical procedures. Specific references describing recommended methods and precision and accuracy of methods not given. Emphasis should be placed on discussing the air lead and blood lead methods since these are the most pertinent to setting an air quality standard.

page 4-1, Section 4.1.1.1, Sampling Methods - The EPA has recommended the Hi-Vol. particulate sample for collecting ambient air particulate for air lead measurement. This is not discussed or referenced. Instead, a short paragraph of the discussion is on sampling particulate lead, using the NASN sample, while two pages are devoted to new dichotomous sample, and an almost untested impactor-electrostatic precipitator.

Items not discussed which should be included are proper siting of the sample, frequency of sampling, and data on efficiency of Hi-Vol. filter samples.

page 4-8, Section 4.1.1.2, Sample Preparation - This very important section includes only a brief two-sentence statement of the recommended procedure with no reference. It does acknowledge that the NASN data prior to 1968 are in error (low) by 50 per cent due to improper sample treatment. This is a very important point and it should be further discussed in view of the many different procedures currently being used.

page 4-9, last paragraph - The discussion of the limitation of the dithizone procedure for measuring lead in ambient air particulate should include information on the precision and accuracy data developed by ASTM in an eight-lab, three-city round-robin test. These data, developed under Project Threshold by ASTM in evaluation of ASTM Method D 3112, showed the recovery (accuracy) of added lead yielded results statistically different from the predicted value. The precision, as estimated by coefficient of variation for lead levels of 0.5 to 1.5 $\mu g/M^3$, varied from 16 to 21 per cent.

These results illustrate the best data and are indicative of the larger errors which probably exist in most data reported in the literature. It should be noted that the ASTM data were results from analysis of total filters, and not a wedge section of a large filter as proposed by EPA and used in almost all air lead data reported to date.

page 4-10, line 1 - The source of this data on organic lead is not given, although I suspect it comes from a paper published in Anal. Chem. by Purdue and Thompson of EPA. If so, the data should be viewed with considerable doubt, since their method had a detection limit of 0.2 μg Pb/M^3 and a deviation at the 2 μg level of ~ 0.5 μg. This should include reference to 1974 EPA symposium which provides more accurate data on this subject.

page 4-11, line 1 - The EPA reference method for air lead has many deficiencies. I have prepared a critique outlining these. It is very strange that EPA proposed a method almost totally different from any described in their recent publications. They did not include precision and accuracy data.

page 4-11, line 21 - This dismisses the methods for lead in biological materials by saying they are reviewed in the NAS report on Lead, now over five years old. As noted above, the dithizone method is good as a screening method for high blood lead levels but is not really adequate for measuring levels of lead in blood in the general population.

page 4-15, line 13 - An error. Should read $PbCl_2$.

page 4-19, last paragraph - This is a hodgepodge of information of a very detailed nature on x-ray analysis. Unfortunately, x-ray diffraction and fluorescence are mixed up and it doesn't have much meaning or use.

SECTION 5, ENVIRONMENTAL APPRISAL

page 5-14, line 2 - Out of date.

page 5-14, Section 5.2.1.2, Ambient Lead Monitoring - It is unfortunate that the NASN air lead data prior to 1968 are not corrected or omitted in view of the known error in these data.

page 5-21, line 8 - NASN data show a 24 per cent decrease in urban air lead levels for the 50th percentile from 1971 to 1974. There is a general decrease beginning in 1970-71 but it is highly variable, possibly due to sampling and analysis errors.

This corresponds closely to our findings. We should send in our report on air lead trends. This would help counteract work of Chow (page 5-36, line 2).

page 5-51, line 13 - The reference for LA catalyst study is not given.

Shouldn't the California ARB air lead data be given? These data also show a downtrend and seasonal variation.

page 5-77, line 15 - This reference should include comment that the sampling procedure missed large particles, thus results are biased to small side.

page 5-79, line 15 - The discussion includes only work by Laveskog. No mention is made of Du Pont and Ethyl data presented at EPA symposium in 1974.

page 5-87, line 21 - J. M. Pierrard work on photolysis of lead halides mentioned. We should cite more recent data showing mechanism in hydrolytic, thus H_X is potential by-product and not free halogen as inferred by photolytic mechanism.

page 5-90, line 13 - Three-city data on alkyl lead is cited. These data are no good.

page 5-90, line 17 - Only data from 1971 NAS report is cited. More definitive data are now known and should be included.

SECTION 6, ENVIRONMENTAL EXPOSURE

page 6-3, line 12 - Can this be supported? If so, an annual average standard should be used.

page 6-4, line 3 - Is this true? This accepts air lead/blood lead relation for general population, but discards for extreme exposure cases, yet only in extreme case can the relationship of air lead/blood lead be supported.

page 6-7, line 12 - This is not clear. It does not show data as stated to support contention of high blood lead association with high lead in soil and dust. Even so, this is only association and does not prove source of high blood levels.

SECTION 8, METABOLISM OF LEAD IN ANIMALS AND PLANTS

page 8-4, line 25 - Text is incomplete.

page 8-9, line 2 - This point seems lost in all other data. I agree with Bill Sprout, this should receive more emphasis.

page 8-34, lines 19 and 24 - This reasoning is probably "ok" on a relative basis, but even in the case of the Du Pont work, I think the analytical method is not capable of showing a trend at these levels.

page 8-36 - Seems like this is the best spot to build a case for air quality standard.

page 8-46 - As noted by both Bill Sprout and Al Pahnke, the SWRI data are suspect and more emphasis on its citing poor data should be noted.

page 9-36, Section 9.7.2 Climatic Implications - The ice nuclei story should include data from Colorado State University which shows combustion particles from unleaded fuel were as effective as leaded fuel exhaust in producing ice nuclei.

ESJacobs/eaa
1/19/77
Attach.

ATMOSPHERIC CHEMISTRY OF AUTOMOTIVE LEAD PARTICLES

J. M. Pierrard

Introduction

There is little published information on the atmospheric chemistry of particulate lead compounds emitted by automobiles. Analyses of halide and lead ions in solutions made from aerosol particles collected at several locations (1, 2, 3) showed that the bromine to lead ratio is less (and sometimes much less) than unity. The unit mole ratio of bromine to lead is expected on the basis of the work of Hirschler, et al (4) who reported that the chief constituents of the inorganic lead compounds leaving the exhaust system are PbBrCl, two forms of $NH_4Cl \cdot 2PbBrCl$ and $2NH_4Cl \cdot PbBrCl$. This bromine deficiency has been explained on the basis of preferential oxidation of bromide, but not the more stable chloride, followed by volatilization of bromine (1, 2, 3). It has also been explained on the basis that PbBrCl is photolyzed by radiation at wavelengths below approximately 380 nm (5, 6), to yield molecular halogens.

It had been presumed that the chief chemical species of automotive emitted lead particulate matter was PbBrCl. Recently however, it was reported (7) that composition of emitted particles varies with particle size. Whereas PbBrCl is the major lead salt in particles of equivalent diameter between 2 and 10 μm, the submicron lead salts are primarily $2PbBrCl \cdot NH_4Cl$. In the same study it was noted that little $2PbBrCl \cdot NH_4Cl$ was found in samples collected at the tail pipe from the hot exhaust gas. It was, however, found after cooling and mixing of the exhaust with the ambient air. While we have no experimental data on the thermal or photo reactions of $2PbBrCl \cdot NH_4Cl$, its layer structure and the presence of the ionic NH_4Cl suggest that it should be less easily photolyzed than PbBrCl.

New Data*

Atmospheric measurements of gaseous halogen components (6, 8, 9, 10) have not discriminated between the hydrogen halides and the molecular halogens. This distinction is an important one however because the molecular halogens, particularly bromine, are more reactive than their corresponding halogen acids.

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* Unpublished personal communication, C. L. Moret and J. M. Pierrard, E. I. Du Pont De Nemours & Company, Inc.

To obtain data on the partitioning of the gaseous atmospheric halogen component among these possible species, weekly samples were taken during most of the period from December, 1969 to July, 1970 at the Du Pont Experimental Station at Wilmington, Delaware. The collection system used a glass fiber filter mat impregnated with a measured amount of disodium fluorescein, and preceded by a similar, but untreated, filter through which outside air was pumped at 40 cfm between 0700 and 1900 local time for seven days per sample. At the conclusion of a one-week sampling period, the reagent was recovered by extraction with ethanol, concentrated, and the concentrated solution analyzed by thin layer chromatography on silica gel G plates with 65:35 (v/v) toluene-glacial acetic acid to separate products. Tests established that halogenation and hydrohalogenation products formed on the filter would resist oxidative degradation during the sampling period. Some of the filters were spiked, over part of their area, with micromole quantities of molecular bromine to ensure that atmospheric halogen, if present, would reach the reagent filter and to provide internal standards. The system sensitivity was approximately 10^{-12} mole l^{-1} for Br_2 and Cl_2 and 10^{-11} mole l^{-1} for HBr and HCl.

HBr and HCl were found in about half the samples. Bromine was found only in the first sample, and is believed to have been an artifact from laboratory contamination.

The water solubility of the lead in collections of atmospheric particulate matter was determined for samples taken at the Experimental Station and immediately adjacent to the toll booths on the heavily-travelled Delaware Memorial Bridge. Results were as shown in Table I. Because of the low water solubility of atmospheric lead particles which has been noted by others (11), samples were washed with organic solvents, as indicated in the table, to remove any oily coating which would inhibit solution. This treatment did not increase water solubility, nor was there any significant difference between the solubility of the "fresh" lead salts collected at the toll gate side and the "aged" lead salts collected at the Experimental Station.

A striking difference is evident, however, in the Br/Pb ratios of the residues after equilibration of the sample for solubility determination. The Br/Pb ratio for the fresh sample is reduced by about one order of magnitude while that of the aged sample is changed only slightly. The suggested explanation for this behavior is that soluble carbonates occurring along with the lead salts in the fresh sample cause precipitation of lead while allowing halogen to go into solution. In order for the same effect not to occur with the aged sample from the Experimental Station, the lead particle surfaces must already have been converted to a relatively insoluble form, such as an oxide, carbonate, or basic halide, Pb(OH)Cl. Conversion of lead halide or the ammonium-lead halide complex to basic lead halides by reaction with atmospheric water vapor would also be consistent with the presence of hydrogen halides and absence of molecular halogens in the air.

Summary

The observation that submicron automotive lead particles are primarily $2PbBrCl \cdot NH_4Cl$, rather than PbBrCl as was formerly believed, modifies our assessment of the importance of photolytic decomposition in atmospheric reactions. The apparently different surface compositions of fresh and aged lead aerosol particles are consistent with a hydrolytic conversion mechanism which would be expected to release hydrogen halide rather than halogen from the particles.

Table I

Water Solubility of Lead in Atmospheric Particulate Matter

Sample Source	Solubility μg Pb/1000 ml H_2O	Br/Pb in Solids	
		Before H_2O	After H_2O
Delaware Memorial Bridge	4800	0.81	0.07
Delaware Memorial Bridge*	5200	0.72	0.06
Experimental Station	4500	0.89	0.74

* Washed with Freon®, then benzene-methanol

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11. Robinson, E. and Ludwig, F., "Size Distributions of Atmospheric Lead Aerosols," Final Report, SRI Project No. PA-4788, 1964.