UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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MEMORANDUM

SUBJECT: Glover Lead SIP - Review of Chemical Mass Balance Source Apportionment of Ambient Lead in Glover, Missouri: Volume I, and Associated Correspondence

FROM: Tom Coulter, Environmental Scientist
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TO: Lisa Haugen, Project Officer
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On your behalf, I have reviewed ASARCO's Chemical Mass Balance Source Apportionment of Ambient Lead in Glover, Missouri: Volume I ("CMB Study"), your November 24, 1993 letter to Mr. Gene Cassin of Missouri's Air Pollution Control Program, and Mr. Gregory Knapp's "clarification" letter back to Mr. Cassin. In your letter, I am most interested in ASARCO's resolution of points #1, 4 & 5 regarding the CMB study as that is my area of expertise. I am also interested in points #5 & 6 regarding ASARCO's Development of ISCST2 Model Inputs for the Prediction of Ambient TSP Lead Concentrations in the Glover, Missouri Area but have not seen the latter document.

In looking back at the second paragraph of Section 4.3 of the Dispersion Modeling Protocol ("Glover Protocol" - September 1992; prepared by TRC and Keystone/NEA) for the Glover Plant, as well as its "Ambient Filter Processing and Analysis Flow Diagram" (Figure 4.1), I find a fundamental point of confusion that transfers to the CMB Study and the subsequent correspondence between ASARCO and regulatory agencies. I regret not having noticed this confusion when I reviewed the Glover Protocol in October 1992.

As a small excursion, it is worth noting that ASARCO's previous CMB studies in support of lead SIP revisions (one in Region VIII and one in your region) have shown similar lack of clarity and inconsistency in terms of reporting. In Section 2.2 of ASARCO's East Helena CMB Source Apportionment Study: Final Report (April 1991; prepared by NEA) is the statement that half of the TSP sample was analyzed at ASARCO for lead while the other half was retained at NEA for speciation. Yet in Figure 2.1.1 (High Volume TSP Quartz Fiber Filter Analysis Flow Diagram) of the same report is the indication that lead (Compliance Analysis) was done at Air Quality Bureau (State of Montana) while other analytes were determined at NEA. Then, in Section 4.2 (Developing the

Source Profile Library), it is stated that lead was "determined by inductively coupled plasma (ICP) spectrometry." This seems at odds with ASARCO's emphasis on flame absorption spectrometry (AA) for lead determination (p.1 of its 12/15/93 letter). In any case, while not explicitly stated, it should be assumed (and hoped) that the ambient samples were also assayed with the same analytical methods.[1]

In Section 5.1.2.3 (Sample Analysis) of ASARCO's Emission Inventory Test Protocol for Omaha (June 1991; prepared by TRC) it is stated that "[a]ll sample ... analyses will be provided by the ASARCO Technical Services Laboratory in Salt Lake City, Utah." In Section 5.1.2 of this protocol (Reference Method 5/12; Particulate and Lead Measurements) is the statement that "[a]ll analyses of the prepared samples will be providing (sic) using an atomic absorption spectrophotometer (AA) or ... ICP following, at a minimum, the standard EPA Reference Method analyses procedures." Again, it is assumed and hoped that ambient samples were also to be analyzed using the same methods.[2] However, in Figure 4.1 (Ambient Filter Processing and Analysis Flow Diagram; analogous to Figure 2.1.1 described in previous paragraph) of ASARCO's Modeling and Reconciliation Protocol (October 1991; prepared by TRC and NEA) is the indication that lead (Compliance Analysis) was to be done at Nebraska Department of Environmental Conservation while other analytes were to be determined at NEA. Moreover, in Table 4.1 of the same protocol is the indication that lead was to be assayed using X-ray fluorescence (XRF) or ICP (AA was only specified for arsenic). Again, this seems at odds with ASARCO's emphasis on flame AA for lead determination (p.1 of its 12/15/93 letter).

The Glover Protocol's flow diagram (for ambient samples), as well as the CMB Study's "Filter Sample Processing and Analysis Protocol" (Figure 2.1.1) indicate that lead is to be analyzed at ASARCO's TSC using Flame Ionization AA Spectrometry (FAA), "the accepted reference method for measuring TSP lead" (p. 1 of ASARCO's 12/15/93 letter).[2] (Figure 2.1.1 would at least imply that lead in both ambient and source samples would be assayed using the same analytical method.) Beyond that, both figures indicate that of the remaining analytes, some will be determined

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[1]This assumption is important for consistence with CMB assumptions, and minimizes biases in the source apportionment: "ambient and source measurements should be considered together. Insofar as practical, similar collection and analysis methods should be used for both types of measurements." (Gordon et al., 1984).

[2]AA Spectrometry following HNO_3 extraction is the EPA certified reference analysis method for lead as specified in Appendix G of 40 CFR 50, but this is explicitly so for compliance purposes and has been joined by 14 equivalent methods.

at TSC while others will be determined at Chester's LabNet.[3] The impression is that the two labs employ complementary analytical methods. While not explicitly stated in the Protocol, it would be assumed that species that could be assayed with accepted reference methods at, say, TSC would be analyzed there. And species that could not be so assayed at TSC but which could be using methods at Labnet would be assayed there. This assumption may have largely held but apparently lead (and cadmium) was assayed at both labs (TSC using AA and LabNet using XRF) with different quantitation results. A key point of confusion is that it was not stated a priori (i.e., in the Glover Protocol) which species would be analyzed at TSC versus those to be analyzed at Labnet, and under what, if any, circumstances would the same species be assayed at both labs (which turned out to be the case for lead)!

I am not sure why lead was ever assayed at both labs using two different analytical methods. It seems to me that assaying the same species with two different analytical systems is begging for differential results. I discussed this matter with Chuck Lewis and Bob Stevens, Source Apportionment Research Branch, AREAL and they feel the same way. In any case, as described in Section 2.4 of the CMB Study and reiterated in ASARCO's 12/15/93 letter, different quantitations were seen. In the first place, analyzing all but the very lightest elements using XRF (**sampled on Teflon filters**[4]) would have been consistent with EPA guidance (Receptor Model Technical Series, Vol. I, Section 3.1.1 and Vol. II, Section 5.2.6). There is nothing sacred about ASARCO's using AA for lead except that it was the original certified reference method for **compliance analyses**;[2] if AA was regarded as the "superior" method the rationale for additional use of an alternative method was also not set out a priori, nor explained in ASARCO's 12/15/93 letter.

Point #1 on your letter is well taken and I am not sure ASARCO fully addressed it. The differential quantitation led ASARCO to its concoction of the "correction" factor, $\chi_{Pb-AA}/\chi_{Pb-XRF}$, to be applied to all species analyzed using XRF. Despite what is claimed in its 12/15/93 letter, the appropriateness of ASARCO's correction factor is questionable for at least two reasons: (1) the XRF analyses were applied to samples taken on quartz filters,[4] and the assumption of the "correct" lead analysis via AA (versus that via XRF) was evidently based on an independent check against an EPA certified reference standard.

On page 2 of its letter, ASARCO said that "...if all the chemical species concentrations in the ambient samples were doubled along with all of the source profile species weight

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[3]Formerly Keystone/NEA

[4]Use of quartz filters for XRF is not recommended (Dzubay and Stevens, 1989).

fractions, the percent mass explained by a given combination of source contribution estimates would be unchanged." This is true, but seems to contradict what it said in Section 2.4 of the CMB Study (p. 2-19): "Although this adjustment to the analytical data would affect the percent TSP mass explained in the CMB analysis, it would not significantly affect the percent lead explained..." Perhaps the first sentence should be revised to read: "...if all the chemical species concentrations in the ambient samples were doubled along with all of the source profile species weight fractions, the percent mass **of a particular species** explained by a given combination of source contribution estimates would be unchanged." Equally unclear is the next sentence in ASARCO's 12/15/93 letter: "If the source profile chemistries were increased more than the ambient samples, then an artificially high percent mass explained would result." Does this suggest that the correction factor was only applied to the source samples? Though it is not clear from the discussion in Section 2.4 (Developing the Source Profile Library) of the CMB Study, this correction factor at the very least should have been applied to both source and ambient samples.[1]

The nominal value for $\chi_{Pb\text{-}AA}/\chi_{Pb\text{-}XRF}$ was omitted in the discussion in Section 2.3 of the CMB Study; it should have been reported. I gather from ASARCO's 12/15/93 letter that is was close to 2. Application of this ratio, however, would have resulted in the artificially high percent TSP mass explained. At best, ASARCO's derivation of the correction factor "used to normalize the two analytical data sets" is unprecedented in any of its other lead apportionment studies that I have reviewed, defies convention, and belies EPA guidance. Beyond that I am not sure what (if any) "harm" was done by this manipulation in a regulatory sense. For all the fuss with deriving and applying the factor, though, I would like to have seen the CMB fitting results for analyses with appropriate use of XRF alone. For the XRF analyses that were done, a rationale should be provided as to how the problems posed by the quartz filters were surmounted. (Again, I stress the importance of the combination of analyte, filter type, and analytical method.)

Regarding points 4 & 5 in your letter, I discovered the same anomaly. I believe the problem is resolved in ASARCO's 12/15/93 letter.

I hope my review comments are helpful. Please keep me apprised on future developments with the lead SIP revision at Glover and feel free to call if you have any questions.

Attachment

cc: J. Irwin
C. Lewis (MD-47)
D. Wilson

References

Dzubay, T.G. and R.K. Stevens, 1989. Sampling and Analysis Methods for Ambient PM-10 Aerosol. In: RECEPTOR MODELING IN AIR QUALITY MANAGEMENT. P.K. Hopke Ed.

Gordon, G.E., W.R. Pierson, J.M. Daisey, P.J. Lioy, J.A. Cooper, J.G. Watson and G.R. Cass, 1984. Consideration for Design of Source Apportionment Studies. Atmos. Environ. 18(8): 1567.