Comments Prior to the April 20 Phone Call
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9 April 2018 (Revised 11 April)

To members of the committee:

I am writing this note to the committee prior to the phone call because I have been advised by Aaron Yeow that call will be the last of the panels activities in connection with the SO_2 review.

The focal point of my comments is material added to the ISA in connection with advice from the committee. It touches only on the parts of the ISA where I have had major input with my viewpoints on SO_s chemistry and the possible importance of emissions from smelters and integrated iron and steel mills, and on major recommendations to EPA in connection with our last review of the ISA. Specifically, it touches on the following from the June 30, 2017 letter to Administrator E. Scott Pruitt in connection with the chapter on atmospheric chemistry and ambient air concentrations. In that letter we made (among others) the following recommendations:

"To improve this chapter, emission trends from 2011-2016 should be added. It is also important to highlight the contributions of emissions from smelters and integrated steel mills as these may explain some high values in the data shown. The importance of pollution sources and the formation of other sulfur compounds such as inorganic and organic particulate S(IV) and organic S(VI) species should be discussed."

The final Revised ISA was released by EPA in December 2017 https://cfpub.epa.gov/ncea/isa/recordisplay.cfm?deid=338596. However, notification of the release was not send to the panel and we will not further review the document.

1. There are comments which follow which I have on each of the items in the quote from the letter to the administrator given above. However, my major concern is with the treatment of literature related to particulate sulfur(IV) compounds in the Final ISA and the implications for this atmospheric chemistry in the treatment of the importance of emissions from smelter and integrated iron and steel mills in the REA which we will discuss on April 20.

I have attached my past comments related to this chemistry and the REA (from my April 29, 2017 final comments on the draft REA) below.

EPA has referenced the chemistry of inorganic S(IV) in particulate matter in the Final ISA (it was completely missing from previous drafts), but they misinterpreted the peer reviewed literature in such a way as to justify not considering it (and the possible importance of emission from smelters and integrated iron and steel mill as modifiers to the effect of SO_2 on asthma) in the REA.

In section 2.3.3. of the Final ISA they cover the question of particulate inorganic S(IV) in emission from smelters and integrated iron and steel mills as follows:

"Particle-phase inorganic and organic sulfur compounds have been identified in early studies (Eatough and Hansen, 1983, 1980; Lee et al., 1980; Eatough et al., 1979; Eatough et al., 1978; Smith et al., 1976). These studies identified inorganic SO32− complexed with Fe(III) in the particles emitted by a smelter near Salt Lake City, UT. In a detailed spectroscopic study of the transient complexes that form between SO2, a source of S(IV) in particles, and Fe(III) in the aqueous phase, Kraft and van Eldik (1989a) and Kraft and van Eldik (1989b) reported that the oxidation of S(IV) by Fe(III) to form SO42− occurs on the order of seconds to minutes and is further accelerated by low pH. Sulfuric acid is well known to absorb water at even low ambient relative humidity (Seinfeld and Pandis, 2006). The highly acidic aqueous conditions that arise once smelter plume particles equilibrate with the ambient atmosphere ensure that S(IV)-Fe(III) complexes have a small probability of persisting and becoming a matter of concern for human exposure."

This is cherry picking of the literature to suit one's desires. This summary does not consider the following from the peer reviewed literature, and which was provided to EPA in my comments (references are from the material in my previous comments given in the Appendix):

Our studies on inorganic S(IV) in aged plume particles come from the study of plumes from a copper smelter, a coal-fired power plant study and an oil-fired power plant. In these studies, the presence of inorganic S(IV) species was identified in both fresh and aged plumes and were found in the plumes of the copper smelter and coal-fired power plant for the relatively long transport times (hours) (Eatough et al, 1982, Eatough et al. 1981a). For the copper smelter plume studied the ratio of the inorganic S(IV) to As increased with plume travel time. Average concentration of the inorganic S(IV) after about four hours of plume travel was about 60% of the particulate sulfate. The data indicated (Eatough et al., 1982) that the formation of stable particulate inorganic S(IV) involved chemical equilibria among the Fe plus Cu aerosol content, aerosol acidity and the concentration of SO_2(g), with the net result that after one or two hour he amount of SO_X present as stable particulate inorganic S(IV) increased with time, rather than decreasing to near zero as assumed in the EPA Final ISA. For the coal-fired power plant plume, again the amount of inorganic S(IV) relative to total SO_X increased with plume travel time and after about 4 hours of plume travel was about 50% of the particulate sulfate. We also conducted a plume study of an oil-fired power plant plume (Eatough et al, 1981a). Particulate inorganic S(IV) was not detected in the primary emissions or plume of the oil-fired power plant. We also studied the chemistry of the formation of sulfate and organic S(IV) and S(IV) compounds in these plume studies. Note that these plume studies are not referenced in the Final ISA but the assumption of non-existence of plume particulate inorganic S(IV) is assumed to be negligible as stated in the material in the Final ISA quoted above. In addition, we have also reported on the laboratory generation of stable Fe(III)-S(IV) aerosol (Hilton et al, 1979). This study is also not quoted. The metals which appear to be associated with the inorganic S(IV) as

outlined in the above referenced studies include Fe, Cu and Zn. The assertion that inorganic S(IV) particulate material has "a small probability of persisting and becoming a matter of concern for human exposure" is simply not supported by the peer reviewed literature.

The importance of this misinterpretation of the literature with respect to the REA is, of course, that EPA can assume that emissions from smelters and integrated iron and steel mills cannot be of special concern.

2. We also requested that in the revision of the ISA the emission trends from 2011-2016 should be added. That was not done. But this exclusion, from my point of view, does not seriously affect the revised ISA in the same way the mistreatment of the literature mentioned above does.

3, We also requested that "It is also important to highlight the contributions of emissions from smelters and integrated steel mills as these may explain some high values in the data shown."

This point is more important than item 2. with respect to the development of the REA because it bears on decisions made in selection of the study areas in that document.

The intent of this request is not covered in the Final ISA. The Final ISA does give the total emissions from copper smelting and combined iron and steel mill facilities on the top of page 2-5. However, consideration of the importance of smelter and iron and steel mill emissions could have been highlighted, but were not in connection with the follow Figures, Figure 2-3 (this is probably the most important because identifying the location of these facilities in this or a similar figure would have meet our intent), Figure 2-13 (There is an integrated iron and steel mill within Cleveland. It could impact the ambient monitors in the city. The effect seems to be as large as any influence of the RGUs to the east or west of the city). Figure 2-18 and Table 2-12 do meet the intent of this request.

The request is important because it could have guided the decisions on selection of study areas in the REA.

Observation

The result of the mistreatment of the plume presence of particulate inorganic S(IV) in plumes is that the incorrect assumption that "The highly acidic aqueous conditions that arise once smelter plume particles equilibrate with the ambient atmosphere ensure that S(IV)-Fe(III) complexes have a small probability of persisting and becoming a matter of concern for human exposure" allows EPA to treat lightly the consideration of emissions from smelters and integrated steel mills, The importance of this omission lies in the possible importance of these particulate inorganic S(IV) species as modifiers on the effect of SO_2 on asmathics. I have outlined the potential

Importance of this in the material final comments on the Draft IRP given in the Appendix where I have suggest EPA should conduct an evaluation of past literature smelter based epidemiological studies to determine if the stable inorganic S(IV) species may be effect modifiers of asthma for exposed populations. .

This suggestion is based on the early laboratory studies of Amdur (1971) and Alarie (1973) which indicated that exposure to both SO_2 and metal oxides present in smelter emissions resulted in an enhanced animal response and that the resulting aerosols were irritating. I have suggested to EPA that a possible fruitful set of data to evaluate the relative importance of aerosol S(IV) species associated with smelter emissions would involve past epidemiological studies from about two to three decades ago when smelter emission were much more significant, for example from the TX smelters in El Paseo (ASARCO Cu smelter, closed in 1999), and Corpus Christi (ASARCO Pb smelter, closed in 1985), Az smelters (ASARCO Cu smelter in Hayden, currently operating and Phelps Dodge Cu smelter in Douglas, closed in 1987), from the Kennecott Cu smelter in Magna, UT prior to construction of the tall stack, from the Tacoma WA smelter (American Smelting and Refining, a Cu smelter specializing in high As ore refining, closed in 1985), or the smelters in Montana (ASARCO Pb smelter in East Helena, closed in 2001, Anaconda Cu smelter in Anaconda, closed in 1981) and Idaho (Bunker Hill Pb smelter in Kellogg, closed in 1982). I know that several epidemiological studies were conducted at these locations, but I am not familiar with the results of these studies with respect to asthma exacerbation. I recommended that EPA look at this older data to see if an estimate of the relative potency of SO_2 and smelter associated aerosol S(IV) species can be determined. There will not be data on the concentrations of S(IV) in the aerosols emitted from these sources, so total particulate exposure might need to be used as a surrogate.
.
I assume that EPA will not conduct this exercise and the possible importance of exposure to particulate inorganic S(IV) species, the possible importance of emission from smelters and integrated iron and steel mills, and possible effect modifying of asthma exposure estimates due to the presence of fine particulate inorganic S(IV) species will all remain unexamined and unknown.

Appendix

The following is from my April 29, 2017 final comments on the Draft IRP and relates directly to m comments on the Final ISA as summarized above"

Relationship to Sources:

A potentially enlightening exercise might be to examine if any relationship exists between the results of epidemiological studies and the source of SO_2 for a given epidemiological study. I suggest this because it might enlighten whether particulate S(IV) (e.g. absorbed SO_2) might be important in exacerbation of asthma. This suggestion is based on the early laboratory studies of Amdur (1971) and Alarie (1973) which indicated that exposure to both SO_2 and metal oxides present in smelter emissions resulted in an

enhanced animal response and that the resulting aerosols were irritating. Postulating that the work of Amdur might reflect the present of stable metal sulfite species in the aerosols studied, and that the formation of such aerosol species, rather than aerosol sulfate, might explain the results of the EPA CHESS study in the Salt Lake City environment with substantial impact from Cu smelter emissions (EPA 1974), we conducted studies on S(IV) associated with ambient aerosols. This work demonstrated that stable transition metal ion - sulfite species existed in aerosols associated with smelter emissions (Smith 1976, Eatough 1979, Eatough 1980) and could be formed in aging smelter plumes (Eatough 1981a, Eatough 1982). The sulfite species were present at from 10 to 30 mol % of the sulfate species in the smelter associated aerosols. The sulfite species were less important in urban or coal-fired power plant plumes (Eatough 1978). We also demonstrated that stable Fe(III) –S(IV) aerosols could be routinely generated in the laboratory (Hilton 1979). The measurement, stability and formation of these inorganic S(IV) species in aerosols has been reviewed (Eatough 1983). These S(IV) species were present in emission from all smelters studied, were present in lower amounts in emissions from coal-fired power plants and additional material was formed during plume transport in smelter plumes. The amount of the S(IV) species, relative to sulfate average 0.1 mol S(IV)/mol sulfate in the coal fired power plant plumes and 0.5 mol S(IV)/mole sulfate in aged smelter plumes. The formation of S(IV) in smelter plumes increased with decreasing acidity of the aerosol.

If these S(IV) containing aerosols identified in the above reviewed research account for the enhanced effect of SO_2 in the presence of transition metal containing aerosols in animal exposure studies, then this class of compounds may be important in the interpretation of the morbidity effects associated with exposure to pollution from refinery sources. A careful review of pertinent epidemiological literature may inform this postulate.

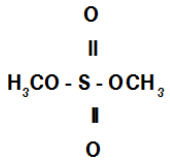
The current set of counties which are nonattainment with respect to the current SO_2 NAAQS will probably not provide the needed information. A review of nonattainment counties with populations near or over 100,000 shows that with two exceptions, the SO_2 exposures are dominated by emissions from coal-fired power plants, where aerosol S(IV) species are less important. The two exceptions are Jefferson County, MO where about 30% of the SO_2 emissions currently are from the Herculaneum Lead Smelter, with the remainder being from coal-fired power plants, and the Steubenville, Weirton region in eastern Ohio and western Pennsylvania, where emission from the Weirton Steel are likewise, a minor portion of the SO_2 emissions in the immediate area, with coal fired power plants being more important. These two locations would only stand out from the other nonattainment areas if the morbidity influence of aerosol S(IV) species was much greater that that associated with SO_2 itself. In addition to being a nonattainment area, Jefferson County, MO was also highlighted in the September 2008 Integrated Science Assessment for Sulfur Oxides, but with no epidemiological discussion associated with this nonattainment area (part of the St. Louis MO MSA).

Probably a more fruitful set of data to evaluate the relative importance of aerosol S(IV) species associated with smelter emissions would involve past epidemiological studies from about two to three

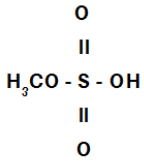
decades ago when smelter emission were much more significant, for example from the TX smelters in El Paseo (ASARCO Cu smelter, closed in 1999), and Corpus Christi (ASARCO Pb smelter, closed in 1985), Az smelters (ASARCO Cu smelter in Hayden, currently operating and Phelps Dodge Cu smelter in Douglas, closed in 1987), from the Kennecott Cu smelter in Magna, UT prior to construction of the tall stack, from the Tacoma WA smelter (American Smelting and Refining, a Cu smelter specializing in high As ore refining, closed in 1985), or the smelters in Montana (ASARCO Pb smelter in East Helena, closed in 2001, Anaconda Cu smelter in Anaconda, closed in 1981) and Idaho (Bunker Hill Pb smelter in Kellogg, closed in 1982). I know that several epidemiological studies were conducted at these locations, but I am not familiar with the results of these studies with respect to asthma exacerbation. I recommend that EPA look at this older data to see if an estimate of the relative potency of SO_2 and smelter associated aerosol S(IV) species can be determined. There will not be data on the concentrations of S(IV) in the aerosols emitted from these sources, so total particulate exposure would need to be used as a surrogate. The importance of elucidating the effect of these exposures is correctly alluded to in the ISA on Page 4-12, Line 11.

Organic Oxysulfur Compounds in the Atmosphere

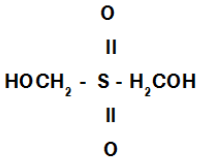
This section was added to my preliminary comments to provide a written response to the question raised in the preliminary comments by Dr. Daniel Jacob. Compounds identified by BYU and discussed below include:



Dimethyl Sulfate



Monomethyl Sulfuric Acid



Bis-Hydroxymethyl Sulfone

Alkyl Sulfates. We have previously identified monomethyl sulfuric acid and dimethyl sulfate in power plant plumes (Lee 1980, Eatough 1981b, Hansen 1987)) and in the Los Angeles Basin (Eatough 1986, Hansen 1986). The alkyl sulfates have been shown to be present in emissions from both coal and oil-fired power plants (Eatough 1981b). In addition, formation of dimethyl sulfate during plume transport has been seen in the plumes of both a oil-fired and a coal-fired power plant (Hansen 1987). Dimethyl sulfate did not form in the plume of the oil-fired power plant studied while it resided in a fog bank, but formation was seen after the plume exited the fog bank. The rate of conversion of SO_2 to dimethyl sulfate was about 0.4 mole %/hr in the oil fired power plant plume and about 0.05 mole %/hr in the coal fired power plant plume. Particulate phase dimethyl sulfate dominated in these two studies. In the Los Angeles Basin studies (Eatough 1986) dimethyl sulfate was only seen in air masses not imbedded in a fog bank, i.e. generally in the inland area. Gas phase dimethyl sulfate was the dominate species in these studies, was present at highest concentrations in transported plumes in the Inland Empire and was seen to exceed 10 mole % of the total sulfur oxides present. It should be pointed out that at the time of these studies, substantial SO_2 emission from power plants were present in the Basin..

Dimethyl sulfate is a mutagen and suspected human carcinogen, so it's presence may be important with respect to toxic species, but I am not aware of any data indicating that inhalation will exacerbate asthma.

Bis Hydroxymethyl Sulfone.

Several different methods of analysis of particulate samples collected from the plumes of coal-fired power plants or from areas heavily impacted by coal-fired boilers indicated that a S(IV) compound distinctly difference form inorganic S(IV) was present in the samples (Eatough 1978, Eatough 1981, Richter 1981). This compound was subsequently identified as bis-hydroxymethyl sulfone (Eatough 1984). The sulfone was usually present in emissions from coal- or oil-fired power plants at mol ratios of about 0.5 (range of 0.1 to 1.0) compared to sulfate (Eatough 1983). First order formation of the sulfone was observed in plumes from six different power plants at rates of from 0.4 to 3.0 % SO_2/hr. with the observed rate being inversely proportional to atmospheric water partial pressure (Eatough 1983). The sulfone was found in highest concentrations in the Las Angeles Basin in inland samples (mol fraction comparable to sulfate), but was not seen in coastal samples impacted by fog or clouds (Farber 1982).

Toxicological data is not available for bis-hydroxymethyl sulfaone.

Other Organic Oxysulf Comounds.

Aerosol phase methane sulfonic acid (Panter 1980) and gas phase ethylene sulfite (Jones 1974) have been identified in atmospheres impacted by emission from coal fired power plants, but only at concentrations much less than the above described species.

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