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Interactive comment

Interactive comment on "Water-soluble iron correlation to primary speciated organics in low-emitting vehicle exhaust" *by* Joseph R. Salazar et al.

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General: This paper characterizes Fe solubility found in tailpipe emissions from different vehicle classes and proposes a mechanism involving Fenton chemistry with aromatic compounds to explain their results. This work is novel and of interest to the aerosol community. On another note, I found it refreshing to read an ACPD paper that was well-written yet concise. I recommend this paper for publication after addressing my minor comments.

Reply: We thank the Reviewer for their comments.

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Discussion paper

Major Comments: 1. The title is a bit awkward and overly complicated. I suggest that the authors simplify their title to something like “Water-soluble iron emitted from vehicle exhaust is linked to cyclic organic compounds”.

Reply: We agree that this would be clearer to the reader, so the title has been changed from “Water-soluble iron correlation to primary speciated organics in low-emitting vehicle exhaust” to “Water-soluble iron emitted from vehicle exhaust is linked to primary speciated organic compounds”

2. The rationale for targeting the IVOCs was not well-explained. I suggest a paragraph in the introduction briefly discussing different organics emitted from vehicles and what their possible role in Fe solubility may be.

Reply: The authors agree that a rational for targeting IVOCs would be beneficial to the introduction. Line 81-89 refers to the research on organic species and solubilized iron. Line 89-92 was added to better explain the rational for targeting IVOCs. Line 81-89 states “A third, broad, iron solubilization hypothesis emphasizes an iron-organic interaction (Baba et al., 2015; Vile et al., 1987). For example, a significant increase in water-soluble iron is observed in the presence of oxalate and formate in ambient aerosols and in cloud droplets (Paris et al., 2011; Zhu et al., 1993). Other studies have suggested that the photolysis of polycyclic aromatic hydrocarbons leads to reduced iron, which may result in greater iron water solubility (Faiola et al., 2011; Haynes et al., 2019; Pehkonen et al., 1993; Zhu et al., 1993).”

Line 89-92: Vehicle exhaust contains many organic species including secondary organic aerosol (SOA) Single-ring aromatic compounds (C6-C9) PAHs, hopanes, steranes, alkanes, organic acids and intermediate volatility organic compound (IVOCs) which are longer chain organic species. (Cheung et al., 2010; Zhao et al., 2016)

Specific Comments: Abstract:

1. Define EC and OC. Reply: For clarification, Line 22-23 now reads “elemental carbon

(EC), organic carbon (OC)"

2. Sentence on lines 21-24 needs to be rephrased. I found it confusing. Reply: We thank the reviewer for this suggestion. To clarify for the reader, Line 23-26 has been divided in to two sentences and changed to "Naphthalene and intermediate volatility organic compounds (IVOC) were quantified for a subset of vehicles. The IVOC quantified contained 12 to 18 carbons and were divided into three subgroups: aliphatic, single ring aromatic (SRA), and polar (material not classified as either aliphatic or SRA)."

3. The end of the abstract should more clearly spell out the mechanism for the increased Fe solubility and include the role of Fenton chemistry.

Reply: To clarify for the reader, line 34-37 has been changed to "These results suggest that the large driver in water-soluble iron from primary vehicle tail-pipe emissions is related to the organic composition of the PM. We hypothesize that, during the extraction process, specific components of the organic fraction of the PM are oxidized and chelate the iron into water"

Introduction:

4. I suggest mentioning the different organics found in vehicle exhaust with attention to cyclic compounds and IVOCs. I also suggest mentioning how those compounds could affect Fe solubility to help establish the rationale for that aspect of your work.

Reply: 81-89 refers to the research on organic species and solubilized iron which led to the rationale to establish a relationship between water soluble iron and IVOCs. Line 81-89 states "A third, broad, iron solubilization hypothesis emphasizes an iron-organic interaction (Baba et al., 2015; Vile et al., 1987). For example, a significant increase in water-soluble iron is observed in the presence of oxalate and formate in ambient aerosols and in cloud droplets (Paris et al., 2011; Zhu et al., 1993). Even when compared to sulfuric acid, oxalic acid results in a greater increase in iron solubility because of the organic iron interaction (Chen and Grassian, 2013). Other studies have suggested that the photolysis of polycyclic aromatic hydrocarbons leads to reduced iron, which may result in greater iron water solubility (Faiola et al., 2011; Haynes and Majestic, 2019; Haynes et al., 2019; Pehkonen et al., 1993; Zhu et al., 1993)." Line 89-92: Vehicle exhaust contains many organic species including secondary organic aerosol (SOA) Single-ring aromatic compounds (C6-C9) PAHs, hopanes, steranes, alkanes, organic acids and intermediate volatility organic compound (IVOCs) which are longer chain organic species. (Cheung et al., 2010; Zhao et al., 2016)

5. I encourage the authors to include and discuss the following papers relevant to this study in the introduction and the results section: [Chen and Grassian, 2013; Fu et al., 2012; Meskhidze et al., 2017]

Reply: We agree that these references are important for this topic, so the following lines have been added. Line 57 "From these combustion sources, it has been shown that the species of iron differed greatly and had an impact in iron solubility (Fu et al., 2012)." Line 84 "Even when compared to sulfuric acid, oxalic acid results in a greater increase in iron solubility because of the organic iron interaction (Chen and Grassian, 2013)" Meskhidze et al., 2017, while important, was not added to the manuscript because a discussion of iron dissolved in seawater might confuse readers in understanding the context of this manuscript.

Methods:

1. Define FID

Reply: For clarity, Line 128-129 now reads "by gas chromatography, with detection by a flame ionization detector (FID)."

Results:

1. Figure SI1 is important for showing that bulk organics and markers of inorganic acid processing (e.g., sulfate and nitrate) do not correlate with Fe and are not important for Fe solubility. I suggest showing at least these two aspects of your correlation analysis

in the main manuscript and not in the SI.

Reply: We agree with this suggestion and a plot showing bulk organic carbon (OC) and sulfate is now Figure 3 in the manuscript and referenced in line 302 and 307.

2. Line 311: Define LFC.

Reply: LCF is defined in section 2.6 Line 191 in the methods “Least-square linear combination fitting (LCF) was subsequently performed in the range 7090 to 7365 eV to confirm iron valence and further identify the major mineral groups present.”

3. Line 324: provide some more rationale for why you targeted these specific organics.

Reply: To clarify for the reader, Line 340 was modified to “leading to the investigation of organic species which resulted in a correlation to longer chain IVOC and naphthalene (Haynes and Majestic, 2019)“

4. Lines 353-354: While these plots are compelling, the authors should provide a sentence or two with some explanation for the scatter in the data. Reply: To address the scatter in the manuscript line 336 was added “The variance of figure 4 could result from the fact that, in addition to the IVOCs, other factors also influence iron water solubility”

Conclusions: 1. I suggest that the authors reiterate that Fe solubility was not related to inorganic acid processing. This is a very important point since many studies assume that sulfuric acid, in particular, is the most important acid that induces changes in Fe solubility.

Reply: We agree that this is one of the key points of the paper. Thus, we have changed line 410 to “This study shows water-soluble iron is directly formed from vehicle exhaust and not correlated to sulfates”

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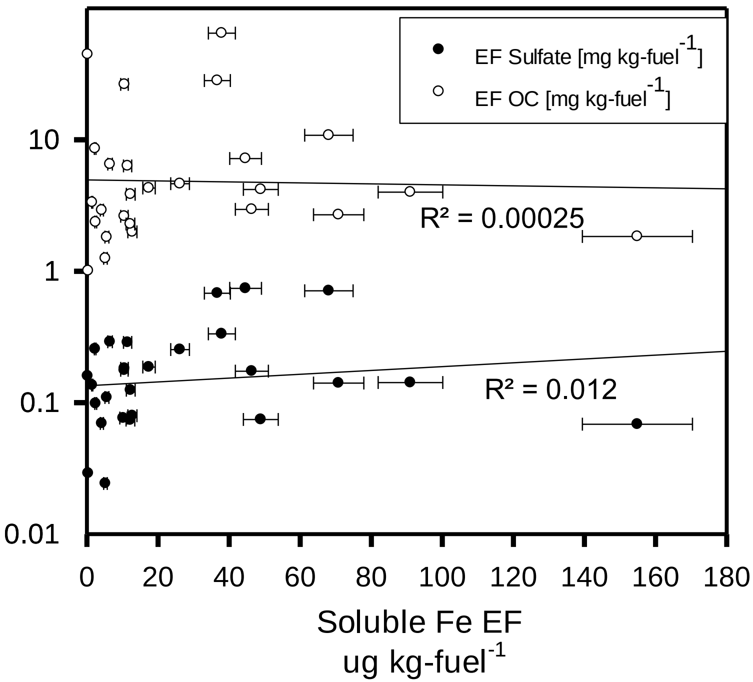

Figure 3: Linear correlation plots representing EF in mg kg-fuel-1 for sulfate and organic carbon (OC) in µg kg-fuel-1 for water-soluble iron. Correlation lines and R2 values for all elements are shown.

Fig. 1.