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Atmospheric Chemistry and Physics Discussions

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

Joseph R. Salazar et al.

joe3salazar@gmail.com

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Summary: The authors present a comprehensive study assessing the iron emitted by a collection of gasoline vehicles spanning a range of emissions certifications. This includes total iron and water-soluble iron as well as complementary analyses to determine the oxidation state of the iron. Interestingly, there is a trend between water-soluble iron emissions and intermediate-volatility organic compound (IVOC) emissions. Through a complementary laboratory study, the authors demonstrate that the iron may interact with some organic compounds, resulting in a transformation to water-soluble iron. Overall, this is a nice paper, and I recommend it for publication in Atmospheric

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Chemistry and Physics, pending adequate response to my comments and those from the other reviewers.

Reply: We thank the Reviewer for the kind words.

General Comments: Some of the manuscript is unnecessarily repetitive. For example:

Lines 100-103, lines 115-118, and lines 126-127 are referring to particle sampling and analysis methods. Please combine to a single location within the document.

Reply: We thank the reviewer for the suggestion to reduce the repetitiveness, lines 100-103, lines 115-118, and lines 126-127 are combined. Line 110-116 now reads "Emission samples were collected using a constant volume sampler from which a slip-stream of dilute exhaust was drawn at a flow rate of 47 L min-1. Particle phase emissions were collected using three sampling trains operated in parallel off of the end of the CVS dilution tunnel. Train 1 contained a Teflon filter (47 mm, Pall-Gelman, Teflo R2PJ047). Train 2 contained two quartz filters (47 mm, Pall-Gelman, Tissuquartz 2500 QAOUP) in series. Train 3 contained an acid-cleaned Teflon filter followed by a quartz filter (47 mm, Teflo, Pall Life Sciences, Ann Arbor, MI) and the flow rate was 0.5 L min-1 through each Tenax tube." Lines 115-118 and 126-127 were deleted.

Lines 129-131 and lines 142-144 both mention the use of a laminar flow hood for handling of samples. Please remove this redundancy. Reply: To make the manuscript more concise, text in line 142 "and handled inside a polypropylene laminar flow hood (NuAire, Plymouth, MN)" was removed

In Figures 1, 2, and 4, please use "μg" rather than "ug". Reply: We thank the Reviewer for bringing this to our attention: We changed ug to μg in Figures 1, 2, and 4

Specific Comments: Lines 61-63: Is the iron present in the gasoline itself, or does it leach from the vehicle components?

Reply: To avoid any misunderstanding, Line 65-69 changed to "Iron is contained in many fuels which has pre-combusted concentrations ranging from 13-1000 μg L-1 (Lee

and Von Lehmden, 1973; Santos et al., 2011; Teixeira et al., 2007). Within the engine, computational models of combustion in engines suggest that iron emissions could also originate from the fuel injector nozzle inside the engine block (Liati et al., 2015)."

Line 118-120: For a field campaign that occurred in 2014, I have a hard time believing that results were published in 2000. Please correct this reference.

Reply: We thank the Reviewer for catching this. We were using the methods, not the data. Thus, line 131-132 is changed to "procedure for these data presented elsewhere" from "these data are presented elsewhere"

Lines 156-159: How was 3% of the filters "measured exactly"? Was this using a filter punch that was precisely 3% of the area of the filters? Please clarify.

Reply: To clarify how the filters were cut Line 166-167 changed to "$\sim$3% of the filters was measured and cut using a ceramic blade" Lines 178-182: I may have missed this definition, but what is "μXRF"? Does it differ from a typical X-ray fluorescence measurement?

Reply: The μ refers to the small spot size that the beam was able to fluoresce, thus line 188 has been changed to "micro X-ray fluorescence (μXRF)" and μXRF has been added to XRF in line 188 and 191 for consistency

Lines 235-241: It is a little unclear to me how the total iron emissions are defined. Is this the sum of the water-soluble iron from the water extractions described in Section 2.3 and the remaining iron that underwent the acid digestion in Section 2.4? Or was water-soluble iron determined from one filter and total iron determined from another filter? Please clarify.

Reply: Yes, the iron is summed from the water extractions described in Section 2.3 and the remaining iron that underwent the acid digestion in Section 2.4. Line 166-169 has been clarified to "First $\sim$3% (measured exactly) of the filters were cut and saved for X-ray absorption near edge structure (XANES) spectroscopy, then the water-soluble

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elements were extracted and, lastly the polymethylpentene ring was removed from the Teflon filters."

Lines 246-248: Why do the authors use the symbol from the periodic table for metals in previous sentence in this paragraph but not here?

Reply: We thank the Reviewer for bringing this to our attention. Elements in line 257 were changed to the names of the elements.

Lines 258-261: "Trace elements km-1" and "per km emissions" are just distance-based emission factors (as opposed to the fuel-based emission factors that the authors have used). I recommend using "distance-based emission factors" in both of these lines.

Reply: We thank the reviewer for the clarification. "Trace elements km-1" and "per km emissions" have been changed to "distance-based emission factors" in Lines 269-272 "Table 2 compares the average exhaust PM composition and trace elements in distance-based emission factors in this study to literature values for other passenger vehicles, including one diesel and three gasoline exhaust studies. For all elements, the distance-based emission factors were greater in the diesel cohort, relative to the gasoline vehicles."

Figures 1 and 2: I'm wondering if it could be more informative to present the total iron emissions as, e.g., Figure 1a, and then have Figure 1b include box plots of the water-soluble iron fraction. This is just a thought that could potentially be more informative to drive home how much of the iron is actually water-soluble.

Reply: This is a great suggestion and we thank the reviewer. Below is the revised graph and the removed graph.

Lines 275-280: I have another thought on the presentation of results here. Given a lack of trend in total iron with emission certification, I'm curious if it would be worth exploring a trend in the ratio of total iron to particulate matter (PM) mass (e.g., EFFe/EFPM). I suspect that the emissions of iron relative to total PM will increase, which could be an

interesting result.

Reply: The authors agree that this could be useful, unfortunately overall PM mass wasn't measured as part of this study.

Lines 377-387: If I am understanding this correctly, it suggests that Fe(III) is emitted yet is rapidly converted to Fe(II). This may be worth stating explicitly.

Reply: Added to Line 406 to restate the above chemistry and clear up any confusion "This overall process suggests that Fe(III) is emitted through car exhaust through interaction with water and organics undergoes a Fenton like reaction and converted to Fe(II) and the iron is chelated by the resulting oxidized organics."

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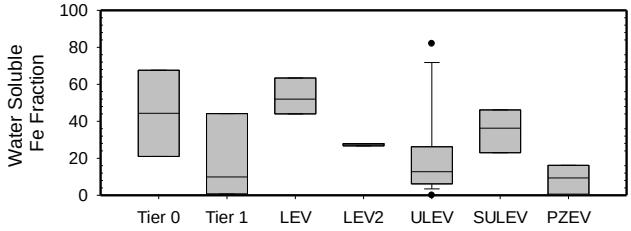
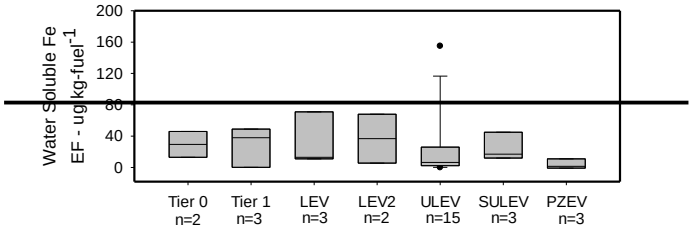


Figure 2: Water-soluble iron from the 32 vehicles tested reported in water-soluble iron fraction. The center black line represents the median value and the edges of the boxes represent the 25th and 75th percentiles while the whiskers are the 10th and 90th percentiles.



~~Figure 2: Water-soluble iron from the 32 vehicles tested reported in EF (μg kg-fuel^{-1}). The center black line represents the median value and the edges of the boxes represent the 25th and 75th percentiles while the whiskers are the 10th and 90th percentiles.~~

Fig. 1.

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