Review of acp-2019-386

Salazar et al., "Water-soluble iron correlation to primary speciated organics in low-emitting vehicle exhaust"

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

## **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.

Lines 129-131 and lines 142-144 both mention the use of a laminar flow hood for handling of samples. Please remove this redundancy.

In Figures 1, 2, and 4, please use "µg" rather than "ug".

## **Specific Comments:**

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

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.

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.

Lines 178-182: I may have missed this definition, but what is "µXRF"? Does it differ from a typical X-ray fluorescence measurement?

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.

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?

Lines 258-261: "Trace elements km<sup>-1</sup>" 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.

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.

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.,  $EF_{Fe}/EF_{PM}$ ). I suspect that the emissions of iron relative to total PM will increase, which could be an interesting result.

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.