Answer to the reviewers' comments

The questions of the referees are answered in purple. We have further added the changes made in the text in green as they are also highlighted in green in the revised manuscript.

Referee 1

1) This paper presents what I would call preliminary results from the development and brief deployment of two instruments for measuring water soluble Fe (ws Fe) in ambient PM2.5 particles and speciation into Fe(II) and Fe(III). The ambient measurements are over two separate periods with a different particle collection system for each and cover a total of 3 weeks of sampling. Measuring ws Fe is difficult due to low concentrations and the measurement depends on the method operational parameters. Possibly one of the biggest difficulties is measuring what is in the ambient particle since it is difficult to sample the particles unaltered using most techniques. This leads to some confusion in this paper that should be addressed. In this study, PM2.5 was analyzed at these two different pHs by two different instruments: pH 4.5, shown to be representative of European cloud water, and as a reference at pH 6.5 – this includes what is stated to be the optimal pH range for the ferrozine method. How does one interpret this measurement data since the pH of PM2.5 that entered the instruments would most likely be much lower than pH 4.5? Why were the measurements made at this pH, ie representative of cloud water? Is one to assume that the reported ws Fe concentrations represent what is in ambient PM2.5? It seems the assumption, (although not stated), is that no matter the pH or concentration of ws Fe in the ambient particles entering the instrument, the pH of the measurement determines the measured concentration of ws Fe. The logic is not clear, nor how one is to interpret soluble Fe concentrations in PM2.5 based on this data.

The ws-Fe concentrations reported here are operationally defined by the extraction and measurement pH and do not directly represent the in situ pH or iron speciation within PM2.5 particles. Instead, the measurements are intended to probe the amount and redox state of iron that becomes water-soluble when particles are exposed to aqueous environments of defined pH. These conditions are relevant to understand the potential impact of iron species on chemical processing in the atmospheric aqueous phase, e.g. when particles are scavenged by cloud or fog droplets. The pH 4.5 condition was chosen to represent cloud- or fog-water-relevant conditions, whereas pH 6.5 serves as a methodological reference condition, which is frequently used for filter extraction and represents neutral aqueous phase conditions. Consequently, differences between the two pHs reflect pH-dependent dissolution and redox transformations. Nevertheless, atmospheric processing impacts the solubility and speciation of atmospheric iron. The presence of oxalate, for example, can increase the solubility and the photo-reduction to Fe(II) under slightly acidic conditions. The extraction and different pH can therefore give important information on dissolution of iron pH conditions relevant for chemical processing in the atmospheric aqueous phase.

To mimic the pH of aerosol water, an extraction pH below 2 would be required. On the one hand, the commercial sampling units used in this study are not designed for such low pHs as we will discuss in comment 16. On the other hand, determining the soluble iron concentration at such acidic conditions would more refer to acid-extractable Fe and not water-soluble Fe.

To facilitate the interpretation of the results regarding the pH conditions we have made several changes throughout the manuscript. We have changed the title to:

~~Real-Time~~ Online Water-Soluble Iron Speciation in Ambient ~~Aerosols at Neutral and Slightly Acidic pH~~ under Cloud-Water Relevant and Neutral Conditions

We have implemented a new section discussing the definition of water-soluble Fe which will be further explained in comment 2. We have made several small changes like adding “cloud relevant conditions” throughout the manuscript to facilitate interpretation of the setup and the data.

2) Another overall issue is the lack of clarity in terminology. A list of the terms with definitions in a table would be useful, and then take careful in how they are used throughout the paper.

This is an excellent idea. As referee 2 had a similar idea, we added a new section in the methodology part to explain the definitions and underline research gaps and challenges when no standardized definition or procedure exists. We hope it now explains better the measured parameter. The new paragraph is added in lines 106-132.

2.2 Definition of Water-Soluble Iron

The lack of a standardized protocol for determining trace metal solubility, including Fe, has been widely discussed in the literature (e.g. Tang et al., 2025; Perron et al., 2020; Meskhidze et al., 2016). Several studies have demonstrated that leaching or extraction procedures, including different chemical composition and pH value of the solutions as well as different contact time, strongly influence the measured metal’s solubility (e.g. Li et al., 2023; Tang et al., 2025; Perron et al., 2020; Meskhidze et al., 2016). Most comparative studies investigating the effect of leaching solutions on iron solubility have used ultrapure water or organic buffers such as formate or acetate with a pH around 4.3 (e.g. Li et al., 2023; Perron et al., 2020; Majestic et al., 2006).

As no standard protocol exists, a variety of operational terms have been used in the literature to describe experimentally mobilised aerosol trace element fractions, including ‘soluble’, ‘labile’, ‘leachable’, dissolved’, ‘readily accessible’, ‘bioaccessible’ and ‘bioavailable’, as summarized by Tang et al. (2025). The use of different extraction or leaching approaches and definitions complicate direct comparison of reported iron solubility and soluble iron concentrations across studies.

This study focuses on the analysis of the iron fraction which is soluble in Seradest water (pH6.5), used as a near-neutral reference condition, and Seradest water adjusted to pH 4.5 with HNO_3, providing mildly acidic, low-ionic-strength aqueous conditions representative of cloud-water acidity while minimizing additional chemistry introduced by adding buffering agents. The pH of the aqueous phase can vary widely, ranging from highly acidic conditions (pH<0) in deliquesced aerosols to neutral pH in rain and fog water (e.g. Pye et al., 2020; Herrmann et al., 2015). As discussed above, the solubility of atmospheric iron depends on particle size, chemical composition, photochemical activity and atmospheric processing, as well as on pH. To allow a clearer interpretation of our data, we therefore use the term *water-soluble iron* throughout this study, emphasizing that the reported values represent the fraction of iron that is soluble under neutral and mildly acidic aqueous conditions relevant to cloud, fog and rain water.

A key advantage of the online approach is the high temporal resolution of the measurements; however, the method requires short extraction and reaction times for both ferrozine and the reducing reagent hydroxylamine (HA), as will be discussed in section 3.1.1. Consequently, the quantity reported as ws-Fe(II) is operationally defined by the reaction time of dissolved Fe(II) with ferrozine. The term total ws-Fe refers to the amount of Fe detected as dissolved Fe(II) after addition of HA, which reduces dissolved Fe(III) to Fe(II) prior to complexation with ferrozine.

Here is my understanding of the terms used.

3) Ws-Fe(II) is clear (line 67). It is the Fe measured by the ferrozine method for any sample pH for short reaction times.

Yes, exactly.

4) Ws Fe is not clear, lines 63... suggest it is the Fe measured in an aqueous sample after liquid filtration also at any pH. But it is not specified how the Fe in the filtrate was detected.

This was summarized by Shi et al. (2012) and no specific method was given. As no standard procedure exists, different methods are used including XRF, IC-MS, ICP-OES, AAS.

5) Total ws-Fe (line 70, and Eq 4)) is the measurement of Fe(II) with the ferrozine method after treatment with HA that converts Fe(III) to Fe(II) at any pH. But the conversion rate depends on time, (line 255) so HA reaction time must also be known and remain constant. Also, likely some composition dependence.

This is correct and an advantage of FIA systems is that the reaction times are always exactly the same with each injection. Reaction and reduction time were already given in Table 1. So even if reduction and ferrozine complexion rates are short they are always the same in the setup. As we changed the whole paragraph where we explained the function of the FIA system (see question 6) we now hope that it is easier to follow.

6) Reducible Fe(III), due to the above limitation with HA conversion of Fe(III) to Fe(II) being operationally defined. Reducible Fe(III) refers to the conditions of these FIA systems. But what about this effect on Total ws-Fe?

Thank you for pointing this out. Of course, the concentration of total ws-Fe isdependent of the FIA system. As there is no standard definition of total ws-Fe as a function of pH, reduction time and reduction solution, the term is operationally defined by the method applied. The advantage of a FIA system compared to batch approach is that reaction times are always exactly the same, and results are reproducible. In section 3.1.1 we have extended the discussion about the reduction of dissolved Fe(III) to Fe(II) to address the importance when comparing the result with other studies. As referee 2 had a similar comment we answered the two comments together in paragraph 3.1.1 lines 311-330:

Reduction efficiency was tested with single dissolved Fe(III) standards of pH 3.5 and showed high efficiency, varying between 80-117% relative to dissolved Fe(II) when standards were freshly prepared. A decrease in reduction efficiency was observed with increasing age of the dissolved Fe(III) standards likely due to the formation of hydrolysed Fe(III) species which are not rapidly reduced by HA. This observation highlights that, under the short reduction times in the FIA system, less reactive or less reducible Fe(III) species may not be fully reduced. Previous studies have used HA as reducing solution in flow injection systems applying very short reaction times (HA and ferrozine together) of approximately 1 minute (e.g. Pullin and Cabaniss, 2001; Teixeira and Rocha, 2007). In the presented systems the reduction times were 20 s for the MARS and 40 s for the PILS system. The reaction times with ferrozine were 78 s for the MARS and 157 s for the PILS system (Table 1). Therefore, the total time for the reduction of dissolved Fe(III) to Fe(II) was 98 s for the MARS and 197 s for the PILS system. Pullin et al. (2007), using an acetate buffer carrier of pH 4.0 and a reaction temperature of 65°C, reported 100 % reduction efficiency by adding acetic acid to the carrier and colour reagent suggesting that the acetate buffer forms a complex with the dissolved Fe(III). As no buffer solution was used in the present FIA apparatus, the addition of acetic acid had no effect on reduction efficiency when injecting aged Fe(III) standards. Heating of the reduction coil in a water-bath as reported by Pullin et al. (2007) was not applied to reduce the technical complexity for a system which is intended to run continuously for a long period of time. Similarly, heating was not applied in many other FIA systems designed for ws-Fe(II) /(III) determination (e.g. Attiyat et al., 2011; Teixeira and Rocha, 2007).

Luther et al. (1996) reported incomplete reduction of dissolved Fe(III) by HA in the presence of humic-like substances.

To acknowledge this limitation imposed by the operational given reduction time, further on we use the term reducible Fe(III) instead of ws-Fe(III). This also underlines that total-ws Fe is defined by the kinetics of the FIA system and might also underestimate the total ws-Fe concentration compared to studies with longer reduction times.

7) Total Fe (line 63) is the total Fe measured in a particle, no method is specified, ie ICPMS, or XRF??

This was summarized by Shi et al. (2012) and no specific method was given. As no standard procedure exists, different methods are used including XRF, IC-MS, ICP-OES, AAS.

8) Fe(II), at times this term is also used, which is unclear. Is this the measurement of ws-Fe(II) but only for the standards?

To avoid misunderstanding of the different forms of Fe(II)/Fe(III) used, we have implemented the following convention: dissolved Fe(II)/Fe(III) is now used to describe chemically the presence of Fe(II)/Fe(III) in the solution, which of course is dependent on the chemical composition and pH of the sample. Ws-Fe(II) is only used when describing our measurement result.

9) Finally, how does the sampling/analysis system not alter the ratio of Fe(II)/Fe(III) from what it was in the ambient aerosol. Line 81 notes in filter sampling the redox state of ws Fe may change. If the proportion of Fe(II) and Fe(III) in the two online sampling systems is altered, what are the implications of this?

Although the online system cannot guarantee preservation of the in-particle Fe(II)/Fe(III) ratio of the ambient aerosol, it substantially reduces redox artefacts associated with filter storage by rapidly dissolving particles and stabilizing Fe(II) under controlled conditions as ferrozine is quickly added to the sample.

Specific Comments

10) Line 6 in Abstract not clear. If the PILS-FIA system at pH 4.5 represent pH of cloud water? What does the measurement for the MARS-FIA system at pH 6.5 represent?

In the PILS-FIA system, pH 4.5 represents conditions in cloud water. In the MARS-FIA system, we used pH 6.5 as a reference measurement as many studies use ultrapure water as extraction medium. Now the sentence is changed to:

In summer 2024, the Metrohm AeRosol Sampler (MARS) was operated with an extraction pH of 6.5 providing neutral reference extraction conditions. In winter 2025, a particle-into-liquid sampler (PILS) was applied using an extraction pH of 4.5 to probe iron solubility and speciation under mildly acidic, cloud-water-relevant extraction conditions.

11) What about the importance of oxalate or other organic Fe ligands? Presumably, the ferrozine forms a stronger complex than Fe-Ox, and so displaces it. So any Fe-Ox is measured as ws Fe(II)? Is this correct? Explain line 289.

Organic ligands such as oxalate can influence iron solubility and redox chemistry in the aqueous phase. It might also interfere with ferrozine even if ferrozine is added in excess (Voelz et al., 2019). Stookey (1970) found an interference of oxalate when concentrations exceeded 500 mg L^{-1}. Furthermore, humic-like substances can affect the reduction efficiency of hydroxylamine hydrochloride as discussed by Luther et al. (1996). However, ferrozine forms a much stronger complex with Fe(II) than oxalate and is added in large excess as done in this study.

Based on oxalate concentrations around 0.05 µg m^{-3} from urban background stations in the UK (Laongsri and Harrison, 2013), oxalate concentrations in the filter extracts can be expected to be around 5.5 µM and in the MARS and FIA samples below 1 µM. Ferrozine concentrations of 2.7 mM were prepared and mixed with the sample in a ratio 1:10 (sample to ferrozine). Therefore, the ferrozine concentration in the sample is 270 µM, thus greatly exceeding the oxalate concentration.

Therefore, most of the dissolved Fe(II), whether present as free Fe(II) or initially complexed by oxalate, should be quantitatively converted to the Fe(II)–ferrozine complex and detected as ws-Fe(II). The presence of ligands may thus affect the amount of dissolved Fe(II) present prior to detection, but should less interfere directly with ferrozine-based Fe(II) quantification.

The sentence in line 289 was deleted and replaced by the following sentences (now in lines 360-365) to underline the effect of extraction:

This enrichment may reflect the mobilisation of Fe that has previously undergone ligand-mediated dissolution and redox processing in the atmosphere, where organic ligands such as oxalate are known to increase iron dissolution by complexation and facilitate photoreduction of Fe(III) to Fe(II) under mildly acidic conditions (Shi et al., 2012). In addition, complexation with organic ligands has been shown to stabilize dissolved Fe(II) in rain water of pH 4.5 (Kieber et al., 2005). Overall, this demonstrates that the extraction pH can affect both the amount and speciation of the water-soluble iron.

The presence of oxalate and its role in ligand-promoted dissolution is discussed later in lines 543-541 as suggested by Referee 2.

In addition to organic compounds emitted directly from exhaust, common atmospheric ligands can enhance solubility, even under moderately acidic conditions (Chen and Grassian, 2013). Deprotonated ligands replace surface OH groups, thus forming a bidentate surface complex, which destabilizes the Fe-O bond (Wang et al., 2017). The formation of organic ligand-Fe complexes in the aqueous phase enhances further Fe dissolution from the aerosol into the liquid water phase (Sakata et al., 2022). Oxalate, which is ubiquitously present in aerosol particles, is considered an important complexing ligand alongside formate and acetate. The complexation of Fe(III) by such ligands can additionally promote the photo-reduction to Fe(II) (Shi et al., 2012). Increased solubility in fog samples in the presence of metal-organic complexes has, for example, been observed by Giorio et al. (2025).

12) Why is Fe(II) and Fe(III) vs Fe2+ and Fe3+ used at various times? It seems random, or is there meaning in this?

Thank you for pointing out this inconsistency. There was no meaning behind it. All Fe^{2+} and Fe^{3+} are replaced by Fe(II) and Fe(III), respectively.

13) Figure 2 schematic could use some clarification, ie label the 6 port valve and 2 way pinch valve (I assume these are the black circles). It is not clear how the 6 port valve works. Eg, in the figure, what is happening? What do the dotted lines mean? How is the sample in the sample loop injected – no pumps (peristaltic channels) are shown – showing these might help?

Thank you for pointing out the missing clarity. We have changed Figure 2. Now, it includes the two positions of the 6-port-valve during inject and load mode. We have further changed the Figure caption as follows:

Figure 1: Schematic diagram of the measurement setup in detail. During LOAD mode, the aerosol sample solution is transferred into the injection loop of the six-port valve, while the carrier stream flows through the FIA system. After the injection loop is filled (10 min for the MARS-FIA and 12 min for the PILS-FIA), the automated six-port valve switches to INJECT mode. In INJECT mode, the carrier stream is directed through the injection loop, thereby pushing the sample toward the FIA. The sample is first transferred to a T-piece connected to a 2-port valve, where HA or H_2O are added alternately to the sample stream before entering the reduction coil. After passing the reduction coil, the sample stream enters a second T-piece where ferrozine is added prior to the reaction coil. Following the reaction coil, the sample enters the LWCC coupled to a spectrophotometer, where absorbance is measured.

We have further changed lines 214-233 to describe better how the FIA system worked. As Referee 2 also had question about the setup, we hope that it is now clear how the FIA setup works:

During LOAD mode of the six-port valve, a continuous sample flow from the MARS or PILS system was collected into the injection loop (600 µL for MARS and 400 µL for PILS), both exceeding at least 1.5 times the volume of the LWCC (see Figure 2). Due to the different sample flow rates (MARS: 0.1 mL min^{-1}; PILS: 0.05 mL min^{-1}), a smaller injection loop volume was used for the PILS–FIA system compared to the MARS–FIA system to achieve comparable injection time resolution. While the sample solution filled the injection loop, the carrier stream passed through the FIA system, providing the baseline signal. The carrier flow rate was set to 1.0 mL min^{-1} for the MARS–FIA system and 0.5 mL min^{-1} for the PILS–FIA system. The pH of the carrier stream was adjusted to match the pH of the respective sample flow (pH 6.5 for MARS and pH 4.5 for PILS).

To ensure complete filling of the injection loop, sampling times of 8 min for the MARS–FIA system and 10 min for the PILS–FIA system were applied. Accordingly, the six-port valve switched from LOAD to INJECT mode after 8 min (MARS–FIA) and 10 min (PILS–FIA). During INJECT mode, the sample solution was injected into the carrier stream (see Figure 2). At the first mixing point, either hydroxylamine hydrochloride (HA) solution or Seradest water (H_2O) was introduced into the carrier stream via a two-port switching valve (flow ratio carrier : HA/H_2O = 10 : 1). The injection valve was switched back to LOAD mode after 2 min, so that fresh extractant solution was filled into the loop thereby decreasing waiting time for the subsequent injection and increasing the sampling frequency.

For each LOAD–INJECT cycle, only one reagent was added to the sample stream. The addition of HA and H_2O was alternated between consecutive LOAD cycles, such that HA was added during one cycle and H_2O during the subsequent cycle. The two-port valve was switched during each LOAD mode after the peak of the previous sample had been fully detected. Because the addition of HA caused a baseline shift, the switching between HA and H_2O was carefully timed to occur between two consecutive peaks.

14) Figure 3. Is the vertical axis label correct? Is it total ws-Fe, not ws-Fe?

You are right, there was an error in the y-axis label which now has been changed. The caption was adapted as well.

15) In Figure 4, state in the Fig caption the pH of the filter extracts. Was the pH of the MARS and Filter extracts the same?

The extraction solution was adapted to the pH of the sampling system as described in the Figure caption. We compared filter extraction with the online system considering the two different used pH values. By this experiment we found out the underestimation at pH 4.5 in the PILS setup underlining the impact of extraction time on the concentration of water-soluble iron at slightly acidic pH. It underlines even more that the measured water-soluble iron concentrations are determined by the methodological approach and that a clear definition might help to compare the results from different methods with each other.

16) Lines 352 to 360. If the argument is that the MARS is higher than the filter due to all the various possible artifacts for the longer filter analysis time at the high pH of 6.5, why not test this with lower pH for both systems?

It is a very interesting point to measure the water-soluble iron fraction at different pH conditions which would represent different environmental conditions. We indeed tried to measure at lower pH values representing aerosol-water pH values. A lower pH was also expected to lead to an increasing signal as concentrations are expected to be higher, which in turn would mean that the system might be also applicable in more remote regions. Unfortunately, the acidification of the sample stream was more complicated than expected as both commercial particle-into liquid samplers are not designed for measurements at such low pH levels. In the PILS system there is a stainless steel wick. With low pH the iron blank value got very high. A system without any metal part would be required. In the MARS system, there is a heater for the steam production which is made out of metal. As we did not want to corrode the systems, we did not acidify the extraction liquids further. Summing it up, lower pH would be an interesting next step with particle-sampling systems adapted for such conditions.

Figure 5 caption, state the sampling method used, MARS (a), PILS (b).

The caption has been adapted.

Regarding the last section of the paper comparing the two measurement periods and seasonal variation; there are other studies on this, for example, https://doi.org/10.1289/EHP2182. https://pubs.acs.org/doi/10.1021/acs.est.0c00483

Thank you for pointing us towards these two very interesting publications. We have now included a discussion about the influence of sulfate on seasonal trends.

We have made the following changes in lines 561-575:
Similarly, Ye et al. (2018) analysed long-term filter samples collected in Atlanta from 1998 to 2013 and found that seasonal and long-term trends in ws-Fe closely followed sulfate concentrations, which were elevated in summer and showed a long-term decline attributed to reduced coal combustion. Based on the same data set, Wong et al. (2020) further concluded that sulfate promotes acidic aerosol conditions and particle water that enhance the dissolution of iron, with ws-Fe variability mainly controlled by particle liquid water and stronger effects in summer, while combustion sources contribute relatively more in winter.

In Europe, sulfate concentrations have decreased by approximately 0.15 µg yr^{-1} between 2000 and 2018 (Tsimpidi et al., 2025). This long-term decline likely contributes to the generally lower ws-Fe concentrations observed during the Berlin campaigns compared to those reported for Atlanta between 2008 and 2013 (average 24.22 ng m^{-3} , Ye et al., 2018). Nevertheless, ws-Fe concentrations measured during one week in March 2025 and during nearly three weeks in June 2025 were comparable, despite representing different seasons.

The absence of a clear seasonal difference in the present study may partly result from comparing measurements at two-nearby sites but still differently influenced by traffic. Importantly, however, the results of the second test campaign underline that the slightly acidic wash flow of pH 4.5 used in the PILS-FIA setup does not significantly affect iron's solubility or oxidation state during sampling compared to sampling in MARS with pH 6.5.

#######Referee 2###########

This manuscript presents the first online instrument capable of simultaneously measuring ws-Fe(II) and total ws-Fe in ambient aerosols using a FIA–LWCC system coupled to two aerosol sampling units (MARS and PILS). The development is technically meaningful, and the instrument shows promising potential for improving the time-resolved quantification of dissolved iron and soluble iron species—key parameters for understanding atmospheric aqueous-phase chemistry and Fe redox cycling.

Before acceptance, however, several scientific and methodological issues require careful clarification and revision. I recommend revision. Detailed comments are provided below.

1) Clarification of lines 45–47 — Misinterpretation of literature

Original statement:

"particularly when exposed to solar radiation and oxalate with nanometer sized, amorphous iron, especially from combustion sources (Baldo et al., 2022; Ito et al., 2019)."

It is unclear what the authors intend to convey. Do you mean that pyrogenic Fe exhibits higher dissolution rates under acidic conditions? If so, this needs to be stated explicitly. However, neither Baldo et al. (2022) nor Ito et al. (2019) make the statement currently implied in your sentence. Baldo et al. found that iron from coal combustion dissolves much faster than mineral dust under simulated atmospheric acidic conditions. Ito et al. emphasized that pyrogenic Fe shows higher solubility relative to crustal Fe.Please rewrite this sentence to clearly reflect the actual conclusions of the cited studies and your intended message.

Thank you for the comment. We intent to summarize under which conditions iron shows high solubility. Pyrogenic iron shows higher solubility compared to mineral dust since the iron is nanometer sized and amorphous. Furthermore, Chen and Grassian (2013), for example, showed that oxalate enhances solubility due to metal-ligand dissolution and enhance photo-reduction of Fe(III) to Fe(II). We added the citation of Chen & Grassian (2013) in the sentence to underline that this statement was neither made by Baldo et al. (2022) nor by Ito et al. (2019) but that it is more a summary:

Over the past decades, research consistently demonstrates that iron dissolution rates are highest under acidic conditions (pH < 4), particularly when exposed to solar radiation and oxalate (e.g. Chen and Grassian, 2013) with nanometer-sized, amorphous iron, especially from combustion sources (e.g. Baldo et al., 2022; Ito et al., 2019).

2) Definition of "water-soluble Fe (ws-Fe)" and discussion of extraction chemistry (Lines 64–66)

You define ws-Fe as Fe extracted either at pH 6.5 (MARS) or at pH 4.5 (PILS), simulating cloud water. Later in the manuscript, ws-Fe appears to be described as the sum of Fe soluble in Milli-Q water plus Fe soluble in slightly acidic solution, which introduces conceptual inconsistency. Currently, the description contradicts standard definitions. Many previous studies quantify soluble Fe using ammonium acetate (pH ~4.3) to approximate "readily soluble" Fe (e.g., Perron et al., 2020, Talanta, https://doi.org/10.1016/j.talanta.2019.120377).

I strongly recommend adding a subsection in Methods explicitly addressing:

- **How this definition compares with commonly used leaching solutions (e.g., acetate buffer).**
- **How the choice of pH affects the interpretation of "soluble Fe" relative to atmospheric processes.**
- **Clear definition and justification are crucial for interpreting the presented ws-Fe and ws-Fe(II) data**.

Thank you for pointing out the importance to define better our operational quantity. We have introduced a section defining the term water-soluble iron. As the concentration of dissolved Fe is dependent on pH and the pH can vary from highly acidic (<0) and neutral conditions (7) in atmospheric waters we used the term water-soluble to underline that our results only represent the iron fraction which is soluble at pH 6.5 and 4.5, thus being in the pH range of rain, fog and cloud water. ws-Fe has not been described as the sum of Fe soluble in Seradest water plus in slightly acidic conditions. The study compares the difference in using the online system at the two different pH conditions. To make that clear we have added the following new section in lines 107-132:

2.2 Definition of Water-Soluble Iron

The lack of a standardized protocol for determining trace metal solubility, including Fe, has been widely discussed in the literature (e.g. Tang et al., 2025; Perron et al., 2020; Meskhidze et al., 2016). Several studies have demonstrated that leaching or extraction procedures, including different chemical composition and pH value of the solutions as well as different contact time, strongly influence the measured metal's solubility (e.g. Li et al., 2023; Tang et al., 2025; Perron et al., 2020; Meskhidze et al., 2016). Most comparative studies investigating the effect of leaching solutions on iron solubility have used ultrapure water or organic buffers such as formate or acetate with a pH around 4.3 (e.g. Li et al., 2023; Perron et al., 2020; Majestic et al., 2006).

As no standard protocol exists, a variety of operational terms have been used in the literature to describe experimentally mobilised aerosol trace element fractions, including 'soluble', 'labile', 'leachable', dissolved', 'readily accessible', 'bioaccessible' and 'bioavailable', as summarized by Tang et al. (2025). The use of different extraction or leaching approaches and definitions complicate direct comparison of reported iron solubility and soluble iron concentrations across studies.

This study focuses on the analysis of the iron fraction which is soluble in Seradest water (pH6.5), used as a near-neutral reference condition, and Seradest water adjusted to pH 4.5 with HNO_3, providing mildly acidic, low-ionic-strength aqueous conditions representative of cloud-water acidity while minimizing additional chemistry introduced by adding buffering agents. The pH of the aqueous phase can vary widely, ranging from highly acidic conditions (pH<0) in deliquesced aerosols to neutral pH in rain and fog water (e.g. Pye et al., 2020; Herrmann et al., 2015). As discussed above, the solubility of atmospheric iron depends on particle size, chemical composition, photochemical activity and atmospheric processing, as well as on pH. To allow a clearer interpretation of our data, we therefore use the term *water-soluble iron* throughout this study, emphasizing that the reported values represent the fraction of iron that is soluble under neutral and mildly acidic aqueous conditions relevant to cloud, fog and rain water.

A key advantage of the online approach is the high temporal resolution of the measurements; however, the method requires short extraction and reaction times for both ferrozine and the reducing reagent hydroxylamine (HA), as will be discussed in section 3.1.1. Consequently, the quantity reported as ws-Fe(II) is operationally defined by the reaction time of dissolved Fe(II) with ferrozine. The term total ws-Fe refers to the amount of Fe detected as dissolved Fe(II) after addition of HA, which reduces dissolved Fe(III) to Fe(II) prior to complexation with ferrozine.

Some questions of the online analysis workflow

3) Time resolution of PILS sampling

"The reduced sample flow also leads to a longer sampling time of 12 min for the PILS system."

Does this mean the temporal resolution of PILS-FIA measurement is 12 min?

Yes, exactly. We get one signal every 12 minutes in the PILS-FIA setup. It includes 10 minutes of sampling and then 2 minutes of injection, before the injection loop is filled again for the next value. We have therefore made some changes from 'near-time' to "online" measurements. Thus , we have also changed the title from Real-Time Water-Soluble Iron Speciation…. To Online Water-Soluble Iron Speciation…

4) Valve switching during Fe(II) and total Fe measurement

During the sequence in which HA or water is introduced for Fe(III) reduction:

Is the six-port valve switched to waste, meaning no aerosol sample solution is injected during Fe(III) reduction and Fe(II)–FZ complex formation? If so, this should be clearly illustrated in Figure 2 and explained in the text. This is essential for understanding how continuous the measurements truly are.

As referee 1 had similar questions about the 6-port-valve we have added the INJECT and LOAD mode in Figure 2. During injection the injection loop is emptied by the carrier and thus cannot be refilled by new sample coming from the particle-into-liquid-sampling unit. This means that during INJECT mode sample coming from the particle-into-liquid sampling is transferred to waste, yes. When the 6-port-walve switches pack to LOAD the injection loop is filled again.

We have rewritten section 2.3.2 lines 214-232 hoping that it now better illustrates how the system works:

During LOAD mode of the six-port valve, a continuous sample flow from the MARS or PILS system was collected into the injection loop (600 µL for MARS and 400 µL for PILS), both exceeding at least 1.5 times the volume of the LWCC (see Figure 2). Due to the different sample flow rates (MARS: 0.1 mL min^{-1}; PILS: 0.05 mL min^{-1}), a smaller injection loop volume was used for the PILS–FIA system compared to the MARS–FIA system to achieve comparable injection time resolution. While the sample solution filled the injection loop, the carrier stream passed through the FIA system, providing the baseline signal. The carrier flow rate was set to 1.0 mL min^{-1} for the MARS–FIA system and 0.5 mL min^{-1} for the PILS–FIA system. The pH of the carrier stream was adjusted to match the pH of the respective sample flow (pH 6.5 for MARS and pH 4.5 for PILS).

To ensure complete filling of the injection loop, sampling times of 8 min for the MARS–FIA system and 10 min for the PILS–FIA system were applied. Accordingly, the six-port valve switched from LOAD to INJECT mode after 8 min (MARS–FIA) and 10 min (PILS–FIA). During INJECT mode, the sample solution was injected into the carrier stream (see Figure 2). At the first mixing point, either hydroxylamine hydrochloride (HA) solution or Seradest water (H_2O) was introduced into the carrier stream via a two-port switching valve (flow ratio carrier : HA/H_2O = 10 : 1). The injection valve was switched back to LOAD mode after 2 min, so that fresh extractant solution was filled into the loop thereby decreasing waiting time for the subsequent injection and increasing the sampling frequency.

For each LOAD–INJECT cycle, only one reagent was added to the sample stream. The addition of HA and H_2O was alternated between consecutive LOAD cycles, such that HA was added during one cycle and H_2O during the subsequent cycle. The two-port valve was switched during each LOAD mode after the peak of the previous sample had been fully detected. Because the addition of HA caused a baseline shift, the switching between HA and H_2O was carefully timed to occur between two consecutive peaks.

5) Reduction of Fe(III) by hydroxylamine – residence time and reaction completeness

In the reduction coil, Fe(III) is reduced to Fe(II) by hydroxylamine hydrochloride (HA). Unlike some batch methods using ascorbic acid that require ~30 min residence time to ensure complete Fe(III) reduction (Perron et al., 2020, Talanta; Zhi et al., 2025, ES&T, https://doi.org/10.1021/acs.est.4c12370), the manuscript does not discuss:

- **the residence time in the reduction coil,**
- **whether the mixing with HA and ferrozine in the tubing is sufficient,**
- **or any calibration tests to confirm complete Fe(III) reduction within the online system.**

Please provide:

- **the internal volume and corresponding residence time in the reduction coil and reaction coil,**
- **experimental evidence (or literature support) that HA achieves complete Fe(III) → Fe(II) reduction within this timeframe,**
- **discussion of potential underestimation of total Fe if reduction is incomplete.**

- **This is a critical issue because incomplete Fe(III) reduction would directly bias the reported total ws-Fe.**

Thank you for pointing out that the reduction time was not discussed enough. The reduction times were included in Table 1 before and are now explicitly mentioned in the text. Reduction efficiency was regularly tested with a single standard and compared with the ws-Fe(II) concentrations. As discussed in response to reviewer 1, we observed a decrease in recovery with aged and non-acidified standards, probably due to hydrolysis of ws-Fe(III) to less soluble and reducible Fe(III). The reduction time is short, but comparable with other FIA methods. As the reduction might not be complete we introduced the term reducible Fe(III). Of course, this in turn means that also total ws-Fe only represents the soluble iron fraction concentration limited by the kinetics of the setup.

We have added the following paragraph in lines 311-330:

Reduction efficiency was tested with single dissolved Fe(III) standards of pH 3.5 and showed high efficiency, varying between 80-117% relative to dissolved Fe(II) when standards were freshly prepared. A decrease in reduction efficiency was observed with increasing age of the dissolved Fe(III) standards likely due to the formation of hydrolysed Fe(III) species which are not rapidly reduced by HA. This observation highlights that, under the short reduction times in the FIA system, less reactive or less reducible Fe(III) species may not be fully reduced. Previous studies have used HA as reducing solution in flow injection systems applying very short reaction times (HA and ferrozine together) of approximately 1 minute (e.g. Pullin and Cabaniss, 2001; Teixeira and Rocha, 2007). In the presented systems the reduction times were 20 s for the MARS and 40 s for the PILS system. The reaction times with ferrozine were 78 s for the MARS and 157 s for the PILS system (Table 1). Therefore, the total time for the reduction of dissolved Fe(III) to Fe(II) was 98 s for the MARS and 197 s for the PILS system. Pullin et al. (2007), using an acetate buffer carrier of pH 4.0 and a reaction temperature of 65°C, reported 100 % reduction efficiency by adding acetic acid to the carrier and colour reagent suggesting that the acetate buffer forms a complex with the dissolved Fe(III). As no buffer solution was used in the present FIA apparatus, the addition of acetic acid had no effect on reduction efficiency when injecting aged Fe(III) standards. Heating of the reduction coil in a water-bath as reported by Pullin et al. (2007) was not applied to reduce the technical complexity for a system which is intended to run continuously for a long period of time. Similarly, heating was not applied in many other FIA systems designed for ws-Fe(II) /(III) determination (e.g. Attiyat et al., 2011; Teixeira and Rocha, 2007).

Luther et al. (1996) reported incomplete reduction of dissolved Fe(III) by HA in the presence of humic-like substances.

To acknowledge this limitation imposed by the operational given reduction time, further on we use the term reducible Fe(III) instead of ws-Fe(III). This also underlines that total-ws Fe is defined by the kinetics of the FIA system and might also underestimate the total ws-Fe concentration compared to studies with longer reduction times.

6) Organic-ligand–driven Fe dissolution

line 445 "They demonstrated that ws-Fe is formed through the dissolution of iron in water mediated by specific organic compounds present in the exhaust."

The current statement focuses on the large driver in water-soluble iron from primary VOCs in exhaust. Please expand it briefly to reflect that, in addition to primary VOC-derived organics, common atmospheric ligands such as formate, acetate, and oxalate can complex Fe^{3+} and enhance both dissolution and photoreduction to Fe^{2+} (Shi et al., 2012, https://doi.org/10.1016/j.aeolia.2012.03.001; Chen and Grassian, 2013, https://doi.org/10.1021/es401285s). Recent observations also show oxalate enrichment in aged supermicron particles (Li et al. 2025, https://doi.org/10.1093/nsr/nwaf221), implying aging-dependent effects.

Please revise this section to incorporate these studies and clarify the organic-mediated pathways promoting Fe solubility.

Thank you for the great idea to incorporate briefly the dissolution pathways by organic ligands. We have added the following paragraph in lines 534-542:

In addition to organic compounds emitted directly from exhaust, common atmospheric ligands can enhance solubility, even under moderately acidic conditions (Chen and Grassian, 2013). Deprotonated ligands replace surface OH groups, thus forming a bidentate surface complex, which destabilizes the Fe-O bond (Wang et al., 2017). The formation of organic ligand-Fe complexes in the aqueous phase enhances further Fe dissolution from the aerosol into the liquid water phase (Sakata et al., 2022). Oxalate, which is ubiquitously present in aerosol particles, is considered an important complexing ligand alongside formate and acetate. Recently, oxalate has been observed in aged dust particles, which can enhance dissolution (Li et al., 2025). The complexation of Fe(III) by such ligands can additionally promote the photo-reduction to Fe(II) (Shi et al., 2012). Increased solubility in fog samples in the presence of metal-organic complexes has, for example, been observed by Giorio et al. (2025).

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