Acid-Catalysed Dissolution of Iron in Brake Wear Aerosol

BY

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Abstract

Identifying sources of water-soluble iron (WS-Fe) in the environment is important in understanding the biogeochemical iron cycle and because of human health impacts associated with exposure to iron-containing aerosol. A main mechanism of iron solubilisation is through acid-catalysed reactions in atmospheric aerosol and cloud droplets. In this study the acid-catalysed dissolution of iron in brake wear aerosol was investigated to determine whether brake wear could be an anthropogenic source of WS-Fe. It was found that the iron in brake wear particles becomes soluble when suspended in solutions similar to atmospheric aerosol pH conditions and that the dissolution happens quickly enough to be atmospherically relevant. In solutions of nitric acid and sulphuric acid at pH 1, 2, and 3, 50-100% of available iron was dissolved within 10 hours. The dissolution was found to be very pH dependent, with an approximately 90% decrease in dissolved iron when pH is increased from 1 to 4, suggesting the reaction is highly proton driven. The dissolved iron was speciated and it was found that 75 ± 2.5% was Fe(III) and 25 ± 2.5% was Fe(II) for solutions of sulphuric acid at all pH levels and nitric acid at pH 2-4. However, in nitric acid solutions at pH 1, Fe(II) was completely oxidised into Fe(III). It was found that this oxidation increased with increasing nitrate concentrations at pH 1, suggesting nitrate has a role in the dissolution of iron. These results show that brake wear aerosol could be an important anthropogenic source of WS-Fe in the atmosphere.

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1. Introduction

1.1 Motivation

Iron is an essential nutrient for most life on earth, and the availability of iron can be a limiting factor in organism growth, for example bioavailable iron is a limiting nutrient for phytoplankton growth in high nutrient low chlorophyll (HNLC) parts of the ocean[1–3]. For iron to be bioavailable it must be in a soluble form. The most biologically, environmentally, and chemically relevant oxidation states of iron are Fe(II) and Fe(III)[4]. Iron in rocks and mineral dust is insoluble, and therefore not bioavailable; however there are several mechanisms in the environment through which it can become soluble[5]. Fe(II) is the most soluble and biologically relevant form of iron, however in neutral to basic conditions it is readily oxidised to the more thermodynamically stable Fe(III)[4,6].

The global iron cycle is the biogeochemical cycling of iron through its different forms and oxidation states in the atmosphere, biosphere, hydrosphere and lithosphere[7]. There is a knowledge gap in accounting for the pathways through which iron becomes bioavailable as the amount of bioavailable iron observed in the biosphere cannot be accounted for by known pathways of iron solubilisation, suggesting either unknown direct sources of WS-Fe or reaction generating WS-Fe from insoluble forms[1,2,7–10].

In addition to environmental implications WS-Fe in the atmosphere is a human health concern. Inhalation of WS-Fe is known to cause the formation of reactive oxygen species (ROS) in the body as Fe(II) participates in the Fenton reaction, where Fe(II) is oxidised to Fe(III) by hydrogen peroxide, which is an ROS[11–13]. Following its formation, ROS reacts and depletes antioxidants in the body, leading to a condition called oxidative stress, which negatively affects cardiovascular and respiratory health[13]. In fact, a recent epidemiological study in the South-eastern region of USA has indicated that emergency hospital admissions for cardiovascular diessiaes issues over a fifteen year periodis most highly correlated to WS-Fe concentration in ambient aerosol compared to all other aerosol chemical components/species and even aerosol particle mass[12].

1.2 Acid-Catalysed Reactions on Aerosol Particles

A major way that iron is solubilised is through reactions occurring in atmospheric aerosol particles[14,10,1,15]. Previous research has shown that during atmospheric transport, aerosol particles containing insoluble iron, such as mineral dust and fly ash, can undergo processing in aqueous aerosol and cloud droplets which solubilises the iron[16–19]. In fact, aerosol deposition of mineral dust was identified to be a major source of iron for the oceans, however, given that the form of iron in mineral dust is predominantly insoluble, it was hypothesised that processing must take place during atmospheric transport to convert the iron into a bioavailable form[1,8,9]. In 1992 Zhuang et al. looked at iron transportation and marine deposition from mineral dust and the mechanisms through which it can be solubilised[2]. They suggested that aerosol acids, specifically sulphuric acid, must react with iron, because cloud (which generally has a higher pH than aerosol), photo-reductive, and ocean processing did not totally account for iron solubilisation. Following this seminal study, natural, anthropogenic, pyrogenic, and lithogenic sources of aerosol iron have been investigated and identified as sources of WS-Fe[2016,21,2,8,22]. Laboratory experimentation has been done to further study the reactions that occur in aerosol conditions[9,23–28]. Such studies have shown that iron dissolution in aerosol conditions is highly pH dependent[9,23–28]. Understanding the rate and pH dependence of these reactions as well as the effect of different acids is important, because it has seasonal and regional implications in the atmosphere, as species of acid and pH of aerosol change by region and season[29]. Nitric acid and sulphuric acid from pH 1 to 4 were chosen as reaction conditions for this study because these range of conditions are representative of atmospheric aerosol.

The dependence of iron dissolution on pH suggests that these reactions are highly proton-driven. Forms of insoluble iron aerosol vary based on the source, however generally it is in the form of iron oxides[23,24,26]. The most likely mechanism for proton-driven dissolution of iron oxides is that protons bond to oxygen atoms, weakening and breaking the Fe-O bond, bringing Fe into solution[9,30,24,26,28,31]. This is illustrated in Figure 1.2.1.

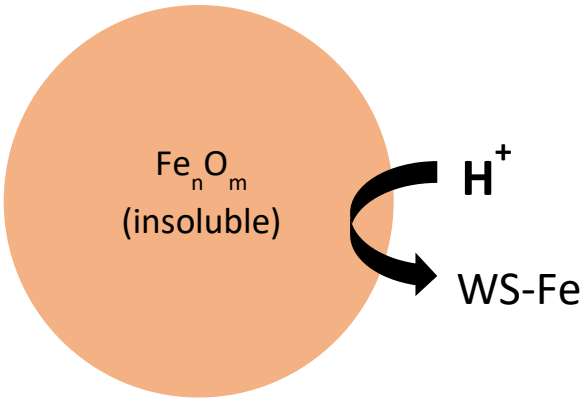

Figure 1.2.1. Illustration of proton-driven dissolution of iron. Insoluble iron in the form of general iron oxides dissolved into water-soluble iron (WS-Fe) by a proton (H^+).

1.3 Brake Wear Aerosol as a Source of Water-Soluble Iron

Brake pads are a disposable part of the braking system in most vehicles. They press against a stainless steel rotor, creating friction which slows the vehicle[32]. Brake pads are designed to wear down and to be replaceable; the friction caused by applying brakes causes the brake pad to wear down into a fine dust[33]. Hagino et al (2016) found that 36-73% of brake wear emissions are unaccounted for and could be contributing to gaseous and aerosol emissions[34]. There are three main types of brake pads: semi-metallic, ceramic, and organic[35]. Semi-metallic brake pads are the most commonly used and are made of a mixture of metallic and organic components, including many transition metals[34]. Gietl et al found that aerosol emissions from semi-metallic brake pads were 47-48% iron[36].

Correlational data has suggested that non-exhaust vehicle emissions may be a source of WS-Fe[37]. Because semi-metallic brake pads are a source of aerosol emission and contain large amounts of iron, they could possibly account for the WS-Fe from non-exhaust emissions[32].

1.4 Research Objectives

The goal of this project was to determine whether the iron in brake wear aerosol becomes soluble through acid processing in atmospheric aerosol conditions. This was done by suspending brake wear particles in solutions acidified to between pH 1 and 4 with sulphuric acid or nitric acid, because these are atmospherically relevant acids and pH conditions[29]. Aliquots were removed from solution periodically, over a 30 hour

reaction time, for determination of iron concentration. The compound 1,10-phenanthroline was used to complex dissolved iron in solution, in order to determine the concentration of iron using colorimetric methods. Another objective was to investigate the effects of acid and counterion species, and their concentration, on dissolution. To determine this, the dissolution of iron in sulphuric acid and nitric acid was compared and differences were analysed. These experiments will enable the assessment of whether or not brake wear aerosol could be an anthropogenic source of WS-Fe.

2. Materials and Methods

2.1 Chemicals

All chemicals were obtained from commercial suppliers and used without further purification. The following chemicals were obtained from Sigma-Aldrich and were ACS reagent grade, listed with percent purity in brackets: Iron(III) chloride (97%); copper(II) sulphate heptahydrate (>99.0%); hydroxylamine hydrochloride (99%); 1,10-phenanthroline monohydrate (99%); sodium fluoride (99%). Sulphuric acid was obtained from EM Science Inc., was ACS reagent grade and was of 95.0-98.0% concentration. Hydrochloric acid was obtained from Sigma-Aldrich and was ACS reagent grade, 37% concentration. Nitric acid was obtained from Anachemia, was ACS reagent grade and 68.0-70.0% concentration.

2.2 Collection of Brake Wear

Brake wear particle samples were collected by manually rubbing a NAPA ProFormer disc brake pad against a NAPA stainless steel rotor. This produced a dust which was used for further experimentation. Note that this was done by hand, and therefore the actual force applied was far less than that during actual braking by a vehicle. The dust was collected from a clean Teflon surface and stored in a small capped plastic centrifuge tube. The dust was collected and used as needed and was stored exposed to air and ambient light.

2.3 Dissolution Experiments

Approximately 1.0 mg of brake wear was added to 50 mL plastic vials, to which 50 mL of acid solution was added. Solutions contained 50 mL of deionised miliQ water

and either sulphuric acid or nitric acid at pH 1, 2, 3, and 4 ±0.01, confirmed with a pH meter. These acids were chosen because both nitric acid and sulphuric acid are very common in the atmosphere and these pH conditions were chosen because they reflect the pH range of aerosol; in Canada pH 1 is typical of aerosol in August and pH 4 is typical of January. To investigate the effect of nitrate ion, solutions were acidified to pH 1 with sulphuric acid and 0.1, 0.01, and 0.05 M sodium nitrate was added. Given the solute and brake pad concentrations, these dissolution experiments best represent reaction conditions that occur in suspended aerosol and cloud droplets in the atmosphere.

Reaction vials were covered with foil throughout the experiment to simulate dark conditions. Vials were kept well mixed on a vortex mixer for 30 hours. Aliquots were periodically removed from solution for analysis.

2.4 Dissolved Iron Quantification and Speciation

To determine the concentration of water-soluble Fe(II) and Fe(III) in solution throughout the reaction, modifications were made to methods used by Cwiertny et al and Chen et al[23,24]. This colorimetric absorbance method quantifies dissolved iron based on the formation of a coordinated complex between 1,10-phenanthroline and Fe(II). Aliquots were filtered using a 0.45 µm syringe filter to remove insoluble particles, leaving only dissolved iron. One (1.0) mL of the filtered solution was added to a 15 mL centrifuge vial, also wrapped in foil and capped, and 200 µL of 0.45 M ammonium acetate buffer was added to bring the solution to a pH suitable for complexation. For determination of Fe(II) 50 µL of 0.45 M sodium fluoride was added, as sodium fluoride ensures that only Fe(II) can complex the 1,10-phenanthroline, because at high concentrations of Fe(III) it can also complex 1,10-phenanthroline. For determination of total dissolved iron in solution, the sum of Fe(II) and Fe(III), 50 µL of 1.5 M hydroxylamine hydrochloride was added. Hydroxylamine hydrochloride reduces Fe(III) to Fe(II). After addition of the reagents, the solutions were left for 30 to 60 minutes, then 200 µL of 5 mM 1,10-phenanthroline was added and left for 10 to 60 minutes. The complex needs at least 10 minutes to form and is stable for up to an hour[38]. Deionised water was then added, bringing the solution to a final volume of 11.45 mL and a Vernier UV-Vis spectrophotometer was used to measure absorbance at 510 nm.

Standards were made using iron(III) chloride to quantify dissolved Fe(II+III) concentration, and iron(II) sulphate heptahydrate was used to quantify dissolved Fe(II). Appropriate volumes of iron stock solution were added to a 15 mL vial and 1 mL of either sulphuric acid or nitric acid between pH 1-4 was added and 200 µL of 0.45 M ammonium acetate was added. To the iron(III) chloride standards 50 µL of 1.5 M hydroxylamine hydrochloride was added to reduce the Fe(III) to Fe(II) for colorimetric determination. To the iron(II) sulphate heptahydrate 50 µL of 0.45 M sodium fluoride was added. The vials were left for 30 minutes, then 200 µL of 5 mM 1,10-phenanthroline was added. The solutions were then diluted with deionised water, and the absorbance at 510 nm was determined. Standards ranged from 0-3.5 ppm, calibration curves were constructed and the linear equation was used to calibrate dissolved iron concentration. Calibration curves were done every couple of weeks to account for any variation in the instrument.

2.5 Total Available Iron Determination

Total available iron represents the total amount of iron that can possibly be dissolved from the particles. For this, much harsher conditions were necessary. Aliquots of sulphuric or nitric acid solutions, of any pH, from the dissolution vials described above, were placed in 50 mL centrifuge vials with a small hole punched in the cap. Aqua regia was made using 1:3 nitric acid to hydrochloric acid and was added to the vial in a 1:5 ratio of dissolution solution to aqua regia. The solution was then sonicated for 2 hours. After sonication the solution was neutralised with sodium hydroxide to a pH between 1 and 4. Aliquots of solution were placed in 15 mL vials and the iron was quantified as described above. This methodology was optimised by trying different volume ratios of aqua regia and various sonication times and comparing the resulting concentrations of iron. Too much or too little aqua regia and sonication caused a decrease in iron signal.

Standards for total available iron were made similar to the standards described above however, instead of nitric or sulphuric acid solution, aqua regia was added to the standards and they were sonicated for 2 hours.

Using the dissolved and total available iron concentrations, the effective percentage of iron in solution was calculated using the following equation:

$$Percentage\ of\ dissolved\ iron = \frac{[dissolved\ iron]}{[total\ available\ iron]}$$

3. Results and Discussion

Brake wear particles were reacted in solutions of sulphuric acid and nitric acid at pH 1, 2, 3, and 4. These pH conditions were chosen because they are representative of the conditions of acidic aerosol in the atmosphere[29]. Dissolution of iron progressed quickly at pH levels 1 to 3. In both acids, at pH 1-3, there was little to no dissolved iron in solution at the beginning of the reaction, but within 10 hours 60-100% of the available iron was dissolved, and between 15 and 30 hours, in most solutions, the percentage of dissolved iron did not increase. These results imply that with respect to time, this reaction is atmospherically relevant. Smaller aerosols can stay in the atmosphere for weeks, so if this reaction occurs in the atmosphere, it happens quickly enough that most of the iron could be dissolved before the particles are deposited[39].

3.1 pH Dependence

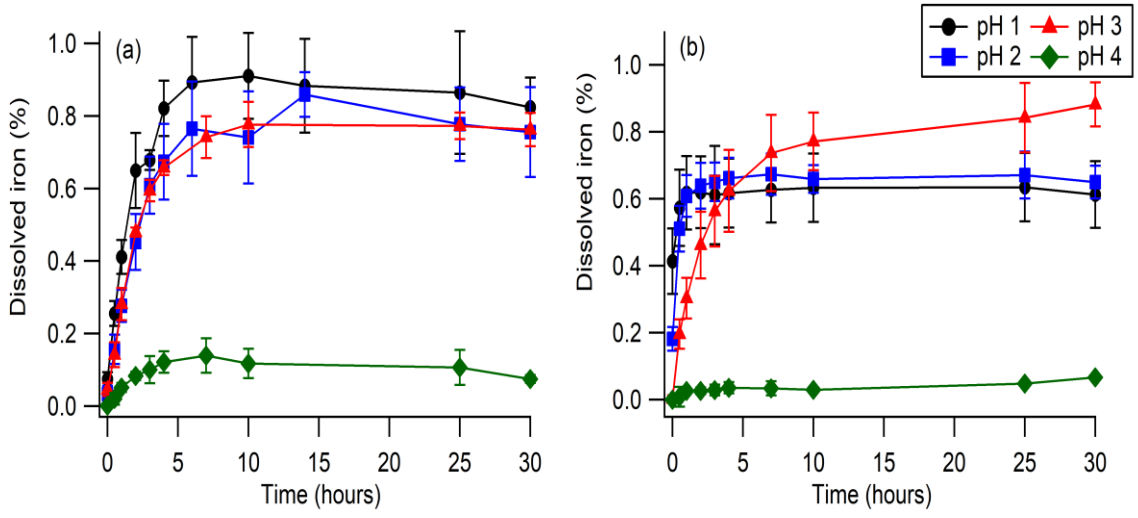

Figure 3.1.1. Dissolved iron (%) as a function of time (hours) at pH 1, 2, 3, and 4. Solutions acidified with (a) sulphuric acid and (b) nitric acid.

The dissolution of iron is pH dependent, as clear from Figure 3.1.1. In both sulphuric and nitric acid solutions, although pH 1, 2, and 3 dissolve a similar amount of

iron, between 50-100%, dissolved iron decreases significantly at pH 4, with those conditions dissolving less than 20% of the available iron. The difference in total dissolved iron between pH 1 and pH 4 in both acids is ~90%. This significant decrease in dissolved iron suggests the reaction is highly proton driven. In nitric acid solutions pH 3 may dissolve more iron than pH 1 and 2, however taking error into account, it is unclear whether this is the case.

In sulphuric acid solutions, at all pH levels, there was almost no dissolved iron at hour zero of the reaction (seen in Figure 3.1.1), which was also seen in nitric acid solution at pH 3 and 4. However in nitric acid solutions there was observed an increased amount of dissolved iron at hour zero of the reaction. In pH 1 and 2 conditions dissolved iron percent was approximately 40% and 20%, respectively, at hour zero of the reaction. This increased dissolved iron could be due to iron contamination in the reagents, specifically the nitric acid, although this is not likely as this increase was not seen in standards or blanks. This increased initial dissolved iron could be because the reaction is happening very quickly. The concentration used for hour zero is in reality 3-7 minutes after the acid has been added to the brake wear particles, which is the time it takes to remove and filter aliquots, stopping the dissolution. In these few minutes the acid could be solubilising iron, leading to the increased dissolved iron. There has been some indication that nitric acid may have an increased rate of dissolution compared to sulphuric acid.

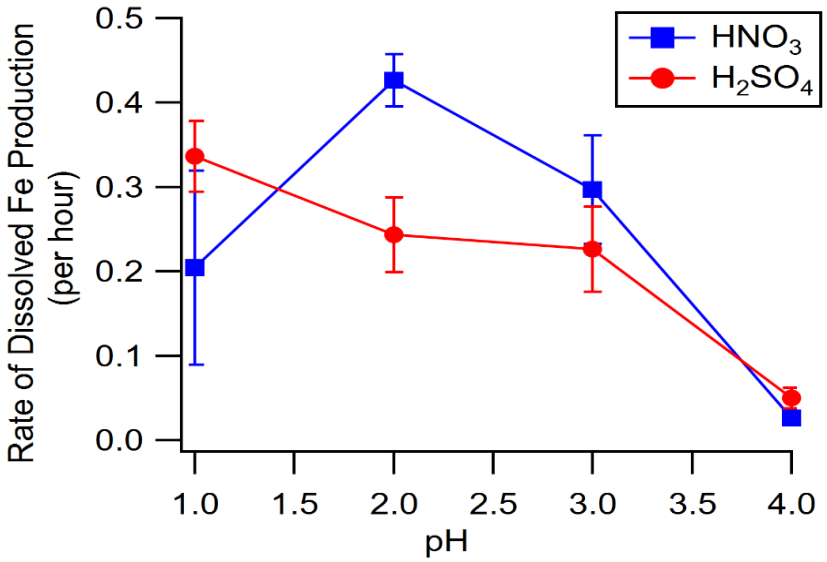

Figure 3.1.2. Rate of dissolved iron production (percentage of dissolved iron per hour) as a function of pH for solutions of nitric acid and sulphuric acid. Rate taken as the slope of the linear plot of the first hour of the reactions.

It was observed that the initial rate of iron dissolution was also pH dependent. Figure 3.1.2 shows that in sulphuric acid solutions the rate of iron dissolution is clearly pH dependent; rate decreases as pH increases. In nitric acid solutions there was an apparent pH dependence between pH 2 to 4, but at pH 1 the rate appears to be lower than both pH 2 and 3 although there is large error is associated with this number. It is unclear whether this is accurately representative of the rate of iron dissolution and no conclusions can be made based on these results.

Previous literature studies have investigated the acid-catalysed dissolution of iron from multiple sources including mineral dusts and fly ash[26,28,40]. These studies also found that the amount of iron dissolved is highly pH dependent. Cwiertny et al (2008) dissolved Arizona test dust (AZTD) in solutions of hydrochloric acid and found that raising pH from 1 to 2 decreased total dissolved iron concentration by 70% and raising it from pH 1 to 3 led to a 90% decrease[24]. The Cwiertny et al study saw much more of a change in dissolved iron between pH 1, 2, and 3 than was observed in this study. Although there was a large decrease in total dissolved iron, approximately 90%, between pH 1 and 4, there is no clear difference in total dissolved iron between pH 1, 2, and 3. This is likely due to differences in the morphology and mineralogy of AZTD and brake wear particles.

In the Cwiertny et al study they determined using ICP-AES that the AZTD contained 1.48 ± 0.06 % mass of iron; this is much less than reported mass percentage of iron in brake wear, which Gietl et al reported to be 47-48% iron by mass[24,36]. Because brake wear particles have a much larger percent of iron by mass compared to AZTD, this may account for differences in observed pH dependence. In brake wear particles, less acid would be required to dissolve the same amount of iron than in AZTD, because in brake wear particles it is more readily accessed by the protons, and thus less of a pH dependence is seen.

The dissolution of iron in brake wear particles is also faster than the dissolution of iron in other sources. In this study, for solutions of both sulphuric and nitric acid at pH 1, 2, and 3, 60-80% of the iron in the brake wear particles was dissolved within 5-10 hours, and the percent of dissolved iron stabilised by 15 hours. In a study by Chen et al (2013) on the dissolution of iron in fly ash, they found that in solutions of sulphuric acid at pH 2, after 45 hours only about 40% of the available iron had been dissolved and that percentage was still increasing[26]. Cwiertny et al. (2008) used sulphuric acid and nitric acid at pH 1 to dissolve iron in several mineral dusts and found that after 30 hours the percentage of dissolved iron was only about 10-15% and still increasing[24]. The increased rate of dissolution in brake wear particles compared to mineral dusts and fly ash may be because the form of iron in brake wear particles is more easily dissolved by acid, or it could be because there is more iron by mass in brake wear particles than in mineral dust or fly ash, so the iron is more accessible to acid.

Although most of the iron in the brake wear particles was dissolved within 7-30 hours, at pH levels of 1 to 3, the total percent of dissolved iron did not (definitively) reach 100% by 30 hours. This could be because there is a fraction of iron that cannot be solubilised in these conditions, or this could be because the reaction has significantly slowed, but not stopped completely. Although the concentration of dissolved iron seems to stabilise between 10 to 30 hours in most of the reactions, seen in Figure 3.1.1, the reaction may still be happening very slowly, and over a longer time the amount of dissolved iron could reach 100%. The reaction could slow down because of depletion of protons in solution, however this is likely not the case because after 30 hours the pH of

the solutions did not raise significantly. The reaction could also slow because the concentration of dissolved iron in solution is so high that it makes dissolution much less favourable. In real atmospheric conditions, if aerosols are mixing, dissolved iron could diffuse from the particle, decreasing the concentration of free iron in solution and possibly increasing dissolution to 100%.

3.2 Speciation of Dissolved Iron

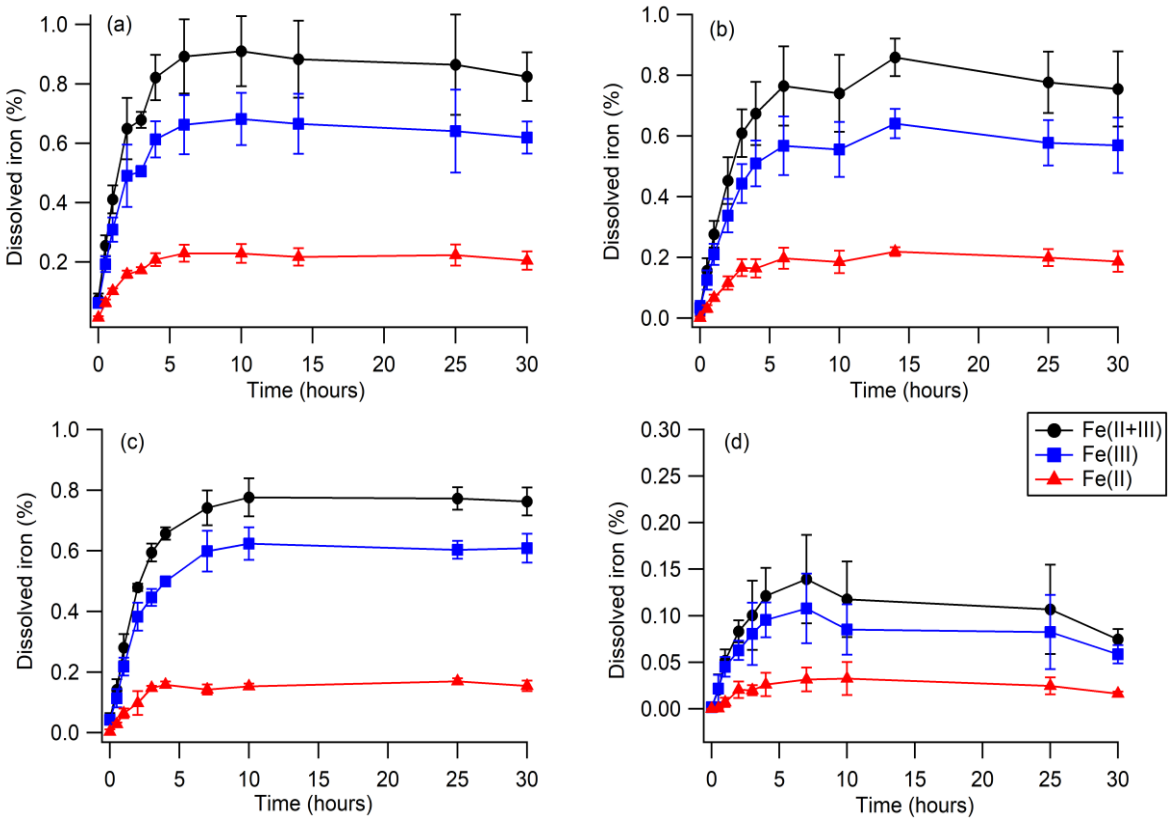

Figure 3.2.1. Dissolved iron (%) as a function of time (hours). Iron in solution speciated into Fe(II) and Fe(III). Solutions acidified with sulphuric acid to pH (a) 1, (b) 2, (c) 3, and (d) 4.

Throughout the dissolution experiments the iron was speciated into Fe(II), Fe(III), and their sum Fe(II+III), or total available iron. The major form of dissolved iron at all pH levels of sulphuric acid was Fe(III) which made up approximately 75 ± 2.5% of iron in solution, with the other 25 ± 2.5% in the form of Fe(II). The ratio of Fe(III) to Fe(II) remained approximately constant throughout the reaction. These observations are consistent with previous studies of dissolution of iron in fly ash and mineral dust in sulphuric acid solutions, where it was observed that the major form of iron was Fe(III), and the Fe(II) remained stable in solution throughout the reaction[23,24,26].

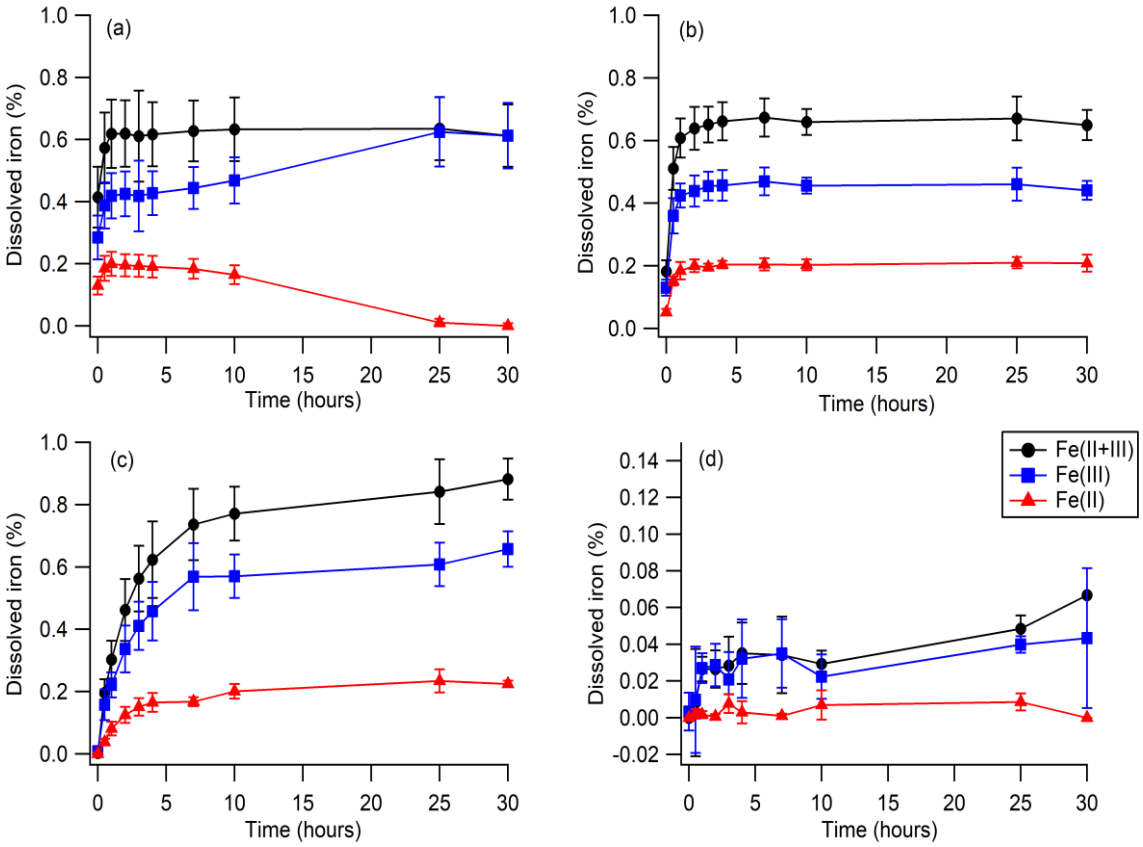

Figure 3.2.2. Dissolved iron (%) from brake wear as a function of time (hours). Brake wear dissolved in solutions of nitric acid at pH (a) 1, (b) 2, (c) 3, and (d) 4 as labelled. Iron is speciated into Fe(II) and Fe(III)

In solutions of nitric acid at pH 2 to 4, the same trends in speciation were observed. Throughout the reaction there was approximately 75 ± 2.5% Fe(III) and 25 ± 2.5% Fe(II) in solution. However in solutions of nitric acid at pH 1, seen in Figure 3.2.2 (a), the percentage of dissolved Fe(II) decreases as it is completely oxidised into Fe(III) between 6 and 30 hours. There was no effect on Fe(II)/Fe(III) ratio at different pH levels

or sulphuric acid solutions, suggesting that the oxidation is not solely dependent on proton concentration. This would suggest that nitrate ion is responsible for the oxidation of Fe(II) to Fe(III).

3.3 Comparison of Sulphuric Acid and Nitric Acid

The dissolution of iron in nitric acid and sulphuric acid was similar however there are some important differences between them. Figure 3.1.2 shows that, although there are unclear results for nitric acid at pH 1, nitric acid solutions at pH 2 and 3 have faster rates of iron dissolution than sulphuric acid at all pH levels tested. This may suggest that the nitrate ion plays a role in dissolution, leading to the increased rate. It has been suggested in previous studies that the nitrate ion dissolves insoluble iron through a ligand-promoted mechanism, in which nitrate directly chelates insoluble iron, weakening the irons other bonds and dissolving it into solution[24,31]. This could explain the faster rate of dissolution in nitric acid solutions of pH 2 and 3 compared to sulphuric acid solutions. The nitric acid dissolves iron from the insoluble particles through both proton-promoted and ligand-promoted mechanisms. Nitrate may also increase the rate of reaction by chelating dissolved iron in solution. This would decrease the concentration of dissolved iron in solution, making the dissolution of more iron increasingly favourable which could increase the rate of dissolution. Sulphate ion may also have this effect, however it may be less effective because sulphate is a weaker ligand for iron[24].

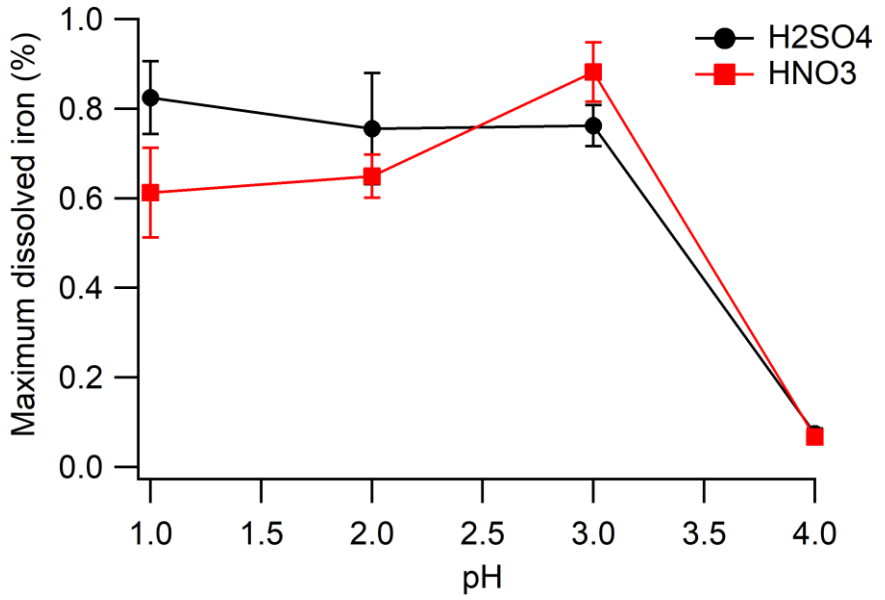

Figure 3.3.1. Maximum percentage of dissolved iron as a function of pH for sulphuric acid and nitric acid. Maximum dissolved iron is dissolved iron at 30 hours.

Although the rate of iron dissolution in nitric acid is faster than in sulphuric acid, it does not dissolve significantly more iron than sulphuric acid. Figure 3.3.1 shows the maximum percentage of dissolved iron at each pH, for each acid. At pH 1 sulphuric acid may dissolve slightly more iron than nitric acid but nitric acid at pH 3 has a similar maximum dissolved iron as pH 1 sulphuric acid. It is unclear whether one acid dissolves more iron than the other in total.

3.4 Nitrate as an Oxidiser

The oxidation of Fe(II) to Fe(III) in solutions of nitric acid at pH 1, seen in Figure 3.2.2 (a), and the fact that this effect is not seen in sulphuric acid solutions at pH 1 where the concentration of protons is the same, or nitric acid solutions at lower pH levels, suggests that the nitrate ion may have an oxidising effect on iron at high concentrations. This oxidising effect has been reported in multiple literature studies. Cwierntny et al. (2008) saw this effect in the dissolution of iron in mineral dust in nitric acid solutions at pH 1[24]. They observed decreased Fe(II) in solutions of nitric acid but not in solutions of

sulphuric acid or hydrochloric acid. They propose that nitrate oxidises iron through the following reactions[24]:

$$2Fe(II) \rightarrow 2Fe(III) + 2e^-$$

$$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O$$

Reaction 1. $Net\ reaction\colon\ 2Fe(II) + NO_3^- + 2H^+ \rightarrow 2Fe(III) + NO_2^- + H_2O$

At pH 1, nitric acid solutions have high concentrations of both nitrate and protons, so it is unclear which of the two, if any, is a limiting factor in the oxidation of Fe(II). To separate the effect of protons and nitrate, as well as to confirm results seen in nitric acid pH 1 solutions, dissolution of the brake wear was carried out in solutions acidified to pH 1 with sulphuric acid, and concentrations of sodium nitrate were varied.

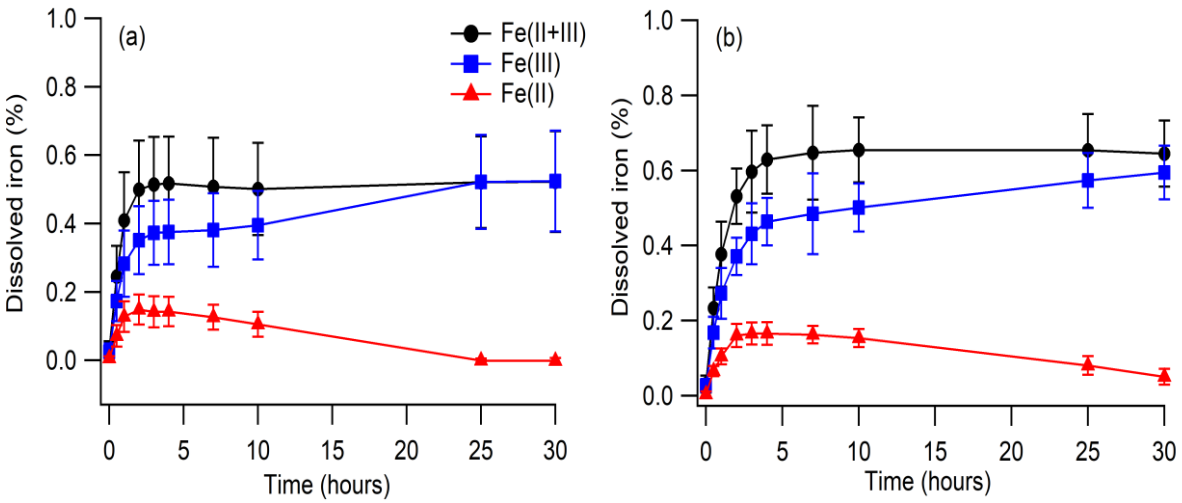

Figure 3.4.1. Dissolved iron (%) as a function of time (hours) in solution acidified to pH 1 with H_2SO_4, containing (a) 0.1 M sodium nitrate and (b) 0.05 M sodium nitrate.

As seen in Figure 3.4.1(a), when solutions of sulphuric acid are spiked with 0.1 M of sodium nitrate, the oxidation of Fe(II) is observed, which confirms the results of the nitric acid at pH 1 solutions. When the pH is kept the same and the concentration of nitrate is lowered by half, dissolved Fe(II) is still oxidised, however compared to solutions with 0.1 M nitrate the oxidation is not as effective.

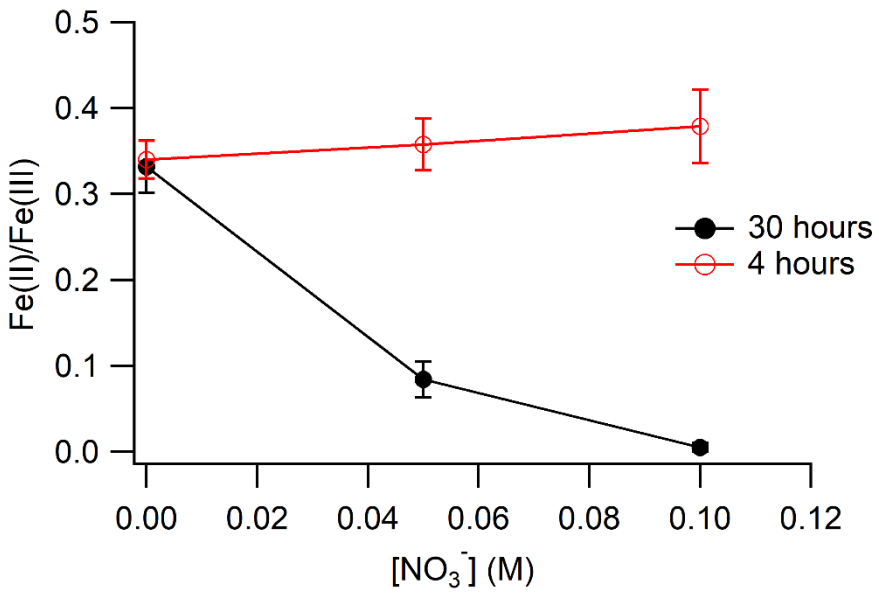

Figure 3.4.2. Ratio of dissolved Fe(II)/Fe(III) as a function of nitrate ion concentration at pH 1 after 4 hours and 30 hours. The 0 M data comes from sulphuric acid pH 1 data, 0.05 M is solution of sulphuric acid pH 1 and 0.05 M sodium nitrate, the 0.1 M data is from sulphuric acid and 0.1 M sodium nitrate

Figure 3.4.2 shows that in the beginning of the reaction, at 4 hours, the ratio of dissolved Fe(II) to Fe(III) is not dependent on nitrate concentration. But at 30 hours the ratio of dissolved Fe(II) to Fe(III) decreases as concentration of nitrate increases. This further indicates that nitrate is responsible for the oxidation of Fe(II) to form Fe(III). The ratio of Fe(II)/Fe(III) is constant across nitrate concentration at 4 hours, suggesting that this redox reaction does not happen until later in the reaction. This may be because Fe(II) concentration must build in solution before the reaction proceeds, because two Fe(II) ions are needed for every one nitrate ion. Protons also participate in the proposed redox reaction (Reaction 1), thus more experiments should be done, changing the concentration of protons and holding nitrate constant, in order to better understand the role of both nitrate ions and protons.

Based on the results that show nitrate plays a role in dissolution, it would be expected that nitric acid would dissolve more iron than sulphuric acid, because both nitrate and protons participate in dissolution, however this is not the case, as evident in Figure 3.3.1. At pH 1 sulphuric acid dissolves more iron than nitric acid. It is possible

this is because of increased consumption of protons in the nitric acid solution at pH 1. In the proposed redox reaction (Reaction 1) two protons are consumed to form water with an oxygen from the nitrate ion. This increased loss of protons, compared to sulphuric acid which does not undergo this redox reaction, could cause the decreased percentage of dissolved iron. Nitrate ion is also consumed in this reaction, which decreases the number of ions available to chelate iron. Competition between dissolution of iron and oxidation of iron could account for why nitric acid, although it has two possible mechanisms of iron dissolution, does not dissolve more iron than sulphuric acid.

4. Conclusions and Future Directions

4.1 Conclusions

In this study the dissolution of iron in brake wear particles and the effect of sulphuric acid, nitric acid, and nitrate ion was investigated. It was found that the iron in brake wear does become soluble through acid-catalysed reactions similar to aerosol conditions, meaning that brake wear could be a significant anthropogenic source of aerosol iron. At pH levels of 1-3 both nitric acid and sulphuric acid dissolved 50-100% of the iron from brake wear particles. These reactions occurred quickly enough to be atmospherically relevant, with most of the iron dissolved within 10 to 30 hours. The dissolution was also highly pH dependent. Increasing pH from 1 to 4 resulted in an 80-90% decrease in total dissolved iron, because the dissolution is proton-driven. The dissolved iron was speciated and found to be 75 ± 2.5% Fe(III) and 25 ± 2.5% Fe(II) in solutions of sulphuric acid at all pH levels, and nitric acid at pH 2-4. In solutions of nitric acid at pH 1 the Fe(II) is completely oxidised to Fe(III). The role of nitrate in the redox reaction was investigated and it was found that at the end of the reaction the ratio of Fe(II) to Fe(III) decreased as nitrate concentration increased, suggesting that nitrate is responsible for the oxidation of Fe(II) to Fe(III). Nitrate may also increase dissolution by chelating iron on the particle surface, dissolving it into solution, as well as chelating dissolved iron in solution, which could make dissolution more favourable. These effects may be responsible for the faster initial rate of dissolution seen in solutions of nitric acid at pH 2 and 3, compared to sulphuric acid. However the rate of dissolution at pH 1 is lower in nitric acid than sulphuric acid. Both acids resulted in a similar amount of total

dissolved iron, however at pH 1 sulphuric acid may dissolve slightly more iron than nitric acid. In conclusion, the iron in brake wear particles is readily solubilised in acidic conditions, meaning brake wear aerosol could be an anthropogenic source of WS-Fe in the atmosphere.

4.2 Future Directions

To further study the effect of nitrate ion on dissolution of iron from brake wear particles, further studies should be conducted. In future work, both proton and nitrate concentration should be varied, in order to better understand the redox reaction and how proton and nitrate concentration affects rate of dissolution and total dissolved iron. Understanding the factors affecting the redox reaction could possibly explain unexpected results. There may be competition between dissolution mechanisms and redox mechanisms which could account for decreased dissolved iron in nitric acid solutions at pH 1. The reaction could also be studied by directly measuring concentration of nitrite in solution, since nitrite is a product of the reaction and absorbs in the UV range between 210-200 nm[41].

These experiments were done under dark conditions, so the results are only representative of reactions occurring at night. Thus, repeating these reactions under simulated-sunlight conditions would demonstrate iron solubility in a wider range of atmospheric conditions. Photochemistry may increase the dissolution rate because of radical formation and it could also have a photo-reductive effect on iron. Some studies show that the presence of light increases rate of dissolution and total dissolved iron, however the effect of light is variable based on morphology of the source particles[25,26,31].

As mentioned before, the brake wear used in this study was collected by hand, by scraping a brake pad against a rotor to generate dust. This is not representative of an actual braking system, where there would be much more force used and the brake pad would be at a higher temperature. Studies have suggested that the temperature of the brake pad affects the morphology and size of the emitted particles[34,34,36,42–44]. Higher temperatures cause emissions of smaller particles[42]. Collecting emitted brake wear aerosol directly from a braking system would more ideally represent real world conditions. However simply sorting the particles by size and using the small, relevant

particles would make further studies more accurate and may decrease error that could be caused by differences in particle size across experiments and replicates.

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