

**The role of transition  
metal ions on HO<sub>x</sub>  
radicals in clouds**

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# The role of transition metal ions on HO<sub>x</sub> radicals in clouds: a numerical evaluation of its impact on multiphase chemistry

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## Abstract

A new modelling study of the role of transition metal ions on cloud chemistry has been performed. Developments of the Model of Multiphase Cloud Chemistry (M2C2; Leriche et al., 2001) are described, including the transition metal ions reactivity emission/deposition processes and variable photolysis in the aqueous phase. The model is then applied to three summertime scenarios under urban, remote and marine conditions, described by Ervens et al. (2003).

Chemical regimes in clouds are analyzed to understand the role of transition metal ions on cloud chemistry and especially, on  $H_xO_y$  chemistry, which consequently influences the sulphur and the VOCs chemistry in droplets. The ratio of Fe(II)/Fe(III) exhibits a diurnal variation with values in agreement with the available measurements of Fe speciation. In the urban case, sensitivity tests with and without TMI chemistry, show an enhancement of OH concentration in the aqueous phase when TMI chemistry is considered.

## 1. Introduction

Cloud, fog and rain chemistry have an important effect on both regional and global scales (Lelieveld and Crutzen, 1991; Jacob, 2000). Actually, there are still some remaining questions about processes in the atmospheric liquid phase related, in particular, to the role of transition metal ions, to the presence of VOCs (Volatile Organic Compounds), and to particulate matter that can act as cloud nuclei (Facchini, 2002).

TMI are incorporated into tropospheric liquid phase via aerosols, which often contain metal oxide particles. This metal oxide can turn into soluble metals by undergoing thermal and photochemical processes at the surface of the particles (Zuo and Hoigné, 1992; Erel et al, 1993; Siefert et al., 1994; Faust, 1994; Hoigné et al., 1994; Sulzberger et al., 1994; Sulzberger and Laubscher, 1995). When aerosol particles act as CCN (Cloud Condensation Nuclei), soluble metals dissolve into cloud droplets.

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Various field campaigns report concentrations of dissolved trace metals into rainwater (Jickells et al., 1984; Ross, 1987; Lim et al., 1993) and in cloud water samples (Anastasio et al., 1994; Sedlak et al., 1997). Laboratory measurements also demonstrate the transfer of trace metals from the solid to the liquid phase (Spokes et al., 1994; Desboeufs et al., 1999). Iron (Fe), manganese (Mn) and copper (Cu) are the most abundant transition metals in the atmospheric liquid water as well as in aerosols. The major effects of transition metals are principally linked to the homogeneous aqueous phase chemistry.

Graedel et al. (1986) first attempted to explain the complex redox chemistry of transition metals in atmospheric water through the development of a detailed kinetic model. Their results indicated that transition metals (Cu(I) and Cu(II), Fe(II) and Fe(III) and Mn(II) and Mn(III)) could play an important role in the radical chemistry of the atmospheric water phases. They predicted that photolysis of Fe(III)-complexes should be important in-cloud sources of OH radicals, and that transition metals should be the most important sinks for HO<sub>2</sub>/O<sub>2</sub><sup>-</sup> radicals in clouds. Following this theoretical study, some aspects of the transition metal redox chemistry in atmospheric waters have been investigated through laboratory studies.

Observed Fe(II) in atmospheric aqueous phases is produced through photolysis of Fe(III) hydroxo species (Faust and Hoigné, 1990), photolysis of Fe(III)-oxalato-complexes (Zuo and Hoigné, 1992; Faust and Zepp, 1993), and also by reactions of HO<sub>2</sub>/O<sub>2</sub><sup>-</sup> radical or Cu(I) with Fe(III)-hydroxo-complexes (Sedlak and Hoigné, 1993). Transition metal ions, Fe(II) and Fe(III) and especially copper (I and II), were shown to be very reactive with HO<sub>2</sub>/O<sub>2</sub><sup>-</sup> radical and catalyse very efficiently the self-reaction of HO<sub>2</sub>/O<sub>2</sub><sup>-</sup> yielding O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> (Sedlak and Hoigné, 1993). Cloud chemistry model calculations suggest that depletion of HO<sub>x</sub> by reactions between copper and HO<sub>2</sub>/O<sub>2</sub><sup>-</sup> radical slow down O<sub>3</sub> production significantly in polluted clouds (Matthijssen et al., 1997; Walcek et al., 1997).

In the atmospheric liquid phase, the speciation of dissolved Fe, Cu and Mn is still subject of major uncertainties. Especially, in the case of Mn, no measurement is avail-

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able. While most of the Fe(II) is thought to be present as the free Fe<sup>2+</sup> ion at pH < 3, most of the Fe(III) is complexed with OH<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and organic ions such as oxalate (Faust, 1994). Copper appears to be present as organic complexes (Spokes et al, 1996; Nimmo and Fones, 1997) which are less reactive towards HO<sub>2</sub>/O<sub>2</sub><sup>-</sup> radicals than towards free ions (von Piekowski et al., 1993). Key uncertainties for Cu and Fe are the complexation state of the metals and the kinetic reaction constants involving the metal complexes.

Transition metal ions are also potential catalysts in the autoxidation of S(IV) (Calvert, et al., 1985; Brandt and van Eldik, 1995). While recent laboratory studies have greatly improved our understanding of the metal ion catalysis, only the role of iron is now reasonably well understood. Catalytic activity of metals ions strongly depends on the reaction system, particularly on the oxidation state of the metal ions, on the pH and on the concentration level of:

- oxidants (e.g. HO<sub>2</sub>/O<sub>2</sub><sup>-</sup>, H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, OH, O<sub>2</sub>),
- reductants (e.g. HO<sub>2</sub>/O<sub>2</sub><sup>-</sup>, Cu(I), S(IV)),
- complexing agents (e.g. organic ligands like oxalate, formate, etc.).

Catalysis of S(IV) autoxidation by iron and manganese has been investigated in many laboratory studies (Conklin and Hoffmann, 1988; Kraft and van Eldik, 1989; Martin et al., 1991; Grgić et al., 1991; Berglund et al., 1993; Kotronarou and Sigg, 1993; Brandt et al., 1994; Berglund and Elding, 1995; Warneck and Ziajka, 1995). In Grgić et al. (1998, 1999), laboratory investigations showed that oxalate has a strong inhibiting effect on the conversion of S(IV) to S(VI) in the presence of Fe(II) or Fe(III) due to the formation of Fe(III)-oxalato-complexes. Moreover, when Fe(II) is initially predominant, an induction period appears where Fe(II) is oxidised into Fe(III) to become catalytically active. In Ziajka et al. (1994) and Nović et al. (1996), it has been shown that a steady state is established between Fe(II) and Fe(III) during the conversion of S(IV) to S(VI).

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The coexistence of two or more catalytically active transition metals in atmospheric liquid water exhibits a significant synergistic effect on the S(IV) autoxidation. (van Eldik et al., 1992). For example, S(IV) autoxidation catalysed with a mixture of Fe and Mn ions is significantly more effective than the catalytic effect of the individual metal ions (Grgić, 2001). Model studies show that catalysed metal reactions prevail on aqueous sulphate formation during the night in fog droplets where the H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> concentrations are low (Pandis and Seinfeld, 1992). The catalysed S(IV) autoxidation may significantly contribute to the total oxidation of SO<sub>2</sub> in continental cloud and fog water droplets in regions with high humidity and under low photochemical activity (Warneck, 1991).

In this paper, we present new developments of the fully explicit multiphase chemistry model M2C2 (Model of Multiphase Cloud Chemistry) from Leriche et al. (2000; 2001) including the incorporation of the transition metal ions chemistry and variable actinic flux in the aqueous phase. The model is then applied to chemical conditions similar to Ervens et al. (2003) who simulated three different chemical scenarios (urban, rural and marine).

After describing the multiphase box model and its new developments, we analyze similarities and discrepancies in the behaviour of the chemical species against results from Ervens et al. (2003) and against the available measurements of the Fe speciation. The radicals, transition metal ions, VOCs and sulphur chemistry are studied in details in order to evaluate the impact of TMI on multiphase chemistry.

## 2. Description of the multiphase box model

### 2.1. Description of the M2C2 model (Leriche et al., 2000, 2001)

The M2C2 model is the result of the coupling (Leriche et al., 2001) between a multiphase chemistry model described in Leriche et al. (2000) and a quasi-spectral microphysics model based upon the parameterisation of Berry and Reinhardt (1974a, b, c,

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d) and Huret et al. (1994). For the purpose of this study, M2C2 is used with prescribed microphysics in order to compare results with Ervens et al. (2003) simulations.

The chemistry included in the chemical module is explicit. The gas-phase mechanism includes the oxidation of methane, the chemistry of NO<sub>y</sub> and ammonia; it is derived and has been updated after Madronich and Calvert (1990). The exchange of chemical species between the gas phase and the aqueous phase is parameterised with the mass transfer kinetic formulation developed by Schwartz (1986). The aqueous phase chemistry includes the detailed chemistry of HO<sub>x</sub>, chlorine, carbonates, NO<sub>y</sub> and sulphur and the oxidation of organic volatile compounds (VOCs) with one carbon atom. This aqueous phase chemical mechanism has been recently updated (Leriche et al., 2003). The droplet pH is calculated at each time step by solving a simplified ionic balance equation.

## 2.2. New developments in M2C2

### 2.2.1. Transition metal ions chemistry

The transition metal ions considered are iron, manganese and copper because these species are known to play a major role on HO<sub>x</sub> and sulphur chemistry. This mechanism includes 47 reactions with iron, 13 reactions with copper, 25 reactions with manganese, 6 coupled TMI reactions and 5 aqueous phase equilibria describing the chemistry of TMI with HO<sub>x</sub>, sulphur, NO<sub>y</sub> and VOCs and is presented in Tables 1–5.

This chemical scheme is updated after the CAPRAM chemical mechanism (Herrmann et al., 2000) and includes the additional processes such as emission/deposition implemented in CAPRAM2.4 (Ervens et al., 2003).

In this section, we like to discuss in details recent aspects of cloud TMI chemistry: the formation of ferryl and manganyl ions, the equilibrium between iron and methyl peroxy radical (CH<sub>3</sub>O<sub>2</sub>) and the equilibrium between iron and sulphate.

In the iron mechanism, the ferryl ion FeO<sup>2+</sup> and its reactivity are taken into account. Until recently, the oxidation of ferrous ion (Fe(II)) by ozone was considered as producing

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OH radicals and Fe(III). However, Logager et al. (1992) provided final evidence that this reaction between Fe(II) and ozone produces Fe(IV) (the ferryl ion) and oxygen (R16). Rate constants and activation energies for reactions of the ferryl ion with selected inorganic and organic compounds present in atmospheric water have been measured by Jacobsen et al. (1997a, 1998b) (reactions R2, R12, R15, R27, R18, R24, R27, R28, R36, R37, R38, R39). In all Fe(IV) reactions, Fe(III) is formed. Fe(III) reacts with HO<sub>x</sub>, sulphite and VOCs (formaldehyde and formic acid). The reaction between the ferryl ion and Fe<sup>2+</sup> ion branches into two reactions forming Fe<sup>3+</sup> or dimer Fe(OH)<sub>2</sub>Fe<sup>4+</sup> (R18 and R19). The formation of dimer Fe(OH)<sub>2</sub>Fe<sup>4+</sup> is favoured at higher temperature (R19). Afterwards, this species produces also Fe<sup>3+</sup> (R20 and R21) but with a very slow rate (Jacobsen et al., 1997a). For a pH around 3, the ferryl ion plays a role mainly as a temporary OH radical sink whereas for more acidic solution, the ferryl ion is more likely to react as a distinct species (Jacobsen et al, 1998b). The reaction between Fe(II) and peroxy radicals allows the formation of a transient intermediate CH<sub>3</sub>O<sub>2</sub>Fe<sup>2+</sup> (R41), which later decomposes into Fe<sup>3+</sup> and CH<sub>3</sub>OOH (R42 and R43) (Khaikin et al., 1996).

In M2C2 model, the equilibrium between sulphate plus Fe<sup>3+</sup> and the iron-sulphato-complex [Fe(SO<sub>4</sub>)]<sup>+</sup> (R44 and R45) is considered, while the reaction between Fe<sup>2+</sup> and SO<sub>4</sub><sup>-</sup> is not taken into account because there is no evidence that this reaction takes place in the cloud phase (Mc Elroy and Waygood, 1990).

Manganese complexes, as well as the manganyl ion, have been added in M2C2. Looking at Mn(II) oxidation by ozone, available information about the kinetic and the mechanism of this reaction is contradictory. Sheng (1993) made this hypothesis that the reaction between Mn<sup>2+</sup> and ozone produced Mn(III) and free OH radical based upon a theoretical study. Jacobsen et al. (1998a) described a mechanism based upon laboratory investigations: Mn(II) reacts with ozone forming the manganyl ion MnO<sup>2+</sup> (Mn(IV)) without formation of free OH radical (R62). Then, MnO<sup>2+</sup> rapidly reacts with Mn<sup>2+</sup> to form Mn(III) (R63). This mechanism is similar to the one describing the reactivity of the ferryl ion.

## 2.2.2. Variable photolysis in the aqueous phase

Photolysis frequencies are calculated using the Tropospheric Ultraviolet-Visible Model (TUV version 4.1) developed by Madronich and Flocke (1999), which has been extended to include calculations of photolysis frequencies in cloud droplets. The conditions used to calculate actinic flux are: 51° N, 0° longitude, 1000 hPa, 288.15 K and an albedo of 0.1, on 24 June 1997. The actinic flux is obtained every 15 minutes after running the TUV model. To calculate the photolysis coefficients inside the droplets, we multiply values of clear sky actinic flux by 1.6 (Ruggaber et al., 1997) and we use available laboratory data (cross sections and quantum yields). Photodissociation coefficients at noon are shown in Table 6. A main difference between M2C2 and CAPRAM2.4 is the accounting of ozone (O<sub>3</sub>) and hydroxymethyl hydroperoxide (OHCH<sub>2</sub>OOH) photolysis in droplets.

## 2.2.3. Emission and deposition

Emission and deposition have to be considered since otherwise species such as SO<sub>2</sub> are oxidised within a short time of simulation. This is particularly critical in the urban scenario, where trace gases were oxidized without any renewal.

Values used for emission and deposition can be found in CAPRAM2.4 home page (<http://www.tropos.de/CHEMIE/multimod/CAPRAM/capram.html>). Emissions were taken from the EDGAR 1° – 1° database of Olivier et al. (1996) for anthropogenic emissions and biogenic emissions from the global database of Guenther et al. (1995). Dry deposition velocities for the most important gas phase species were taken from Ganzeveld et al. (1998).

## 3. Results and validation of M2C2

In order to evaluate the role of the transition metal ions on cloud chemistry, three simulations have been performed with different initial chemical conditions and are compared

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with results from CAPRAM2.4 model (Ervens et al., 2003). These three chemical scenarios correspond to marine, averaged continental (remote) and polluted continental (urban) conditions and are described in details by Ervens et al. (2003). Same conditions are also used for prescribed microphysics: the liquid water content ( $0.3 \text{ g/m}^3$ ), the temperature (288.15 K), the pressure (1000 hPa) and the droplet radius ( $10 \mu\text{m}$ ) are set constant during the simulation, which lasts 72 h. Results are discussed only for the two last days. The simulated values of the pH are around 2.6, 3.4, 3.5 for the urban, the remote and the marine scenarios, respectively.

### 3.1. Transition metal ions chemistry

The transition metals are initialized as  $\text{Fe}^{3+}$ ,  $\text{Cu}^+$  and  $\text{Mn}^{3+}$ . In the urban case, iron initial concentration is 10 and 100 times larger than, respectively, in the remote case and in the marine case. The initial concentrations of manganese and copper are the same and the ratio  $\text{Fe}/(\text{Mn or Cu})$  is equal to 20 in the two continental cases and to 50 in the marine scenario. For manganese and copper, initial concentrations in the urban case are 10 and 250 times larger than, respectively, in the remote case and in the marine case. All these conditions are similar to the scenarios described by Ervens et al. (2003).

Figure 1 represents the time evolution of the  $\text{Fe(II)}$  and  $\text{Fe(III)}$  concentrations and of the  $\text{Fe(II)}/\text{Fe(III)}$  ratio in the urban conditions for which iron concentrations are particularly important. During the day,  $\text{Fe(III)}$  is converted into  $\text{Fe(II)}$  and a strong dependency of  $\text{Fe(II)}/\text{Fe(III)}$  ratio on the photolysis is observed. The same behaviour is obtained for the two other scenarios.

To go into more details, Fig. 2 shows the relative contribution of iron redox reactions at noon (a) and at midnight (b) in the urban case.

Apart from the dominant contribution of photolysis processes in the total production of  $\text{Fe(II)}$  (P1, P2, P3 and P4), the main differences between day and night are due to the redox reactions between  $\text{Cu(I)}$  and  $\text{Fe(III)}$  (R87, R88, R89) and to the reactions between  $\text{Fe(III)}$  and  $\text{HO}_2/\text{O}_2^-$  radicals (R8, R9, R10 and R13). Concerning the produc-

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tion of Fe(III), reactions between Fe(II) and radicals play a major role during the day. During the night, reactions with radicals play no significant role in Fe(III) production and the most important sources for Fe(III) are the reactions of Fe(II) with Mn(III). The reaction of Fe(II) with O<sub>3</sub> producing the ferryl ion Fe(IV) (Logager et al., 1992) is one order of magnitude lower than the direct conversion pathways of Fe(II) to Fe(III) during the day as well as during the night. Due to high NO emission in the urban case, ozone is destroyed during the whole simulation and reduce the effect of this reaction in the conversion of Fe(II) to Fe(III). The diurnal behaviour of the Fe(II)/Fe(III) ratio differs from Ervens et al. (2003), and will be discussed in Sect. 4.

### 3.2. Aqueous phase radicals and radical anions

#### 3.2.1. OH radical

OH is one of the most important radical in both gas and aqueous phases. The aqueous phase concentrations of OH radical versus time are shown in Fig. 3 for the three different scenarios. The maximum concentrations in the urban, remote and marine cases are, respectively,  $1.2 \cdot 10^{-12}$ ,  $1.5 \cdot 10^{-12}$  and  $4.8 \cdot 10^{-13}$  M.

Figure 4 represents the relative contribution of the corresponding sources and sinks for OH radical in the aqueous phase for the three cases at noon, the second day. In the remote and marine cases, the transfer from the gas phase represents an important source for OH radicals (37 and 50%, respectively). In the urban case, it only represents 13% of the total OH production. Indeed, the photolysis of Fe(III)-complexes (P1, P2, P3 and P4) contributes around 74% to the production of the OH radical in this scenario. The Fenton-type reactions of metals ions (Fe<sup>2+</sup> and Cu<sup>+</sup>) (R1 and R51) also lead to the production of OH in significant amount in the three scenarios (respectively 9%, 41% and 16% in the urban, remote and marine cases). These results are explained by the initial concentrations of TMI and by the H<sub>2</sub>O<sub>2</sub> regime which are different in the three scenarios. In the urban case, Fe(III) initial concentration is ten times larger than in the remote scenario and one hundred times larger than in the maritime case. Due to the

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high SO<sub>2</sub> emission in the urban case, H<sub>2</sub>O<sub>2</sub> is efficiently consumed and has a relatively low concentration ( $3 \cdot 10^{-6}$  M at noon the second day) compared to the two other cases ( $1.1 \cdot 10^{-4}$  M and  $2.4 \cdot 10^{-4}$  M for the remote and marine cases, respectively). With these urban conditions of high TMI and low H<sub>2</sub>O<sub>2</sub>, the Fenton-type reactions show a rather low contribution in the most polluted case. For the same reasons, there is a high relative contribution of the photolysis of Fe(III)-complexes in the urban case and a dominant effect of the H<sub>2</sub>O<sub>2</sub> photolysis in the two other cases.

Concerning the OH destruction, the oxidation of organic species is an important sink, especially in the continental cases where initial concentrations and emissions of organic species in the gas phase are larger than in the marine case. Another important destruction of OH radical occurs via the equilibrium between OH plus Cl<sup>-</sup> and ClOH<sup>-</sup> which is shifted towards production of ClOH<sup>-</sup>. This contribution is more important in the marine case than in the two continental cases because, in the marine case, initial concentration of chlorine in the gas phase and in the aqueous phase are larger than in the continental cases. Due to high H<sub>2</sub>O<sub>2</sub> concentration in the remote and marine cases, reaction between H<sub>2</sub>O<sub>2</sub> and OH radical plays a significant role in the OH destruction (36 and 39%, respectively). Finally, reaction between OH and Fe(II) (R14) also contributes to the destruction of OH in the continental cases where initial TMI concentrations are larger.

Concentrations for OH radicals computed in M2C2 seem quite reasonable since they are in the range of previous modelling studies (Jacob et al., 1989; Herrmann et al., 2000; Warneck, 2000). Going into details of the scenarios simulated by M2C2, one can observe that OH is comparable to Ervens et al. (2003) in the marine case. However, for the continental cases, there is one order of magnitude difference in the OH concentration in our runs compared to CAPRAM2.4 runs. This difference is essentially due to the fact that VOCs oxidation in gas phase results in the production of CH<sub>2</sub>O, which is oxidized by OH<sub>(aq)</sub>. Since in CAPRAM2.4, more emissions of VOCs including C2 compounds are considered compared to our simulation, the urban scenario, rich in VOCs, exhibits the lowest OH<sub>(aq)</sub> concentration levels.

### 3.2.2. Radical anions

The same analysis than for OH has been performed for the dichloride radical anion  $\text{Cl}_2^-$  (not shown). The sources for the  $\text{Cl}_2^-$  correspond to those of Cl atom because  $\text{Cl}_2^-$  is formed through a fast equilibrium between  $\text{Cl}^-$  plus Cl atom and  $\text{Cl}_2^-$  radical (Buxton et al., 1998). At noon, two sources of Cl atom dominate. First, the most important source of Cl atom occurs via the equilibrium between  $\text{ClOH}^-$  and Cl plus  $\text{OH}^-$  (85% of Cl atom production in the urban case). Since  $\text{ClOH}^-$  is formed after the equilibrium between  $\text{Cl}^-$  plus OH and  $\text{ClOH}^-$ , the evolution of  $\text{Cl}_2^-$  follows the one of  $\text{OH}(\text{aq})$  (Fig. 3). The second source for chlorine atoms is the reaction of chloride with  $\text{SO}_4^-$  (15%), due to the high  $\text{SO}_2$  emission in the urban case. The main sinks of this radical anion are the reactions between  $\text{Cl}_2^-$  with  $\text{HO}_2/\text{O}_2^-$  radical (48%), with Fe(II) (40%) and with  $\text{HSO}_3^-/\text{SO}_3^{2-}$  (10%). Reaction of  $\text{Cl}_2^-$  with  $\text{H}_2\text{O}_2$  is negligible (2%) since  $\text{H}_2\text{O}_2$  concentration is very low in the urban case.

The other two radical anions, the sulphate radical anion,  $\text{SO}_4^-$  and the carbonate radical anion  $\text{CO}_3^-$  are present in very low concentrations. Their time evolution is similar to the one of the dichloride radical anion but with higher concentrations in the urban case at noon of  $1.1 \cdot 10^{-14}$  M for  $\text{SO}_4^-$  and of  $5.5 \cdot 10^{-14}$  M for  $\text{CO}_3^-$ . These two radicals are mainly influenced by the concentration of  $\text{OH}(\text{aq})$  during the day and by the concentration of  $\text{NO}_3$  during the night.

### 3.3. VOCs chemistry

Figure 5 presents the main aqueous phase pathways of soluble volatile organic compounds at noon in the urban case. In this scenario, the effect of TMI on  $\text{HO}_x$  radicals is the most important and, therefore the most significant for aqueous phase oxidation of soluble VOCs. The contribution of the ferryl ion ( $\text{FeO}^{2+}$ ) in the oxidation of formaldehyde (R39) and formic acid (R37 and R38) is indicated and shows that the direct role of TMI on VOCs chemistry is negligible.

The effect of transition metal ions on aqueous phase soluble VOCs chemistry is

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indirect. TMI chemistry increases  $\text{OH}_{(\text{aq})}$  concentrations leading to a more important oxidation of VOCs yielding to more  $\text{HO}_{2(\text{aq})}$  production.

### 3.4. Sulphur chemistry

Figure 6 displays the main pathways of S(IV) oxidation leading to sulphate formation for the urban scenario at noon. This scenario was chosen because the chemistry of TMI is very efficient due to high initial concentrations for TMI and for sulphur dioxide and also to high emissions of  $\text{SO}_2$ .

In the sulphate formation, two pathways can be distinguished:

- A direct production of sulphate through the oxidation of S(IV) by  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ ,  $\text{HNO}_4$ ,
- An indirect pathway through TMI catalysis which is initiated by the oxidation of S(IV) by  $\text{OH}$ ,  $\text{Cl}_2^-$  and  $\text{FeO}^{2+}$ .

The  $\text{HSO}_3^-/\text{SO}_3^{2-}$  concentration decreases from  $8.5 \cdot 10^{-7}$  M to  $1.0 \cdot 10^{-7}$  M over a time period of 72 h. In the urban case, due to the high  $\text{NO}_x$  level, the direct conversion pathway of S(IV) to S(VI) by pernitric acid plays a significant role (10%) whereas due to the low ozone concentration and to the acidic pH value, ozone does not contribute significantly in the S(IV) to S(VI) conversion.

In M2C2 model, the indirect pathway is found to be less efficient by a factor 100 compared to the direct oxidation flux of S(IV) into S(VI) by  $\text{H}_2\text{O}_2$  and  $\text{HNO}_4$ . Although  $\text{H}_2\text{O}_2$  concentration is low, oxidation of S(IV) by  $\text{H}_2\text{O}_2$  remains dominant throughout the simulation. Indeed, the reaction of  $\text{Cu}^+$  with oxygen (R50) leads to high  $\text{HO}_2/\text{O}_2^-$  concentration in the aqueous phase, which results in a continuously  $\text{H}_2\text{O}_2$  formation through reactions of  $\text{HO}_2/\text{O}_2^-$  with Fe(II) and  $\text{Cu}^+$  (R7, R11 and R52, R53). Indeed, iron is mainly present as Fe(II) during the day and concentration of  $\text{Cu}^+$  is maintained (maximum at noon  $1.3 \cdot 10^{-9}$  M) by reaction of  $\text{Cu}^{2+}$  with  $\text{HO}_2/\text{O}_2^-$  radical (R54, R55).

The direct conversion pathway of S(IV) to S(VI) is about the same order of magnitude than the transfer of  $\text{SO}_2$  from the gas phase. This continuous transfer of  $\text{SO}_2$  from the

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gas phase, due to high SO<sub>2</sub> emission considered in the urban scenario, explains the low hydrogen peroxide concentration.

In CAPRAM2.4, SO<sub>2</sub> concentration increases throughout the simulation in the urban case. This difference with our SO<sub>2</sub> evolution is due to the fact that iron is mainly present as Fe(III) during the day in Ervens et al. (2003) runs leading to a lower hydrogen peroxide production than in M2C2.

#### 4. Discussion

In this section, the original features of the TMI mechanism introduced in M2C2 are reviewed in order to highlight new findings and to discuss them not only in the context of Ervens et al. (2003) scenarios but also against other available model results and field measurements.

The analysis of TMI chemistry in M2C2 shows a diurnal variation of the Fe(II)/Fe(III) ratio due to the Fe(III) photolysis as described in Sect. 3.1. Some measurements of the iron speciation in atmospheric liquid phase are available and exhibit a very high variability in the Fe(II)/Fe(III) ratio. This information about speciation is important because it is directly linked to the efficiency of atmospheric redox cycles in atmospheric liquid phase. The results obtained with M2C2 model for the percentage of Fe(II) towards dissolved Fe for the three cases are given in Table 7 as well as values from field measurements in clouds found in the literature. Measurements indicate higher values during the day than during the night. This particular feature is quite well reproduced by M2C2 model, contrary to the two versions of CAPRAM. While CAPRAM2.3 exhibits no diurnal variation with iron mainly present as Fe(II), CAPRAM2.4 strongly underestimates day time values and simulates iron mainly as Fe(III). Ervens et al. (2003) explains this result by the formation of Fe(III)-oxalato- complexes, which it is not considered in M2C2. In conclusion, results from M2C2 on the Fe(II)/Fe(III) ratio agree quite favourably with the available measurements and is able to reproduce the natural diurnal variability of this ratio among various scenarios.

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The analysis of the major sinks and sources for OH in the aqueous phase shows the importance of the TMI chemistry in the concentration levels of the OH radical, especially due to the photolysis of Fe(III)-complexes and to the Fenton-type reactions of metal ions (Fe<sup>2+</sup> and Cu<sup>+</sup>) in the continental scenarios. To specify this effect of TMI chemistry on HO<sub>x</sub> multiphase chemistry, we have performed a sensitivity test which consists in considering or not the transition metal ions chemistry (Fig. 7). Neglecting TMI leads to a maximum concentration of OH<sub>(aq)</sub> of  $2.7 \cdot 10^{-13}$  M at noon in the urban case, lower by a factor of 4.4 compared to the simulation with TMI chemistry. This result is in agreement with Matthijssen et al. (1997) who found an increase of about 2.55 of OH<sub>(aq)</sub> in the presence of TMI. HO<sub>2</sub> radical exhibits a different behaviour than OH<sub>(aq)</sub> if TMI chemistry is neglected. For the urban case, the HO<sub>2(aq)</sub> concentration at noon increases from  $4.0 \cdot 10^{-9}$  M considering TMI to  $1.1 \cdot 10^{-7}$  M neglecting TMI because its main sinks, reactions with Cu(I and II), and with Fe(II and III) are missing (R52, R53, R54, R55 and R7, R8, R9, R10, R11, R13). Finally, this sensitivity test permits to quantify the role of TMI chemistry on HO<sub>x</sub> radicals concentrations in aqueous phase and shows that, among TMI, dissolved iron has a leader role on HO<sub>x</sub> chemistry and that copper plays a significant role in the chemistry of H<sub>x</sub>O<sub>y</sub>.

## 5. Conclusions

This study presents new developments of the multiphase model of cloud chemistry M2C2 including the incorporation of transition metal ions and the capability to use variable photolysis frequencies in aqueous phase. This new version of the model has been applied to three different chemical scenarios in order to evaluate the impact of transition metal ions on multiphase chemistry. These three scenarios represent urban, remote and marine conditions following Ervens et al. (2003).

The chemistry of transition metal ions, of radicals, of sulphur and of VOCs is analyzed in details with special focus on new developments which leads to differences with Ervens et al. (2003) model. The main difference concerns the Fe(II)/Fe(III) ratio, which

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is compared directly with available measurements and shows that the M2C2 model is able to represent the natural diurnal variability of this ratio. The analysis of the most important sources and sinks of the OH radical in the aqueous phase shows that its concentration are partly controlled by the iron. Indeed, its highest production pathway is the photolysis of Fe(III)-hydroxo-complexes. For sulphur chemistry, results show a negligible contribution of the iron and manganese catalysis of the S(IV) oxidation to the production of sulphate. Conversion of S(IV) into S(VI) is mainly due to hydrogen peroxide (90%) and pernitric acid (10%). The role of TMI in this conversion is indirect: iron and copper control the chemistry of H<sub>x</sub>O<sub>y</sub> as shown by the sensitivity test comparing urban simulation with and without TMI chemistry.

An important issue, in atmospheric chemistry, concerns the clouds/aerosols interaction via the quantification of the indirect effect of aerosols on the radiative budget of the Earth, which is still subject to many uncertainties. On a global point of view, chemical reactions in clouds modify the composition of cloud droplets and, hence, of the aerosol population released into the atmosphere after cloud evaporation. The consequence is an enhancement of the efficiency of aerosols to form CCN leading to smaller and more numerous droplets, this is the first indirect effect (Twomey, 1977). Then, the efficiency of precipitation formation is modified inhibiting rain and enhancing cloud lifetime. This is the second indirect effect (Albrecht, 1989). In this study, the calculated pH is acidic and the introduction of TMI chemistry enhances H<sub>2</sub>O<sub>2</sub> production in droplets leading to an efficient conversion of S(IV) into S(VI) by reaction with H<sub>2</sub>O<sub>2</sub>, which contributes to the acidification of droplets. This chemical pathway associated with other SO<sub>2</sub> sources (advective and vertical transport, ..., considered in chemistry/transport models) will lead to a constant acidification of droplets resulting in large changes in aerosol population (aerosol size distribution, aerosol surface properties, hygroscopicity). This process will enhance the efficiency of aerosols to form CCN. Since the chemistry of clouds is controlled by all these series of processes, only modelling of specified scenarios will help to learn how different conditions affect the overall impact of clouds on climate such as the indirect effect. For this, M2C2 provides a powerful tool to focus on individual



processes.

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**Table 1.** Iron chemistry

Reactants	Products	No.	$k_{298}$ ( $M^{-n+1}s^{-1}$ )	$E_a/R$ ( $^{\circ}K$ )	References
$H_2O_2 + Fe^{2+}$	$Fe^{3+} + OH + OH^{-}$	R1	70	5050	Christensen et al. (1993)
$H_2O_2 + FeO^{2+}$	$Fe^{3+} + HO_2 + OH^{-}$	R2	$9.5 \cdot 10^3$	2800	Jacobsen et al. (1998a)
$H_2O_2 + [Fe(OH)]^{+}$	$[Fe(OH)]^{2+} + OH + OH^{-}$	R3	$1.9 \cdot 10^6$	6200	Moffett and Zika (1987)
$H_2O_2 + Fe^{3+}$	$Fe^{2+} + HO_2 + H^{+}$	R4	$2.0 \cdot 10^{-3}$		Walling and Goosen (1973)
$H_2O_2 + [Fe(OH)]^{2+}$	$Fe^{2+} + HO_2 + H_2O$	R5	$2.0 \cdot 10^{-3} = k_7$		estimated
$H_2O_2 + [Fe(OH)_2]^{+}$	$Fe^{2+} + HO_2 + OH^{-} + H_2O$	R6	$2.0 \cdot 10^{-3} = k_7$		estimated
$O_2^{-} + Fe^{2+} + 2H^{+}$	$H_2O_2 + Fe^{3+}$	R7	$1.0 \cdot 10^7$		Rush and Bielski (1985)
$O_2^{-} + Fe^{3+}$	$Fe^{2+} + O_2$	R8	$1.5 \cdot 10^8$		Rush and Bielski (1985)
$O_2^{-} + [Fe(OH)]^{2+}$	$Fe^{2+} + O_2 + OH^{-}$	R9	$1.5 \cdot 10^8$		Rush and Bielski (1985)
$O_2^{-} + [Fe(OH)_2]^{+}$	$Fe^{2+} + O_2 + 2OH^{-}$	R10	$1.5 \cdot 10^8$		Rush and Bielski (1985)
$HO_2 + Fe^{2+} + H^{+}$	$Fe^{3+} + H_2O_2$	R11	$1.2 \cdot 10^6$	5050	Jayson et al. 1973b
$HO_2 + Fe(O)^{2+}$	$Fe^{3+} + O_2 + OH^{-}$	R12	$2.0 \cdot 10^6$		Jacobsen et al. (1998b)
$HO_2 + [Fe(OH)]^{2+}$	$Fe^{2+} + O_2 + H_2O$	R13	$1.3 \cdot 10^5$		Ziajka et al. (1994)
$OH + Fe^{2+}$	$[Fe(OH)]^{2+}$	R14	$4.6 \cdot 10^8$	1100	Christensen and Sehested (1981)
$OH + FeO^{2+} + H^{+}$	$Fe^{3+} + H_2O_2$	R15	$1.0 \cdot 10^7$		Logager et al. (1992)
$O_3 + Fe^{2+}$	$FeO^{2+} + O_2$	R16	$8.2 \cdot 10^5$		Logager et al. (1992)
$FeO^{2+} + H_2O$	$Fe^{3+} + OH + OH^{-}$	R17	$1.3 \cdot 10^{-2}$	4100	Jacobsen et al. (1998b)
$FeO^{2+} + Fe^{2+} + H_2O$	$2Fe^{3+} + 2OH^{-}$	R18	$7.2 \cdot 10^4$	842	Jacobsen et al. (1997a)
$FeO^{2+} + Fe^{2+} + H_2O$	$Fe(OH)_2Fe^{4+}$	R19	$1.8 \cdot 10^4$	5052	Jacobsen et al. (1997a)
$Fe(OH)_2Fe^{4+}$	$2Fe^{3+} + 2OH^{-}$	R20	0.49	8780	Jacobsen et al. (1997a)
$Fe(OH)_2Fe^{4+} + 2H^{+}$	$2Fe^{3+} + 2H_2O$	R21	1.95	5653	Jacobsen et al. (1997a)

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Table 1. Continued

Reactants	Products	No.	$k_{298}$ ( $M^{-n+1}s^{-1}$ )	$E_a/R$ ( $^{\circ}K$ )	References
$Cl_2^- + Fe^{2+}$	$Fe^{3+} + 2Cl^-$	R22	$1.0 \cdot 10^7$	3060	Thornton and Laurence (1973)
$Cl_2^- + Fe^{2+}$	$[FeCl]^{2+} + Cl^-$	R23	$4.0 \cdot 10^6$	3700	Thornton and Laurence (1973)
$Cl^- + FeO^{2+} + H^+$	$Fe^{3+} + ClOH^-$	R24	100		Jacobsen et al. (1998b)
$NO_3 + Fe^{2+}$	$Fe^{3+} + NO_3^-$	R25	$8.0 \cdot 10^6$		Pikaev et al. (1974)
$NO_2 + Fe^{2+}$	$Fe^{3+} + NO_2^-$	R26	$3.1 \cdot 10^4$		Epstein et al. (1982)
$HNO_2 + FeO^{2+}$	$Fe^{3+} + NO_2 + OH^-$	R27	$1.1 \cdot 10^4$	4150	Jacobsen et al. (1998b)
$NO_2^- + FeO^{2+} + H^+$	$Fe^{3+} + NO_2 + OH^-$	R28	$1.0 \cdot 10^5$		Jacobsen et al. (1998b)
$HSO_3^- + [Fe(OH)]^{2+}$	$Fe^{2+} + SO_3^- + H_2O$	R29	30		Ziajka et al. (1994)
$SO_5^- + Fe^{2+} + H_2O$	$[Fe(OH)]^{2+} + HSO_5^-$	R30	$2.65 \cdot 10^7$		Williams (1996)
$HSO_5^- + Fe^{2+}$	$[Fe(OH)]^{2+} + SO_4^{2-}$	R31	$3.0 \cdot 10^4$		Gilbert et al. (1990)
$SO_4^- + Fe^{2+} + H_2O$	$[Fe(OH)]^{2+} + SO_4^{2-} + H^+$	R32	$4.1 \cdot 10^9$	-2165	Buxton et al. (1997)
$O_2^- + [Fe(SO_4)]^+$	$Fe^{2+} + SO_4^{2-} + O_2$	R33	$1.5 \cdot 10^8$		Rush and Bielski (1985)
$HO_2 + [Fe(SO_4)]^+$	$Fe^{2+} + SO_4^{2-} + O_2 + H^+$	R34	$1.0 \cdot 10^3$		Rush and Bielski (1985)
$S_2O_8^{2-} + Fe^{2+} + H_2O$	$[Fe(OH)]^{2+} + 2SO_4^{2-} + H^+$	R35	17		Buxton et al. (1997)
$HSO_3^- + FeO^{2+}$	$Fe^{3+} + SO_3^- + OH^-$	R36	$2.5 \cdot 10^5$		Jacobsen et al. (1998b)
$HCOOH + FeO^{2+} + O_2 + H^+$	$Fe^{3+} + CO_2 + HO_2 + H_2O$	R37	160	2680	Jacobsen et al. (1998b)
$HCOO^- + FeO^{2+} + O_2 + H^+$	$Fe^{3+} + CO_2 + HO_2 + OH^-$	R38	$3.0 \cdot 10^5$		Jacobsen et al. (1998b)
$CH_2(OH)_2 + FeO^{2+} + O_2$	$Fe^{3+} + HCOOH + HO_2 + OH^-$	R39	400	5352	Jacobsen et al. (1998b)
$CO_3^- + Fe^{2+}$	$Fe^{3+} + CO_3^{2-}$	R40	$2.0 \cdot 10^7$		estimated from Herrmann et al. (2000)
$CH_3O_2 + Fe^{2+}$	$CH_3O_2Fe^{2+}$	R41	$8.6 \cdot 10^5$		Khaikin et al. (1996)
$CH_3O_2Fe^{2+} + H_2O$	$Fe^{3+} + CH_3OOH + OH^-$	R42	100		Khaikin et al. (1996)

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**Table 1.** Continued

Reactants	Products	No.	$k_{298}$ ( $M^{-n+1}s^{-1}$ )	$E_a/R$ ( $^{\circ}K$ )	References
$CH_3O_2Fe^{2+} + H^+$	$Fe^{3+} + CH_3OOH$	R43	$3.0 \cdot 10^4$		Khaikin et al. (1996)
$Fe^{3+} + SO_4^{2-}$	$[Fe(SO_4)]^+$	R44	$3.2 \cdot 10^3$		Jayson et al. (1973a)
$[Fe(SO_4)]^+$	$Fe^{3+} + SO_4^{2-}$	R45	27		Jayson et al. (1973a)
$Fe^{3+} + Cl^-$	$[FeCl]^{2+}$	R46	4.8		Xu et al. (1985)
$[FeCl]^{2+}$	$Fe^{3+} + Cl^-$	R47	$9.2 \cdot 10^{-1}$		estimated

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**Table 2.** Copper-chemistry

Reactants	Products	No.	$k_{298}$ ( $M^{-n+1}s^{-1}$ )	$E_a/R$ (° K)	References
OH + Cu <sup>+</sup>	Cu <sup>2+</sup> + OH <sup>-</sup>	R48	$3.0 \cdot 10^9$		Goldstein et al. 1992
O <sub>3</sub> + Cu <sup>+</sup> + H <sup>+</sup>	Cu <sup>2+</sup> + OH + O <sub>2</sub>	R49	$3.0 \cdot 10^7$		Hoigné and Bühler (1996)
O <sub>2</sub> + Cu <sup>+</sup>	Cu <sup>2+</sup> + O <sub>2</sub> <sup>-</sup>	R50	$4.6 \times 10^5$		Bjergbakke et al. (1976)
H <sub>2</sub> O <sub>2</sub> + Cu <sup>+</sup>	Cu <sup>2+</sup> + OH + OH <sup>-</sup>	R51	$7.0 \cdot 10^3$		Berdnikov et al. (1973)
HO <sub>2</sub> + Cu <sup>+</sup> + H <sup>+</sup>	Cu <sup>2+</sup> + H <sub>2</sub> O <sub>2</sub>	R52	$3.5 \cdot 10^9$		Berdnikov et al. (1973)
O <sub>2</sub> <sup>-</sup> + Cu <sup>+</sup> + 2H <sup>+</sup>	Cu <sup>2+</sup> + H <sub>2</sub> O <sub>2</sub>	R53	$9.4 \cdot 10^9$		Von Piechowski et al. (1993)
HO <sub>2</sub> + Cu <sup>2+</sup>	Cu <sup>+</sup> + O <sub>2</sub> + H <sup>+</sup>	R54	$1.0 \cdot 10^8$		Rabani et al. (1973)
O <sub>2</sub> <sup>-</sup> + Cu <sup>2+</sup>	Cu <sup>+</sup> + O <sub>2</sub>	R55	$8.0 \cdot 10^9$		Rabani et al. (1973)
Cl <sub>2</sub> <sup>-</sup> + Cu <sup>+</sup>	Cu <sup>2+</sup> + 2Cl <sup>-</sup>	R56	$1.0 \cdot 10^7 = k_{22}$		estimated
SO <sub>4</sub> <sup>-</sup> + Cu <sup>+</sup>	Cu <sup>2+</sup> + SO <sub>4</sub> <sup>2-</sup>	R57	$1.4 \cdot 10^7 = k_{75}$	4089	estimated
CO <sub>3</sub> <sup>3-</sup> + Cu <sup>+</sup>	Cu <sup>2+</sup> + CO <sub>3</sub> <sup>2-</sup>	R58	$2.0 \cdot 10^7$	estimated from	Herrmann et al. (2000)
Cu <sup>2+</sup> + OH	[Cu(OH)] <sup>2+</sup>	R59	$3.5 \cdot 10^8$		Baxendale et al. (1971)
[Cu(OH)] <sup>2+</sup>	Cu <sup>2+</sup> + OH	R60	$3.0 \cdot 10^4$		Meyerstein (1971)

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Table 3. Manganese-chemistry

Reactants	Products	No.	$k_{298}$ ( $M^{-n+1} s^{-1}$ )	$E_a/R$ ( $^{\circ} K$ )	References
$OH + Mn^{2+}$	$[Mn(OH)]^{2+}$	R61	$2.0 \cdot 10^7$		Jacobsen et al. (1997b)
$O_3 + Mn^{2+}$	$MnO_2^+ + O_2$	R62	$1.65 \cdot 10^3$	4750	Jacobsen et al. (1998a)
$MnO^{2+} + Mn^{2+} + 2H^+$	$2Mn^{3+} + H_2O$	R63	$1.0 \cdot 10^5$		Jacobsen et al. (1998a)
$MnO_2^+ + MnO_2^+ + 2H^+$	$2Mn^{2+} + H_2O_2 + O_2$	R64	$6.0 \cdot 10^6$		Jacobsen et al. (1997b)
$MnO_2^+ + HO_2 + H^+$	$Mn_2^+ + H_2O_2 + O_2$	R65	$1.0 \cdot 10^7$		Jacobsen et al. (1997b)
$H_2O_2 + Mn^{3+}$	$Mn_2^+ + HO_2 + H^+$	R66	$7.3 \cdot 10^4$		Davies et al. (1968)
$H_2O_2 + [Mn(OH)]^{2+}$	$MnO_2^+ + H^+ + H_2O$	R67	$2.8 \cdot 10^3$		Jacobsen et al. (1997b)
$H_2O_2 + Mn^{4+}$	$Mn^{2+} + 2H^+ + O_2$	R68	$1.25 \cdot 10^8$		estimated from Jacobsen et al. (1998a)
$NO_3 + Mn^{2+}$	$Mn^{3+} + NO_3^-$	R69	$1.1 \cdot 10^6$		Neta and Huie (1986)
$Cl_2^- + Mn^{2+}$	$Mn^{3+} + 2Cl^-$	R70	$8.5 \cdot 10^6$	4090	Laurence and Thornton (1973)
$Cl_2^- + Mn^{2+}$	$MnCl_2^+$	R71	$2.0 \cdot 10^7$	4090	Laurence and Thornton (1973)
$MnCl_2^+$	$Mn^{2+} + Cl_2^-$	R72	$3.0 \cdot 10^5$		Laurence and Thornton (1973)
$MnCl_2^+$	$Mn^{3+} + 2Cl^-$	R73	$2.1 \cdot 10^5$	2100	Laurence and Thornton (1973)
$HSO_5^- + Mn^{2+}$	$Mn^{3+} + SO_4^- + OH^-$	R74	$3.0 \cdot 10^4 = k_{31}$		estimated
$SO_4^- + Mn^{2+}$	$Mn^{3+} + SO_4^{2-}$	R75	$1.8 \cdot 10^7$	4100	Buxton et al. (1997)
$SO_5^- + Mn^{2+} + H_2O$	$Mn^{3+} + HSO_5^- + OH^-$	R76	$1.0 \cdot 10^{10}$		Berglund et al. (1994)
$MnHSO_3^+ + Mn^{3+}$	$2Mn^{2+} + SO_3^- + H^+$	R77	$1.3 \cdot 10^6$		Berglund et al. (1994)
$CO_3^- + Mn^{2+}$	$Mn^{3+} + CO_3^{2-}$	R78	$1.5 \cdot 10^7$		Cope et al. (1978)
$Mn_2^+ + O_2^-$	$MnO_2^+$	R79	$9.5 \cdot 10^7$		Jacobsen et al. (1997b)
$MnO_2^+$	$Mn^{2+} + O_2^-$	R80	$7.5 \cdot 10^3$		Jacobsen et al. (1997b)

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**Table 3.** Continued

Reactants	Products	No.	$k_{298}$ (M <sup>-n+1</sup> s <sup>-1</sup> )	$E_a/R$ (°K)	References
Mn <sup>2+</sup> + HO <sup>2</sup>	MnO <sup>2+</sup> + H <sup>+</sup>	R81	1.1 · 10 <sup>6</sup>		Jacobsen et al. (1997b)
MnO <sub>2</sub> <sup>+</sup> + H <sup>+</sup>	Mn <sup>2+</sup> + HO <sub>2</sub>	R82	1.4 · 10 <sup>7</sup>		Jacobsen et al. (1997b)
Mn <sup>3+</sup> + Mn <sup>3+</sup>	Mn <sup>2+</sup> + Mn <sup>4+</sup>	R83	1.0 · 10 <sup>7</sup>		estimated from Jacobsen et al. (1998a); Rosseinsky (1963)
Mn <sup>2+</sup> + Mn <sup>4+</sup>	Mn <sup>3+</sup> + Mn <sup>3+</sup>	R84	1.0 · 10 <sup>7</sup>		estimated from Jacobsen et al. (1998a); Rosseinsky (1963)
Mn <sup>2+</sup> + HSO <sub>3</sub> <sup>-</sup>	MnHSO <sub>3</sub> <sup>+</sup>	R85	3.1 · 10 <sup>7</sup>		Berglund et al. (1993)
MnHSO <sub>3</sub> <sup>+</sup>	Mn <sup>2+</sup> + HSO <sub>3</sub> <sup>-</sup>	R86	1.03 · 10 <sup>3</sup>		Berglund et al. (1993)

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**Table 4.** Coupled TMI chemistry

Reactants	Products	No.	$k_{298}$ ( $M^{-n+1}s^{-1}$ )	$E_a/R$ (°K)	References
$Fe^{3+} + Cu^+$	$Fe^{2+} + Cu^{2+}$	R87	$1.3 \cdot 10^7$		Buxton et al. (1995)
$[Fe(OH)]^{2+} + Cu^+$	$Fe^{2+} + Cu^{2+} + OH^-$	R88	$1.3 \cdot 10^7 = k_{87}$		estimated
$[Fe(OH)_2]^+ + Cu^+$	$Fe^{2+} + Cu^{2+} + 2OH^-$	R89	$1.3 \cdot 10^7 = k_{87}$		estimated
$Mn^{3+} + Fe^{2+}$	$Mn^{2+} + Fe^{3+}$	R90	$1.3 \cdot 10^4$		Davies (1969)
$[Mn(OH)]^{2+} + Fe^{2+}$	$Mn^{2+} + [Fe(OH)]^{2+}$	R91	$2.1 \cdot 10^4$		Davies (1969)
$Mn^{2+} + FeO^{2+} + 2H^+$	$Mn^{3+} + Fe^{3+} + H_2O$	R92	$1.0 \cdot 10^4$	2700	Jacobsen et al. (1998b)

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**Table 5.** Aqueous phase equilibria

Reactants	No.	K (M)	$\Delta H/R$ (K)	References
$\text{Fe}^{2+} + \text{H}_2\text{O} \leftrightarrow [\text{Fe}(\text{OH})]^+ + \text{H}^+$	E1	$3.22 \cdot 10^{-10}$		Mesmer (1971)
$\text{Fe}^{3+} + \text{H}_2\text{O} \leftrightarrow [\text{Fe}(\text{OH})]^{2+} + \text{H}^+$	E2	$6 \cdot 10^{-3}$		Brandt and van Eldik (1995)
$[\text{Fe}(\text{OH})]^{2+} + \text{H}_2\text{O} \leftrightarrow [\text{Fe}(\text{OH})_2]^+ + \text{H}^+$	E3	$7.62 \cdot 10^{-6}$		Hemmes et al. (1971)
$\text{Mn}^{3+} + \text{H}_2\text{O} \leftrightarrow [\text{Mn}(\text{OH})]^{2+} + \text{H}^+$	E4	$9.30 \cdot 10^{-1}$		Wells and Davies (1967)
$[\text{Mn}(\text{OH})]^{2+} + \text{H}_2\text{O} \leftrightarrow [\text{Mn}(\text{OH})_2]^+ + \text{H}^+$	E5	$1.00 \cdot 10^{-5}$		Baral et al., 1986

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**Table 6.** Photolysis rates (aqueous phase) at noon

Reactants	Products	No.	J[s <sup>-1</sup> ]	References
O <sub>3</sub> + H <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	P1	2.98 · 10 <sup>-4</sup>	Graedel and Weschler (1981)
H <sub>2</sub> O <sub>2</sub>	2 OH	P2	4.81 · 10 <sup>-6</sup>	Graedel and Weschler (1981); Zellner et al. (1990)
HNO <sub>2</sub>	NO + OH	P3	1.72 · 10 <sup>-4</sup>	Graedel and Weschler (1981)
NO <sub>2</sub> <sup>-</sup> + H <sub>2</sub> O	NO + OH + OH <sup>-</sup>	P4	4.19 · 10 <sup>-5</sup>	Graedel and Weschler (1981); Zellner et al. (1990)
NO <sub>3</sub> <sup>-</sup> + H <sub>2</sub> O	NO <sub>2</sub> + OH + OH <sup>-</sup>	P5	2.99 · 10 <sup>-7</sup>	Graedel and Weschler (1981); Zellner et al. (1990)
NO <sub>3</sub>	NO + O <sub>2</sub>	P6	4.45 · 10 <sup>-2</sup>	Graedel and Weschler (1981)
OHCH <sub>2</sub> OOH + O <sub>2</sub>	HCOOH + OH + HO <sub>2</sub>	P7	8.53 · 10 <sup>-6</sup>	Lerliche et al. (2000)
CH <sub>3</sub> OOH + O <sub>2</sub>	CH <sub>2</sub> O + OH + HO <sub>2</sub>	P8	8.53 · 10 <sup>-6</sup>	Lerliche et al. (2000)
Fe <sup>3+</sup> + H <sub>2</sub> O	Fe <sup>2+</sup> + OH + H <sup>+</sup>	P9	6.41 · 10 <sup>-6</sup>	Benkelberg and Warneck (1995)
[Fe(OH)] <sup>2+</sup>	Fe <sup>2+</sup> + OH	P10	5.63 · 10 <sup>-3</sup>	Benkelberg and Warneck (1995)
[Fe(OH) <sub>2</sub> ] <sup>+</sup>	Fe <sup>2+</sup> + OH + OH <sup>-</sup>	P11	7.52 · 10 <sup>-3</sup>	Weschler et al. (1986); Benkelberg et al. (1991)
[Fe(SO <sub>4</sub> )] <sup>+</sup>	Fe <sup>2+</sup> + SO <sub>4</sub> <sup>-</sup>	P12	4.51 · 10 <sup>-5</sup>	Benkelberg and Warneck (1995)

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**Table 7.** Percentage of Fe(II) out of dissolved Fe during the day and during the night for the three scenarios and from available measurements

	DAY			
	M2C2	CAPRAM2.3	CAPRAM2.4	measured
Urban				90 <sup>*,a</sup>
	85	99.7	4	40–80 <sup>d</sup>
Remote	80	98	N.A.	62 <sup>f</sup> 76 <sup>c</sup>
Marine	80	85	N.A.	70–80 <sup>\$b</sup>
	NIGHT			
	M2C2	CAPRAM2.3	CAPRAM2.4	measured
Urban				20–60 <sup>*,a</sup>
	1	99.7	2	0 <sup>#</sup> –40 <sup>d</sup>
Remote	20	98	N.A.	45–60 <sup>e</sup>
Marine	20	85	N.A.	50 <sup>f</sup> 26–55 <sup>c</sup> N.A.

\* percentage of Fe(II) out of total amount of Fe,

# Fe(II) is below detection limits,

\$ marine air mass with anthropogenic influence.

<sup>a</sup> Behra and Sigg (1990),

<sup>b</sup> Pehkonen et al. (1992),

<sup>c</sup> Erel et al. (1993),

<sup>d</sup> Sedlak et al. (1997),

<sup>e</sup> Schwanz et al. (1998),

<sup>f</sup> Deutsch et al. (2001).

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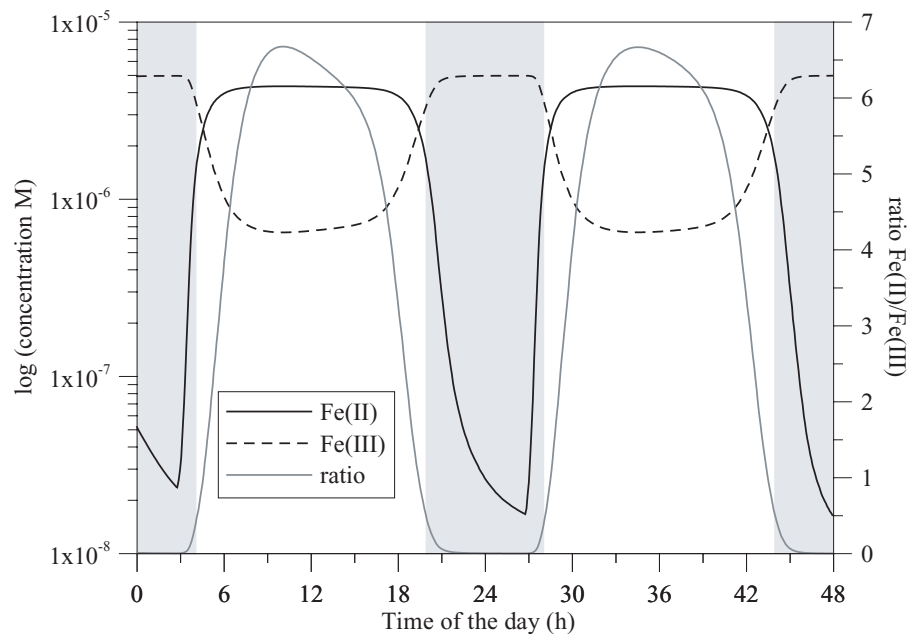
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**Fig. 1.** Time evolution of Fe(III) and Fe(II) concentrations and of the ratio Fe(II)/Fe(III) for the urban scenario. Shaded areas correspond to night-time periods.

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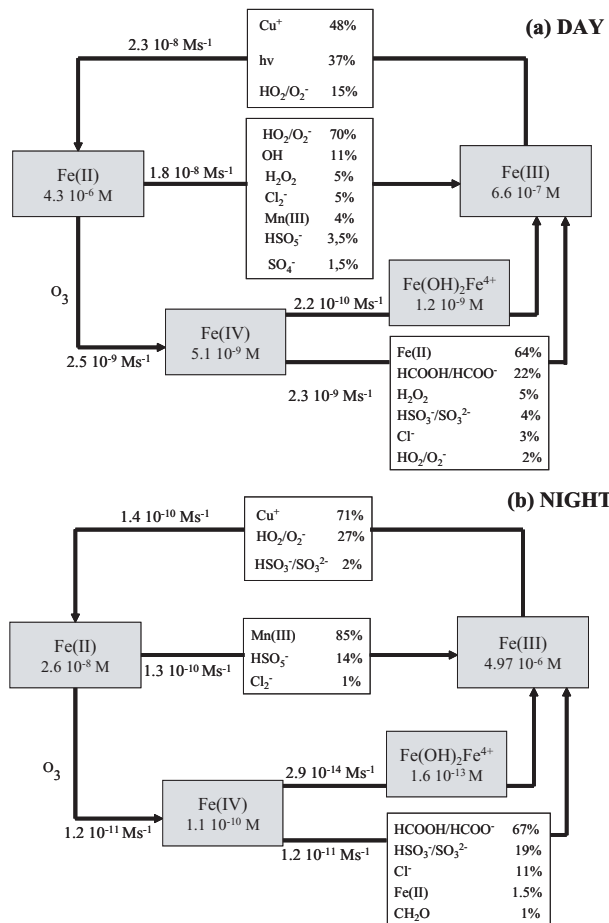


Fig. 2. Iron redox reactions during the day (a) and at night (b) for the urban scenario.

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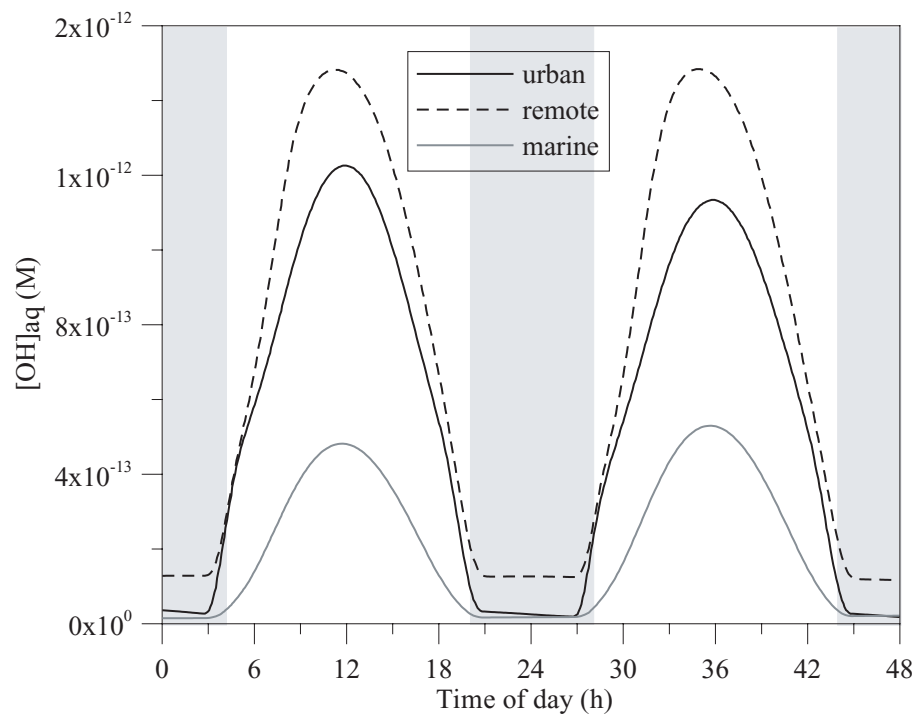
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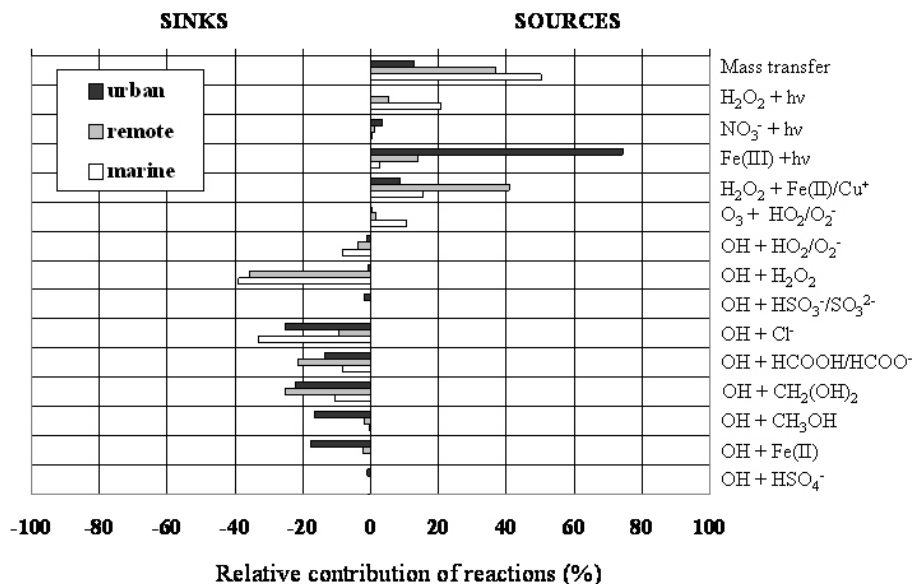
**Fig. 3.** Simulated time evolution of  $\text{OH}_{(\text{aq})}$  for urban, remote and marine conditions. Shaded areas correspond to night-time periods.

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**Fig. 4.** Sinks and sources for OH<sub>(aq)</sub> for urban, remote and marine conditions at noon 2nd day. Values of production and loss fluxes are identical and are in [M s<sup>-1</sup>]: urban  $1.1 \cdot 10^{-8}$ , remote  $9.5 \cdot 10^{-9}$ , marine  $5.5 \cdot 10^{-9}$ .

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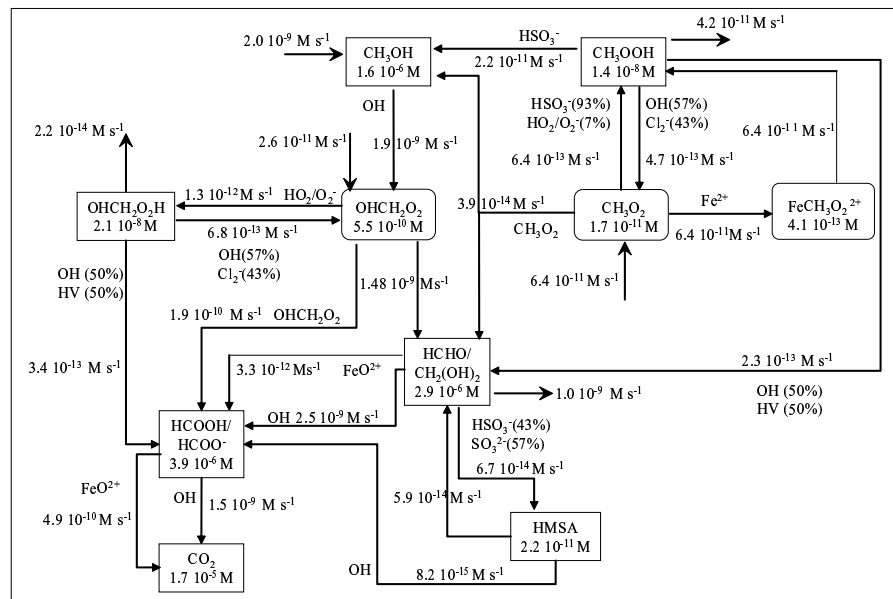
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**Fig. 5.** Concentration/flux diagram for oxidation of VOCs at noon in urban case. Concentration values are reported in the boxes and fluxes are indicated with the arrows.

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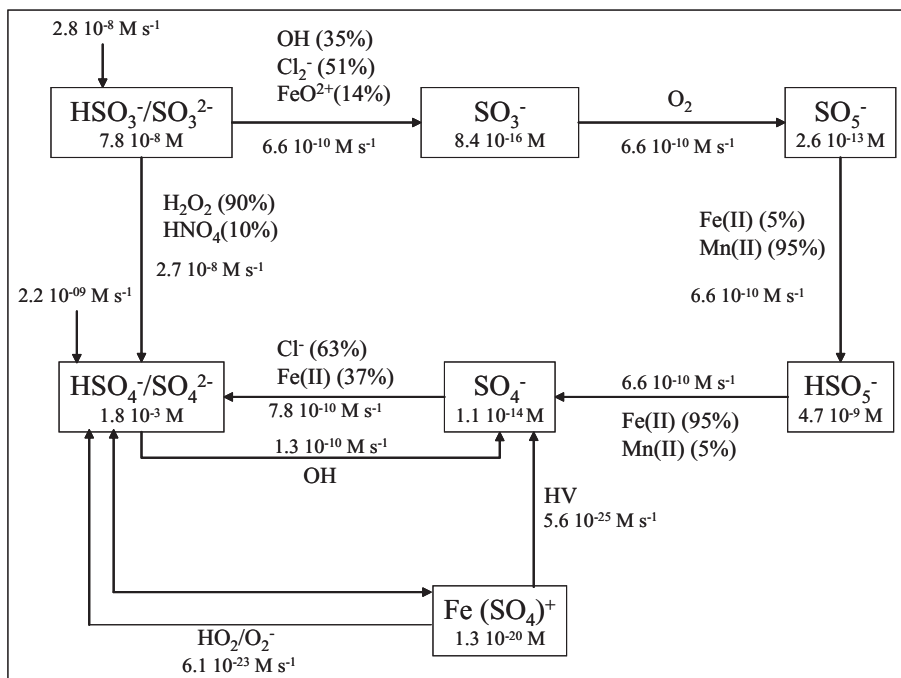
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**Fig. 6.** Concentration/flux diagram for oxidation pathways of S(IV) into S(VI) at noon in urban case. Concentration values are reported in the boxes and fluxes are indicated with the arrows.

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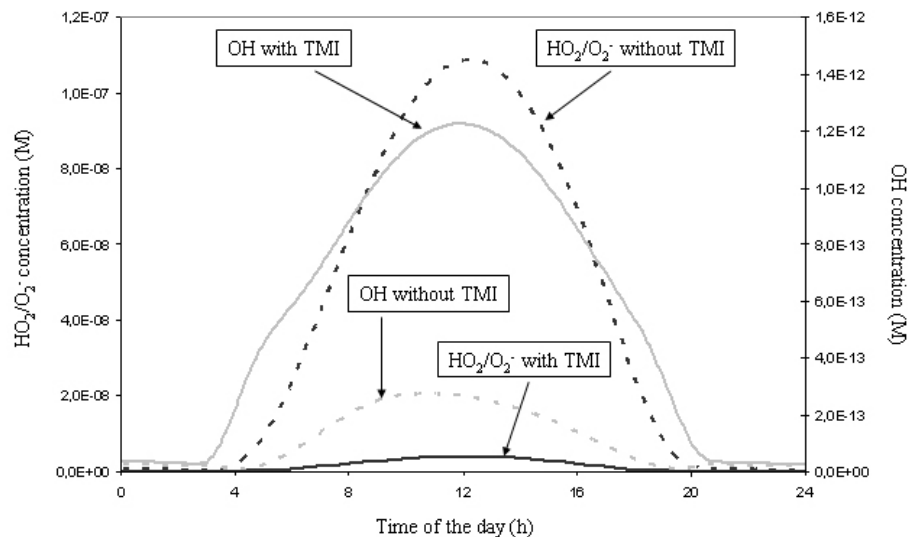
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**Fig. 7.** Time evolution of OH<sub>(aq)</sub> and HO<sub>2</sub>/O<sub>2</sub><sup>-</sup> concentration for urban conditions over one day simulation with and without TMI.

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