

The role of transition metal ions on HO_x 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, oxo-hydroxide and silicate 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.

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 HO₂/O₂⁻ 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 HO₂/O₂⁻ 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 HO₂/O₂⁻ radical and catalyse very efficiently the self-reaction of HO₂/O₂⁻ yielding O₂ and H₂O₂ (Sedlak and Hoigné, 1993). Cloud chemistry model

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calculations suggest that depletion of HO_x by reactions between copper and HO₂/O₂⁻ radical slow down O₃ production significantly in polluted clouds (Matthijsen 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 available. While most of the Fe(II) is thought to be present as the free Fe²⁺ ion at pH < 3, most of the Fe(III) is complexed with OH⁻, SO₄²⁻, 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 HO₂/O₂⁻ 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. HO₂/O₂⁻, H₂O₂, O₃, OH, O₂),
- reductants (e.g. HO₂/O₂⁻, 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 Novi 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).

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 H₂O₂ and O₃ concentrations are low (Pandis and Seinfeld, 1992). The catalysed S(IV) autoxidation may significantly contribute to the total oxidation of SO₂ 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; 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_y 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_x, chlorine, carbonates, NO_y 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_x 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_x, sulphur, NO_y 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 (CH₃O₂) and the equilibrium between iron and sulphate.

In the iron mechanism, the ferryl ion FeO²⁺ and its reactivity are taken into account. Until recently, the oxidation of ferrous ion (Fe(II)) by ozone was considered as producing 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_x, sulphite and VOCs (formaldehyde and formic acid). The reaction between the ferryl ion and Fe²⁺ ion branches into two reactions forming Fe³⁺ or dimer Fe(OH)₂Fe⁴⁺ (R18 and R19). The formation of dimer Fe(OH)₂Fe⁴⁺ is favoured at higher temperature (R19). Afterwards, this species produces also Fe³⁺ (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 CH₃O₂Fe²⁺ (R41), which later decomposes into Fe³⁺ and CH₃OOH (R42 and R43) (Khaikin et al., 1996).

In M2C2 model, the equilibrium between sulphate plus Fe³⁺ and the iron-sulphate-complex [Fe(SO₄)]⁺ (R44 and R45) is considered, while the reaction between Fe²⁺ and SO₄⁻ 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 Mn²⁺ 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 MnO²⁺ (Mn(IV)) without formation of free OH radical (R62). Then, MnO²⁺ rapidly reacts with Mn²⁺ 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 min 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 (O₃) and hydroxymethyl hydroperoxide (OHCH₂OOH) photolysis in droplets.

2.2.3 Emission and deposition

Emission and deposition have to be considered since otherwise species such as SO₂ 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 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 g/m³),

Table 1. Iron chemistry.

Reactants	Products	N ^o	k ₂₉₈ (M ⁻ⁿ⁺¹ s ⁻¹)	E _a /R (K)	References
H ₂ O ₂ +Fe ²⁺	Fe ³⁺ +OH+OH ⁻	R1	70	5050	Christensen et al. (1993)
H ₂ O ₂ +FeO ²⁺	Fe ³⁺ +HO ₂ +OH ⁻	R2	9.5 10 ³	2800	Jacobsen et al. (1997a)
H ₂ O ₂ +Fe(OH) ⁺	Fe(OH) ₂ ²⁺ +OH+OH ⁻	R3	1.9 10 ⁶	6200	Moffett et Zika (1987)
H ₂ O ₂ +Fe ³⁺	Fe ²⁺ +HO ₂ +H ⁺	R4	2.0 10 ⁻³		Walling et Goosen (1973)
H ₂ O ₂ +Fe(OH) ²⁺	Fe ²⁺ +HO ₂ +H ₂ O	R5	2.0 10 ⁻³ =k ₄		estimated
H ₂ O ₂ +Fe(OH) ²⁺	Fe ²⁺ +HO ₂ +OH ⁻ +H ₂ O	R6	2.0 10 ⁻³ =k ₄		estimated
O ₂ ⁻ +Fe ²⁺ +2H ⁺	H ₂ O ₂ +Fe ³⁺	R7	1.0 10 ⁷		Rush and Bielski (1985)
O ₂ ⁻ +Fe ³⁺	Fe ²⁺ +O ₂	R8	1.5 10 ⁸		Rush and Bielski (1985)
O ₂ ⁻ +Fe(OH) ²⁺	Fe ²⁺ +O ₂ +OH ⁻	R9	1.5 10 ⁸		Rush and Bielski (1985)
O ₂ ⁻ +Fe(OH) ²⁺	Fe ²⁺ +O ₂ +2OH ⁻	R10	1.5 10 ⁸		Rush and Bielski (1985)
HO ₂ +Fe ²⁺ +H ⁺	Fe ³⁺ +H ₂ O ₂	R11	1.2 10 ⁶	5050	Jayson et al. (1973b)
HO ₂ +FeO ²⁺	Fe ³⁺ +O ₂ +OH ⁻	R12	2.0 10 ⁶		Jacobsen et al. (1998b)
HO ₂ +Fe(OH) ²⁺	Fe ²⁺ +O ₂ +H ₂ O	R13	1.3 10 ⁵		Ziajka et al. (1994)
OH+Fe ²⁺	Fe(OH) ²⁺	R14	4.6 10 ⁸	1100	Christensen and Sehested (1981)
OH+FeO ²⁺ +H ⁺	Fe ³⁺ +H ₂ O ₂	R15	1.0 10 ⁷		Logager et al. (1992)
O ₃ +Fe ²⁺	FeO ²⁺ +O ₂	R16	8.2 10 ⁵		Logager et al. (1992)
FeO ²⁺ +H ₂ O	Fe ³⁺ +OH+OH ⁻	R17	1.3 10 ⁻²	4100	Jacobsen et al. (1998b)
FeO ²⁺ +Fe ²⁺ +H ₂ O	2Fe ³⁺ +2OH ⁻	R18	7.2 10 ⁴	842	Jacobsen et al. (1997a)
FeO ²⁺ +Fe ²⁺ +H ₂ O	Fe(OH) ₂ Fe ⁴⁺	R19	1.8 10 ⁴	5052	Jacobsen et al. (1997a)
Fe(OH) ₂ Fe ⁴⁺	2Fe ³⁺ +2OH ⁻	R20	0.49	8780	Jacobsen et al. (1997a)
Fe(OH) ₂ Fe ⁴⁺ +2H ⁺	2Fe ³⁺ +2H ₂ O	R21	1.95	5653	Jacobsen et al. (1997a)
Cl ₂ ⁻ +Fe ²⁺	Fe ³⁺ +2Cl ⁻	R22	1.0 10 ⁷	3060	Thornton and Laurence (1973)
Cl ₂ ⁻ +Fe ²⁺	FeCl ²⁺ +Cl ⁻	R23	4.0 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 10 ⁶		Pikaev et al. (1974)
NO ₂ +Fe ²⁺	Fe ³⁺ +NO ₂ ⁻	R26	3.1 10 ⁴		Epstein et al. (1982)
HNO ₂ +FeO ²⁺	Fe ³⁺ +NO ₂ +OH ⁻	R27	1.1 10 ⁴	4150	Jacobsen et al. (1998b)
NO ₂ ⁻ +FeO ²⁺ +H ⁺	Fe ³⁺ +NO ₂ +OH ⁻	R28	1.0 10 ⁵		Jacobsen et al. (1998b)
HSO ₃ ⁻ +Fe(OH) ²⁺	Fe ²⁺ +SO ₃ ⁻ +H ₂ O	R29	30		Ziajka et al. (1994)
SO ₅ ⁻ +Fe ²⁺ +H ₂ O	Fe(OH) ²⁺ +HSO ₅ ⁻	R30	2.65 10 ⁷		Williams (1996)
HSO ₅ ⁻ +Fe ²⁺	Fe(OH) ²⁺ +SO ₄ ⁻	R31	3.0 10 ⁴		Gilbert et al. (1990)
SO ₄ ⁻ +Fe ²⁺ +H ₂ O	Fe(OH) ²⁺ +SO ₄ ⁻ +H ⁺	R32	4.1 10 ⁹	-2165	Buxton et al. (1997)
O ₂ ⁻ +Fe(SO ₄) ⁺	Fe ²⁺ +SO ₄ ²⁻ +O ₂	R33	1.5 10 ⁸		Rush and Bielski (1985)
HO ₂ +Fe(SO ₄) ⁺	Fe ²⁺ +SO ₄ ²⁻ +O ₂ +H ⁺	R34	1.0 10 ³		Rush and Bielski (1985)
S ₂ O ₈ ²⁻ +Fe ²⁺ +H ₂ O	Fe(OH) ²⁺ +2SO ₄ ²⁻ +H ⁺	R35	17		Buxton et al. (1997)
HSO ₃ ⁻ +FeO ²⁺	Fe ³⁺ +SO ₃ ⁻ +OH ⁻	R36	2.5 105		Jacobsen et al. (1998b)
HCOOH+FeO ²⁺ +O ₂ +H ⁺	Fe ³⁺ +CO ₂ +HO ₂ +H ₂ O	R37	160	2680	Jacobsen et al. (1998b)
HCOO ⁻ +FeO ²⁺ +O ₂ +H ⁺	Fe ³⁺ +CO ₂ +HO ₂ +OH ⁻	R38	3.0 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 10 ⁷		estimated from Herrmann et al. (2000)
CH ₃ O ₂ +Fe ²⁺	CH ₃ O ₂ Fe ³⁺	R41	8.6 10 ⁵		Khaikin et al. (1996)
CH ₃ O ₂ Fe ²⁺ +H ₂ O	Fe ³⁺ +CH ₃ OOH+OH ⁻	R42	100		Khaikin et al. (1996)
CH ₃ O ₂ Fe ²⁺ +H ⁺	Fe ³⁺ +CH ₃ OOH	R43	3.0 10 ⁴		Khaikin et al. (1996)
Fe ³⁺ +SO ₄ ²⁻	Fe(SO ₄) ⁺	R44	3.2 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 10 ⁻¹		estimated

Table 2. Copper-chemistry.

Reactants	Products	N°	k ₂₉₈ (M ⁻ⁿ⁺¹ s ⁻¹)	E _a /R (K)	References
OH+Cu ⁺	Cu ²⁺ +OH ⁻	R48	3.0 10 ⁹		Goldstein et al. (1992)
O ₃ +Cu ⁺ +H ⁺	Cu ²⁺ +OH+O ₂	R49	3.0 10 ⁷		Hoigné and Bühler (1996)
O ₂ +Cu ⁺	Cu ²⁺ +O ₂ ⁻	R50	4.6 10 ⁵		Bjergbakke et al. (1976)
H ₂ O ₂ +Cu ⁺	Cu ²⁺ +OH+OH ⁻	R51	7.0 10 ³		Berdnikov et al. (1973)
HO ₂ +Cu ⁺ +H ⁺	Cu ²⁺ +H ₂ O ₂	R52	3.5 10 ⁹		Berdnikov et al. (1973)
O ₂ ⁻ +Cu ⁺ +2H ⁺	Cu ²⁺ +H ₂ O ₂	R53	9.4 10 ⁹		Von Piechowski et al. (1993)
HO ₂ +Cu ²⁺	Cu ⁺ +O ₂ +H ⁺	R54	1.0 10 ⁸		Rabani et al. (1973)
O ₂ ⁻ +Cu ²⁺	Cu ⁺ +O ₂	R55	8.0 10 ⁹		Rabani et al. (1973)
Cl ₂ ⁻ +Cu ⁺	Cu ²⁺ +2Cl ⁻	R56	1.0 10 ⁷ =k ₂₂		estimated
SO ₄ ⁻ +Cu ⁺	Cu ²⁺ +SO ₄ ²⁻	R57	1.8 10 ⁷ =k ₇₅	4100	estimated
CO ₃ ⁻ +Cu ⁺	Cu ²⁺ +CO ₃ ²⁻	R58	2.0 10 ⁷		estimated from Herrmann et al. (2000)
Cu ²⁺ +OH	Cu(OH) ²⁺	R59	3.5 10 ⁸		Baxendale et al. (1971)
Cu(OH) ²⁺	Cu ²⁺ +OH	R60	3.0 10 ⁴		Meyerstein (1971)

Table 3. Manganese-chemistry.

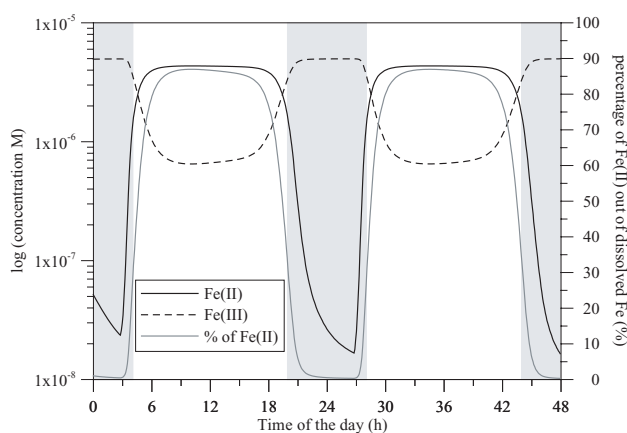
Reactants	Products	N°	k ₂₉₈ (M ⁻ⁿ⁺¹ s ⁻¹)	E _a /R (K)	References
OH+Mn ²⁺	Mn(OH) ²⁺	R61	2.0 10 ⁷		Jacobsen et al. (1997b)
O ₃ +Mn ²⁺	MnO ²⁺ +O ₂	R62	1.65 10 ³	4750	Jacobsen et al. (1998a)
MnO ²⁺ +Mn ²⁺ +2H ⁺	2Mn ³⁺ +H ₂ O	R63	1.0 10 ⁵		Jacobsen et al. (1998a)
MnO ²⁺ +MnO ²⁺ +2H ⁺	2Mn ²⁺ +H ₂ O ₂ +O ₂	R64	6.0 10 ⁶		Jacobsen et al. (1997b)
MnO ₂ ⁺ +HO ₂ +H ⁺	Mn ²⁺ +H ₂ O ₂ +O ₂	R65	1.0 10 ⁷		Jacobsen et al. (1997b)
H ₂ O ₂ +Mn ³⁺	Mn ²⁺ +HO ₂ +H ⁺	R66	7.3 10 ⁴		Davies et al. (1968)
H ₂ O ₂ +Mn(OH) ²⁺	MnO ²⁺ +H ⁺ +H ₂ O	R67	2.8 10 ³		Jacobsen et al. (1997b)
H ₂ O ₂ +Mn ⁴⁺	Mn ²⁺ +2H ⁺ +O ₂	R68	1.25 10 ⁸		estimated from Jacobsen et al. (1998a)
NO ₃ +Mn ²⁺	Mn ³⁺ +NO ₃ ⁻	R69	1.1 10 ⁶		Neta and Huie (1986)
Cl ₂ ⁻ +Mn ²⁺	Mn ³⁺ +2Cl ⁻	R70	8.5 10 ⁶	4090	Laurence and Thornton (1973)
Cl ₂ ⁻ +Mn ²⁺	MnCl ₂ ⁺	R71	2.0 10 ⁷	4090	Laurence and Thornton (1973)
MnCl ₂ ⁺	Mn ²⁺ +Cl ₂ ⁻	R72	3.0 10 ⁵		Laurence and Thornton (1973)
MnCl ₂ ⁺	Mn ³⁺ +2Cl ⁻	R73	2.1 10 ⁵	2100	Laurence and Thornton (1973)
HSO ₅ ⁻ +Mn ²⁺	Mn ³⁺ +SO ₄ ⁻ +OH ⁻	R74	3.0 10 ⁴ =k ₃₁		estimated
SO ₄ ⁻ +Mn ²⁺	Mn ³⁺ +SO ₄ ²⁻	R75	1.8 10 ⁷	4100	Buxton et al. (1997)
SO ₅ ⁻ +Mn ²⁺ +H ₂ O	Mn ³⁺ +HSO ₅ ⁻ +OH ⁻	R76	1.0 10 ¹⁰		Berglund et al. (1994)
MnHSO ₃ ⁺ +Mn ³⁺	2Mn ²⁺ +SO ₃ ⁻ +H ⁺	R77	1.3 10 ⁶		Berglund et al. (1994)
CO ₃ ⁻ +Mn ²⁺	Mn ³⁺ +CO ₃ ²⁻	R78	1.5 10 ⁷		Cope et al. (1978)
Mn ²⁺ +O ₂ ⁻	MnO ²⁺	R79	9.5 10 ⁷		Jacobsen et al. (1997b)
MnO ²⁺	Mn ²⁺ +O ₂ ⁻	R80	7.5 10 ³		Jacobsen et al. (1997b)
Mn ²⁺ +HO ₂	MnO ₂ ⁺ +H ⁺	R81	1.45 10 ⁶		Jacobsen et al. (1997b)
MnO ²⁺ +H ⁺	Mn ²⁺ +HO ₂	R82	1.4 10 ⁷		Jacobsen et al. (1997b)
Mn ³⁺ +Mn ³⁺	Mn ²⁺ +Mn ⁴⁺	R83	1.0 10 ⁷		estimated from Jacobsen et al. (1998a) and Rosseinsky (1963)
Mn ²⁺ +Mn ⁴⁺	Mn ³⁺ +Mn ³⁺	R84	1.0 10 ⁷		estimated from Jacobsen et al. (1998a) and Rosseinsky (1963)
Mn ²⁺ +HSO ₃ ⁻	MnHSO ₃ ⁺	R85	3.1 10 ⁷		Berglund et al. (1993)
MnHSO ₃ ⁺	Mn ²⁺ +HSO ₃ ⁻	R86	1.03 10 ³		Berglund et al. (1993)

Table 4. Coupled TMI chemistry.

Reactants	Products	N°	k ₂₉₈ (M ⁻ⁿ⁺¹ s ⁻¹)	E _a /R (K)	References
Fe ³⁺ +Cu ⁺	Fe ²⁺ +Cu ²⁺	R87	1.3 10 ⁷		Buxton et al. (1995)
Fe(OH) ²⁺ +Cu ⁺	Fe ²⁺ +Cu ²⁺ +OH ⁻	R88	1.3 10 ⁷ =k ₈₇		estimated
Fe(OH) ₂ ⁺ +Cu ⁺	Fe ²⁺ +Cu ²⁺ +2OH ⁻	R89	1.3 10 ⁷ =k ₈₇		estimated
Mn ³⁺ +Fe ²⁺	Mn ²⁺ +Fe ³⁺	R90	1.3 10 ⁴		Davies (1969)
Mn(OH) ²⁺ +Fe ²⁺	Mn ²⁺ +Fe(OH) ²⁺	R91	2.1 10 ⁴		Davies (1969)
Mn ²⁺ +FeO ²⁺ +2H ⁺	Mn ³⁺ +Fe ³⁺ +H ₂ O	R92	1.0 10 ⁴	2700	Jacobsen et al. (1998b)

Table 5. Aqueous phase equilibria.

Reactions	N°	K (M)	ΔH/R (K)	References
Fe ²⁺ +H ₂ O=Fe(OH) ⁺ +H ⁺	E1	3.22 10 ⁻¹⁰		Mesmer (1971)
Fe ³⁺ +H ₂ O=Fe(OH) ²⁺ +H ⁺	E2	6.0 10 ⁻³		Brandt and van Eldik (1995)
Fe(OH) ²⁺ +H ₂ O=Fe(OH) ₂ ⁺ +H ⁺	E3	7.62 10 ⁻⁶		Hemmes et al. (1971)
Mn ³⁺ +H ₂ O=Mn(OH) ²⁺ +H ⁺	E4	9.30 10 ⁻¹		Wells and Davies (1967)
Mn(OH) ²⁺ +H ₂ O=Mn(OH) ₂ ⁺ +H ⁺	E5	1.00 10 ⁻⁵		Baral et al. (1986)

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

the temperature (288.15 K), the pressure (1000 hPa) and the droplet radius (10 μm) are set constant during the simulation, which lasts 72 h. Results are discussed only for the two last days. The pH conditions are calculated at each time step by solving the electro-neutrality equation, which contains the main ionic species such as carbonates, ammoniac, sulphate, nitrate, TMI and chlorine. 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

Table 7 presents the initialization of transition metal ions used for the three scenarios (urban, remote, marine). The

transition metals are initialized as Fe³⁺, Mn³⁺ and Cu⁺. Initial concentrations of transition metal ions are the highest in the urban case and iron is the dominant species. The initial concentrations of manganese and copper are the same and the ratio between iron and manganese (or copper) is equal to 20 in the two continental cases and to 50 in the marine scenario. All these conditions are similar to the scenarios described by Ervens et al. (2003).

Figure 1 represents the time evolution of the Fe(II) and Fe(III) concentrations and of the Fe(II)/Fe(III) ratio in the urban conditions for which iron concentrations are particularly important. During the day, Fe(III) is converted into Fe(II) and a strong dependency of Fe(II)/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 Fe(II) (P1, P2, P3 and P4), the main differences between day and night are due to the redox reactions between Cu(I) and Fe(III) (R87, R88, R89) and to the reactions between Fe(III) and HO₂/O₂⁻ radicals (R8, R9, R10 and R13). Concerning the production 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 O₃ 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

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

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

Table 7. Initialization of transition metal ions for the three scenarios (urban, remote, marine).

Transition metal	Initial species	Urban (M)	Remote (M)	Marine (M)
Iron	Fe ³⁺	5.0 10 ⁻⁶	5.0 10 ⁻⁷	5.0 10 ⁻⁸
Manganese	Mn ³⁺	2.5 10 ⁻⁷	2.5 10 ⁻⁸	1.0 10 ⁻⁹
Copper	Cu ⁺	2.5 10 ⁻⁷	2.5 10 ⁻⁸	1.0 10 ⁻⁹

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 the 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 10⁻¹², 1.5 10⁻¹² and 4.8 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 (Fe²⁺ and Cu⁺) (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 H₂O₂ 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 high SO₂ emission in the urban case, H₂O₂ is efficiently consumed and has a relatively low concentration (3 10⁻⁶ M at noon the second day) compared to the two other cases (1.1 10⁻⁴ M and 2.4 10⁻⁴ M for the remote and marine cases respectively). With these urban conditions of high TMI and low H₂O₂, 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 H₂O₂ 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⁻ and ClOH⁻ which is shifted towards production of ClOH⁻. This contribution is more important in the marine case than in the two continental cases because, in the marine case, initial concentration of

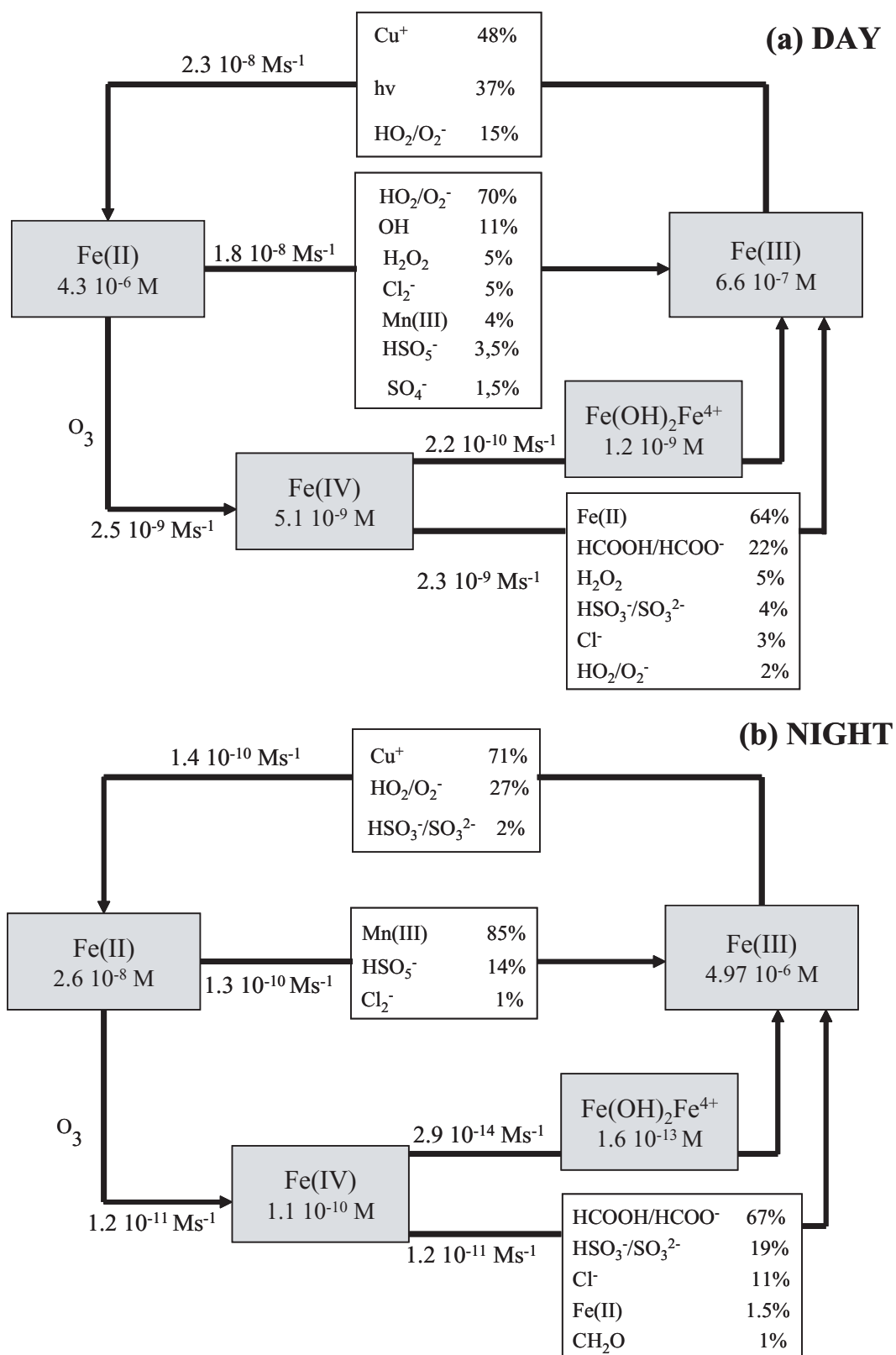


Fig. 2. Iron redox reactions during the day (a) and at night (b) for the urban scenario.

chlorine in the gas phase and in the aqueous phase are larger than in the continental cases. Due to high H₂O₂ concentration in the remote and marine cases, reaction between H₂O₂ 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 CH₂O, which is oxidized by OH_(aq). 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_(aq) concentration levels.

3.2.2 Radical anions

The same analysis than for OH has been performed for the dichloride radical anion Cl₂⁻ (not shown). The sources for the Cl₂⁻ correspond to those of Cl atom because Cl₂⁻ is formed through a fast equilibrium between Cl⁻ plus Cl atom and Cl₂⁻ 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 ClOH⁻ and Cl plus OH⁻ (85% of Cl atom production in the urban case). Since ClOH⁻ is formed after the equilibrium between Cl⁻ plus OH and ClOH⁻, the evolution of Cl₂⁻ follows the one of OH_(aq) (Fig. 3). The second source for chlorine atoms is the reaction of chloride with SO₄⁻ (15%), due to the high SO₂ emission in the urban case. The main sinks of this radical anion are the reactions between Cl₂⁻ with HO₂/O₂⁻ radical (48%), with Fe(II) (40%) and with HSO₃⁻/SO₃²⁻ (10%). Reaction of Cl₂⁻ with H₂O₂ is negligible (2%) since H₂O₂ concentration is very low in the urban case.

The other two radical anions, the sulphate radical anion, SO₄⁻ and the carbonate radical anion CO₃⁻ 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 10⁻¹⁴ M for SO₄⁻ and of 5.5 10⁻¹⁴ M for CO₃⁻. These two radicals are mainly influenced by the concentration of OH_(aq) during the day and by the concentration of NO₃ 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 HO_x radicals is the

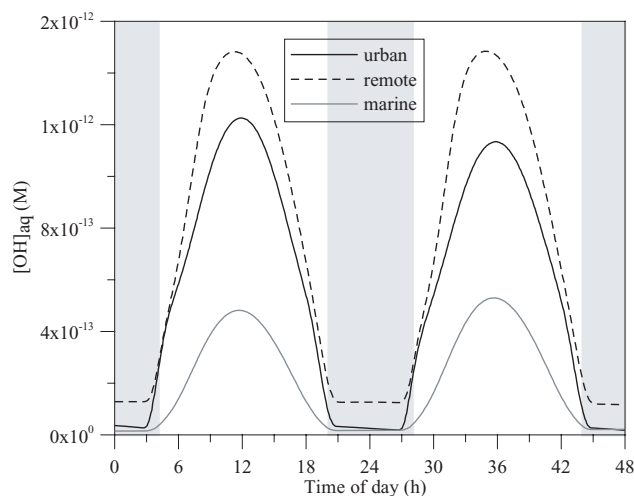


Fig. 3. Simulated time evolution of OH_(aq) for urban, remote and marine conditions. Shaded areas correspond to night-time periods.

most important and, therefore the most significant for aqueous phase oxidation of soluble VOCs. The contribution of the ferryl ion (FeO²⁺) 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 indirect. TMI chemistry increases OH_(aq) concentrations leading to a more important oxidation of VOCs yielding to more HO_{2(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 SO₂.

In the sulphate formation, two pathways can be distinguished:

- A direct production of sulphate through the oxidation of S(IV) by H₂O₂, O₃, HNO₄,
- An indirect pathway through TMI catalysis which is initiated by the oxidation of S(IV) by OH, Cl₂⁻ and FeO²⁺.

The HSO₃⁻/SO₃²⁻ concentration decreases from 8.5 10⁻⁷ M to 1.0 10⁻⁷ M over a time period of 72 h. In the urban case, due to the high 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 H₂O₂ and HNO₄. Although H₂O₂

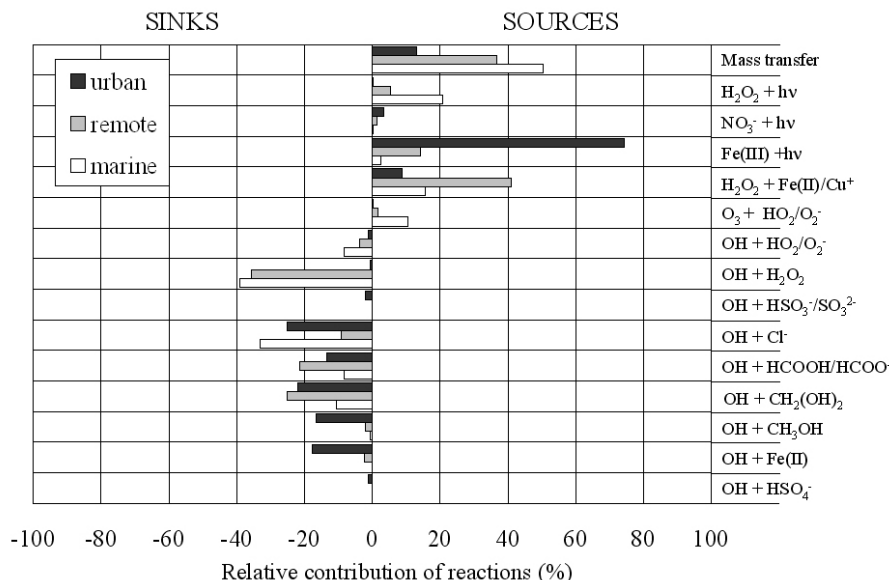


Fig. 4. Sinks and sources for OH_(aq) for urban, remote and marine conditions at noon 2 day. Values of production and loss fluxes are identical and are in [M s⁻¹]: urban 1.1 10⁻⁸, remote 9.5 10⁻⁹, marine 5.5 10⁻⁹.

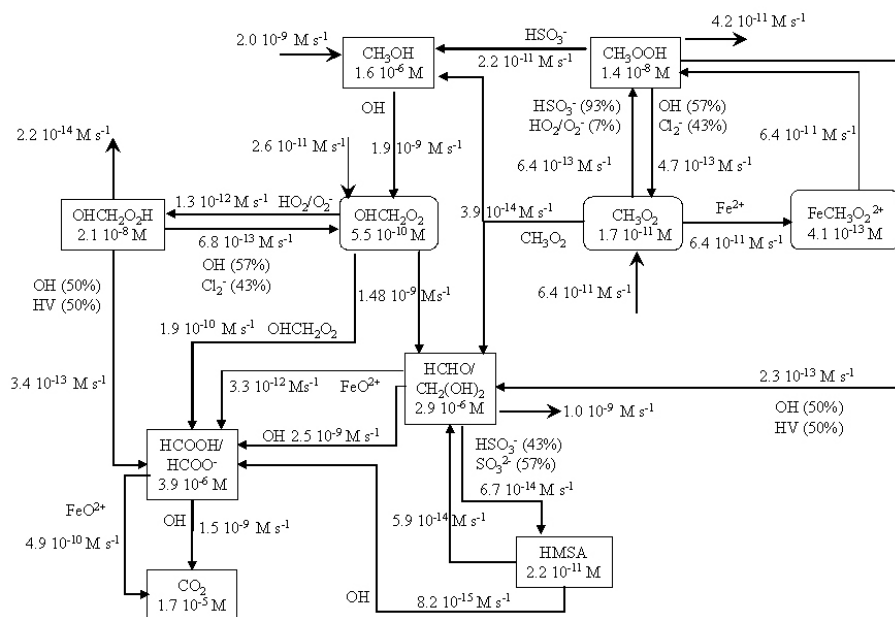


Fig. 5. Concentration/flux diagram for oxidation of VOCs at noon in urban case. Concentration values are reported in the boxes and fluxes are indicated with the arrows.

concentration is low, oxidation of S(IV) by H₂O₂ remains dominant throughout the simulation. Indeed, the reaction of Cu⁺ with oxygen (R50) leads to high HO₂/O₂⁻ concentration in the aqueous phase, which results in a continuously H₂O₂ formation through reactions of HO₂/O₂⁻ with Fe(II) and Cu⁺ (R7, R11 and R52, R53). Indeed, iron is mainly present as Fe(II) during the day and concentration of Cu⁺ is maintained

(maximum at noon 1.3 10⁻⁹ M) by reaction of Cu²⁺ with HO₂/O₂⁻ radical (R54, R55).

The direct conversion pathway of S(IV) to S(VI) is about the same order of magnitude than the transfer of SO₂ from the gas phase. This continuous transfer of SO₂ from the gas phase, due to high SO₂ emission considered in the urban scenario, explains the low hydrogen peroxide concentration.

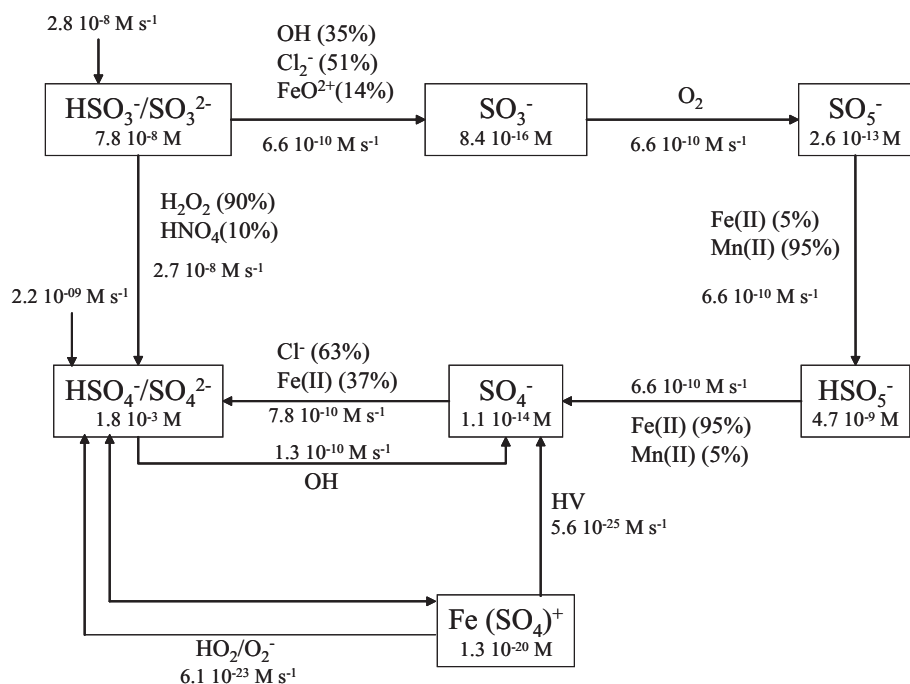


Fig. 6. Concentration/flux diagram for oxidation pathways of S(IV) into S(VI) at noon in urban case. Concentration values are reported in the boxes and fluxes are indicated with the arrows.

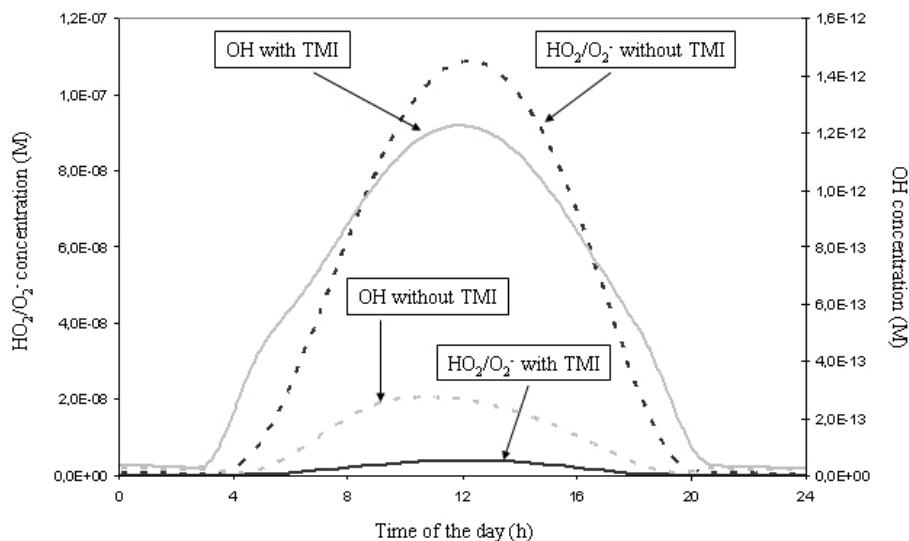


Fig. 7. Time evolution of $\text{OH}_{(\text{aq})}$ and HO_2/O_2^- concentration for urban conditions over one day simulation with and without TMI.

In CAPRAM2.4, SO_2 concentration increases throughout the simulation in the urban case. This difference with our SO_2 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.

Table 8. 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	85	99.7	4	90 ^{1a} 40–80 ^d 62 ^f
Remote	80	98	N.A.	76 ^c
Marine	80	85	N.A.	70–80 ^{3b}
NIGHT				
	M2C2	CAPRAM2.3	CAPRAM2.4	measured
Urban	1	99.7	2	20–60 ^{1a} 0 ² –40 ^d 45–60 ^e 50 ^f
Remote	20	98	N.A.	26–55 ^c
Marine	20	85	N.A.	N.A.

¹percentage of Fe(II) out of total amount of Fe,

²Fe(II) is below detection limits, marine air mass with anthropogenic influence.

^aBehra and Sigg, 1990;

^bPehkonen et al., 1992;

^cErel et al., 1993;

^dSedlak et al., 1997.

^eSchwanz et al., 1998;

^fDeutsch et al., 2001.

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 8 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.

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 (Fe²⁺ and Cu⁺) in the continental scenarios. To specify this effect of TMI chemistry on HO_x 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_(aq) of 2.7 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 Matthijsen et al. (1997) who found an increase of about 2.55 of OH_(aq) in the presence of TMI. HO₂ radical exhibits a different behaviour than OH_(aq) if TMI chemistry is neglected. For the urban case, the HO_{2(aq)} concentration at noon increases from 4.0 10⁻⁹ M considering TMI to 1.1 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_x radicals concentrations in aqueous phase and shows that, among TMI, dissolved iron has a leader role on HO_x chemistry and that copper plays a significant role in the chemistry of H_xO_y.

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 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_xO_y as shown by the sensitivity test comparing urban simulation with and without TMI chemistry.

More measurements on iron speciation are needed as a function of light conditions (night and day), together with H₂O₂ and oxalate concentrations in order to evaluate the sensitive parameter of the iron speciation. Future laboratory experiments should include irradiation tests on real cloud water samples to complement the field experiments with controlled temperature, concentration levels and light conditions. Also, the Fenton reaction, which is still subject to many controversies (Gozzo, 2001; Dunford, 2002; Kremer, 2003), needs some more investigations.

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 H₂O₂ production in droplets leading to an efficient conversion of

S(IV) into S(VI) by reaction with H₂O₂, which contributes to the acidification of droplets. This chemical pathway associated with other SO₂ 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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