Supplementary material

Iron(III)-induced activation of chloride from artificial sea-salt aerosol

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Table S1.   Composition of the prepared artificial seawater applied according to Kester et al. [1]
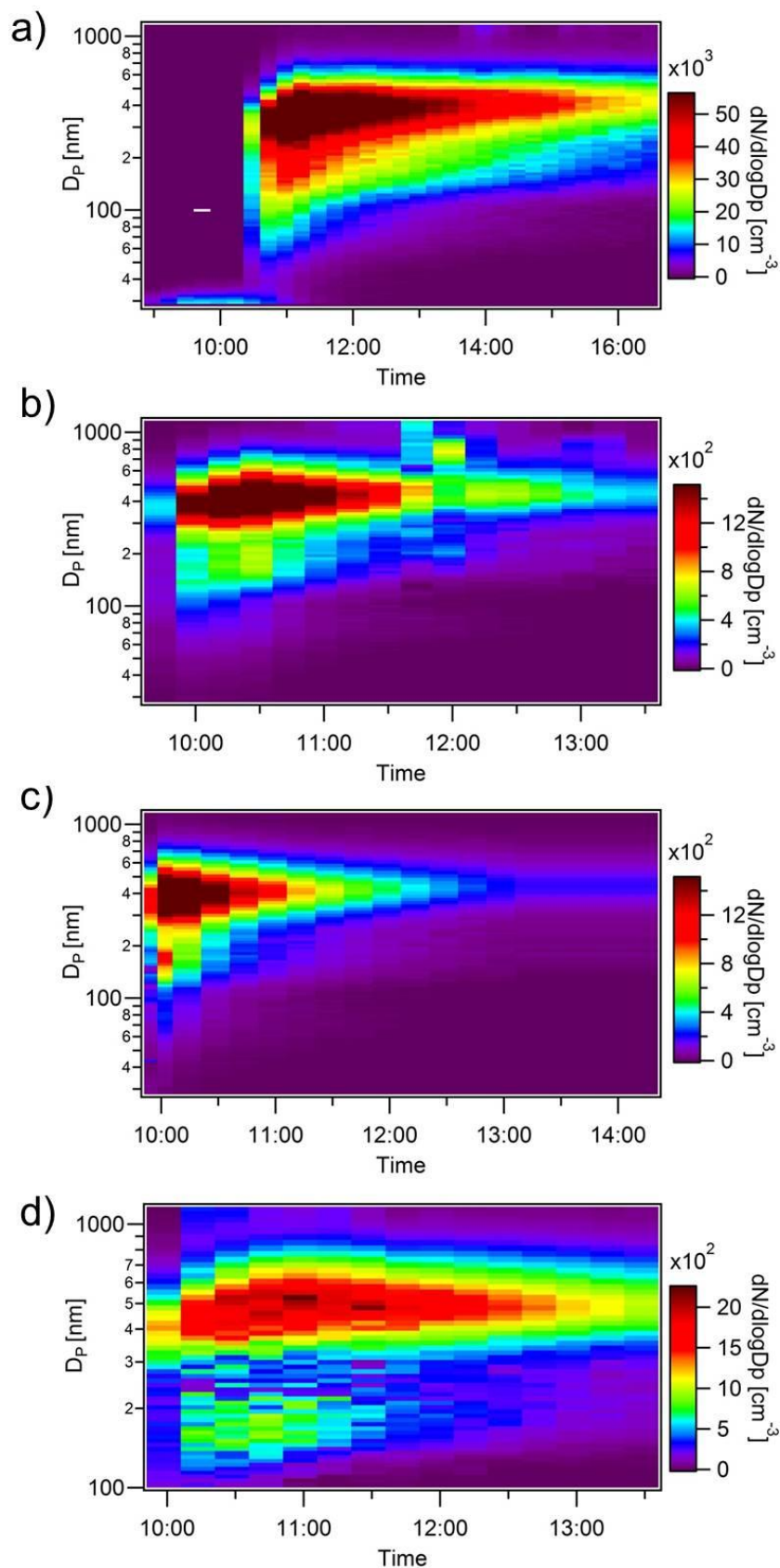
Salt	Manufacturer	Weighed amount (g) in 1 L H_2O
Artificial seawater		
NaCl	Sigma–Aldrich, ACS	23.9
$Na_2SO_4 \cdot 10H_2O$	Merck, ACS	9.09
KCl	Roth, ACS	0.68
$NaHCO_3$	Merck, for analysis	0.20
KBr	Merck, for analysis	0.098
H_3BO_3	Grüssing GmbH, 99.5 %	0.026
NaF	Riedel de Haën, for analysis	0.003
$MgCl_2$	Sigma–Aldrich, 98 %	5.07
$CaCl_2 \cdot 2H_2O$	Grüssing, 99 %	1.52

Table S2.   Rate constants for the reactions of methane and the reference hydrocarbons used as radical tracers for OH, Cl and Br at 298 K
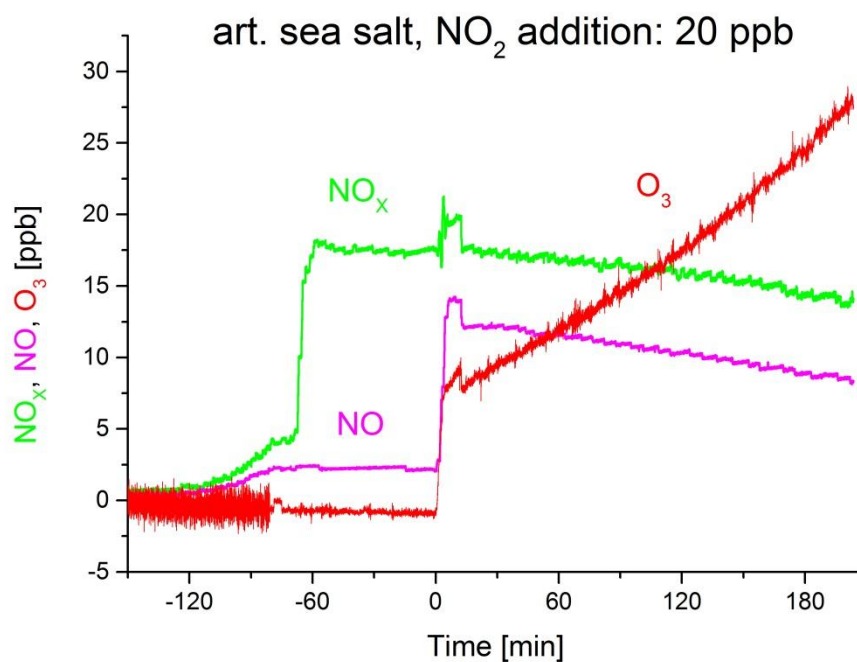
Hydrocarbon	k_{OH} ($cm^3\ s^{-1}$)	k_{Cl} ($cm^3\ s^{-1}$)	k_{Br} ($cm^3\ s^{-1}$)
Methane (CH_4)	6.7×10^{-15} [2]	1.07×10^{-13} [2]	4×10^{-24} [3]
2,2-Dimethylpropane (DMP)	8.3×10^{-13} [2]	1.1×10^{-10} [4]	$\leq 1 \times 10^{-20}$ [5]
2,2-Dimethylbutane (DMB)	2.2×10^{-12} [2]	1.7×10^{-10} [6]	–
2,2,4-Trimethylpentane (TMP)	3.3×10^{-12} [2]	2.3×10^{-10} [7]	6.8×10^{-15} [8]
Toluene	6.2×10^{-12} [9]	5.9×10^{-11} [10]	1.3×10^{-14} [11]
n-Perfluorohexane	–	–	–

Table S3. Main equilibrium constants ($\log_{10}K$) for the formation of low-molecular-weight Fe^{III} complexes with several ligands at zero ionic strength and 298 K
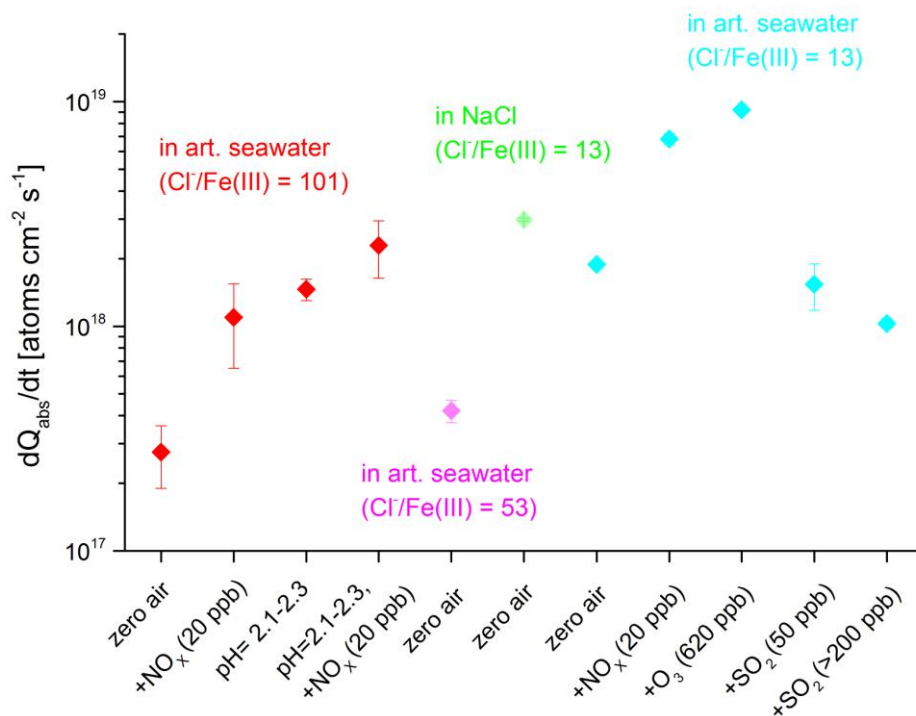
Equilibrium constants	$\log_{10}K$
Water	
	−2.19[12]
	−5.67[12]
	−12.0[12]
	−21.6[12]
Chloride	
	1.48[13]
	2.13[14]
	1.13[15]
Bromide	
	0.61[16]
	0.2[16]
Fluoride	
	6.2[17]
	10.8[17]
	14.0[17]
Sulfate	
	3.92[18]
	5.42[18]

Fig. S1. Contour plots of selected experiments with nebulised (a) NaCl (1 g L^{-1}); (b) NaCl + FeCl$_3$ (~18 mmol L^{-1} Cl$^-$, Cl$^-$/Fe^{III} = 13); (c) artificial seawater + FeCl$_3$ (~29 mmol L^{-1} Cl$^-$, Cl$^-$/Fe^{III} = 101); and (d) artificial seawater + FeCl$_3$ (~37 mmol L^{-1} Cl$^-$, Cl$^-$/Fe^{III} = 13)

Fig. S2. Time profiles of NO_x, NO and O_3 during the experiment with Fe^{III}-free artificial seawater and 20 ppb NO_2.

Fig. S3. Overview of the initial minimum absolute Cl production rate dQ_{abs}/dt (atoms cm^{-2} s^{-1}) for each experiment with Fe^{III}-containing samples and various air contaminants (NO_x, O_3, SO_2).

References

[1]   D. R. Kester, I. W. Duedall, D. N. Connors, R. M. Pytkowicz, Preparation of artificial seawater. *Limnol. Oceanogr.* **1967**, *12*, 176. doi:10.4319/lo.1967.12.1.0176

[2]   R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr, M. J. Rossi, J. Troe, Evaluated kinetic, photochemical and heterogeneous data for atmospheric chemistry: supplement V. IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. *J. Phys. Chem. Ref. Data* **1997**, *26*, 521. doi:10.1063/1.556011

[3]   D. L. Baulch, J. Duxbury, S. J. Grant, D. C. Montague, Evaluated kinetic data for high temperature reactions. Volume 4. Homogeneous gas phase reactions of halogen-and cyanide-containing species. *J. Phys. Chem. Ref. Data* **1981**, *10*, 723.

[4]   R. Atkinson, S. M. Aschmann, Kinetics of the gas phase reaction of Cl atoms with a series of organics at 296 ± 2 K and atmospheric pressure. *Int. J. Chem. Kinet.* **1985**, *17*, 33. doi:10.1002/kin.550170105

[5]   J. C. Amphlett, E. Whittle, Bromination of fluoroalkanes. Part 4. Kinetics of thermal bromination of fluoroform and pentafluoroethane. *Trans. Faraday Soc.* **1968**, *64*, 2130. doi:10.1039/tf9686402130

[6]   M. E. Jenkin, S. M. Saunders, M. J. Pilling, The tropospheric degradation of volatile organic compounds: a protocol for mechanism development. *Atmos. Environ.* **1997**, *31*, 81. doi:10.1016/S1352-2310(96)00105-7

[7]   S. M. Aschmann, R. Atkinson, Rate constants for the gas-phase reactions of alkanes with Cl atoms at 296 ± 2 K. *Int. J. Chem. Kinet.* **1995**, *27*, 613. doi:10.1002/kin.550270611

[8]   I. Barnes, V. Bastian, K. H. Becker, R. Overath, Z. Tong, Rate constants for the reactions of Br atoms with a series of alkanes, alkenes, and alkynes in the presence of O_2. *Int. J. Chem. Kinet.* **1989**, *21*, 499. doi:10.1002/kin.550210703

[9]   R. Atkinson, Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions. *Chem. Rev.* **1986**, *86*, 69. doi:10.1021/cr00071a004

[10]   J. Shi, M. J. Bernhard, Kinetic studies of Cl atom reactions with selected aromatic compounds using the photochemical reactor-FTIR spectroscopy technique. *Int. J. Chem. Kinet.* **1997**, *29*, 349. doi:10.1002/(SICI)1097-4601(1997)29:5<349::AID-KIN5>3.0.CO;2-U

[11]   A. Bierbach, I. Barnes, K. H. Becker, Rate constants of the Br-initiated gas-phase oxidation of a series of alcohols, furans and benzenes at 300 ± 2 K. *Atmos. Environ.* **1999**, *33*, 2981. doi:10.1016/S1352-2310(99)00084-9

[12]   C. F. Baes, R. E. Mesmer, *The Hydrolysis of Cations* **1976** (Wiley: New York).

[13]   D. R. Kester, R. H. Byrne, Y.-J. Liang, Redox reactions and solution complexes of iron in marine systems, in *Marine Chemistry in the Coastal Environment, Vol. 18* (Ed. T. M. Church) **1975**, pp. 56–79 (American Chemical Society: Washington, DC).

[14]   A. E. Martell, R. M. Smith, *Critical Stability Constants. Volume 4. Inorganic Complexes* **1976** (Plenum: New York).

[15]   K. B. Yatsimirskii, V. P. Vasil'ev, *Instability Constants of Complex Compounds* **1960** (Pergamon Press: Oxford, UK).

[16]   M. W. Lister, D. E. Rivington, Some ferric halide complexes, and ternary complexes with thiocyanate ions. *Can. J. Chem.* **1955**, *33*, 1603. doi:10.1139/v55-194

[17]   D. K. Nordstrom, E. A. Jenne, Fluorite solubility equilibria in selected geothermal waters. *Geochim. Cosmochim. Acta* **1977**, *41*, 175. doi:10.1016/0016-7037(77)90224-1

[18]   J. De Laat, T. G. Le, Kinetics and modeling of the Fe^{III}/H_2O_2 system in the presence of sulfate in acidic aqueous solutions. *Environ. Sci. Technol.* **2005**, *39*, 1811. doi:10.1021/es0493648