

D.E.A. CHIMIE DE LA POLLUTION ATMOSPHERIQUE ET PHYSIQUE DE L'ENVIRONNEMENT

UNIVERSITE DE PARIS VII
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Processus de dépôt - Physico-Chimie des précipitations , J.L. Colin

I) Introduction

- Cycle atmosphérique des éléments
- Mécanismes de dépôt sec et humide
- Importance relative des deux mécanismes

II) Le cycle de l'eau

- Echanges entre les différents réservoirs
- Formation des nuages et des pluies

III) Interaction liquide-solide

- Propriétés Physico-Chimiques des aérosols
- Incorporation par nucléation (ICS)
- Incorporation par abattement sous le nuage (BCS)
- Evolution chimique du solide

IV) Interaction liquide-gaz

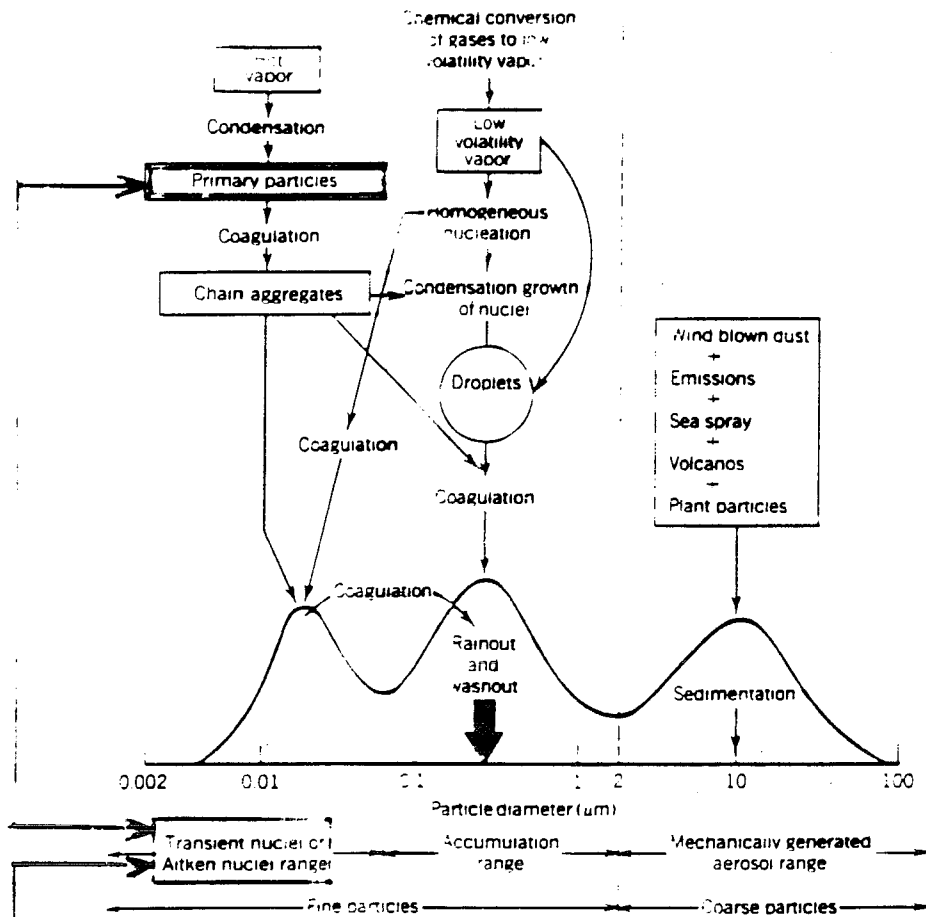
- Dissolution des gaz
- Aspect cinétique
- Réactions en phase liquide

V) Bilan ionique des pluies

- Techniques de collecte et d'analyse
- Balance ionique
- Influence des sources (exemples)
- Influence des facteurs météorologiques (exemples)

VI) Acidité des précipitations

- pH en milieu non contaminé
- les pluies acides
- Implications sur le milieu naturel.



Schematic of an atmospheric aerosol size distribution showing the three modes, the main source of mass for each mode, and the principal processes involved in inserting mass into and removing mass from each mode (from Whalley and Sverdrup, 1980).

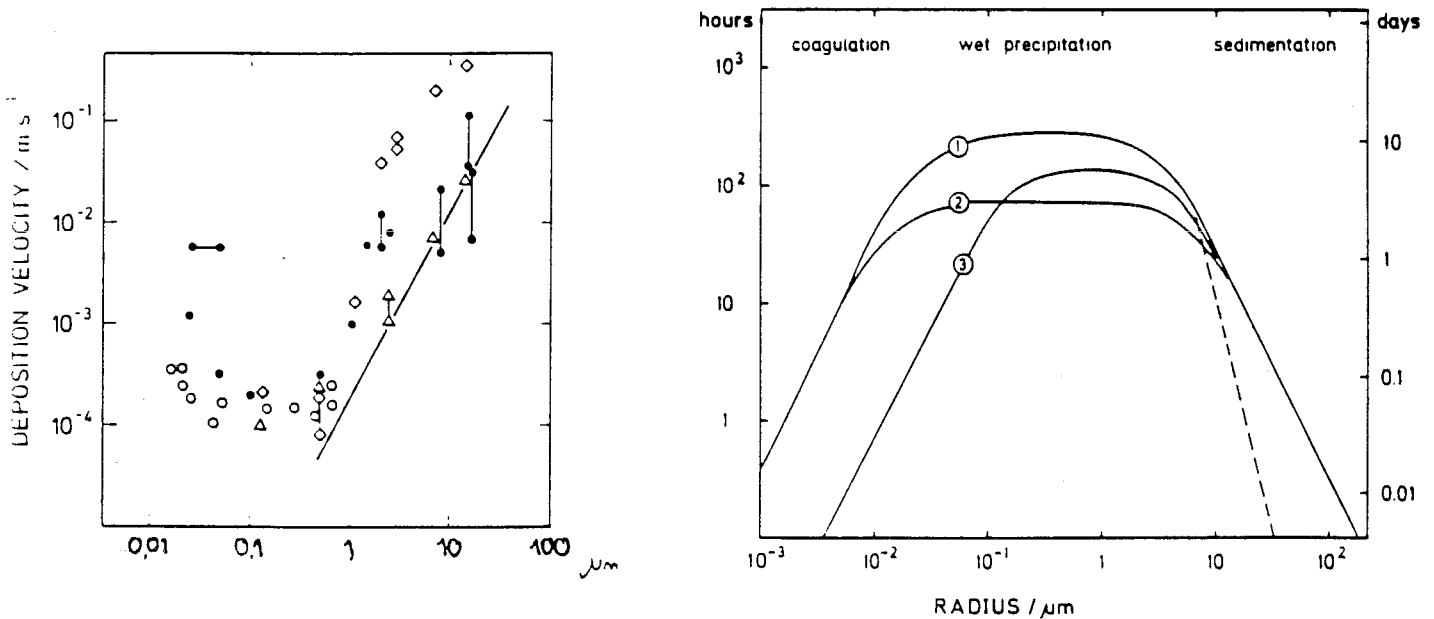


Fig. 7-28. Combined residence lifetimes of aerosol particles as a function of size. [Adapted from Jaenicke (1978c, 1980).] Important removal processes, active in various size ranges, are

Comparaison des flux de dépôt humide et de dépôt sec estimés pour
différents bassins océaniques (GESAMP, 1989).

		Sec	Humide	Humide/Sec
		(g.m ⁻² .an ⁻¹)		
Pacifique nord	Al	1,52	3,76	2,5
	Pb	0,03	0,17	5,7
Pacifique sud	Al	0,13	0,23	1,8
	Pb	0,003	0,02	6,7
Atlantique nord	Al	2,91	1,11	0,4
	Pb	0,18	0,85	4,7
Atlantique sud	Al	0,20	0,27	1,3
	Pb	0,02	0,06	3,0
Océan indien nord	Al	2,01	5,07	2,5
	Pb	0,06	0,27	4,5
Océan indien sud	Al	0,22	0,60	2,7
	Pb	0,01	0,04	4,0
Global	Al	0,97	1,45	1,5
	Pb	0,04	0,20	5,0

Ø Al grosses particules

(a) Arimoto et al., 1985. (b) Arimoto et al., 1987. (c) GESAMP (1989). (d) Lim & Jickells (1990).

Ø Pb finis particules

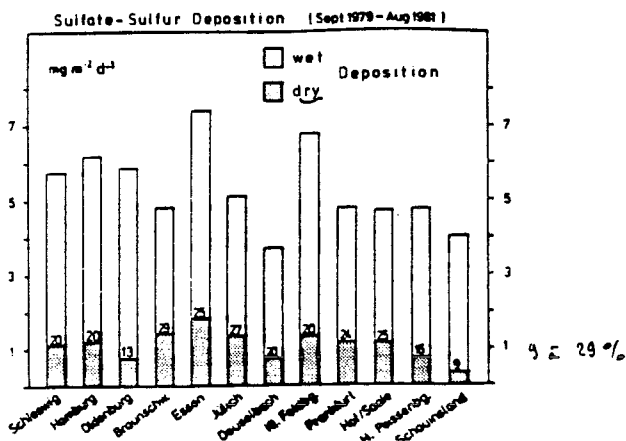


Fig. 2 Comparison of wet and dry sulfate deposition (figures: δ - dry deposition)

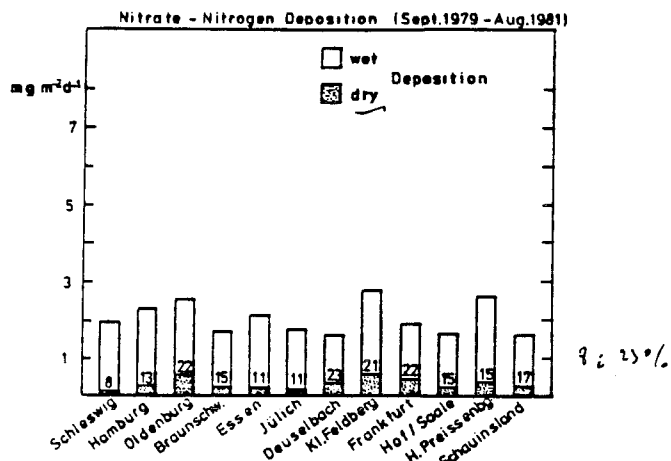
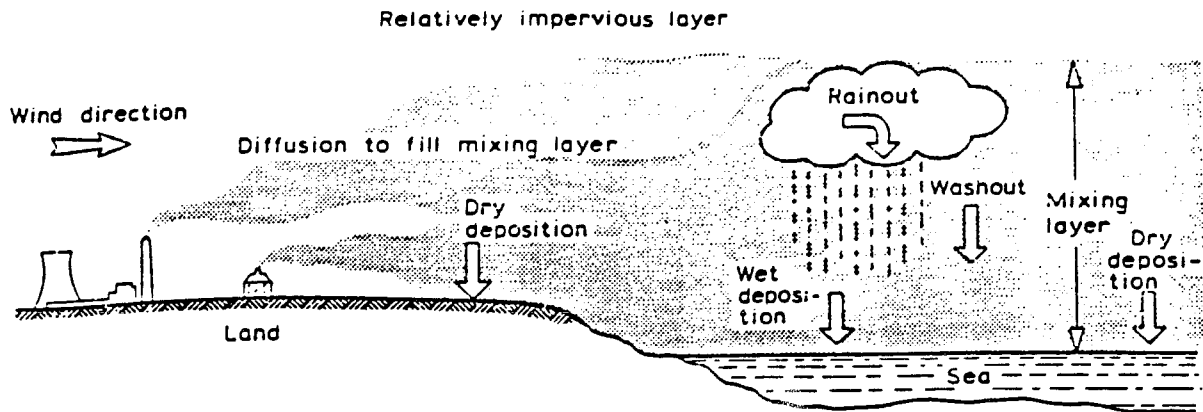


Fig. 3 Comparison of wet and dry nitrate deposition (figures: δ - dry deposition)

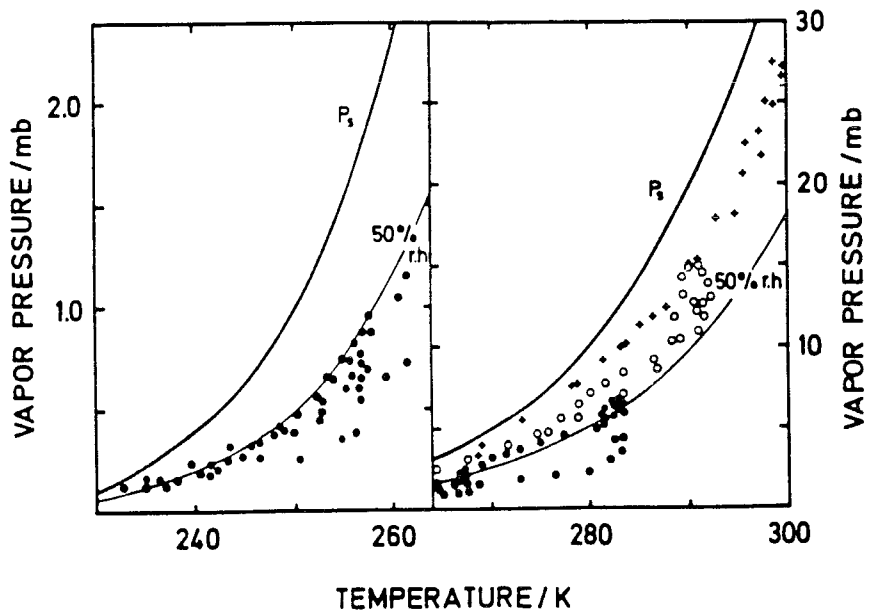
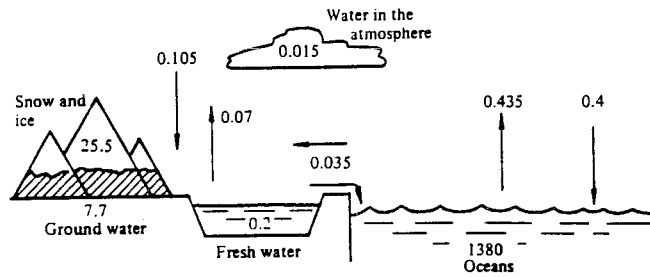
M.W. UGARCI et al. (1983)
in Acid Deposition

En l'air (1 an de mesure) | 30% sec
20% humide



La couche de mélange et les processus d'élimination des rejets.

Fig. 1.8. A global cycle for water. The numbers beside the arrows give the flux of water from one reservoir to another in $10^{18} \text{ kg a}^{-1}$. The numbers within each of the reservoirs give the size in 10^{18} kg .



**Some Compounds Observed in Aerosols by
a Roadway at Argonne National Laboratory Using X-Ray
Diffraction**

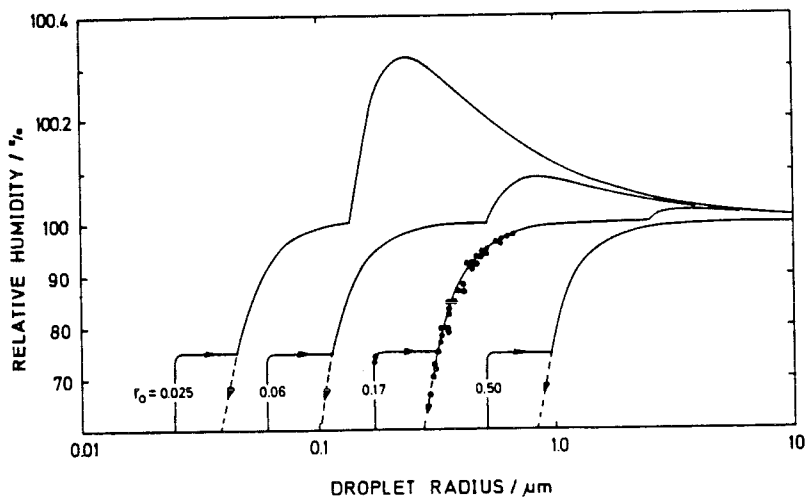
SiO ₂	K ₂ Sn(SO ₄) ₂
CaCO ₃	(NH ₄) ₂ Co(SO ₄) ₂ · 6H ₂ O
CaMg(CO ₃) ₂	(NH ₄) ₃ H(SO ₄) ₂ (letovicite)
CaSO ₄ · 2H ₂ O	3(NH ₄ NO ₃) · (NH ₄) ₂ SO ₄
(NH ₄) ₂ Pb(SO ₄) ₂	2(NH ₄ NO ₃) · (NH ₄) ₂ SO ₄
(NH ₄) ₂ Ca(SO ₄) ₂ · H ₂ O	NH ₄ MgCl ₃ · 6H ₂ O
(NH ₄)HSO ₄	NaCl
(NH ₄) ₂ SO ₄	(NH ₄) ₂ Ni(SO ₄) ₂ · 6H ₂ O

Source: Tani et al., 1983.

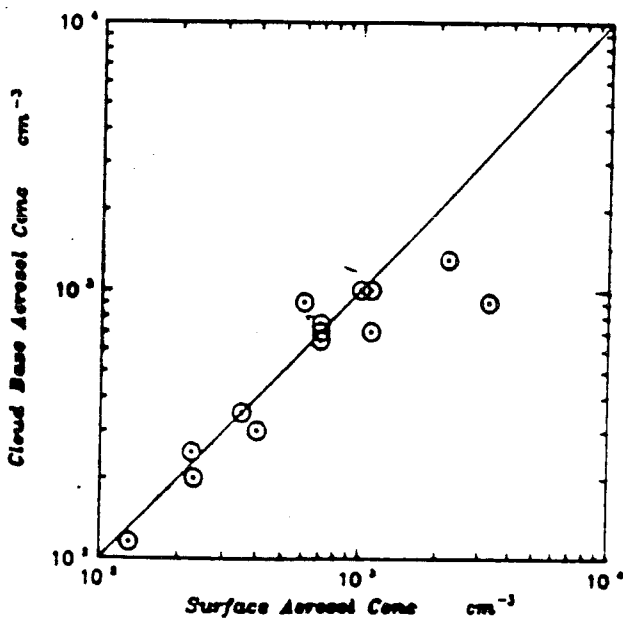
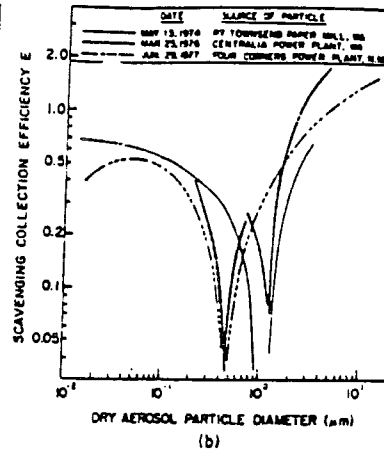
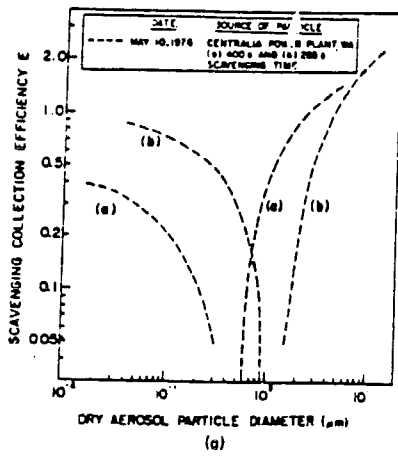
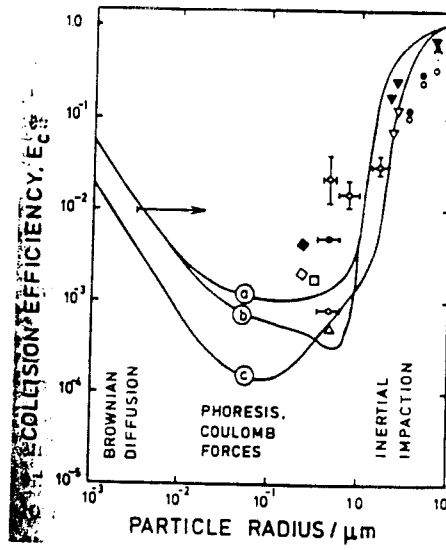
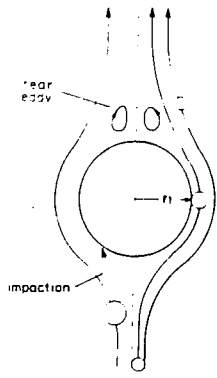
**Deliquescence Points of Some Salts
Commonly Found in Ambient Air at 25°**

Composition	Deliquescence Humidity (%)
(NH ₄) ₂ SO ₄	79.5
(NH ₄)HSO ₄	39.0
(NH ₄) ₃ H(SO ₄) ₂	69.0
2NH ₄ NO ₃ · (NH ₄) ₂ SO ₄	56.4
NaCl	75.7
KCl	84.3
NaCl-KCl	73.8

Source: Tang, 1980a.



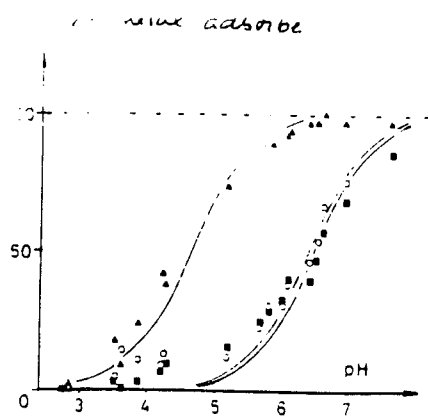
Variation of particle size with relative humidity (Köhler diagram) for sodium chloride particles having different dry radii. Deliquescence occurs at 75% r.h. Note the hysteresis effect when the humidity is raised or lowered beyond the critical value. Curves for relative humidities greater than 75% were calculated. The scale above 100% is expanded. The experimental points refer to observations of Tang *et al.* (1977) on submicrometer-sized monodisperse sodium chloride particles.



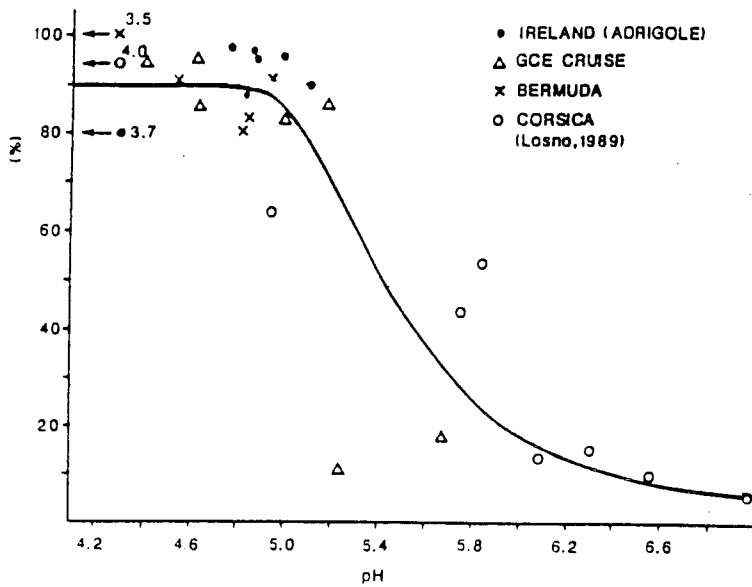
$$W = \frac{[X] \text{ pluie}}{[X] \text{ aérosol}} * \rho$$

$$\begin{cases} [X] \text{ pluie} : 10^{-6} \text{ g/g} \\ [X] \text{ aérosol} : 10^{-6} \text{ g/m}^3 \\ \rho = 1200 \text{ g/m}^3 \end{cases}$$

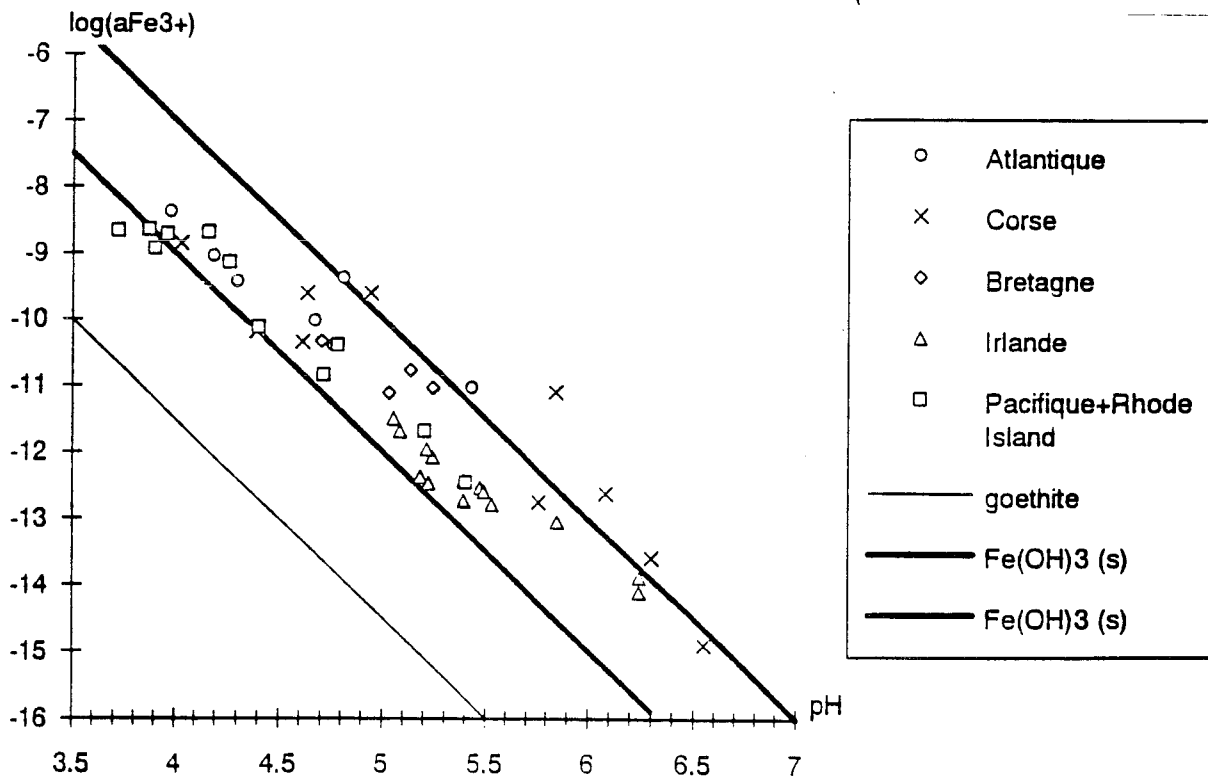
Fig. 2. Comparison of PMS ASASP-100X aerosol number concentrations just below cloud base and at the surface. Measurements pertain to takeoff or landing profiles on days of cloud water collection shown in Table I.



Curbes d'adsorption expérimentales de Cu (\blacktriangle), Zn (\circ) et Cd (\blacksquare) sur des sédiments. (Buffle, 1983)



(Lim, 1991) Solubilité du plomb



Concentrations du fer libre ($\log a_{Fe^{3+}}$) en fonction du pH

TABLE 11.1. Henry's Law Coefficients (H) of Some Atmospheric Gases Dissolving in Liquid Water at 25°C

Gas	H (mole L ⁻¹ atm ⁻¹)	Reference
O ₂	1.3×10^{-3}	Loomis, 1928
NO	1.9×10^{-3}	Loomis, 1928
C ₂ H ₄	4.9×10^{-3}	Loomis, 1928
NO ₂ ^a	1×10^{-2}	Schwartz and White, 1983
O ₃	1.3×10^{-2}	Briner and Perrottet, 1939
N ₂ O	2.5×10^{-2}	Loomis, 1928
CO ₂ ^b	3.4×10^{-2}	Loomis, 1928
SO ₂ ^b	1.24	Maahs, 1982
HONO ^b	49	Schwartz and White, 1981
NH ₃ ^b	62	Van Krevelen et al., 1949
H ₂ CO	6.3×10^3	Blair and Ledbury, 1925
H ₂ O ₂	$(0.7-1.0) \times 10^5$	Martin and Damschen, 1981
	1.4×10^5	Yoshizumi et al., 1984 ^c
	6.9×10^4	Hwang and Dasgupta, 1985 ^d
HNO ₃	2.1×10^5	Schwartz and White, 1981
HO ₂	$(1-3) \times 10^3$	Schwartz, 1984b
PAN	5	Holdren et al., 1984
CH ₃ SCH ₃	0.56	Dacey et al., 1984

Source: Adapted from Schwartz, 1984a.

^aPhysical solubility; reacts with liquid water.

^bPhysical solubility exclusive of acid-base equilibria.

^cAt 20°C.

^dTemperature dependence also reported as $H = \exp [7.92 \times 10^3/T(^{\circ}\text{K}) - 15.44]$.

TABLE 11.2. S(IV) Equilibria in Aqueous Solutions Containing Aldehydes and Fe³⁺

Reaction	pK ^a	$\Delta H_{298.15^{\circ}\text{K}}^{\circ}$ (kcal mole ⁻¹)	Reference ^b
H ₂ O(l) ⇌ H ⁺ + OH ⁻	14.00	13.35	SM
SO _{2(g)} + H ₂ O ⇌ SO ₂ · H ₂ O	-0.095	-6.25	SM
SO ₂ · H ₂ O ⇌ H ⁺ + HSO ₃ ⁻	1.89	-4.16	SM
HSO ₃ ⁻ ⇌ H ⁺ + SO ₃ ²⁻	7.22	-2.23	SM
HNO _{3(g)} ⇌ H ⁺ + NO ₃ ⁻	-6.51	-17.3	SW
HNO _{2(g)} ⇌ HNO _{2(l)}	-1.7	-9.5	SW
HNO _{2(l)} ⇌ H ⁺ + NO ₂ ⁻	3.29	2.5	SW
CO _{2(g)} + H ₂ O ⇌ CO ₂ · H ₂ O	1.47	-4.85	SM
CO ₂ · H ₂ O ⇌ H ⁺ + HCO ₃ ⁻	6.37	1.83	SM
HCO ₃ ⁻ ⇌ H ⁺ + CO ₃ ²⁻	10.33	3.55	SM
CH ₂ O _(g) + H ₂ O ⇌ CH ₂ O · H ₂ O	-3.85	-12.85	LB
HOCH ₂ SO ₃ H ⇌ H ⁺ + HOCH ₂ SO ₃ ⁻	<0 ^c	U ^d	R
HOCH ₂ SO ₃ ⁻ ⇌ H ⁺ + ⁻ OCH ₂ SO ₃ ⁻	11.7	U	SA
NH _{3(g)} + H ₂ O ⇌ NH ₃ · H ₂ O	-1.77	-8.17	SM
NH ₃ · H ₂ O ⇌ NH ₄ ⁺ + OH ⁻	4.77	0.9	SM
O _{2(g)} ⇌ O _{2(l)}	2.90	-3.58	P
H ₂ O _{2(g)} ⇌ H ₂ O _{2(l)}	-4.85	-14.5	MD
O _{3(g)} ⇌ O _{3(l)}	2.03	-5.04	L-B
CaHCO ₃ ⁺ ⇌ Ca ²⁺ + HCO ₃ ⁻	11.6	-2.78	SM
CaSO _{4(l)} ⇌ Ca ²⁺ + SO ₄ ²⁻	2.30	-1.65	SM
NaSO ₄ ⁻ ⇌ Na ⁺ + SO ₄ ²⁻	0.70	-2.23	SM
FeSO ₄ ⁺ ⇌ Fe ³⁺ + SO ₄ ²⁻	4.20	5.4	SM
Fe(SO ₄) ₂ ⁻ ⇌ Fe ³⁺ + 2SO ₄ ²⁻	5.60	U	SM
FeCl ₂ ⁺ ⇌ Fe ³⁺ + Cl ⁻	1.40	-7.91	SM
FeOH ²⁺ ⇌ Fe ³⁺ + OH ⁻	12.30	0.04	SM
Fe(OH) ₂ ⁺ ⇌ Fe ³⁺ + 2OH ⁻	23.3	U	SM
Fe(OH) ₃ ⇌ Fe ³⁺ + 3OH ⁻	39.0	20.7	SM
Fe ₂ (OH) ₂ ⁴⁺ ⇌ 2Fe ³⁺ + 2OH ⁻	25.7	16.2	SM
FeSO ₃ ⁺ ⇌ Fe ³⁺ + SO ₃ ²⁻	10.0 ^c	U	H
MnSO _{4(l)} ⇌ Mn ²⁺ + SO ₄ ²⁻	2.30	-3.39	SM
MnCl ⁺ ⇌ Mn ²⁺ + Cl ⁻	1.10	-8.01	SM
HSO ₄ ⁻ ⇌ H ⁺ + SO ₄ ²⁻	2.20	-4.91	SM

Source: Jacob and Hoffmann, 1983.

^aK is in M atm⁻¹ or Mⁿ. Temperature is 298°K.

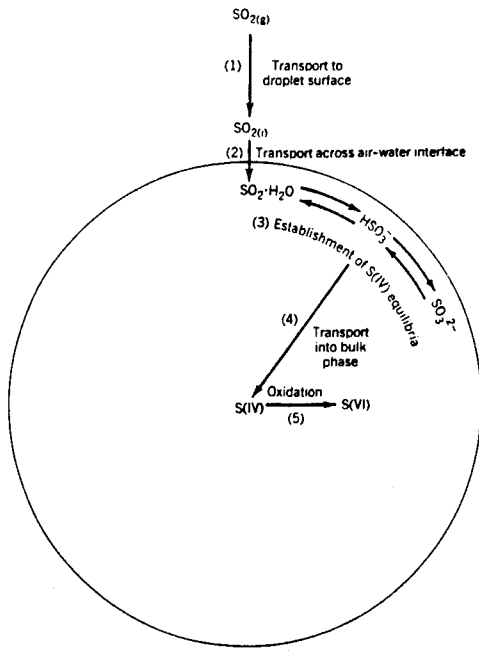


FIGURE 11.3. Schematic of steps involved in the transfer of SO₂ from the gas phase to the aqueous phase of an atmospheric water droplet and its oxidation in the liquid phase. SO_{2(g)} = gas phase SO₂. SO_{2(l)} = SO₂ at water-gas interface.

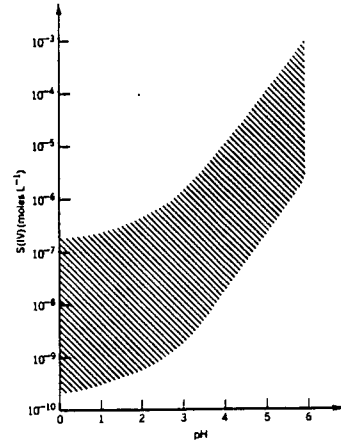


FIGURE 11.2. Range of expected aqueous S(IV) concentrations as a function of acidity for gas phase SO₂ concentrations of 0.2–200 ppb (from Martin, 1984).

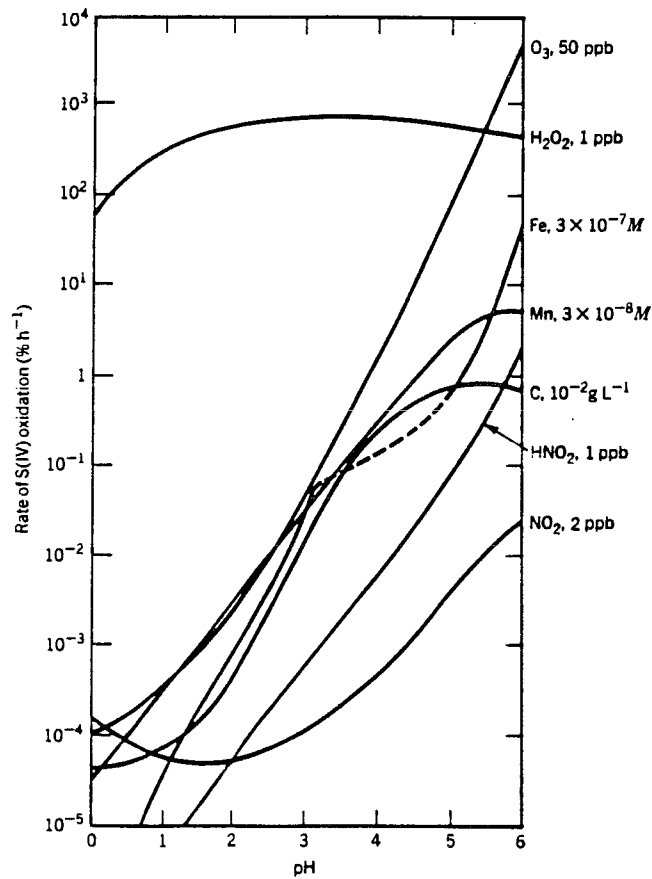


FIGURE 11.9. Estimated rates of oxidation of S(IV) in solution and on carbon surfaces as a function of pH (from Martin, 1984).

BILANS IONIQUES

() en mEq/l

$$|X^-| = (X^-)_{exc} + (X^-)_m$$

\swarrow \searrow
 anion lié à l'acide fort anion lié au sel neutre d'origine marine

→ Evaluation de $(X^-)_m$ à l'aide des F.E

$$(X^-)_m = (Na^+) - ((X^-)/(Na^+))_{mer}$$

modèle de l'eau de mer
 Holland
 Sunderup
 Stumm & Morgan
 Brewer

$$(SO_4^{2-})_m = 0,12 (Na^+)$$

$$(Cl^-)_m = 1,13 (Na^+)$$

$$(NO_3^-)_m = 0$$

$$(SO_4^{2-})_{exc} = (SO_4^{2-}) - 0,12 (Na^+)$$

$$(Cl^-)_{exc} = (Cl^-) - 1,13 (Na^+)$$

$$(NO_3^-)_{exc} = (NO_3^-)$$

$$(H^+)_{calculé} = (SO_4^{2-})_{exc} + (Cl^-)_{exc} + (NO_3^-)_{exc}$$

Et fait $(H^+)_{calculé} \geq (H^+)_{mesuré}$
 car neutre électriq par NH_3 & HCO_3^-

$$(H^+)_{calculé} - (H^+)_{mesuré} = \text{Capacité neutralisante}$$

les faibles de ions à sol peu basiques (Suède, Norvège)
 les forts ions calcis + basique (France)

→ ELEMENTS ANALYSES

- Elements traceurs de principale source :
 - marine Na, Mg, I
 - crustale Al, Si, B, K, Ca
 - anthropique Cu, Zn, Pb
- + Autres espèces majeures pour compléter le bilan ionique
 - H^+ , SO_4^{2-} , NO_3^- , NH_4^+ , HCO_3^-
- Partion soluble / insoluble
 - part: insoluble : Al, Si, Fe
 (part soluble en équilibre avec hydroxydes de surface des aluminosilicates)
 - part: soluble : Na, Mg, Cl, Ca
 - mixtes : Mn, K, Zn

→ BILAN IONIQUE (en q. soluble)

$$\left\{ \begin{array}{l} (Ca^{2+}) + (Mg^{2+}) + (K^+) + (Na^+) + (NH_4^+) + (H^+) = S^+ \\ (SO_4^{2-}) + (NO_3^-) + (Cl^-) + (HCO_3^-) = S^- \end{array} \right. \text{ (mEq/l)}$$

$S^+ \uparrow S^-$ } plus majeurs facile analytique

deficits anioniques fréquents relevés dans la littérature

non pris en compte les acides organiques
 phosphates
 carbonates
 ...

Table 8-6. Inorganic Ion Composition ($\mu\text{mol/liter}$) of Rainwater at Various Locations

	Continental					Maritime			
	North Sweden ^a 1969	Belgium ^a 1969	European, U.S.S.R. ^b 1961-1964	Hubbard Brook, New Hampshire ^c 1963-1974	California ^d 1978-1979	San Carlos, Venezuela ^e 1979-1980	Cape Grim, Tasmania ^f 1977-1981	Amsterdam Island, ^g 1979-1980	Bermuda, ^h 1979-1980
SO ₄ ²⁻	21	63	82.0	29.8 ± 1.2	19.5	1.6 ± 1.25	79.1	26.3 ± 22.4	24.4 ± 23.8
Cl ⁻	11	55	60.0	14.4 ± 2.5	28	4.3 ± 3.4	1349	406 ± 467	264 ± 337
NO ₃ ⁻	5	36	17.7	23.1 ± 1.7	31	3.5 ± 3.6	5.0	2.7 ± 2.1	7.9 ± 9.1
HCO ₃ ⁻	21	—	71.7	—	—	—	—	—	—
HCO ₃ ⁻ ^k	—	0.15	1.73	0.077	0.15	0.33	5.6	0.315	0.27
NH ₄ ⁺	6	25	52.8	12.1 ± 0.7	21	17.0 ± 10	2.0	5.1 ± 7.0	4.8 ± 7.1
Na ⁺	13	42	65.2	5.4 ± 0.6	24	2.7 ± 2.0	1297	334 ± 371	221 ± 282
K ⁺	5	6	17.3	1.9 ± 0.5	2	1.1 ± 1.7	32.3	7.2 ± 7.8	6.5 ± 8.0
Ca ²⁺	16	33	38.1	4.3 ± 0.6	3.5	0.25 ± 0.35	42.9	7.7 ± 8.6	7.2 ± 7.1
Mg ²⁺	5	15	52.5	1.8 ± 0.4	3.5	0.4 ± 0.45	122	36.4 ± 40	24.6 ± 30.4
H ⁺	—	38	3.3	73.9 ± 3.0	39	17 ± 10	1.02	18.2 ± 12.7	21.1 ± 26.9
pH (av.)	—	4.42	5.48	4.13	4.41	4.77	5.99	4.74	4.68
Sum of anions ^h	79	217	313	97.1	98	11	1512	461	321
Sum of cations ^h	66	207	320	105	93	39	1662	453	273
Number of samples	180	180	n.g. ⁱ	n.g.	n.g.	14	56	26	67
Annual precip. ⁱ	360	648	—	1310	697	4000	1120	1120	1131

^a Granat (1972).

^b Petrenchuk and Selezneva (1970).

^c Likens *et al.* (1977).

^d Liljestrand and Morgan (1980), Morgan (1982).

^e Galloway *et al.* (1982).

^f Ayers (1982).

^g Calculated from pH.

^h Sum of charges in $\mu\text{equiv./liter}$.

ⁱ Average annual amount of precipitation in mm.

^j n.g., Not given.

Table 8-7. Concentrations ($\mu\text{mol/liter}$) of Major Inorganic Ions in Cloud and Fog Waters

	European U.S.S.R. ^a		Southern England, ^b nonprecipitating	Whiteface Mt., New York, ^c intercepted clouds	Central Germany, ^d mountain fogs	Pasadena, California, ^e ground fogs
	Frontal precipitating	Nonprecipitating				
SO ₄ ²⁻	29	117	40	26-70	387	240-472
Cl ⁻	22.2	76.8	94	1.7-3.1	205	480-730
NO ₃ ⁻	3.2	16.1	18.6	140-215	450	1220-3250
HCO ₃ ⁻	11.5	16.4	—	—	—	—
HCO ₃ ⁻ ^f	1.1	0.06	0.14-91	0.023-0.045	0.72	0.4-0.005
NH ₄ ⁺	28.8	11.1	22.1	32-89	710	1290-2380
Na ⁺	17	29.8	95.2	2.3-11	295	320-500
K ⁺	5.1	20.4	12.5	13-20	85	33-53
Ca ²⁺	10	29.3	33.2	5-10	110	70-265
Mg ²⁺	12.3	40.0	12.3	1.1-3.1	—	45-160
H ⁺	5.0	94.4	0.06-40	126-251	12.6	14-1200
pH	5.3	4.02	4.4-7.2	3.6-3.9	5.1	4.85-2.92
Sum of anions ^f	95	327	193	194-358	1429	2180-4924
Sum of cations ^f	100	294	220	185-397	1323	1887-4983
Number of samples	125	194	23	Not given	19	4

^a Petrenchuk and Selezneva (1970).

^b Oddie (1962).

^c Munger *et al.* (1983).

^d Mrose (1966).

^e Calculated from pH.

^f Sum of charges in $\mu\text{equiv./liter}$.

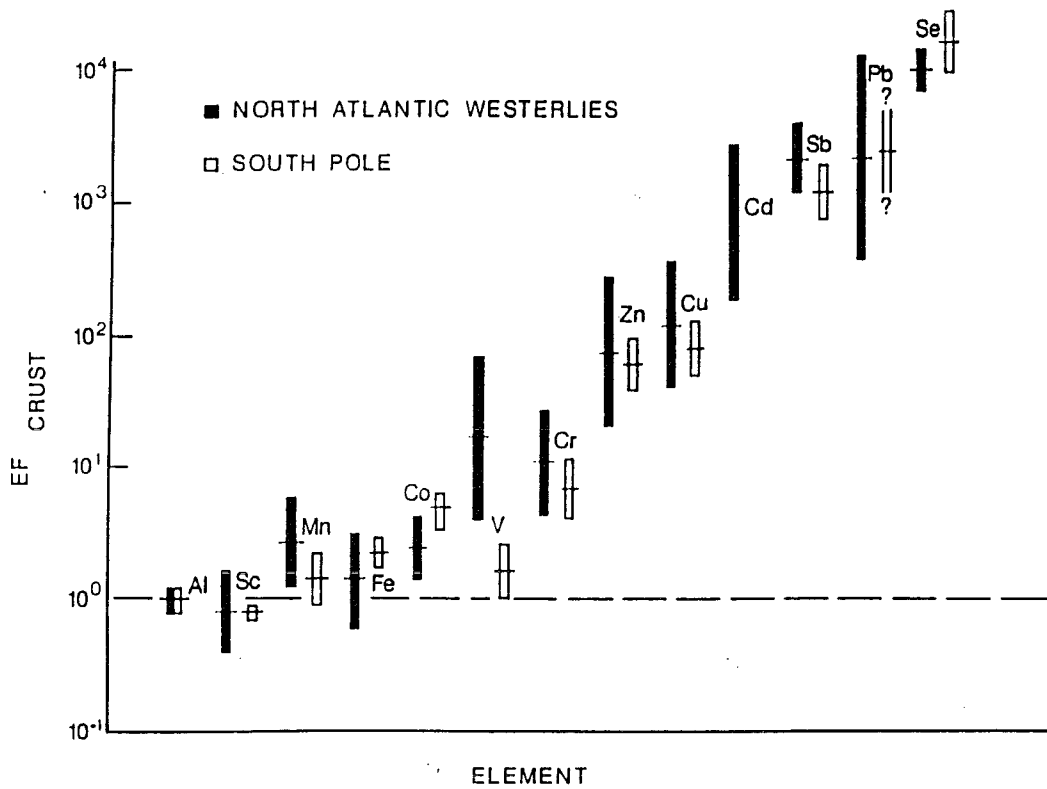
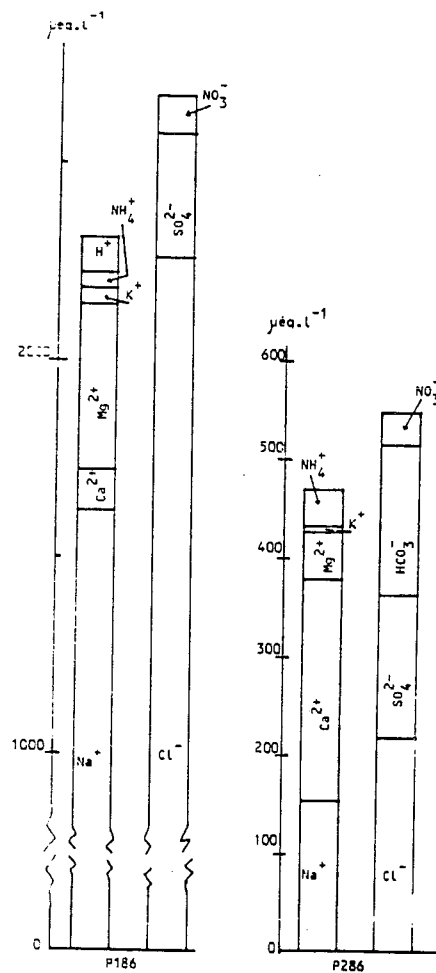
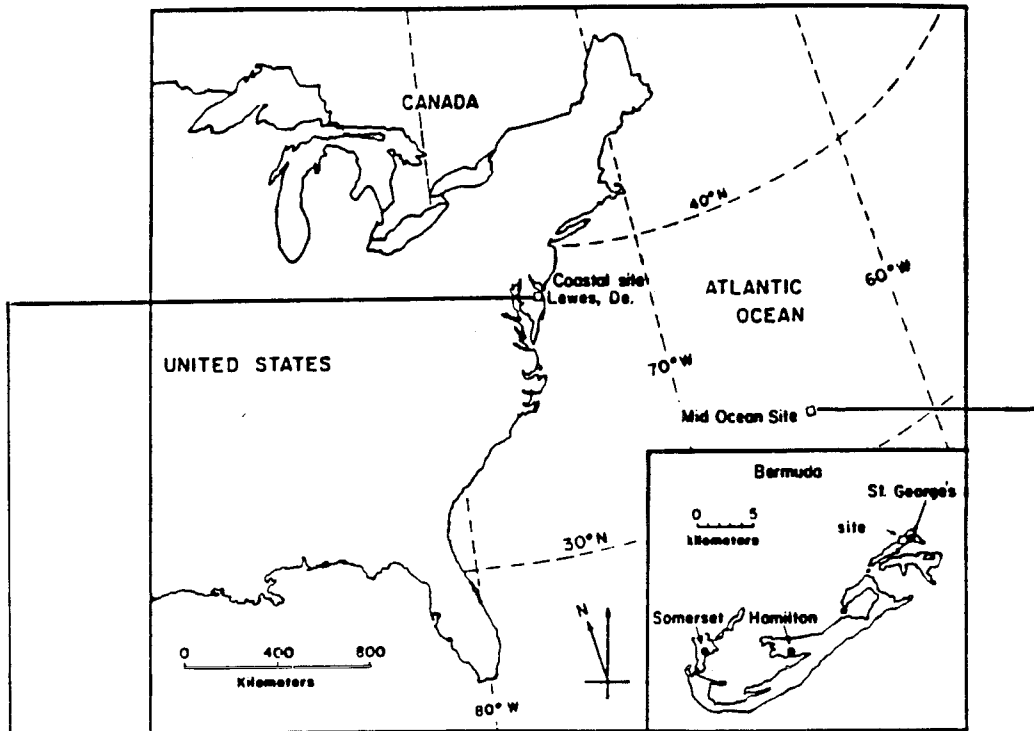


Figure 1.2. Crustal enrichment factors for atmospheric trace metals collected in the North Atlantic westerlies and at the South Pole (After Duce *et al.*, 1975)





Lewes, Delaware

Bermuda

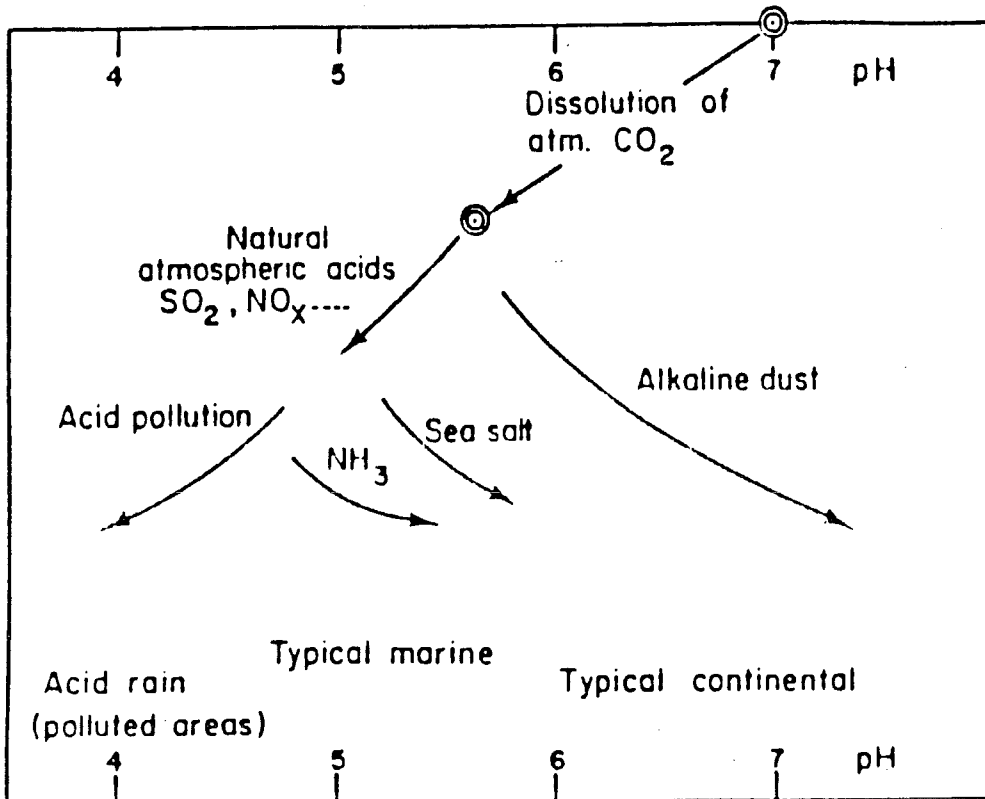
	$\mu\text{Eq/l}$
Ppt. (cm)	68.0
Cations	average:
H ⁺	53.4
Na ⁺	56.5
K ⁺	1.91
Mg ⁺²	12.6
Ca ⁺²	8.53
NH ₄ ⁺	18.9
Anions	
Cl ⁻	46.4
SO ₄	62.5
SO ₄ ²⁻	53.2
NO ₃ ⁻	25.2
SC	151.8
SA	134.1

	$\mu\text{Eq/l}$
Ppt. (cm)	119.
Cations	average:
H ⁺	18.4
Na ⁺	148
K ⁺	4.03
Mg ⁺²	40.0
Ca ⁺²	15.3
NH ₄ ⁺	4.54
Anions	
Cl ⁻	191.
Σ SO ₄	36.3
SO ₄ ²⁻	18.2
NO ₃ ⁻	6.57
SC	230.
SA	233.

eau de mer				croûte terrestre		
concentrations (ppm)	rapport à Na		équivalent	concentrations (ppm)	rapport à Al	
	massique	molaire			massique	molaire
Cl	10800	1.75	1.13	(Cl ⁻) 1.13	130	1.60 10 ⁻³ 1.22 10 ⁻³
SO ₄	2715	2.52 10 ⁻¹	6.83 10 ⁻²	(SO ₄ ⁺) 12.06 10 ⁻²	780	9.59 10 ⁻³ 2.73 10 ⁻³
Na	10770	1	1	(Na ⁺) 1	28300	3.48 10 ⁻¹ 4.09 10 ⁻¹
K	380	3.53 10 ⁻²	2.07 10 ⁻²	(K ⁺) 2.07 10 ⁻²	25900	3.19 10 ⁻¹ 2.29 10 ⁻¹
Mg	1290	1.20 10 ⁻¹	1.13 10 ⁻¹	(Mg ²⁺) 2.26 10 ⁻¹	20900	2.57 10 ⁻¹ 2.85 10 ⁻¹
Ca	412	3.83 10 ⁻²	2.19 10 ⁻²	(Ca ²⁺) 4.38 10 ⁻²	36300	4.46 10 ⁻¹ 3.01 10 ⁻¹
Zn	0.005	4.54 10 ⁻⁷	1.71 10 ⁻⁷	(Zn ²⁺) 3.42 10 ⁻²	70	6.61 10 ⁻⁴ 3.55 10 ⁻⁴
Al	0.002	1.96 10 ⁻⁷	1.49 10 ⁻⁷	-	81300	1 1
Si	2	1.96 10 ⁻⁴	1.49 10 ⁻⁴	-	277200	3.41 3.27
Fe	0.002	1.86 10 ⁻⁷	8.54 10 ⁻⁸	-	50000	6.15 10 ⁻¹ 2.97 10 ⁻¹

Exemples de Modèles

- eau de mer (Brewer, 1975)
- croûte terrestre (Kosm, 1966)



Delmas et al. (1983)

