

W1 : IFEP/MODEL Workshop

Modeling iron biogeochemistry and ocean ecosystems

「Determination of iron solubility of Asian dust in the surface seawater」

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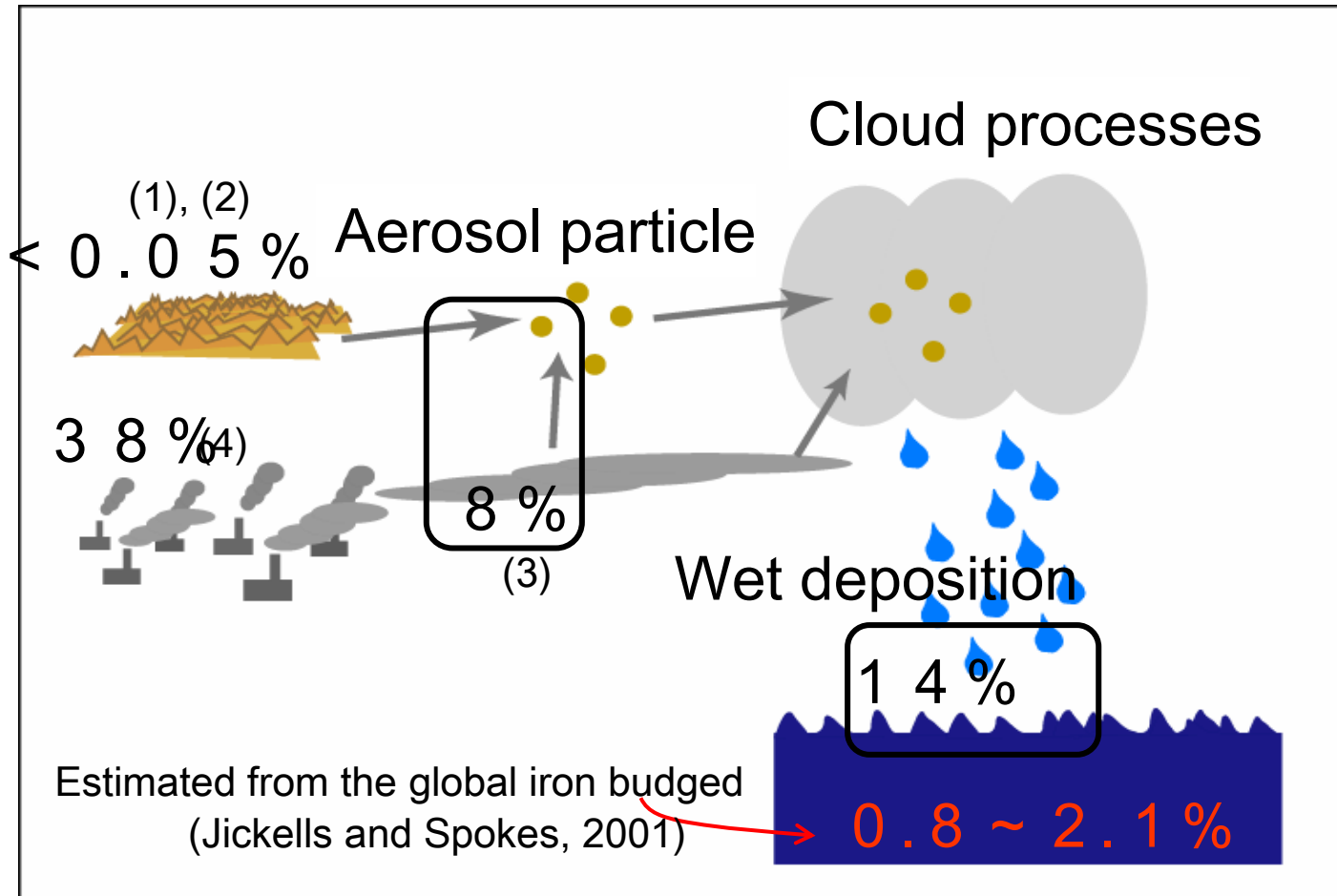
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Yokohama, Japan
13, Oct. 2006

Iron solubility in atmospheric particles

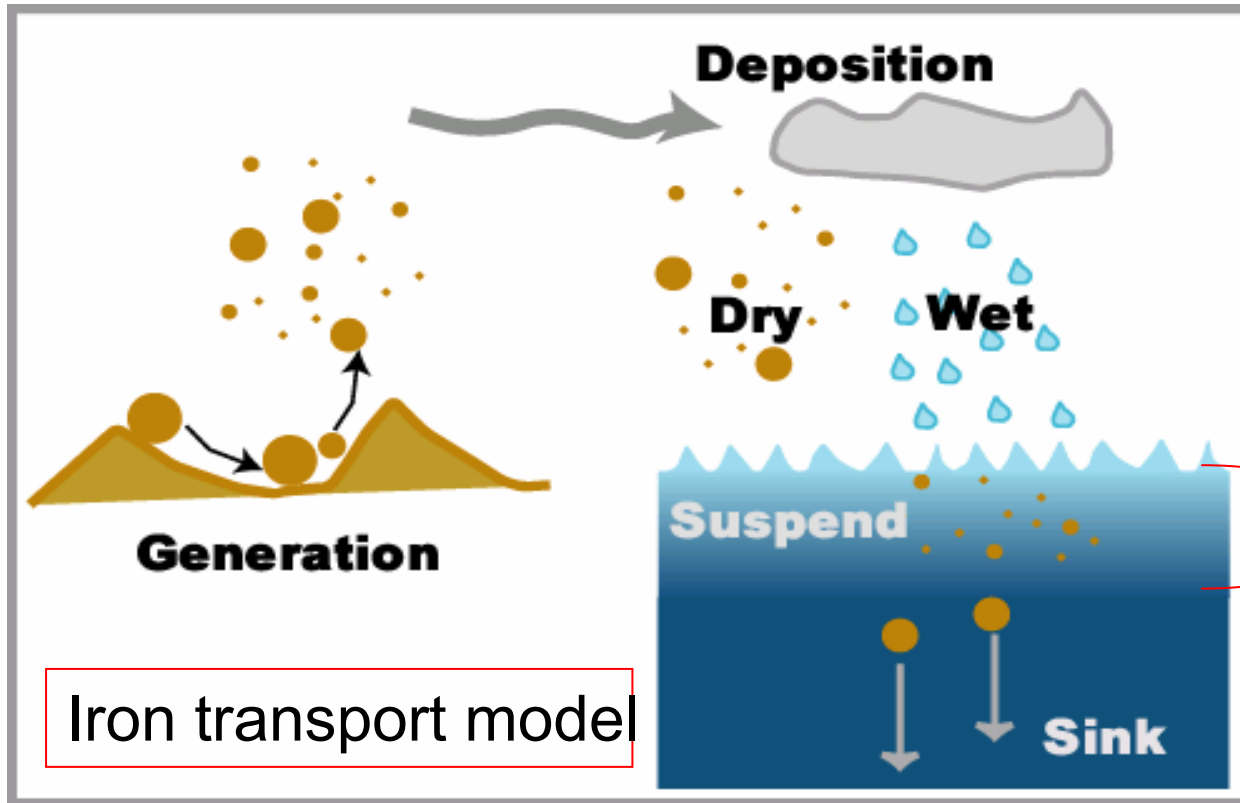


- (1) Bonnet and Guieu., 2004 (2) Guieu and Thomas, 1996 (3) Crecelius, 1980
(4) Desboeufs et al., 2001

“There is no consensus about the iron dissolution experiment “

(Mahowald et al., 2005)

Particle size determine the motion of mineral dust



Iron budged
in sea surface

Recent iron solubility studies

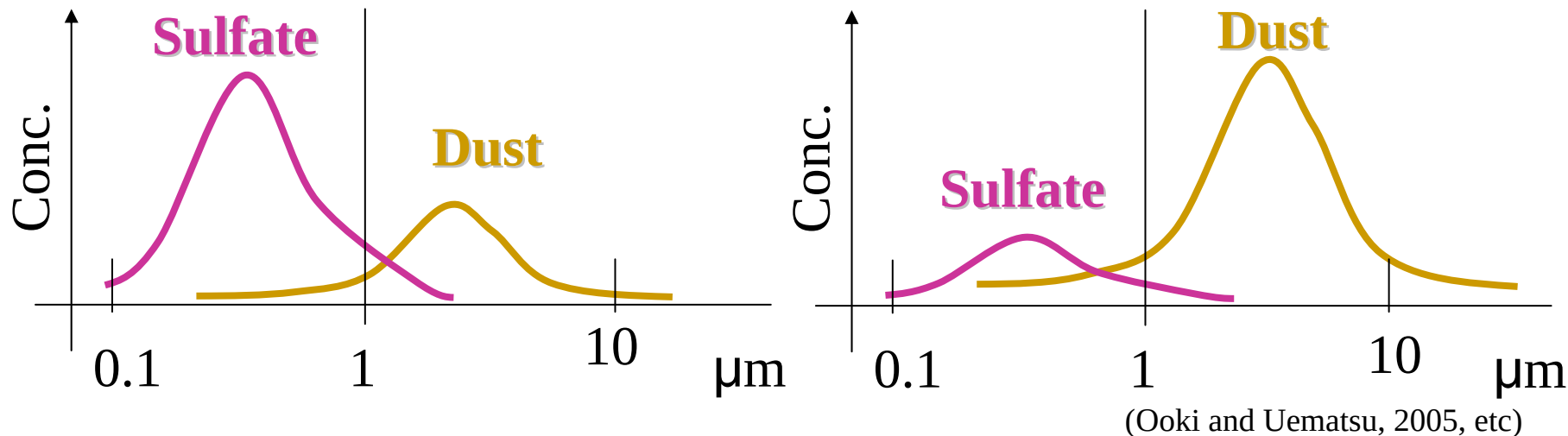
- Aerosol iron solubility (two size fractions)

Fine particle size > Coarse particle size

($D < 1 \mu\text{m}$)

($D > 1 \mu\text{m}$)

(Siefert et al., 1999; Johansen et al., 2000; Chen and Siefert, 2004; Hand et al., 2004; Luo et al., 2005; Baker et al., 2006)

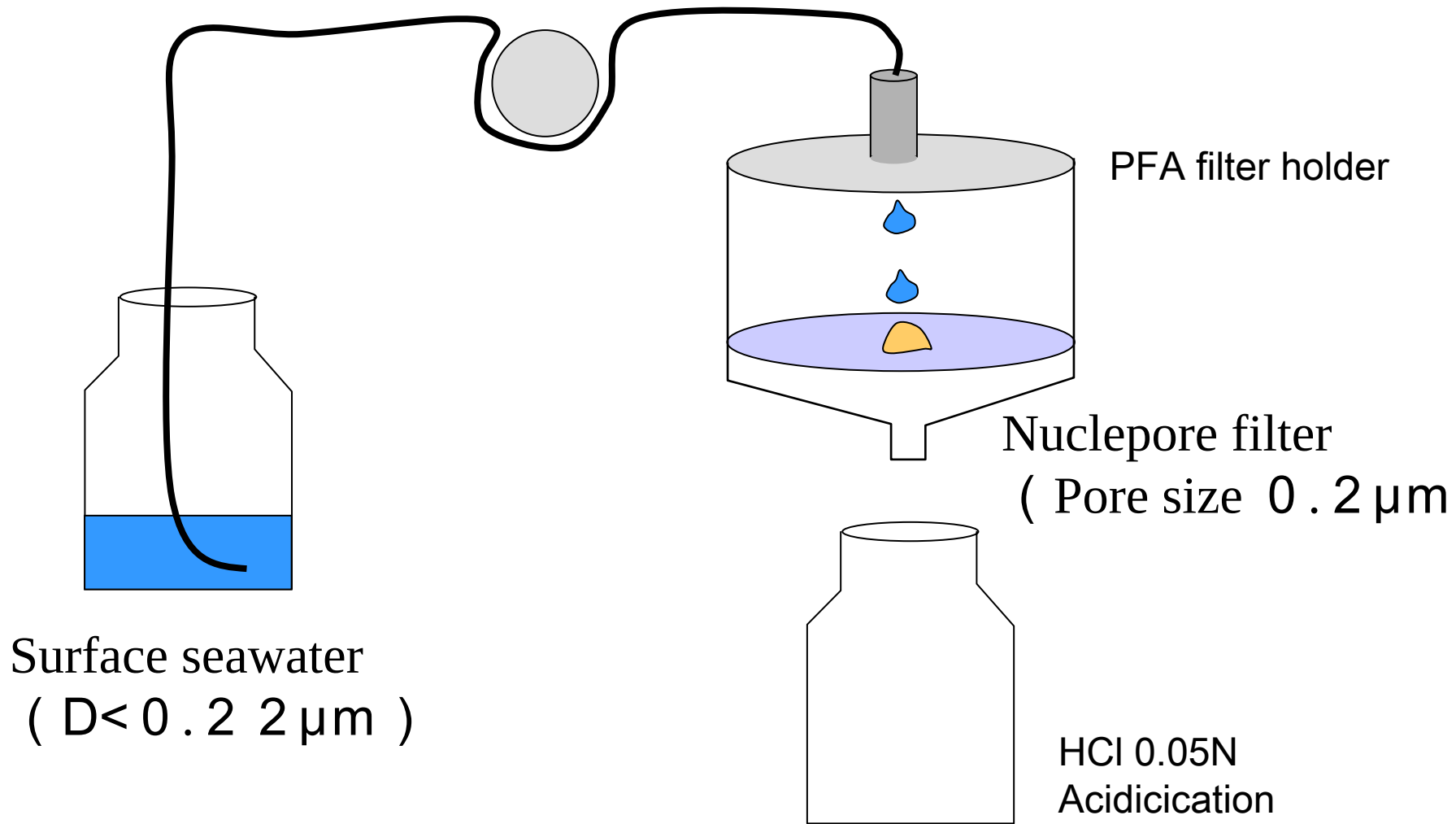


Size-segregate analysis of iron solubility in the coarse size range would develop the iron budget model.

This Study

- Establish the iron dissolution experiment
- Measure the iron solubility of size-segregated aerosol
- Estimate the iron solubility of atmospheric depositions over the North Pacific based on the size-segregated analysis

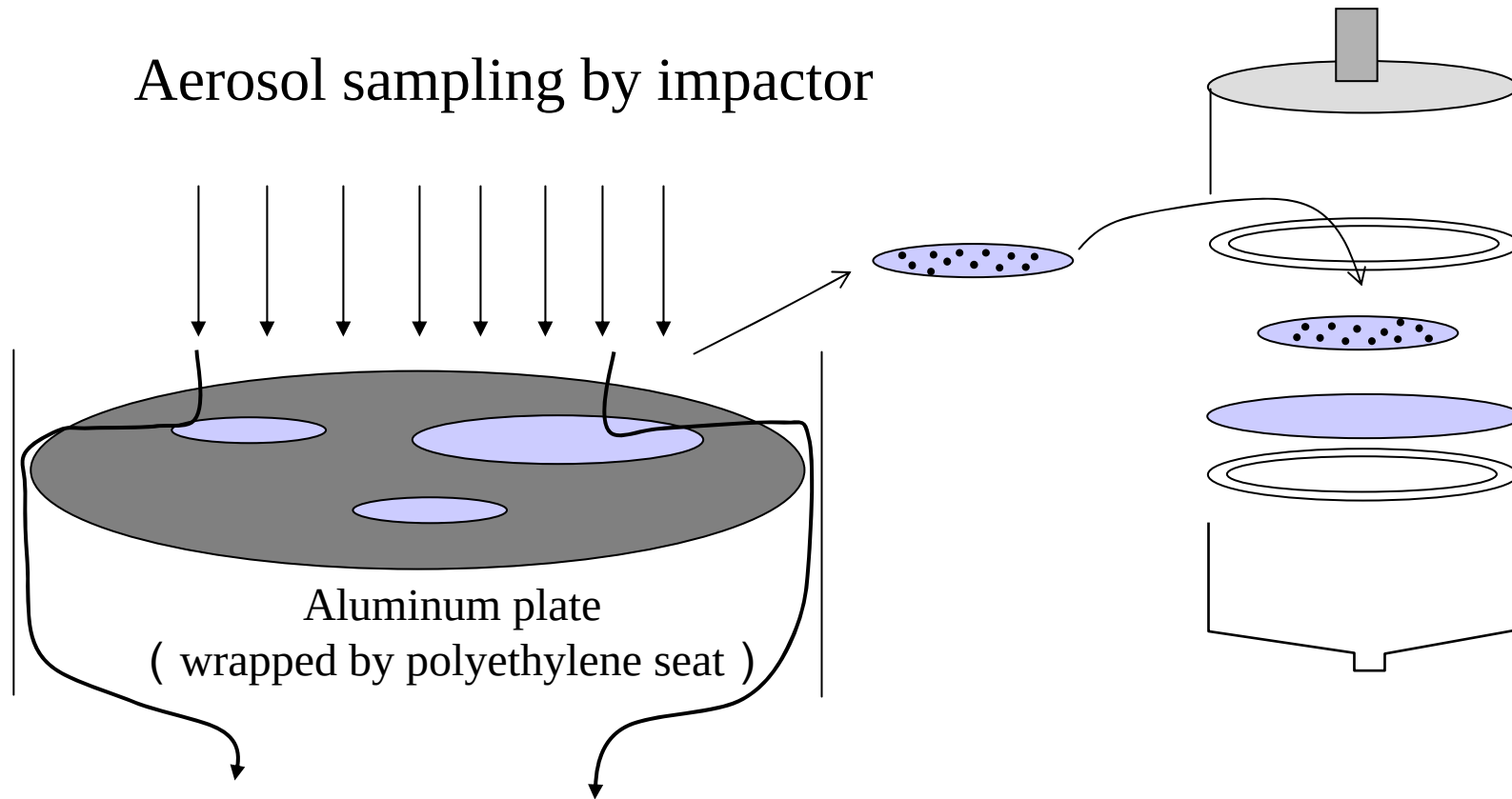
Iron dissolution experiment (1)



Initial study for iron dissolution experiment by filtration method: Buck et al., 2006

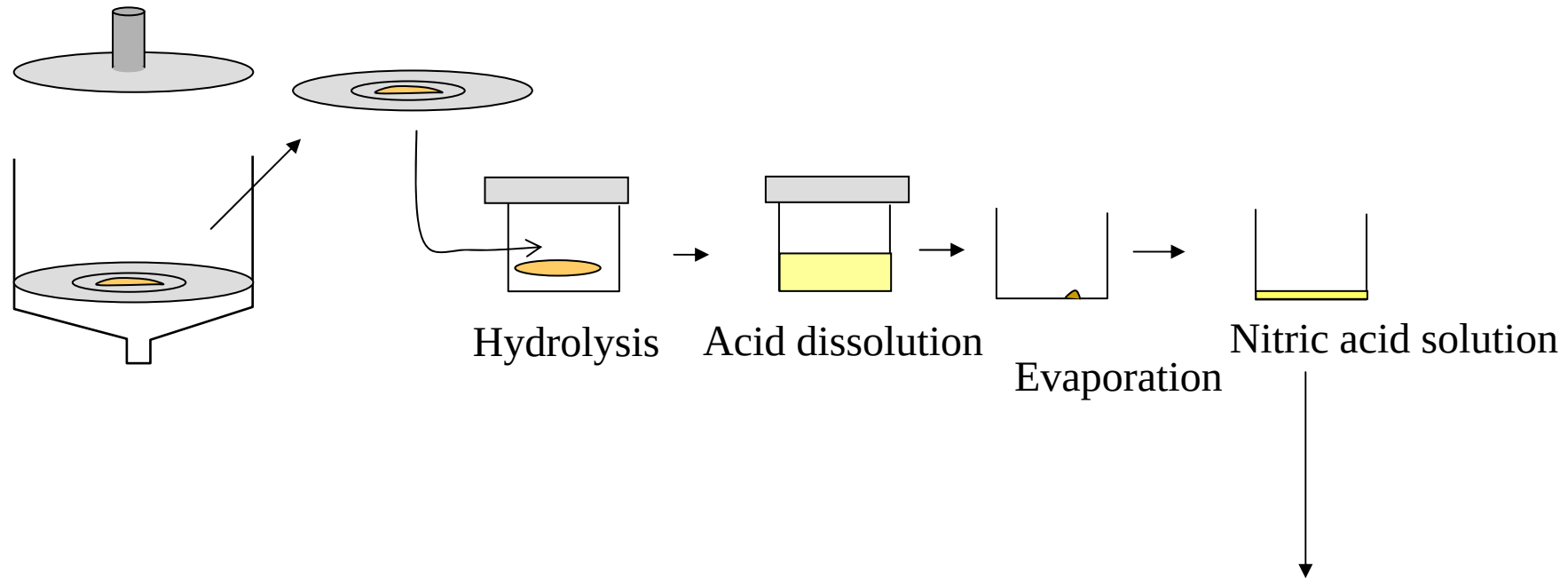
Iron dissolution experiment (2)

Size-segregated aerosol sampling and iron dissolution experiment



Iron dissolution experiment (3)

Determination of insoluble fraction of iron



Samplings

Aerosol samples

- Period and location: April – May, 2006, Hokkaido (North of Japan)
- Total size : Filter holder system
- Size-segregate: Andersen type system
(50% cutoff diameters: 0.43, 0.65, 1.1, 3.3, 4.7, 11 μm)

Wet deposition (snow) sample

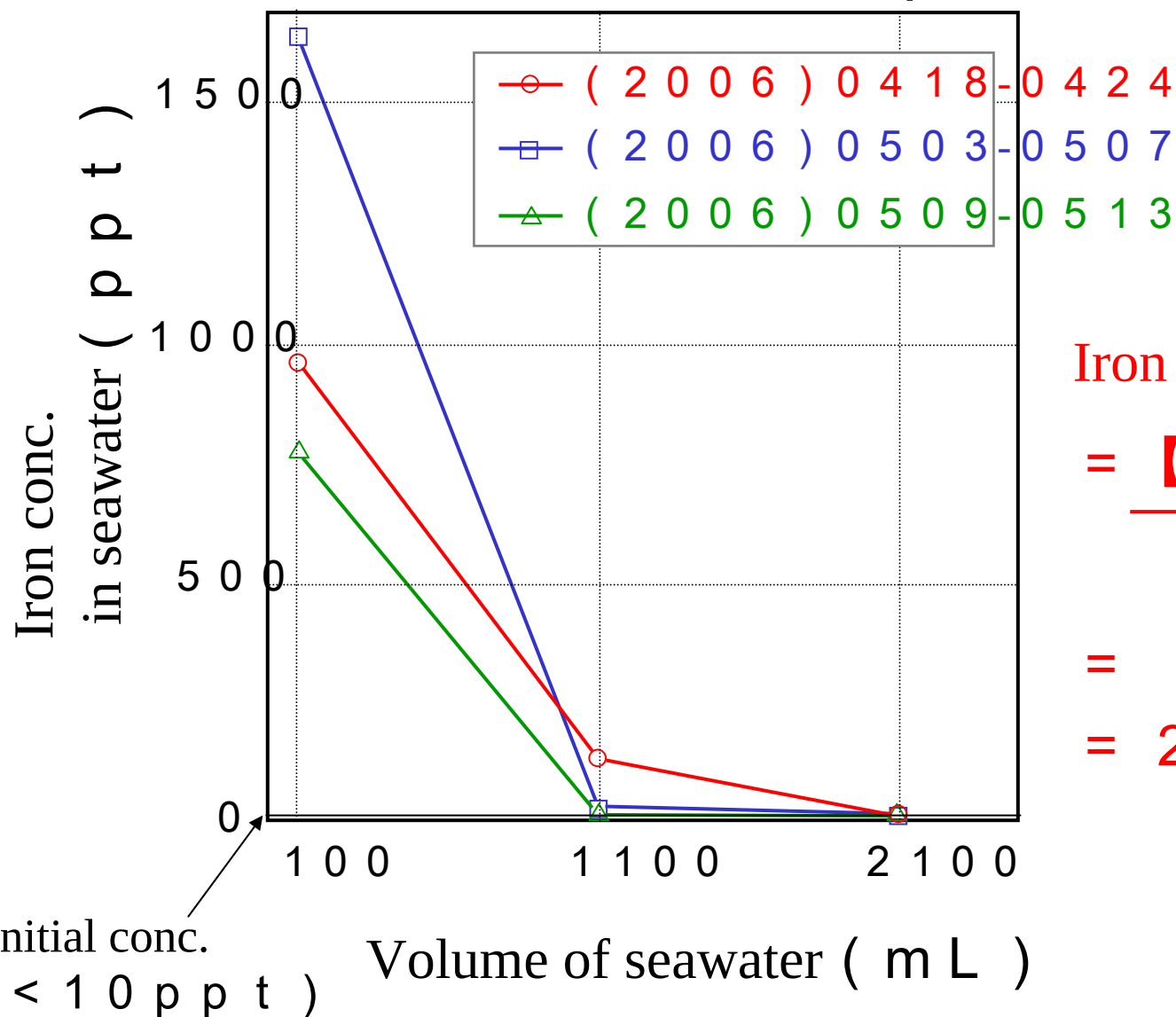
- Period : 11 March, 2006, during the Asian dust episode.
- Location : Top of Mt. Teine (1000m height) in Hokkaido

Surface seawater (10m depth) samples

- Sub-arctic western North Pacific (St. KNOT), January, 2006
D<0.22 μm (PTFE membrane)
- Sub-tropical western North Pacific (Ogasawara), August, 1995
D<0.03 μm (hollow fiber membrane)

Iron dissolution experiment result (1)

Total size aerosol samples



Iron solubility

= **【Total dissolved iron】**

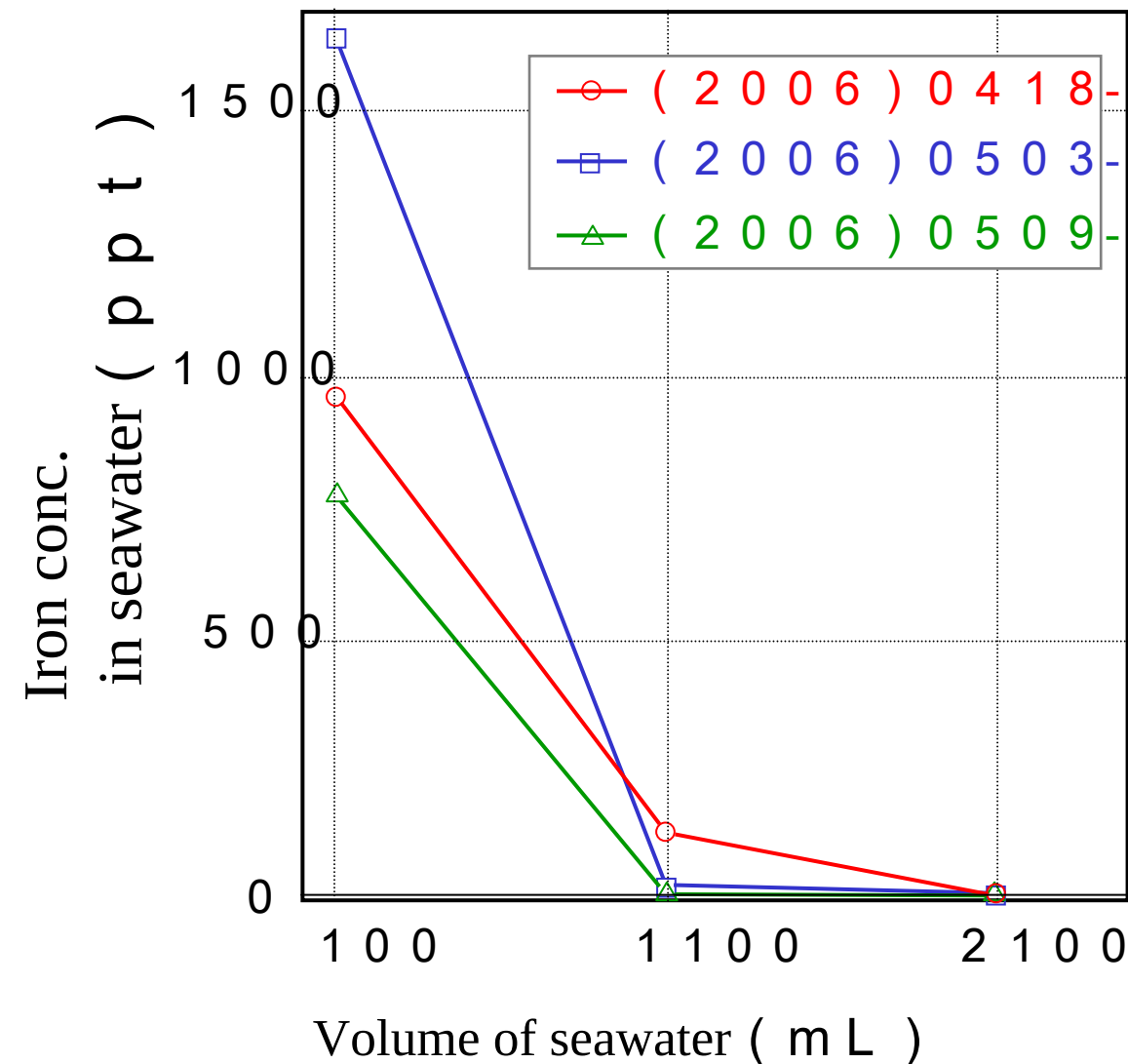
【Total iron】

= 0 . 2 2 / 1 0 . 5

= 2 . 1 %

Results

Total size aerosol samples



Iron solubility

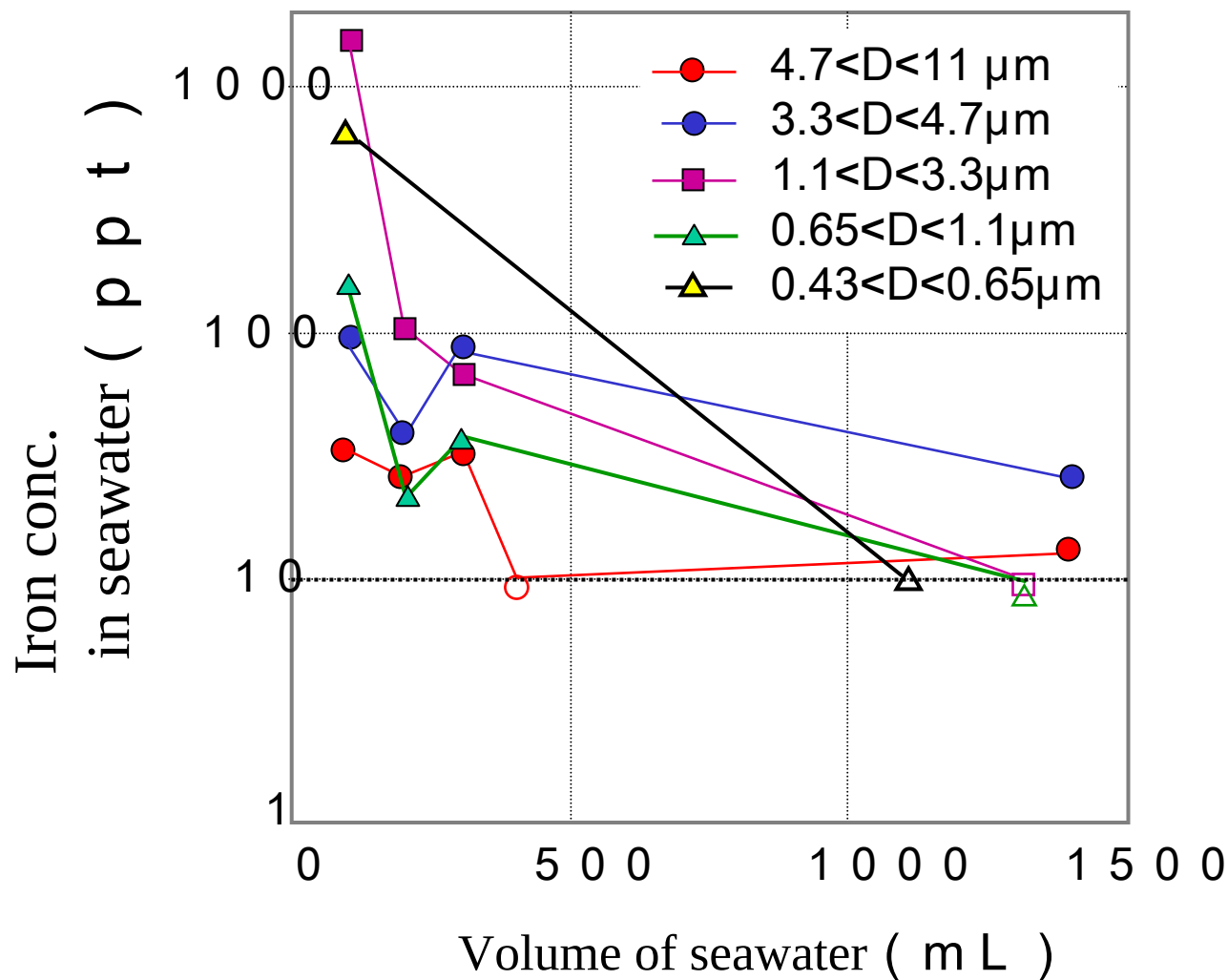
(2 0 0 6) 0 4 1 8 - 0 4 2 4
2.0 ~ 2.2 %

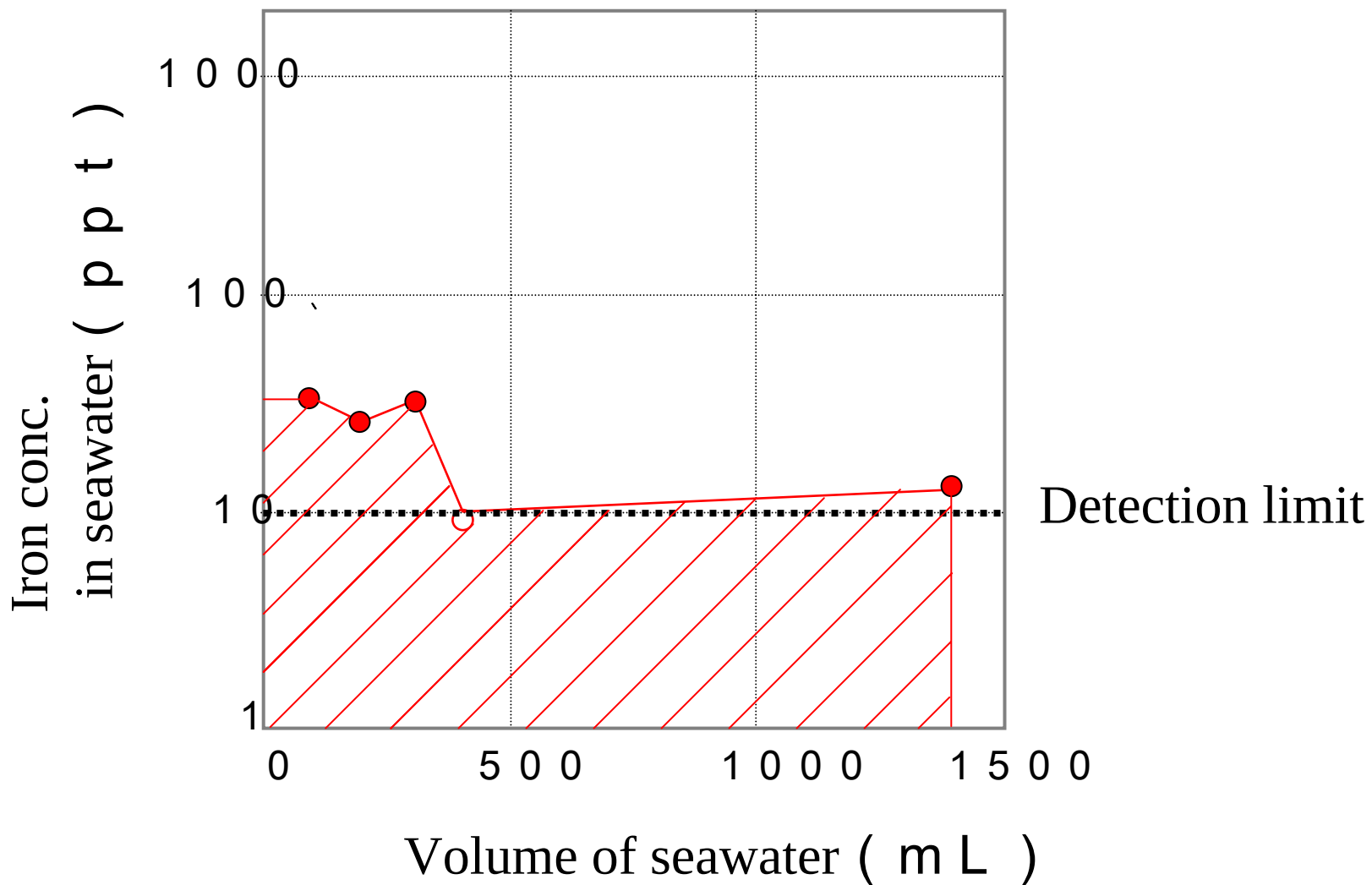
(2 0 0 6) 0 5 0 3 - 0 5 0 7
2.2 ~ 2.4 %

(2 0 0 6) 0 5 0 9 - 0 5 1 3
1.2 ~ 1.4 %

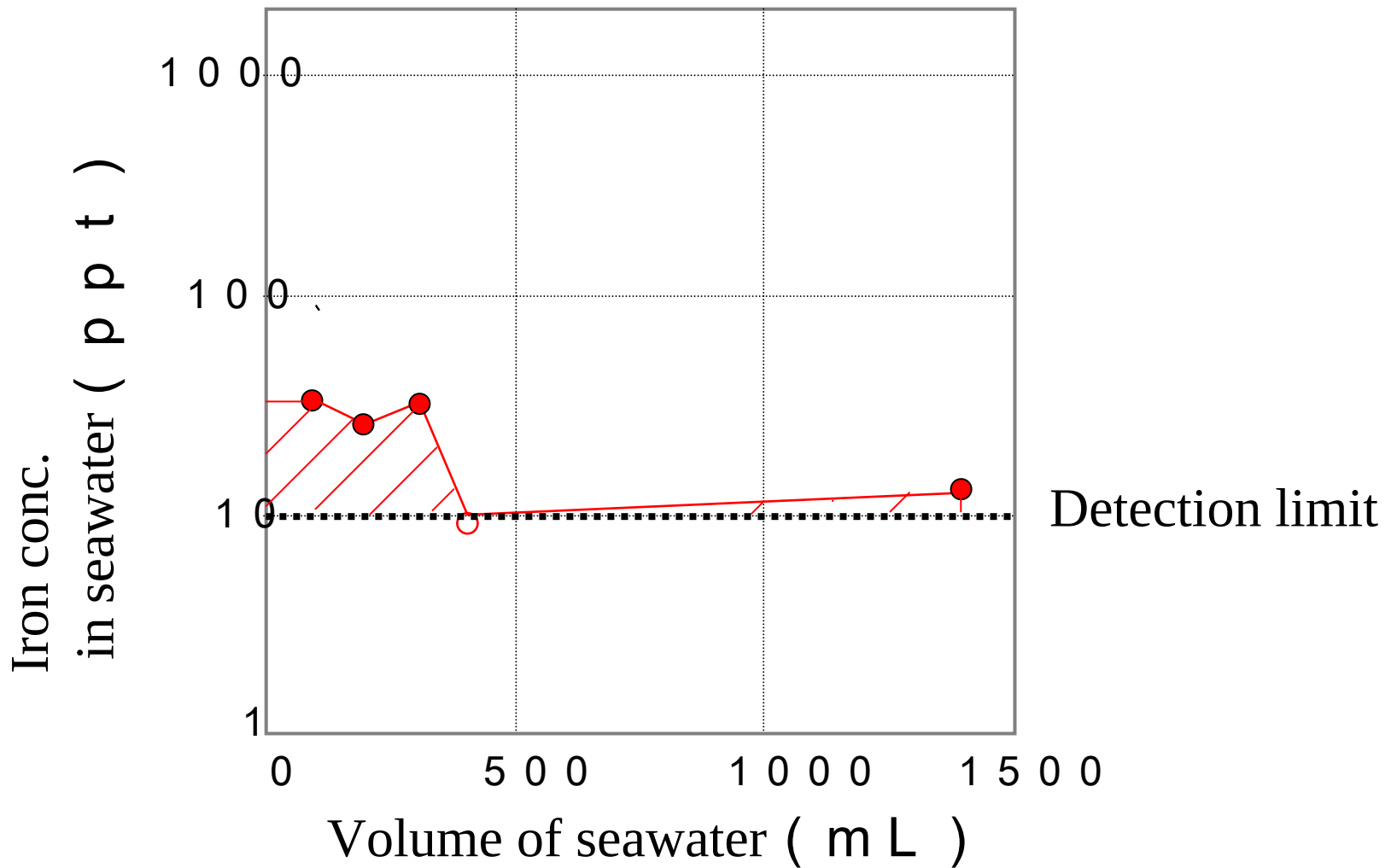
→ 1.2 ~ 2.4 %

Size-segregated aerosol sample (18-24, April, 2006)





Dissolved iron (Maximum) : $0.23 \mu\text{g}$



Dissolved iron (Minimum) : $0.0089 \mu\text{g}$

Range (Min ~ Max) of iron solubility : $0.36 \sim 0.92\%$

Size-segregated aerosol sample (18-24, April, 2006)

Aerosol size range	Dissolved iron (n g)	Insoluble iron (μ g)	Range of Iron solubility
4.7 < D < 11 μm	8.9 ~ 23	2.5	0.36 ~ 0.92 %
3.3 < D < 4.7 μm	35 ~ 48	1.5	2.3 ~ 3.2 %
1.1 < D < 3.3 μm	168 ~ 181	1.9	8.0 ~ 8.6 %
0.65 < D < 1.1 μm	53 ~ 66	1.6	3.2 ~ 3.9 %
0.43 < D < 0.65 μm	62 ~ 73	0.47	1.2 ~ 1.3 %

Size dependence of iron solubility

Aerosol size range	Mode	Iron solubility
$4.7 < D < 11 \mu\text{m}$	< Coarse mode > Mineral dust	0.36 ~ 0.92 %
$3.3 < D < 4.7 \mu\text{m}$		2.3 ~ 3.2 %
$1.1 < D < 3.3 \mu\text{m}$		8.0 ~ 8.6 %
$0.65 < D < 1.1 \mu\text{m}$	< Fine mode > Secondary particles	3.2 ~ 3.9 %
$0.43 < D < 0.65 \mu\text{m}$		1.2 ~ 1.3 %

Assumption : < Iron dissolution $\propto$ Surface area >

$$\text{Iron solubility} = \frac{\text{Dissolved iron}}{\text{Total iron}} = \frac{A \cdot S[d^2]}{\rho \cdot V[d^3]} = \frac{B}{d}$$

$S[d^2]$: Area、 A , B : Constant

$V[d^3]$: Volume、 ρ : Density

$$\text{Iron dissolution} \propto \text{Surface area} \rightarrow \text{Iron solubility} \propto 1 / d$$

Size dependence of iron solubility

Aerosol size	Average size(d)	Size ratio* (D)	$\frac{1}{D}$	=	Iron solubility ratio (R)**
4.7 < D < 11 μm	7.2	3.8	0.26		0.05 ~ 0.1
3.3 < D < 4.7 μm	3.9	2.1	0.49		0.28 ~ 0.37
1.1 < D < 3.3 μm	1.9	1	1		1

* $D_i = d_i / 1.9(\mu\text{m})$

** Iron solubility of size (d) : $r(d)$

Iron solubility ratio: $R_i = r(d_i) / r(1.9 \mu\text{m})$

Aerosol size	$\frac{1}{D}$	$\left(\frac{1}{D}\right)^2 \propto$	Iron solubility ratio
$4.7 < D < 11 \mu\text{m}$	0.26	0.07	0.05 ~ 0.1
$3.3 < D < 4.7 \mu\text{m}$	0.49	0.23	0.28 ~ 0.37
$1.1 < D < 3.3 \mu\text{m}$	1	1	1

$$\text{Iron solubility} = \frac{\text{Dissolved iron}}{\text{Total iron}} = \frac{A[1/d] \cdot S[d^2]}{\rho \cdot V[d^3]} = \frac{B}{d^2}$$

$S[d^2]$: Area、 A : Coefficient
 $V[d^3]$: Volume、 ρ : Density

$A[1/d]$: Size effect of iron solubility on mineral composition

(Mineral particle with high iron solubility would be easily weathered)

Estimation of iron solubility of Asian dust in the snow sample (Mt. Teine)



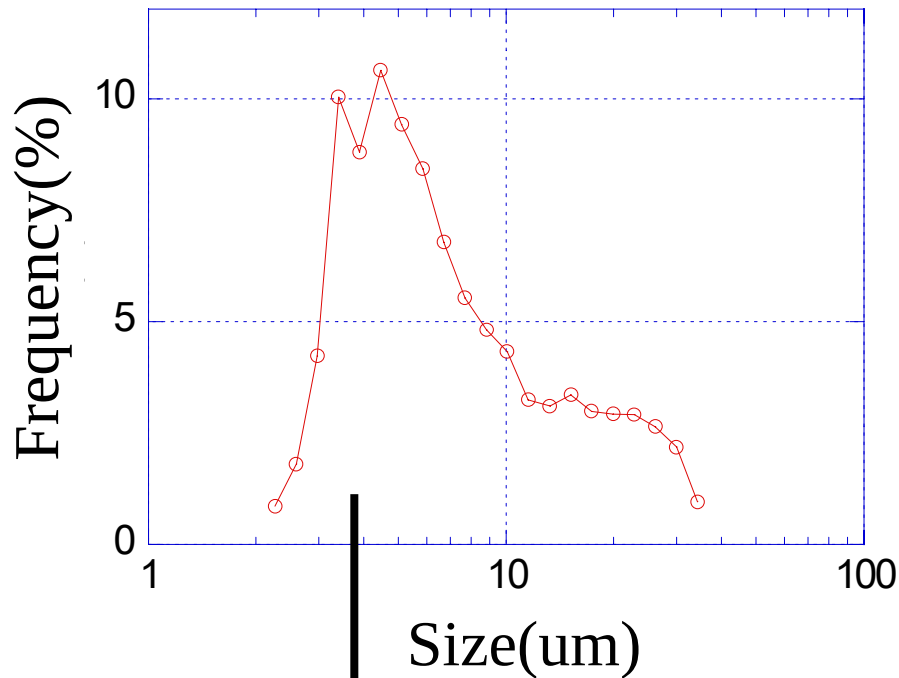
Iron dissolution experiment
(measure the iron solubility)



Optical particle size analyzer
(measure the particle size distribution)

Estimation of iron solubility of Asian dust in the snow sample (Mt. Teine)

Particle size distribution of Asian dust particle



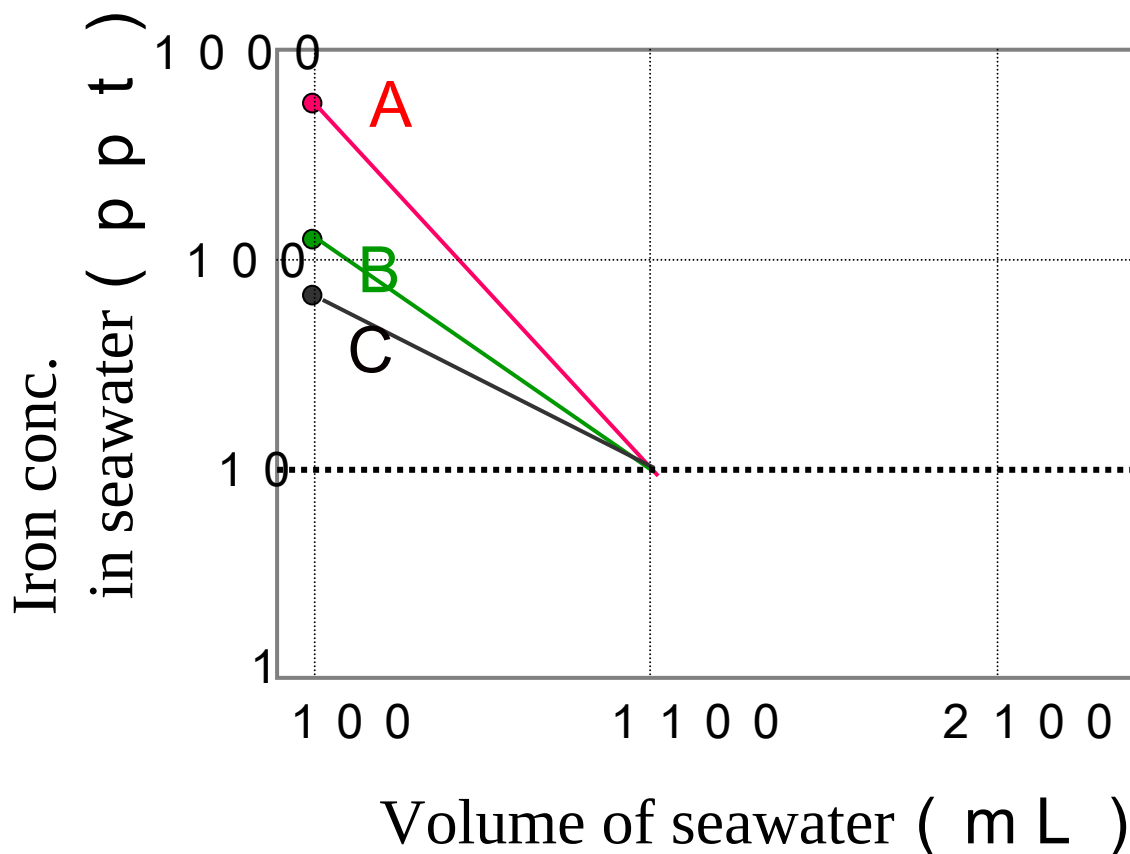
Assumption

$$\text{Iron solubility} \propto \left(\frac{1}{d} \right)^2$$

$$\text{Iron solubility (1.9 } \mu\text{m)} = 8.3 \%$$

Iron solubility of 1.2 % (estimation)

Measurement of iron solubility of Asian dust in the snow sample (Mt. Teine)



Iron solubility
(Measurement)

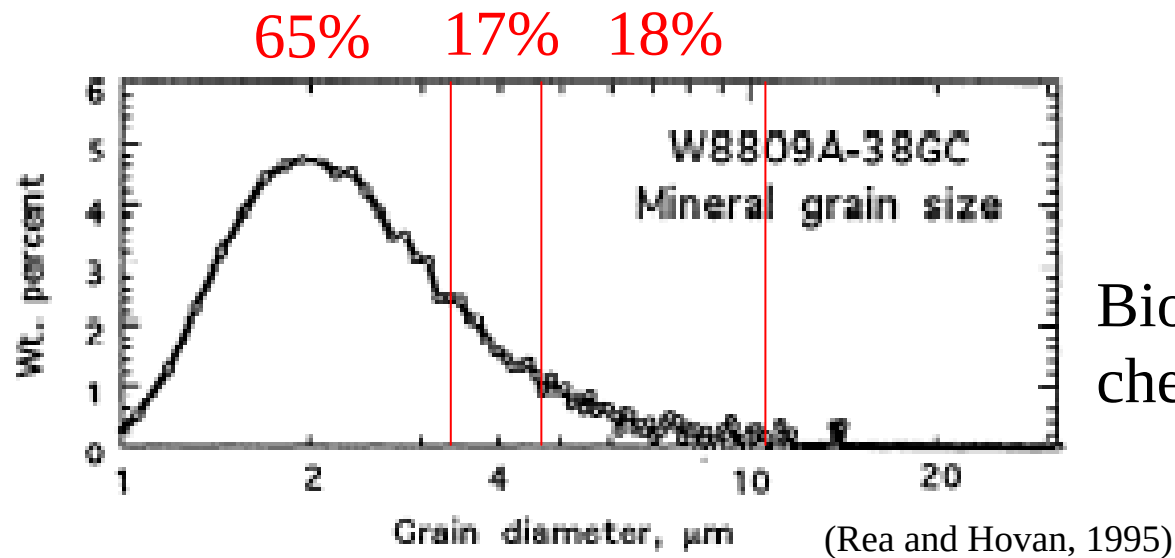
A	0.90 ~ 1.2	%
B	0.47 ~ 1.3	%
C	0.11 ~ 0.49	%

(Estimation)

1.2 %

Estimation of iron solubility of Asian dust deposited on the sub-arctic eastern North Pacific (41°N, 134 ° W)

Particle size distribution of mineral particle in the ocean sediment



Biological particles was chemically removed.

→ Iron solubility : 5.9 %

Assumptions

- Particle size of mineral particle in the ocean sediment is equal to that in the atmospheric depositions.
- Sinking of mineral particles occurred in the same area (horizontal injections were ignored).

Summary and suggestion

- In-line filter holder system measure the **iron solubility** of atmospheric particles. (total size range : 1.2 – 2.4%)
- **Particle size distribution** controls the iron solubility of aerosol.

$$\text{Iron solubility} = \frac{A[1/d] \cdot S[d^2]}{\rho \cdot V[d^3]} = \frac{B}{d^2}$$

$$\text{Iron solubility (1.9 } \mu\text{m)} = 8.3 \%$$

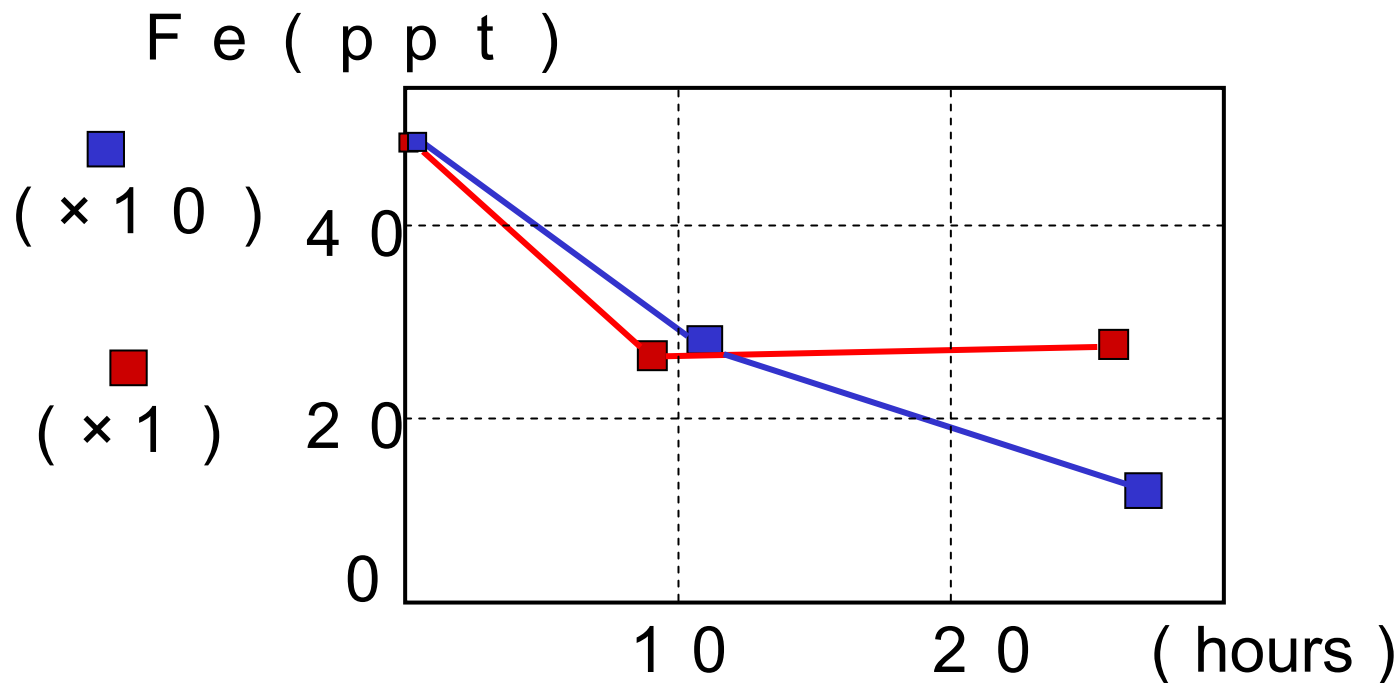
We suggest that the size-segregated analysis should be applied to the future iron budgeted model (including dissolution process).

Iron dissolved from atmospheric particle into seawater in containers

Loss of iron is serious problem

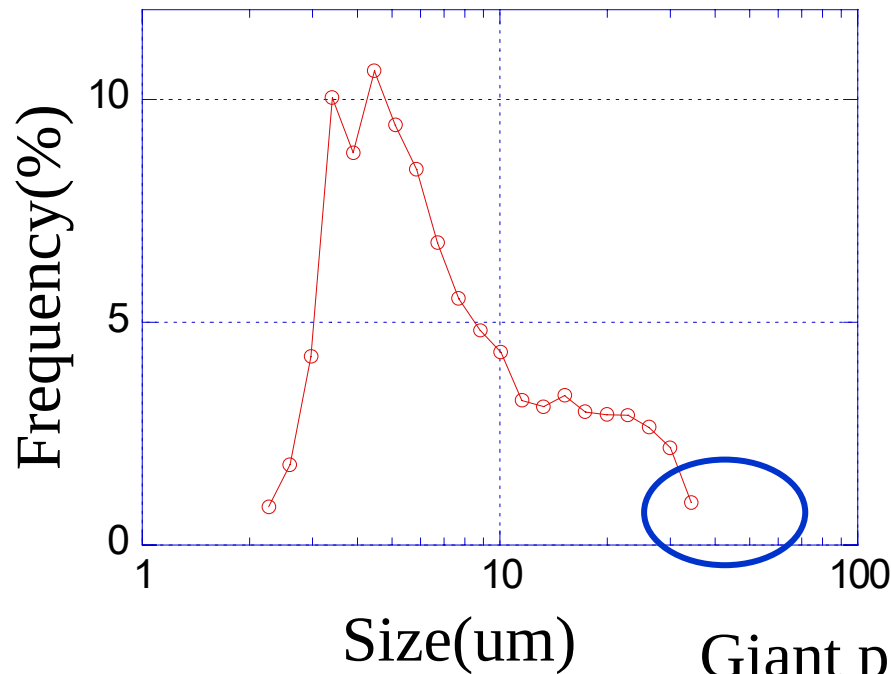
Loss of iron to the inner wall of low-density polyethylene bottle

(Initial conc. of iron 500 ppt (red square) 5000 ppt (blue square))



Giant particle of mineral dust in snow sample may be in high anomaly

Size distribution of mineral dust in snow sample



Giant particle – anomaly ?

If there is a giant particle in snow sample, the iron solubility decrease.

“There is no consensus about the iron dissolution experiment “

(Mahowald et al., 2005)

Dissolution methods

1. Filtering system; Buck et al., (2006) ---cup holder
This study --- in-line holder
2. Bottle dissolution ; Former studies.

Materials

3. Seawater; Bonnet and Guieu., 2004
Buck et al., (2006)
This study
4. Acid solution(pH1, pH4); Former studies
5. Alkaline solution (ph8) ; Former stidies

Iron solubility in the fine mode range

$0.65 < D < 1.1 \mu\text{m}$ 3.2 ~ 3.9 %

$0.43 < D < 0.65 \mu\text{m}$ 1.2 ~ 1.3 %

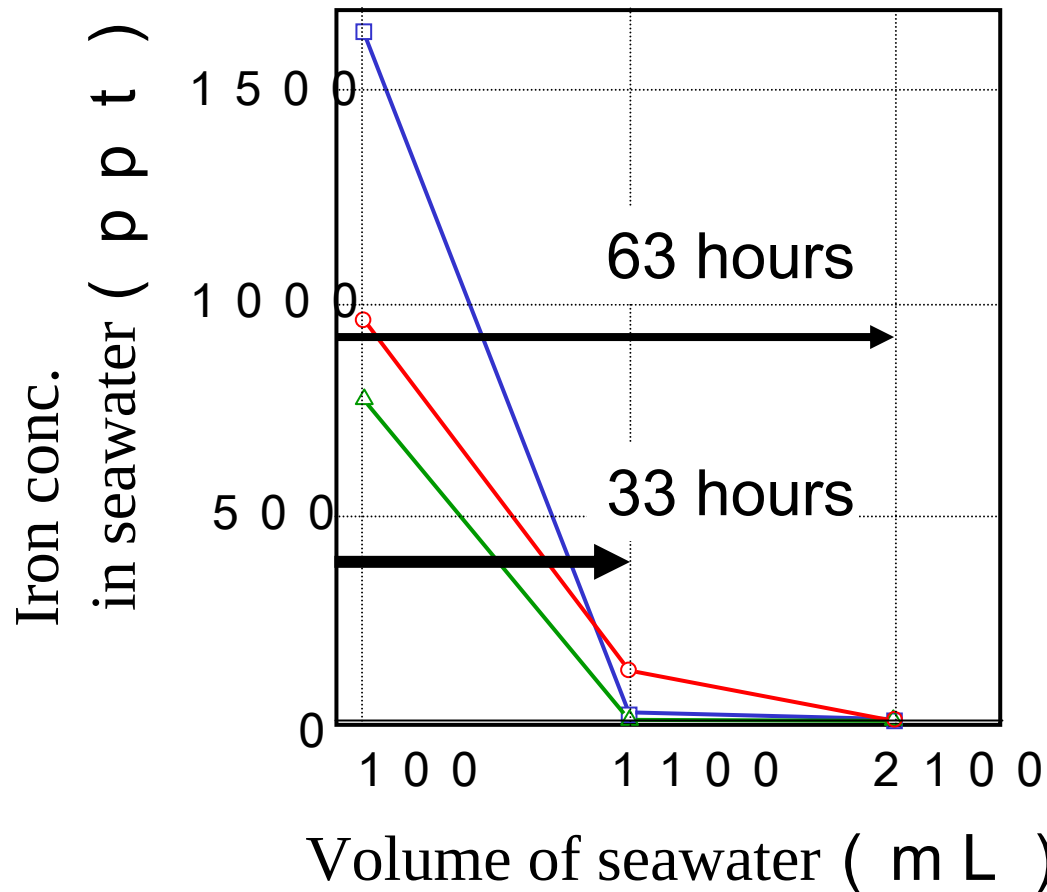
Source of iron in urban air : “Anthropogenic fuel burning” = 40%
(溝畑・真室, 1980)

Power plant exhaust iron : “Iron sulfate” = 80% (Weber et al., 2000)

Iron solubility of power plant particle = 38% (Desboeufs et al., 2001)

- In the polluted air, anthropogenic fuel burning is the main source of iron.
- Anthropogenic fuel burning particles have high iron solubility.
- Burning particles in the fine size range can be globally transported to the ocean.

Dissolution experiment don't give the “time scale ” in real ocean



In real ocean dissolution speed would be faster than this experiment.
Dissolution experiment result indicate the amount of iron supplied into the surface seawater.