Chemical characteristics of aerosols over Arabian Sea & Bay of Bengal: Impact of Anthropogenic Sources

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Rationale:

Climate Change: One of the most important societal concerns for the 21st century

Atmospheric Chemistry: Plays a critical role

-Abundances & distributions of natural and anthropogenic constituents

Greenhouse gases, aerosols and clouds

-Influence incoming and/or outgoing solar radiation, temperature and precipitation

Climate Forcing by Anthropogenic Aerosols

Key issue : **Role of atmospheric chemistry in amplifying/damping climate change**

Questions : **What are the effects of aerosols on clouds, their optical properties, precipitation and regional hydrologic cycle?**

African drought

Rosenfeld et al [2001]:

Correlation between increasing dust frequency
&
Rainfall in Sahelian region (African Monsoon)
(from 1950s through 1980s)

Conclusion:

- **Dust aerosols act as cloud condensation nuclei (CCN)**
- **Increased dust frequency** —Cause of→ **decreased precipitation (cloud life-time effect)**

- **Atmospheric Dust, Chemistry and Transport**

⬇ **Variety of individual minerals (quartz, calcite, gypsum, clays, etc.) (different physical/chemical properties)**

⬇

Requires quantification of its global impacts

⬇

Information on dust emission sources, transport, particle size and compositional data

- **Mineral Dust**

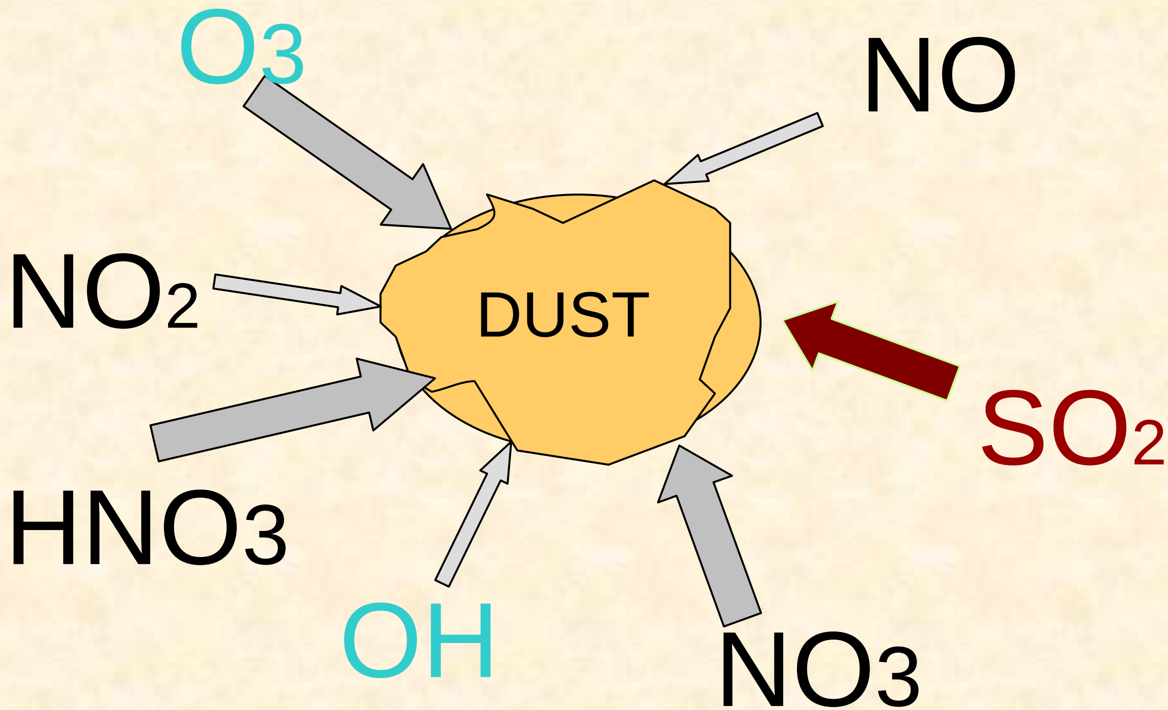
⇓

Atmospheric chemistry is over-simplified in current models
(Global transport/chemistry model & dust model)

⇓

Considered as single entity aerosol with single kinetic parameter for chemical reactions

Mineral dust & Atmospheric Chemistry



- **Alkaline nature favours uptake of SO_2 and NO_x**
- **Changes surface properties: Hydrophobic → Hydrophilic**
- **Ozone decomposition on mineral surface ($2O_3$ → $3O_2$)**

(mediated via POC, Organic complexes, Fe & Mn)

Mineral dust : Recent work

* Provide stoichiometric/catalytic reaction centers - to perturb important gas-phase cycles

* Enhances kinetics of SO_2/NO_2 oxidation

* Perturbation of photo-oxidation cycles of: O_3, HNO_3 & HO_2^* – radicals

* Heterogeneous loss of organic compounds:
Acetaldehyde, acetone ....
Comparable to loss by direct photolysis

Influence of Dust on Sulphate

Asian regions: High SO_2

⬇

Present estimates of SO_4 cooling ignore reactions with mineral aerosols

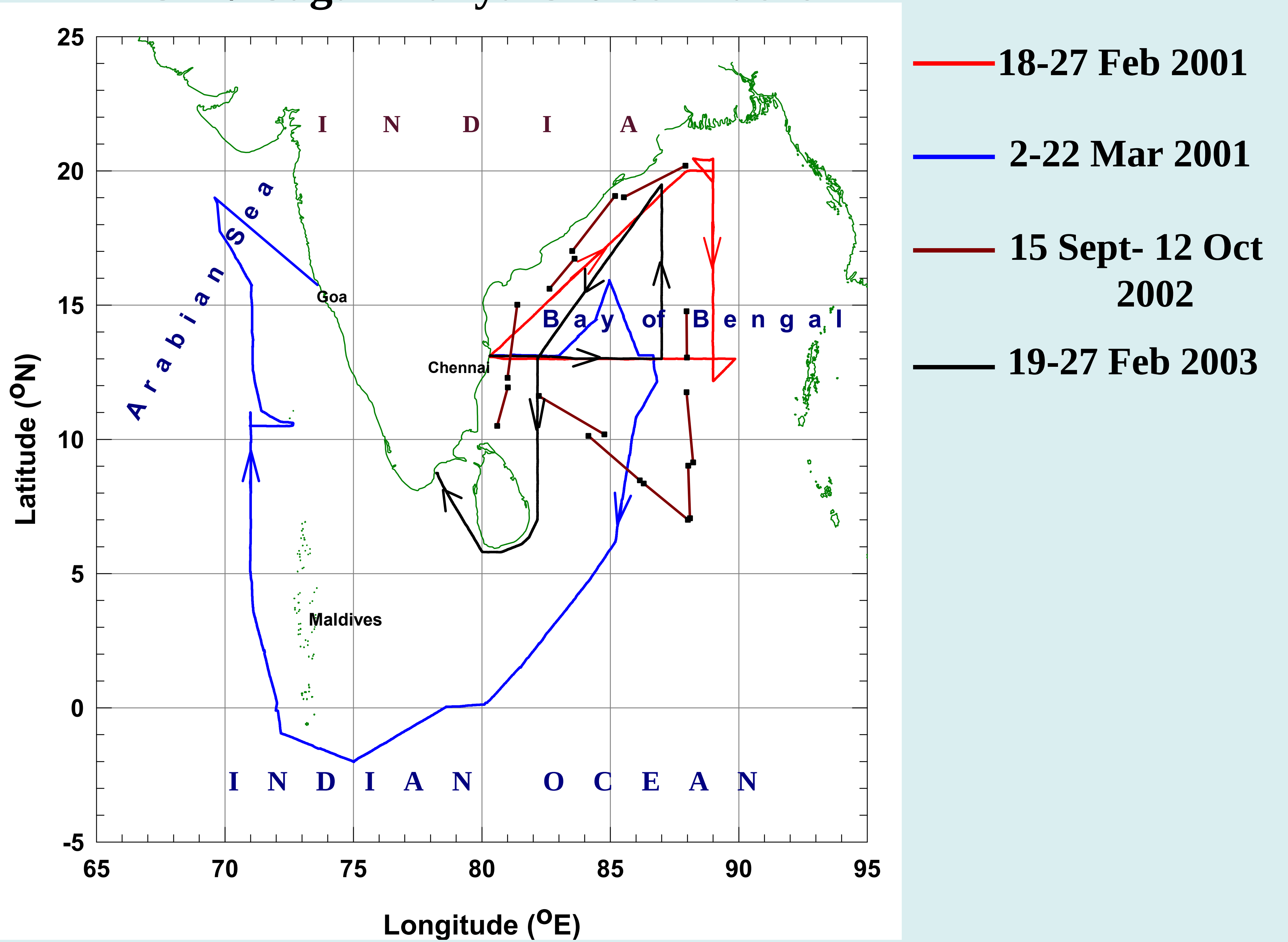
$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$$

(fine) (coarse)

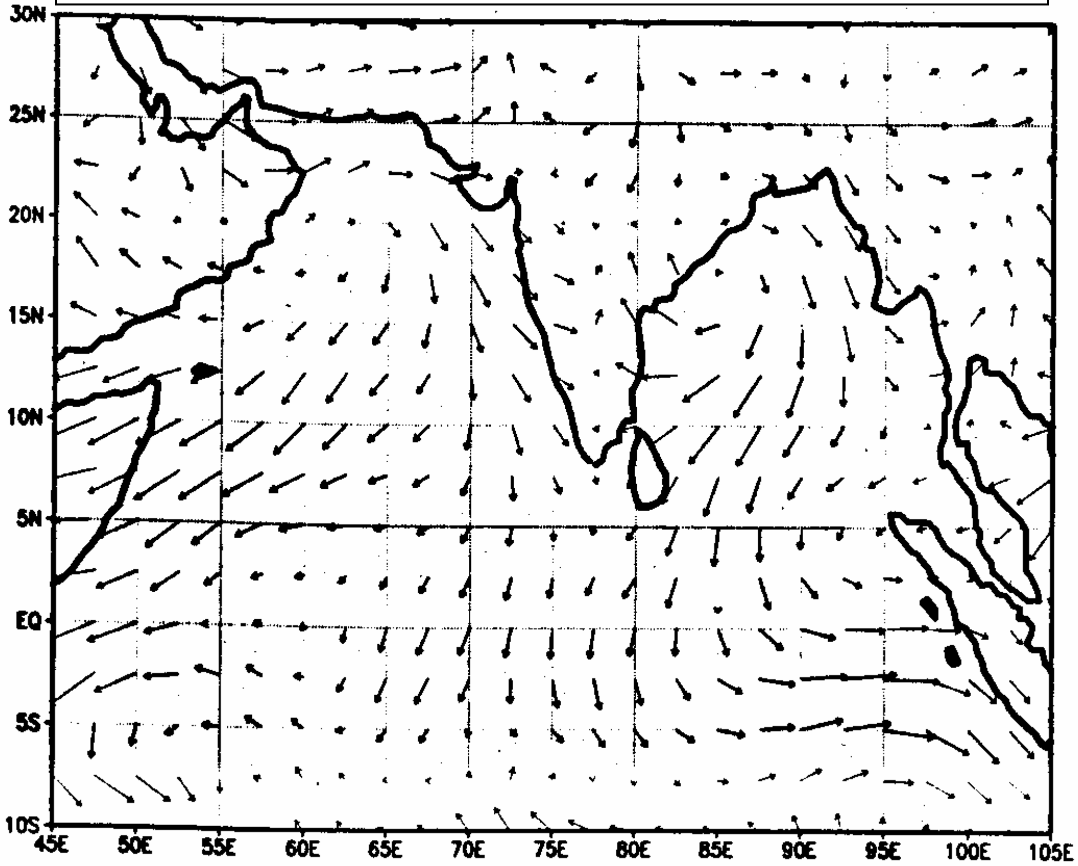
⬇

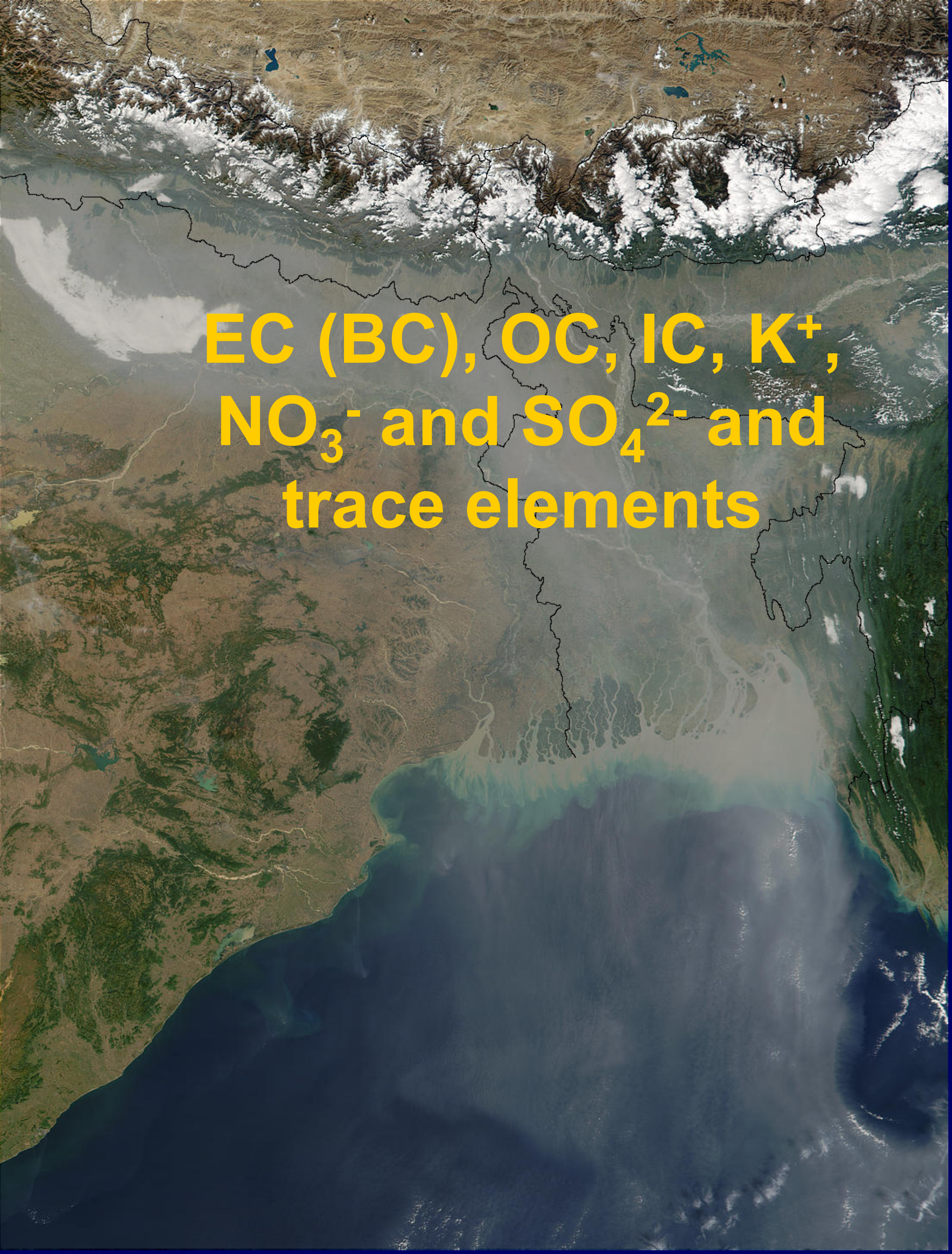
Overestimate the forcing during high dust season

ORV Sagar Kanya Cruise Tracks

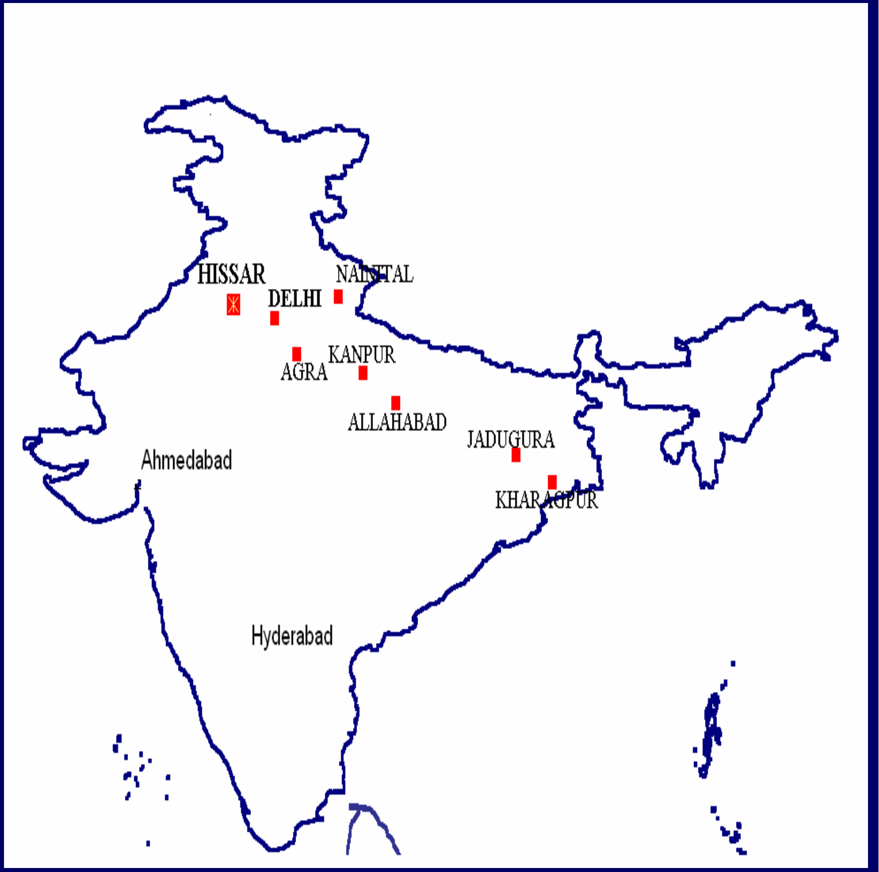


BOB Mean Wind Streamlines
(March 2001)

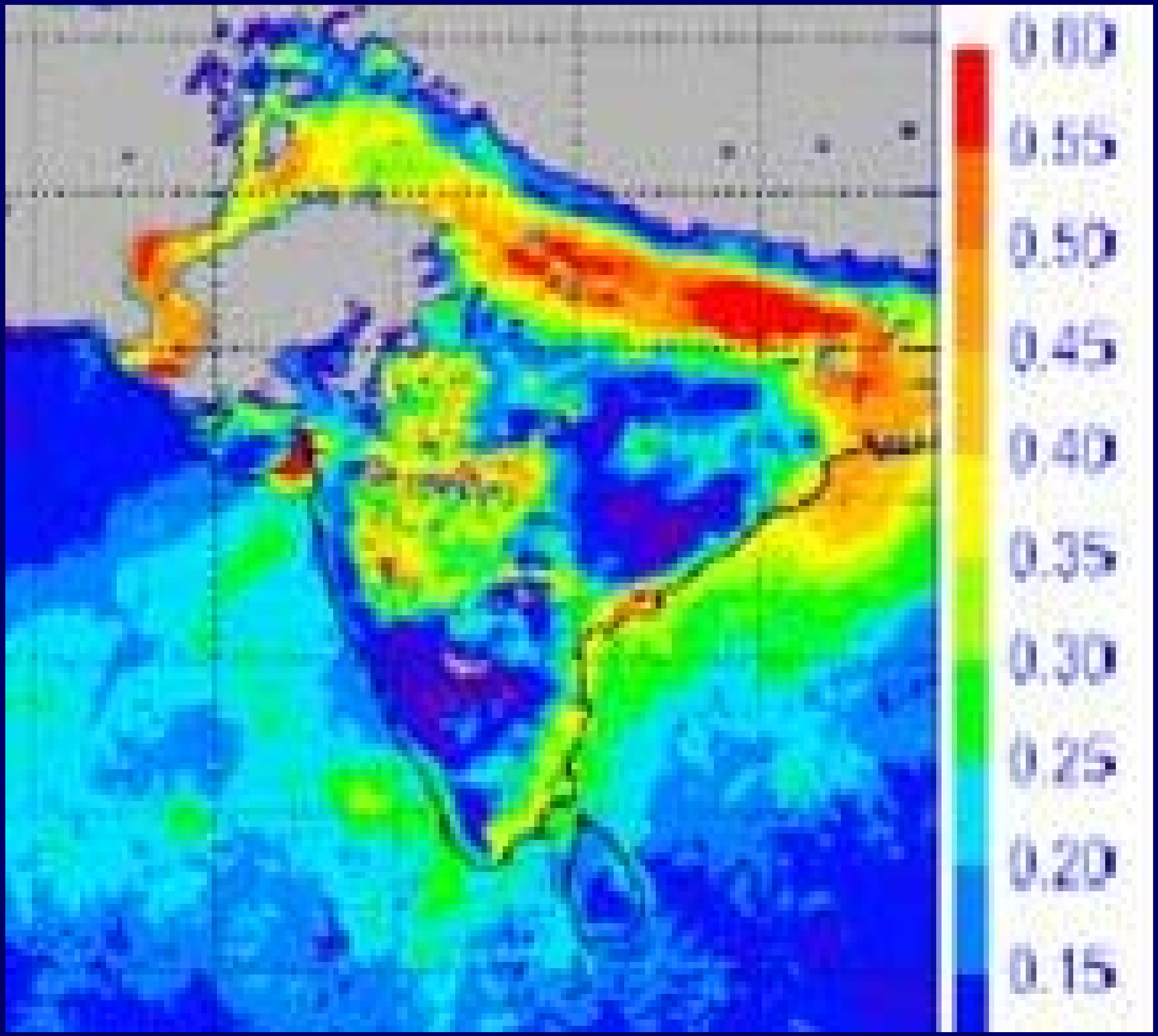




EC (BC), OC, IC, K^+, NO_3^- and SO_4^{2-} and trace elements



MODIS AOD for Dec. month



Objectives

1. **Characterize the temporal and spatial variability in chemical and isotopic composition of aerosols.**

2. **How this variability is related to atmospheric transport processes (physical and chemical).**

3. **Deposition fluxes of natural and anthropogenic constituents across the air-sea interface.**

IMPLICATIONS:

Long-range transport of air pollutants from the south & south-east Asia towards the Indian Ocean.

Experiment :

Sampling : Aerosols samples collected on quartz filters

(using high-volume air samplers)

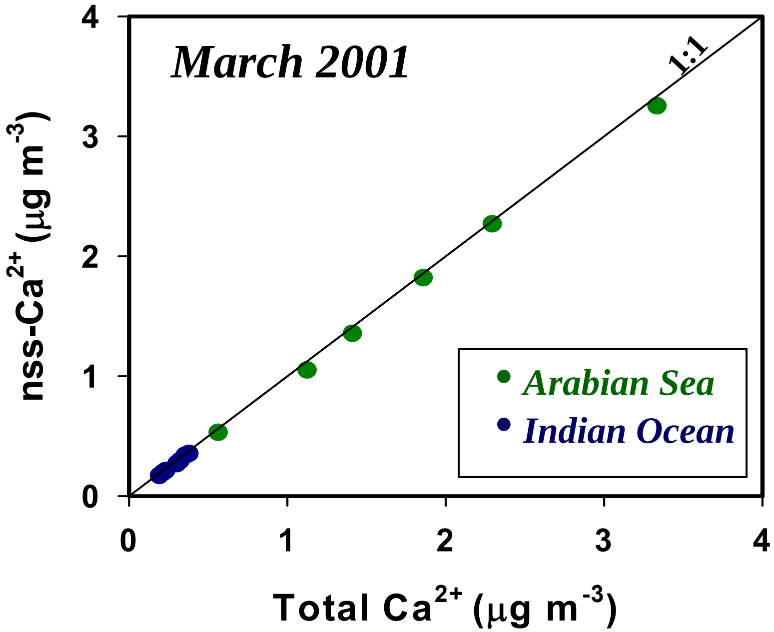
Analysis :

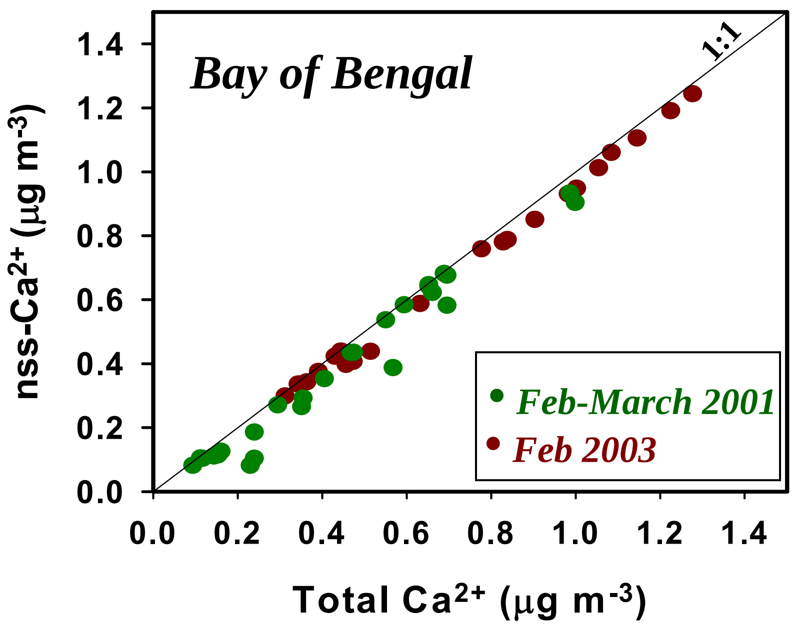
→ **Water soluble constituents :**
NH_4^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , SO_4^{2-} , Cl^- , NO_3^-

→ **Acid soluble constituents :**
Al, Fe, Ca, Mg, Mn, Cu, Zn, Pb

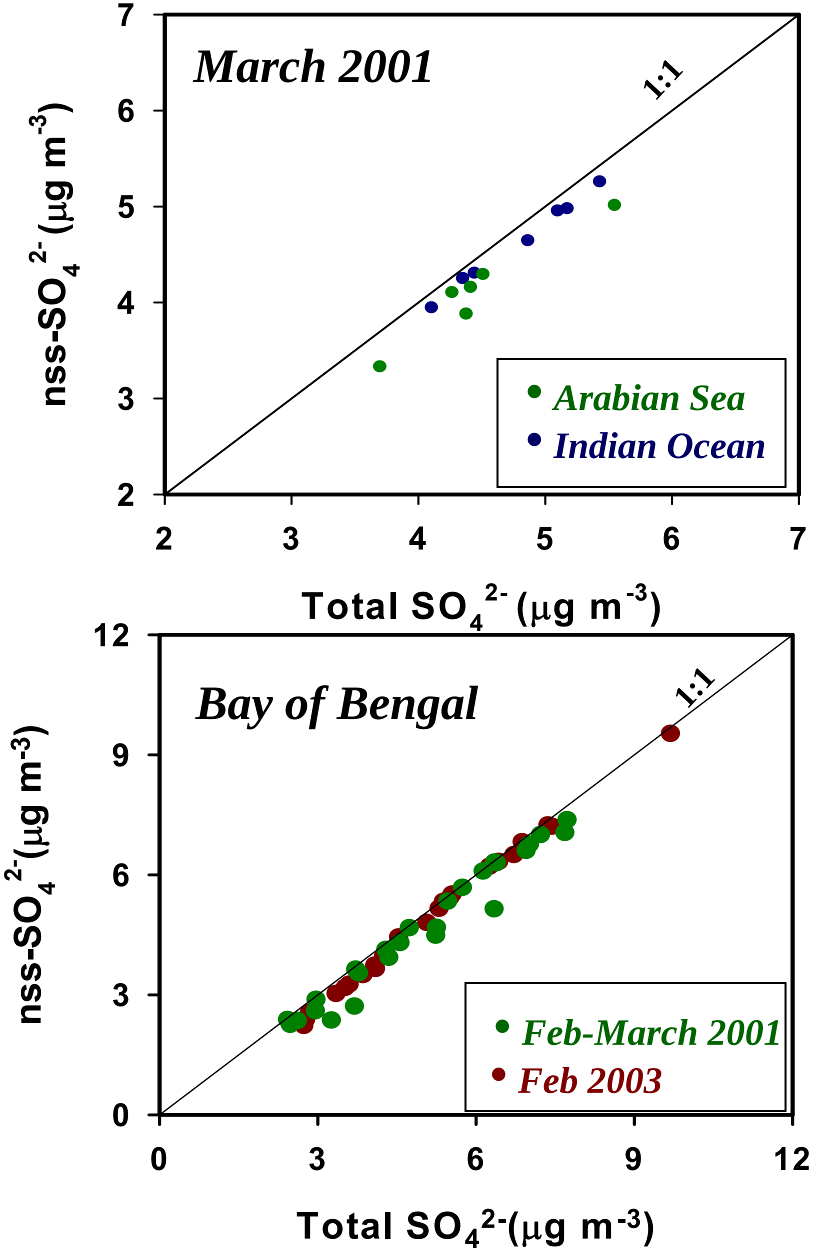
→ **Atmospheric nuclides :**
^{7}Be (53.3 d) & ^{210}Pb (22.3 yr)

Dust & Biogenic Sources



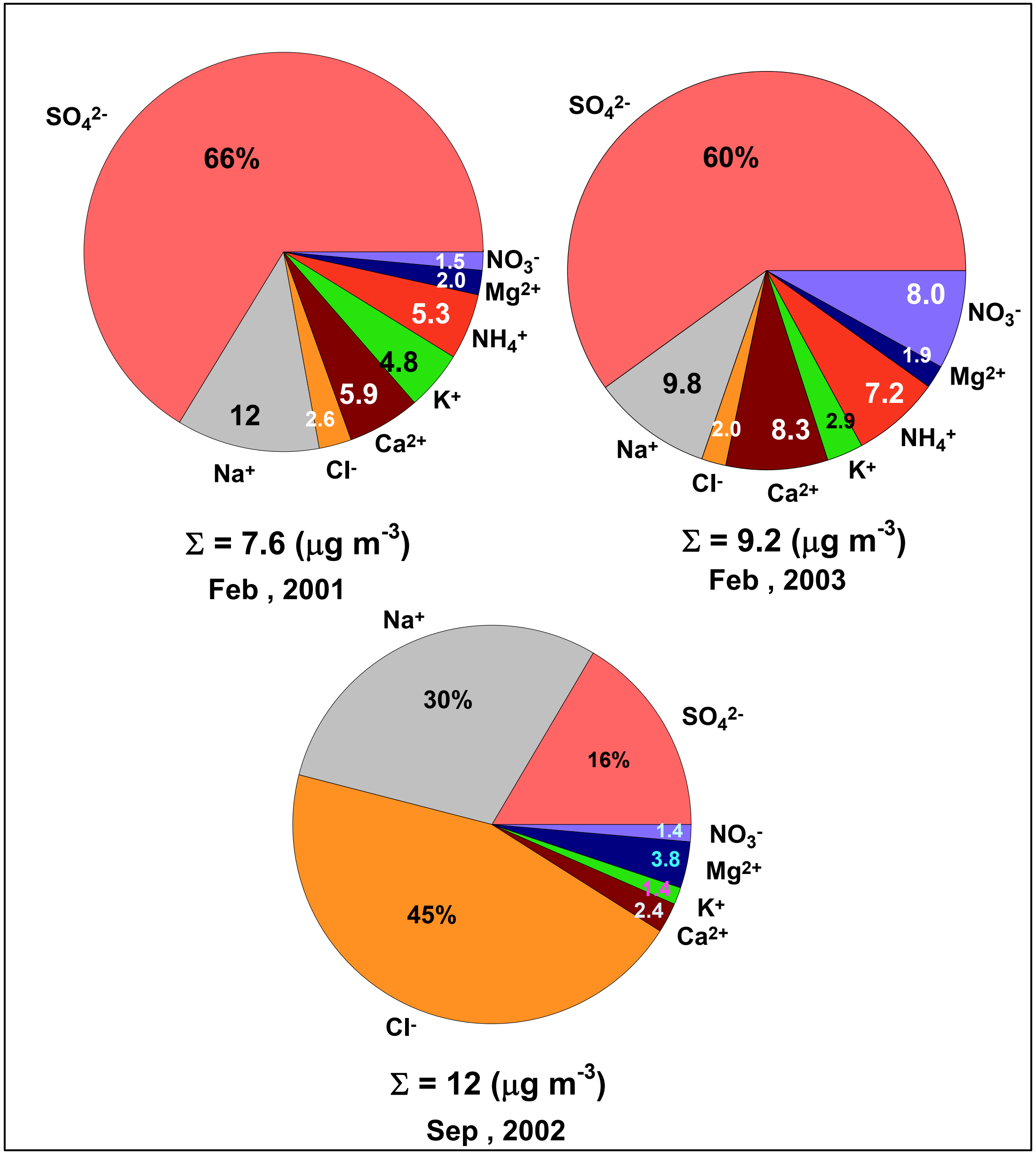


Dominance of Anthropogenic Sources



Average Composition: Water-soluble Constituents

Bay of Bengal



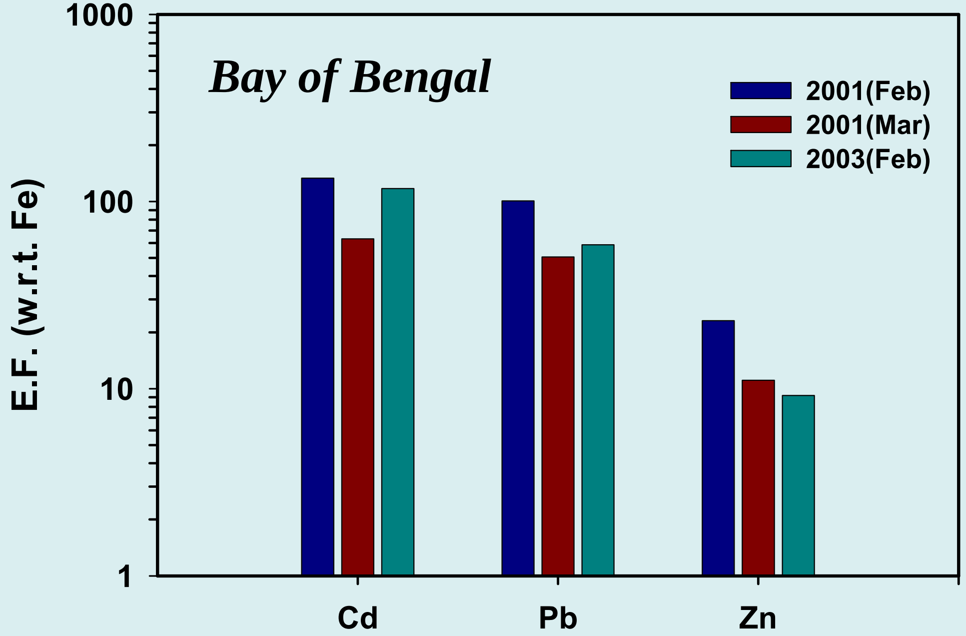
SO_4^{2-} → in marine boundary layer (MBL)

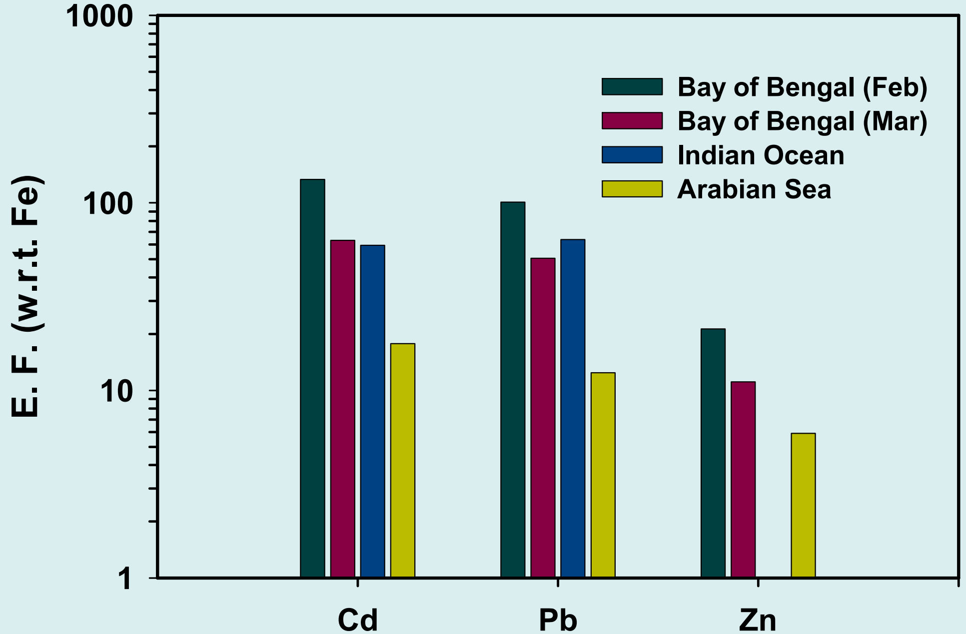
- **Sea-salts**
- **Biogenic:** DMS $\xrightarrow{oxi}$ SO_2 $\xrightarrow{oxi}$ SO_4^{2-}
- **Anthropogenic :** SO_2 $\xrightarrow{oxi}$ SO_4^{2-}
- **Dust , $CaSO_4$ (gypsum)**
  (cement industries)
- **Biomass Burning ?**
- **Volcanic (transient)**

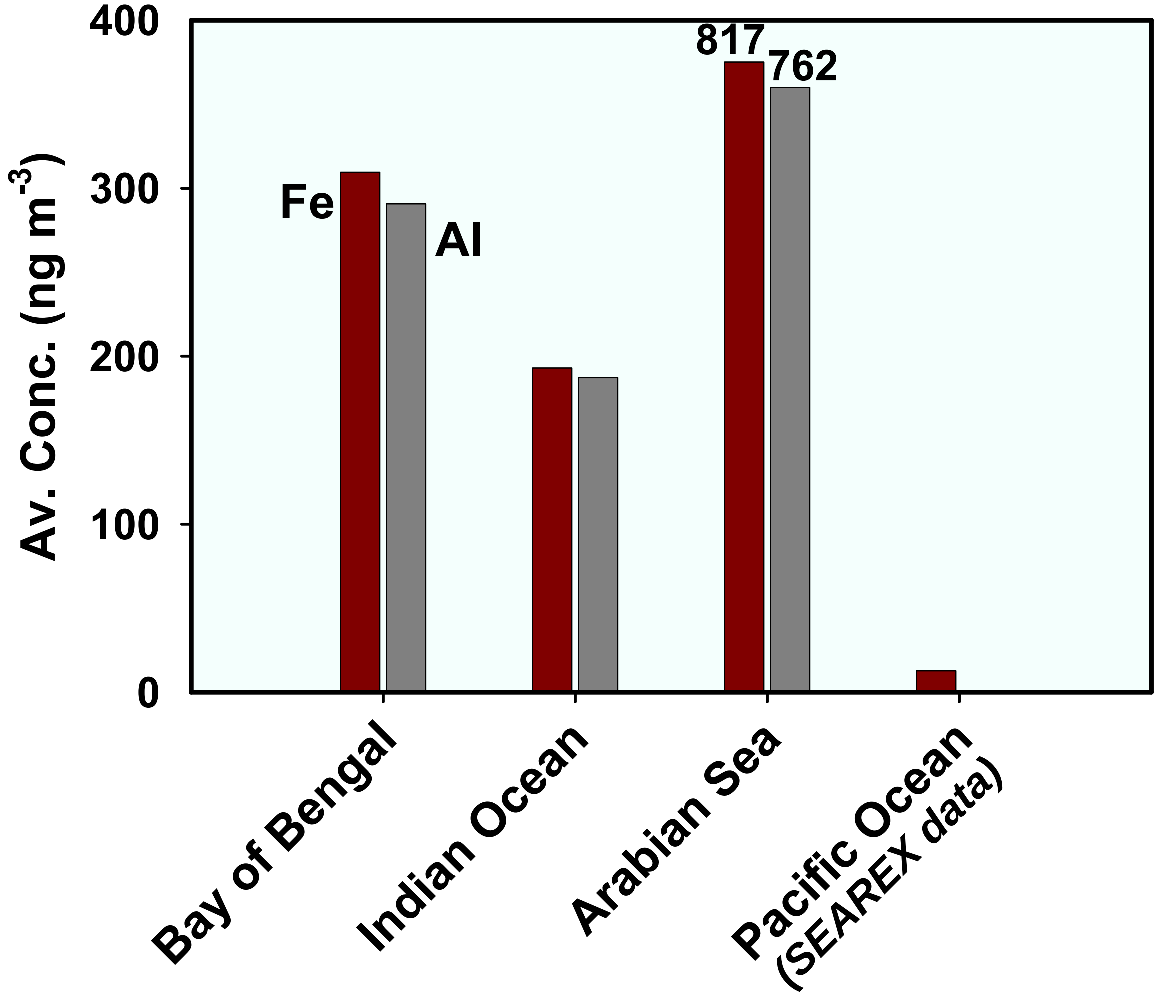
$$\text{nss-}SO_4^{2-} = \Sigma SO_4^{2-} - 0.25Na^+$$

(non-sea-salt)

SO_4^{2-} / Na^+ in sea water = 0.25

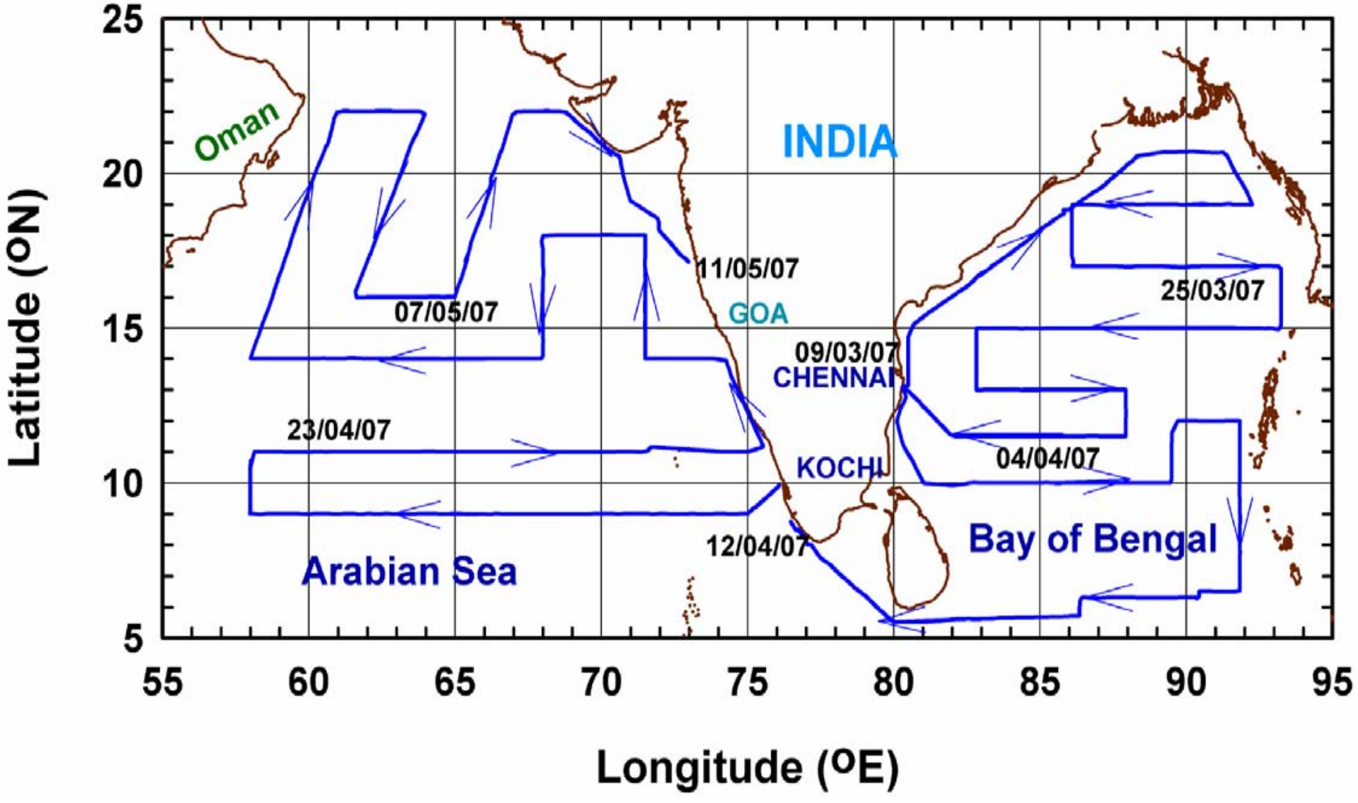

Bay of Bengal
2001(Feb)
2001(Mar)
2003(Feb)
E.F. (w.r.t. Fe)
1000
100
10
1
Cd
Pb
Zn


Bay of Bengal (Feb)
Bay of Bengal (Mar)
Indian Ocean
Arabian Sea
E. F. (w.r.t. Fe)
1000
100
10
1
Cd
Pb
Zn



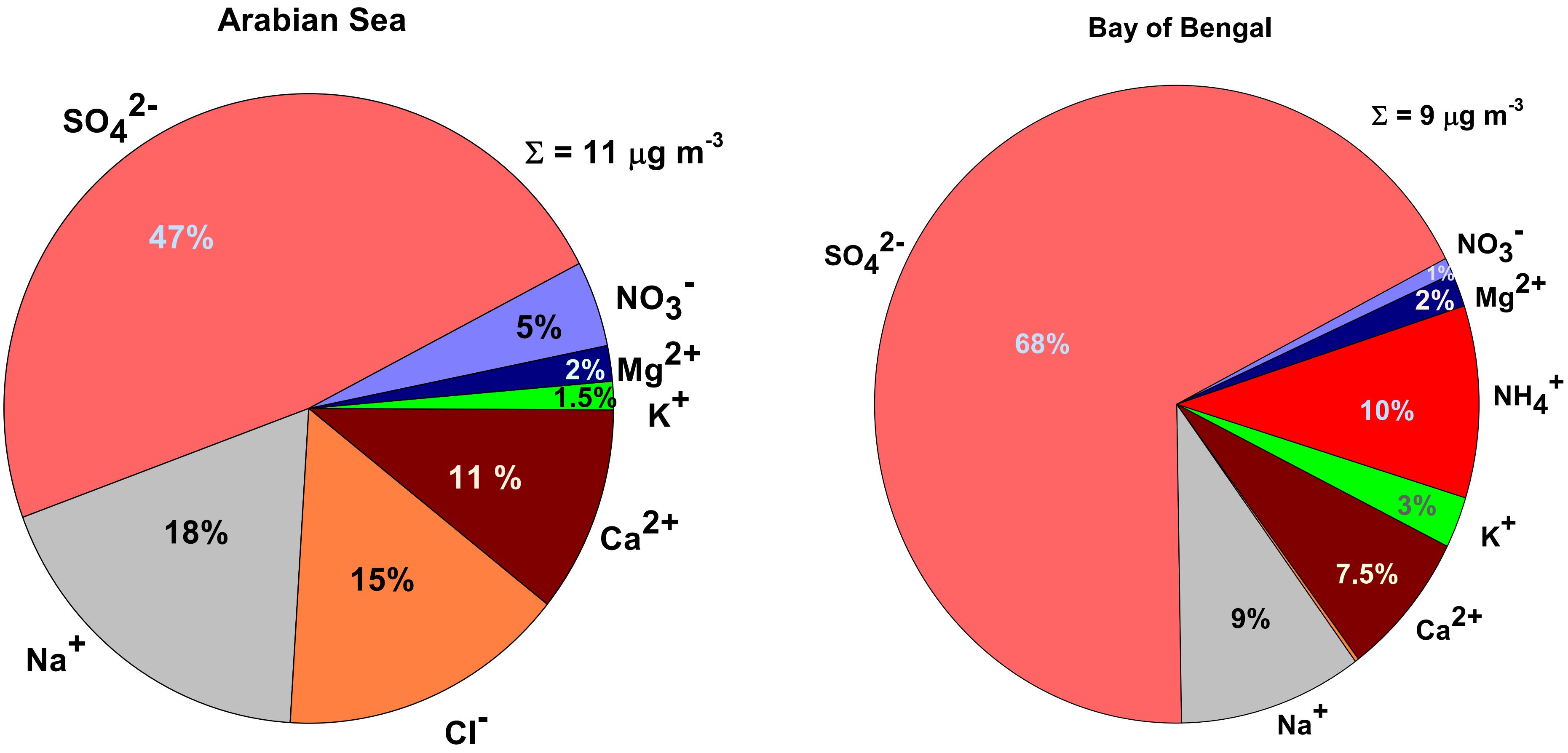
Av. Conc. (ng m^{-3})
400
300
200
100
0
817
762
Fe
Al
Bay of Bengal
Indian Ocean
Arabian Sea
Pacific Ocean
(SEAREX data)

ICARB Sampling Track

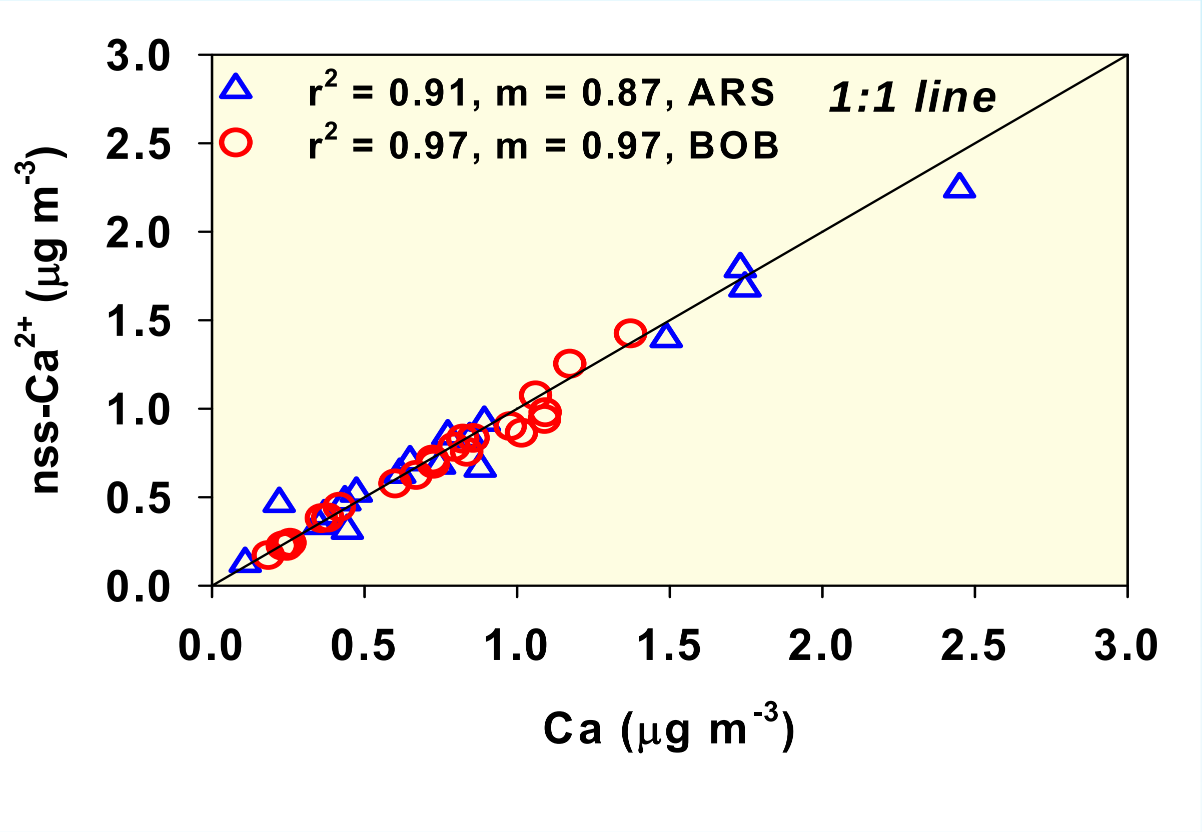


The cruise transects carried out in the Bay of Bengal and Arabian Sea for collection of bulk-aerosol samples during spring inter-monsoon (March-May)

Average water-soluble composition of aerosols over Bay of Bengal and Arabian Sea, reflecting dominance of SO_4^{2-}

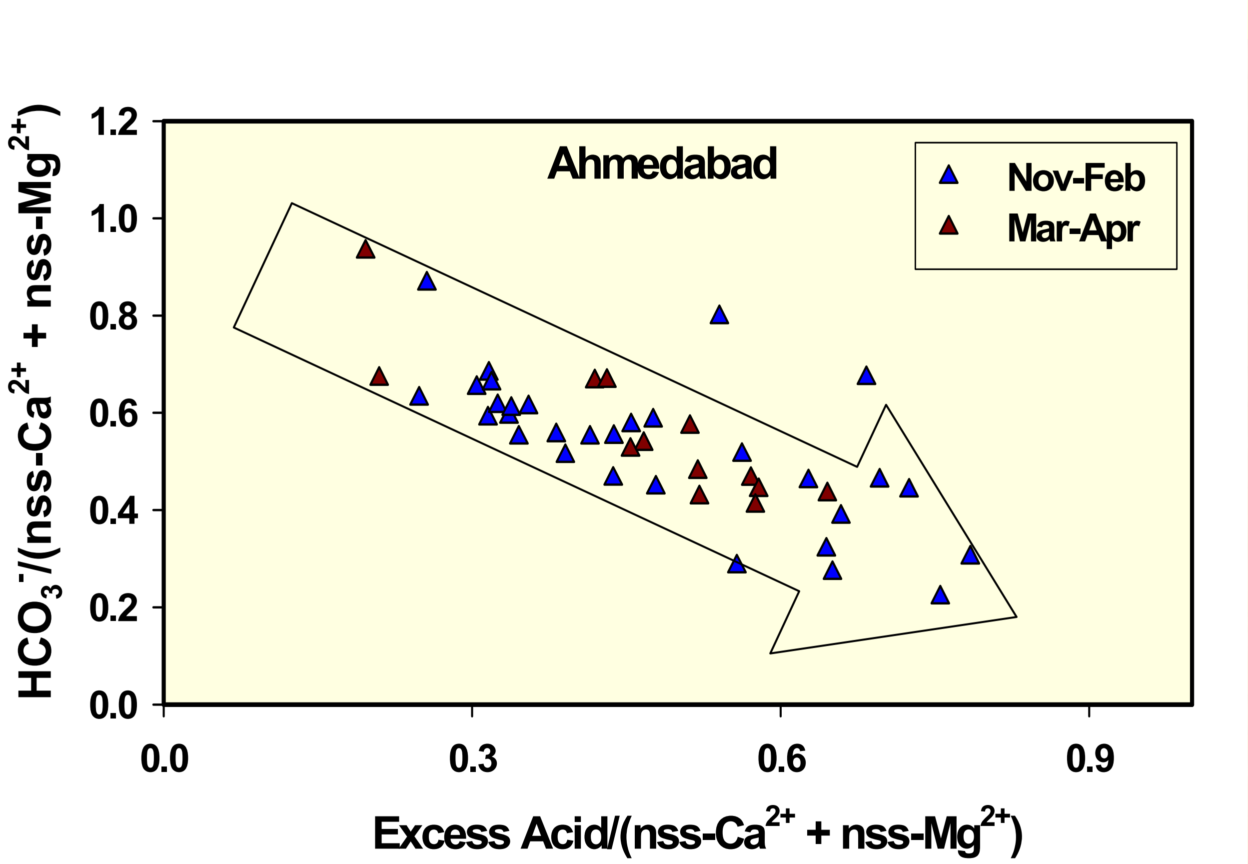


Kumar, AKS, MMS (JESS 2008)



Enhanced solubility of Calcium as dust ($CaCO_3$) undergoes neutralization process with acidic species

Unequivocal evidence: Acid uptake by mineral dust



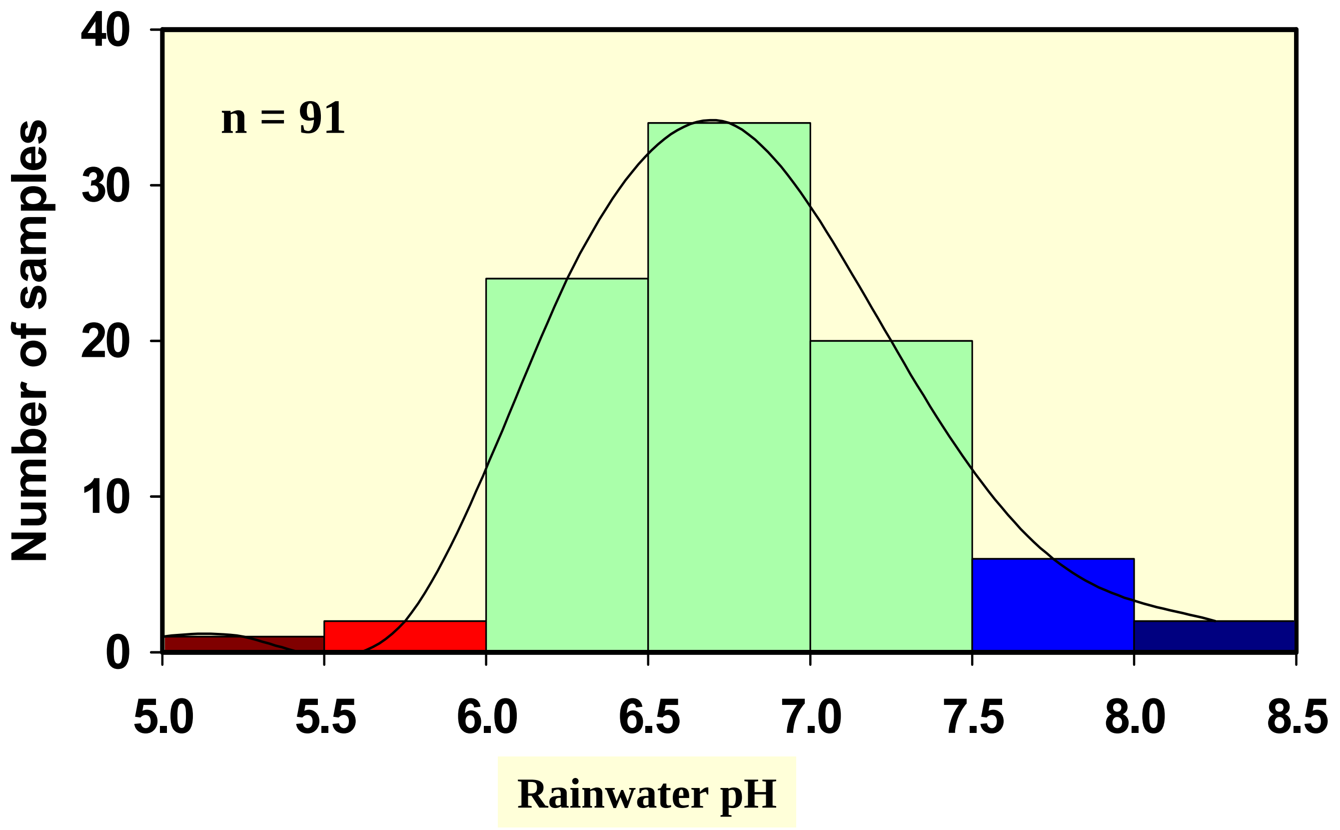
$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$

$CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + CO_2 + H_2O$

(neutralization reactions)

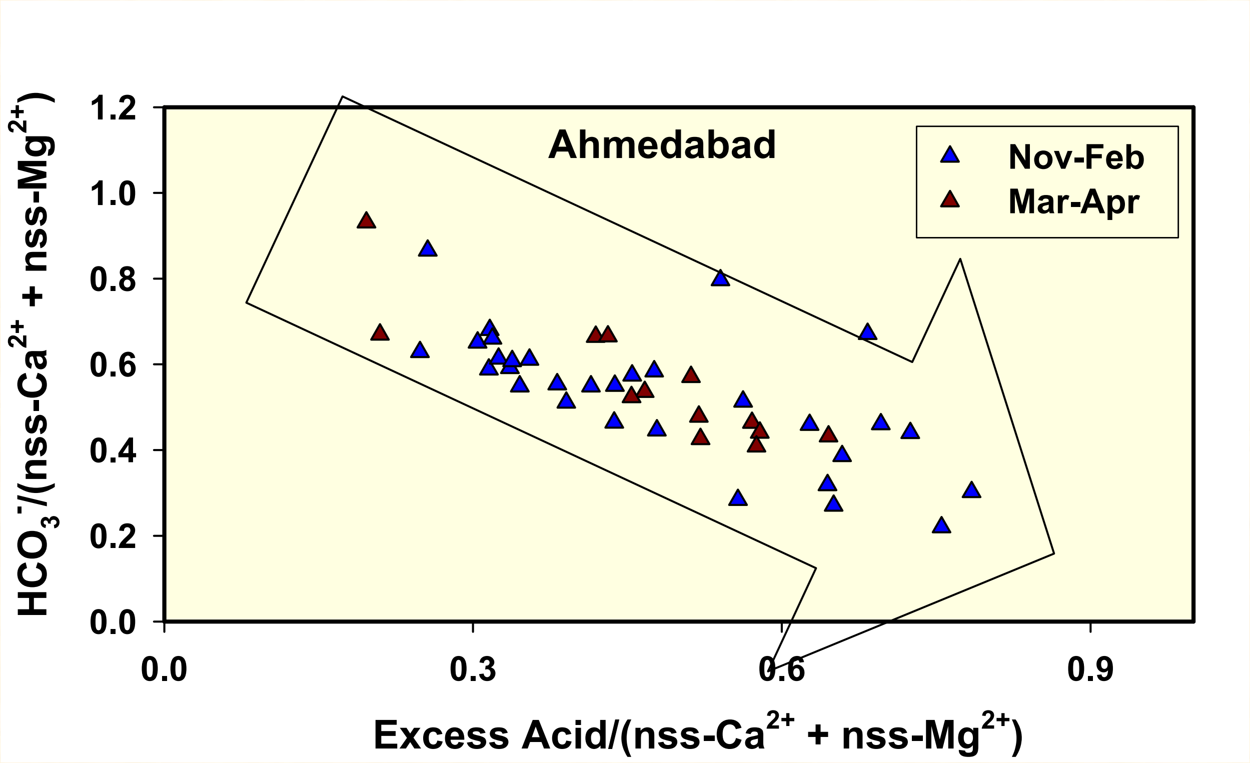
Atmos. Environ, 2005a

Rainwater



Avg. pH = 6.7 ± 0.5 indicating "Alkaline" nature of rainwater

Atmos. Environ, 2005b



IMPLICATIONS:

Change in size distribution of SO_4^{2-} and NO_3^- aerosols from fine to coarse mode

Decrease in Cloud Condensation Nuclei

Present-day models need to account for such chemical reactions to infer climate cooling due to Sulphate aerosols

Atmos. Environ, 2005a

Chloride depletion in MBL

Complete degassing of HCl from NaCl

(Deliquescent sea-salt aerosols)

- ❖ **97--100% RH, buffered pH ~8**

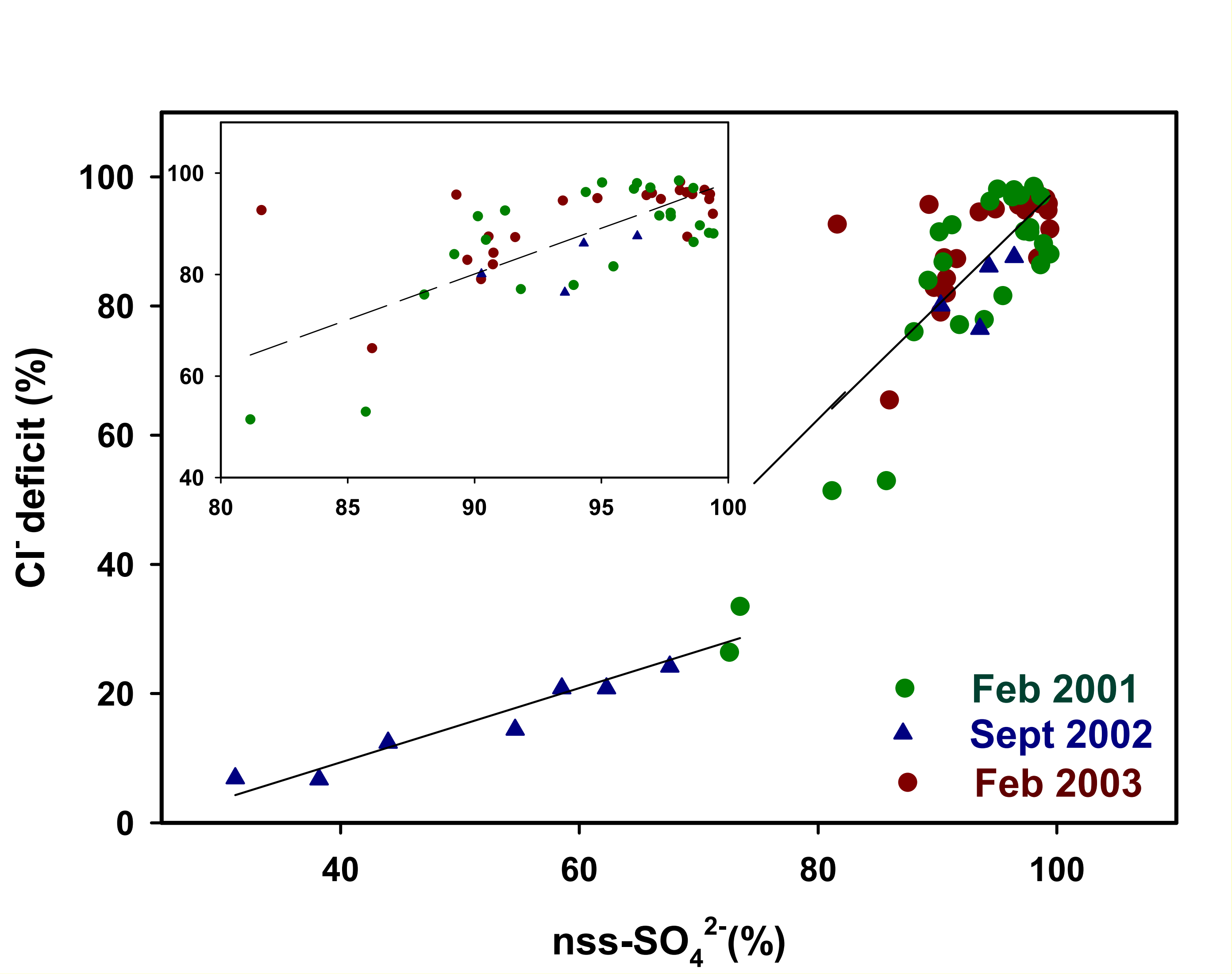
----------------oxi.------------------

nss-SO_4^{2-} → SO_2 (S +4) ⟶ SO_4^{2-} (S +6)

- ❖ $2NaCl + H_2SO_4 \longrightarrow 2HCl\uparrow + Na_2SO_4$
- ❖ $NaCl + HNO_3 \longrightarrow HCl\uparrow + NaNO_3$

- ➢ **Consequence of decreasing aerosol pH as droplets evaporate**
- ➢ **HCl(aq.) reaches saturation**
- ➢ **HCl (g) Aqueous phase ⟶ gas phase**

SO_4^{2-} -rich aerosols: Implications to Cl^- loss



Implications :

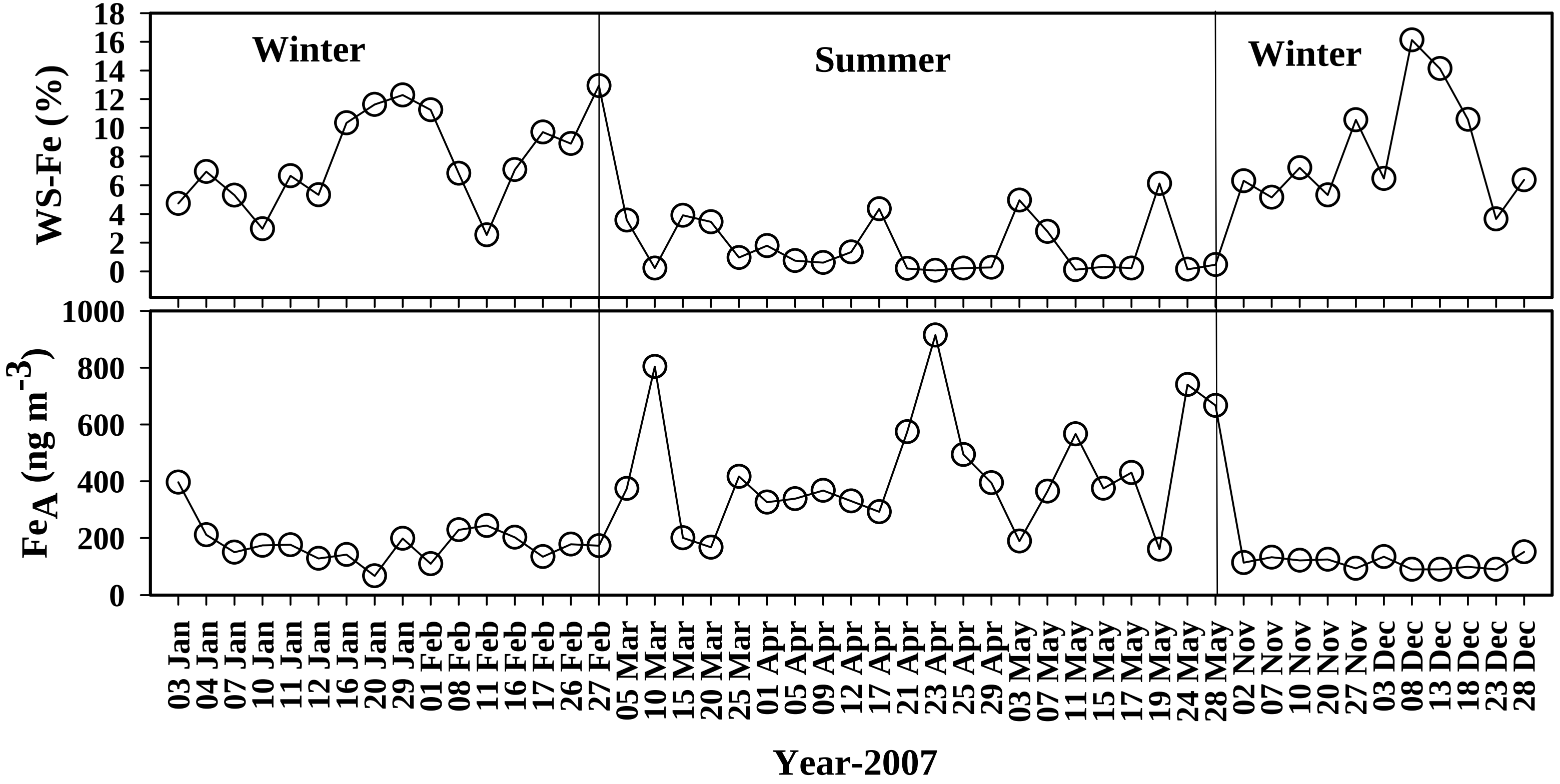
- (SO_2) SO_4^{2-} —*Sea-salt*→ **limit CCN**
- **Enhanced anthropogenic** (SO_2) SO_4^{2-} —*Sink*→ **Not adequate**

Increase Ozone loss :

1. $O_3 + S_{iv}\,(SO_2) \xrightarrow{\text{oxi.}} SO_4^{2-} + O_2$ **[major O_3 sink]**
   (at pH : ~6-8 , Rate constant 4 x 10^{11})

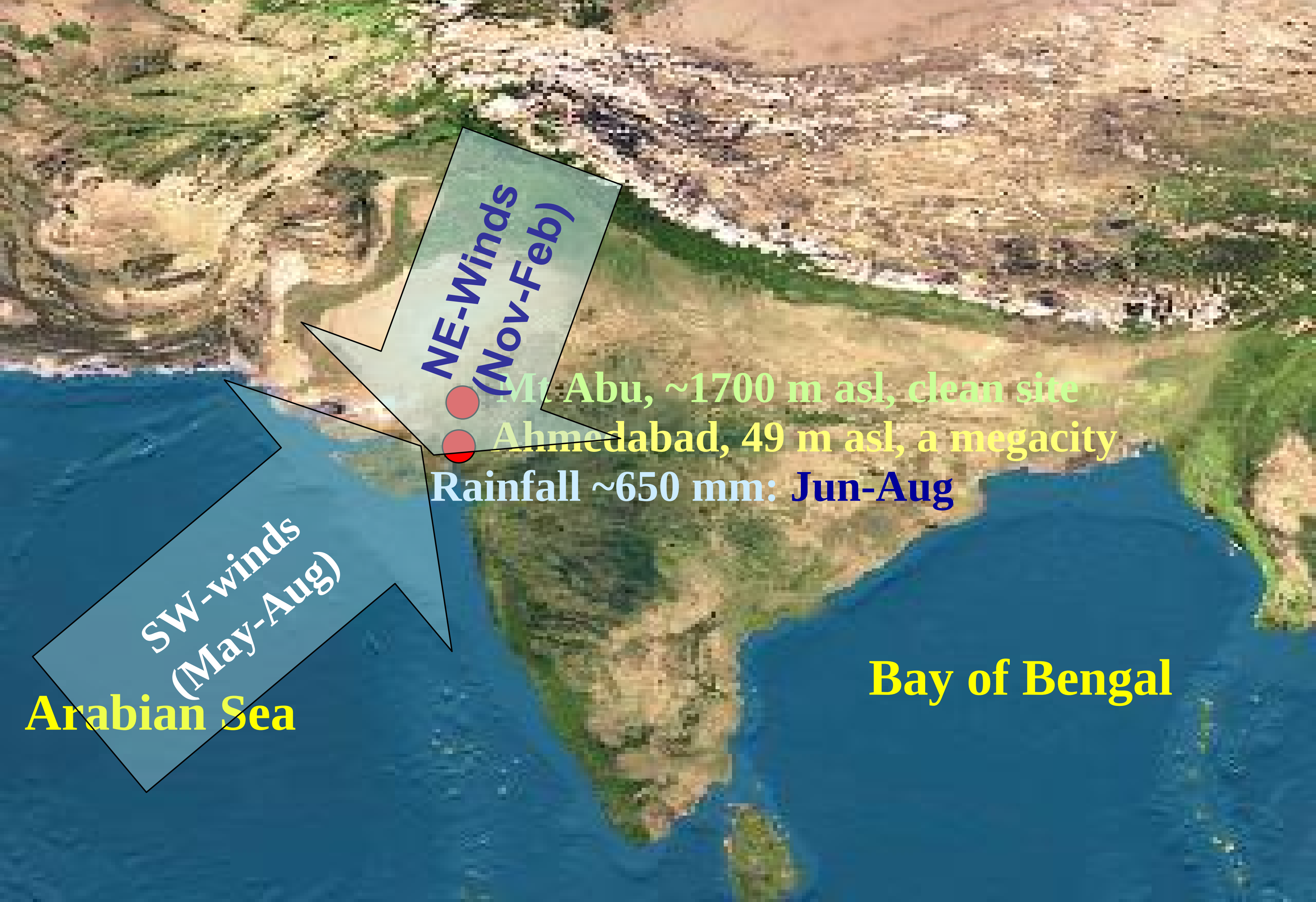
2. $O_3 + Cl^- \xrightarrow{\text{oxi.}} ClO^- + O_2$ **[slow rate]**
   (Unaccounted O_3 sink !)
   (Cl^- ↑ **HCl degassing from sea-salt**)

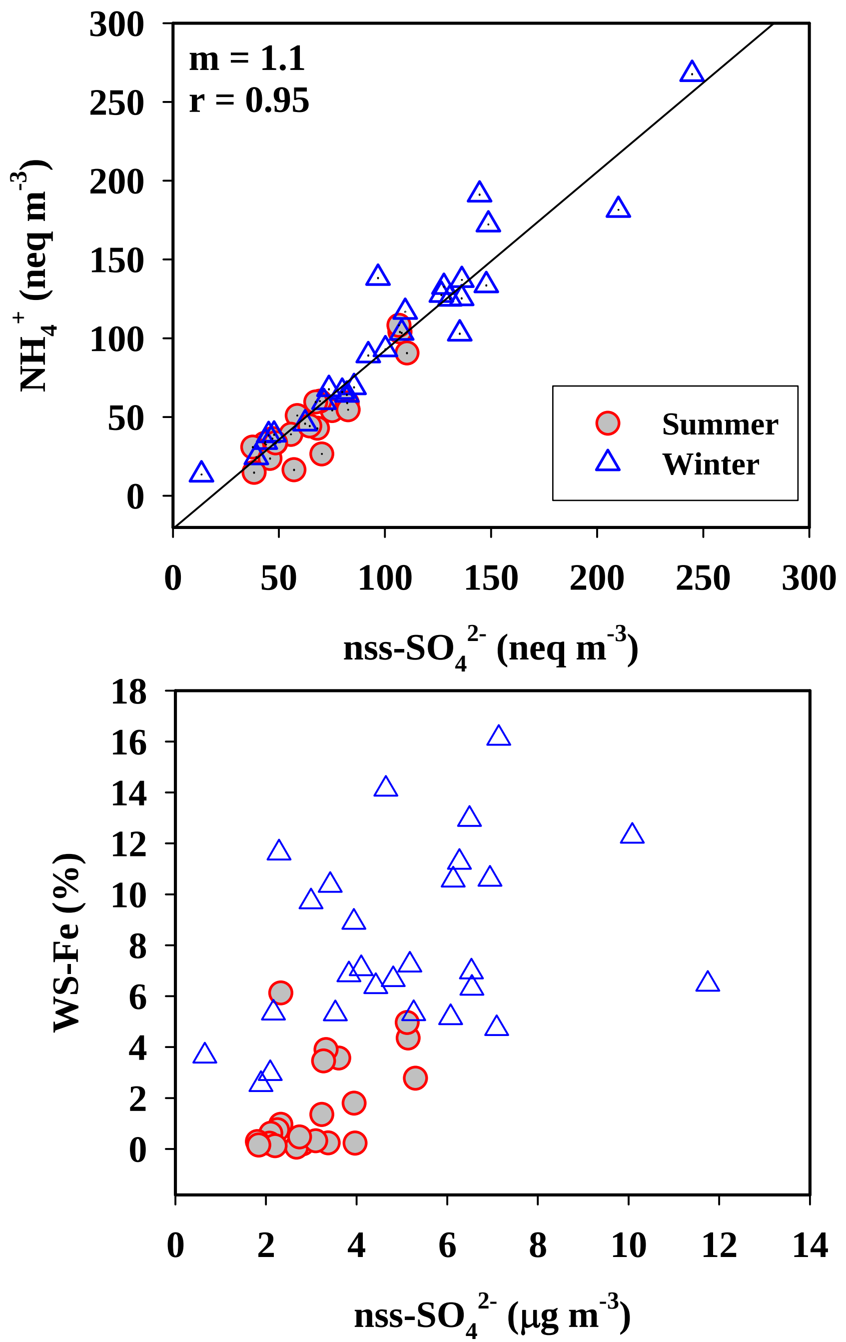
High-altitude Stn: Temporal variability of aerosol iron (Fe_A) and water-soluble iron (WS-Fe)



Bio-available Fe & surface ocean bio-geochemistry

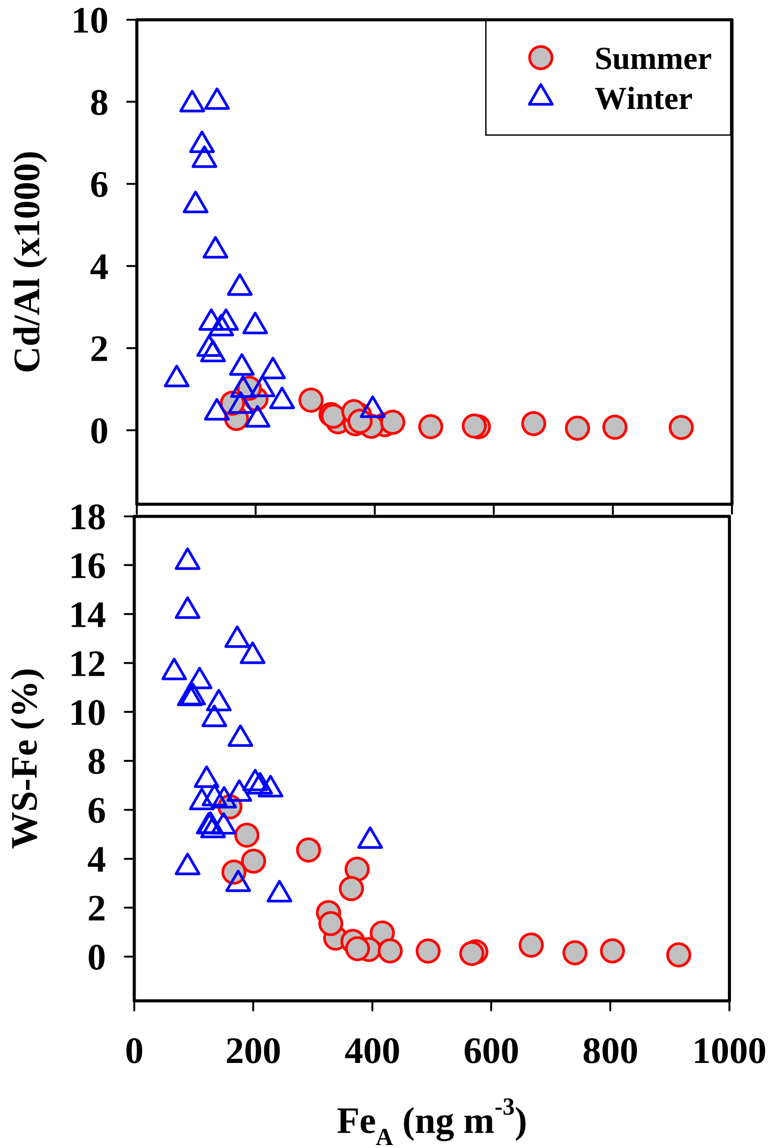
Study sites

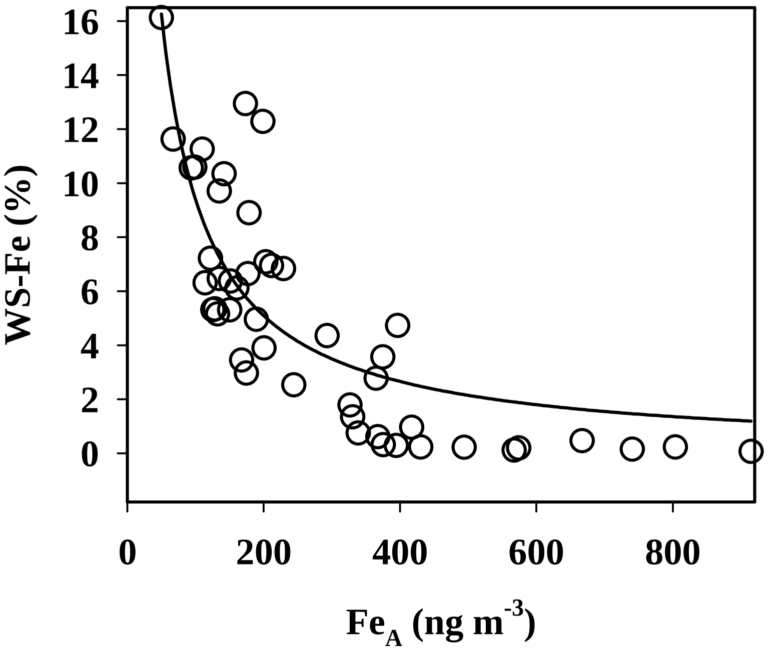

NE-Winds
(Nov-Feb)
Mt Abu, ~1700 m asl, clean site
Ahmedabad, 49 m asl, a megacity
Rainfall ~650 mm: Jun-Aug
SW-winds
(May-Aug)
Arabian Sea
Bay of Bengal



m = 1.1
r = 0.95
Summer
Winter
NH_4^+ (neq m^{-3})
nss-SO_4^{2-} (neq m^{-3})
0
50
100
150
200
250
300
WS-Fe (%)
nss-SO_4^{2-} (µg m^{-3})
0
2
4
6
8
10
12
14
16
18

Solubility of aerosol iron and Direct emission (fossil fuel combustion)





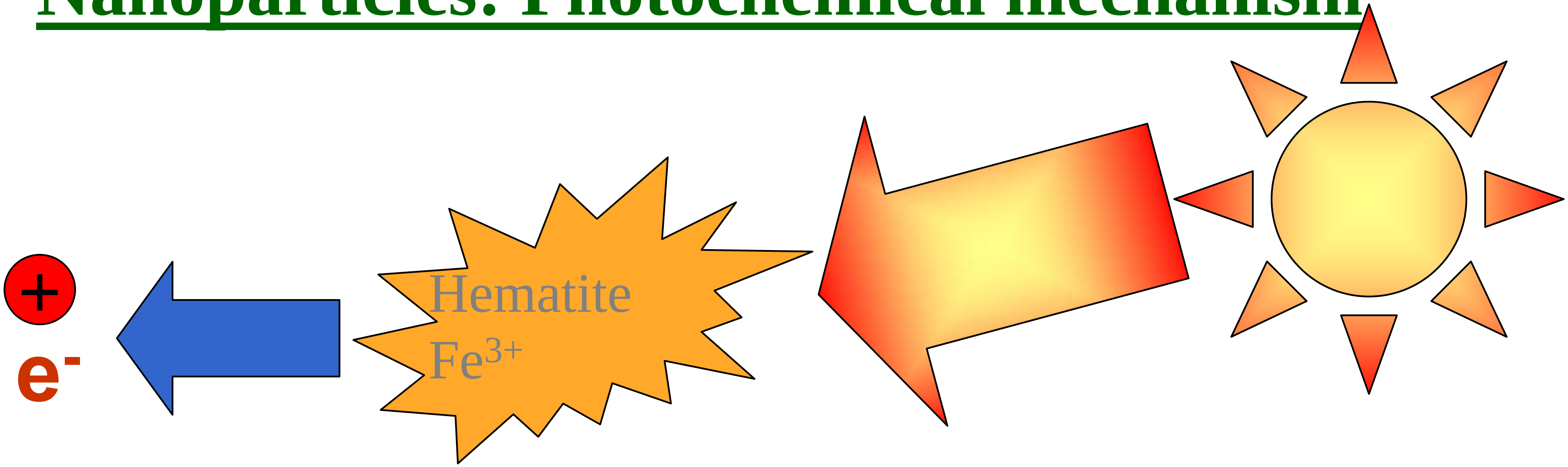
WS-Fe = 0.06 % and Fe_A = 915 ng m^{-3} during summer season (as end member);

WS-Fe of 16.1 % and Fe_A = 50 ng m^{-3} (2nd end member) during winter season.

Kumar and Sarin
***Tellus 'B'*, 2009**
(Under Review)

Fe solubility in semi-arid western India is controlled by composition and chemical nature of aerosols rather than chemical processing during long-range transport.

Nanoparticles: Photochemical mechanism



Generate electron-hole pairs

Mineral Aerosols

$C_2O_4^{2-} \rightarrow CO_2$

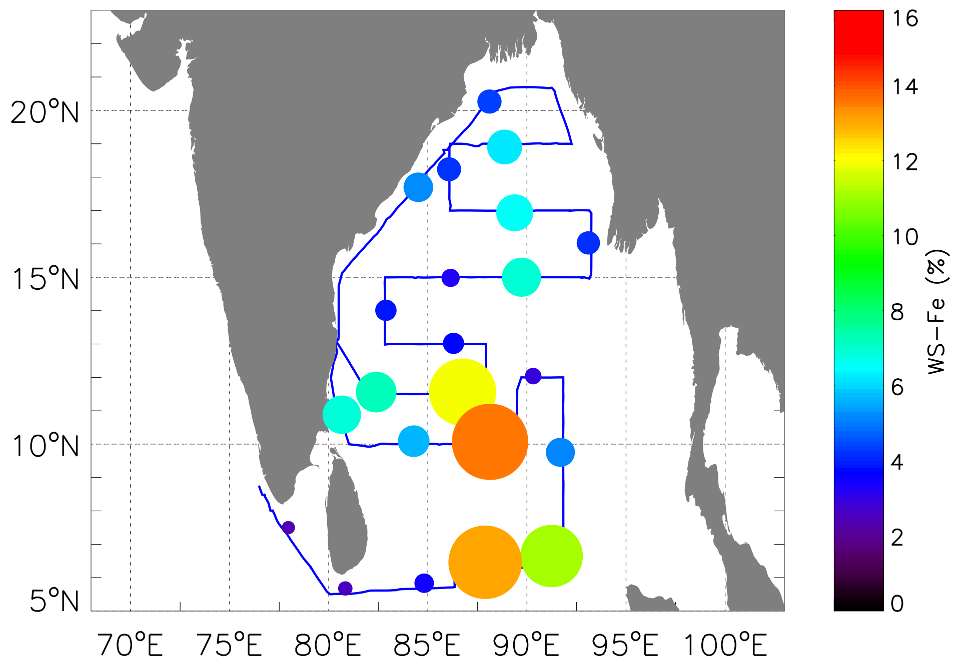
$HSO_3^- \rightarrow SO_4^{2-}$

Oxidation

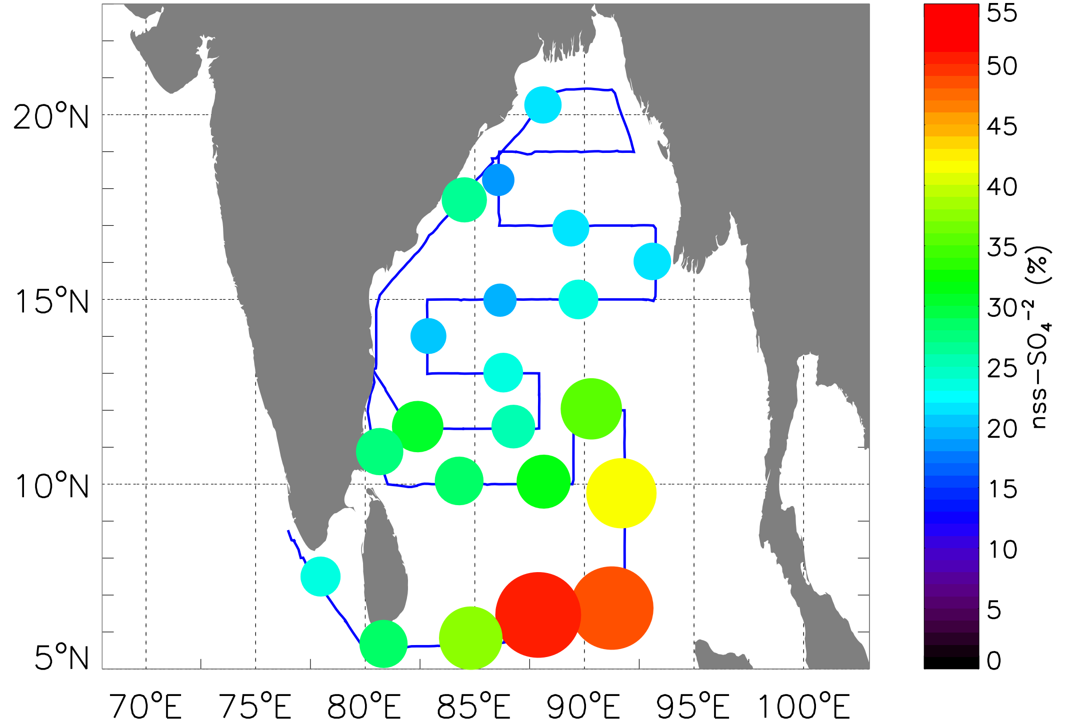
By product: $Fe^{3+} \rightarrow Fe^{2+}$

Reduction

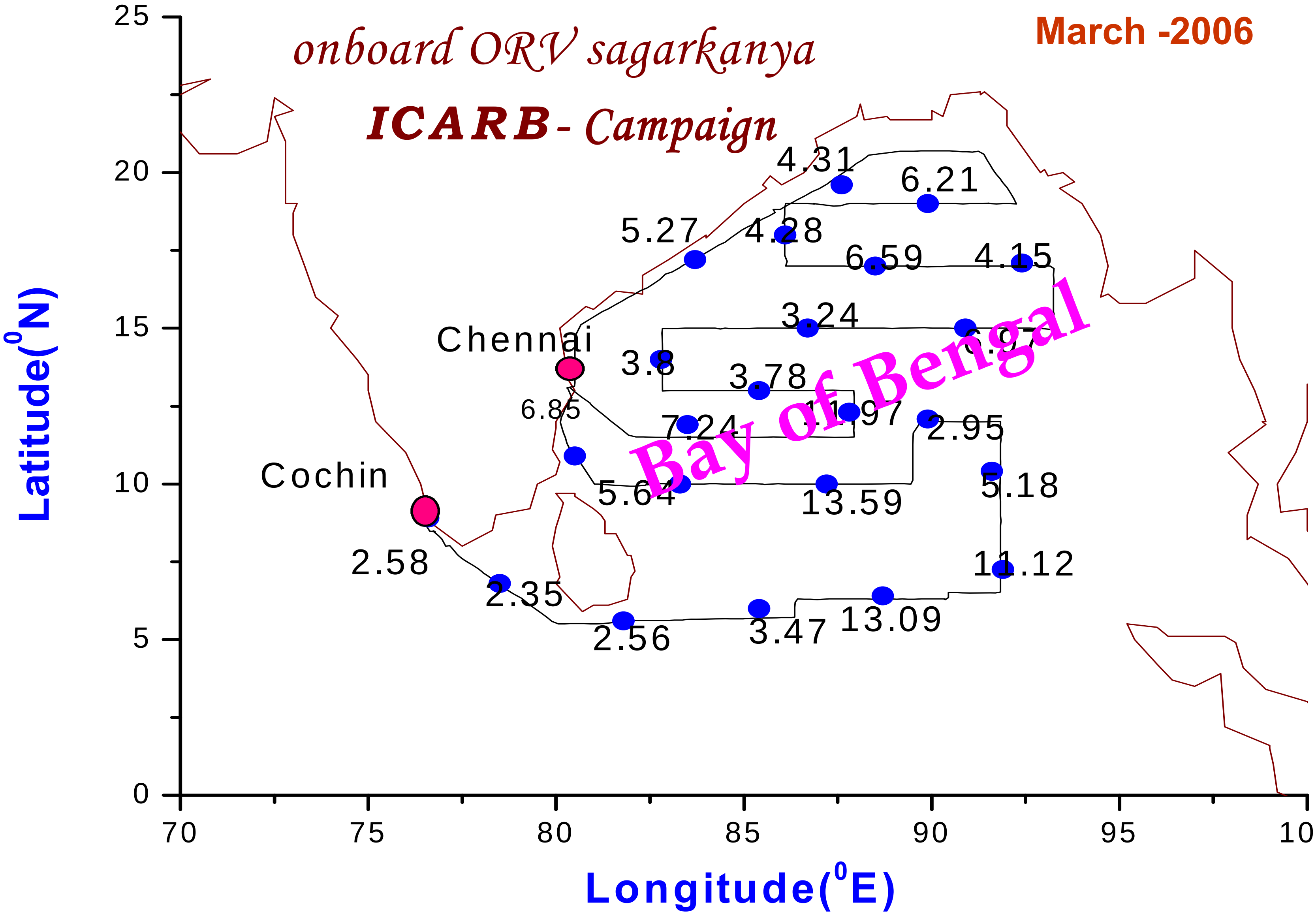
Dissolution (cloud droplet)

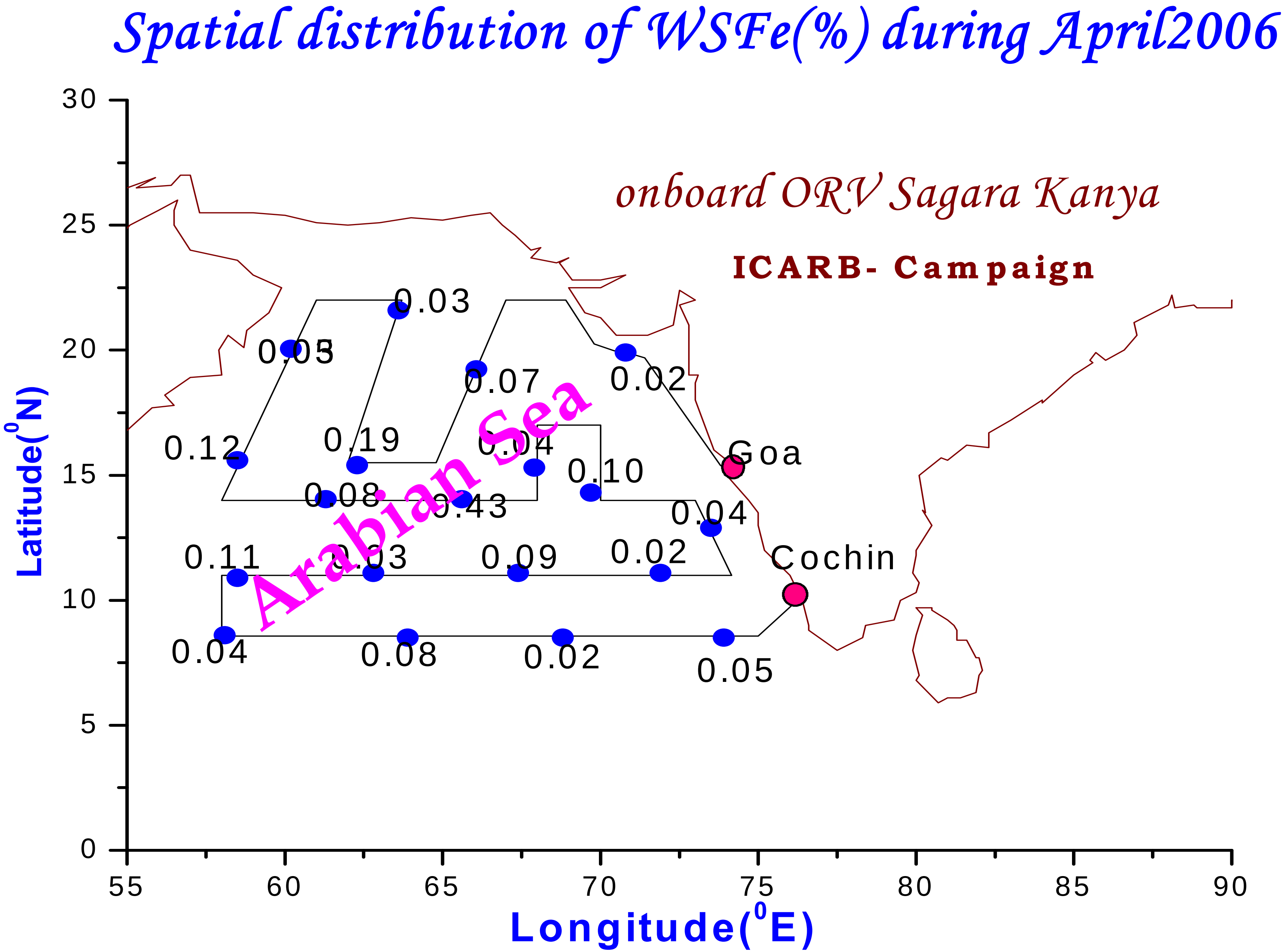


Bay of Bengal (March-April' 06)

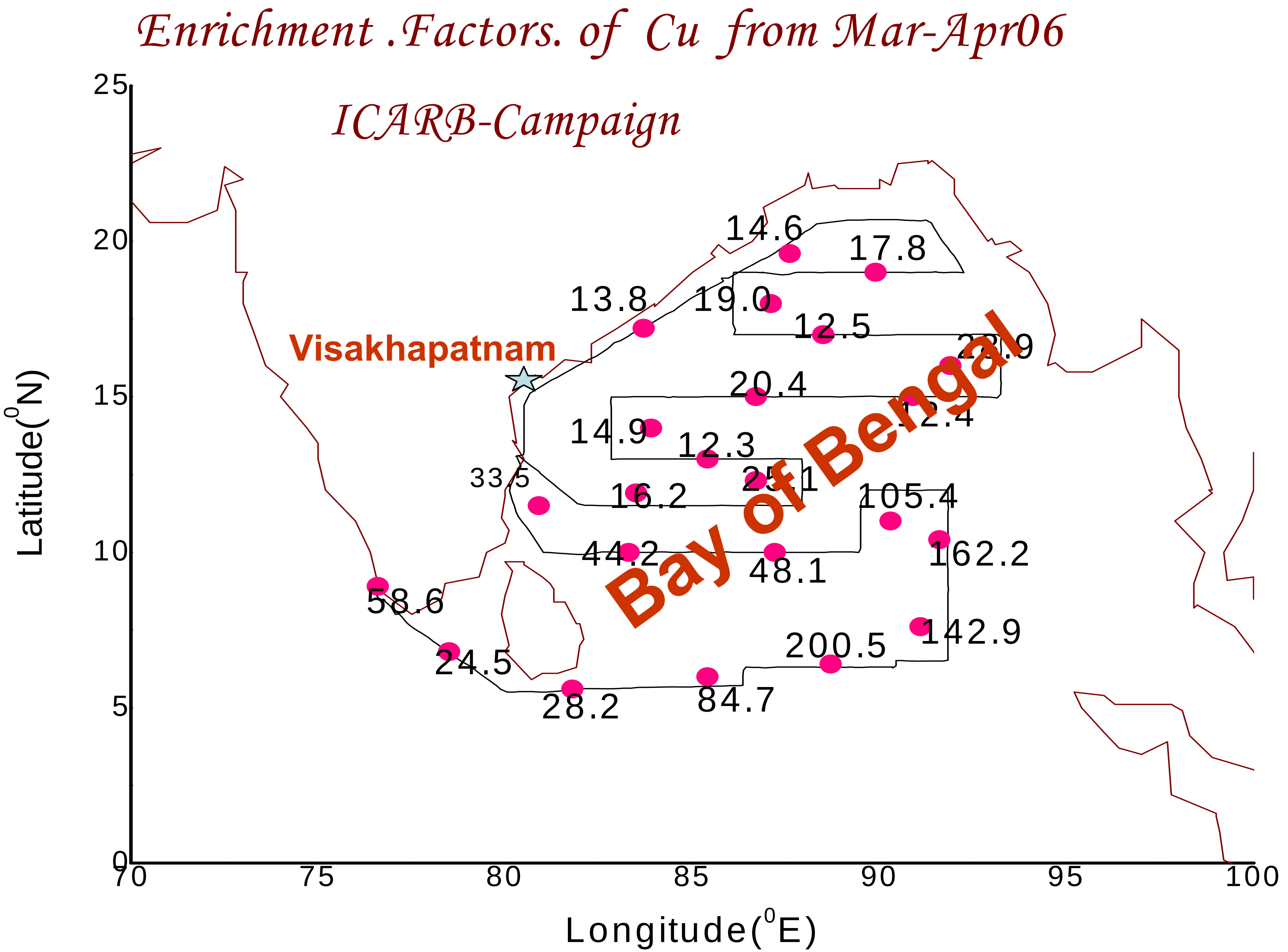


Spatial distributions of Water SolubleFe(%)

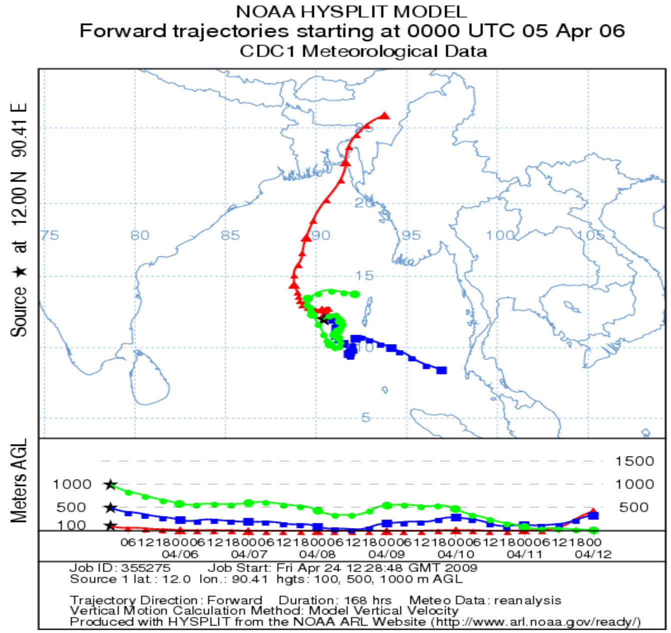


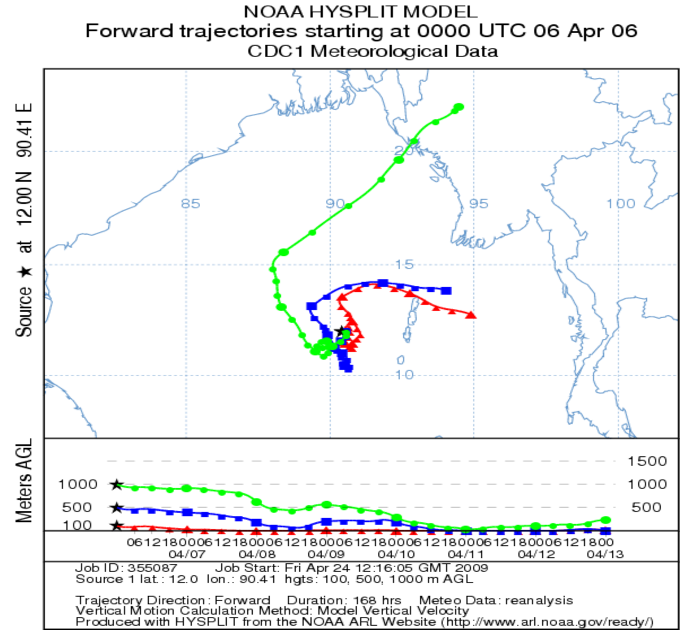


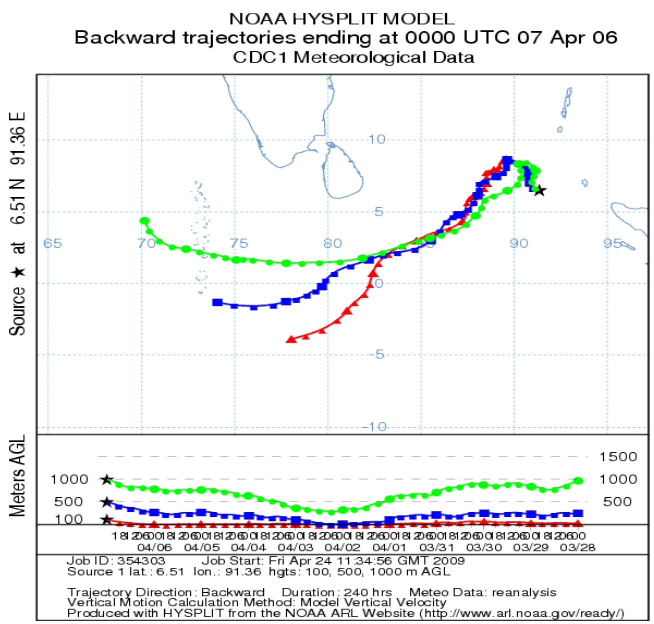
Spatial distribution of WSFe(%) during April2006
onboard ORV Sagara Kanya
ICARB- Campaign
Arabian Sea
Goa
Cochin
0.03
0.05
0.07
0.02
0.12
0.19
0.04
0.10
0.08
0.43
0.04
0.11
0.03
0.09
0.02
0.04
0.08
0.02
0.05
Latitude(0N)
Longitude(0E)

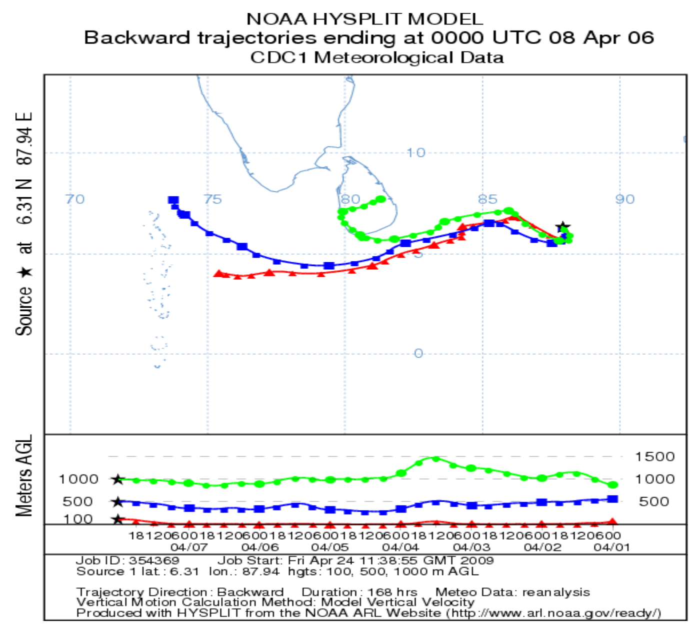


Enrichment .Factors. of Cu from Mar-Apr06
ICARB-Campaign
Visakhapatnam
Bay of Bengal
14.6
17.8
13.8
19.0
12.5
20.4
14.9
12.3
33.5
16.2
105.4
44.2
48.1
162.2
58.6
24.5
28.2
84.7
200.5
142.9
Latitude(⁰N)
Longitude(⁰E)
0
5
10
15
20
25
70
75
80
85
90
95
100


NOAA HYSPLIT MODEL
Forward trajectories starting at 0000 UTC 05 Apr 06
CDC1 Meteorological Data
Source ★ at 12.00 N 90.41 E
Meters AGL
Job ID: 355275 Job Start: Fri Apr 24 12:28:48 GMT 2009
Source 1 lat.: 12.0 lon.: 90.41 hgts: 100, 500, 1000 m AGL
Trajectory Direction: Forward Duration: 168 hrs Meteo Data: reanalysis
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)


NOAA HYSPLIT MODEL
Forward trajectories starting at 0000 UTC 06 Apr 06
CDC1 Meteorological Data
Source ★ at 12.00 N 90.41 E
Meters AGL
Job ID: 355087 Job Start: Fri Apr 24 12:16:05 GMT 2009
Source 1 lat.: 12.0 lon.: 90.41 hgts: 100, 500, 1000 m AGL
Trajectory Direction: Forward Duration: 168 hrs Meteo Data: reanalysis
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)


NOAA HYSPLIT MODEL
Backward trajectories ending at 0000 UTC 07 Apr 06
CDC1 Meteorological Data
Source ★ at 6.51 N 91.36 E
Meters AGL
Job ID: 354303 Job Start: Fri Apr 24 11:34:56 GMT 2009
Source 1 lat.: 6.51 lon.: 91.36 hgts: 100, 500, 1000 m AGL
Trajectory Direction: Backward Duration: 240 hrs Meteo Data: reanalysis
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)


NOAA HYSPLIT MODEL
Backward trajectories ending at 0000 UTC 08 Apr 06
CDC1 Meteorological Data
Source ★ at 6.31 N 87.94 E
Meters AGL
Job ID: 354369 Job Start: Fri Apr 24 11:38:55 GMT 2009
Source 1 lat.: 6.31 lon.: 87.94 hgts: 100, 500, 1000 m AGL
Trajectory Direction: Backward Duration: 168 hrs Meteo Data: reanalysis
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)

Conclusions :

1. **Long-range transport of dust, biogenic and pollution-derived components dominate the aerosol composition in the MABL of Bay of Bengal & Arabian Sea.**

2. **On average, non-sea-salt-SO_4^{2-} accounts for nearly 60% of the water soluble components indicating highly acidic environment (MABL of BOB).**

3. **Enhanced Fe deposition fluxes over Bay of Bengal and Arabian Sea could serve as dominant source for surface waters.**