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Field Monitoring of the Performance of PRB at Vapokon Site in Denmark

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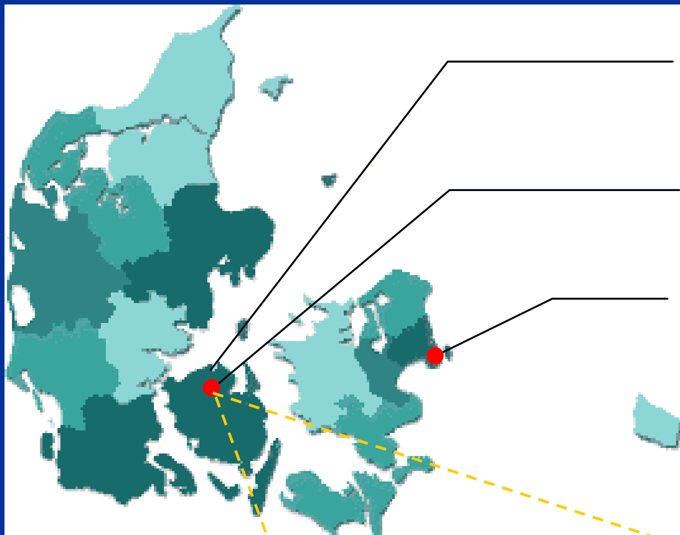
Objectives

- Study the performance of Fe^0 PRB on the removal of chlorinated organics.
- Study the changes in geochemistry of groundwater and identify the possible precipitates.
- Investigate if there are any contributions from microbial degradation and Fe^0 adsorption in PRB.
- Investigate the variations of porosity, hydraulic gradient and water table distribution across the PRB.

Vapokon Site



Fuen Island

Søndersø

Copenhagen

Geology

- Unconfined aquifer
- An unsaturated layer of loam of 1.5 m
- A sandy aquifer of ~10 m
- An impermeable clay layer of >15 m

Groundwater

- 400 to 500 m/yr
- Southeast direction towards a nearby rain water pond & creek

Vapokon Site

Rain Water Pond

Characteristics	mg/L	Characteristics	mg/L
Ca^{2+}	**178**	Cl^-	47.3
Mg^{2+}	14.1	**SO_4^{2-}**	**121**
NH_3-N & NH_4^+-N	0.28	NO_3^-	0.065
Na^+	31.3	NO_2^-	0.022
K^+	3.16	H_2S	0.109
Fe_T	6.65	Conductivity (µS/cm)	*823*
TAL (as $CaCO_3$)	**317**	**pH**	*7.55*

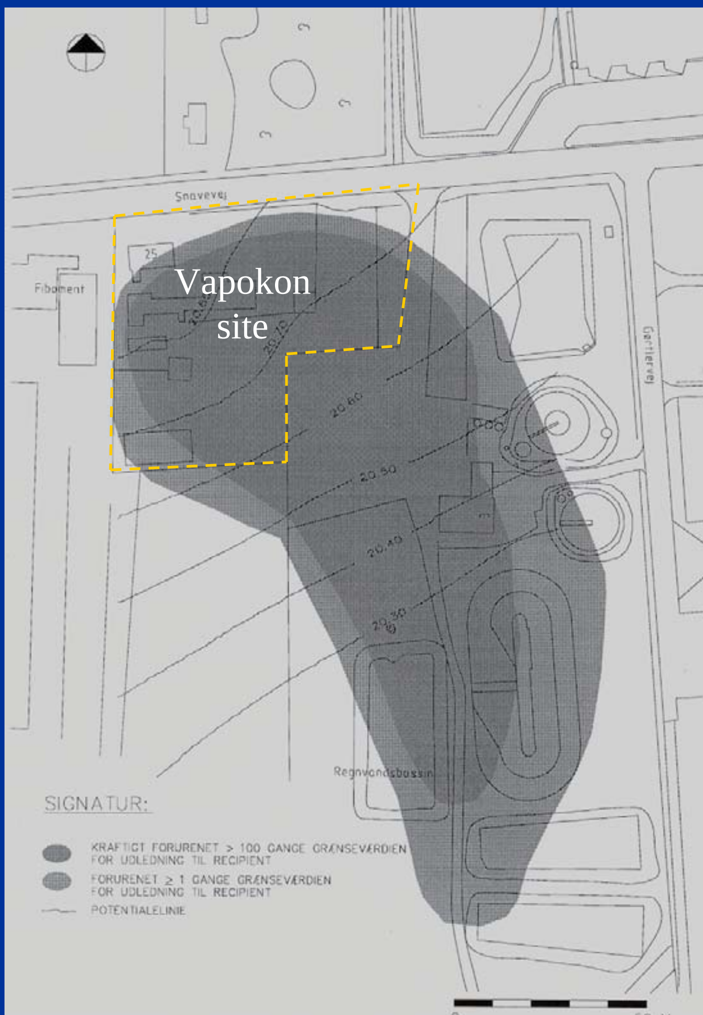
Historical Background

From 1976 to 1997, the site was operated by Vapokon Petrochemical Works to treat and recycle the used solvents and paints.

Spills from the stored drums

Groundwater Contamination

Approximately 200 × 80 m (L ×W) of a contaminated groundwater plume



Contaminants	***Concentration (mg/L)**
[1]Chloroform (TCM)	0.77
[1]Trichloroethane (TCA)	**37**
[1]Tetrachloromethane (TeCM)	0.0011
[1]Trichloroethylene (TCE)	**34**
[1]Perchloroethylene (PCE)	**20**
[2]Vinyl Chloride (VC)	0.71
[2]1,1-Dichloroethylene (11-DCE)	0.32
[2]Trans-1,2-dichloroethylene (t-DCE)	0.10
[2]Cis-1,2-dichloroethylene (c-DCE)	**30**
[2]Dichloromethane (DCM)	**33**
[2]1,2-Dichloroethane (12-DCA)	6.1
[2]1,1-Dichloroethane (11-DCA)	0.77
Benzene	**9.8**
Toluene	**11**
Ethylbenzene	**7.5**
m + p-Xylene	**29**

* Maximum Concentration

Funnel-and-Gate Fe^0 PRB

1) Ramming down of the sheet piling case

3) Construction of a metal frame for filling of the Fe^0

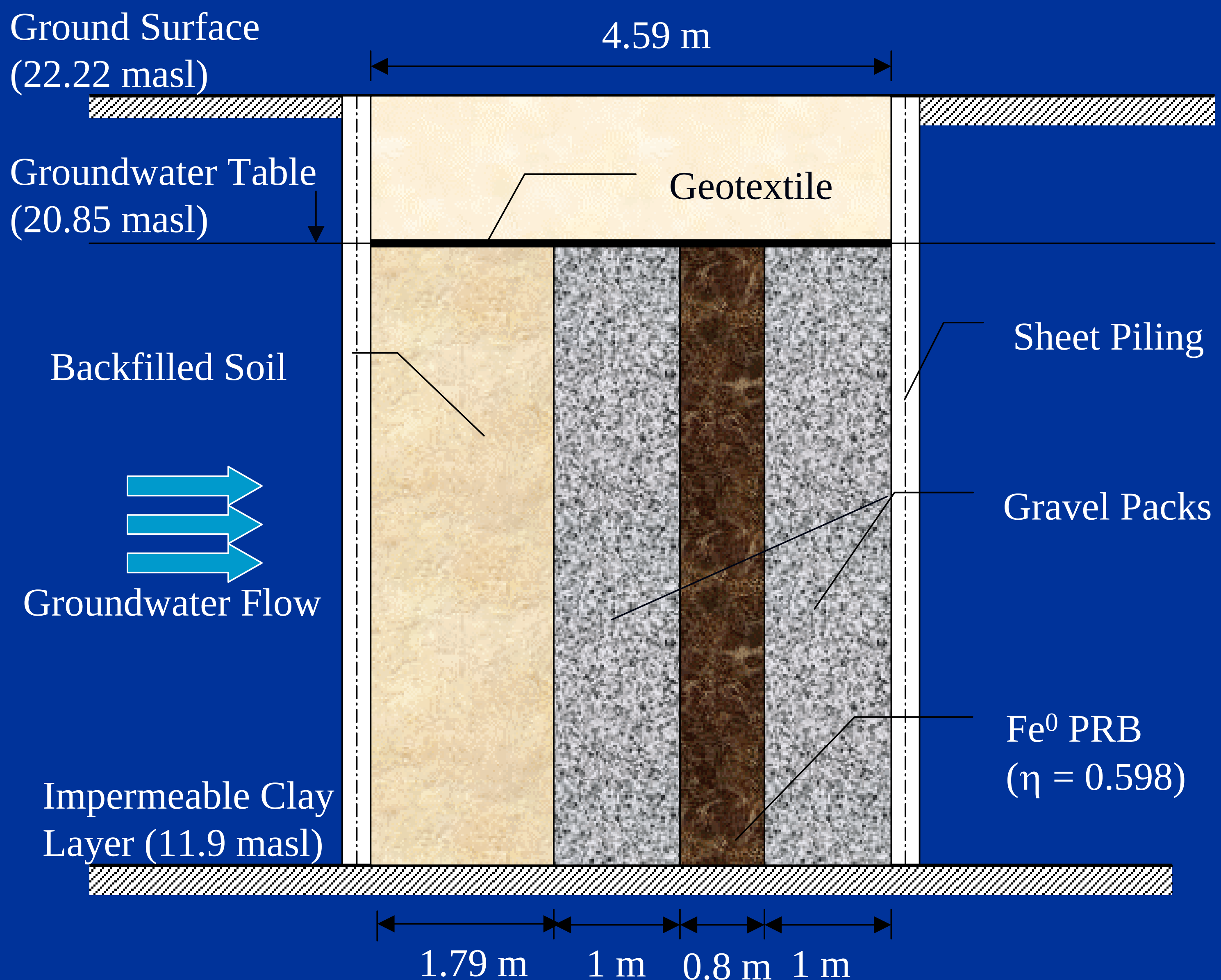
2) Removal of the soil & water from the case

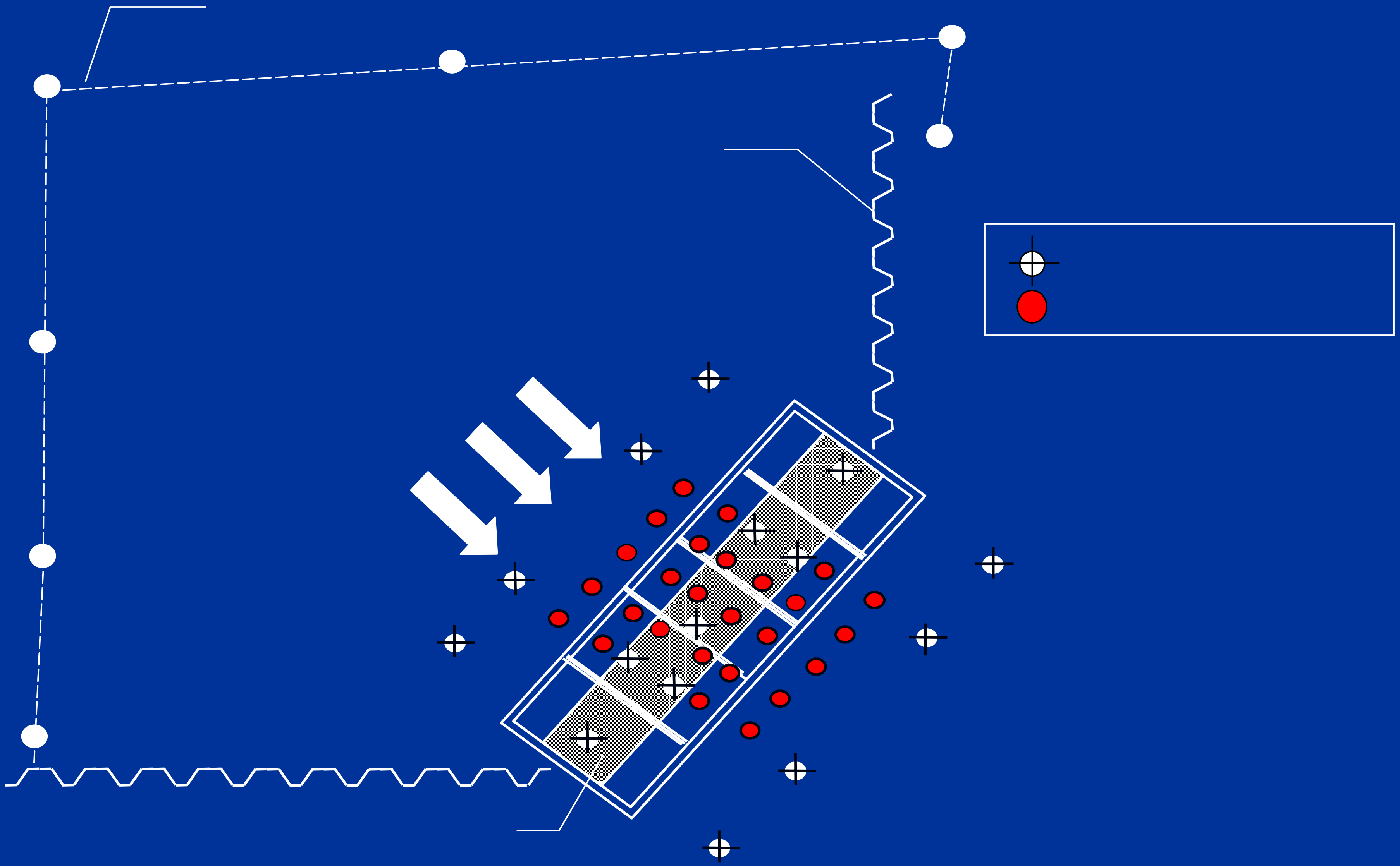
4) Filling of 270 ton of the Fe^0

Fe^0 PRB

14.5 × 9 × 0.8 m (W × D × L)

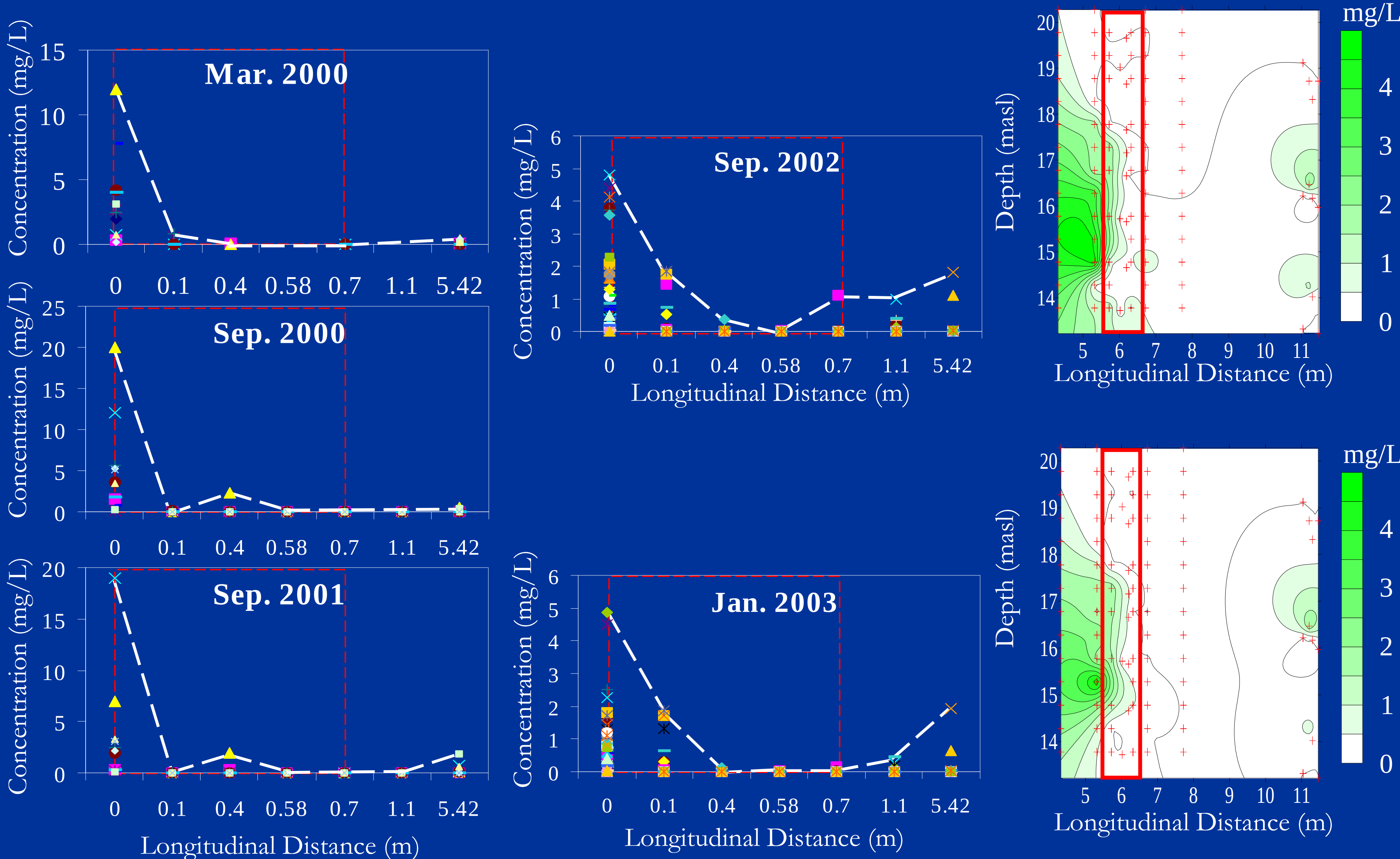
Schematic Diagram of the Fe^0 PRB



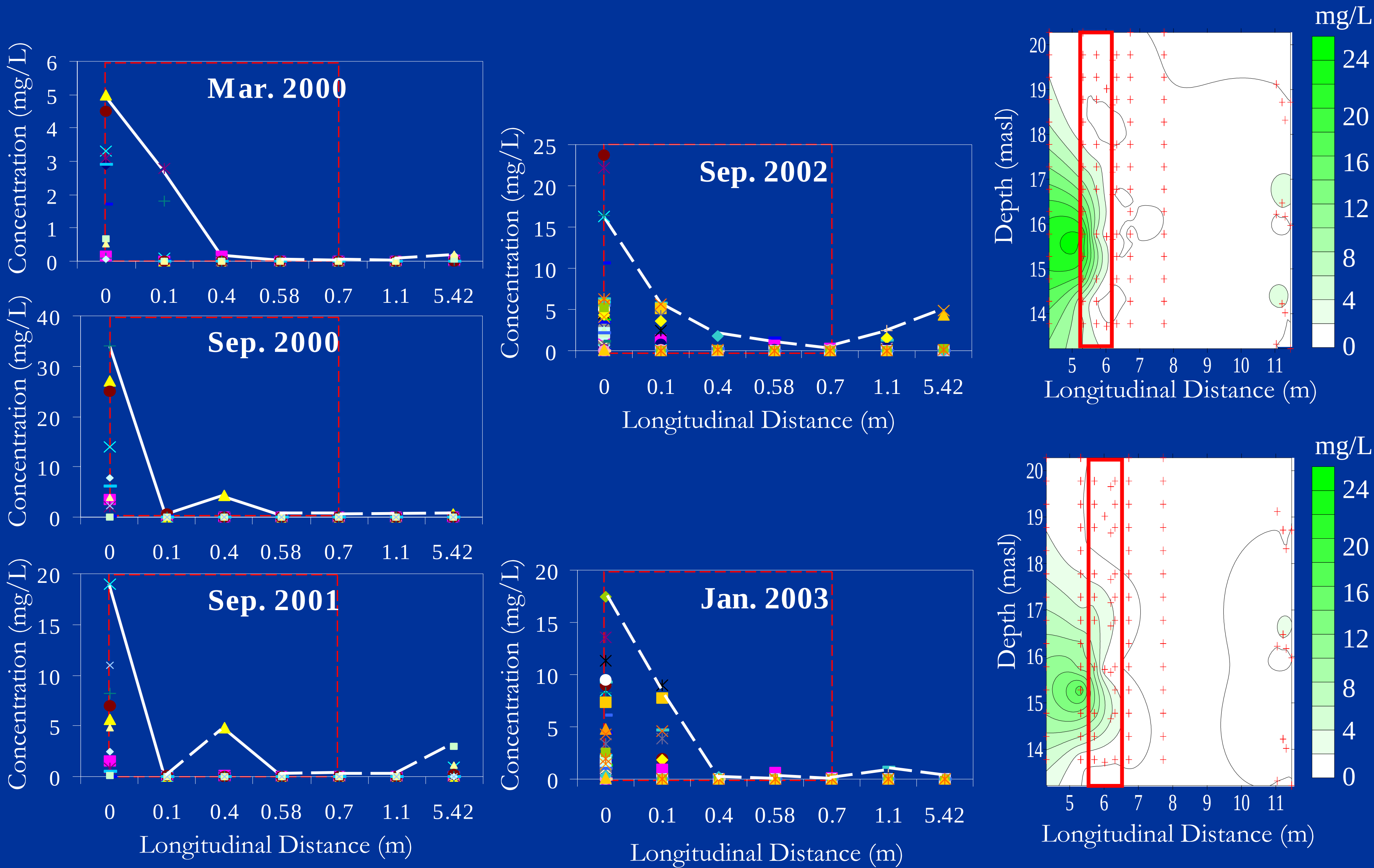


- Mar. 2000, Sep. 2000 & Sep. 2001 ⇒ monitoring wells only
- Sep. 2002 & Jan. 2003 ⇒ monitoring wells and multilevel samplers

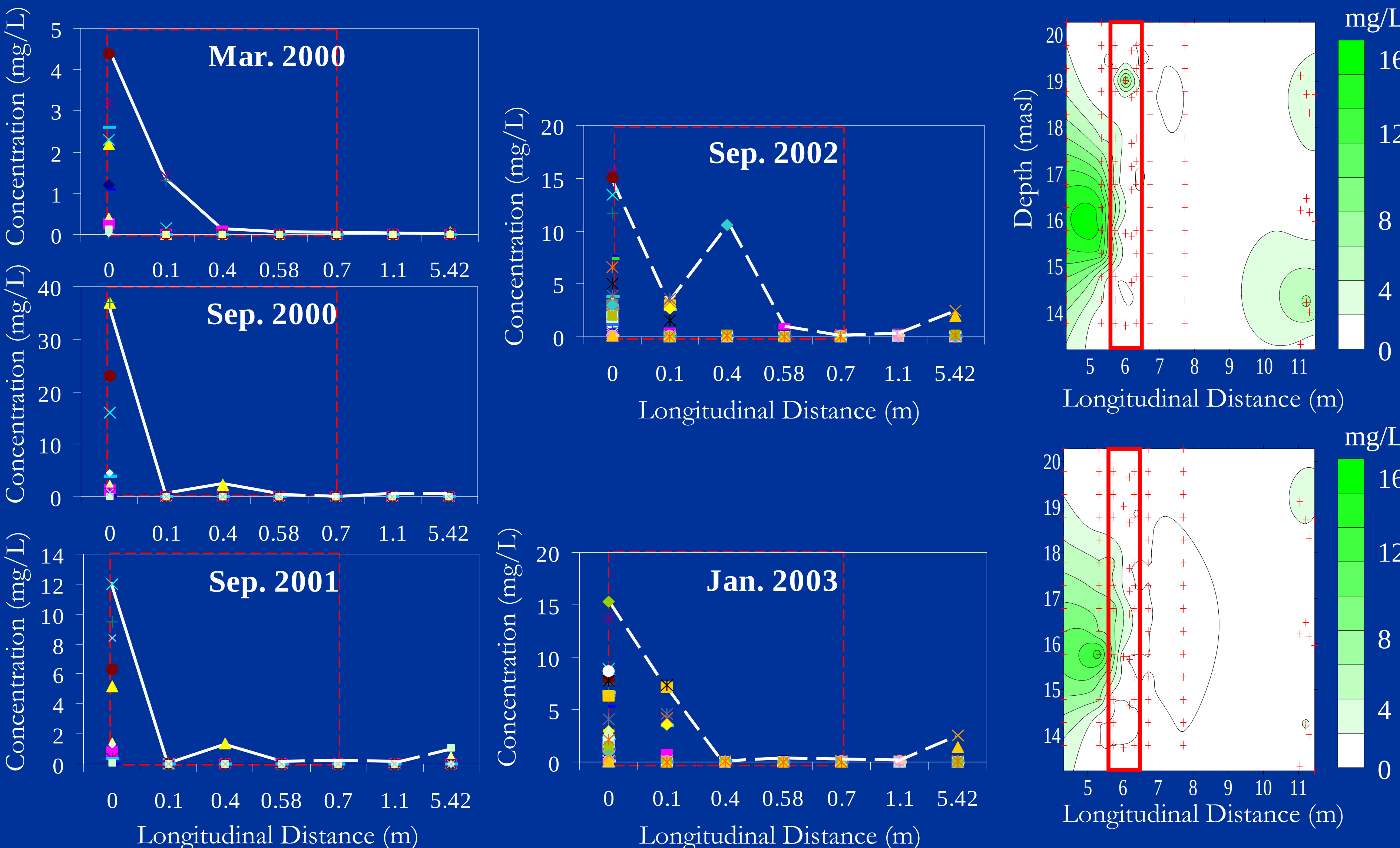
Effectiveness on PCE Dechlorination



Effectiveness on TCE Dechlorination



Effectiveness on 111-TCA Dechlorination

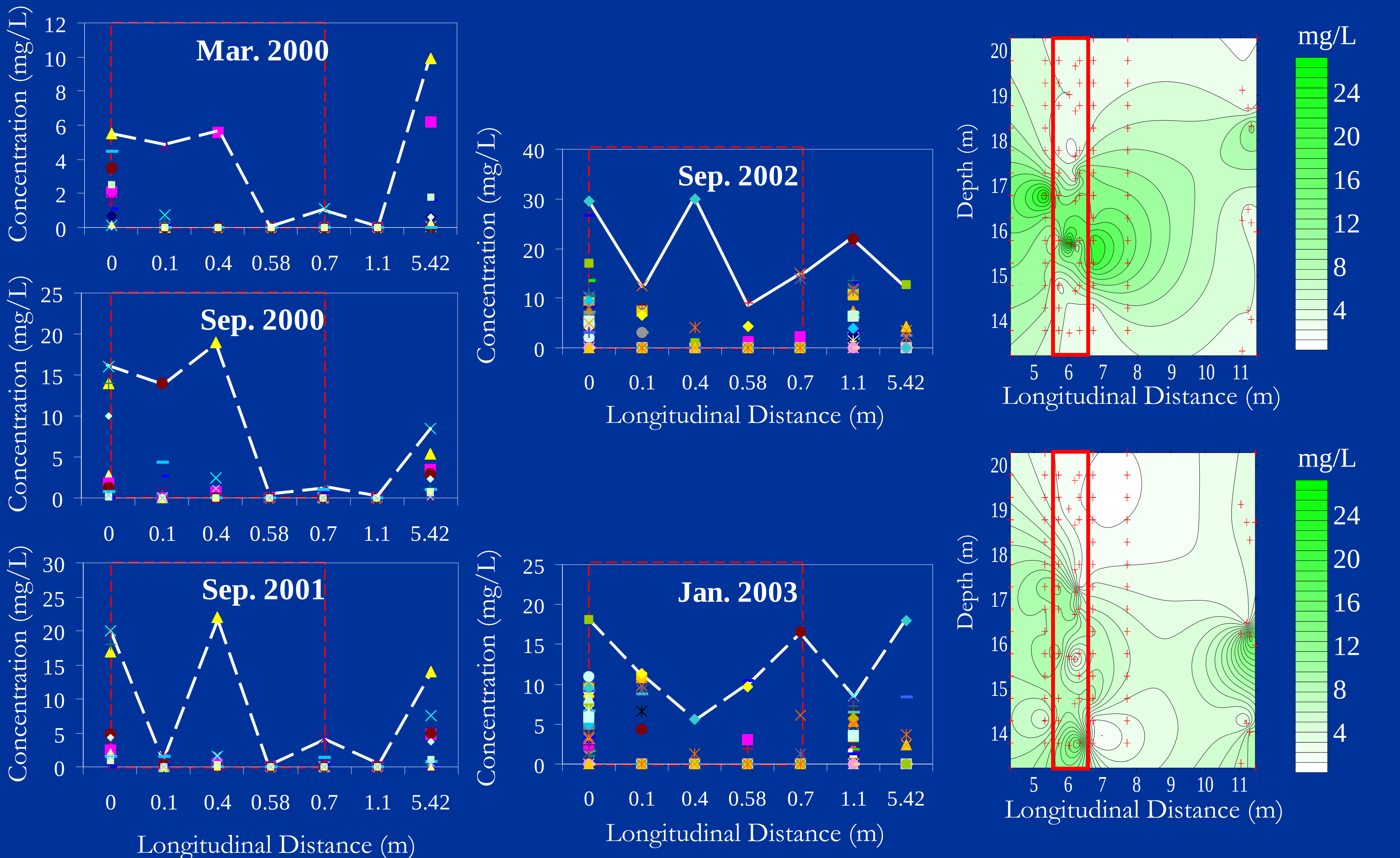


Removal Efficiencies of PCE, TCE & 111-TCA

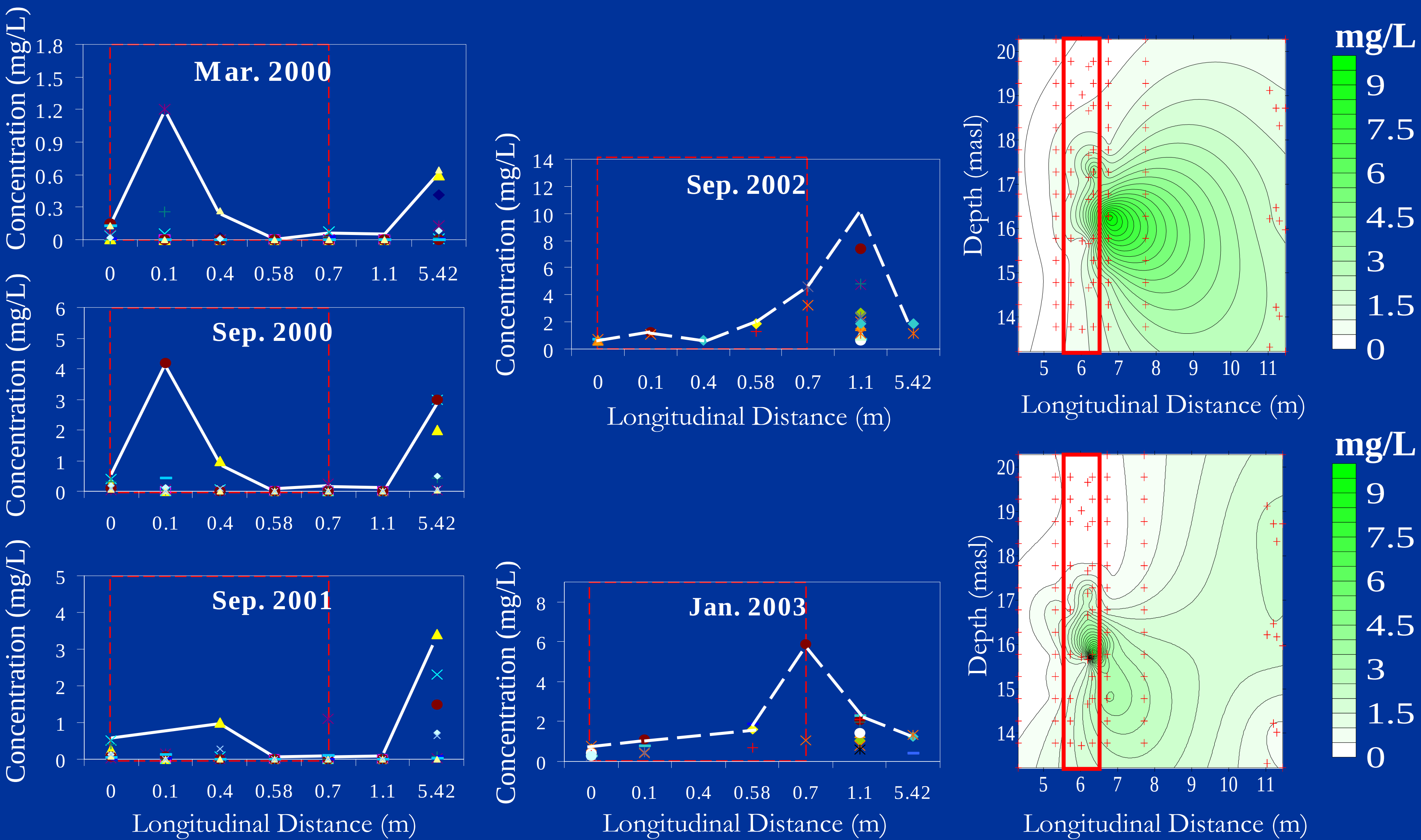
Over the past 3 years,

- 98 % removal of PCE, TCE and 111-TCA
- Over 89 % of removal ⇒ at the first half of the Fe^0 PRB
- No significant deterioration over the past 3 years
- Some PCE, TCE & 111-TCA observed in the downgradient monitoring wells ⇒ probably due to desorption from the downgradient aquifer

Effectiveness on c-DCE Dechlorination



Effectiveness on 11-DCA Dechlorination



Removal Efficiencies of c-DCE & 11-DCA

In the past 3 years,

- Significant **deterioration** in performance

  c-DCE : 80 to 94 % removal → 8.3 to 49 % removal

  11-DCA: 53 to 59 % removal → 6 to 7-fold increase

- Reason: Passivation by **mineral precipitates** e.g. calcite ($CaCO_3$) and pyrite (FeS)

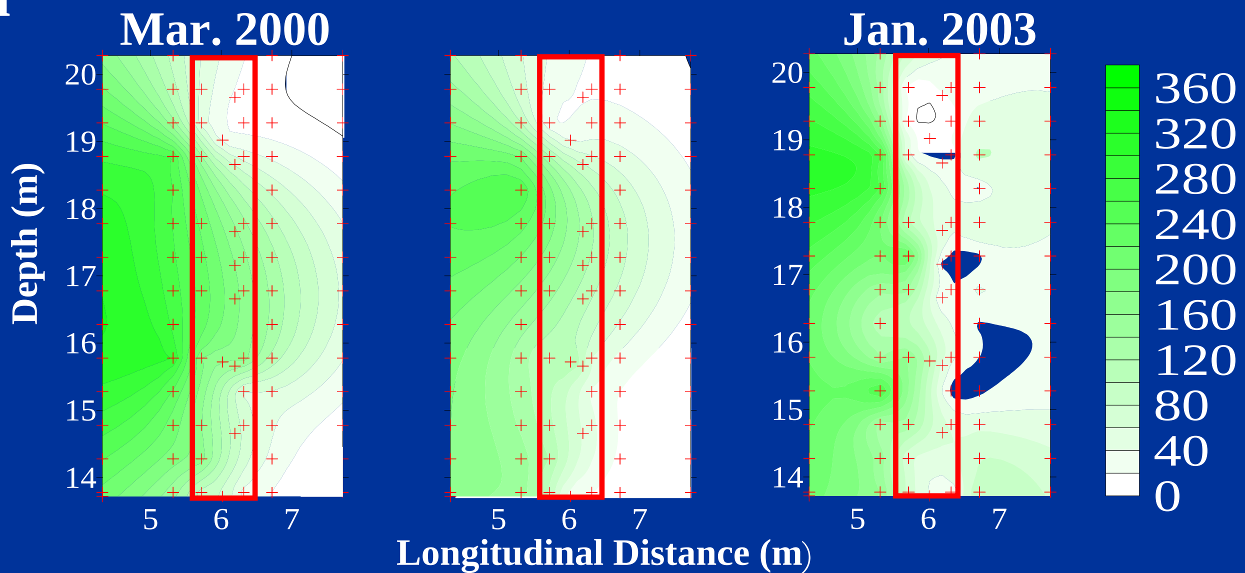
  (i) reduction of dechlorination rates of c-DCE and 11-DCA

  (ii) postponement of sequential production of c-DCE and 11-DCA

  ∴ shifting of peak concentration from the middle to the end of the PRB

Changes in Groundwater Geochemistry

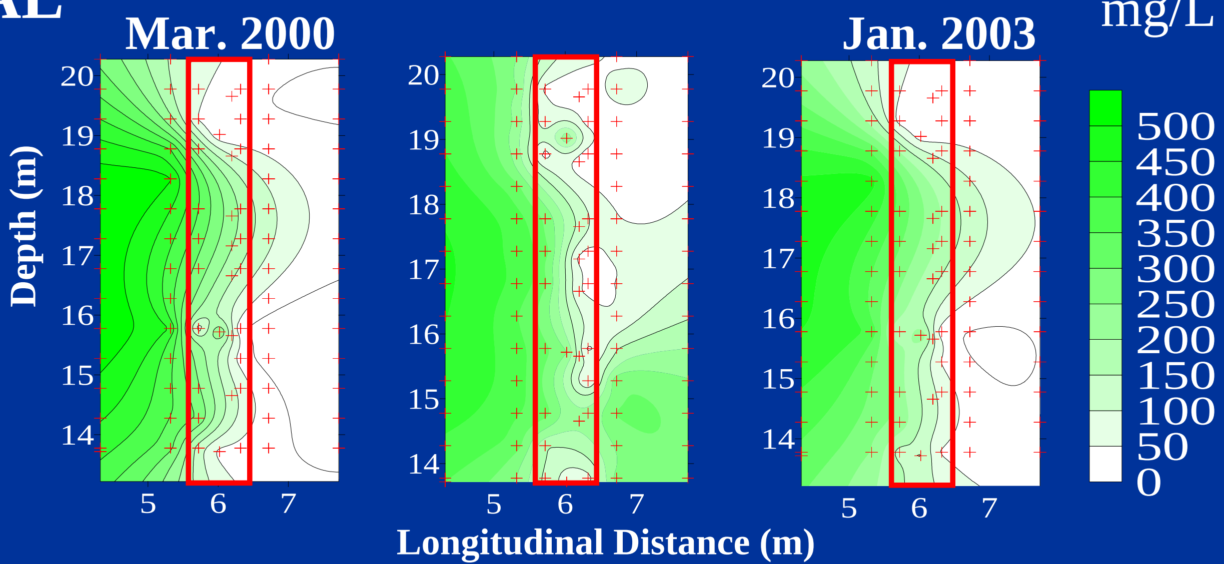
Ca^{2+}



76 to 90 % decrease in Ca^{2+}

TAL

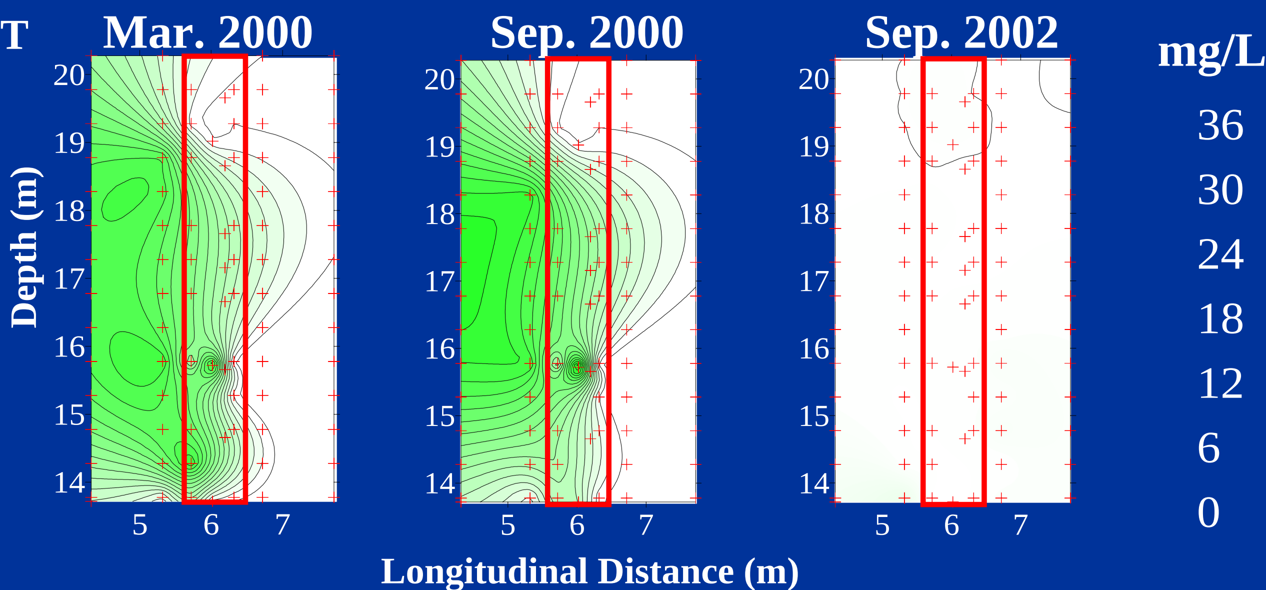
mg/L as



86 to 96 % reduction in TAL

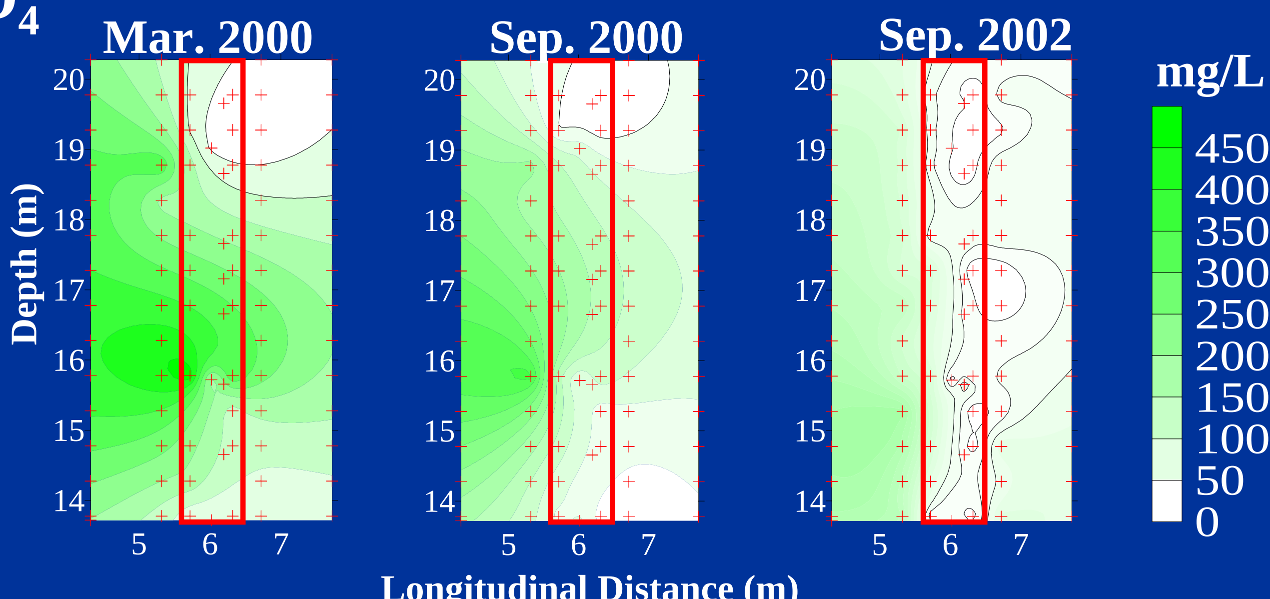
Changes in Groundwater Geochemistry

Fe_T



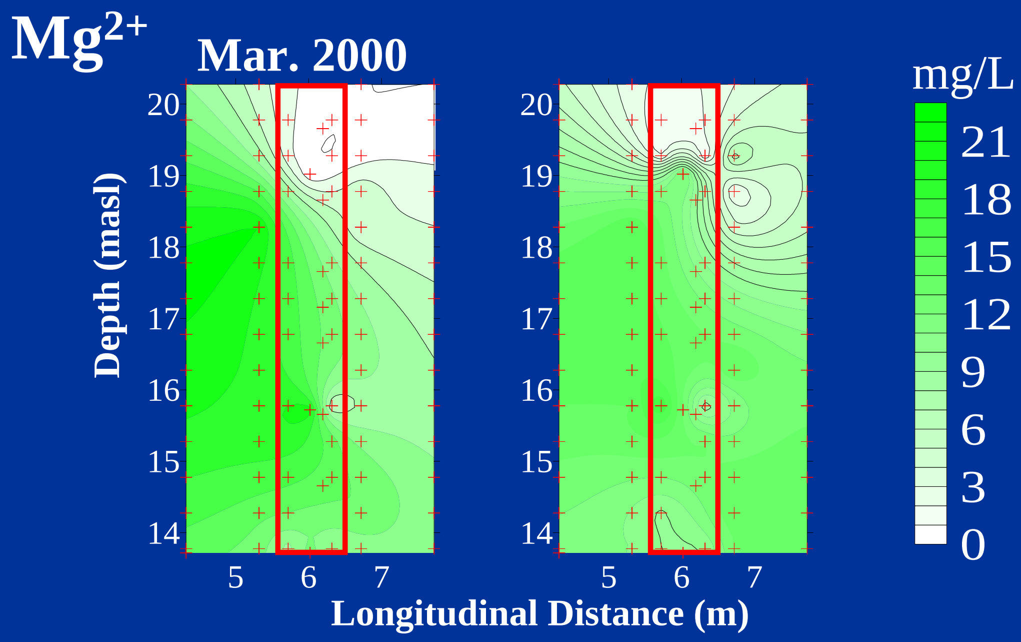
No increase in Fe_T

SO_4^{2-}



53 to 94 % reduction in SO_4^{2-}

Changes in Groundwater Geochemistry

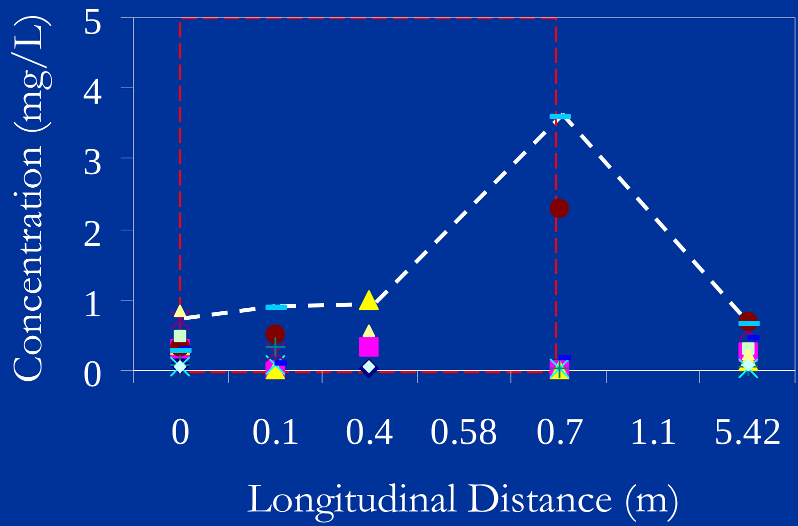


Insignificant decrease in Mg^{2+}

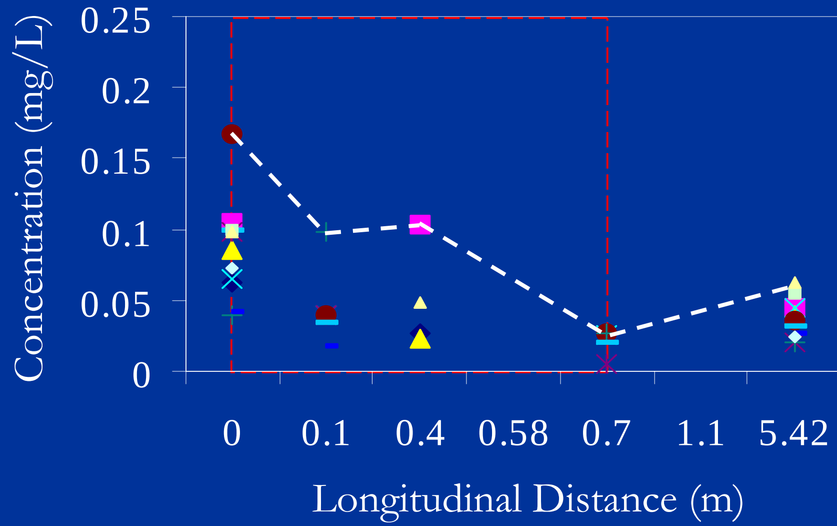
- Decreases in Ca^{2+}, TAL & SO_4^{2-} and no increase in Fe_T
  $\Rightarrow$ significant precipitations of **$CaCO_3$ & FeS**
  $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_{3(s)}$ $\log K_{10} = 8.18$
  $4Fe^0_{(s)} + SO_4^{2-} + 6H_2O \rightarrow 4Fe^{2+} + H_2S_{(aq)} + 10OH^-$ $\log K_{10} = -43.4$
  $Fe^{2+} + S^{2-} \rightarrow FeS_{(s)}$ $\log K_{10} = 17.9$
  (Waybrant et al. 1995)

Changes in Groundwater Geochemistry

NH_3-N & NH_4^+-N



NO_2^- & NO_3^-



- 2-fold increase in NH_3-N & NH_4^+-N
- 76 % reductions in NO_2^- & NO_3^-

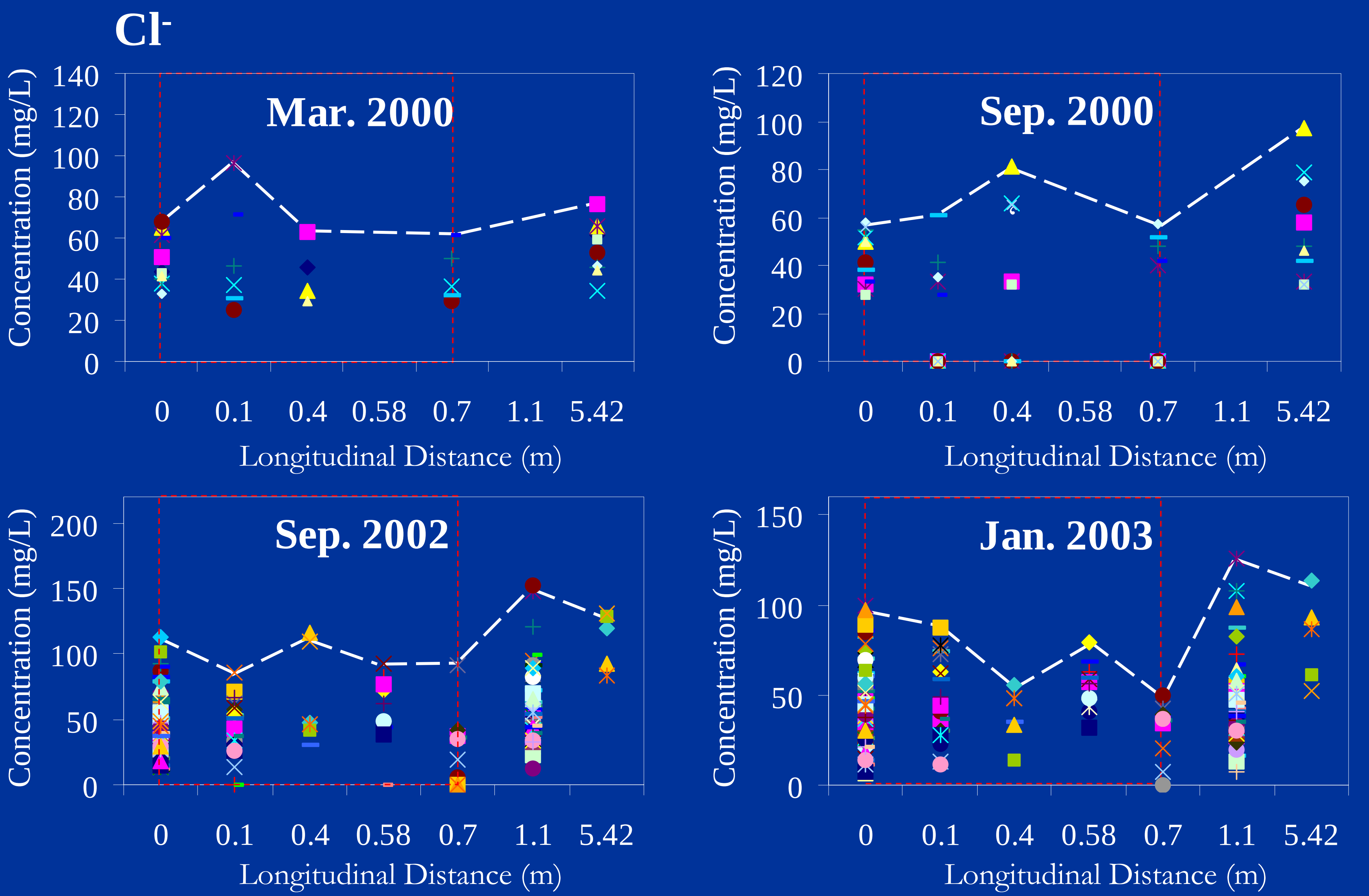
$\Rightarrow$ Reduction from NO_2^- & NO_3^- to NH_4^+

$$3Fe^0_{(s)} + NO_2^- + 6H_2O_{(l)} \rightarrow 3Fe^{2+} + NH_4^+ + 8OH^- \quad \log K_{10} = 24.8$$

$$4Fe^0_{(s)} + NO_3^- + 7H_2O_{(l)} \rightarrow 4Fe^{2+} + NH_4^+ + 10OH^- \quad \log K_{10} = 39.8$$

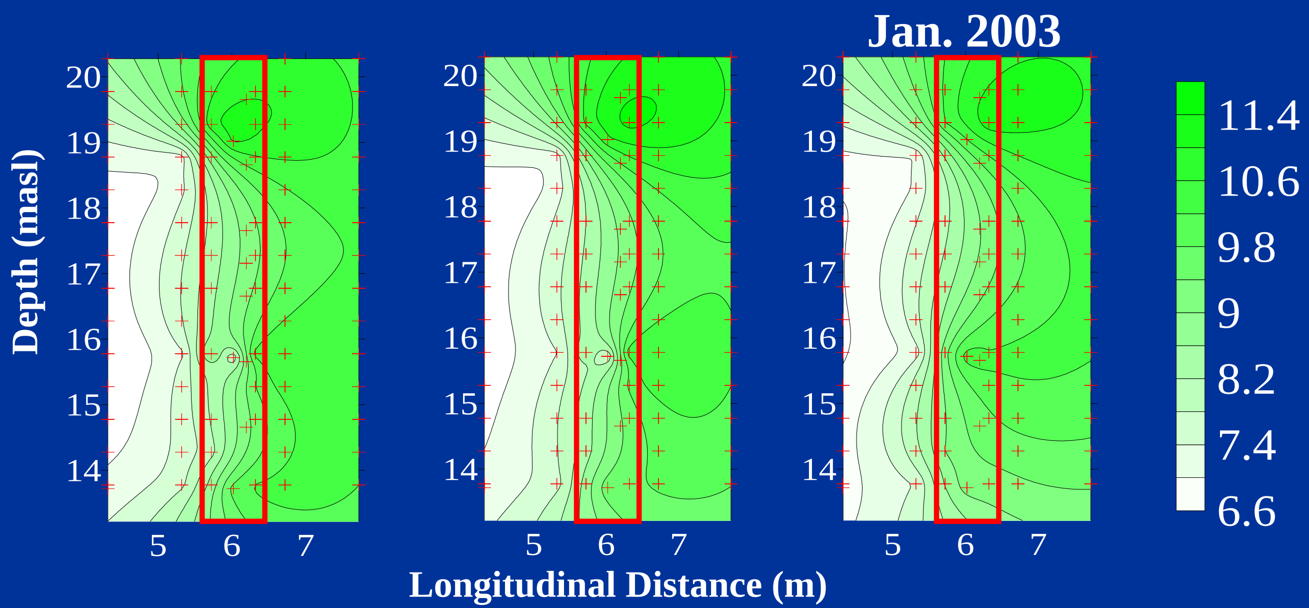
(Choe *et al.* 2000)

Changes in Groundwater Geochemistry

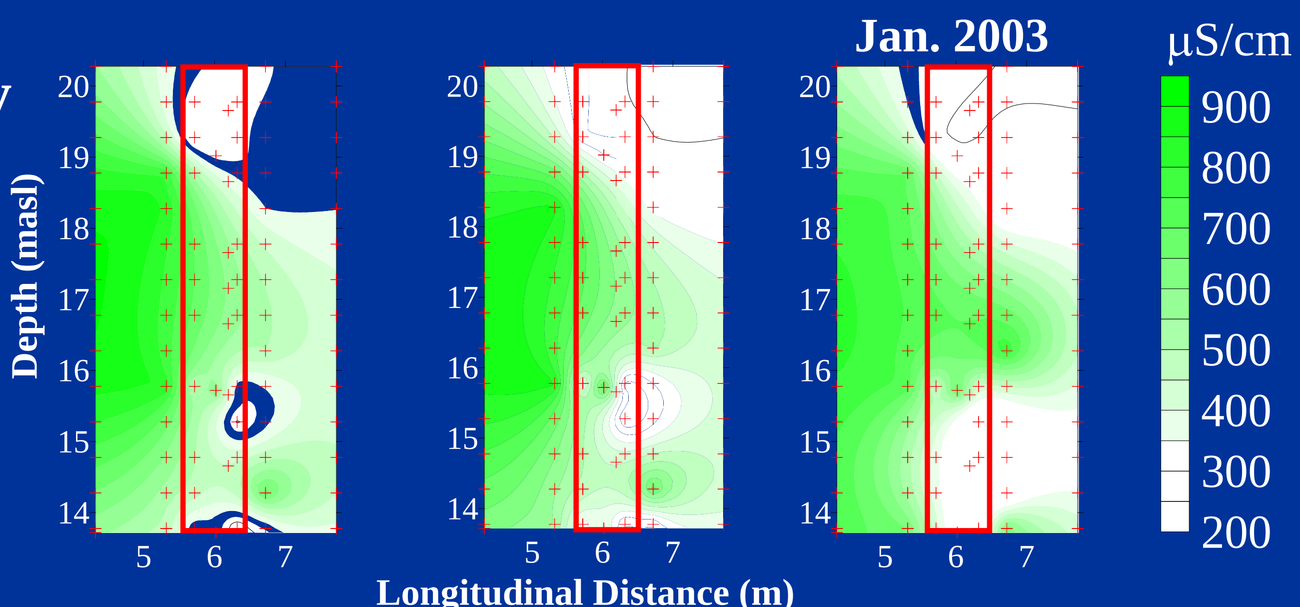


Changes in Physical Parameters

pH

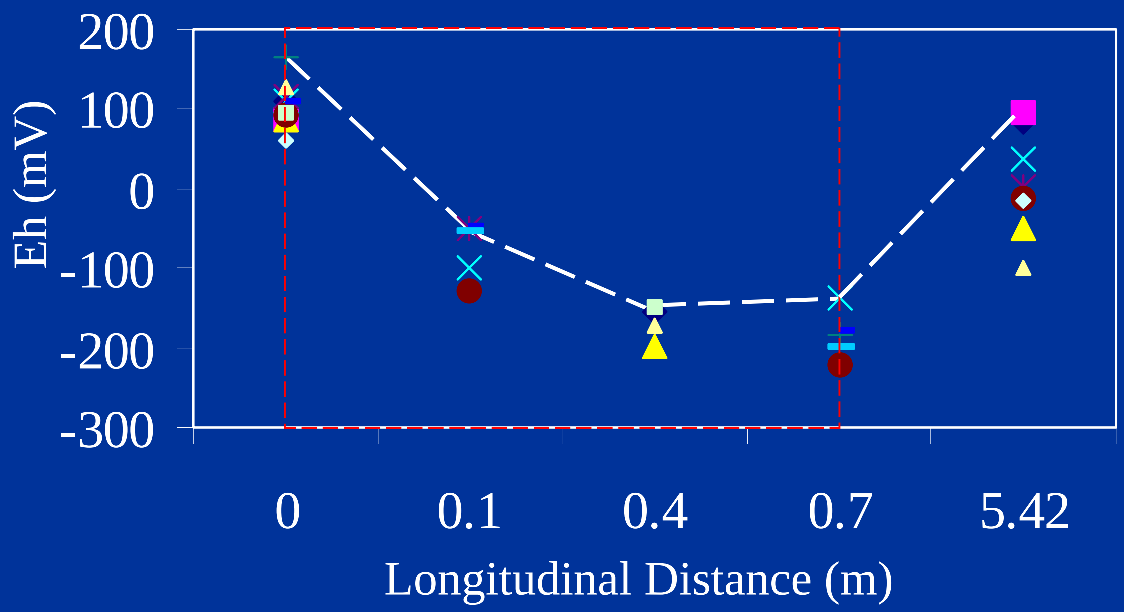


Electrical Conductivity



Changes in Physical Parameters

Redox Potential



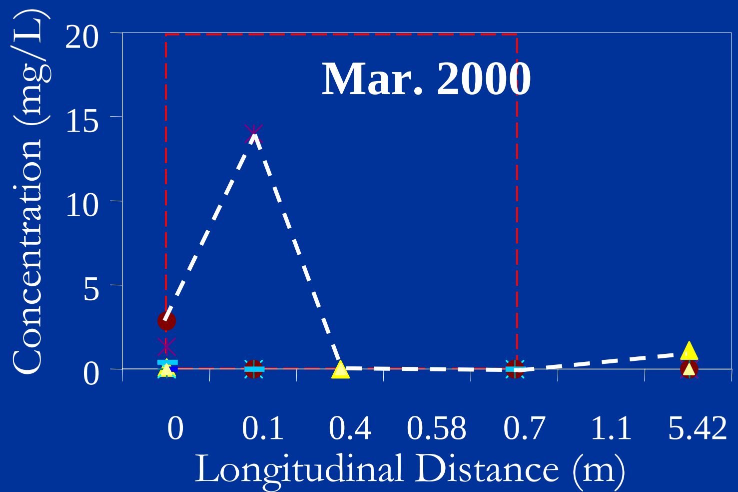
- 2.5 to 3.3 units increase in pH
- 420 (65 %) to 790 (69 %) μS/cm reduction of conductivity

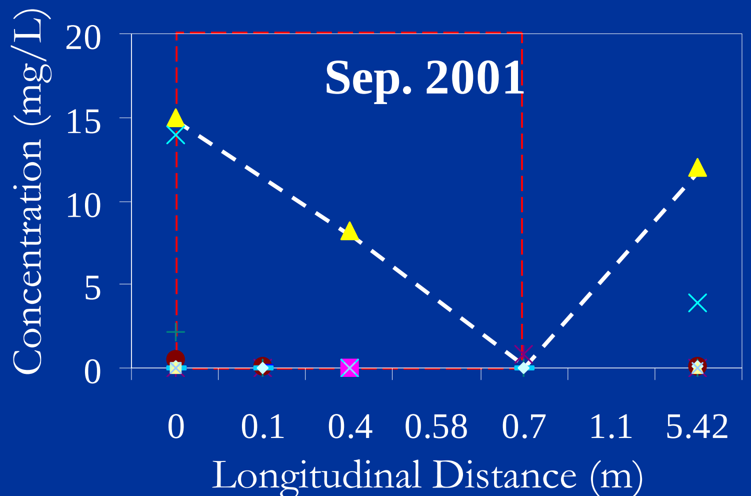
  ⇒ precipitations of dissolved ions
- Nearly 300 mV decrease in Eh & -200 mV of Eh within the barrier

  ⇒ occurrence of reductive dechlorination of chlorinated organics

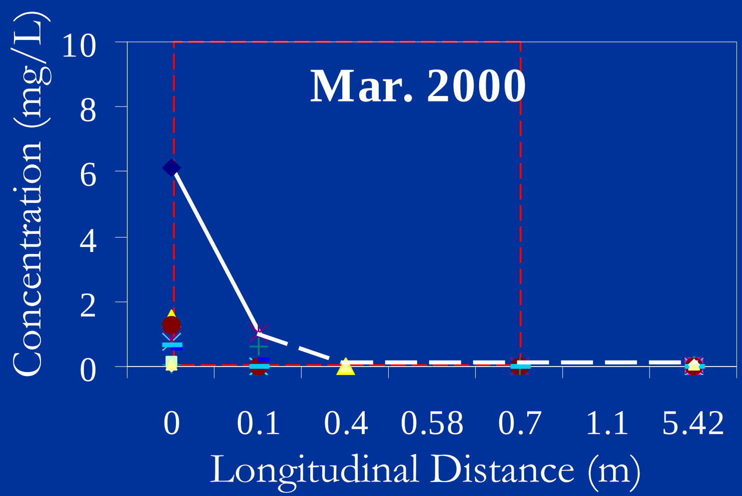
Removal of DCM & 12-DCA

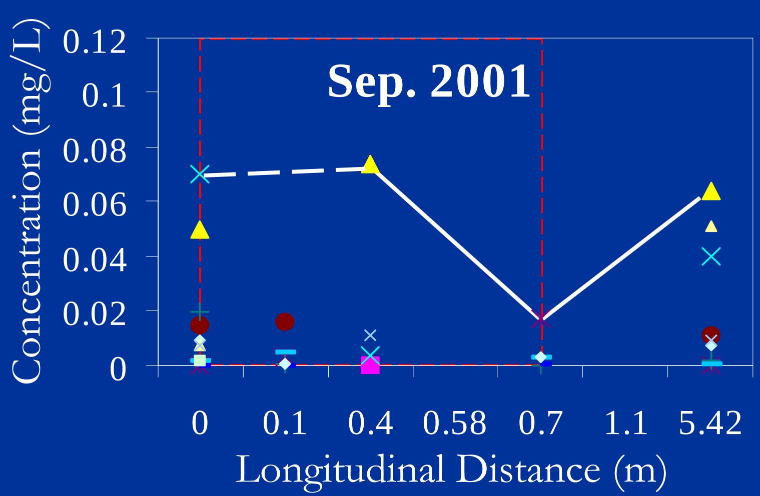
DCM





12-DCA





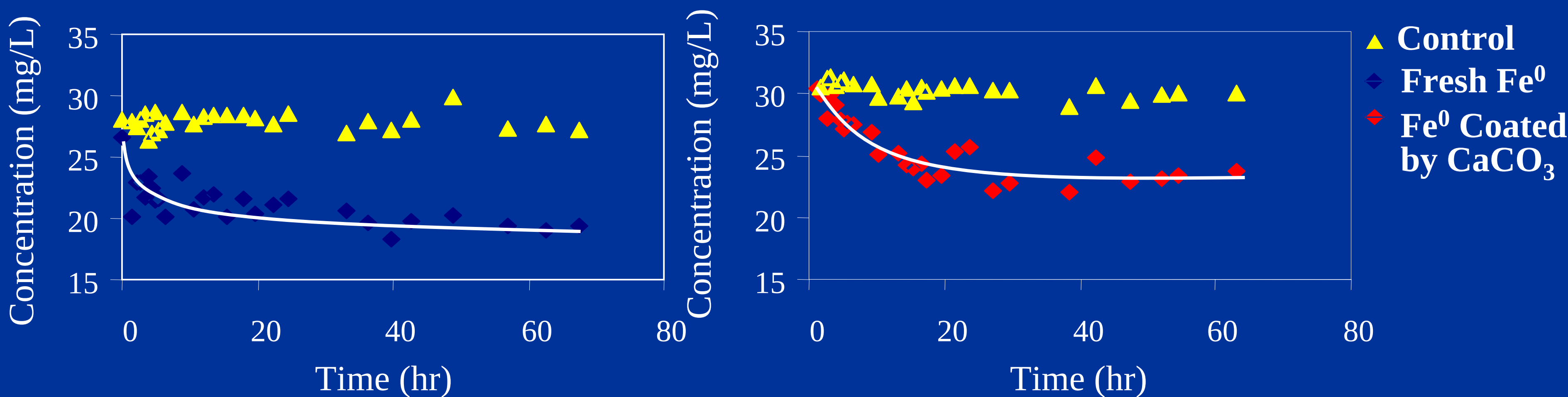
Microbial Degradation

or

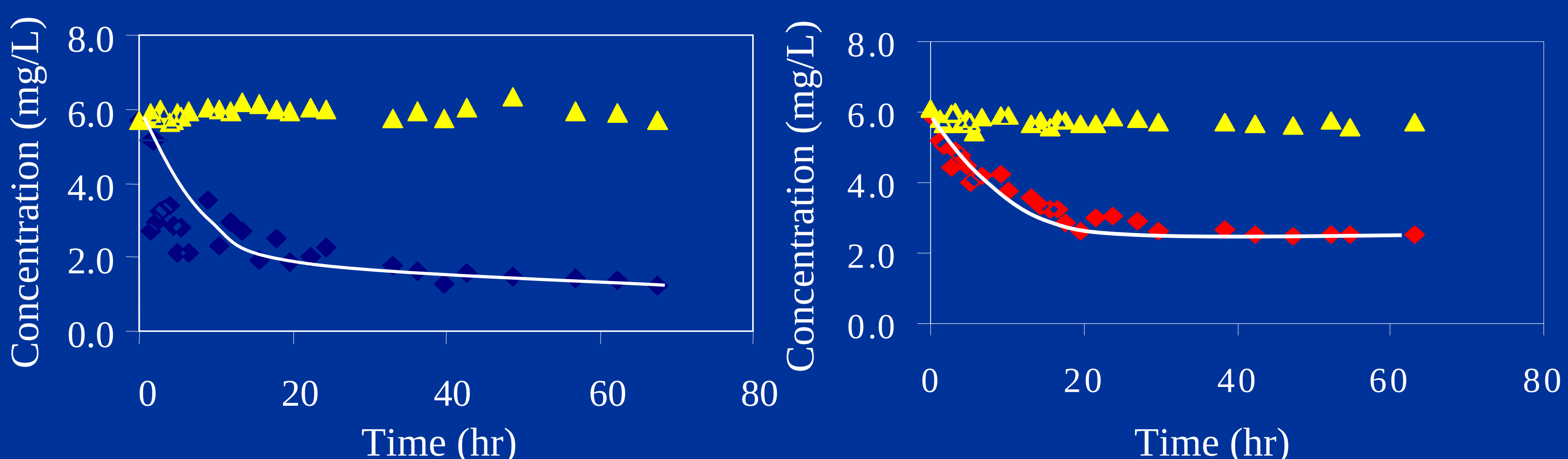
Adsorption by Fe^0

Adsorption of DCM & 12-DCA by Fe^0

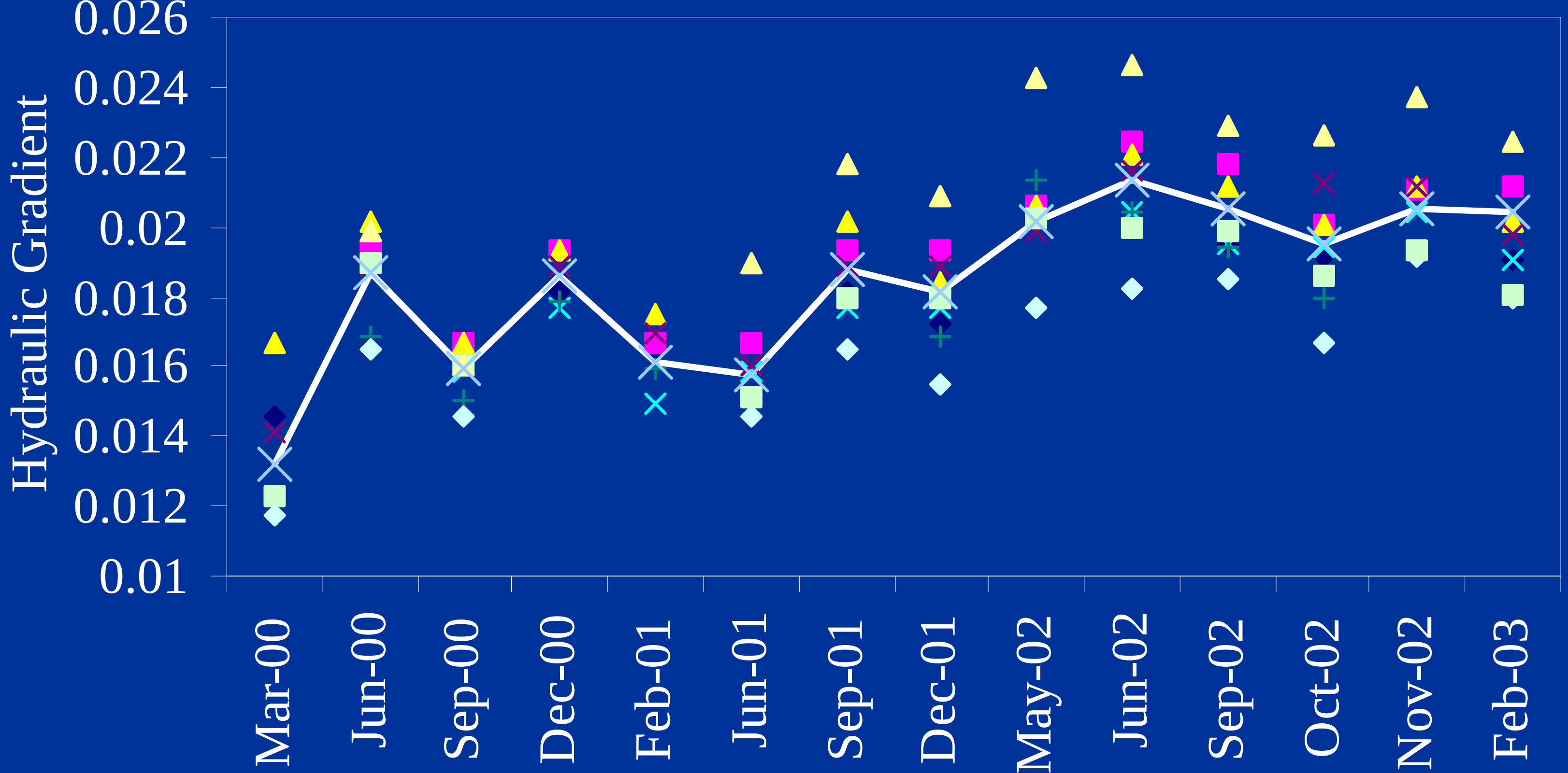
DCM



12-DCA



Hydraulic Gradient & Porosity

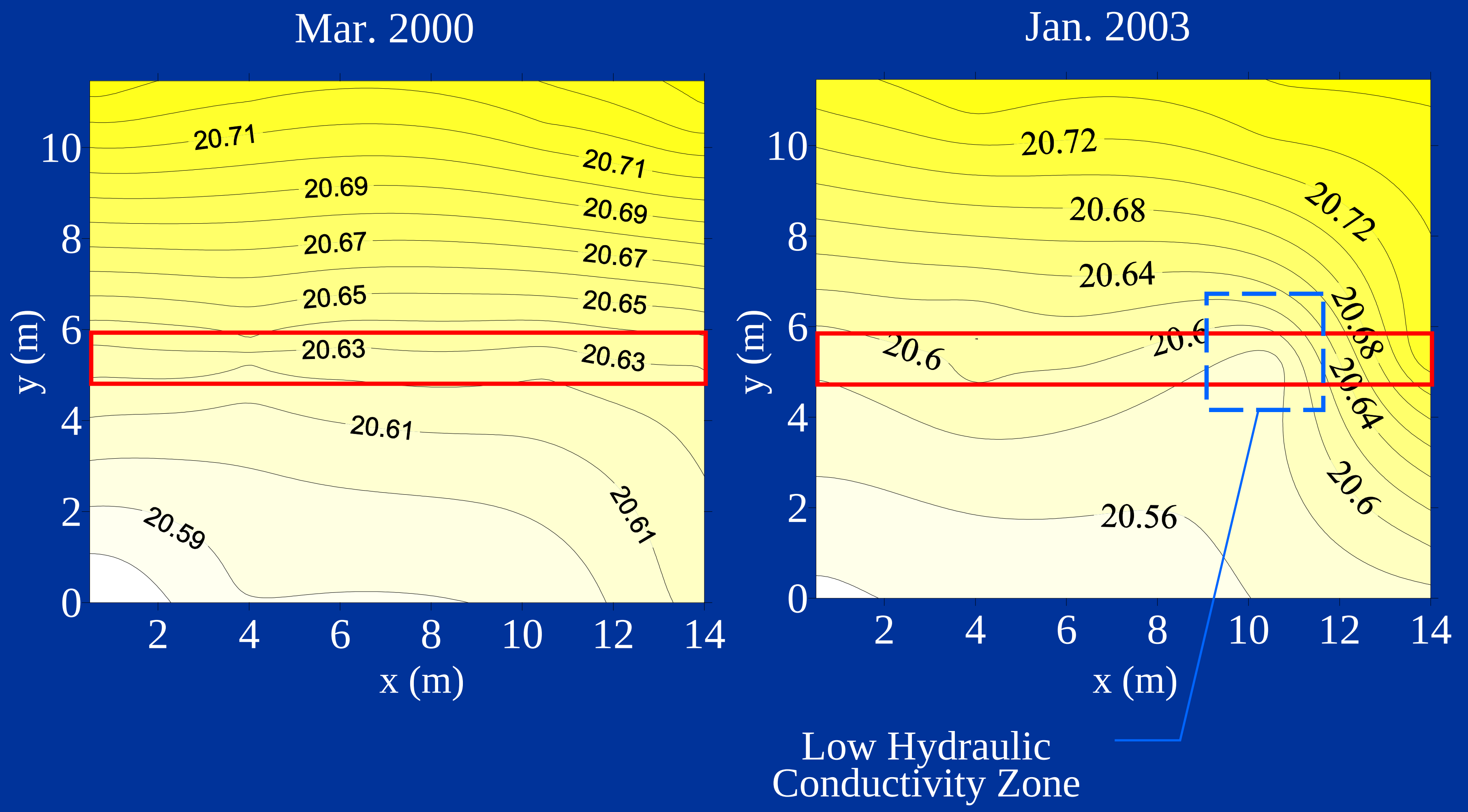


- 55 % increase in hydraulic gradient (0.0132 to 0.0204)
- 2.3 m^3 loss of void volume throughout the barrier

  ⇒ Overall 3.7 % loss of porosity
- Decrease in Ca^{2+}, TAL & SO_4^{2-} ⇒ first half of the PRB

  ⇒ 5.7 % loss of porosity in the front part of the PRB

Water Table Distribution



Conclusion

Organic Study

- PCE, TCE & 111-TCA
  ⇒ 98 % removal without pronounced deterioration of performance with time
- c-DCE and 11-DCA
  ⇒ significant deterioration of the removal efficiency

Geochemical Study

- Significant formation of $CaCO_3$ & FeS
- Reduction from NO_2^- & NO_3^- to NH_4^+
- No significant change in Cl^- because of high background concentration and fluctuation of Cl^-

Physical Study

- 2.5 to 3.3 units increase in pH
- 65 to 69 % reduction of electrical conductivity
- Nearly 300 mV decrease in Eh across the PRB

Others

- Removals of DCM & 12-DCA
  $\Rightarrow$ microbial degradation or adsorption by Fe^0
- Mineral precipitation
  $\Rightarrow$ 55 % increase in hydraulic gradient
  $\Rightarrow$ 3.7 % loss of porosity
  $\Rightarrow$ Disturbance of the water table distribution

Acknowledgements

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