

IRON SPECIATION AND ISOTOPIC FRACTIONATION IN THE RIO NEGRO AND RIO SOLIMÕES MIXING ZONE

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IRON

4th most abundant element in the Earth's crust

Lateritic soils  Covers 1/3 of the continents and drains half of continents waters

Essential for most living organisms

Controls the phytoplankton growth in the ocean  Influence on the global carbon cycle

Amazon Basin

Continental scale erosion and weathering processes
Different geological features, soils and forest formations



Allows to study many biogeochemical processes and define the input of Fe from the continent to the ocean

THE MIXING ZONE



Water different chemical compositions

- ▣ **Rio Solimões:**

- ▣ Circumneutral pH \longrightarrow Fe^{3+} oxyhydroxides or Fe^{3+} associated with clays \longrightarrow Low dissolved [Fe]
 - ▣ Cations-rich \longrightarrow High Electrical Conductivity
 - ▣ High Particulate Suspended Matter
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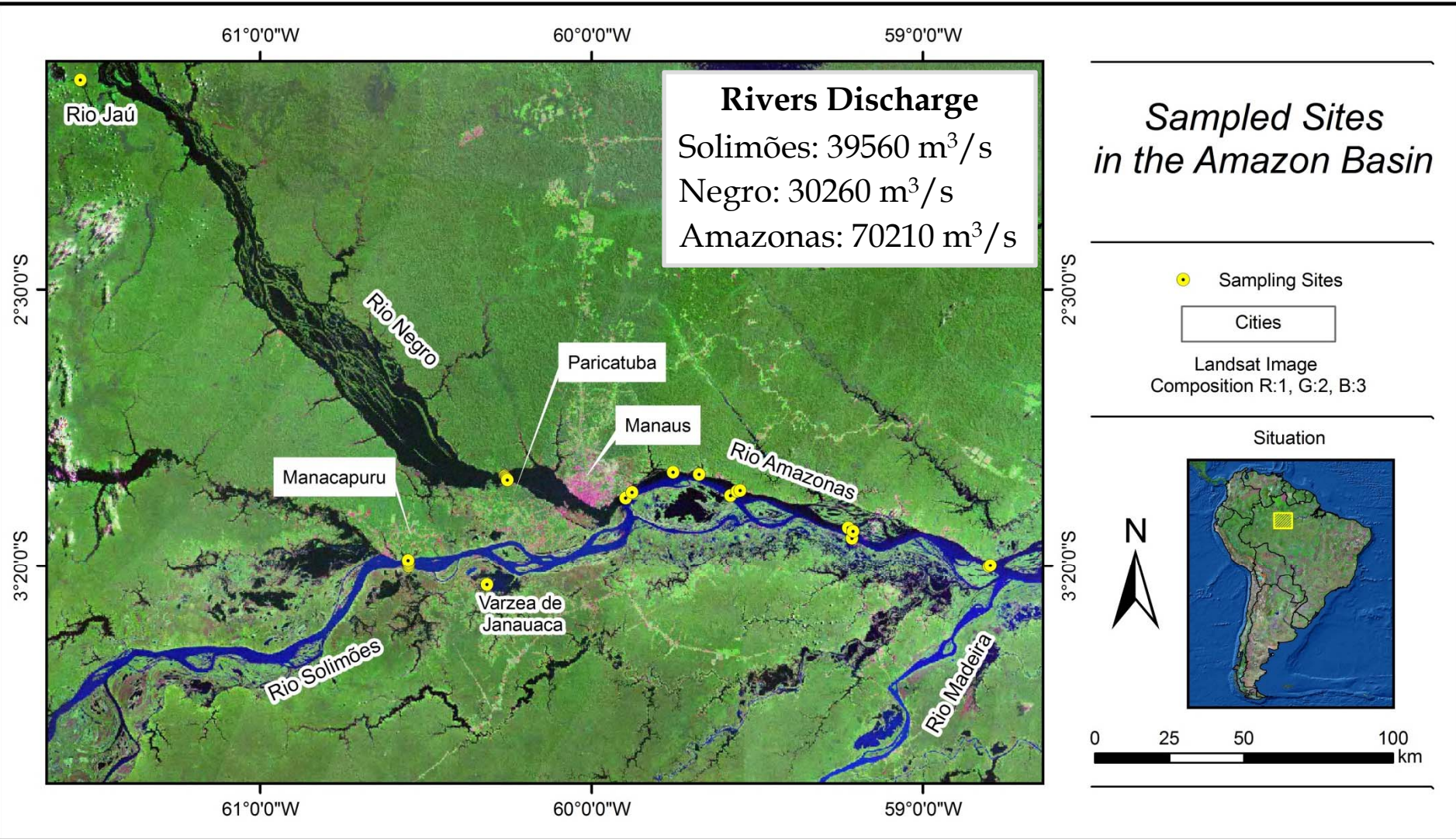
- ▣ **Rio Negro:**

- ▣ Acidic water \longrightarrow “Humic carbon” Fe^{3+} -OM \longrightarrow High Dissolved [Fe]
 - ▣ Cations-poor \longrightarrow Low Electrical Conductivity
 - ▣ Low Particulate Suspended Matter
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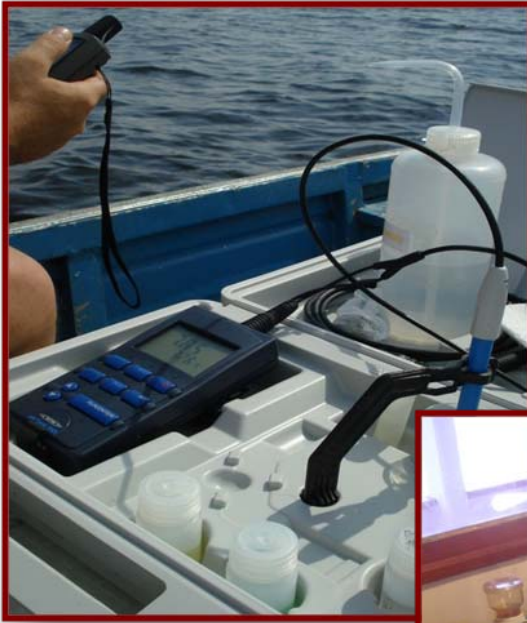
What is the Fe behavior during the rivers mixture?

Field Mission

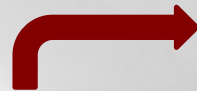
(extreme dry season - October 2010)



Analytical Methods



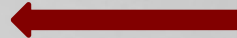
Physical-chemical parameters
(pH, E.C., Temp.)



Vacuum Filtration ($0.45\mu\text{m}$)



Tangencial Ultrafiltration
($0.2\mu\text{m}$ and 5KD)



Analytical Methods



Iron Speciation

Ferrozine Method

Total Fe, Fe(II) and Fe(III)

(Viollier, 2000)



Iron Isotopes



Sample Digestion (HCl , HNO_3 , H_2O_2 , HF)

Anionic Exchange Chromatography

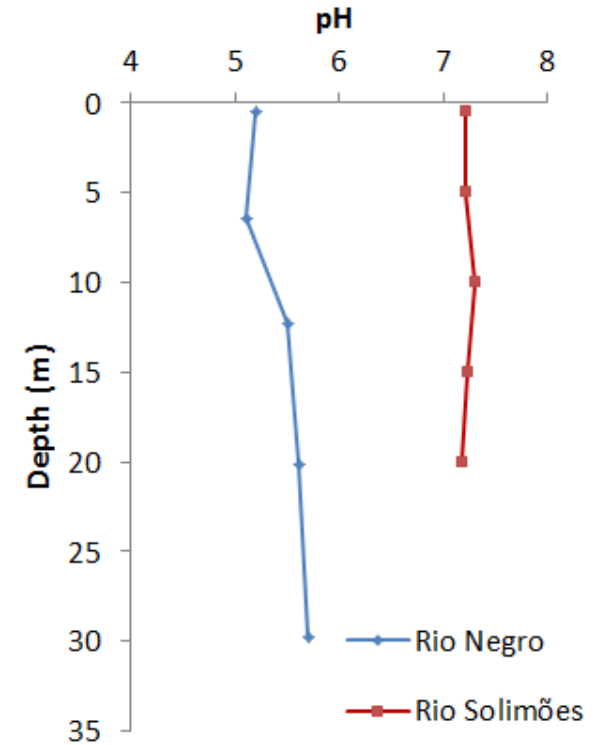
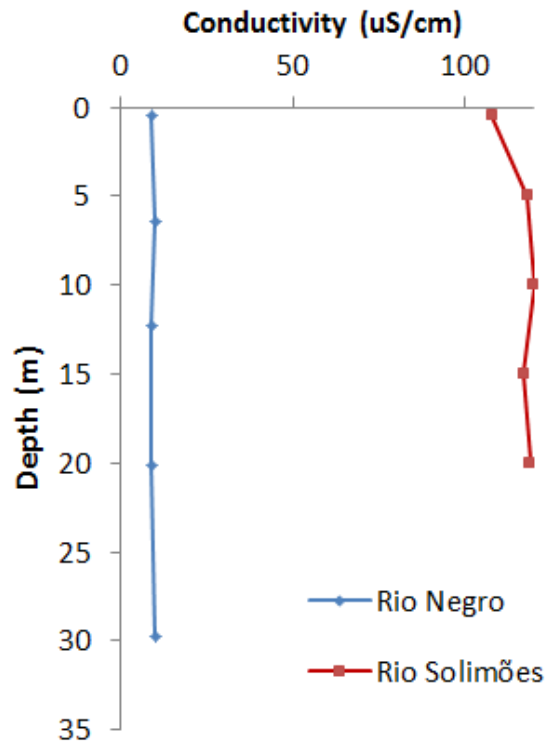
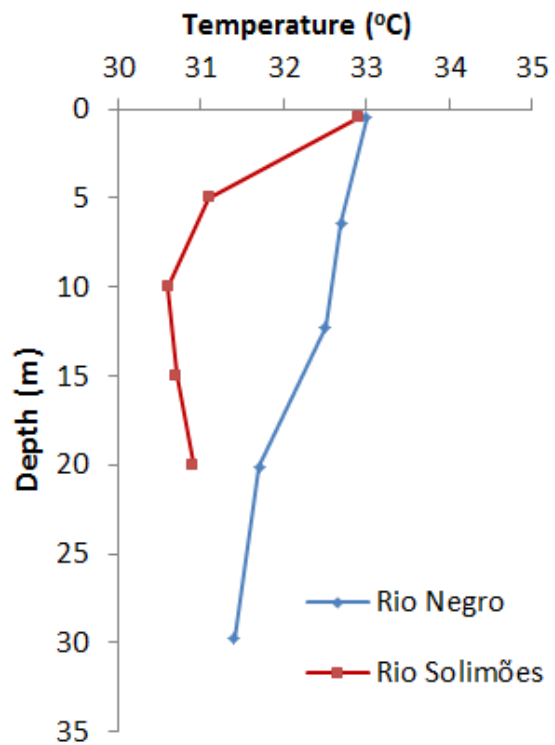
Neptune, MC-ICP-MS

(Poitrasson & Freydier, 2005)



The EndMembers

Physical-chemical parameters



The EndMembers

Iron Speciation

Surface water:

> 99% of Fe(III)

Depth Profile

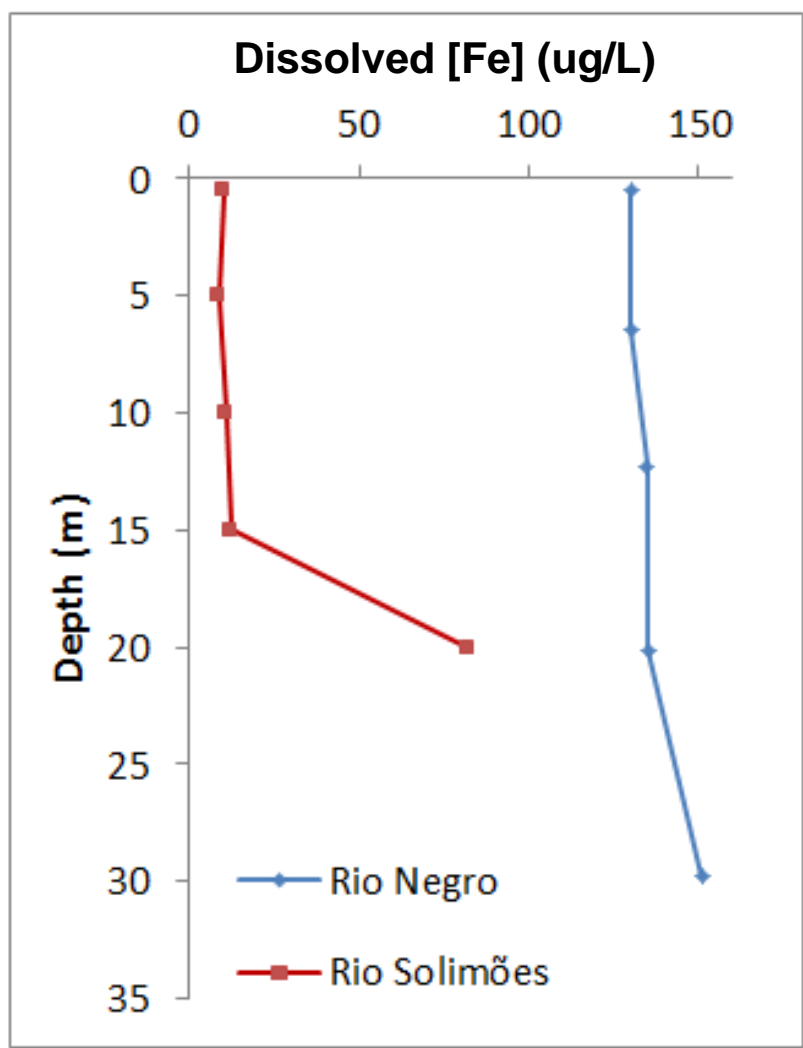
Solimões: 20m – 54 % of Fe(II)

Negro: 30m – 7% of Fe (II)

Fe re-mobilization due its reduction



Increase Fe content in the river's bottom



Tracing the Rivers Mixture

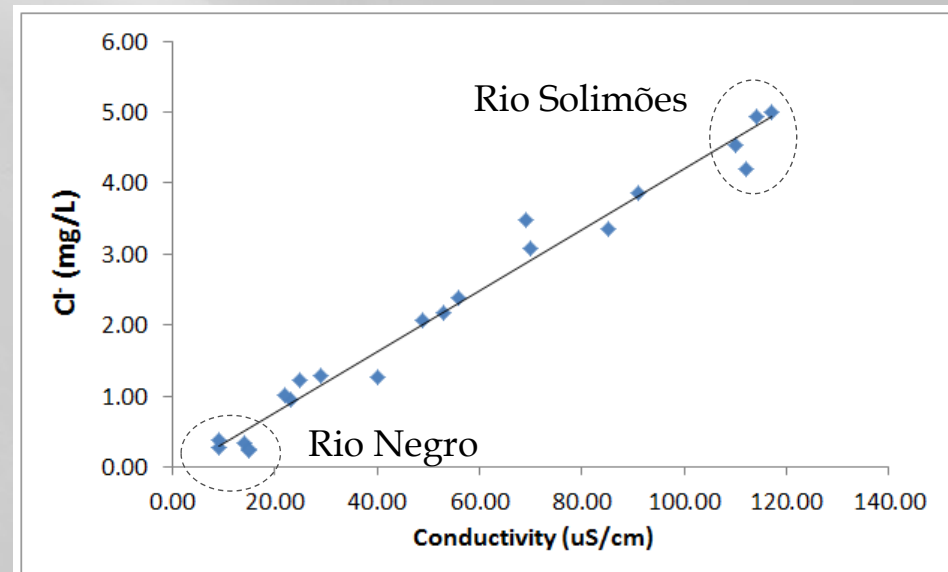
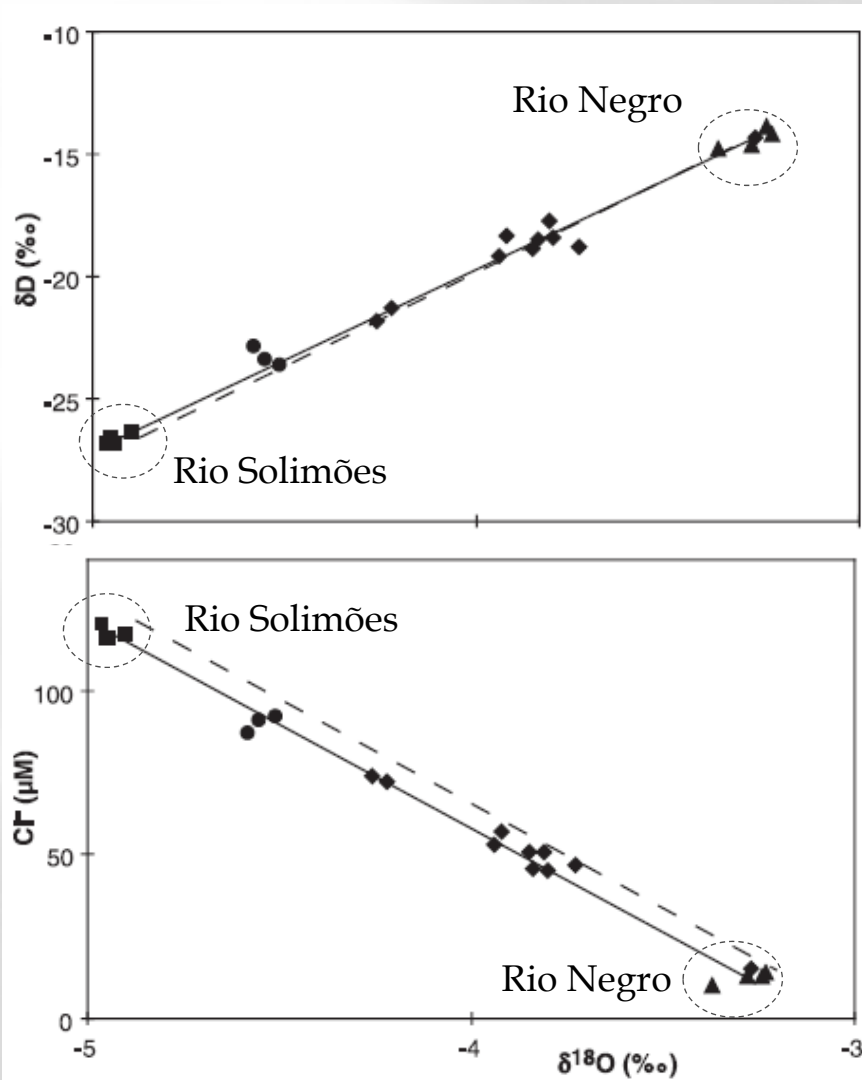
Differentiate water masses



Conservative parameters



Electrical Conductivity

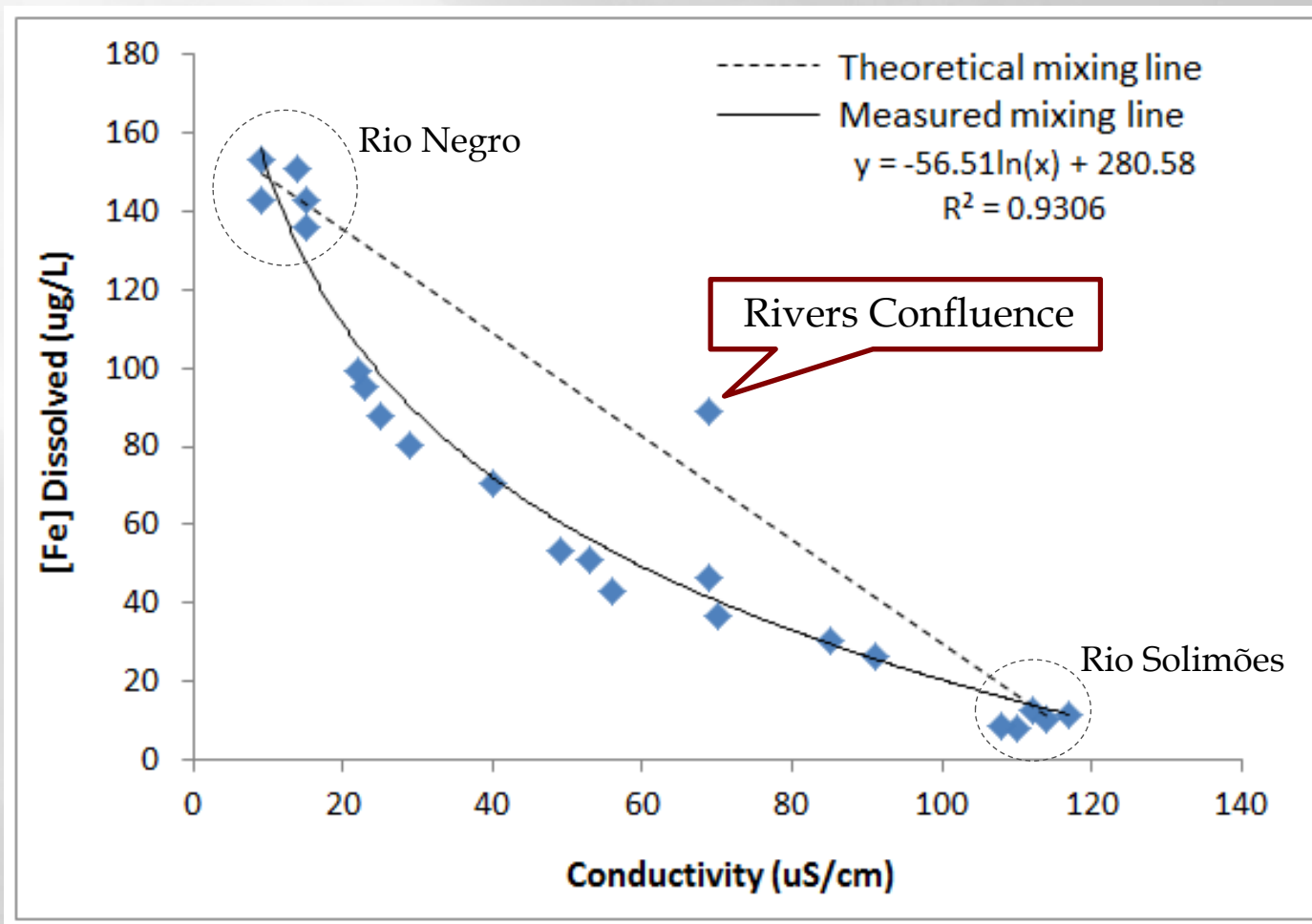


Aucour et al (2003)

Dissolved Fe behavior in the mixing zone

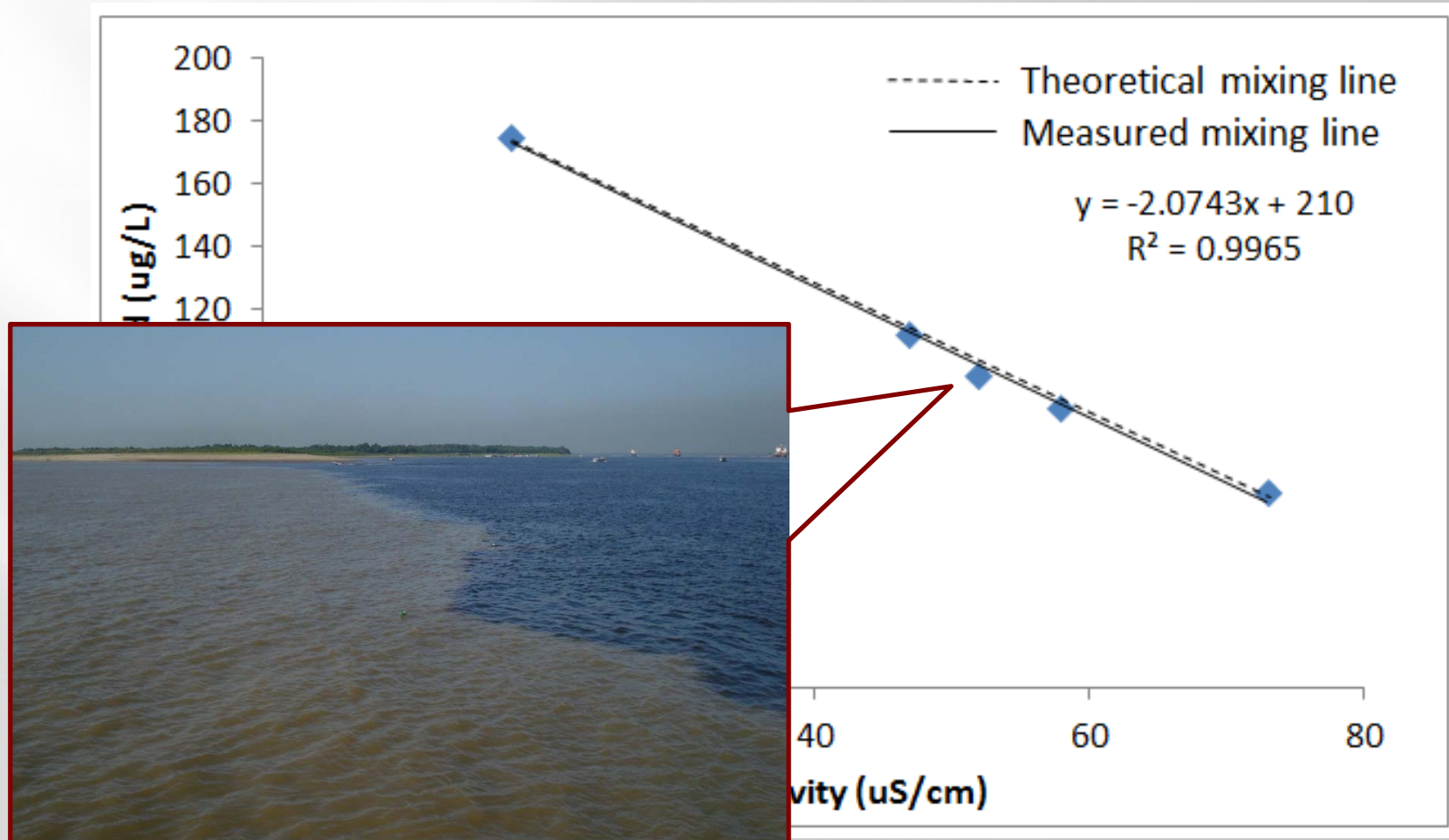
Mixing Zone - (October 2010)

Non-conservative: Fe loss: 12 to 43 $\mu\text{g/L}$
24 to 50 %

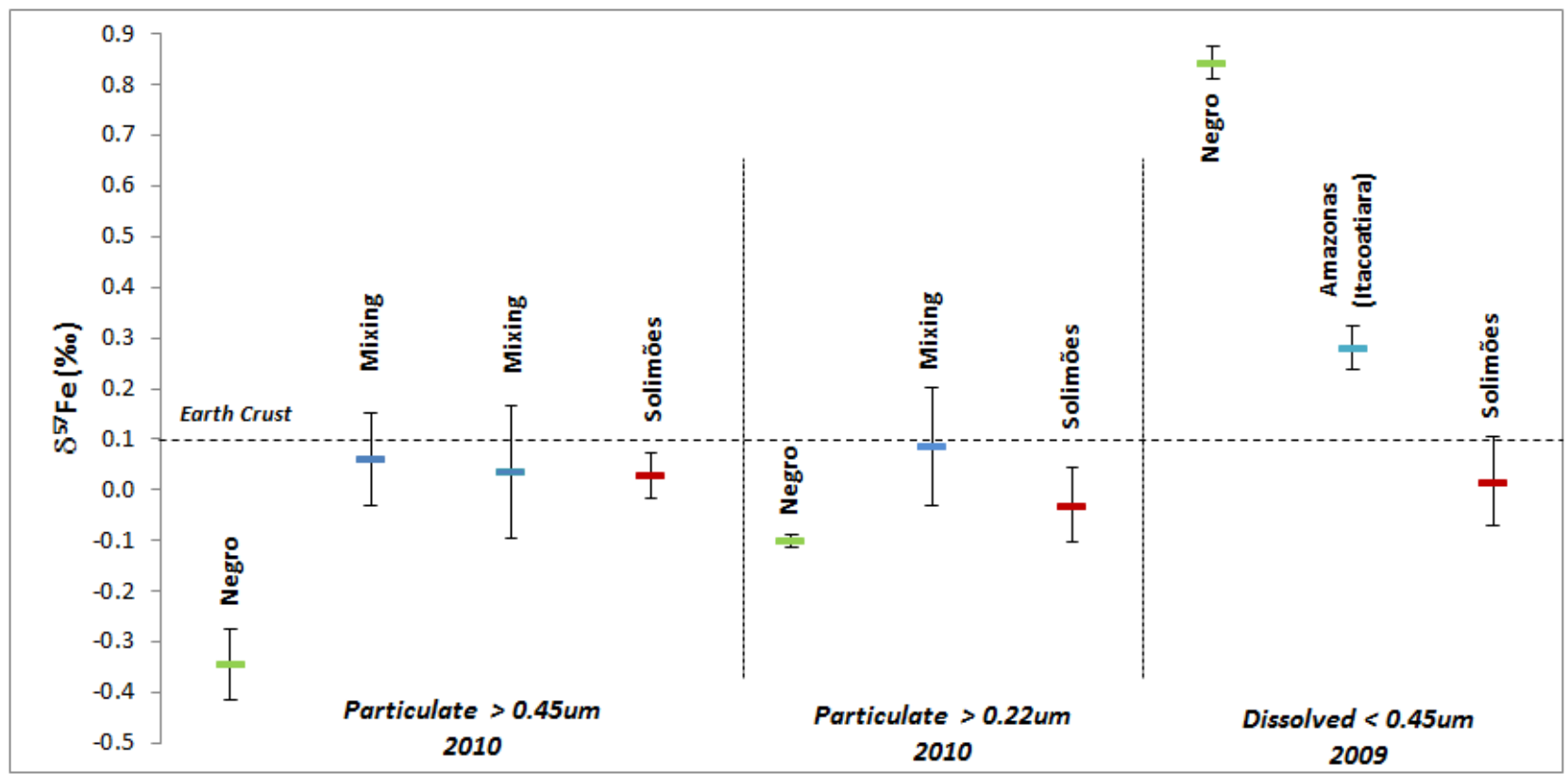


Dissolved Fe behavior in the mixing zone

Beginning of Rivers Confluence (June 2011)
Conservative behavior



Isotopic Signature of the Mixing Zone



Particulate fraction of the mixing zone is enriched in heavy isotopes compared with endmembers



Coagulation of Negro dissolved Fe-OM due physical-chemical changes

Loss of Negro's particulate

Conclusions

- ▣ Contrasted Negro and Solimões waters lead to progressively non-conservative mixing of iron
- ▣ Iron isotopes suggest:
 - Loss of Negro's particulate in the beginning of the mixing process
 - Incorporation of Negro's dissolved Fe into the particulate fraction during the mixing
- ▣ Iron isotopes give us a better insight into the chemical reactions involving iron that occur in the mixing zone