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Role of Oxalic acid on Fractional Solubility of Aerosol Iron over Coastal Ocean: Evidence from compound-specific stable carbon isotopic composition and diagnostic mass ratios

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PRL

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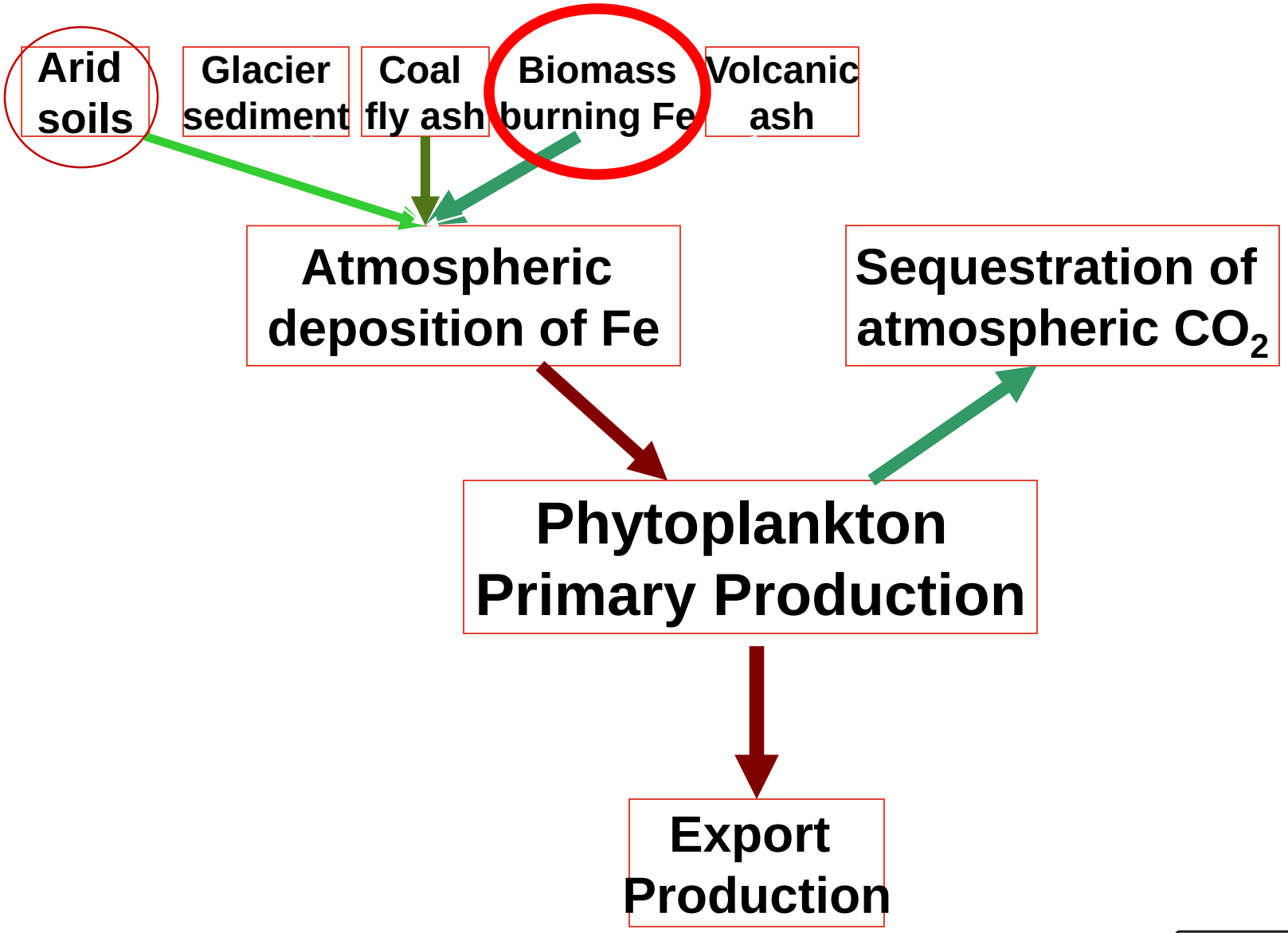
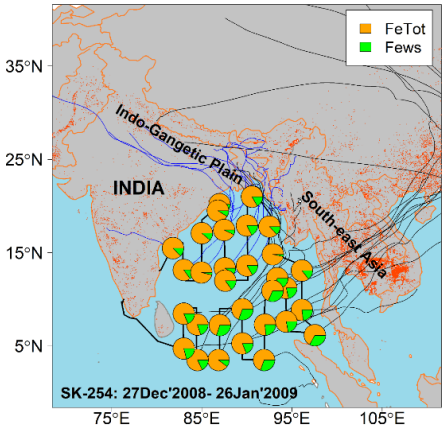
Aerosol iron solubility

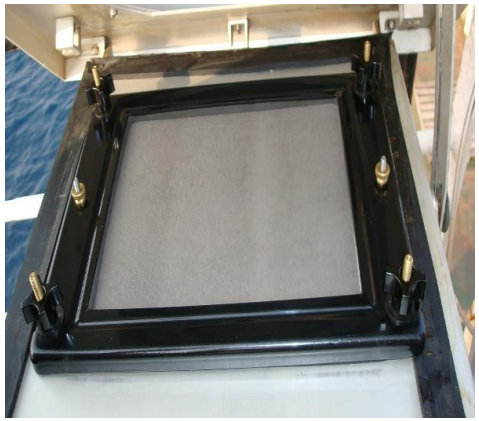


factors affecting aerosol Fe Solubility

- Particle Size (Coarse & fine) – surface area (Baker et al., 2003)
- Mineralogy (Schroth et al., 2009)
- Acid-processing of Mineral dust (PRL Study; Li et al., 2017)
- Source variability (Sholkovitz et al., 2012, Sedwick et al., 2007, PRL study)
- Organic Complexation & Photochemical reduction: Fe(III)-L => Fe (II)-L
- Cloud processing (Desbouefs et al., 2001)

Study region: Bay of Bengal ($PM_{2.5}$, high-volume air sampler; N = 31)





Total aerosol iron, Fe_{Tot} → digested with HF/HNO_3 & measured on ICP-AES

Water-soluble iron, Fe_{ws} → extracted in Milli-Q & adjusted to pH < 2.0
→ measured on GF-AAS
(Bikkina et al., Geochem. Geophys. Geosys., 2013, doi: 10.1002/2014GC005395)

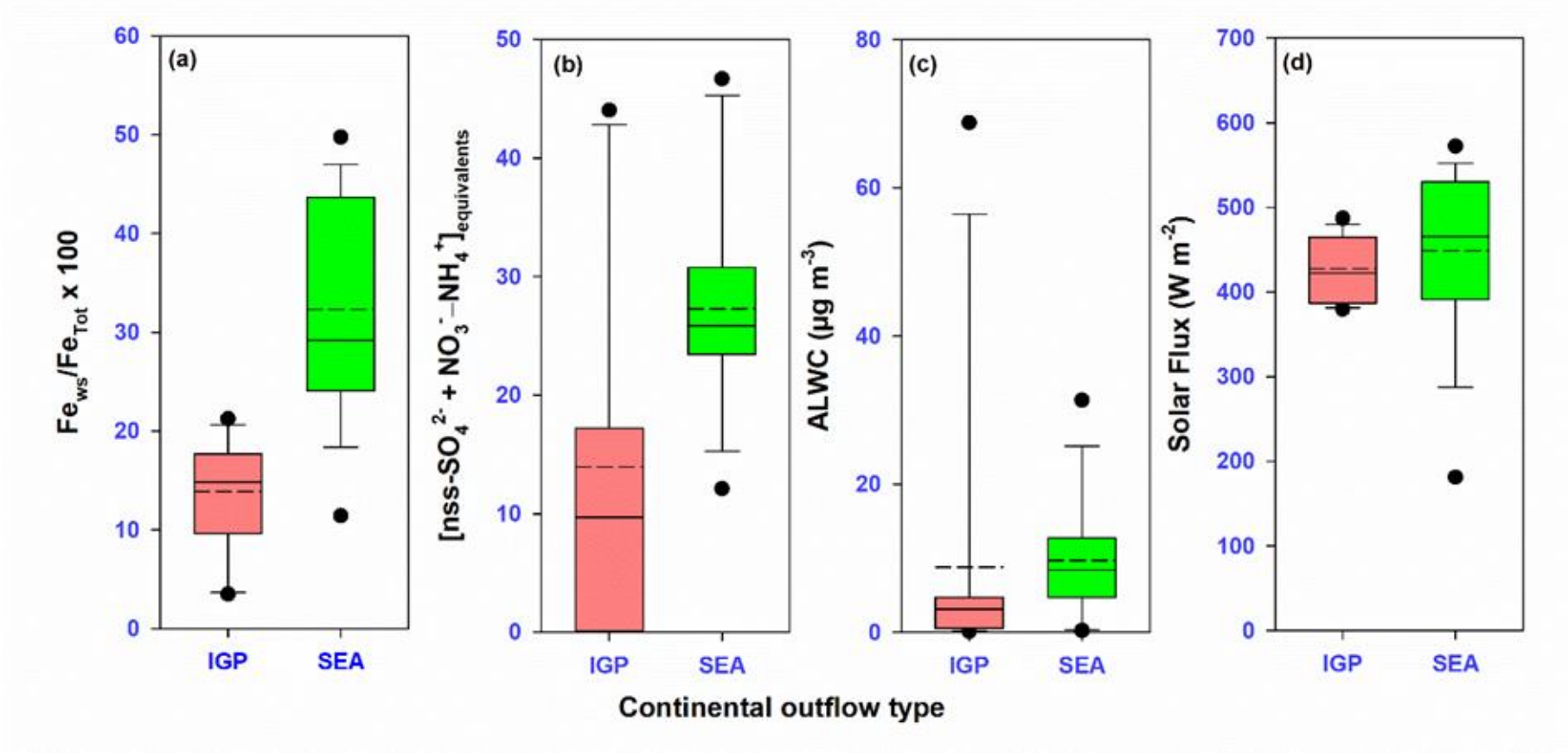
Oxalic acid/precursor organics → extracted in Milli-Q (adjusted pH≈ 8.5-9.0), preconcentrated, dried, derivatized with BF_3/n-butanol (100ºC, 1 h); derivatesextracted in n-hexane → measured on GC-FID & GC-MS **(Bikkina et al., Environ. Sci. Tech., 2017).**

Stable carbon isotopic composition of Oxalic acid

$$\delta^{13}C_{oxalic} = \left(\frac{R_{sample}}{R_{PDB}} - 1\right) \times 1000; R = {}^{13}C/{}^{12}C$$

(**Kawamura and Watanabe, Analytical Chemistry, 2004**)

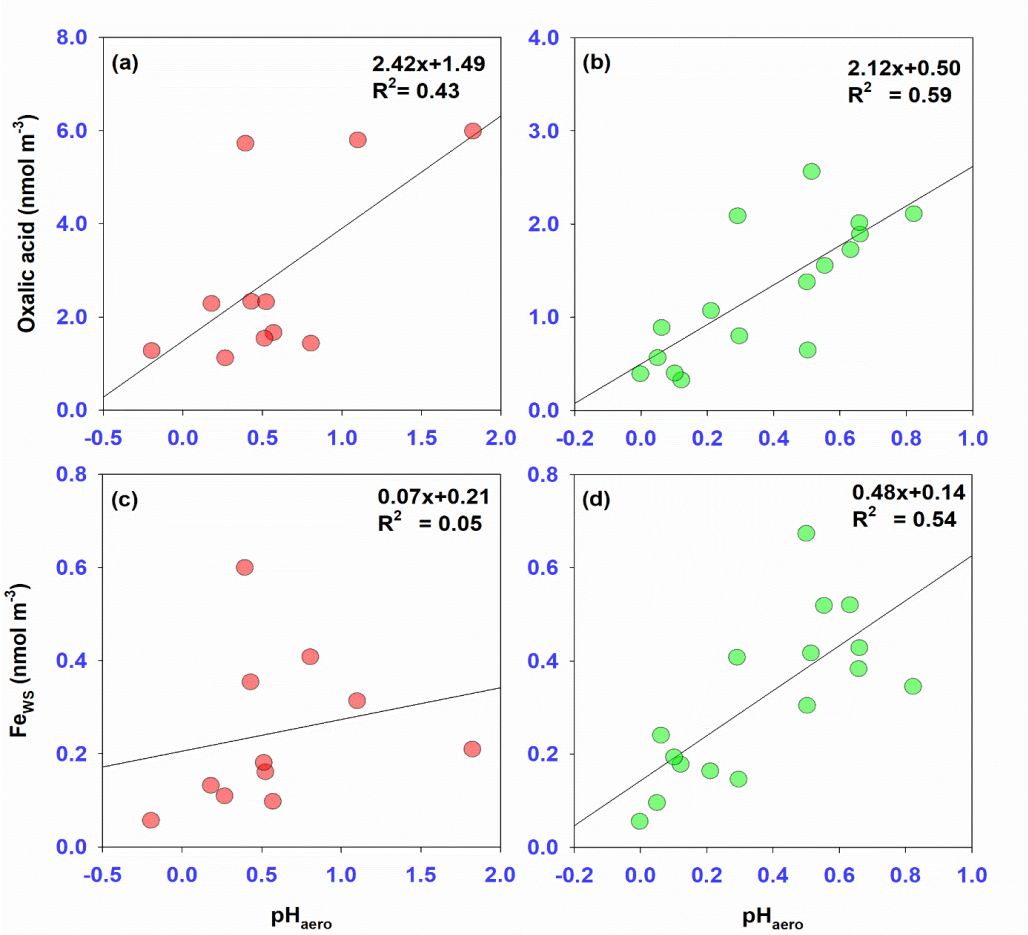
Differences in the fractional solubility of aerosol iron and other influential factors between IGP & SEA-outflow



☞ **Higher Fe-solubility concides with more acidic character, water-content, and slightly higher solar insolation**

(Bikkina et la., submitted to Earth & Space Chemistry)

Relationship of oxalic acid and soluble-Fe with aerosol-pH (from E-AIM II)



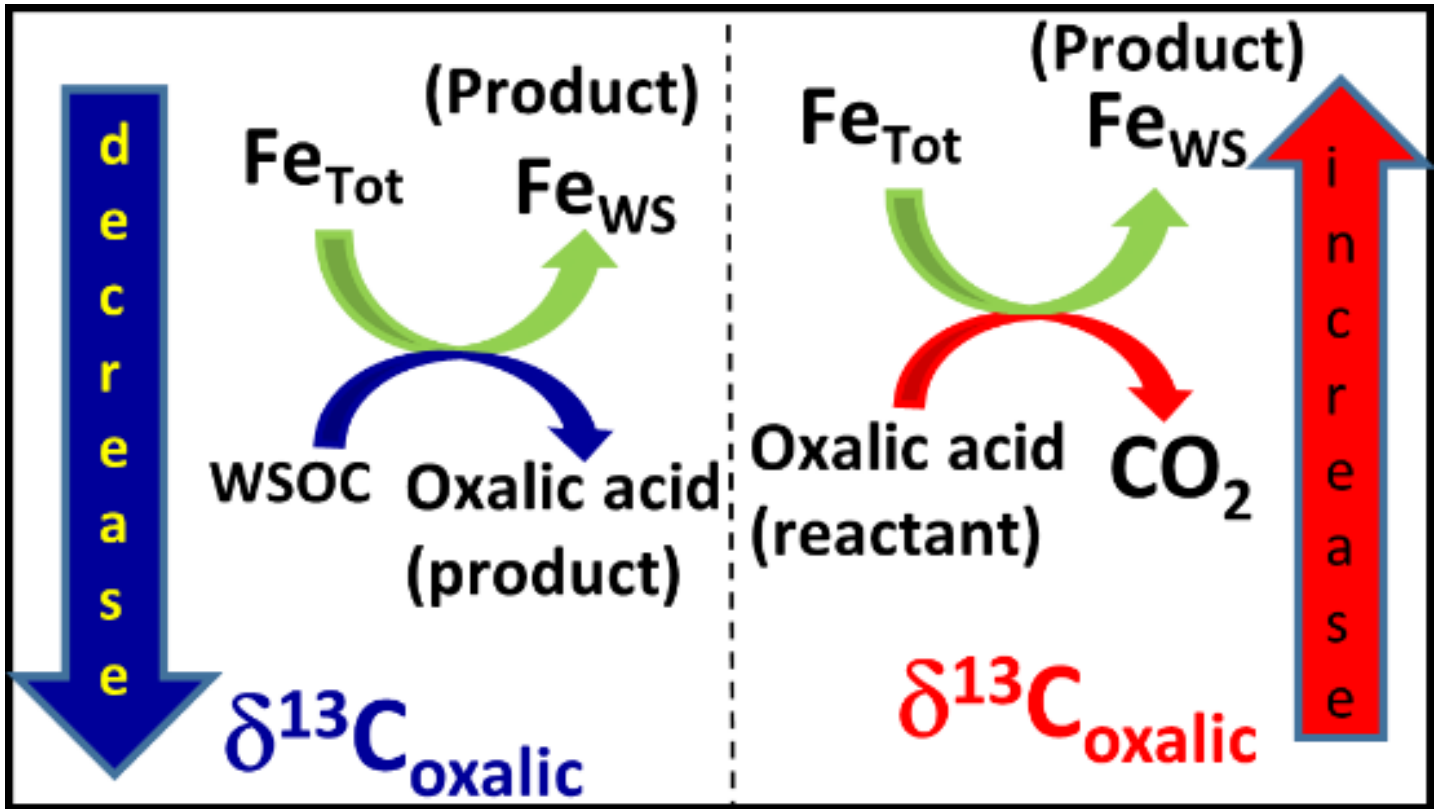
☞ **Better correlations in the continental outflow from Southeast Asia or these aerosols sampled far away from source emissions (hence, more acidity)**

(Bikkina et la., submitted to Earth & Space Chemistry)

Role of Oxalic acid in modulating Fe-solubility

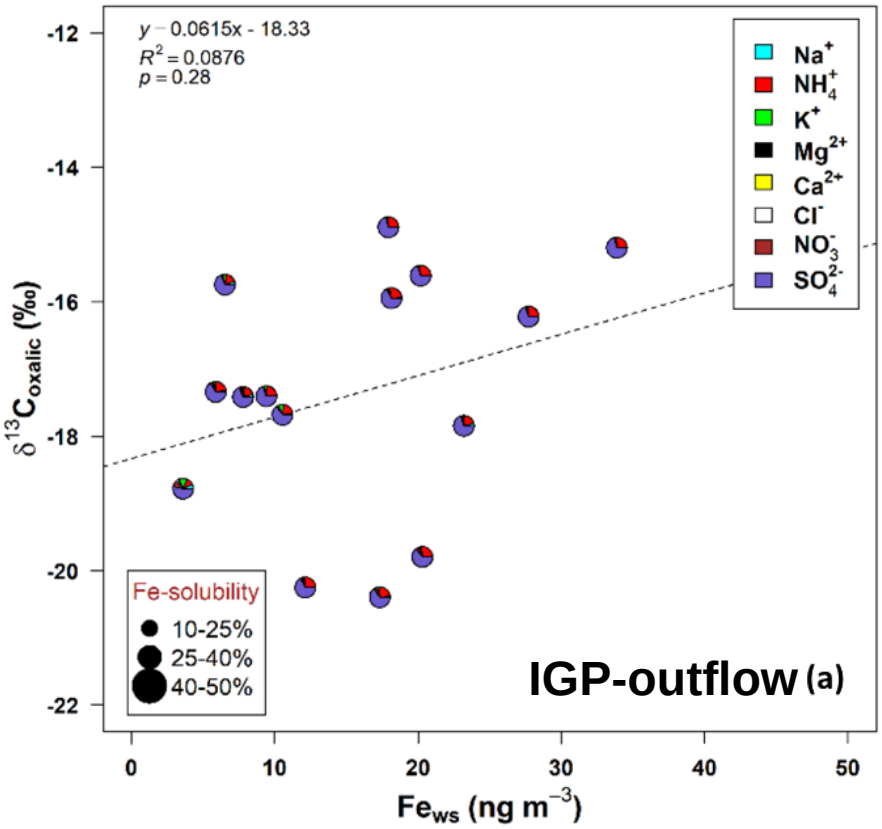
Case (i): WSOC + Fe_{Tot} (i.e., largely Fe^{3+}) → Oxalic acid + Fews (i.e., Fe^{2+})

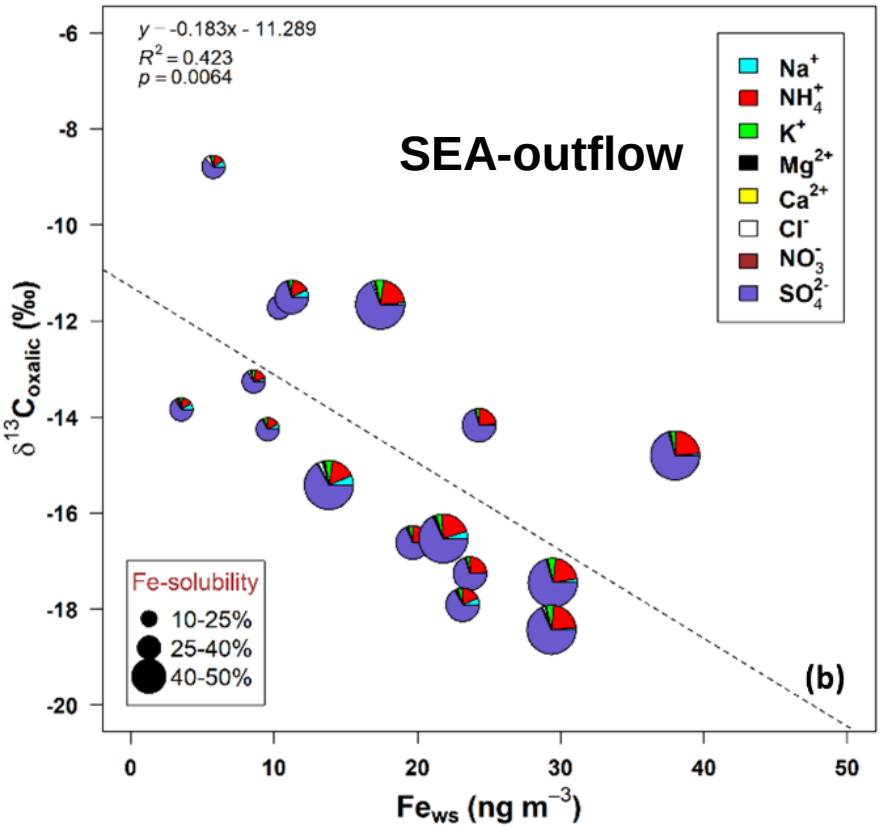
Case (ii): Oxalic acid + Fe_{Tot} (i.e., largely Fe^{3+}) → CO_2 + Fe_{ws} (i.e., Fe^{2+})



(Bikkina et la., submitted to Earth & Space Chemistry)

Relationship between soluble-Fe and $\delta^{13}C_{oxalic}$

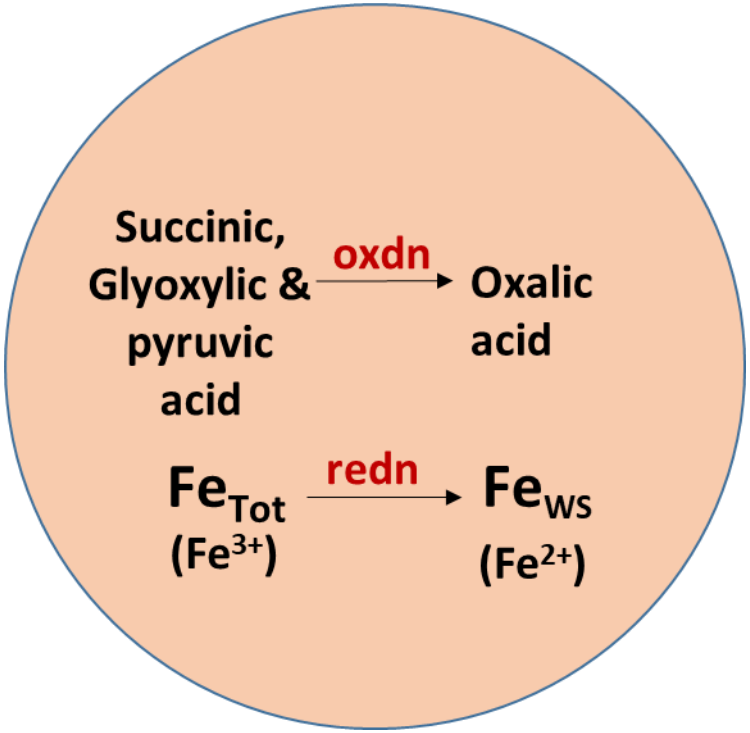


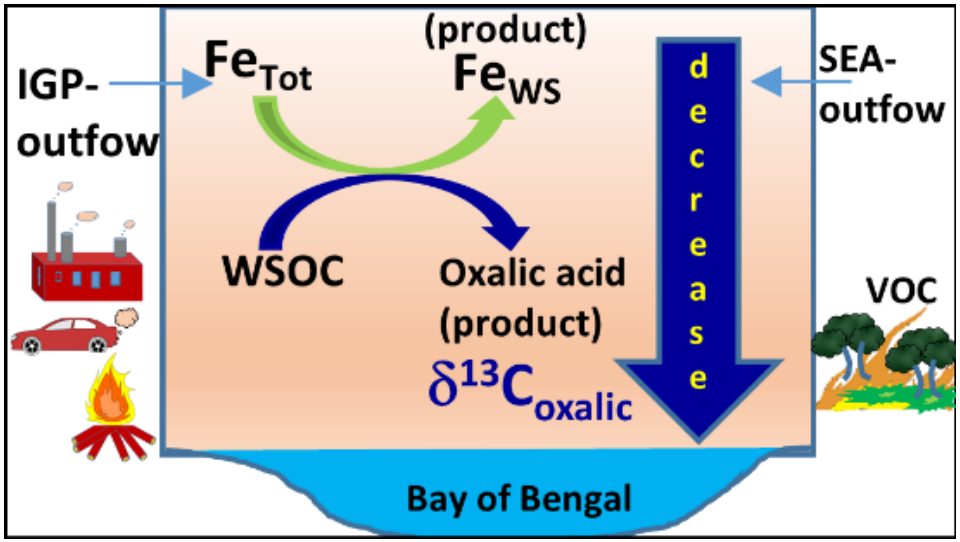


Case (i) => WSOC + Fe_{Tot} → Oxalic acid + Fe_{ws} (i.e., Fe^{2+})

(Bikkina et la., submitted to Earth & Space Chemistry)

☞ **Does the oxalate formation in the atmosphere promote more dust (Fe) dissolution and hence more soluble iron??**





☞ **In clouds/wet aerosols, aqueous phase photochemical oxidation of precursor organic acids to oxalic acid can cause dissolution of mineral dust.**

(Bikkina et la., submitted to Earth & Space Chemistry)

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