# Photochemical activity of seawater contaminated with red soil in the northern part of Okinawa

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## Introduction

Hydroxyl radical (·OH) as a most reactive oxidant, posses an oxidizing power to control the lifetime of many synthetic and natural organic compounds in natural waters. Northern part of Okinawa Main Island is experiencing high soil erosion rate, particularly by acidic reddish soil that contains about 3.3-5.3% of Fe. Past work has shown that low pH and high iron concentration favour OH formation in aquatic systems (Faust and Hoigné, 1990).

## Results and Discussion:

OH radical and Fe (II) photoproduction was examined in the mixture of either red soil in Milli-Q water or in Seawater. To study the effects of red soil particles, samples were divided into filtered (0.45µm) and unfiltered portions. The results are summarized in the table below.

| | OH formation rate (µM/hr) | Fe (II) formation rate (nM/hr) |
|---|---|---|
| Red soil in Milli-Q | | |
| Filtered | 0.08 | 21 |
| Unfiltered | 0.103 (+29%) | 47(+124%) |
| Fil. +130µM HOOH | 3.2 | - |
| Unf. +130µM HOOH | 8.5 (168%) | - |
| Red soil in seawater | | |
| Filtered | 0.086 | 13 |
| Unfiltered | 0.092 (7%) | 14 (+8%) |
| Fil. +130µM HOOH | 1.64 | - |
| Unf. +130µM HOOH | 1.76 (7%) | - |

The results suggest that irradiation of Fe particles could be a source of Fe (II) in solution as in the reaction; Fe (particulate) ? Fe (II). Photo-produced Fe (II) reacts faster with HOOH to form more ·OH radicals in the Fenton's reaction; Fe (II) + HOOH _ Fe (III) + ·OH + $OH^-$

## Conclusion:

Photo-dissolution of particulate iron in red soil polluted waters could be a source of Fe (II). In the presence of HOOH, red soil polluted waters could have higher oxidizing power.

## Reference

Faust B.C. and Hoigné J. (1990) *Atmos. Environ.*, 24A, 79-87.

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# Concentration and carbon isotope profiles of $CH_4$ in paddy rice canopy

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Methane concentration ($[CH_4]$) and carbon isotope fractionation ($\delta^{13}CH_4$) were measured (at 0.1, 0.3, 0.6, 1.0, and 5.0m above ground) within and above paddy rice canopy during the late growing season (plant heights varied from 0.8 to 1.1m). $[CH_4]$ and $\delta^{13}CH_4$ showed strong linear stratifications with height (in logarithmic scale) when the fields were flooded. The highest $[CH_4]$ and lowest $\delta^{13}CH_4$ values occurred near the soil surface. Maximum $[CH_4]$ and $\delta^{13}CH_4$ gradients (between the highest and lowest heights) were 0.75 ppm and 6.6 ‰, respectively. Daily fluctuations were found in the flooded and drained periods both, generally giving low $[CH_4]$ and high $\delta^{13}CH_4$ in daytime, high $[CH_4]$ and low $\delta^{13}CH_4$ in nighttime (approximately 1.0 ppm more concentrated and 5.0 ‰ lighter). Surface drainage initially caused both $[CH_4]$ and $\delta^{13}CH_4$ gradients to be more large (3.96 ppm and 19.8 ‰ on the 5th day after drainage) while maintaining the vertical stratifications of $[CH_4]$ and $\delta^{13}CH_4$ as in the flooded period. However, larger $[CH_4]$ gradients were found in daytime, which may indicate the post-drainage emissions were mainly controlled by soil temperature. 10 days after drainage, gradients and vertical stratification of $\delta^{13}CH_4$ were significantly reduced. It implies that $CH_4$ emission became less constant and that there was no dominant emission pathway, i.e., either through the soil surface or through the aerenchyma of the rice plants. By comparison with $\delta^{13}CH_4$ values from inverted dome and soil core samples, it was concluded that $CH_4$ emitted during the early period of drainage were originally stored in soils and that they were quickly released into air by disappearance of the diffusion barrier between soil and atmosphere. This change in transport pathways corresponded to the sudden emission peak of $CH_4$ (measured by the flux-gradient method). The enhanced $CH_4$ emission reached almost double the maximum emission rate (100 mg $CH_4$ $m^{-2}$ $d^{-1}$) during the flooded period and lasted for around 10 days. Throughout the experiment, highly significant relationship was observed between $[CH_4]$ and $\delta^{13}CH_4$ in canopy and canopy boundary layer. However, the normal Keeling plot approach (based on a linear relationship between $1/[CH_4]$ and $\delta^{13}CH_4$) was not successful to give a representative isotopic composition of the ecosystem. We tried to revise the Keeling plot method for $CH_4$ in several ways based on $[CH_4]$ and sampling heights, and examined their application to separation of $CH_4$ transport pathways during the flooded and drained periods.