STABLE CARBON AND NITROGEN ISOTOPIC COMPOSITION OF BIOMASS BURNING AEROSOLS AND THEIR MOLECULAR COMPOSITION OF DIACIDS AND RELATED COMPOUNDS: LBA-SMOCC CAMPAIGN FROM RONDÔNIA, BRAZIL

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Biomass burning aerosols & their role in atmosphere

1. TC & TN

2. δ[13]C of TC, WISOC and estimated WSOC

3. δ[15]N of TN, WISON & estimated WSN

4. Inorganic ions

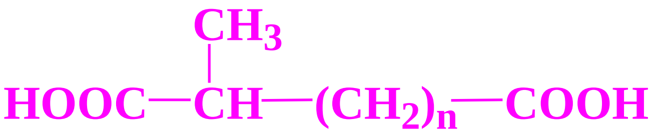
5. WSOC

6. WISOC & EC

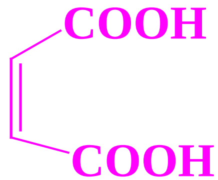
7. Pyrolysis products (Hoffer et al., 2006)

HOOC—$(CH_2)_n$—COOH

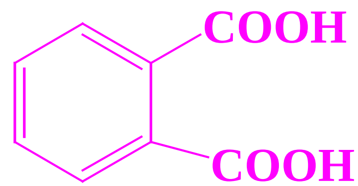
Straight chain diacids (n = 0-9)



Branched chain diacids n = (0-2)

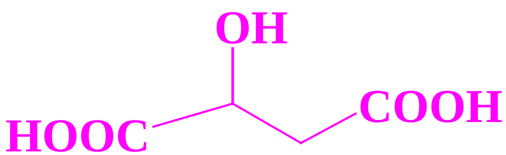


Maleic acid (M)

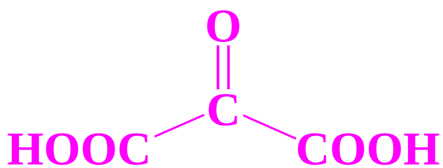


Phthalic acid (Ph)

Unsaturated diacids



Malic acid (hC4)

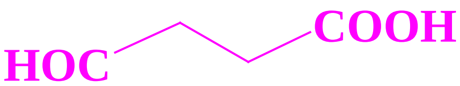


Ketomalonic acid (kC3)

Multifunctional diacids

HOC—COOH

Glyxylic acid (C2w)

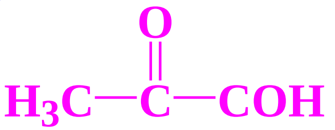


4-oxobutanoic acid (C4w)

Oxocarboxylic acids

HOC—COH

Glyoxal (Gly)



Methylglyoxal (Gly)

Dicarbonyls

Selected diacids and related compounds

Purpose of this study

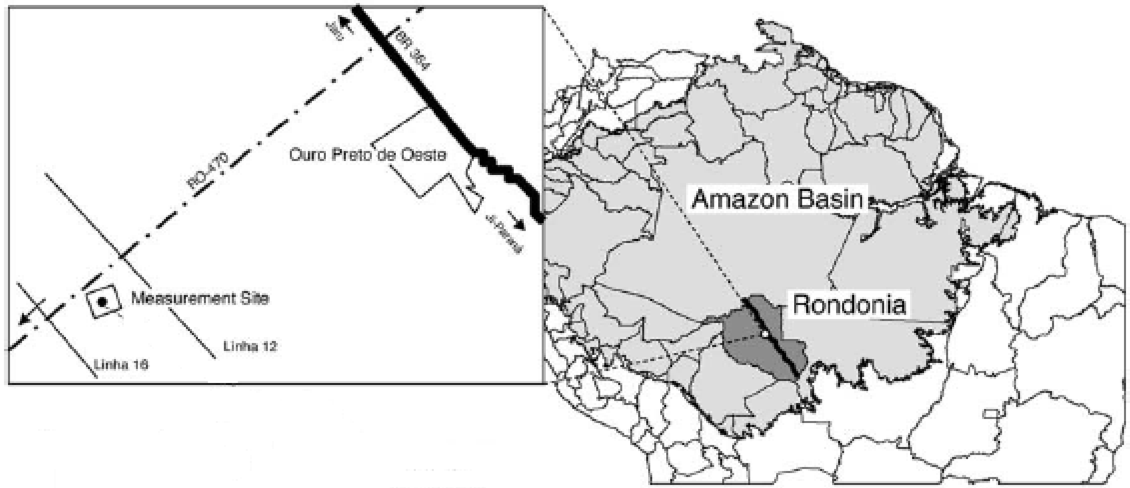
1. To better understand the molecular composition of diacids and related compounds in biomass burning influenced aerosols.

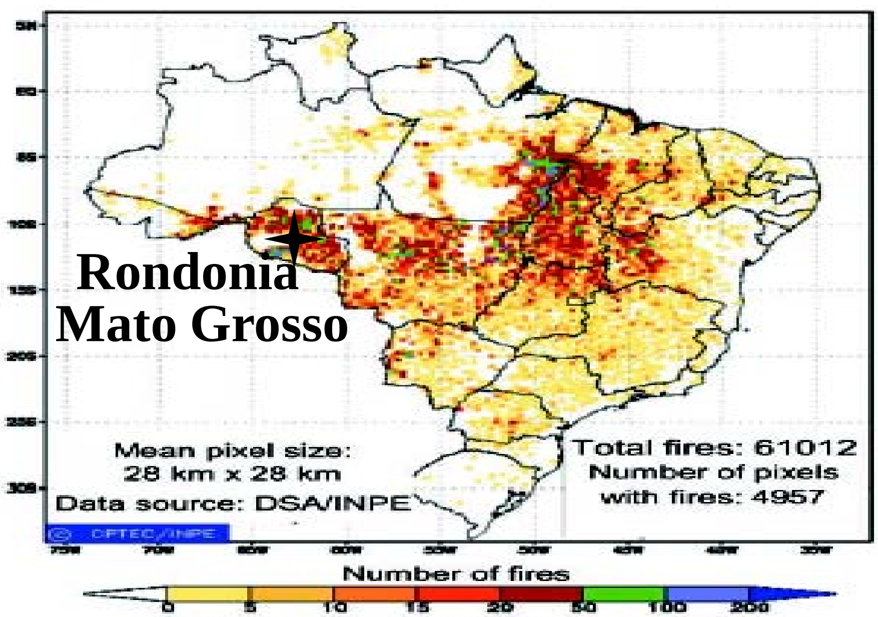
2. To understand the source of diacids and related compounds. Are they directly emitted from biomass burning or secondarily produced by the photo-oxidation of their products?

3. To apply the stable carbon and nitrogen isotopic ratios to better understand the sources of aerosol carbon and nitrogen in biomass burning aerosols.

Sampling site

Kirkman et al., 2002





Fuzzi et al., 2007

Filter sampling:

Sampler: High volume dichotomous sampler

Front: 11 samples

Back: 11 samples

Sampling period:

September 16 to 25, 2002

Duration: ~12 hours, 9 night-time samples and 2 day- time samples.

Meteorology:

CBL: 200-250 m at night while 1800-2000 m at noon

Analytical Techniques

1. Water extracts of aerosols are esterified by n-Butanol/BF_3 and then determined by GC-FID and GC-MS

2. TC & TN (EA)

3. $\delta^{13}C$ of TC, WISOC and estimated WSOC (EA/IRMS)

4. $\delta^{15}N$ of TN, WISON & estimated WSN (EA/IRMS)

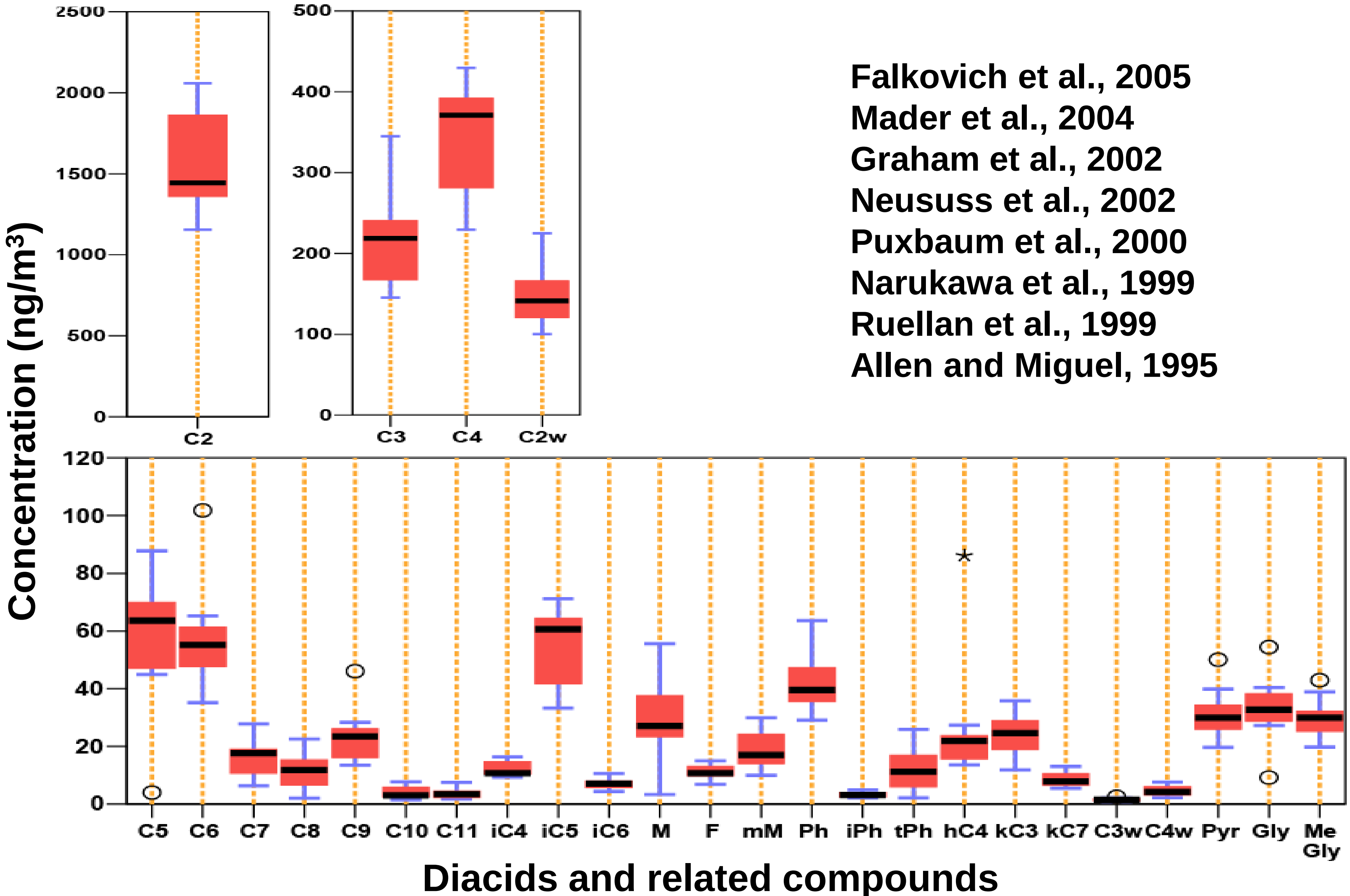
5. Major cations and anions (Metrohm IC)

6. WSOC (Shimadzu TOC 5000)

7. WISOC & EC (Sunset Lab OC/EC analyzer)

8. Pyrolysis products (GC/MS)

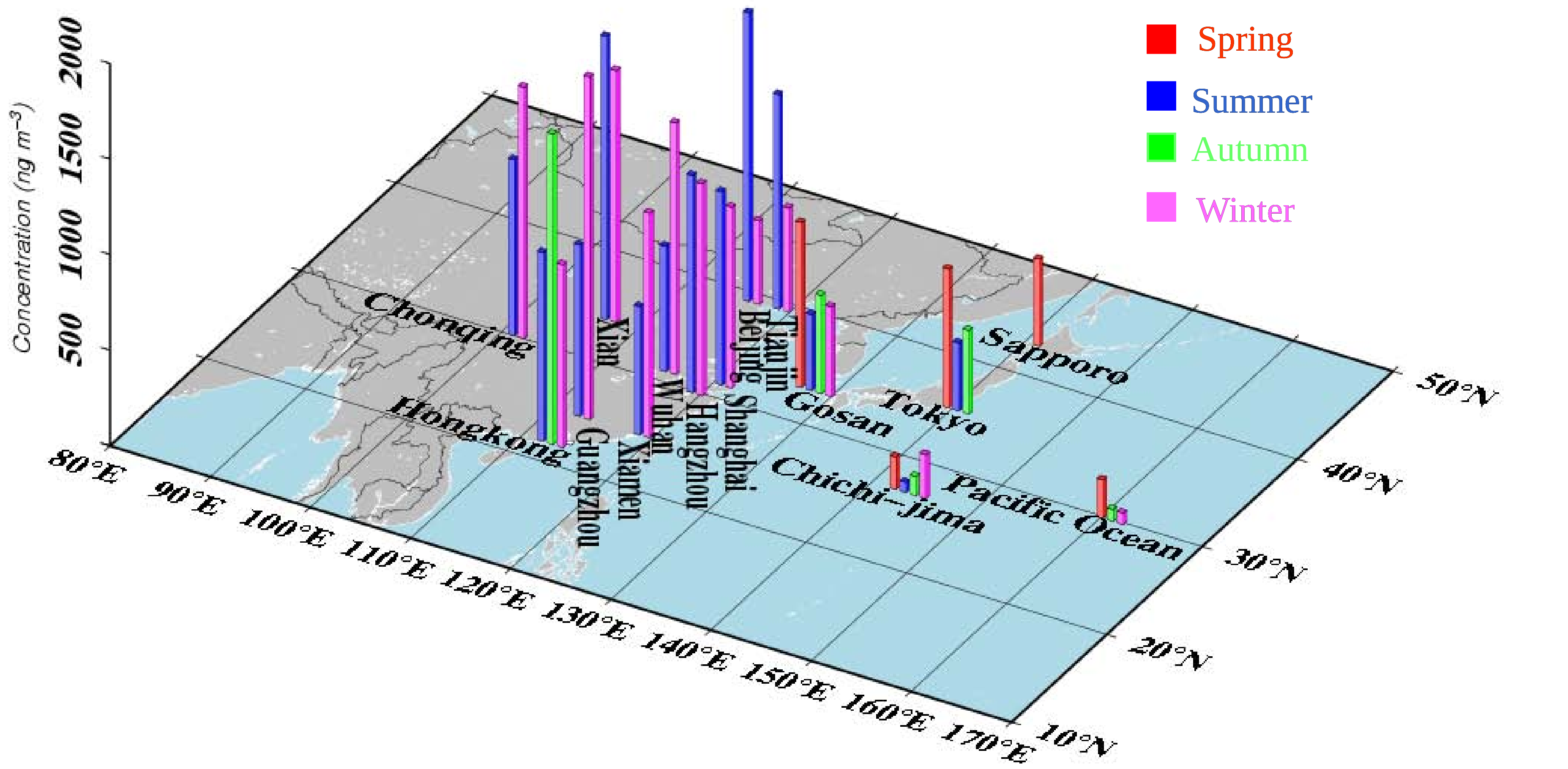
Molecular distributions and concentrations of diacids and related compounds in the biomass burning influenced aerosols (n=11)



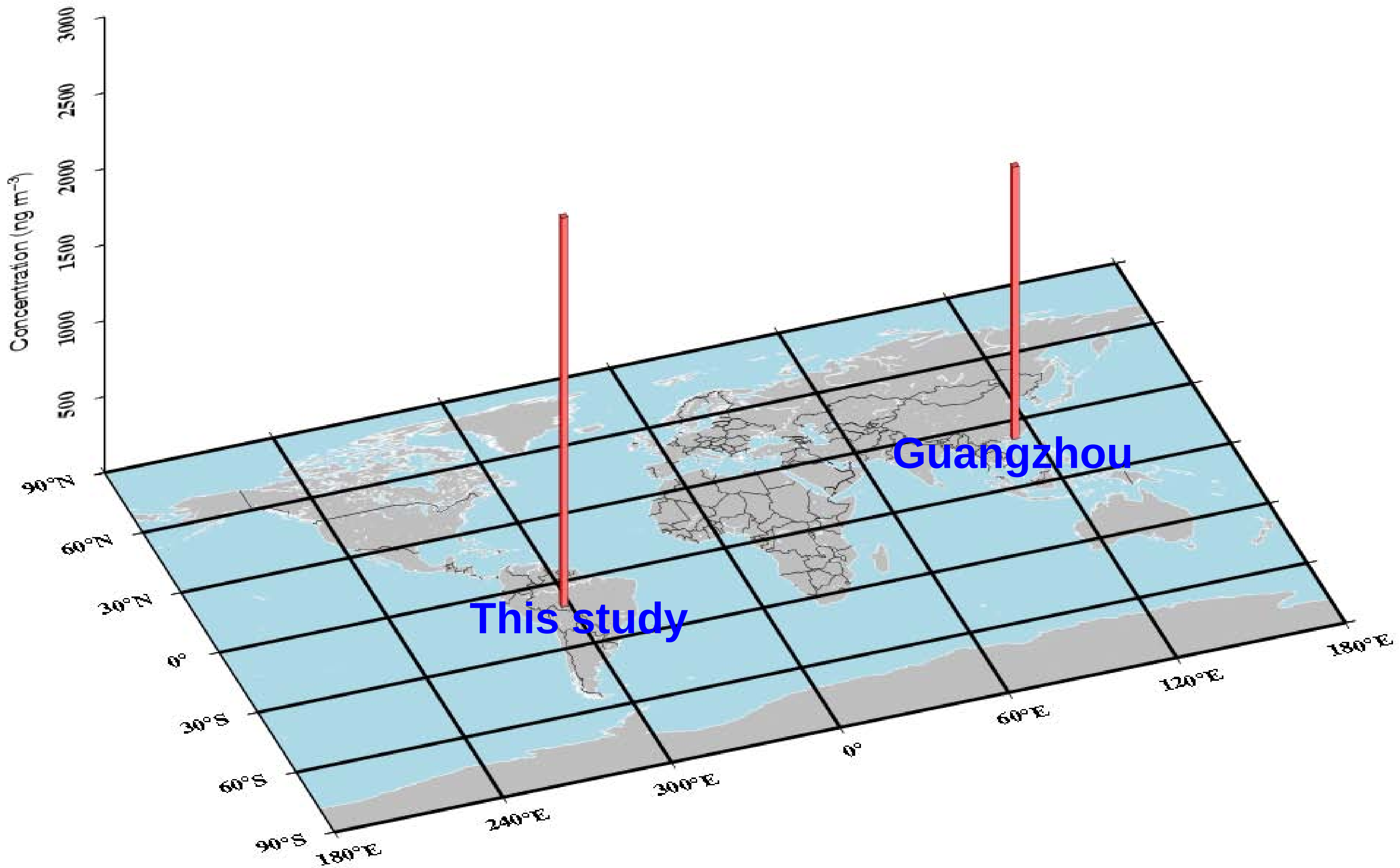
Falkovich et al., 2005
Mader et al., 2004
Graham et al., 2002
Neususs et al., 2002
Puxbaum et al., 2000
Narukawa et al., 1999
Ruellan et al., 1999
Allen and Miguel, 1995

Total diacids concentrations in aerosols from mega-cities in East Asia and remote marine atmosphere

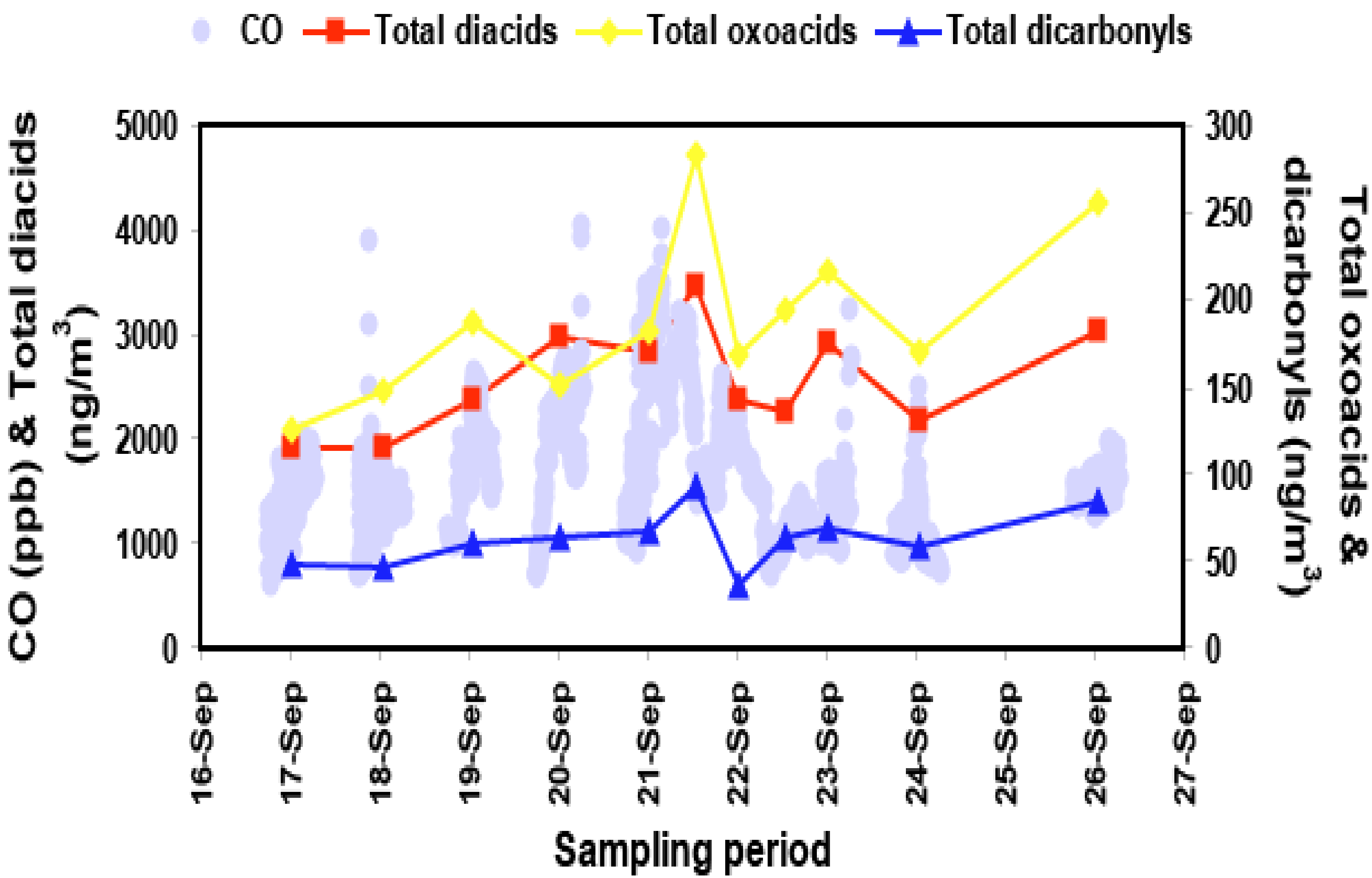
Datasets were collected from different papers.
All of these papers were published by Kawamura's group.



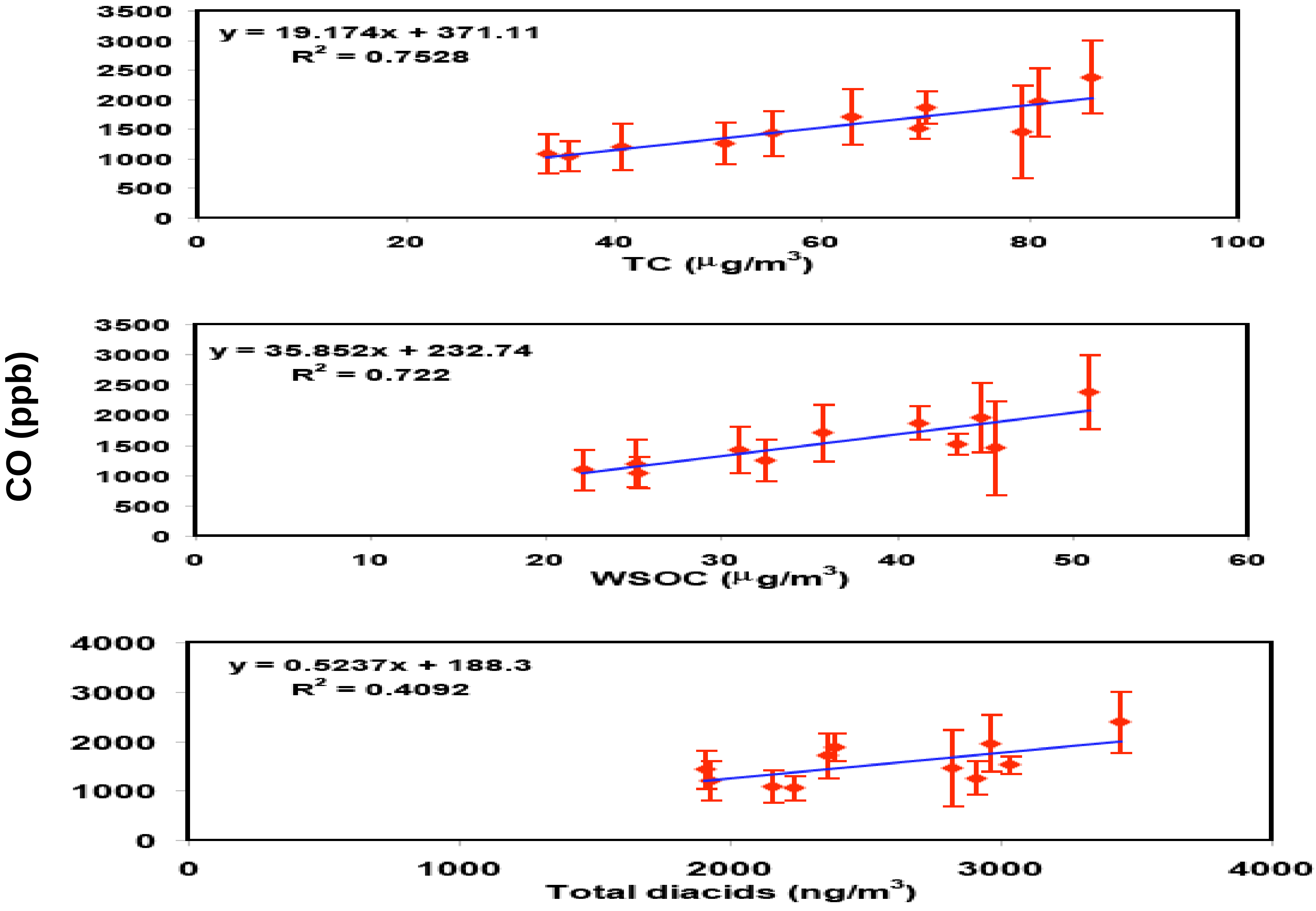
Average concentrations of total diacids in Rondonia and comparison to urban aerosols from Guangzhou, China



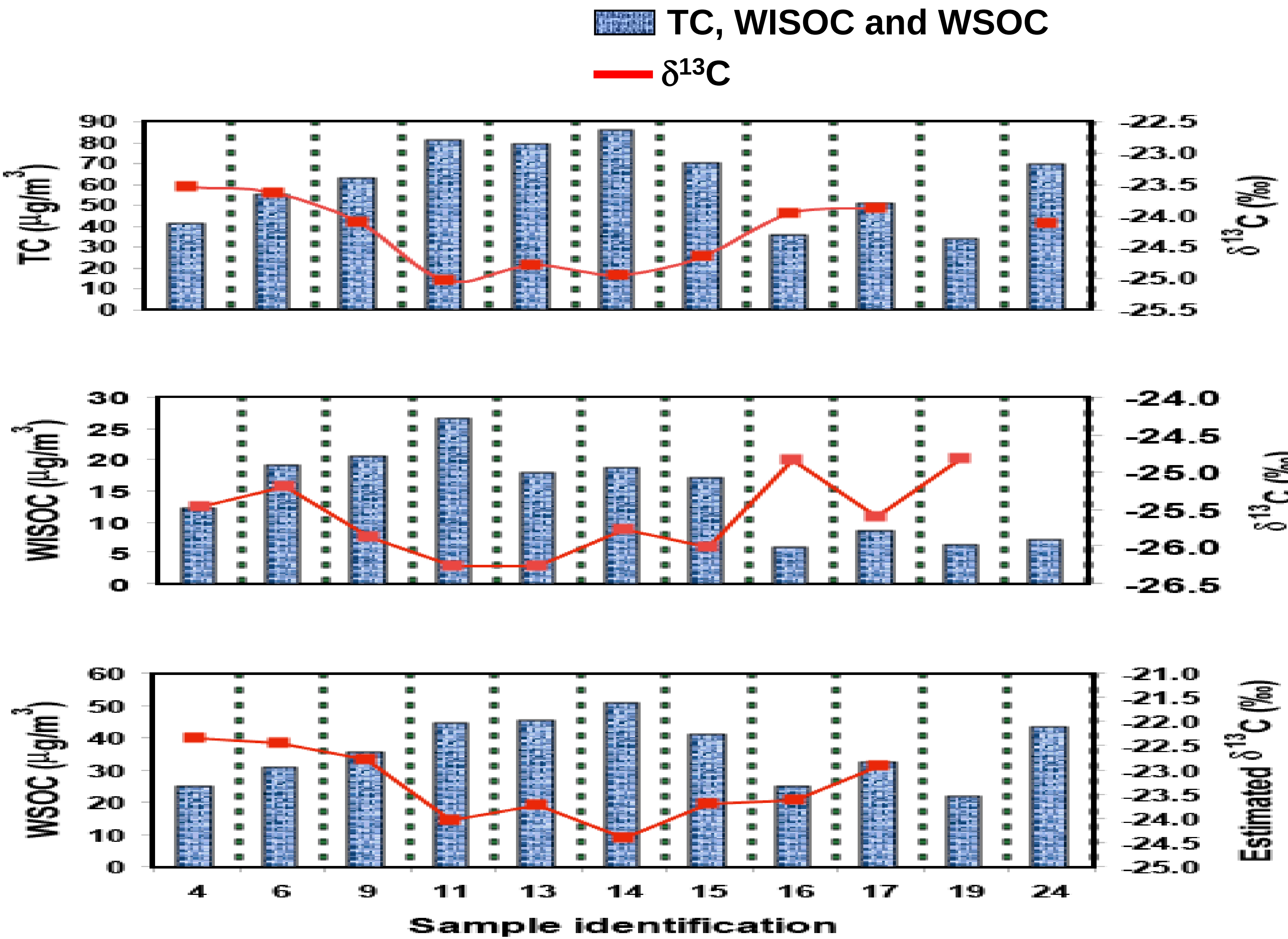
Temporal variation of diacids and related compounds with combustion tracer carbon monoxide (CO)



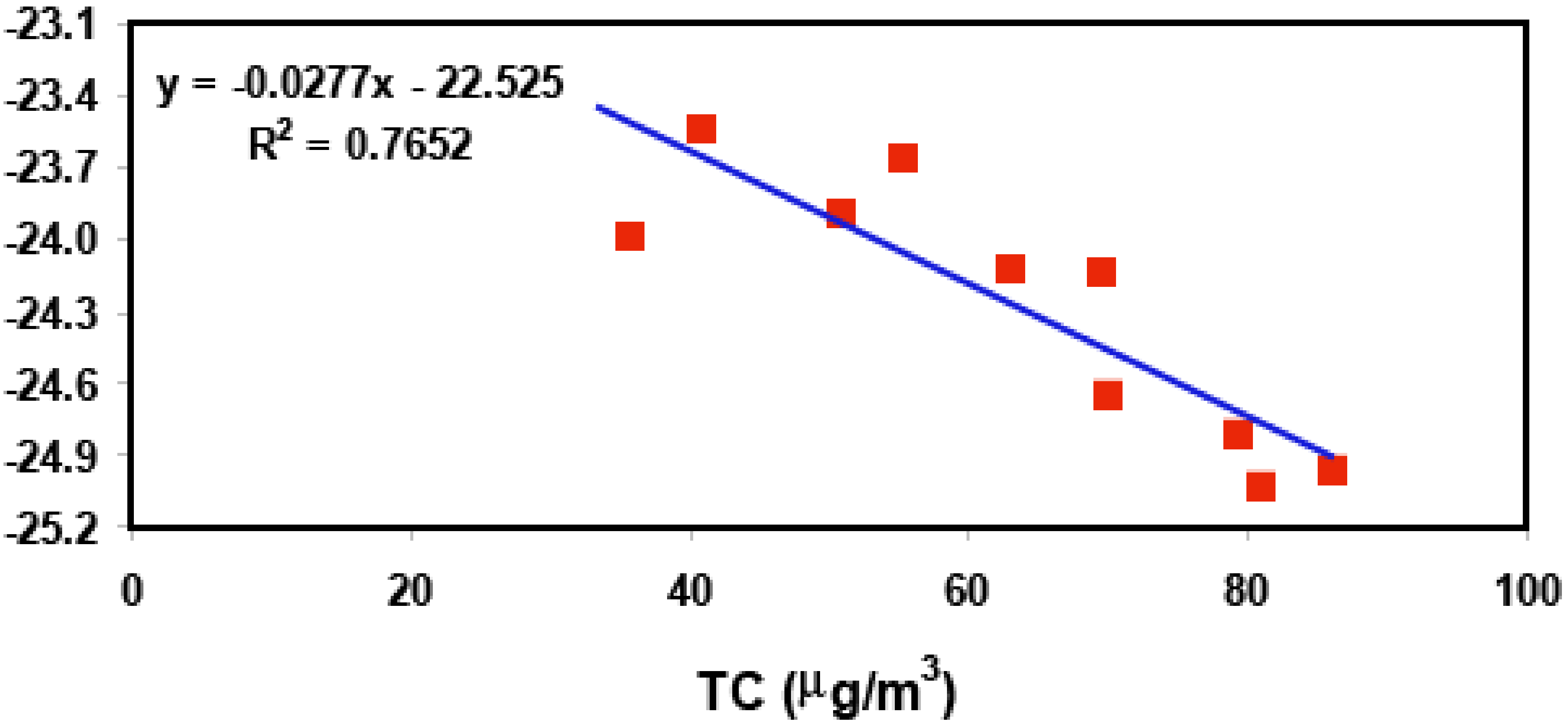
Correlation between (CO) and TC, WSOC and Total diacids



Stable carbon isotopic ratio of TC, WSOC and WISOC

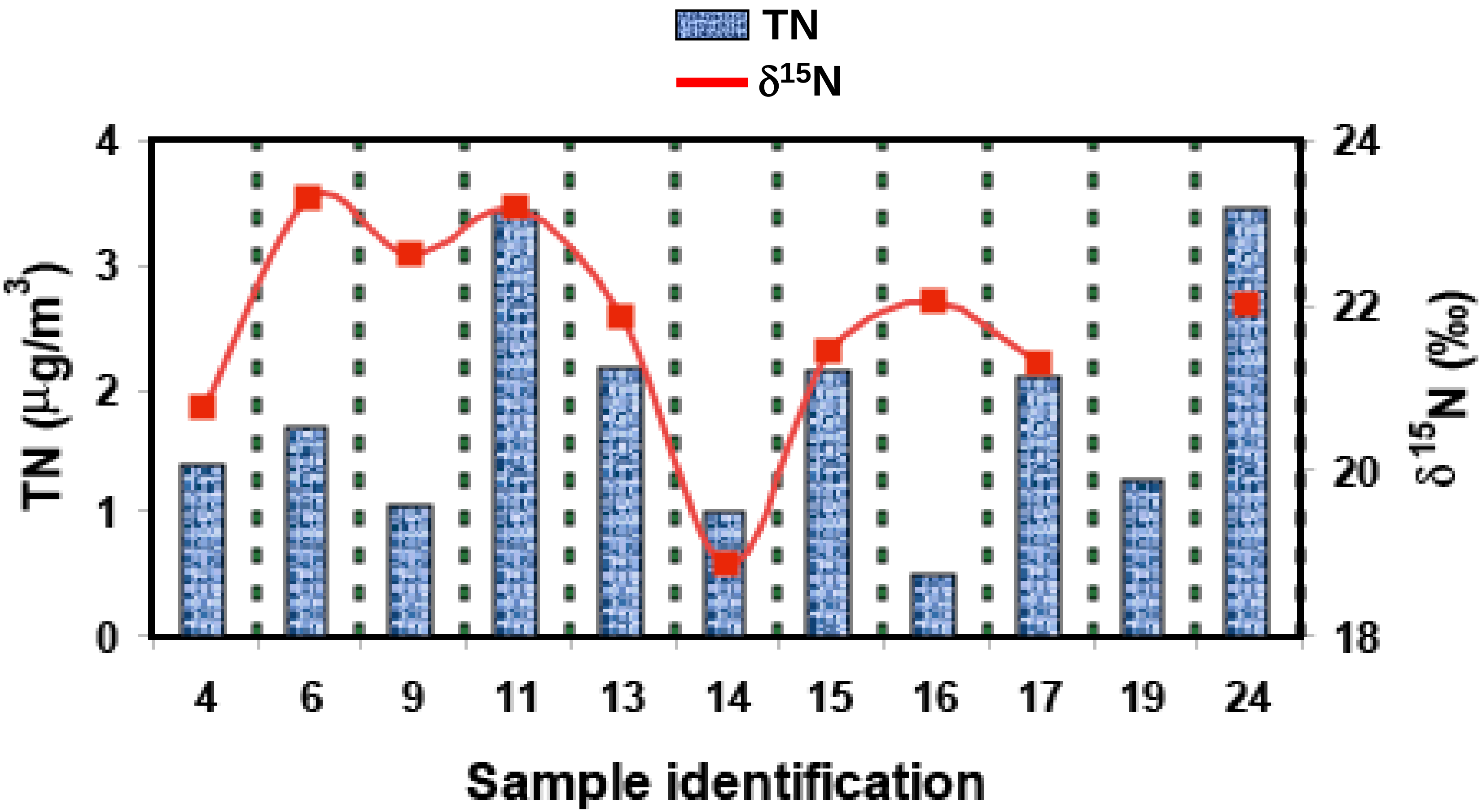


Relationship between stable carbon isotopic ratio and bulk carbon



Similar anti-correlation was obtained between $\delta^{13}C$ of WISOC and estimated WSOC versus WISOC and WSOC.

Nitrogen isotopic ratio of TN



Water insoluble organic nitrogen (WISON): 8.5 to 15.3‰, av. 11.8 ± 2.2‰

Estimated water soluble nitrogen (WSN): 22.73 ± 1.55‰

Conclusion

1. Biomass burning aerosols show high loadings of diacids and related compounds. This is the first report on diacids and related compounds in a range of C_2-C_{11} in biomass burning aerosols in Amazonia.

2. We found the predominance of oxalic acid (C_2) followed by C_4 and C_3. In the high molecular weight range, a large peak of azelaic acid (C_9) was found suggesting photooxidation of unsturated fatty acids.

3. A well correlation between diacids and related compounds with CO, K and EC suggests that diacids are directly emitted from biomass burning. However, secondary production of diacids should be important as no correlation was obtained between oxalic acid and levoglucosan.

4. Based on the anti-correlation between bulk carbon (TC, WSOC, & WISOC) and their $\delta^{13}C$, we suggest that biomass burning is the primary source of aerosol carbon, but its contribution changed significantly during the campaign.

5. Measured $\delta^{15}N$ of WISON is lower than that of TN and estimated WSN.

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1. ICCPA organizing committee for providing travel grant
2. Stefano Decessari for supplying CO, fire points and mass of $PM_{2.5}$ data
3. Ministry of Education Japan for providing the financial support of my Ph.D. study

THANKS

Mass balance equation for estimation of $\delta^{13}C_{WSOC}$

$$F_{WISOC} + F_{WSOC} = 1$$

$$F_{WISOC} = WISOC/TC$$

$$F_{WSOC} = (TC- WISOC)/TC$$

$$\delta^{13}C_{TC} = F_{WISOC} \quad \delta^{13}C_{WISOC} + F_{WSOC} \quad \delta^{13}C_{WSOC}$$

Mass balance equation for estimation of $\delta^{15}N_{WSN}$

$$F_{WISON} + F_{WSN} = 1$$

$$F_{WISON} = WISON/TN$$

$$F_{WSN} = (TN- WISON)/TN$$

$$\delta^{15}N_{TN} = F_{WISON} \quad \delta^{15}N_{WISON} + F_{WSN} \quad \delta^{15}N_{WSN}$$