# Journal Club LFA

## Análise Isotópica de Carbono para Identificação e Quantificação de Fontes de Aerossóis Carbonáceos

### Resultados Recentes e Perspectivas Científicas Futuras

**Djacinto Santos Junior**

djunior@if.usp.br

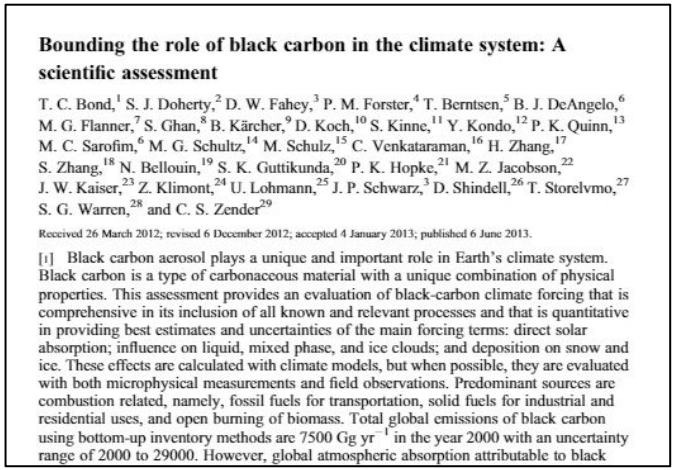
**30 Jan 2020**

# Aerossóis Carbonáceos

- Partículas contendo carbono em sua composição - exceto carbonatos.
- Efeitos diretos e indiretos no clima
- Qualidade do ar e impactos na saúde humana

Tradicionalmente dividido em:

- Carbono Orgânico (OC)
  - Centenas de compostos diferentes contendo carbono combinado com outros elementos como H, O, N, P, Cl, etc.
  - Primário ou Secundário
- Carbono Elementar (EC) ou Black Carbon (BC)
  - material refratário
  - *light-absorbing properties*
  - Aerossol Primário

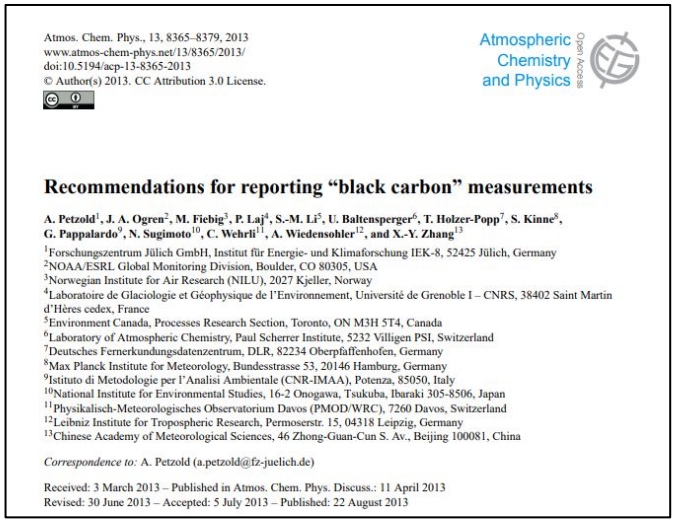


**Bounding the role of black carbon in the climate system: A scientific assessment**

T. C. Bond,[1] S. J. Doherty,[2] D. W. Fahey,[3] P. M. Forster,[4] T. Berntsen,[5] B. J. DeAngelo,[6] M. G. Flanner,[7] S. Ghan,[8] B. Kärcher,[9] D. Koch,[10] S. Kinne,[11] Y. Kondo,[12] P. K. Quinn,[13] M. C. Sarofim,[6] M. G. Schultz,[14] M. Schulz,[15] C. Venkataraman,[16] H. Zhang,[17] S. Zhang,[18] N. Bellouin,[19] S. K. Guttikunda,[20] P. K. Hopke,[21] M. Z. Jacobson,[22] J. W. Kaiser,[23] Z. Klimont,[24] U. Lohmann,[25] J. P. Schwarz,[3] D. Shindell,[26] T. Storelvmo,[27] S. G. Warren,[28] and C. S. Zender[29]

Received 26 March 2012; revised 6 December 2012; accepted 4 January 2013; published 6 June 2013.

[1] Black carbon aerosol plays a unique and important role in Earth's climate system. Black carbon is a type of carbonaceous material with a unique combination of physical properties. This assessment provides an evaluation of black-carbon climate forcing that is comprehensive in its inclusion of all known and relevant processes and that is quantitative in providing best estimates and uncertainties of the main forcing terms: direct solar absorption; influence on liquid, mixed phase, and ice clouds; and deposition on snow and ice. These effects are calculated with climate models, but when possible, they are evaluated with both microphysical measurements and field observations. Predominant sources are combustion related, namely, fossil fuels for transportation, solid fuels for industrial and residential uses, and open burning of biomass. Total global emissions of black carbon using bottom-up inventory methods are 7500 Gg $yr^{-1}$ in the year 2000 with an uncertainty range of 2000 to 29000. However, global atmospheric absorption attributable to black



Atmos. Chem. Phys., 13, 8365–8379, 2013
www.atmos-chem-phys.net/13/8365/2013/
doi:10.5194/acp-13-8365-2013


Atmospheric Chemistry and Physics Open Access

**Recommendations for reporting "black carbon" measurements**

**A. Petzold[1], J. A. Ogren[2], M. Fiebig[3], P. Laj[4], S.-M. Li[5], U. Baltensperger[6], T. Holzer-Popp[7], S. Kinne[8], G. Pappalardo[9], N. Sugimoto[10], C. Wehrli[11], A. Wiedensohler[12], and X.-Y. Zhang[13]**

[1]Forschungszentrum Jülich GmbH, Institut für Energie- und Klimaforschung IEK-8, 52425 Jülich, Germany
[2]NOAA/ESRL Global Monitoring Division, Boulder, CO 80305, USA
[3]Norwegian Institute for Air Research (NILU), 2027 Kjeller, Norway
[4]Laboratoire de Glaciologie et Géophysique de l'Environnement, Université de Grenoble I – CNRS, 38402 Saint Martin d'Hères cedex, France
[5]Environment Canada, Processes Research Section, Toronto, ON M3H 5T4, Canada
[6]Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland
[7]Deutsches Fernerkundungsdatenzentrum, DLR, 82234 Oberpfaffenhofen, Germany
[8]Max Planck Institute for Meteorology, Bundesstrasse 53, 20146 Hamburg, Germany
[9]Istituto di Metodologie per l'Analisi Ambientale (CNR-IMAA), Potenza, 85050, Italy
[10]National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Ibaraki 305-8506, Japan
[11]Physikalisch-Meteorologisches Observatorium Davos (PMOD/WRC), 7260 Davos, Switzerland
[12]Leibniz Institute for Tropospheric Research, Permoserstr. 15, 04318 Leipzig, Germany
[13]Chinese Academy of Meteorological Sciences, 46 Zhong-Guan-Cun S. Av., Beijing 100081, China

*Correspondence to:* A. Petzold (a.petzold@fz-juelich.de)

Received: 3 March 2013 – Published in Atmos. Chem. Phys. Discuss.: 11 April 2013
Revised: 30 June 2013 – Accepted: 5 July 2013 – Published: 22 August 2013

Atmospheric Environment 144 (2016) 226–233

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

# Ambient concentrations and insights on organic and elemental carbon dynamics in São Paulo, Brazil

Djacinto A. Monteiro dos Santos [a, *], Joel F. Brito [a, 1], José Marcus Godoy [b], Paulo Artaxo [a]

[a] Instituto de Física, Universidade de São Paulo, Rua do Matão 1371, CEP 05508-090, São Paulo, SP, Brazil
[b] Departamento de Química, Pontifícia Universidade Católica do Rio de Janeiro, Rua Marquês de São Vicente 225, Gávea, 22453-900, Rio de Janeiro, RJ, Brazil

## HIGHLIGHTS

- Carbonaceous particles dominate $PM_{2.5}$ concentrations in São Paulo.
- Campaign averaged OC:EC ratio for the sampling sites ranged from 0.56 to 1.89.
- Contribution of secondary OC was estimated around 30–40% for all sites.
- The OC3 and OC4 fractions depict a more regional behavior across sampling sites.
- The OC1 fraction is identified to be more dependent of local sources.

Atmos. Chem. Phys., 13, 12199–12213, 2013
www.atmos-chem-phys.net/13/12199/2013/
doi:10.5194/acp-13-12199-2013


Atmospheric Chemistry and Physics Open Access

# Physical–chemical characterisation of the particulate matter inside two road tunnels in the São Paulo Metropolitan Area

**J. Brito[1], L. V. Rizzo[2], P. Herckes[3], P. C. Vasconcellos[4], S. E. S. Caumo[4], A. Fornaro[5], R. Y. Ynoue[5], P. Artaxo[1], and M. F. Andrade[5]**

[1]Physics Institute, University of São Paulo, Brazil
[2]Department of Earth and Exact Sciences, Federal University of São Paulo, Brazil
[3]Department of Chemistry and Biochemistry, Arizona State University, Tempe, USA
[4]Chemistry Institute, University of São Paulo, Brazil
[5]Institute of Astronomy, Geophysics, and Atmospheric Sciences, University of São Paulo, Brazil

*Correspondence to:* J. Brito (jbrito@if.usp.br)

cuss.: 9 August 2013
Published: 17 December 2013

bonaceous aerosol measurement, polycyclic aromatic hydro-

Atmos. Chem. Phys., 11, 2747–2764, 2011
www.atmos-chem-phys.net/11/2747/2011/
doi:10.5194/acp-11-2747-2011


Atmospheric Chemistry and Physics

# Sources of carbonaceous aerosol in the Amazon basin

**S. Gilardoni[1], E. Vignati[1], E. Marmer[1], F. Cavalli[1], C. Belis[1], V. Gianelle[2], A. Loureiro[3], and P. Artaxo[3]**

[1]Joint Research Centre, Institute for Environment and Sustainability, Climate Change Unit, Ispra, Italy
[2]ARPA Lombardia, via F. Restelli 3/1, Milan, Italy
[3]Instituto de Fisica, Universidade de São Paolo, Rua do Matao, Sao Paulo, Brazil

Received: 6 October 2010 – Published in Atmos. Chem. Phys. Discuss.: 9 December 2010
Revised: 14 March 2011 – Accepted: 15 March 2011 – Published: 24 March 2011

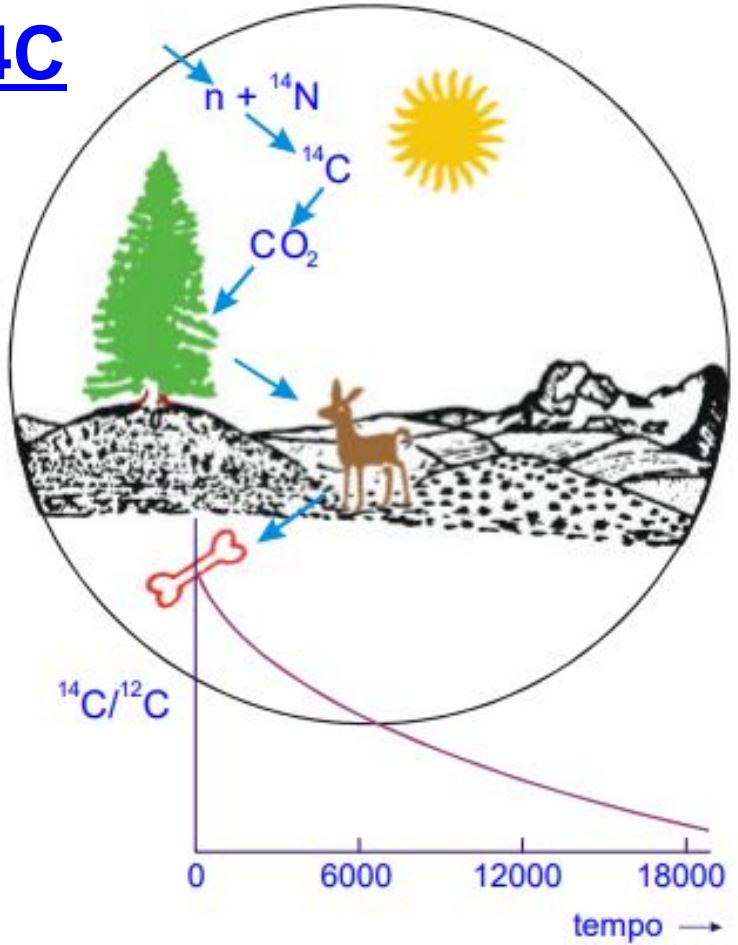
**Abstract.** The quantification of sources of carbonaceous aerosol is important to understand their atmospheric concentrations and regulating processes and to study possible effects on climate and air quality, in addition to develop mitigation strategies.

In the framework of the European Integrated Project on

ground site. The comparison showed an overestimation of elemental carbon (EC) by the TM5 model during the dry season and OC both during the dry and wet periods. The overestimation was likely due to the overestimation of biomass burning emission inventories and SOA production over tropical areas.

# O método de datação por 14C

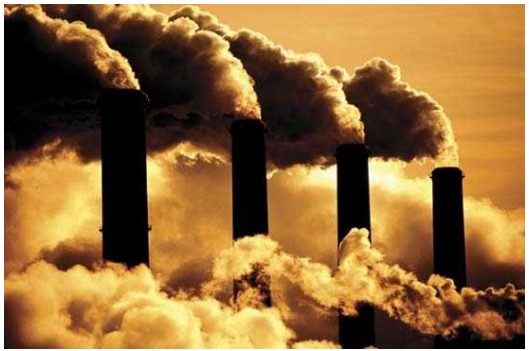
- Produção contínua de carbono radioativo (14C) na alta atmosfera, pela interação de nêutrons cósmicos com átomos de nitrogênio
- O 14C é oxidado a 14CO2 e entra no ciclo global do carbono
- Plantas assimilam 14C durante a fotossíntese e animais comem plantas
- Na morte das plantas ou animais a entrada do 14C cessa



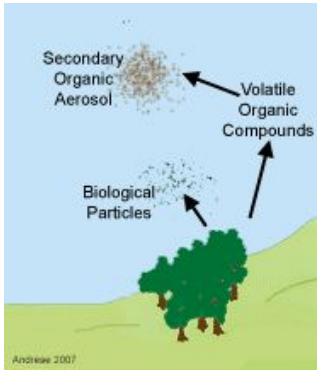

Fonte:http://apostilas.cena.usp.br/moodle/pessenda/livro/

# Uso da assinatura de 14C em aerossóis carbonáceos

- Emissões resultantes da queima de combustíveis **fósseis** são **livres de 14C**



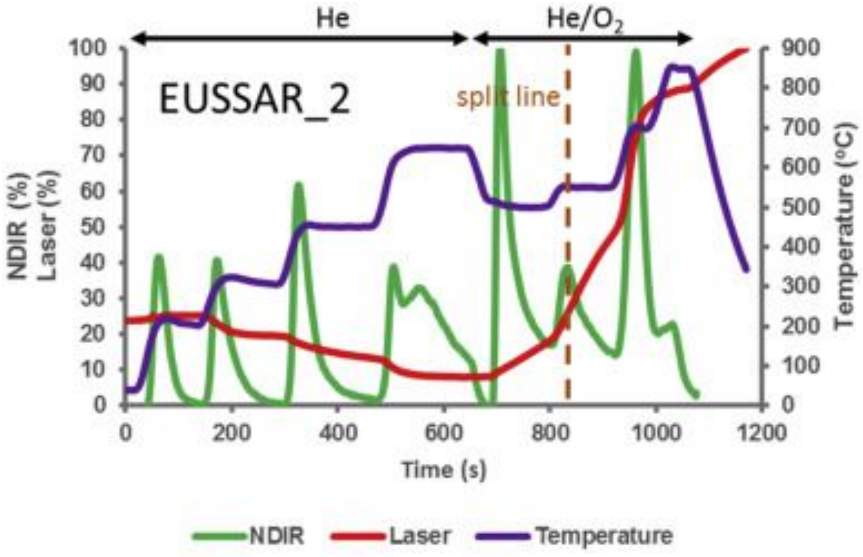
- Emissões resultantes de **biomassa contemporânea** têm **razão 14C/12C característica**



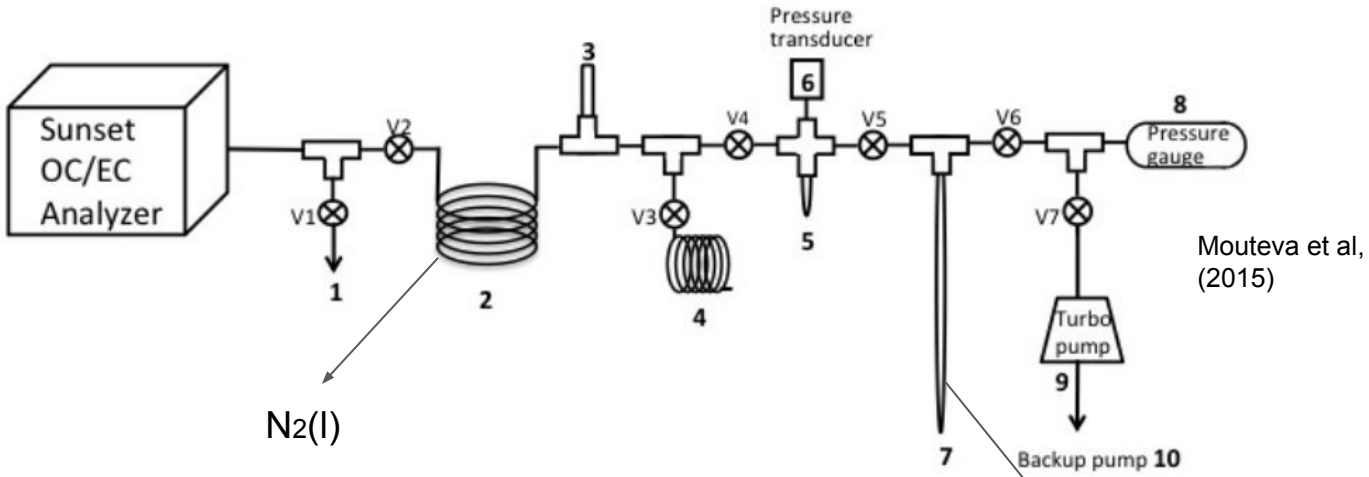

**Ideia central:** separar as componentes fóssil e de biomassa contemporânea no aerossol carbonáceo (EC e OC)

# Analisador de Carbono Sunset

- Método termo-óptico
- Rampas de temperatura
- Evaporação de frações de OC em atmosfera inerte (He)
- Oxidação de frações de EC em atmosfera de He/Ox
- Fragmentos de carbono são convertidos em CO2 e medidos pelo detector por ionização de chama (FID)
- Protocolo de temperatura EUSAAR2
- OC/EC split point definido pela transmitância do laser



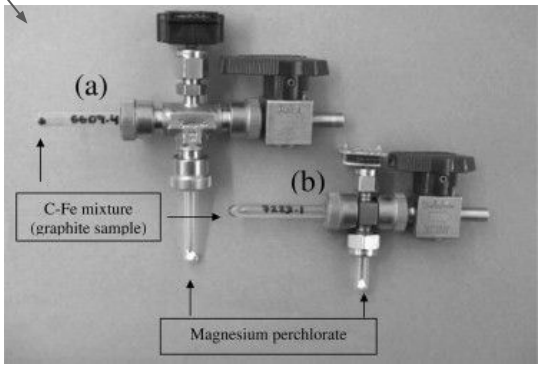
- Analisador de carbono acoplado a uma linha de vácuo




Mouteva et al, (2015)

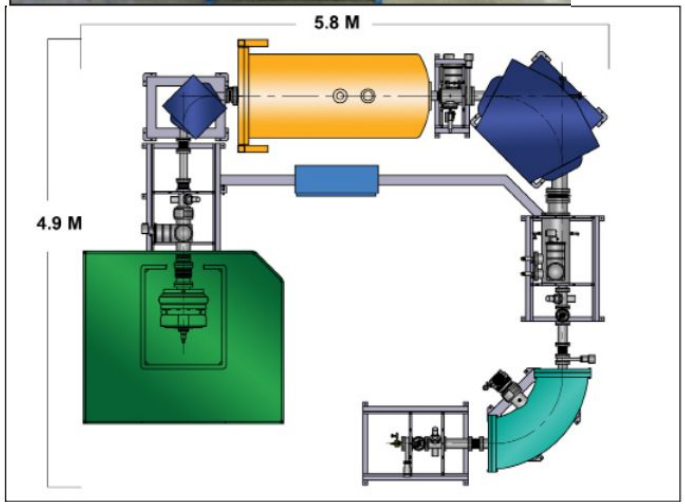
- Aprisionamento criogênico de CO2

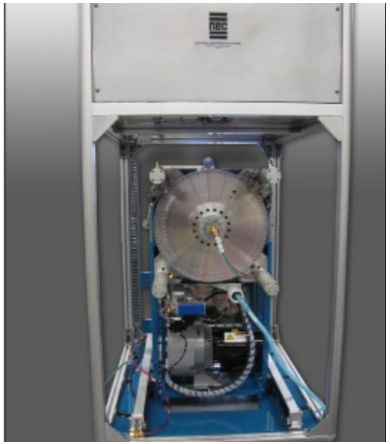
- **CO2 é is reduced to graphite** at 450°C using hydrogen gas over pre-cleaned iron powder as a catalyst.




Santos et al (2007)

# Accelerator Mass Spectrometry (KKCAMS)



https://sites.uci.edu/kccams
http://www.pelletron.com/products/

- High precision measurement of carbon radioisotope ratios
- The sample is converted to negative ions and is accelerated through the spectrometer for a mass separation

**modern fraction $f_M$** - the deviation of the 14C/12C ratio of the sample from modern, defined as 95% of the 14C concentration of the standard OX-I (or NIST HOxI SRM 4990B) in 1950 [Stuiver and Polach, 1977] (Beverly et al. 2010)

# Radiocarbon-Based Source Apportionment

$$f_{M(C)} \times C = f_{M(fossil)} \times C_{fossil} + f_{M(bio)} \times (C - C_{fossil})$$

- $C$ - Concentração medida (BC ou OC)
- $f_M$ - fração moderna medida (BC ou OC)
- $f_{M(fóssil)}$ - assinatura de combustíveis fósseis ( = 0, 14C free)
- $f_{M(bio)}$ - assinatura de biomassa ( > 0, material contemporâneo)
  - folhas (proxy for emissions of biogenic VOCs), fM = 1.019
  - fumaça de queima de lenha (proxy for emissions from wood burning), fM = 1.041

# Using radiocarbon to constrain black and organic carbon aerosol sources in Salt Lake City

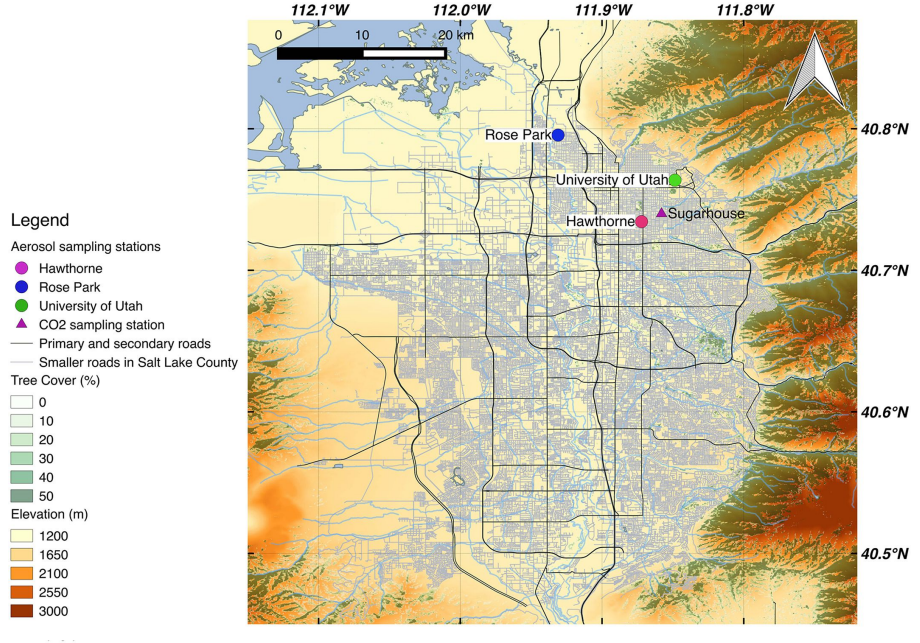
**Gergana O. Mouteva[1], James T. Randerson[1], Simon M. Fahrni[1,2], Susan E. Bush[3], James R. Ehleringer[3], Xiaomei Xu[1], Guaciara M. Santos[1], Roman Kuprov[4], Bret A. Schichtel[5], and Claudia I. Czimczik[1]**

[1]Department of Earth System Science, University of California, Irvine, California, USA, [2]Now at the Eidgenössische Technische Hochschule (ETH), Zürich, Switzerland, [3]Department of Biology, University of Utah, Salt Lake City, Utah, USA, [4]Division of Air Quality, Utah Department of Environmental Quality, Salt Lake City, Utah, USA, [5]National Park Service, Washington, District of Columbia, USA

**Abstract** Black carbon (BC) and organic carbon (OC) aerosols are important components of fine particulate matter ($PM_{2.5}$) in polluted urban environments. Quantifying the contribution of fossil fuel and biomass combustion to BC and OC concentrations is critical for developing and validating effective air quality

# BC and OC aerosols sources in Salt Lake City

- Três sítios - urban, industrial and suburban
- Outubro de 2012 a agosto de 2013 (41 amostras)
- Episódios de inversão térmica durante o inverno com elevadas concentrações de PM2.5 (> 35 ugm-3, 24h average)

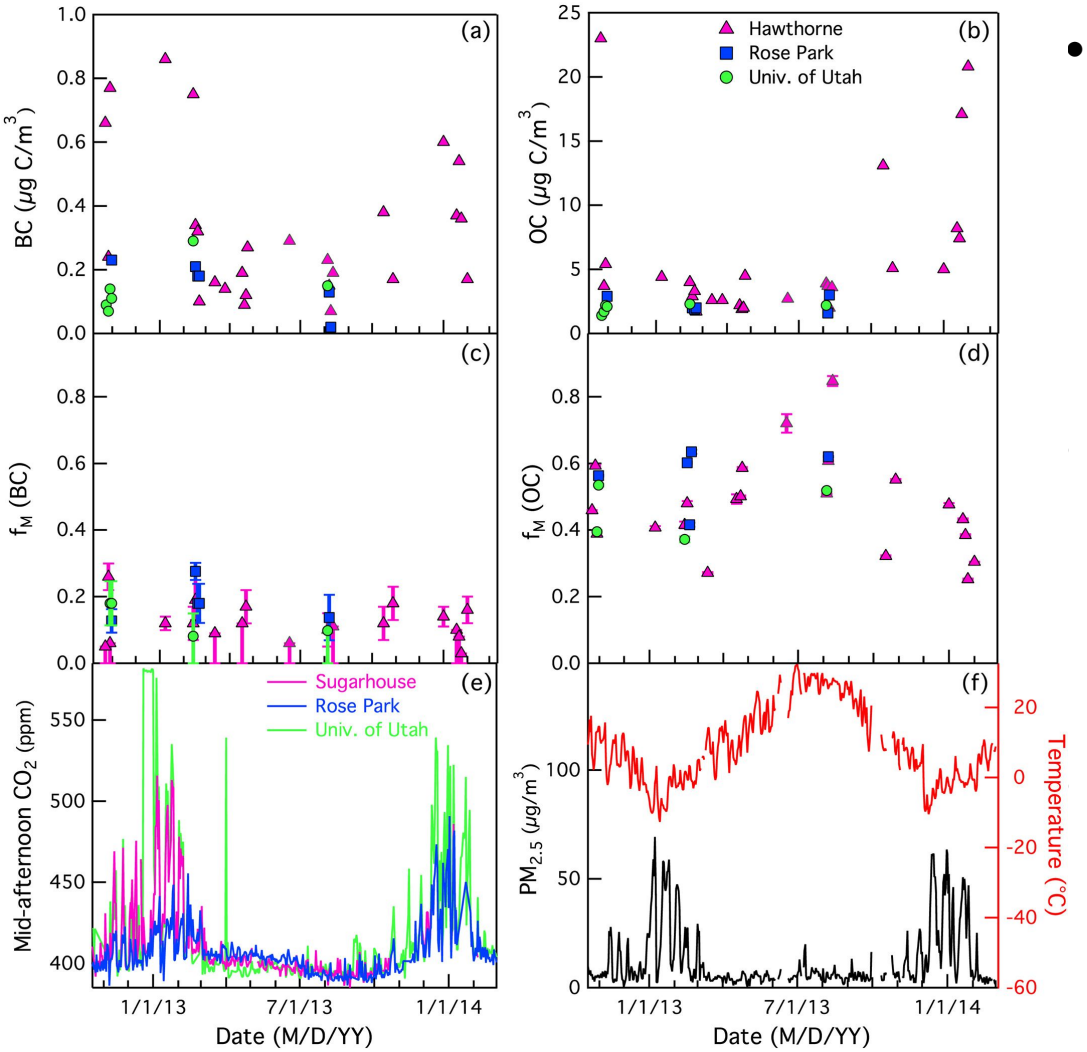



- Emissões veiculares são a principal fonte de PM2.5.
- *Area sources* (home heating, construção, agricultural burning, geração de energia, wildfires e emissões biogênicas) são a segunda maior fonte

- Concentrações de BC mais elevadas durante o inverno (0.38 ugm-3) e mais baixas no verão (0.15 ugm-3)

- *f*M do BC relativamente uniforme ao longo do ano (*f*M = 0.13)

- Nenhuma variação significativa entre os diferentes sítios tanto para BC quanto OC.



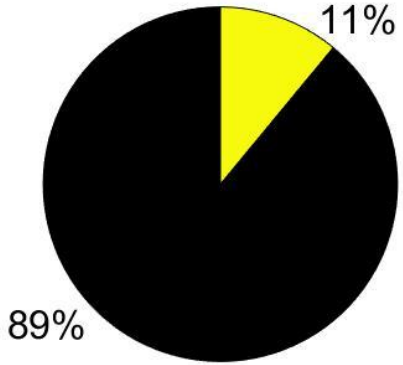

- Maior variabilidade. Concentrações mais elevadas durante o outono (6.1ugm-3) e mais baixas durante a primavera (2.6ugm-3)

average *f*M = 0.50 para OC. Valores menores no inverno (0.43) e significativamente maiores no verão (0.64).

Nenhuma distinção entre o *f*M para OC ou BC nos episódios de inversão térmica

# fossil x non-fossil carbonaceous aerosols

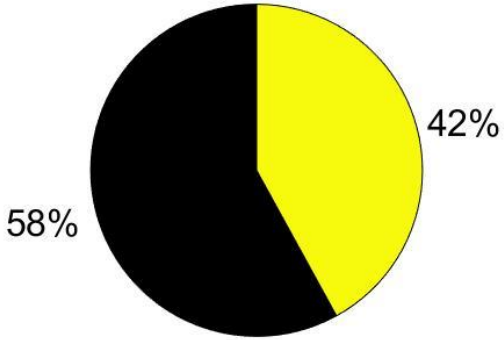
## Black Carbon



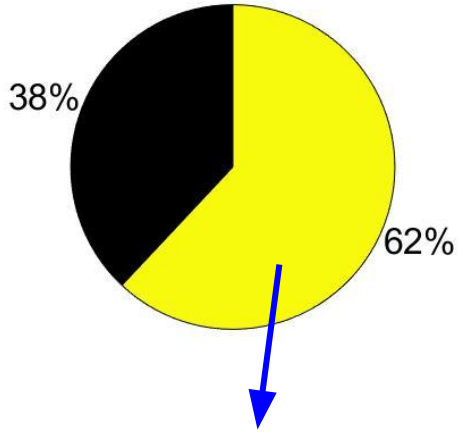


## Organic Carbon

### Inverno




### Verão




**Oxidação de BVOC's**

# Conclusões

- **First study in the U.S.** which separately evaluates the 14C content of BC and OC aerosols.
- **Similar results have been observed in other metropolitan areas** (Milan, Zurich, London and for Chinese megacities). Fossil fuel = 75-93% BC e 32-45% OC.
- **One major challenge** with respect to the successful application of 14C for source apportionment of BC and OC is the complete physical separation of the two fractions without cross-fraction interference and with minimal contamination from background carbon.
- Aside from the time-consuming nature of these measurements, **another limiting factor is the collection of sufficient aerosol mass** to prepare targets suitable for the accelerator mass spectrometer
- Our results suggest that the use of 14C for monitoring BC and OC aerosols **may improve our understanding of source composition in other nonattainment areas**, and **long-term time series** may provide information about the success of different climate and air pollution mitigation policies.

PNAS

# Smoke radiocarbon measurements from Indonesian fires provide evidence for burning of millennia-aged peat

Elizabeth B. Wiggins[a,1], Claudia I. Czimczik[a], Guaciara M. Santos[a], Yang Chen[a], Xiaomei Xu[a], Sandra R. Holden[a], James T. Randerson[a,1], Charles F. Harvey[b,c], Fuu Ming Kai[b,2], and Liya E. Yu[d,e]

[a]Department of Earth System Science, University of California, Irvine, CA 92697; [b]Center for Environmental Sensing and Modeling, Singapore-MIT Alliance for Research and Technology, 138602 Singapore; [c]Parsons Laboratory, Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, MA, 02139; [d]Department of Civil & Environmental Engineering, National University of Singapore, 119260 Singapore; and [e]National University of Singapore Environmental Research Institute, National University of Singapore, 119260 Singapore

Contributed by James T. Randerson, October 11, 2018 (sent for review April 13, 2018; reviewed by Meinrat O. Andreae, Robert D. Field, and Susan E. Page)

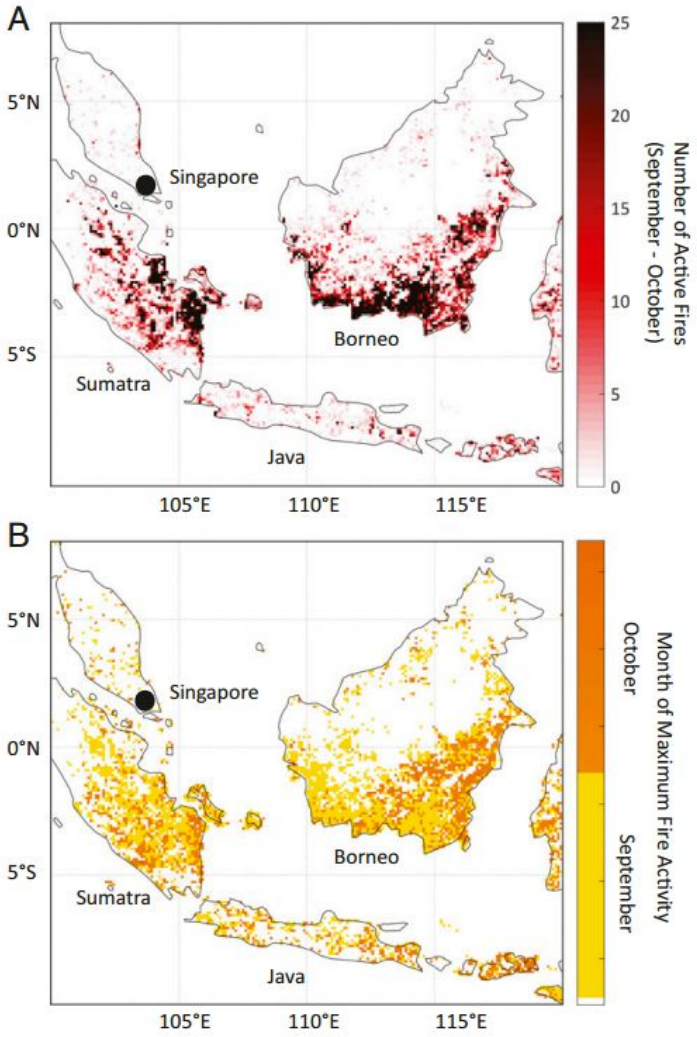
**In response to a strong El Niño, fires in Indonesia during September and October 2015 released a large amount of carbon dioxide and created a massive regional smoke cloud that severely degraded air quality in many urban centers across Southeast Asia. Although several lines of evidence indicate that peat burning was a dominant contributor to emissions in the region, El Niño-induced drought is**

and benefits of these land use practices operate on different spatial and temporal scales, making it difficult to design effective policy and management solutions (13).

The extreme 2015 fire season was a part of a broader set of climate–human–ecosystem interactions across the Maritime Continent that have been evolving over a period of decades from

# Materials and Methods

- Weekly air samples of PM2.5 at the National University of Singapore
- September–October fire seasons of 2014 and 2015 (strong El Niño)
- PM2.5 samples were analyzed for their 14C and TC content at the KCCAMS at the University of California, Irvine

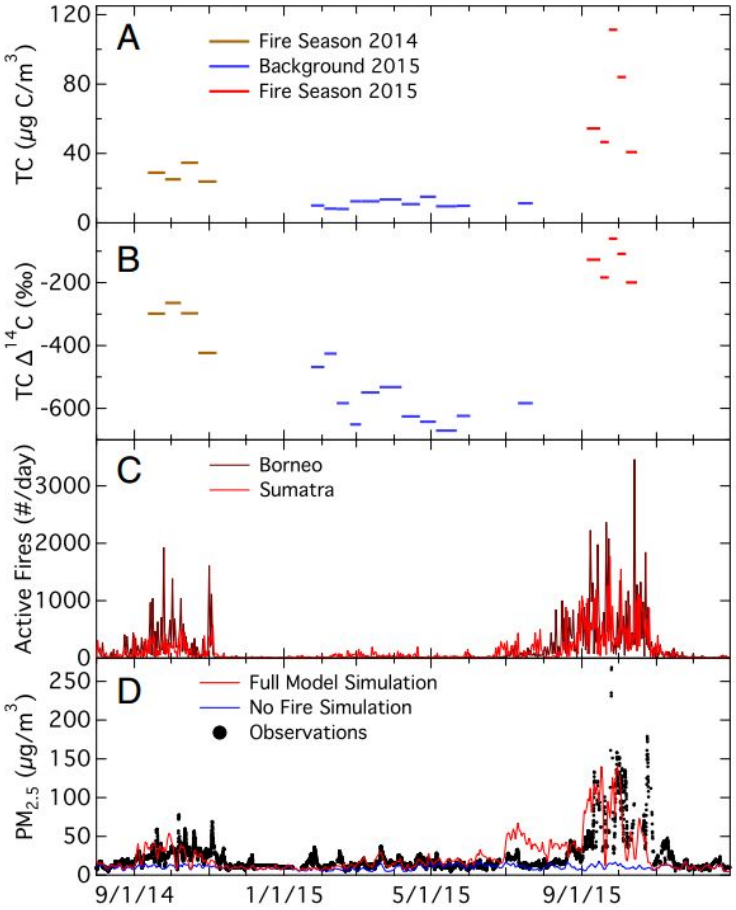


# Burning of millenia-aged peat

- **Peat burning** was a **dominant contributor** to emissions in the region.
- **Droughts increase** deforestation **fires** and agricultural waste burning in plantations.
- Peatland burning is well established as an important source of fire emissions during drought events in Indonesia, but **uncertainties remain with respect to partitioning emissions among different ecosystem and fire types.**
- **Peat fires emit three or more times the amount of PM2.5** released by deforestation fires per kilogram of fuel consumed
- Identifying the age and origin of fire-emitted fine particulate matter

# Bomb-labeled carbonaceous aerosol

- The isotopic constraint comes from a unique **14C labeling** of terrestrial biomass that has occurred during the last 60 y as a consequence of **aboveground nuclear weapons testing**.
- Carbonaceous aerosol originating from the combustion of **aboveground biomass**, as expected for emissions from **deforestation fires or agricultural waste burning in plantations**, should be bomb-labeled. Using isotope definitions, this means the **Δ14 C should be above the contemporary level** observed for atmospheric CO2.
- In contrast, **carbonaceous aerosol from older peat should have a negative Δ14C**, reflecting the longer-term cumulative effects of radioactive decay in organic carbon layers deposited over a period of centuries or millennia
- We use this information to estimate the mean age of the combusted organic material and to **distinguish among agricultural waste burning, deforestation, and peat sources**.

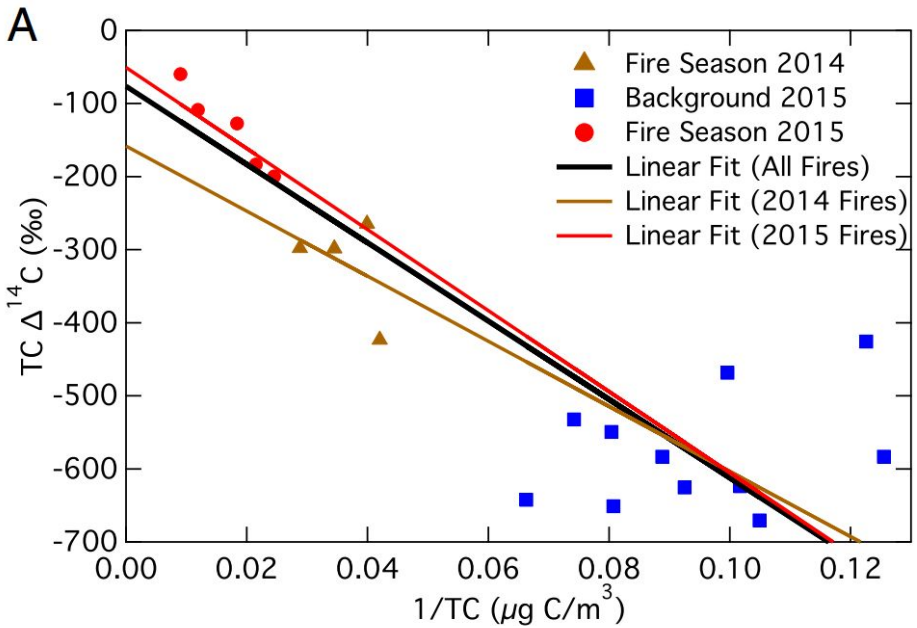



- Carbonaceous aerosol had a mean concentration of **67.4 ± 29.6 μgCm−3 during September and October 2015** (six times urban background levels and **28.1±4.9 μgC m−3 in 2014**

- Mean Δ14C was
  - −578±78‰ (urban background)
  - −321±70‰ (2014)
  - −136 ± 57‰ (2015)

- Intervals with elevated carbonaceous aerosols in Singapore were synchronized with high numbers of satellite active fire detections on Borneo and Sumatra

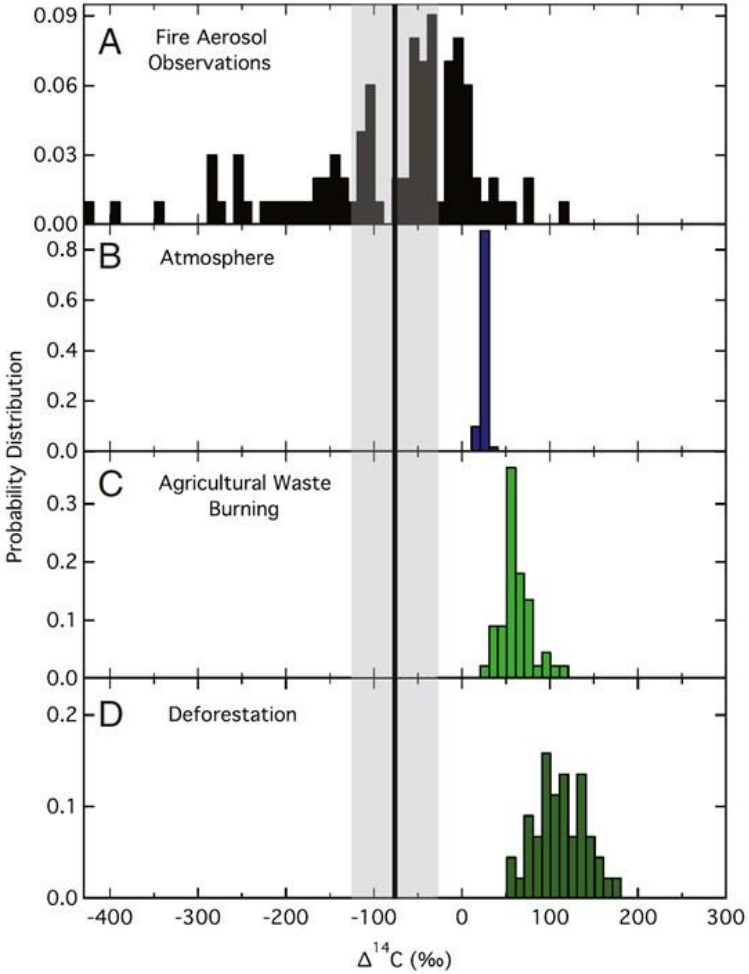
- Atmospheric model simulations with GEOS Chem indicated **fires accounted for more than 80% of the total PM2.5** observed during September and October 2015




- **Estimated the Δ14C of fire-emitted carbonaceous aerosol** using a Keeling plot approach to separate urban background contributions from our weekly observations collected during the 2014 and 2015 fire seasons

- Fire-emitted carbonaceous aerosols during 2014 and 2015 had a mean **Δ14C of −76±51‰** (estimated that the mean turnover time of the combusted carbon was 800±420 y)

- **2014 fire season** had a **more negative Δ14C** (−158±87‰) **than the 2015** fire season (−51±69‰)




- Histogram of the radiocarbon content (Δ14C) of fire-derived carbonaceous aerosols
- Δ14C value of the 2014–2015 atmosphere, using a Monte-Carlo approach with a mean of 25±3‰
- For agricultural waste burning in plantations with an estimated turnover time of 7.5±4 y, the expected Δ14C in 2015 would have been 52±17‰
- For combustion of forest biomass stocks with an estimated turnover time of 55±28 y, the expected Δ14C in 2015 would have been 114±26‰

- If we assume that peat emissions originated from the top meter of the profile with a mean Δ14C of −109‰, and that deforestation fires had a mean Δ14 C of 114‰, then about **85 ±21% of fire aerosol emissions originated from peat**, based on a Monte Carlo analysis.

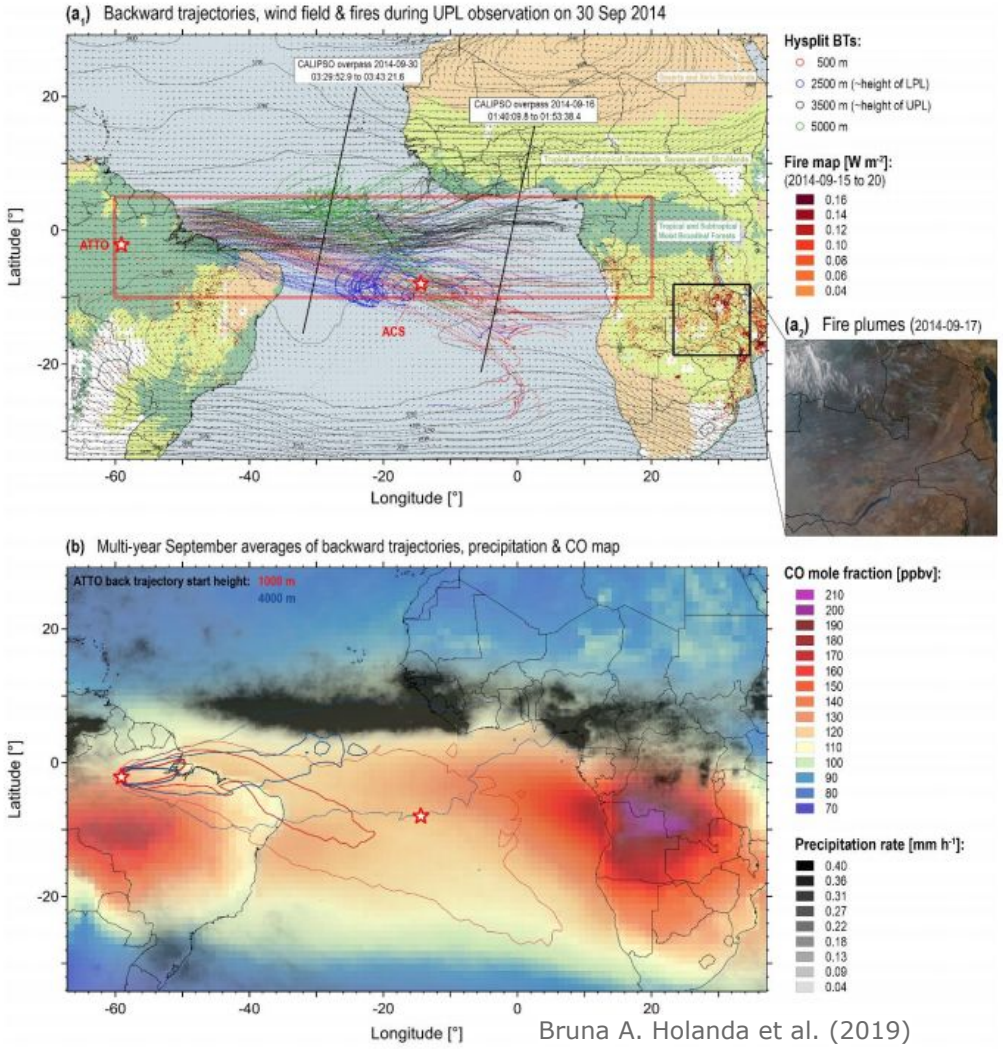
# Conclusões

- Aerosol **Δ14C measurements may provide quantitative constraints on the composition of sources** contributing to TC emissions from fires when these observations are combined with emission factors and peat Δ14 C profiles.
- **Most of the fire aerosol** we measured in Singapore **originated from the burning of peat**

# Conclusões

- **Without improvements in land management and peatland conservation**, we hypothesize that the **Δ14C of regional fire emissions during future El Niño events will decrease** over the next several decades as lowering water tables **expose older peat layers to decomposition and combustion**.
- Our measurements confirm that Indonesian fires are predominantly **releasing CO2 to the** atmosphere that has been out of contact with the atmosphere for centuries and millennia, and thus **represent a net perturbation to the global carbon budget.**
- Systematic **long-term monitoring of 14C content of fire aerosols** in the future may be useful for evaluating the **effectiveness of mitigation policies** designed to protect existing peatland areas, particularly at an integrated province-to-country spatial scale.

- O método KKCAMS para medida de 14C é muito preciso
- Caracterizar melhor a componente de contemporary OC:
  - Traçadores químicos: mz60 e mz73; mz53 e mz82; mz44
  - BBOA fresh, BBOA aged, IEPOX-SOA, OOA, HOA, etc ...
- Investigar relações com propriedades físicas e ópticas
- Separar emissões de HDV e LDV:
  - Etanol (biocombustível) e gasolina/diesel (fóssil)
- Caracterizar diferentes tipos de queimadas:
  - Diferentes assinaturas $f_M$ (ou Δ14C)




Bruna A. Holanda et al. (2019)

**Transatlantic transport of African BB smoke layers** has a strong impact on the north-central Amazonian aerosol population during the BB-influenced season (July to November).

The **early BB season** in this part of the Amazon appears to be **dominated by African smoke**, whereas the later BB season appears to be dominated by South American fires.

The African BB aerosol act as efficient cloud condensation nuclei (CCN) with potentially important implications for aerosol-cloud interactions and the hydrological cycle in the Amazon Basin

During their typical atmospheric lifetime of several days, **BC particles undergo atmospheric aging**, creating internally mixed BC aerosols via the condensation of low and semi-volatile compounds, coagulation, and cloud processing.

The formation of non-absorbing coatings on the BC cores **changes the particle optical, chemical, and physical properties**, with implications for their atmospheric cycling and lifetime.

# Randerson Lab

We study human modification of biogeochemical cycles and climate using satellite observations, field measurements, and models

Santa Ana fire smoke plumes. MODIS mage from NASA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## News from the Randerson Lab

Updates on the 2019 Amazon fires August 30, 2019

Liz Wiggins' paper on the carbon age of smoke from Indonesian fires published in PNAS

https://sites.uci.edu/randersonlab/

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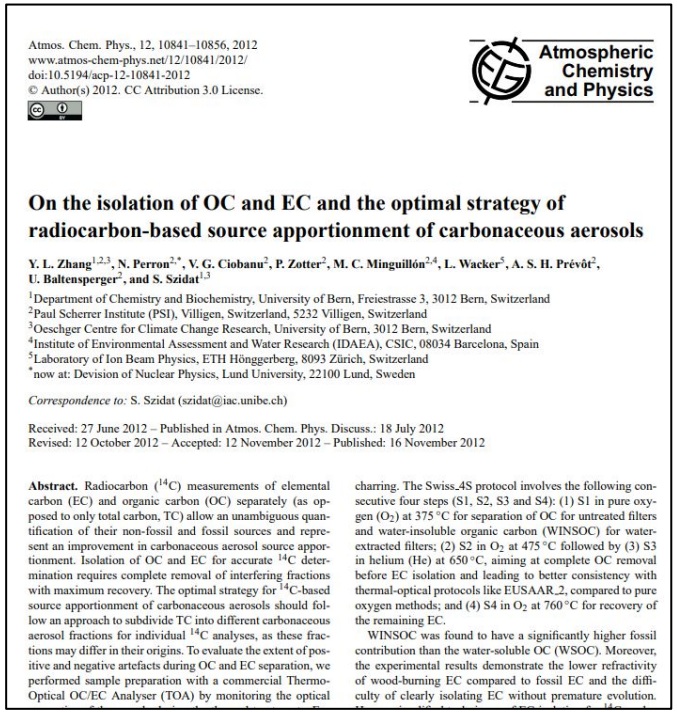
Obrigado pela atenção !!!

# Material adicional

# Análise de Carbono: protocolo Swiss_4S



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www.atmos-chem-phys.net/12/10841/2012/
doi:10.5194/acp-12-10841-2012


Atmospheric Chemistry and Physics

**On the isolation of OC and EC and the optimal strategy of radiocarbon-based source apportionment of carbonaceous aerosols**

Y. L. Zhang[1,2,3], N. Perron[2,*], V. G. Ciobanu[2], P. Zotter[2], M. C. Minguillón[2,4], L. Wacker[5], A. S. H. Prévôt[2], U. Baltensperger[2], and S. Szidat[1,3]

[1]Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland
[2]Paul Scherrer Institute (PSI), Villigen, Switzerland, 5232 Villigen, Switzerland
[3]Oeschger Centre for Climate Change Research, University of Bern, 3012 Bern, Switzerland
[4]Institute of Environmental Assessment and Water Research (IDAEA), CSIC, 08034 Barcelona, Spain
[5]Laboratory of Ion Beam Physics, ETH Hönggerberg, 8093 Zürich, Switzerland
[*]now at: Devision of Nuclear Physics, Lund University, 22100 Lund, Sweden

*Correspondence to:* S. Szidat (szidat@iac.unibe.ch)

Received: 27 June 2012 – Published in Atmos. Chem. Phys. Discuss.: 18 July 2012
Revised: 12 October 2012 – Accepted: 12 November 2012 – Published: 16 November 2012

**Abstract.** Radiocarbon ($^{14}C$) measurements of elemental carbon (EC) and organic carbon (OC) separately (as opposed to only total carbon, TC) allow an unambiguous quantification of their non-fossil and fossil sources and represent an improvement in carbonaceous aerosol source apportionment. Isolation of OC and EC for accurate $^{14}C$ determination requires complete removal of interfering fractions with maximum recovery. The optimal strategy for $^{14}C$-based source apportionment of carbonaceous aerosols should follow an approach to subdivide TC into different carbonaceous aerosol fractions for individual $^{14}C$ analyses, as these fractions may differ in their origins. To evaluate the extent of positive and negative artefacts during OC and EC separation, we performed sample preparation with a commercial Thermo-Optical OC/EC Analyser (TOA) by monitoring the optical charring. The Swiss_4S protocol involves the following consecutive four steps (S1, S2, S3 and S4): (1) S1 in pure oxygen ($O_2$) at 375 °C for separation of OC for untreated filters and water-insoluble organic carbon (WINSOC) for water-extracted filters; (2) S2 in $O_2$ at 475 °C followed by (3) S3 in helium (He) at 650 °C, aiming at complete OC removal before EC isolation and leading to better consistency with thermal-optical protocols like EUSAAR_2, compared to pure oxygen methods; and (4) S4 in $O_2$ at 760 °C for recovery of the remaining EC.

WINSOC was found to have a significantly higher fossil contribution than the water-soluble OC (WSOC). Moreover, the experimental results demonstrate the lower refractivity of wood-burning EC compared to fossil EC and the difficulty of clearly isolating EC without premature evolution.

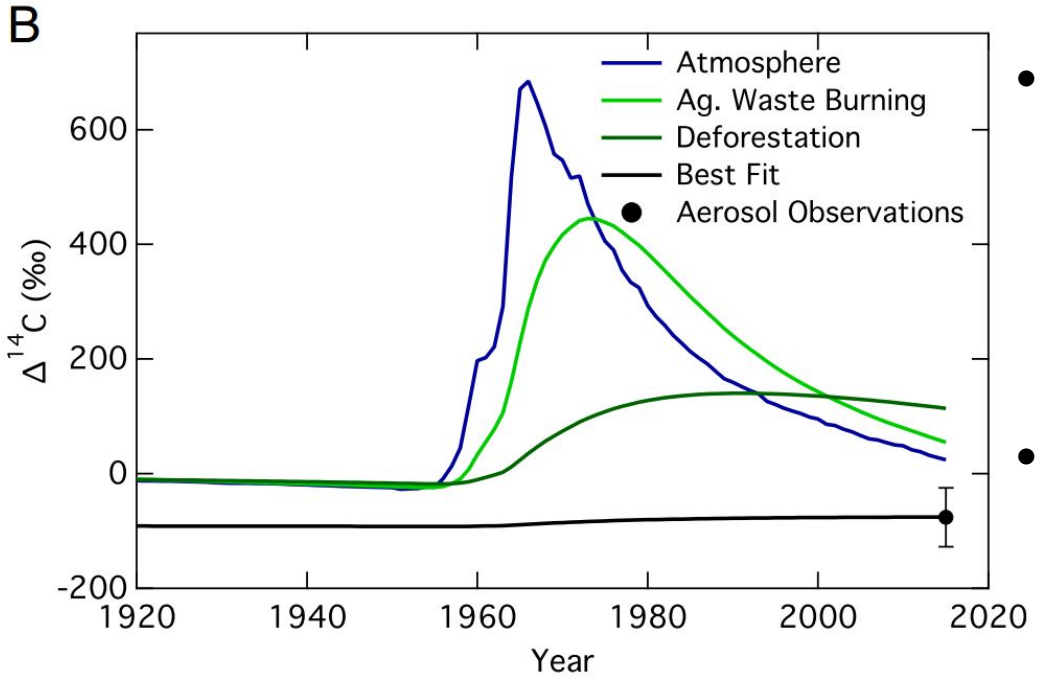
- Desenvolvido por Zhang et al. (2012)
- Condições termo-ópticas otimizadas para minimizar o “charring” de OC
- Four steps:
  - (S1) pure O2 at 375 ◦C for evaporation/oxidation of OC without premature EC evolution, (S2) pure O2 at 475 ◦C followed by (S3) in He at 650 ◦C, both of which aim to achieve complete OC removal before EC isolation (pure O2 reduces OC charring) and (S4) pure O2 at 760 ◦C for desorption and recovery of EC
  - The material evolving during (S3) is defined as a mixture of OC and EC and is not included in the analysis
- Os filtros são “lavados” com Milli-Q water e secos a 60°C para remoção de WSOC

**Table 2.** Radiocarbon Composition of Samples Used to Estimate the Biomass End-Member

| Description of Samples | *n* | Fraction Modern |
|---|---|---|
| Aspen leaves | | |
| 1.4 km radius of Hawthorne | 5 | 1.018 ± 0.006 |
| 0.3 km radius of Rose Park | 4 | 1.021 ± 0.003 |
| 0.4 km radius of University of Utah | 5 | 1.020 ± 0.004 |
| Average ± SD | | 1.019 ± 0.002 |
| Wood | | |
| Pine | 2 | 1.078 ± 0.028 |
| Oak | 1 | 1.035 ± 0.002 |
| Maple | 1 | 1.009 ± 0.002 |
| Average ± SD | | 1.041 ± 0.035 |

# Medida de Total Carbon

- TC é analisado separadamente
- Conventional “sealed-tube”procedure convert TC into CO2. Then measures the mass of the TC derived CO2 and collected the CO2 in a reaction tube for subsequent graphitization and 14C analysis
- A concentração de OC é calculada pela diferença entre carbono total e carbono elementar (TC = OC + EC)
- Balanço isotópico de massa: estimativa do conteúdo de 14C no OC




- Δ14C of:
  - atmospheric CO2 (blue line)
  - model estimates of agricultural waste burning emissions (light green line)
  - model estimates of deforestation (dark green line)

- A source with a **turnover time of 800 ±420 y** (black line) was required to match the observed Δ14C of the fire-emitted aerosols (black circle)