Caracterização química e toxicológica da matéria particulada emitida pelas principais fontes em atmosferas urbanas

CÉLIA ALVES

celia.alves@ua.pt

universidade de aveiro

unesp

Araraquara, 20/02/2019

OUTLINE

- Project identification
- Institutions
- Scientific component
  - Motivation and objectives
  - Work packages and tasks
  - Postgraduate programmes

PROJECT IDENTIFICATION

Chemical and toxicological SOurce PROfiling of particulate matter in urban air (SOPRO)

Projeto de Investigação Científica e Desenvolvimento Tecnológico (IC&DT) nº 29574
Call 02/SAICT/2017

PORTUGAL 2020

FCT
Fundação para a Ciência e a Tecnologia
MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E ENSINO SUPERIOR

FAPESP
FUNDAÇÃO DE AMPARO À PESQUISA
DO ESTADO DE SÃO PAULO

INSTITUTIONS

universidade de aveiro

dao
departamento de ambiente e ordenamento

departamento de biologia

Universidade de São Paulo

INSTITUTO DE ASTRONOMIA, GEOFÍSICA E CIÊNCIAS ATMOSFÉRICAS

Universidade de São Paulo
Instituto de Química

EACH

Escola de Artes, Ciências e Humanidades
da Universidade de São Paulo

COLLABORATING INSTITUTIONS

KIT Karlsruher Institut für Technologie

idæa CSIC

Institute of Environmental Assessment and Water Research, Spanish Research Council

Ciemat Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas

UNIVERSITÀ DEGLI STUDI FIRENZE

ARPA LOMBARDIA Agenzia Regionale per la Protezione dell'Ambiente

Analytical task

vti

Swedish National Road and Transport Research Institute

IFSTTAR

French Institute of Science and Technology for Transport, Development and Networks

CETESB

Environmental Agency of the State of São Paulo

UERJ Universidade do Estado do Rio de Janeiro

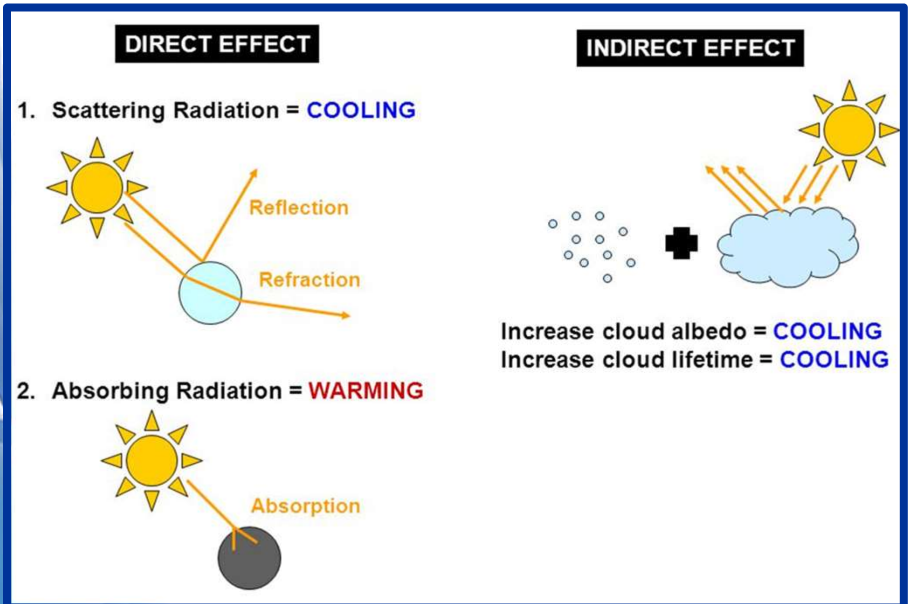
Sampling tasks

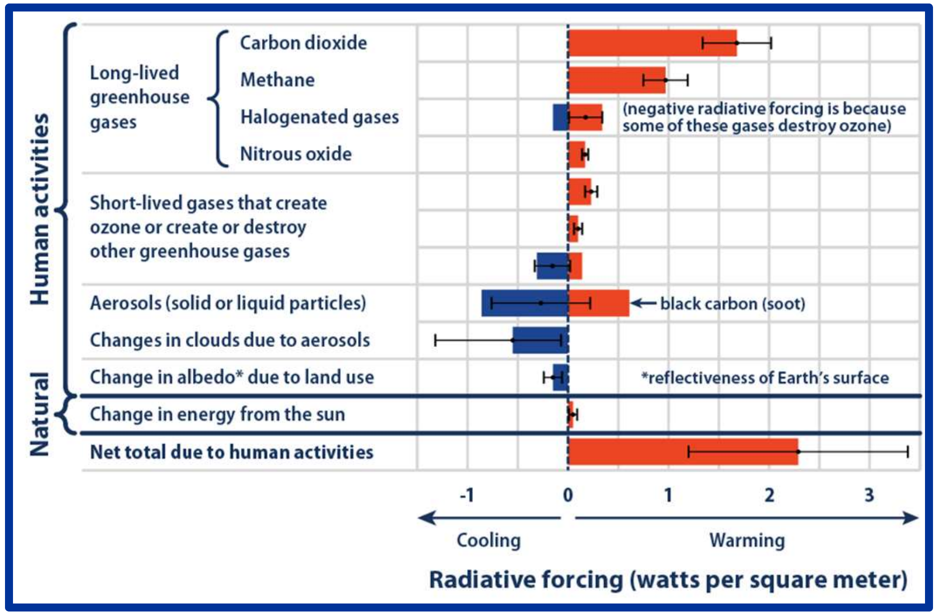
SCIENTIFIC COMPONENT

Motivation

– Why atmospheric particulate matter is so important?

- Interaction with climate

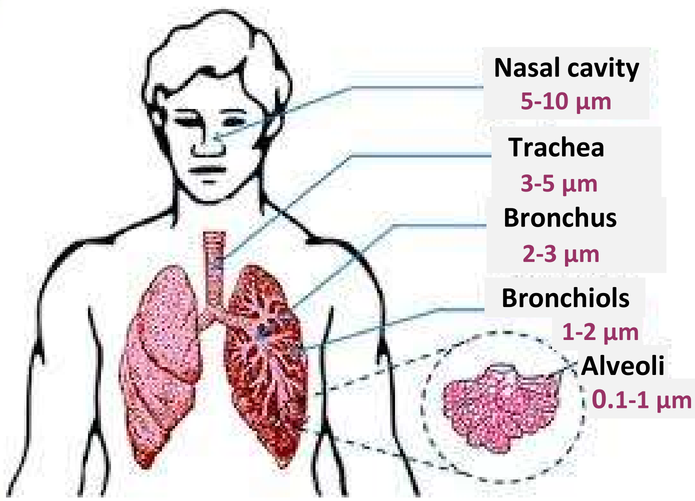




(IPCC AR5, 2014)

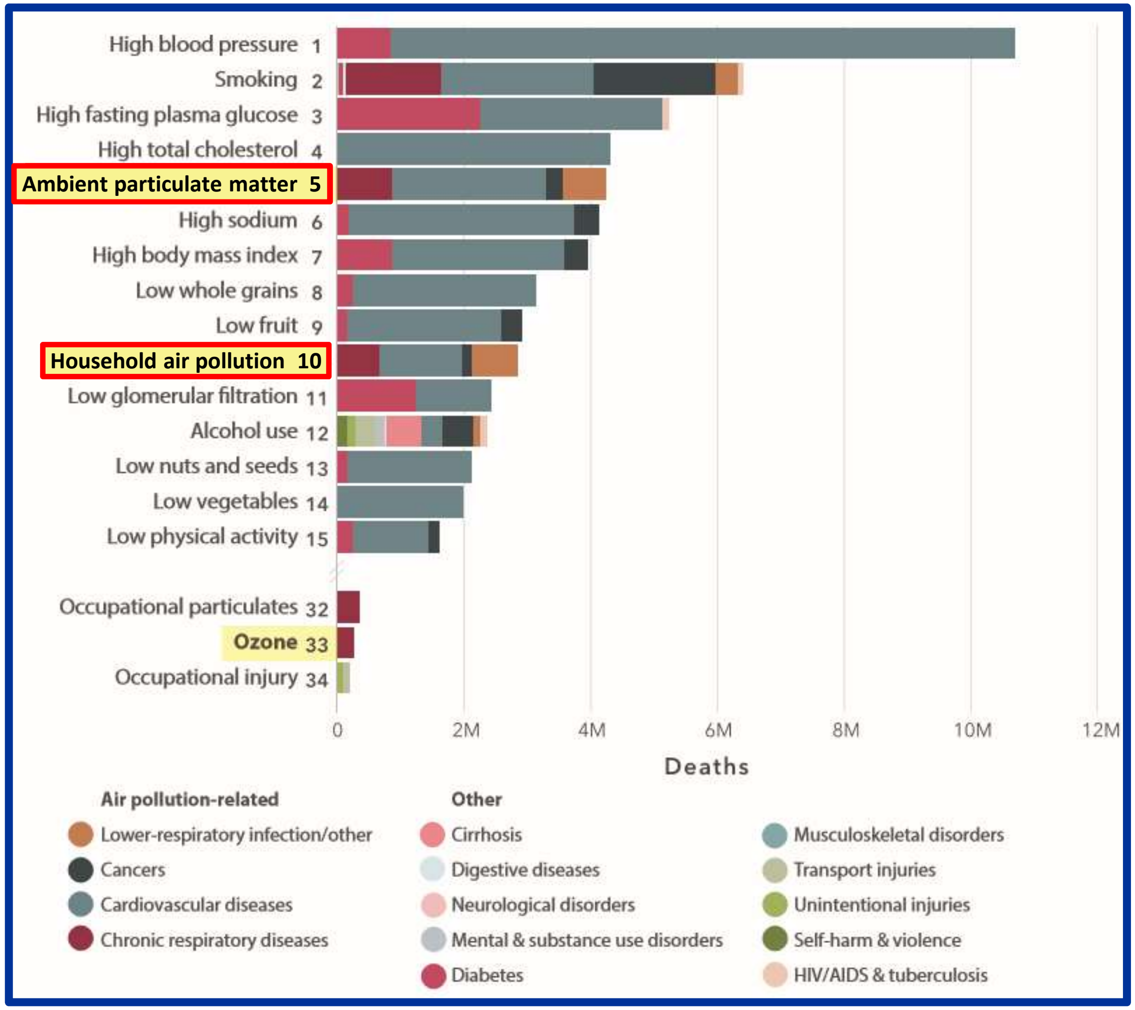
– Why atmospheric particulate matter is so important?

▸ Health effects



The International Agency for Research on Cancer (IARC) has classified particulate matter (PM) in outdoor air pollution as carcinogenic to humans (Class 1)

Global ranking of risk factors for total deaths from all causes for all ages and sexes in 2015



(Institute for Health Metrics, Evaluation's Global Burden of Disease Project, Health Effects Institute, 2017)

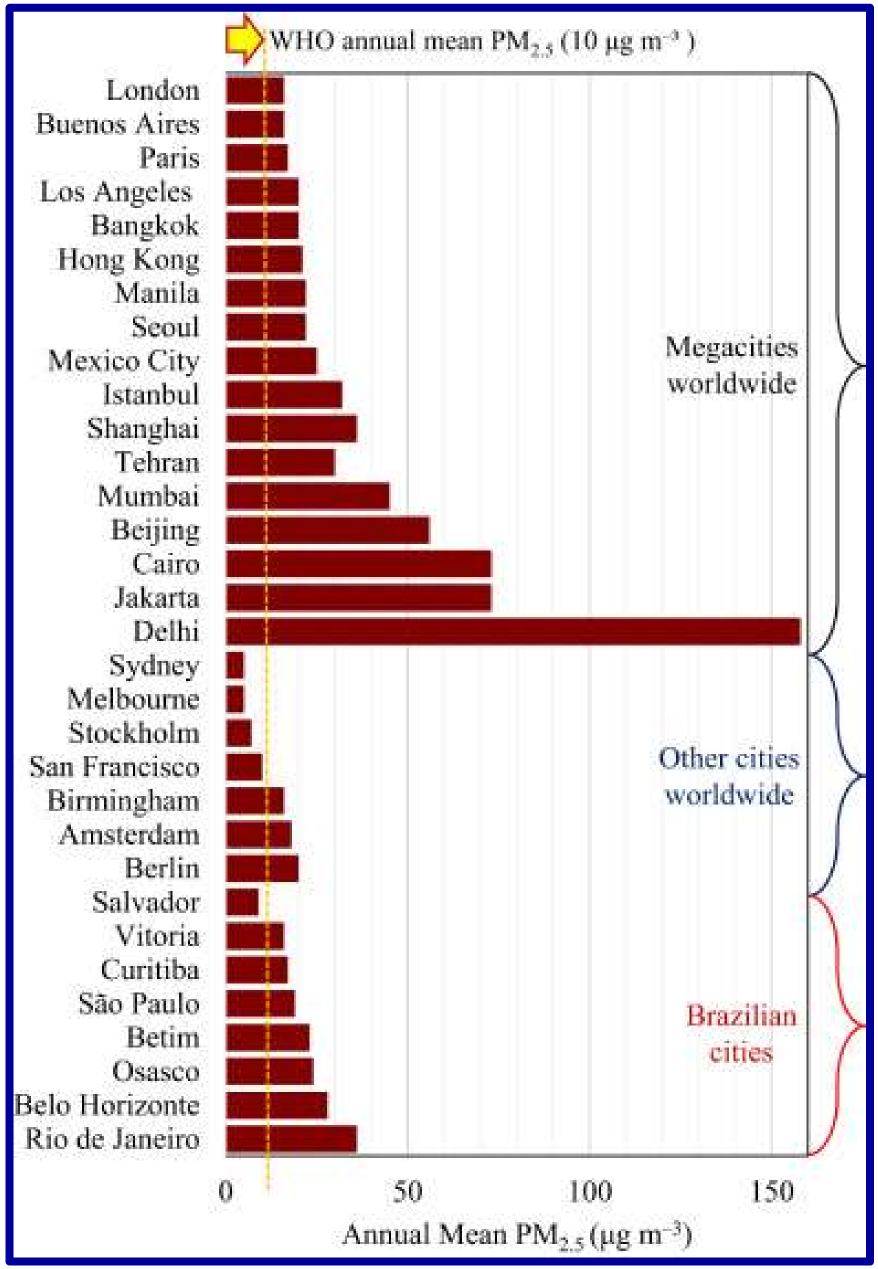
– Why atmospheric particulate matter is so important?

▸ Health effects

% of the urban population in the EU-28 exposed to PM concentrations above the WHO Air Quality Guidelines

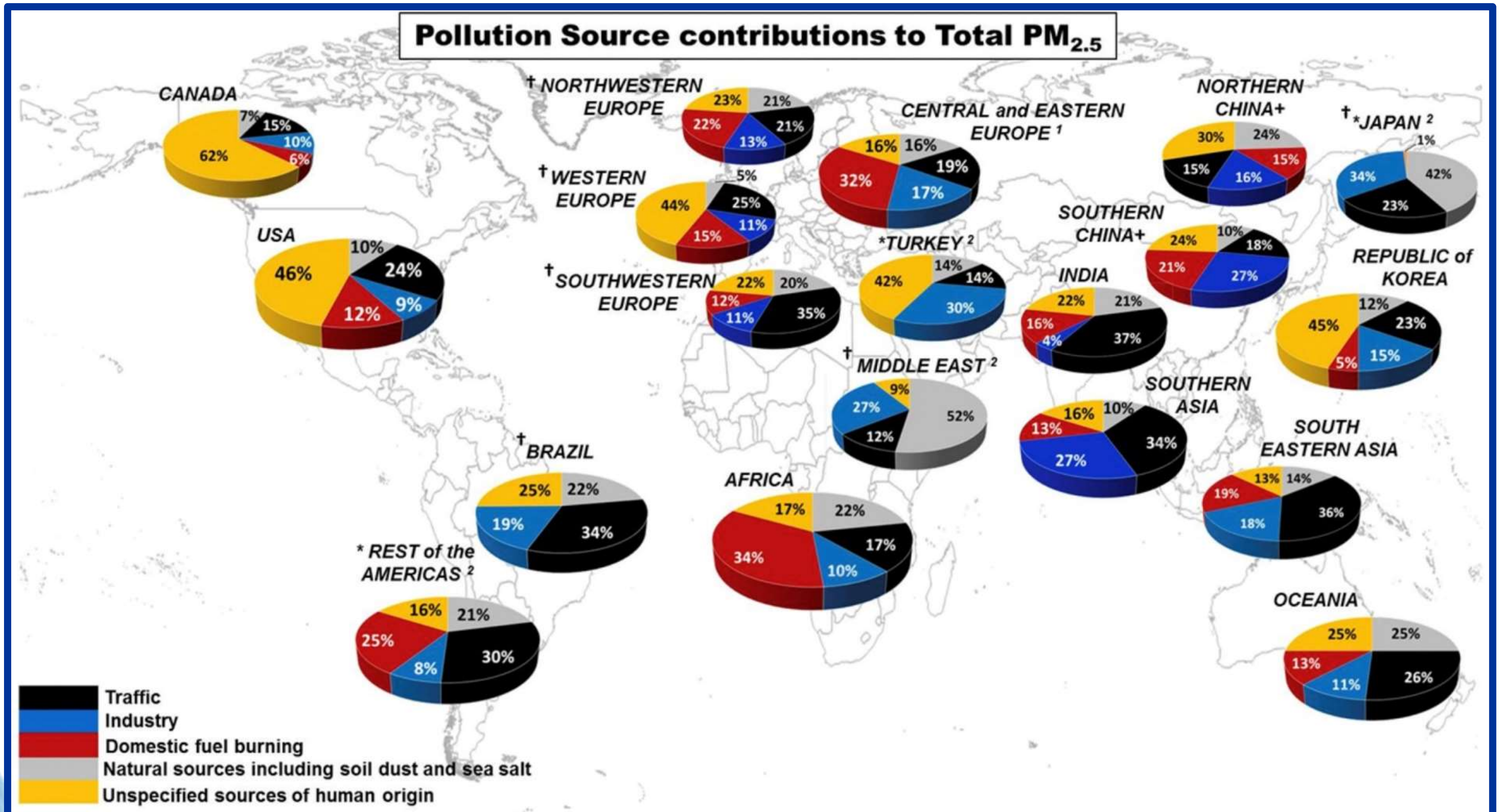
	WHO AQG (µg/m³)	Exposure estimate (%)
$PM_{2.5}$	10 (year)	82 - 85
PM_{10}	20 (year)	50 - 62

(EEA, 2017)



(Pacheco et al., 2017. J Transp Health 4, 53)

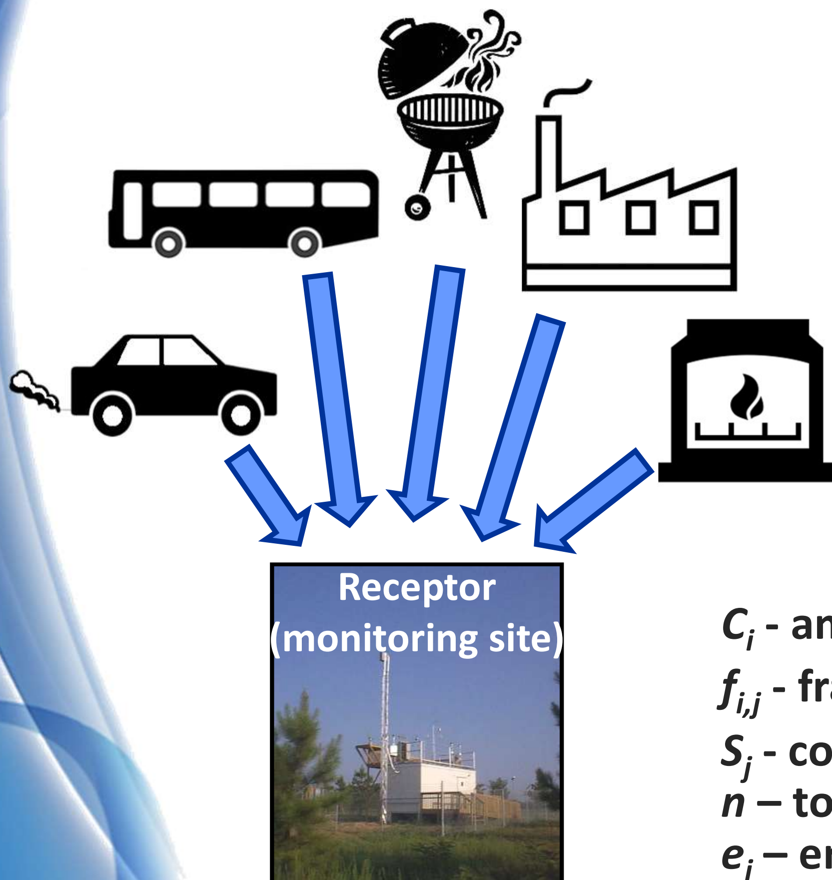
Main sources of fine particulate matter worldwide



(Karagulian et al., 2015. Atmos Environ 120, 475)

Source-apportionment by receptor modelling

- Positive Matrix Factorisation (PMF)
- Chemical Mass Balance (CMB)

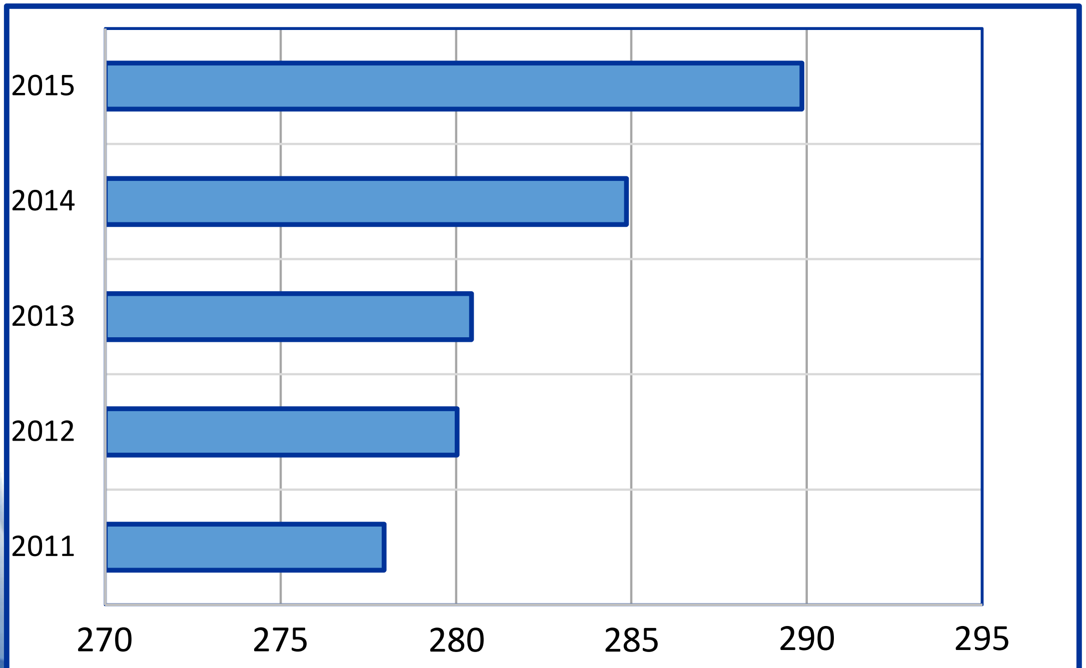


$$C_i = \sum_{j=1}^{n} f_{i,j} S_j + e_i$$

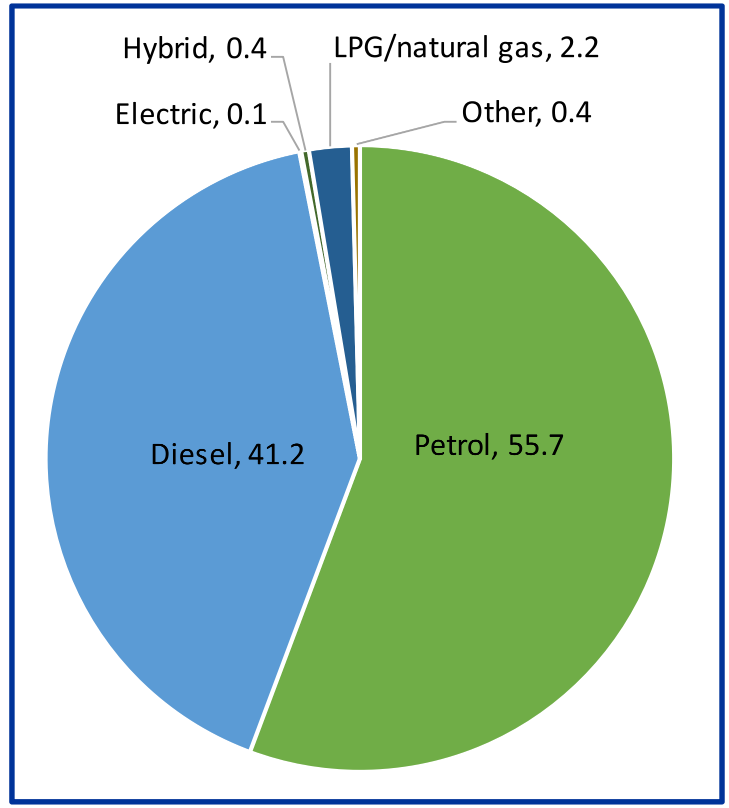
C_i - ambient concentration of specie i (μg/m^3)
$f_{i,j}$ - fraction of species i in emissions from source j
S_j - contribution (source-strength) of source j (μg/m^3)
n – total number of sources
e_i – error term to be minimised (to obtain best fit)
S_j are the unknowns (C_i, $f_{i,j}$, n – required input)

The importance of road traffic emissions

Million vehicles in the EU



Percentage distribution of passenger cars in use by fuel type in the EU



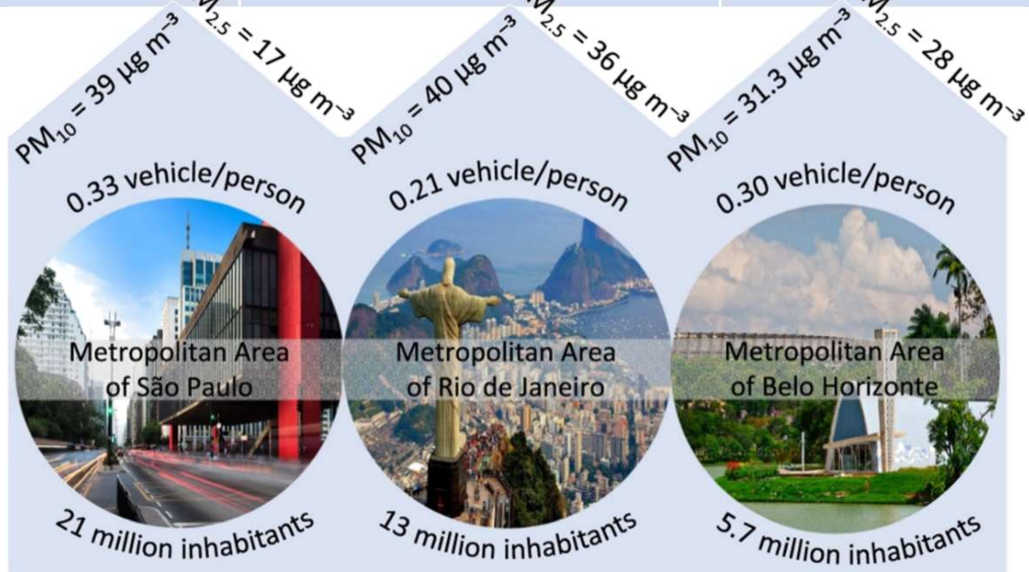
Source: Automobile Manufacturers' Association, 2017.
Report "Vehicles in Use in Europe"

The importance of road traffic emissions

	São Paulo	Rio de Janeiro	Belo Horizonte
Local sources	Transportation, industries	Transportation, petrochemical industries, refinery	Transportation, minery, refinery
Nº gasohol vehicles	3,877,098	1,040,321	633,242
Nº etanol vehicles	495,946	139,801	54,768
Nº flex fuel vehicles	2,615,055	854,556	885,515
Nº diesel vehicles	364,797	124,110	100,092
Nº electric cars	848	42	29
Nº travels/day (x1000)	43715	22594	13060
% travels by public transportation	36.9	48.7	31.0
% travels by passenger cars	31.1	19.5	31.0
% travels by foot	31.4	29.4	37.0
% travels by bicycle	0.6	2.4	1.0

WHO annual means:

- $PM_{2.5}$ 10 µg/m³
- PM_{10} 20 µg/m³



(Pacheco et al., 2017. J Transp Health 4, 53)

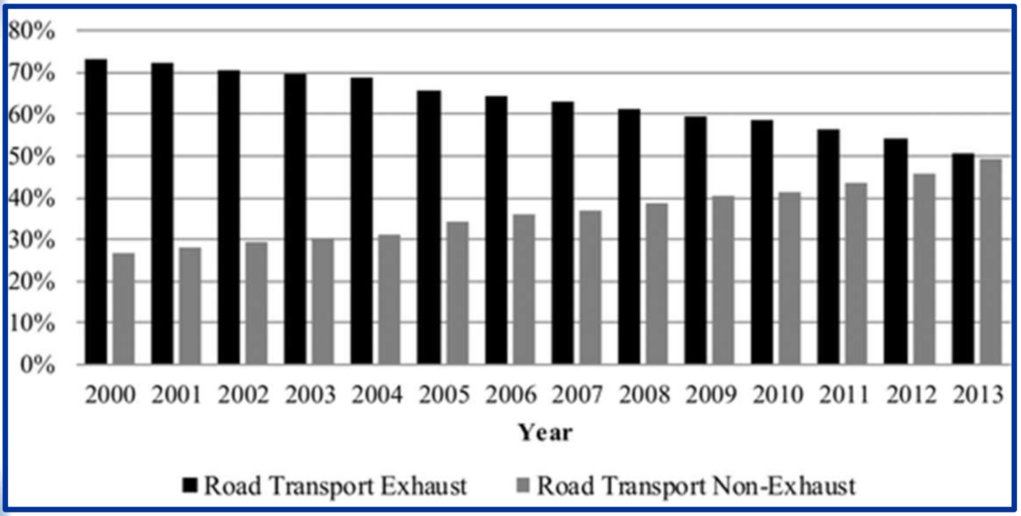
Types of traffic-related particles

Road traffic emissions

- Exhaust
- Non-exhaust
  - Brake wear
  - Tyre wear
  - Road wear
  - Resuspension of road dust

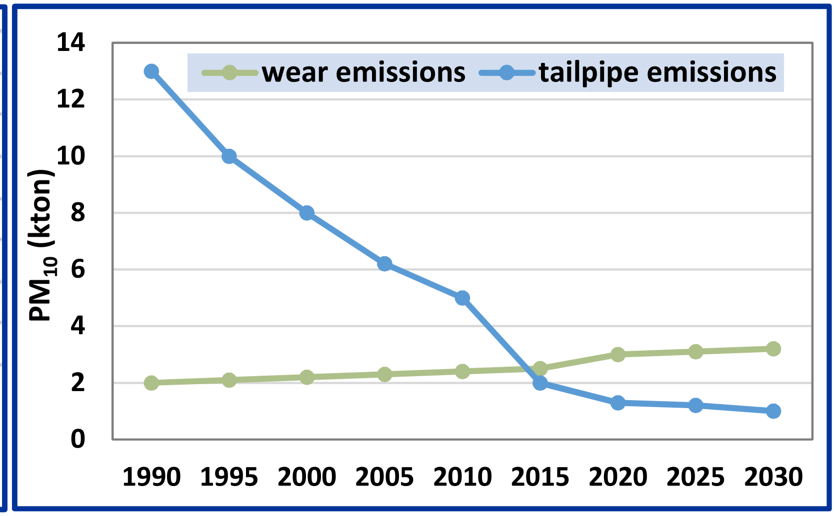
Exhaust *versus* non-exhaust particulate emissions

Trend of the contribution (%) of exhaust and non-exhaust emissions in total road transport PM_{10} emission in the EU-28 region



(Guevara, 2016. In *Airborne Particulate Matter: Sources, Atmospheric Processes and Health)*

PM_{10} emissions from road traffic (Netherlands)



(Krijgsheld, 2011. International workshop road transport wear emissions, Amsterdam)

- Non-exhaust emissions are equal to or surpass exhaust contributions
- Reductions in exhaust PM_{10} have been registered due to stricter emission controls and technological advances
- As exhaust emissions decrease, the unregulated emissions from non-exhaust sources will become even more important
- Large uncertainties associated with non-exhaust emission factors and wear rates

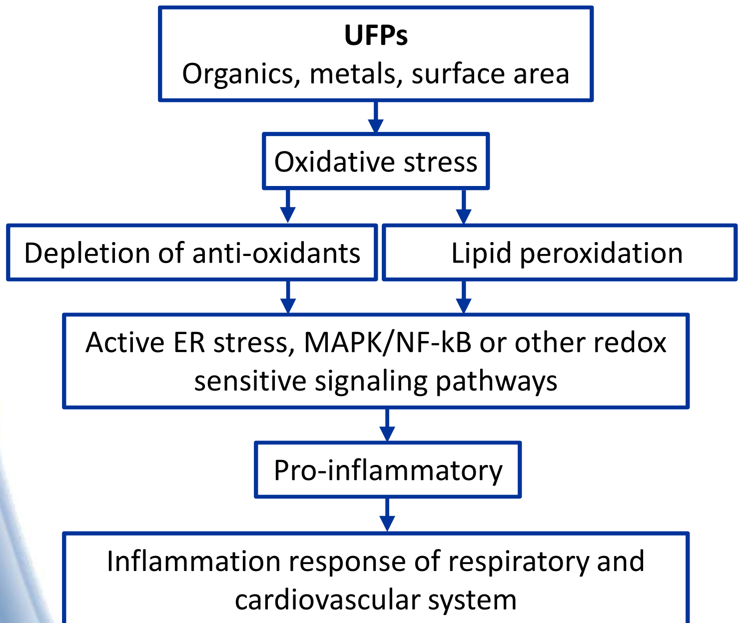
Difficulties in apportioning road traffic emissions

Exhaust	Non-exhaust
• Emission data are outdated and there is limited information on HDVs, motorcycles and flex-fuel vehicles	• Brake and tyre wear particles: composition highly dependent on commercial formulations • Resuspension: heavily affected by climate

NEED TO:

Obtain detailed chemical profiles representing the Luso-Brazilian road traffic patterns to more correctly apportion the contribution of these sources to PM

Health relevance of traffic emissions



- Though the toxicity of exhaust emissions is quite well documented, the re-evaluation has been suggested because the properties of engines and fuels have improved and the emissions are constantly changing.

- Except some bioassays that have identified nitro-PAHs as major mutagenic drivers, few approaches have been used to determine the chemical species forcing the health hazards.

- The toxicological properties of non-exhaust particles are little known and some of the few existing studies have reached contradictory conclusions.

The importance of cooking emissions

Particulate emissions in the USA from commercial cooking and highway vehicles (ton/year)

	Total charbroiling	Flat griddle frying	Clamshell griddle frying	Under-fired charbroiling	Conveyorised charbroiling	Highway vehicles
$PM_{2.5}$	79,300	11,900	910	58,300	8200	135,000
PM_{10}	85,500	15,700	110	60,300	8500	192,000

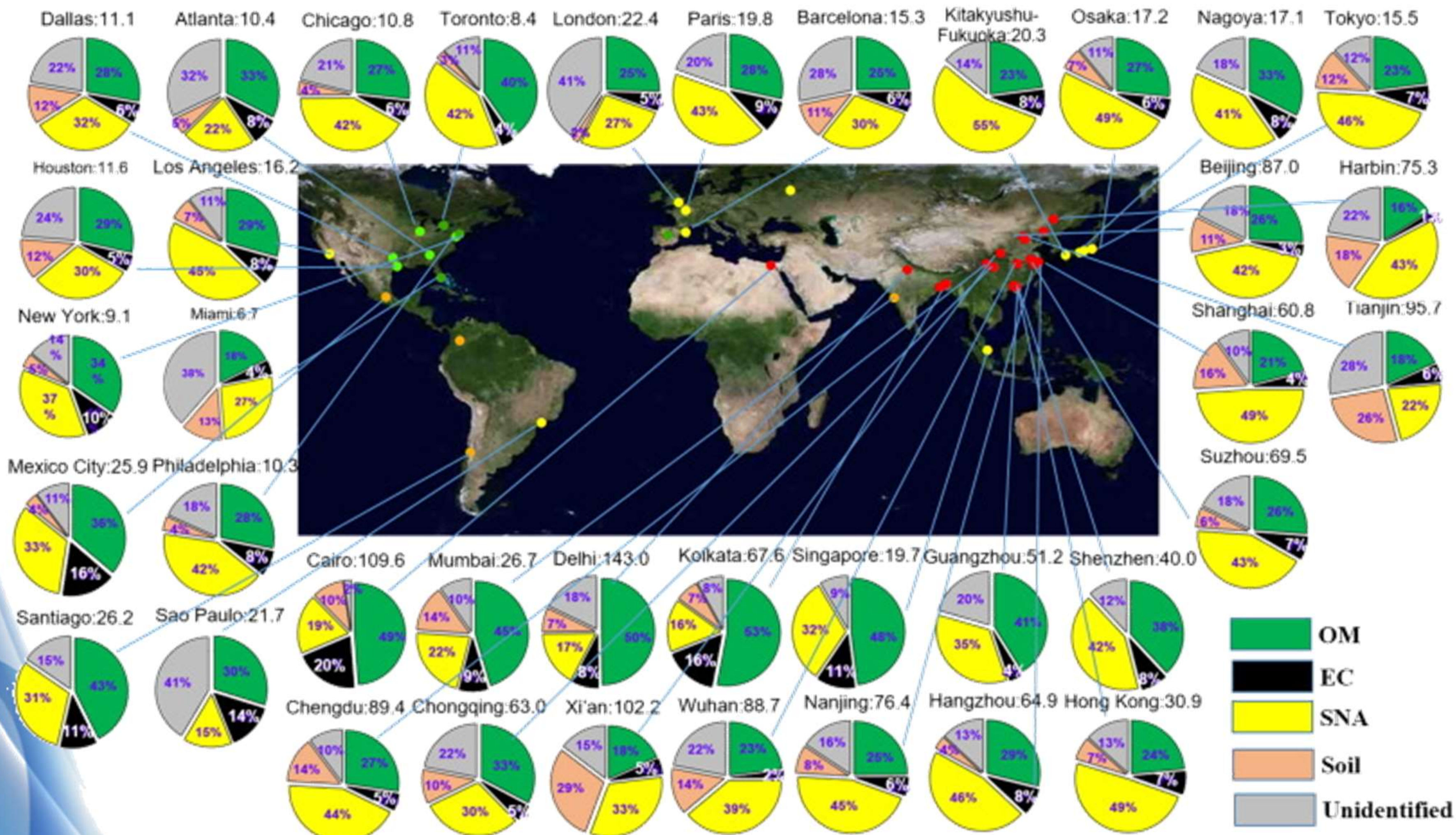
(Abdullahi et al., 2013. Atmos Environ 71, 260)

	Nº of restaurants
USA	700,000
China	2,400,000
Worldwide	16,000,000

- The majority of residential and commercial cooking emissions remains uncontrolled.

The importance of cooking emissions

$PM_{2.5}$ chemical composition for global megacities



OM = 1.4 x OC
SNA = sulphate, nitrate and ammonium
soil = 2.2 Al + 2.49 Si + 1.63Ca + 2.42Fe + 1.94Ti
unidentified = $PM_{2.5}$ - OM - EC - SNA - soil

Numbers after the name of the cities represent the mean $PM_{2.5}$ annual levels in 2013

(Cheng et al., 2016. Environ Int 89-90, 212)

The importance of cooking emissions

City	COA	Ref.
Paris	35%	Crippa et al. (2011)
London & Manchester	34%	Allan et al. (2010)
Barcelona	17%	Mohr et al. (2012)
New York	16%	Sun et al. (2011)
Toronto	33%	Slowik et al. (2010)
Fresno	19%	Ge et al. (2012)
Hong Kong	39%	Lee et al. (2015)
Beijing	33%	Xu et al. (2018)

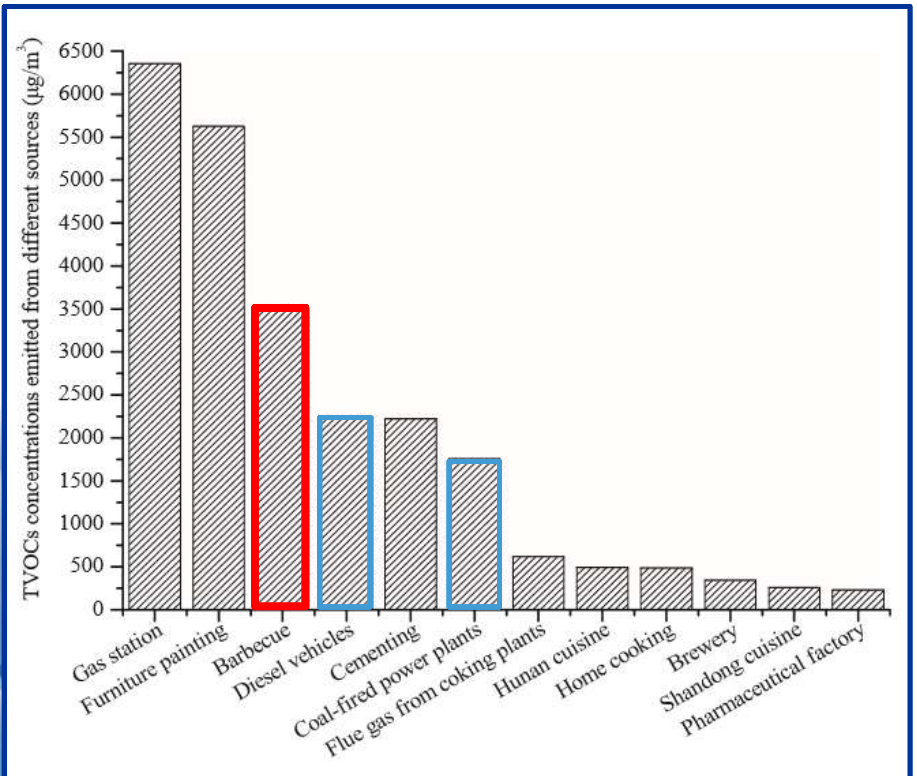
Apportionment of cooking organic aerosol (COA) by PMF applied to ambient measurements by HR-ToF-AMS

- COA is currently not included in European and Brazilian emission inventories
- Model simulations with EMEP4UK for the UK estimated **COA emissions** of **7.4 Gg year^{-1}**, which is an almost **10%** addition to the officially reported UK national **total anthropogenic emissions** of $PM_{2.5}$ (82 Gg in 2012), corresponding to **320 mg person^{-1} day^{-1}**, on average.

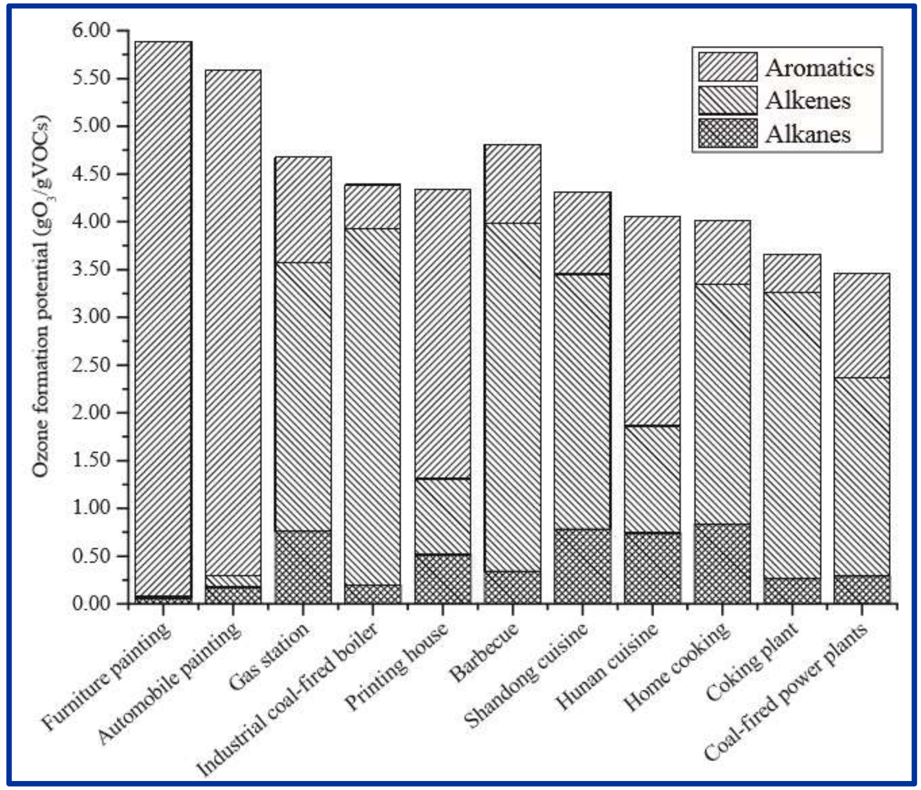
(Ots et al., 2016. Atmos Chem Phys 16, 13773)

The importance of cooking emissions

TVOCs concentrations emitted from different sources

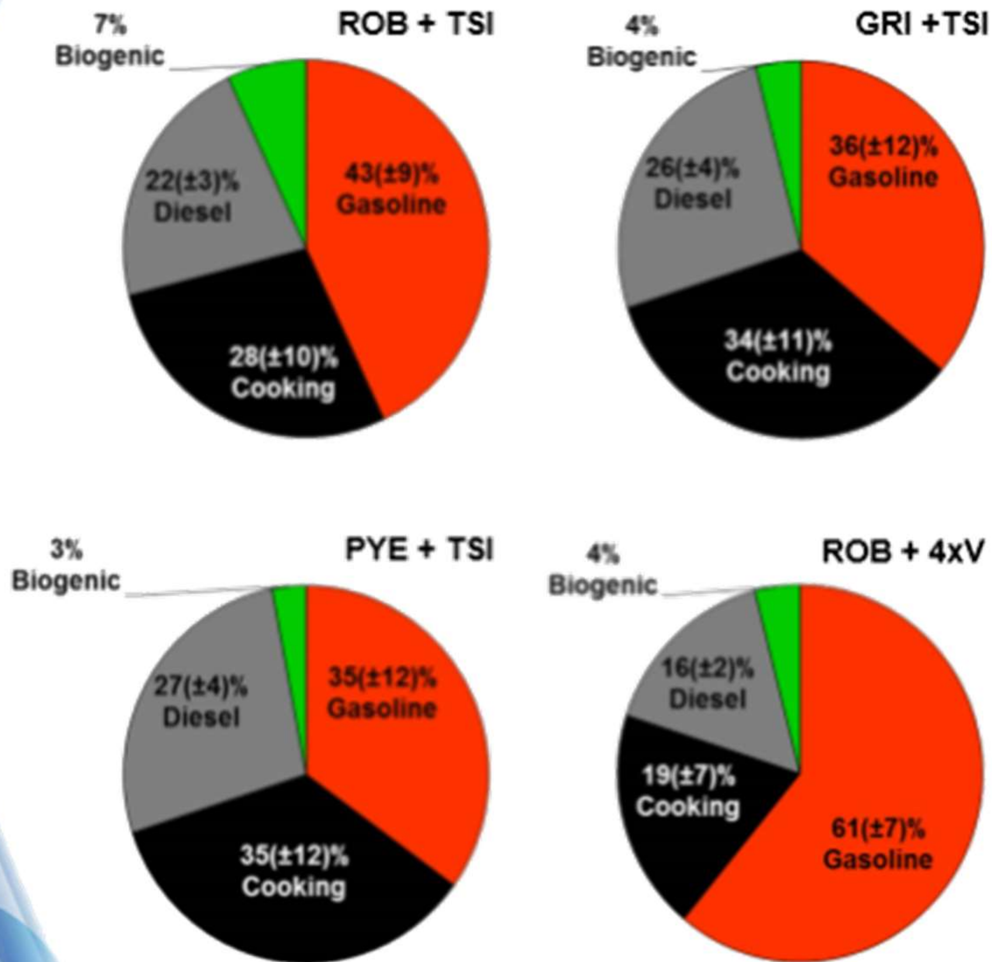


OFP of VOCs from different emission sources



(Cheng et al., 2016. Atmos Environ 145, 299)

The importance of cooking emissions



Secondary organic aerosols (SOA) in Los Angeles

Cooking accounts for 19-34% of the SOA mass concentration in LA

Four different literature parameterisations for the formation and evolution of urban SOA using a box model:

ROB+TSI - Robinson et al. (2007), Tsimpidi et al. (2010)
GRI+TSI - Grieshop et al. (2009), Tsimpidi et al. (2010)
PYE+TSI - Pye and Seinfeld (2010), Tsimpidi et al. (2010)
ROB+4xV - Tsimpidi et al. (2010), Robinson et al. (2007), Zhang et al. (2014)

(Hayes et al., 2015. Atmos Chem Phys 15, 5773)

Environ. Sci. Technol. **2002**, *36*, 567−575

Measurement of Emissions from Air Pollution Sources. 4. C_1−C_{27} Organic Compounds from Cooking with Seed Oils

organic compounds found in the urban atmospheric fine particulate mixture (*1*). These particle-phase acids are known to be emitted from many sources such as meat cooking operations, wood combustion, motor vehicle exhaust, and road dust (*2*), but air pollution modeling results for the Los Angeles Basin indicate that there must be additional as yet unquantified sources of these compounds (*3, 4*). Seed oils are comprised largely of esters of *n*-alkanoic acids (*5*), and

JAM
MIC
GLE
BER
Envir
Unive
Envir
Techn
Ocean
Corva

TECHNICAL PAPER

ISSN 1047-3289 *J. Air & Waste Manage. Assoc.* 53:185–194

Emi

ELSEVIE

AE International – Asia

ATMOSPHERIC ENVIRONMENT

eef

Environ. Sci. Technol. **2007**, *41*, 99−105

Meas

Chem
Parti
from

ᵃStat

YUNL
SJAAK
State Ke
Pollutio
Universi

ELSE

Atmospheric Environment 145 (2016) 299–307

Char
emis

Shuiy

[a] Key Labo
[b] Collabor
[c] Beijing M

Science of the Total Environment 621 (2018) 1300–1309

Contents lists available at ScienceDirect

Science of the Total Environment

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

ELSEVIER

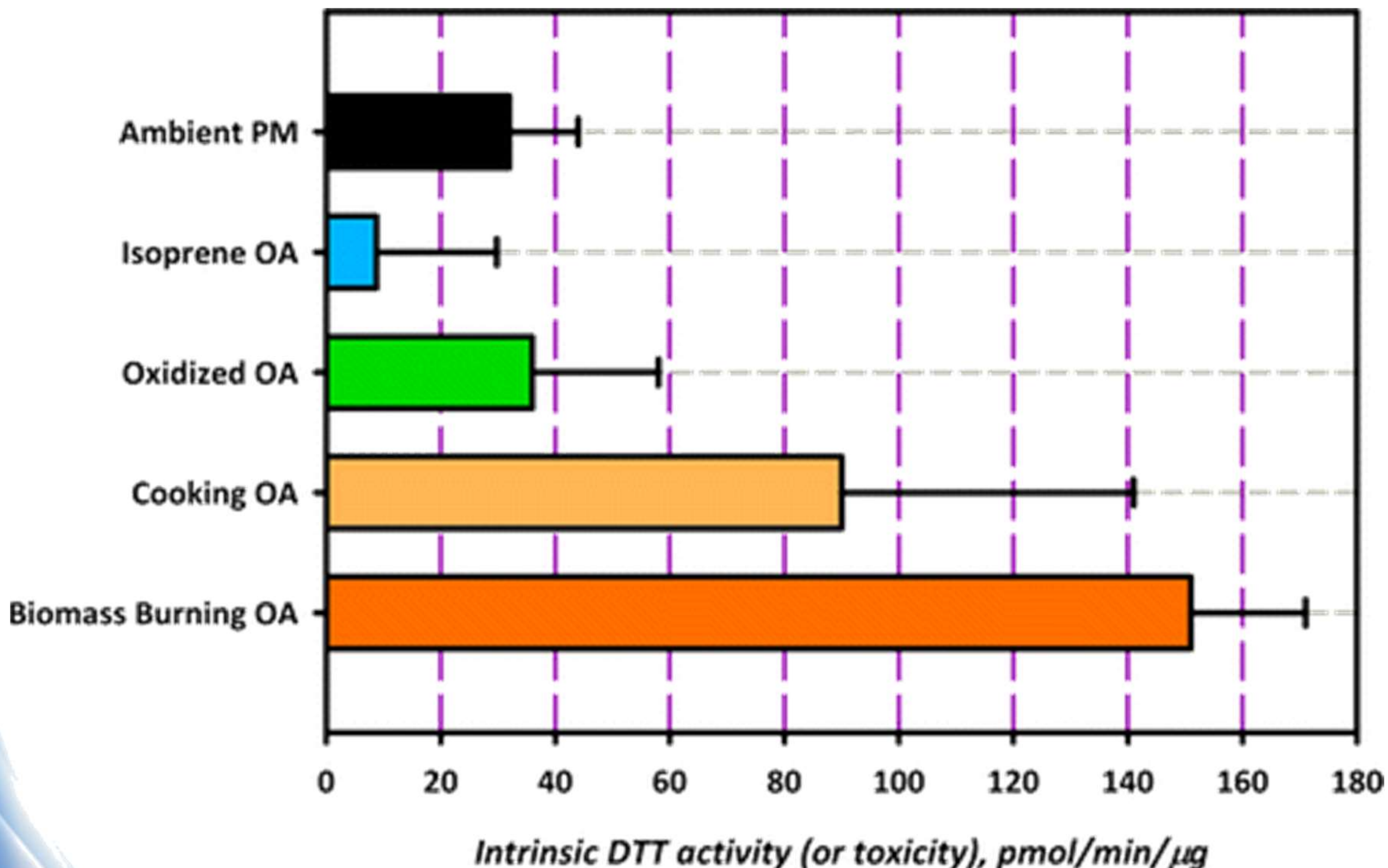
Emissions of volatile organic compounds (VOCs) from cooking and their speciation: A case study for Shanghai with implications for China

Hongli Wang [a,1], Zhiyuan Xiang [b,1], Lina Wang [b,e,*], Shengao Jing [a], Shengrong Lou [a], Shikang Tao [a], Jing Liu [c], Mingzhou Yu [d], Li Li [a], Li Lin [a], Ying Chen [e,f], Alfred Wiedensohler [e], Changhong Chen [a]

[a] *State Environmental Protection Key Laboratory of Formation and Prevention of Urban Air Pollution Complex, Shanghai Academy of Environmental Sciences, Shanghai 200233, China*
[b] *State Environmental Protection Key Laboratory of Risk Assessment and Control on Chemical processes, East China University of Science and Technology, Shanghai 200237, China*
[c] *School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150001, China*
[d] *China Jiliang University, Hangzhou 310018, China*
[e] *Leibniz-Institute for Tropospheric Research, Leipzig, Germany*
[f] *Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, UK*

Health relevance of cooking emissions

Reactive oxygen species (ROS) generating capability of the water-soluble extracts from PM measured by the dithiothreitol (DTT) assay



(Verma et al., 2015. Environ Sci Technol 49, 4646)

Health relevance of cooking emissions

Dangerous constituintes in cooking fumes	Effects
• VOCs • PAHs • Heterocyclic aromatic amines	• Oxidative stress • Respiratory problems • Cancer • DNA and cell damage • Neurotoxic effects

However…

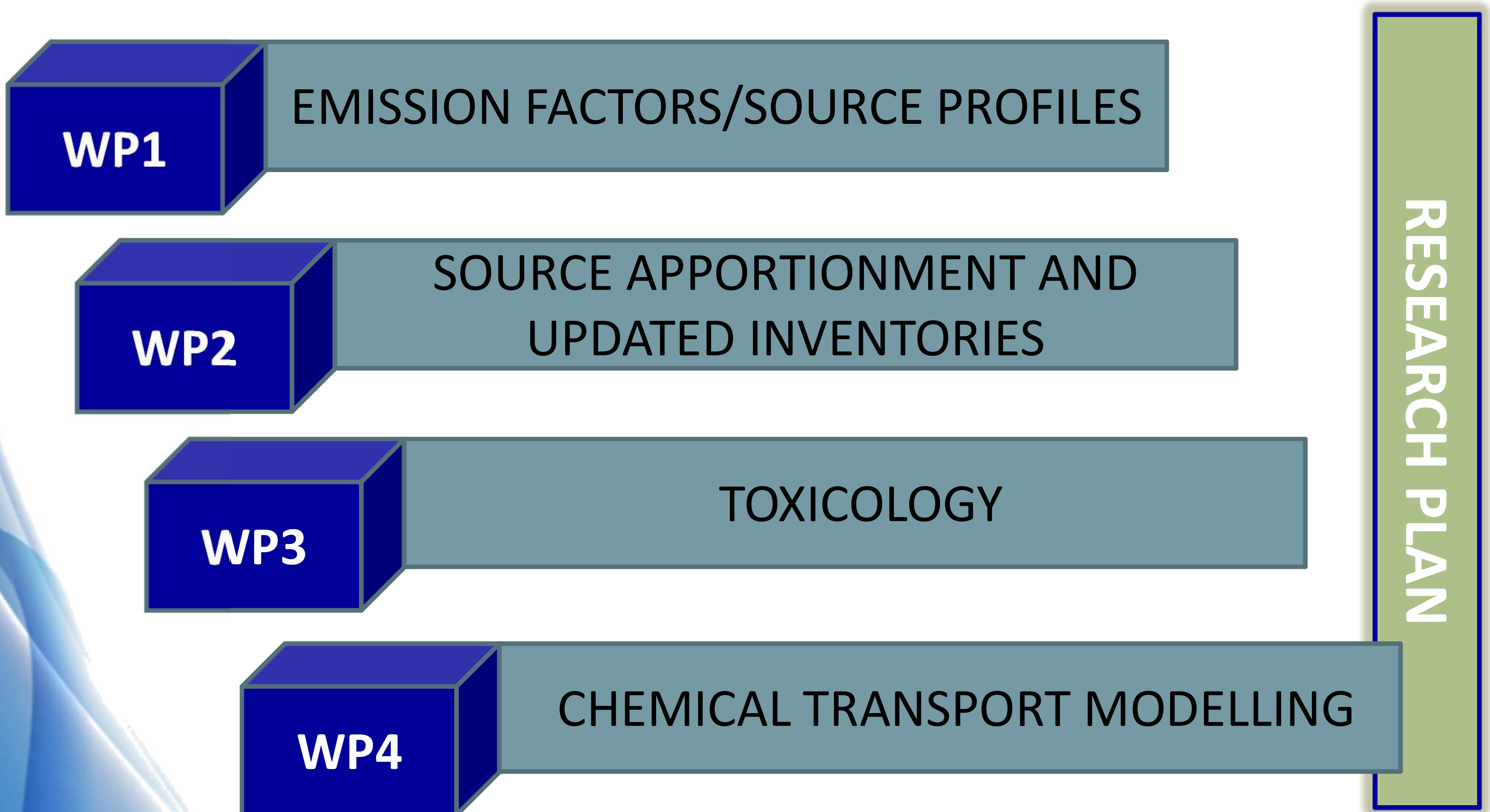
the toxicological studies were only carried out for a limited number of culinary styles, most of them focusing on the cooking fuels

NEED TO:

Obtain chemical fingerprints and assess the toxicology of particles from Luso-Brazilian cooking styles

SOPRO main objective:

To develop hitherto unavailable Luso-Brazilian chemical and toxicological emission profiles for major urban sources of particulate matter



WP1 - Emission Factors/Source Profiles

Task 1.1 - Non-exhaust particle emissions: tyre and brake wear

Task 1.2 - Non-exhaust particle emissions: pavement-tyre interaction

Task 1.3 - Non-exhaust particle emissions: road dust resuspension

Task 1.4 - Vehicle exhaust emissions

Task 1.5 - Road tunnel measurements

Task 1.6 - Cooking emissions

Task 1.7 - Chemical characterisation

WP1 - Emission Factors/Source Profiles

Task 1.1 - Non-exhaust particle emissions: tyre and brake wear

Measurement of tread depth

Tyre weight loss

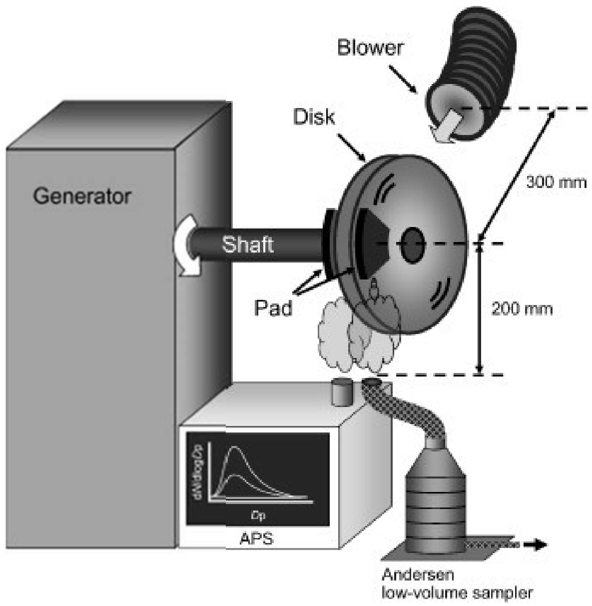
Brake (discs and pads) wear loss

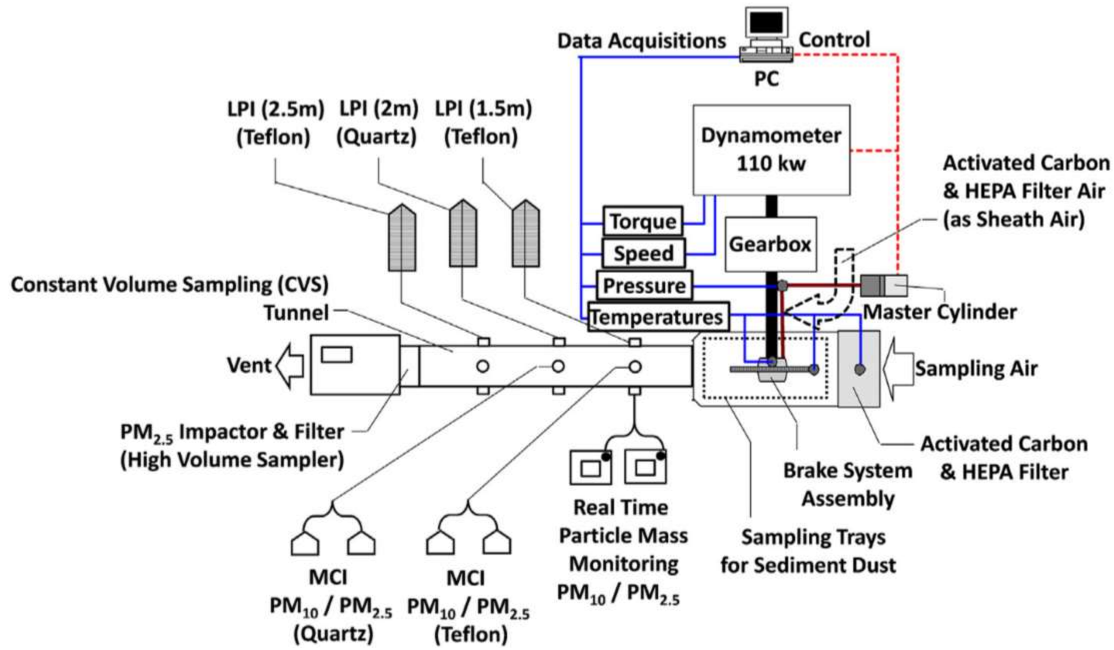
DRIVING LOG

Date & Time	Driving environment (rural, city, motorway, etc)	Driving time	Distance travelled	Weather conditions

WP1 - Emission Factors/Source Profiles

Task 1.1 - Non-exhaust particle emissions: tyre and brake wear





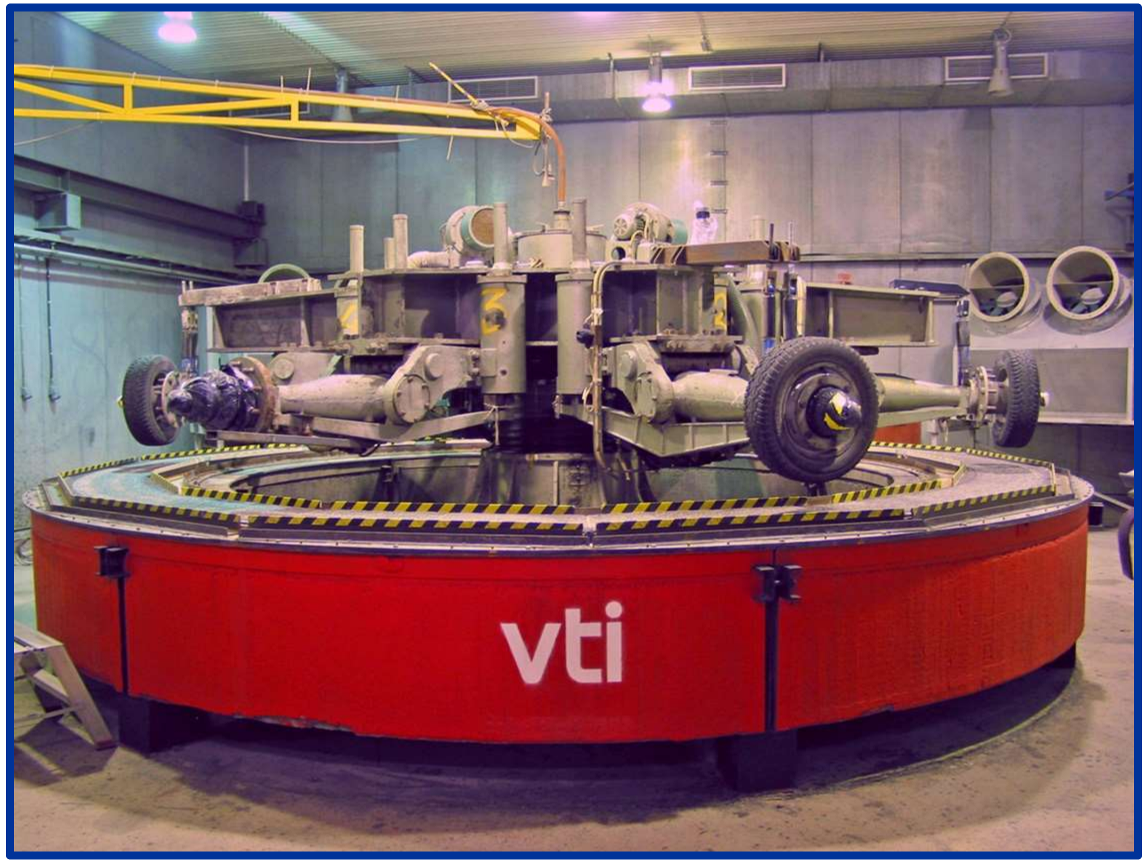
Iijima et al.
Gunma Prefectural Institute of Public Health and Environmental Sciences, Japan

Hagino et al.
Japan Automobile Research Institute

WP1 - Emission Factors/Source Profiles

Task 1.2 - Non-exhaust particle emissions: pavement-tyre interaction

- Road simulador is electrically actuated (no contamination from exhaust pipes)
- Different tyres and pavements can be tested
- Wear particles can be generated under different vehicle velocities



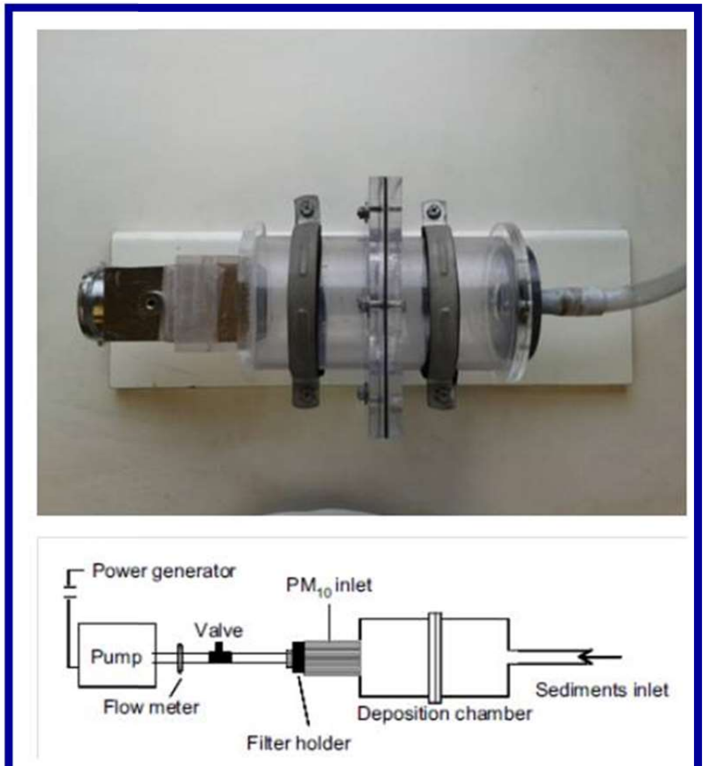
- Hi-vol PM sampling onto filters
- Particle size distributions

WP1 - Emission Factors/Source Profiles

Task 1.3 - Non-exhaust particle emissions: road dust resuspension

SAMPLING METHODOLOGY I

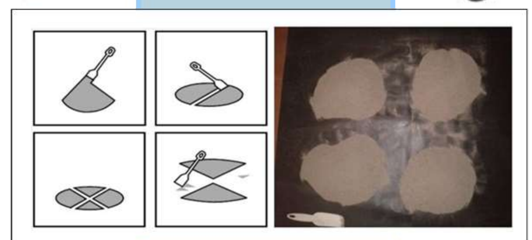
In situ resuspension chamber
(Amato et al., 2011)



Flow = 25 L/min; Area = 1 m^2
Δt = 30 min

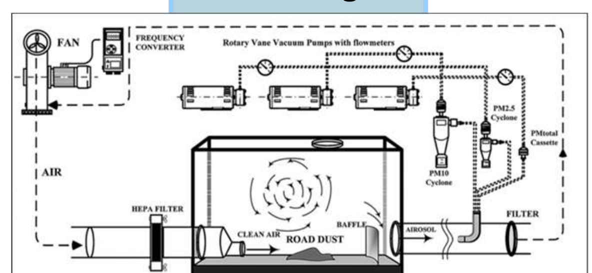
SAMPLING METHODOLOGY II

Broom sweeping
Vacuuming



Coning and quartering

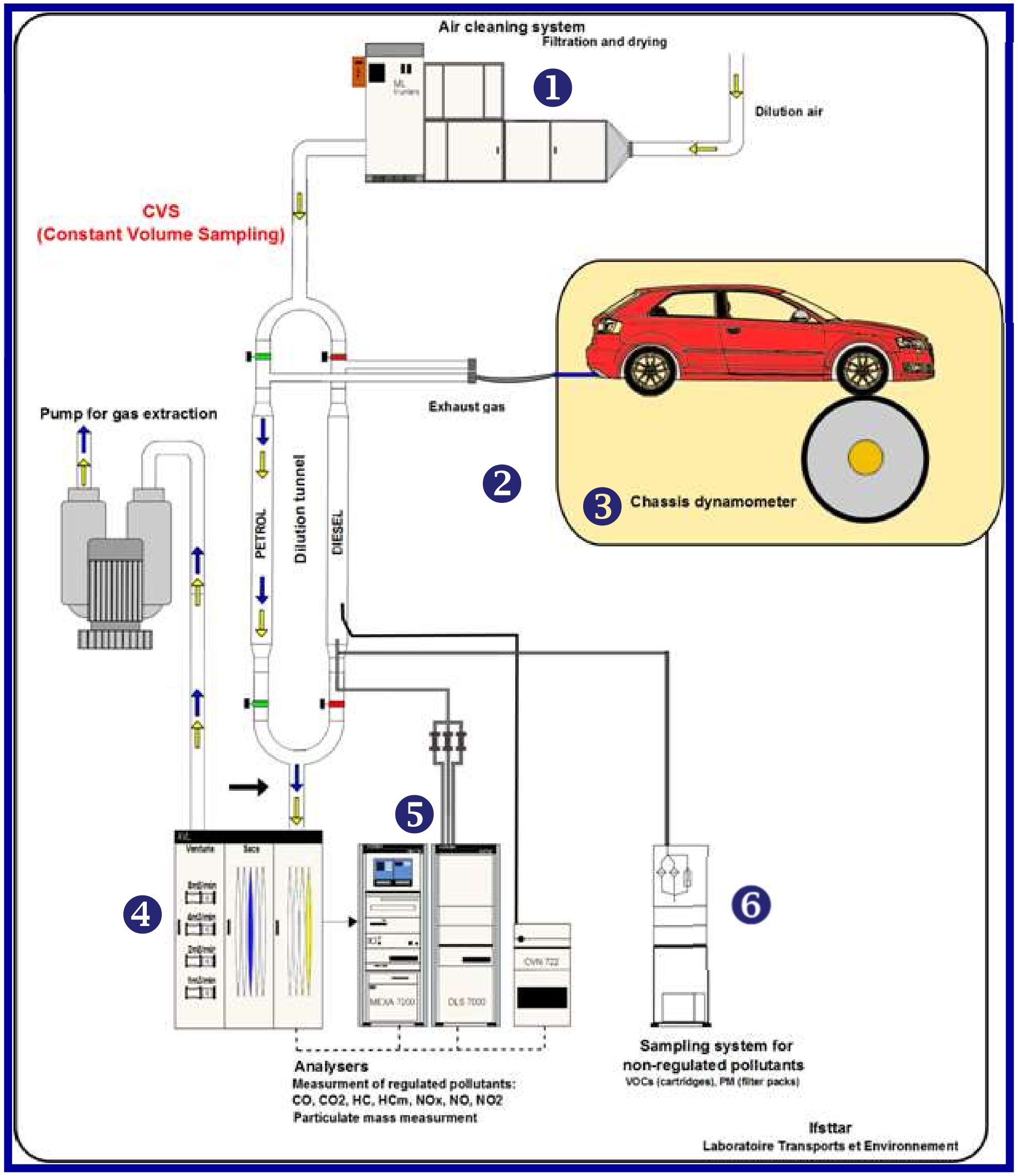
Sieving



Resuspension in a chamber
PM$_{10}$ sampling

WP1 - Emission Factors/Source Profiles

Task 1.4 - Vehicle exhaust emissions



WP1 - Emission Factors/Source Profiles

Task 1.5 - Road tunnel measurements

Rodoanel Mário Covas - HDV

Jânio Quadros - LDV

WP1 - Emission Factors/Source Profiles

Task 1.5 - Road tunnel measurements

João XXI

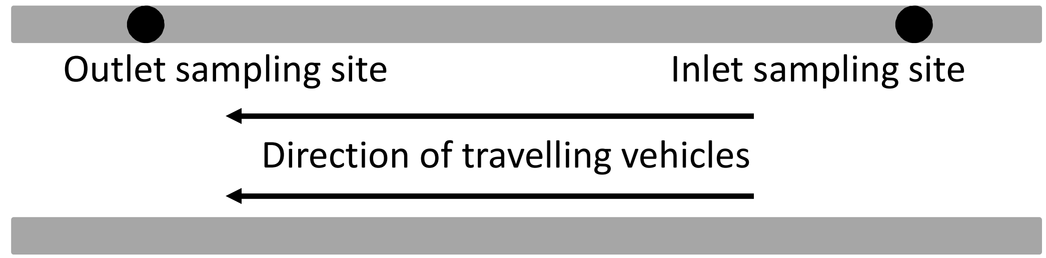
Badal

- Traffic countings
- Airflow through the tunnels
- Real time measurement of CO_2, CO and NO_x
- Aethalometers
- Particle size distributions
- Particle collection onto quartz and teflon filters

La Rovira

WP1 - Emission Factors/Source Profiles

Task 1.5 - Road tunnel measurements



$$EF = \frac{\Delta[P]}{\Delta[CO_2] + \Delta[CO]} Wc$$

EF - emission factor (g/kg of fuel burned)

Δ[P] = concentration of the pollutant subtracted from the background value measured outside the tunnel (µg/m^3)

Δ[CO$_2$] - CO_2 concentration subtracted from the background value (µg C/m^3)

Δ[CO] - CO concentration subtracted from the background value (µg C/m^3)

W_c - weight fraction of fuel carbon (g C/g fuel)

$$EF = \frac{C_{out} - C_{in}}{N.L} A.U.t$$

EF - emission factor (mg/vehicle/km travelled)

C_{out} and C_{in} - pollutant mass concentrations (mg/m^3) at the exit and entrance of the tunnel, respectively

A - tunnel cross-sectional area (m^2)

U - wind speed (m/s)

t - sampling duration (s)

N - total number of vehicles during the sampling period

L - distance between the two monitoring stations (km)

WP1 - Emission Factors/Source Profiles

Task 1.6 – Cooking emissions

Sardinha assada

Leitão à Bairrada

Jaquinzinhos

Bacalhau com natas

Polvo à lagareiro

Vatapá

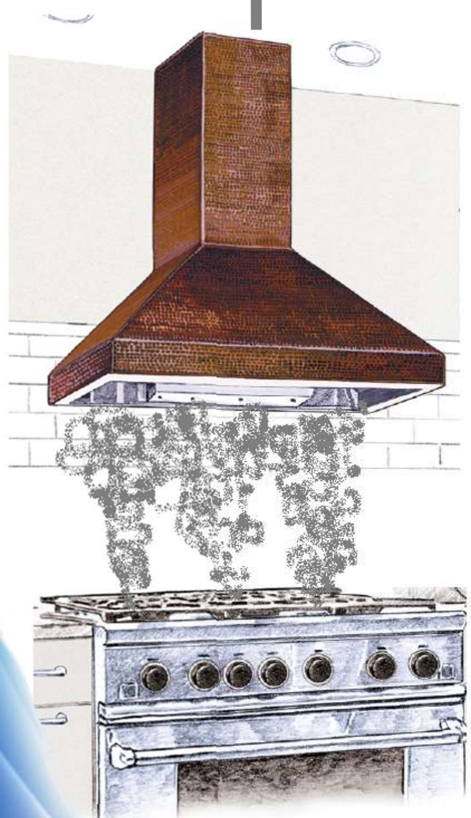
Moqueca

Feijoada

Churrasco

WP1 - Emission Factors/Source Profiles

Task 1.6 – Cooking emissions



VOC sampling onto sorbent tubes

Carbonyl sampling onto DNPH cartridges

$PM_{2.5}$ sampling onto quartz filters

Flow velocity measurement with a Pitot tube

WP1 - Emission Factors/Source Profiles

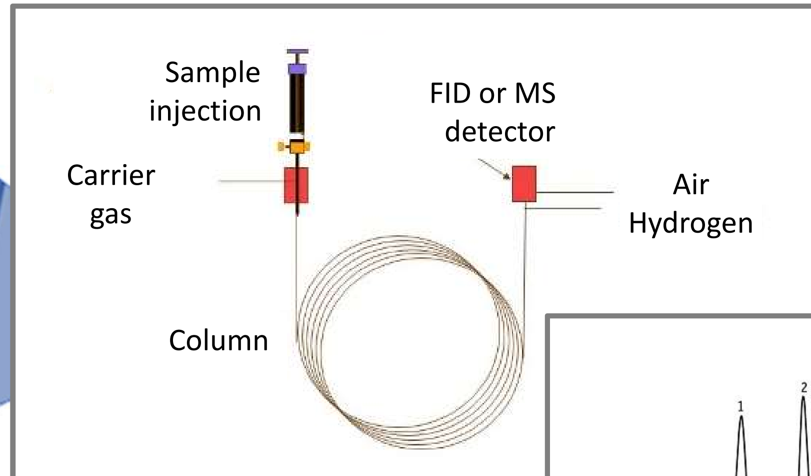
Task 1.7 – Chemical characterisation

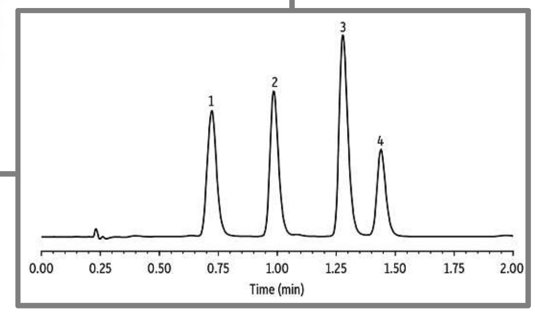
Thermo-optical technique	OC and EC
ICP-MS, ICP-AES, PIXE	Elements
Ion chromatography	Water-soluble ions
GC-MS HPLC-MS/MS HPLC-AECD	Organics
SEM	Morphology
XRD	Mineralogy

WP1 - Emission Factors/Source Profiles

Task 1.7 – Chemical characterisation

Volatile organic compounds





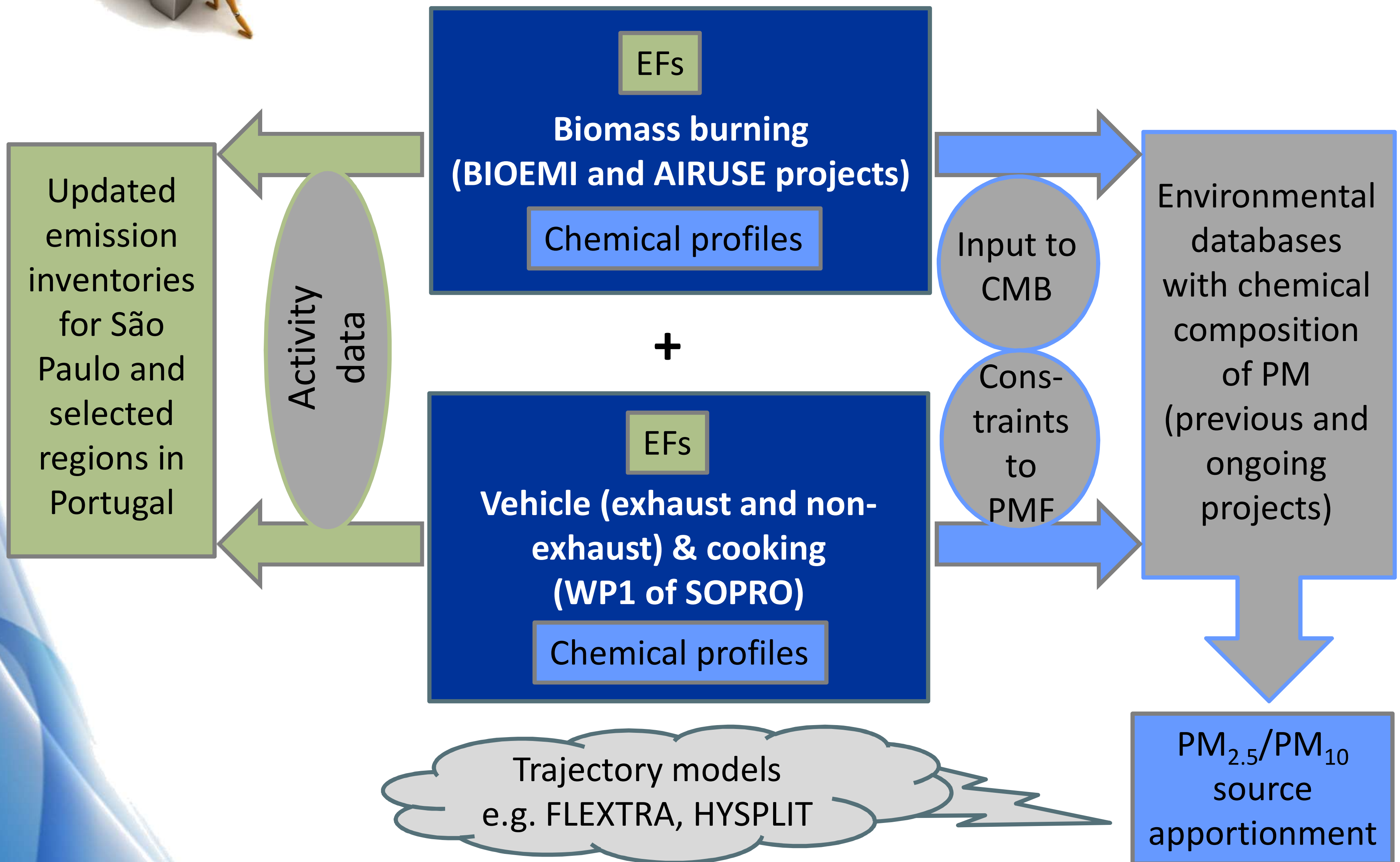
Carbonyl compounds

Acetonitrile extraction

Gradient separation of DNPH derivatives
High-performance liquid chromatography
Photodiode array detector

WP2 – Source apportionment & updated inventories

(Task 2)

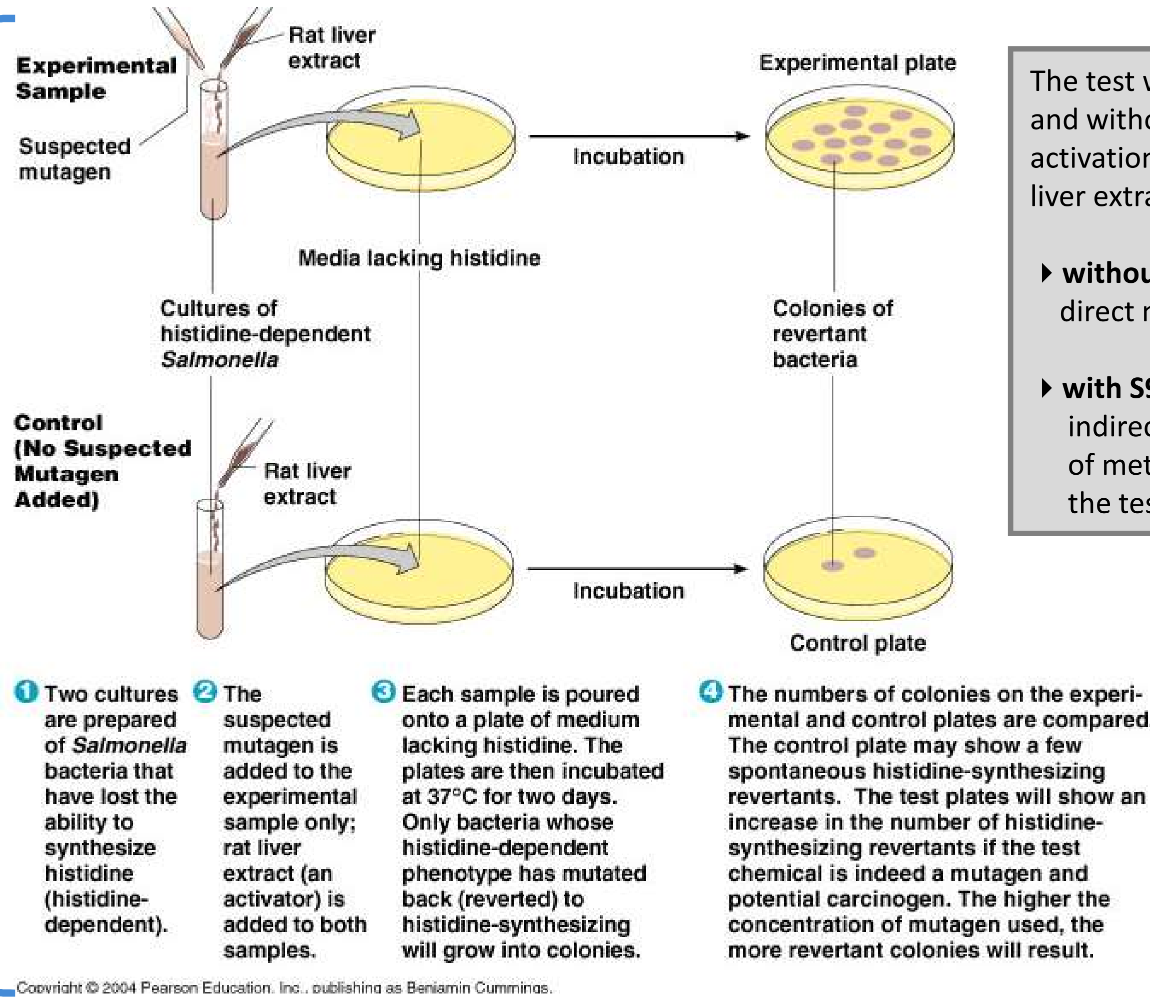


WP3 – Toxicology

Task 3.1 - Mutagenic evaluation

$PM_{10/2.5}$ filters

Organic extracts with PAH, NPAH and OPAH



The test will be repeated with and without metabolic activation by the S9 mix (rat liver extract):

- **without S9** – to evaluate direct mutagenic activity
- **with S9** – to detect the indirect mutagenic activity of metabolic products of the tested PAHs

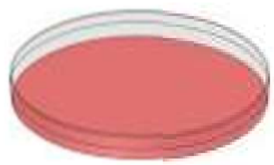
(Maron and Ames, 1983; Mortelmans and Zieger, 2000)

WP3 – Toxicology

Task 3.2 - In vitro screening of the cytotoxicity

Cell culture → Exposure → Biological assays

Cell culture



PM samples

Cell type	Cell line	Description
Lung epithelium	BEAS-2B cells	normal human bronchial epithelium
Lung fibroblasts	MRC-5	primary fetal lung fibroblast cells
Alveolar macrophages	NR8383 cells	murine blood macrophages

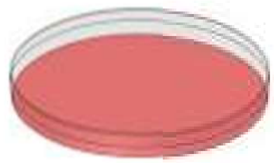
- **Cell viability**
  - LDH; WST-1
    - ✓ Dose-response curves
    - ✓ Selection of concentrations for further studies
- **Oxidative stress**
  - Intracellular ROS generation
  - Nitric oxide production
  - Intracellular catalase and superoxide dismutase activities

WP3 – Toxicology

Task 3.2 - In vitro screening of the cytotoxicity

Cell culture → Exposure → Biological assays

Cell culture



⇐ PM samples

Cell type	Cell line	Description
Lung epithelium	BEAS-2B cells	normal human bronchial epithelium
Lung fibroblasts	MRC-5	primary fetal lung fibroblast cells
Alveolar macrophages	NR8383 cells	murine blood macrophages

- **Inflammation**
  - proinflammatory cytokines (e.g. IL-6, IL-8) and the tumor necrosis factor-alpha (TNF-alpha)
- **Oxidative DNA damage**
  - hOGG1 - modified comet assay
- **cell cycle dynamics**
- **Nuclear and mitotic abnormalities**
  - Cytokinesis-Block Micronucleus Cytome (CBMNCyt) Assay

WP4 – Chemical transport modelling

(Task 4)

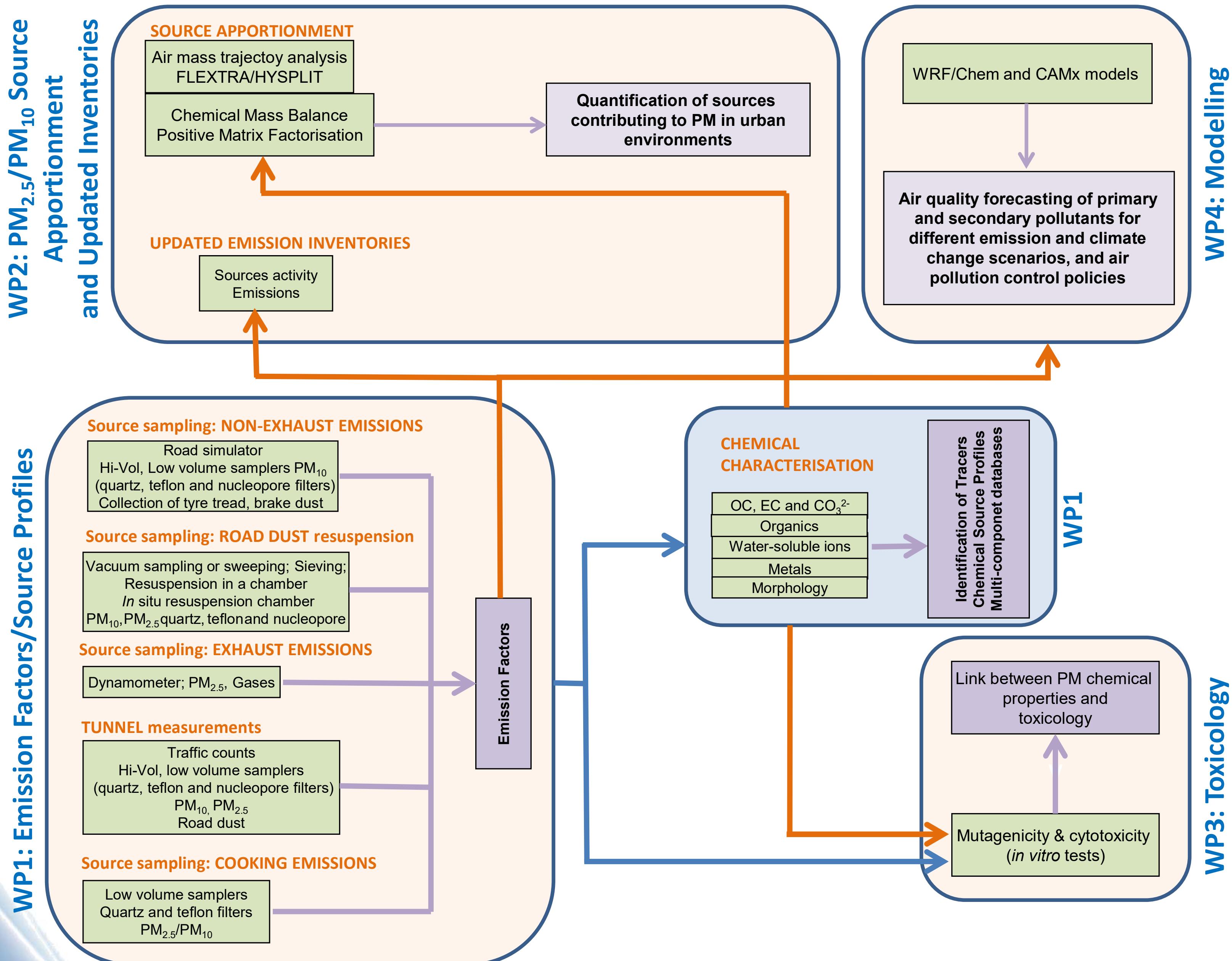
❶ Comprehensive Air Quality Model with Extensions (CAMx)

❷ Weather Research and Forecasting model coupled with Chemistry (WRF-Chem)

❑ Air quality forecasting of primary and secondary pollutants for MASP and a case study in Portugal by incorporating the new emission profiles and updated inventories

❑ Sensitivity tests in terms of air pollution control policies, considering different emission scenarios under climate change conditions

Relashionships between WPs and tasks



POSTGRADUATE PROGRAMME 1:

Title: Physico-chemical profiles of exhaust and non-exhaust emission from motor vehicles

Source sampling: NON-EXHAUST EMISSIONS

Road simulador; Brake dynamometer
PM_{10} samples; size distributions
Collection of tyre tread, brake dust

Source sampling: ROAD DUST resuspension

Vacuum sampling or sweeping; Sieving;
Resuspension in a chamber
In situ resuspension chamber
PM_{10} samples

Source sampling: EXHAUST EMISSIONS

Dynamometer;
$PM_{2.5}$, Combustion gases

TUNNEL measurements

Traffic counts
PM_{10}, $PM_{2.5}$ samples; size distributions
BC; combustion gases
Road dust

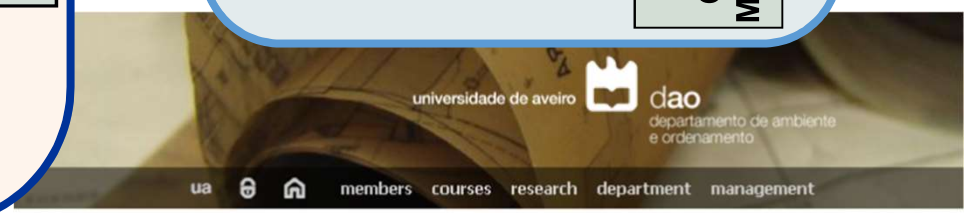
→ **Emission Factors** →

WP1: Emission Factors/Source Profiles

CHEMICAL CHARACTERISATION

OC, EC and CO_3^{2-}
Organics
Water-soluble ions
Metals
Morphology

→ **Identification of Tracers**
Chemical Source Profiles
Multi-component databases



universidade de aveiro
dao departamento de ambiente e ordenamento
1978 2018 a inovar o ambiente

Development of chemically detailed profiles for exhaust and non-exhaust emissions representing the European and Brazilian vehicle fleets

POSTGRADUATE PROGRAMME 2:

Title - Cooking emissions: an overlooked contributor to air pollution?

Source sampling: COOKING EMISSIONS

PM low volume samplers
Flow velocity measurement
VOC and carbonyls in sorbent tubes

→ **Emission Factors**

WP1: Emission Factors/Source Profiles

CHEMICAL CHARACTERISATION

OC, EC
Organic speciation
Water-soluble ions
Metals
VOCs and carbonyls

Identification of Tracers
Chemical Source Profiles
Multi-componet databases

SOURCE APPORTIONMENT

Air mass trajectoy analysis
FLEXTRA/HYSPLIT

Chemical Mass Balance
Positive Matrix Factorisation

UPDATED EMISSION INVENTORIES

Activity information
Emissions

Quantification of cooking emissions to PM in urban environments

WP2: $PM_{2.5}/PM_{10}$ Source Apportionment and Updated Inventories

universidade de aveiro
dao departamento de ambiente e ordenamento

Obtain chemical profiles for hitherto unavailable cooking emissions;
Estimate: i) carcinogenic and mutagenic potencies of these emissions, ii) O_3 and SOA formation potentials of VOCs, and iii) the contribution of cooking emissions to the atmospheric pollution loads at several Brazilian and Portuguese sites

Acknowledgments:

FCT
Fundação para a Ciência e a Tecnologia
MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E ENSINO SUPERIOR

COMPETE 2020

PORTUGAL 2020

UNIÃO EUROPEIA
Fundo Europeu de Desenvolvimento Regional

FAPESP


Casimiro Pio
Teresa Nunes
Mário Cerqueira
Mª Fátima Andrade
Pérola Vasconcellos
Edmilson Freitas
Thiago Nogueira
Margarita Evtyugina
Ana Vicente
Nuno Canha
Regina Miranda
Sofia Caumo
Guilherme Pereira
Postdoc
Researcher
Estela Vicente
Ana Isabel Neto
Xavier Querol
Sérgio Corrêa
Mats Gustafsson
Ana Isabel Miranda
Joana Ferreira
Master fellow
Isabel Lopes
Helena Oliveira
Benjamin Bandowe
Vorne Gianelle
Franco Lucarelli
Esther Coz