Trazadores Moleculares como Finger Prints en Contaminación Atmosférica.

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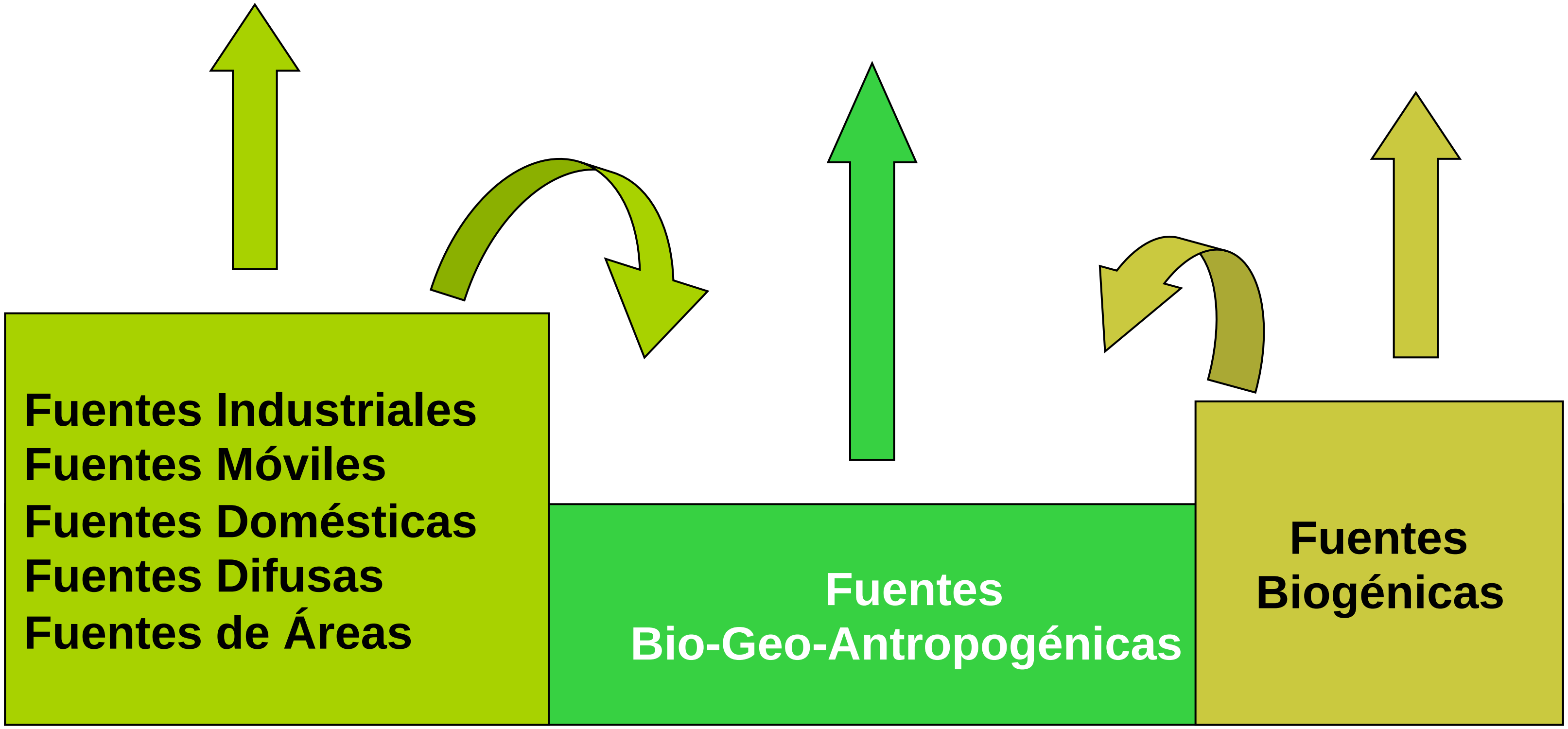
5 y 6 de Abril de 2016

ATMOSFERA: Sistema de Fases

Gas/Líquida/Sólida



Fuentes Industriales
Fuentes Móviles
Fuentes Domésticas
Fuentes Difusas
Fuentes de Áreas

Fuentes
Bio-Geo-Antropogénicas

Fuentes
Biogénicas

EMISIONES

DINAMICA DE GASES Y PARTICULAS EN LA ATMOSFERA

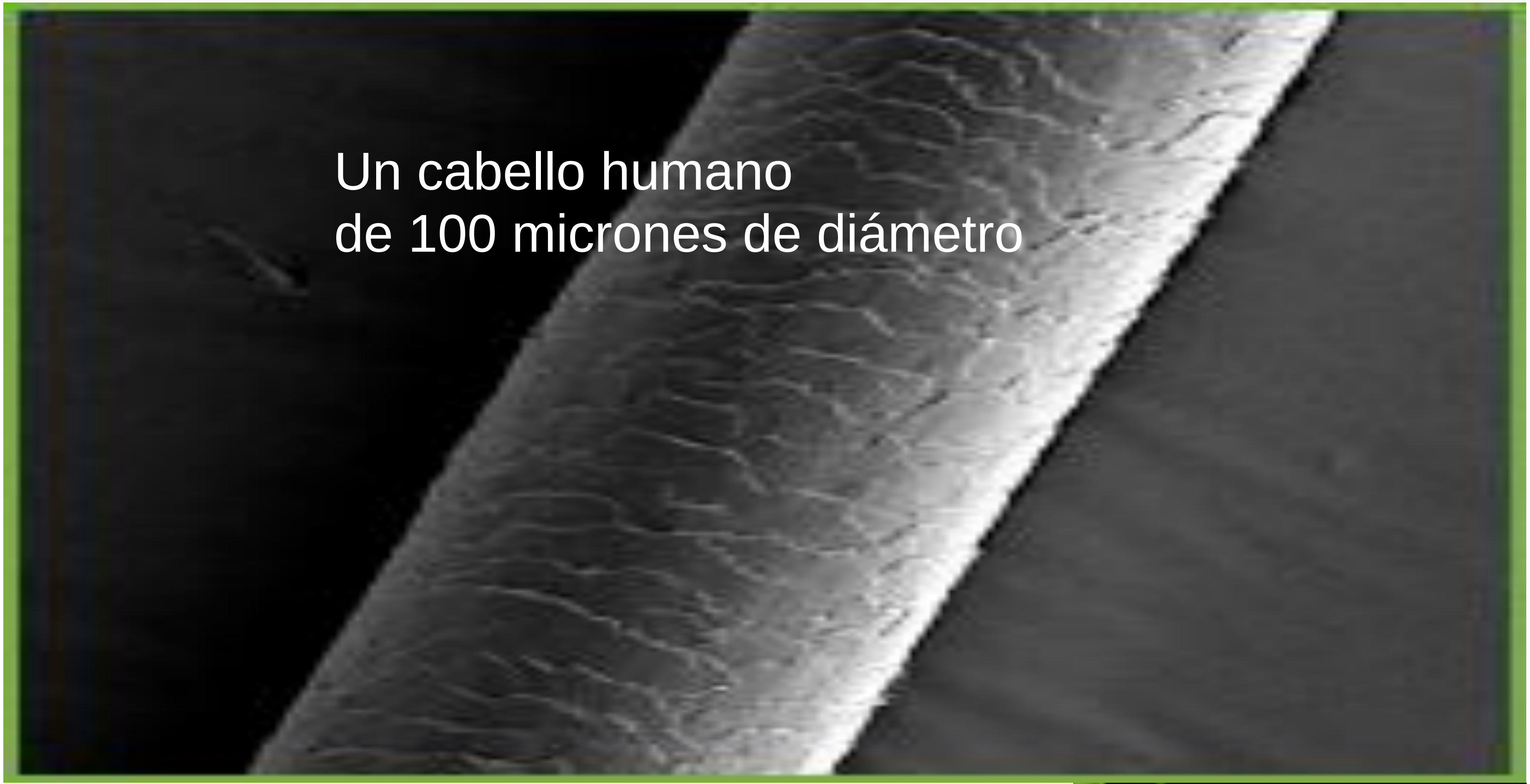
Se pueden originar desde fuentes naturales o antrópicas y se denominan **emisiones primarias** y **aerosoles primarios**. También pueden generarse en la fase aérea por acción fotoquímica, colisional y por coagulación, se denominan gases o **aerosoles secundarios** según corresponda.

Aerosoles: Partículas inorgánicas u orgánicas suspendidas en la fase aérea, las cuales pueden ser de naturaleza sólida, líquida o micro-organismos.

RECEPTOR

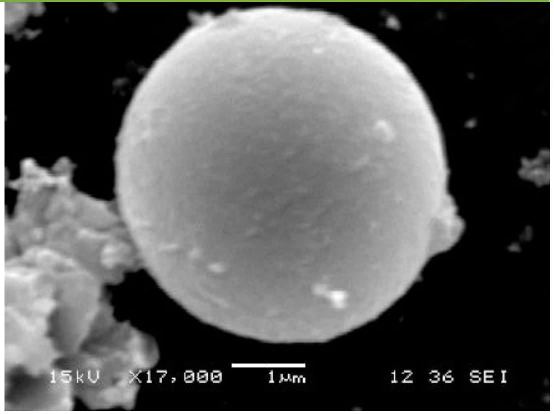
TRANSPORTE
Y
TRANSFORMACIONES QUIMICAS Y CAMBIOS FISICOS

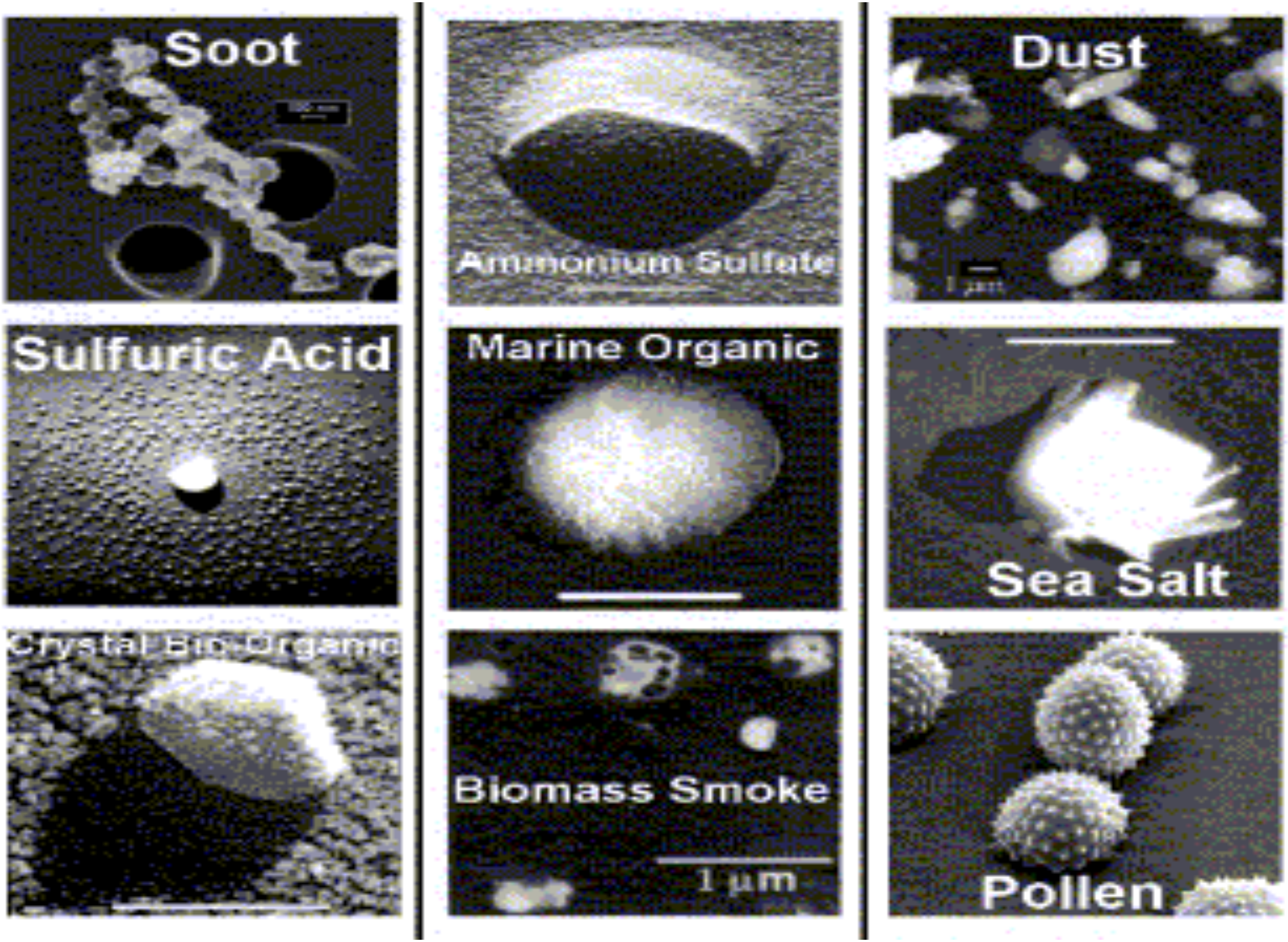
EMISIONES



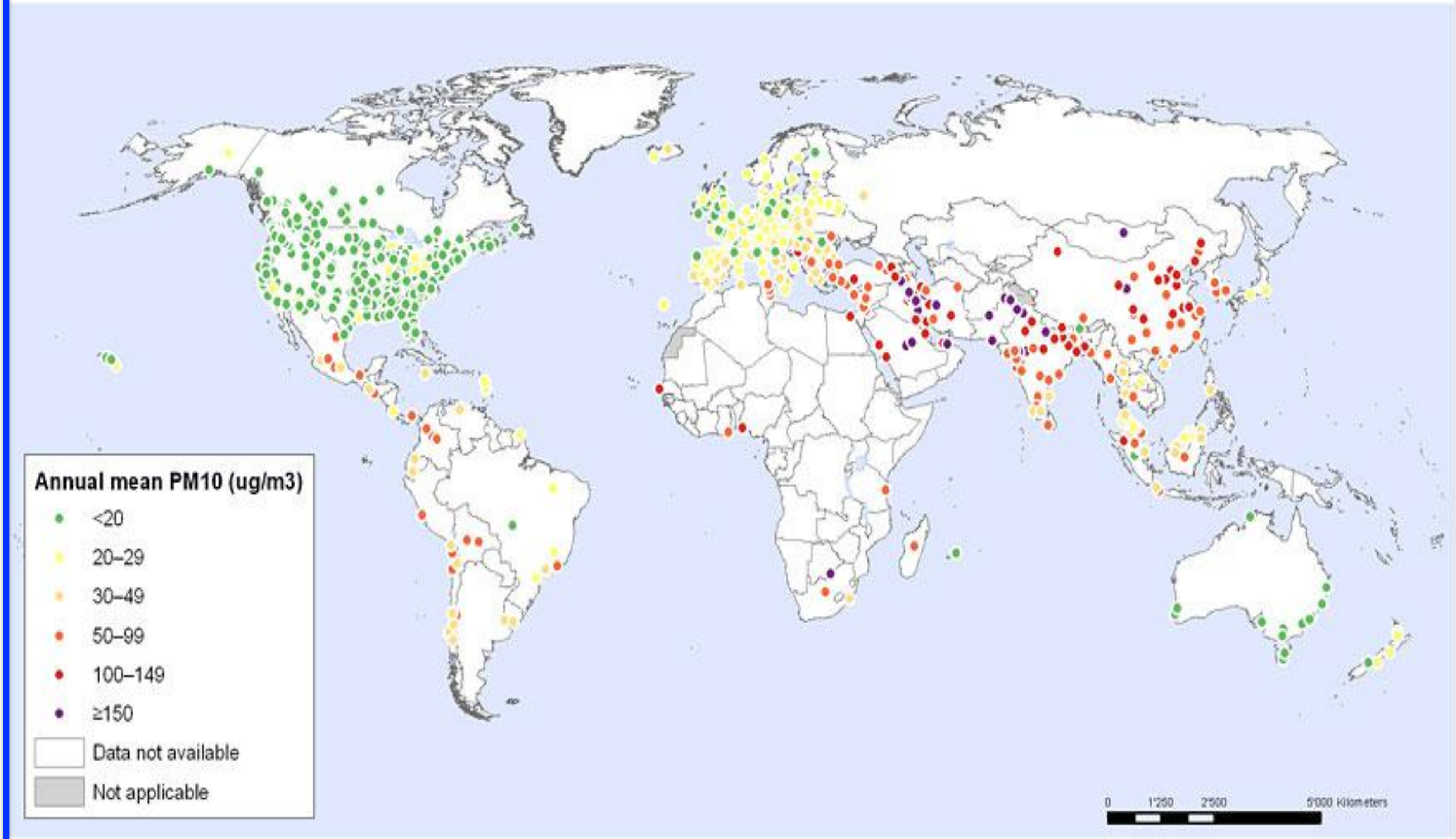
Un cabello humano
de 100 micrones de diámetro

Material Particulado (MP-10) de la fracción respirable están en la escala de 10 micrones o menos.
MP-10 Partículas Gruesas
MP-2,5 Partículas Finas




Soot
Ammonium Sulfate
Dust
1 µm
Sulfuric Acid
Marine Organic
Sea Salt
Crystal Bio-Organic
Biomass Smoke
1 µm
Pollen

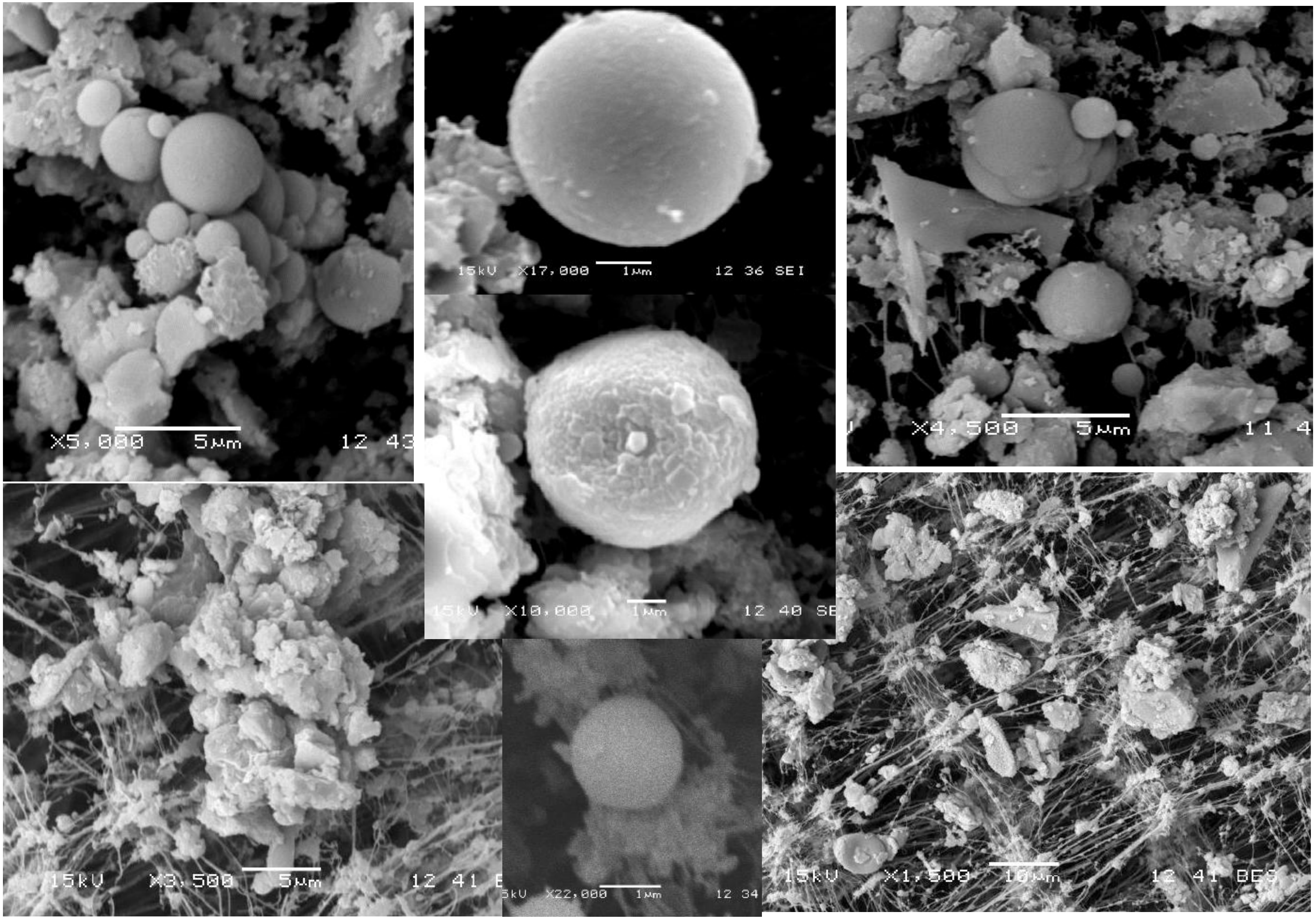
Exposure to particulate matter with an aerodynamic diameter of 10 μm or less (PM10) in 1081 cities, 2003–2010



Data Source: World Health Organization
Map Production: Public Health Information
and Geographic Information Systems (GIS)
World Health Organization

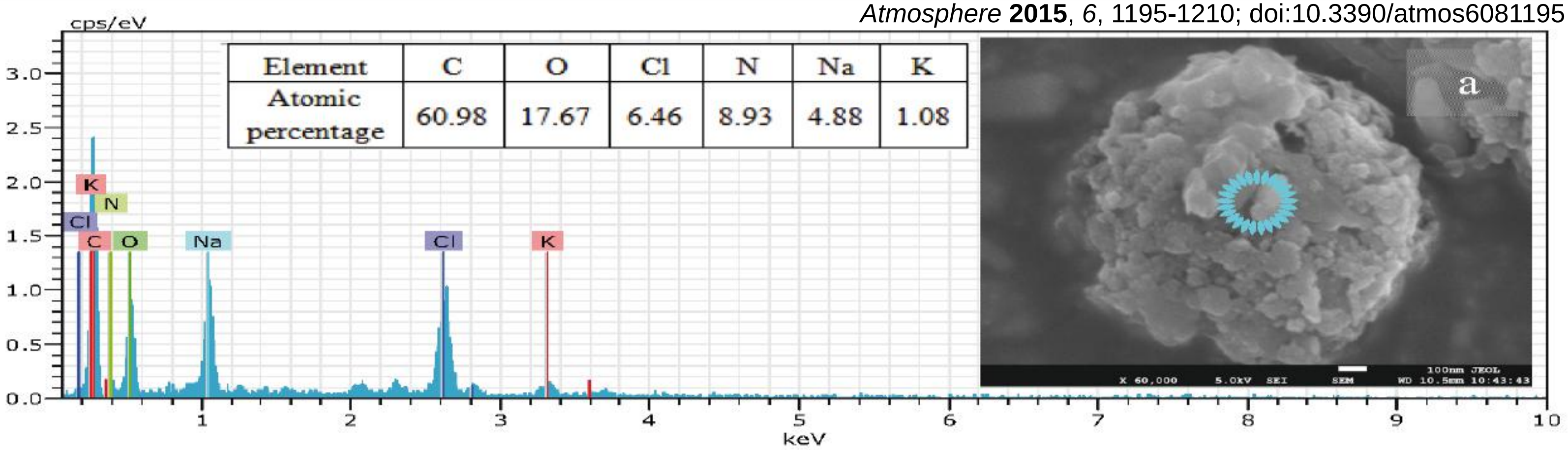
World Health Organization

Material Particulado Típico de Aire Urbano (MP-10 and MP2.5)

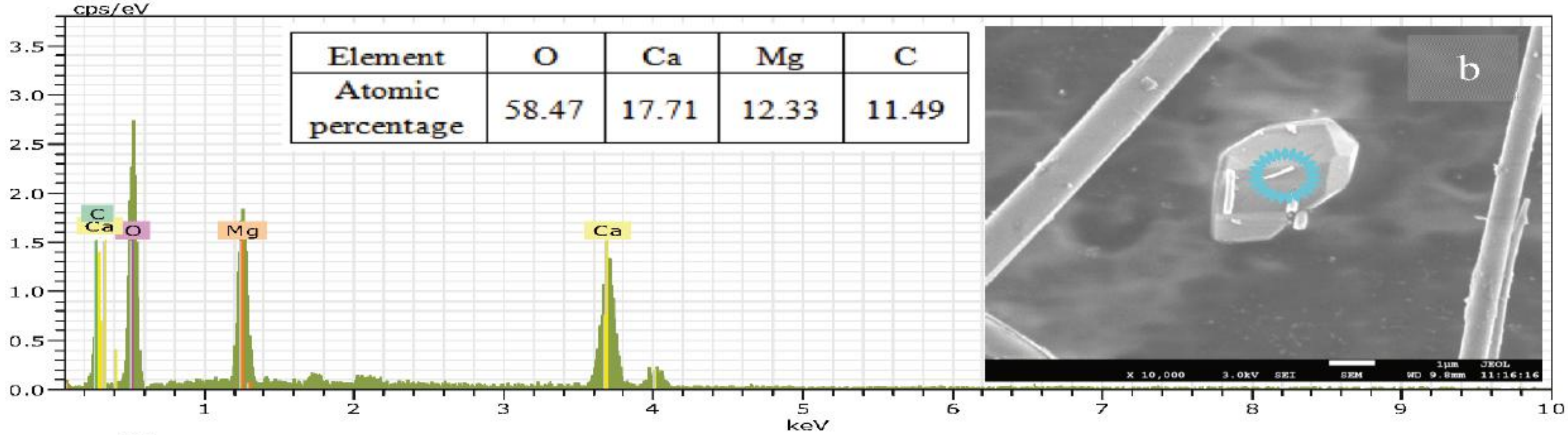


Agradecimientos al Dr. José Sepúlveda por estudio de Microscopía en la UAM, México

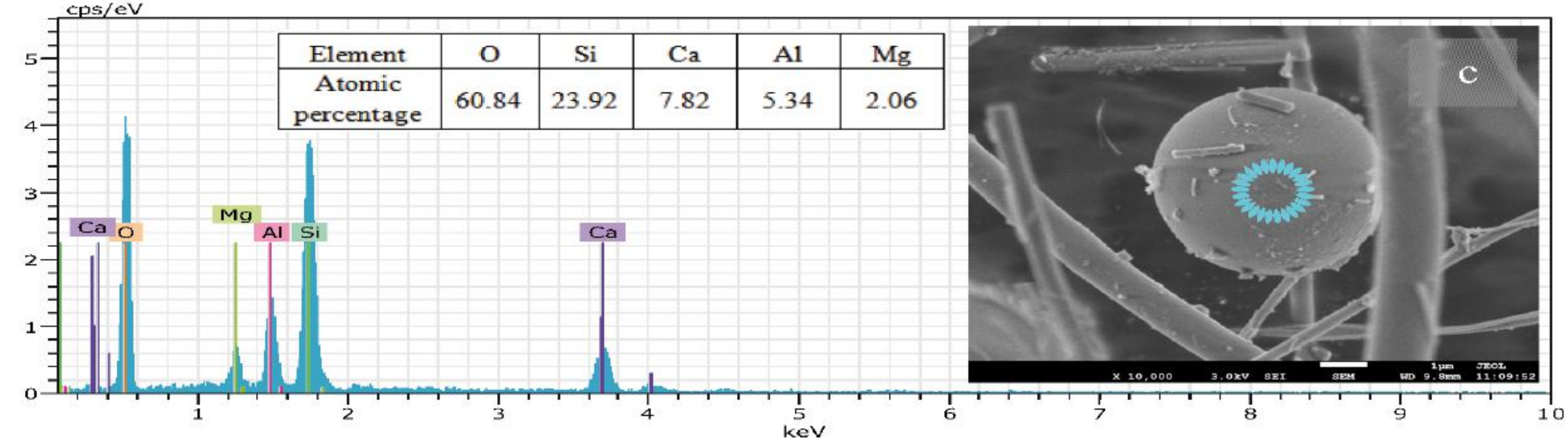
Atmosphere **2015**, *6*, 1195-1210; doi:10.3390/atmos6081195



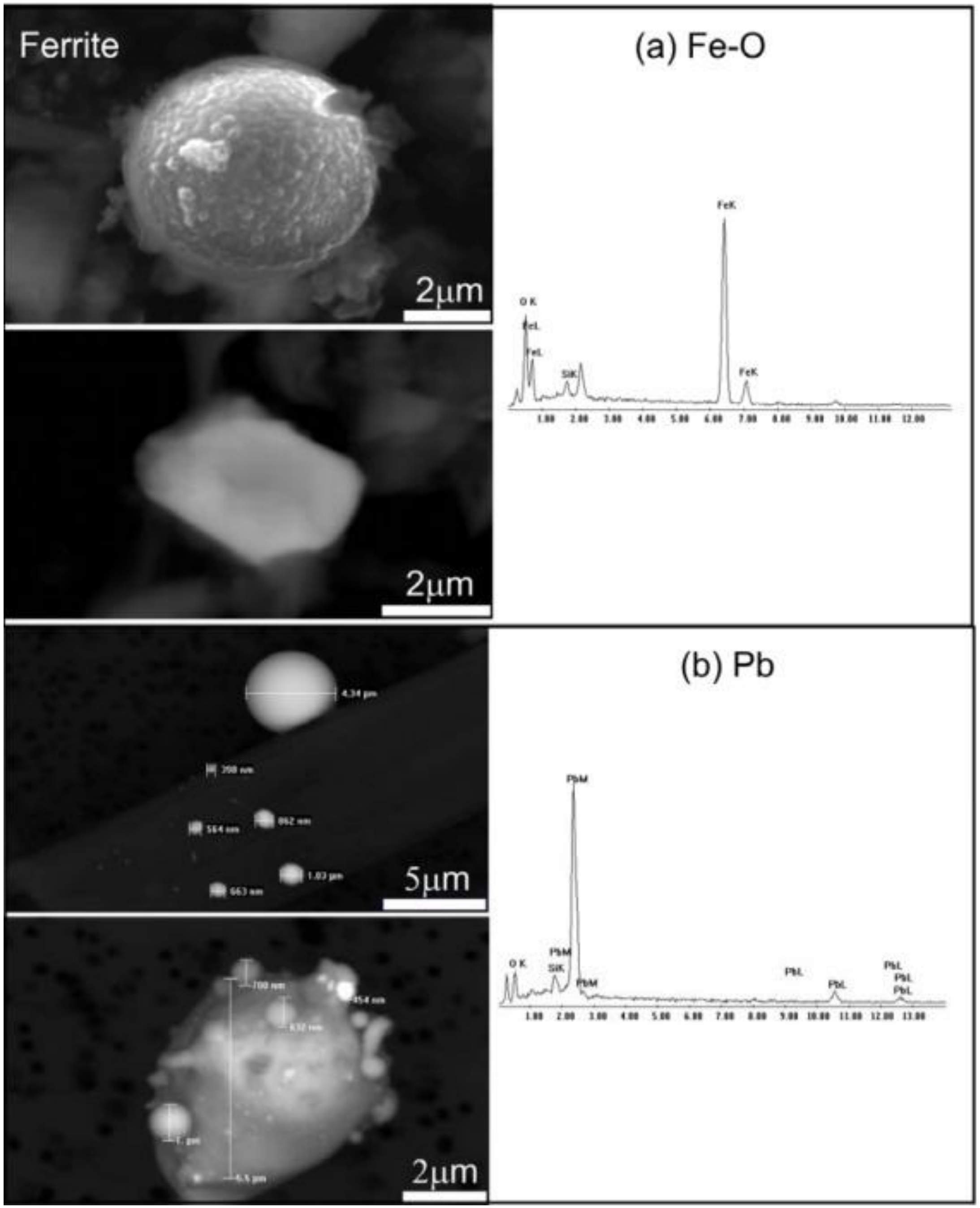
Element	C	O	Cl	N	Na	K
Atomic percentage	60.98	17.67	6.46	8.93	4.88	1.08



Element	O	Ca	Mg	C
Atomic percentage	58.47	17.71	12.33	11.49

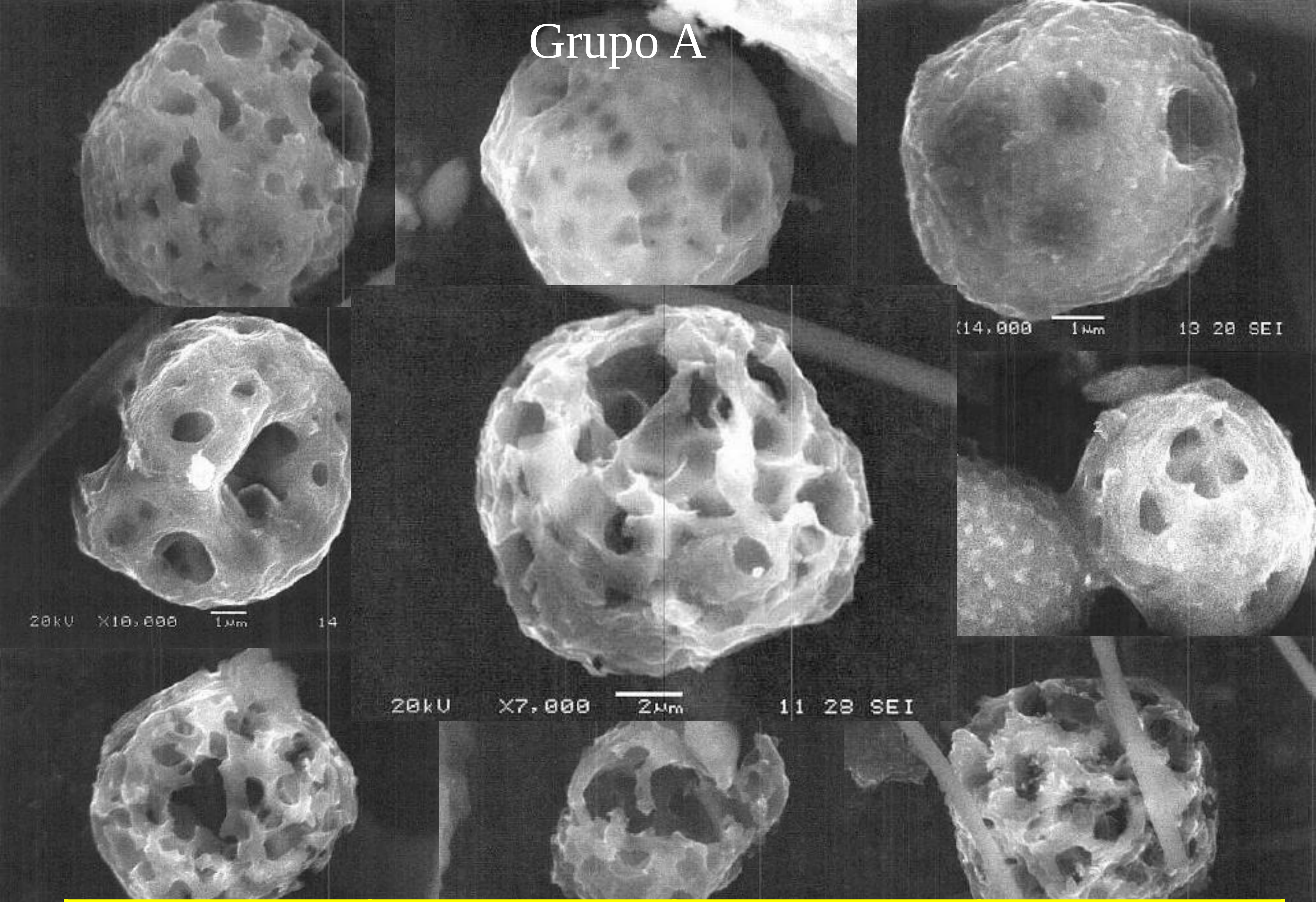


Element	O	Si	Ca	Al	Mg
Atomic percentage	60.84	23.92	7.82	5.34	2.06



Atmospheric Pollution Research, Volume 3, Issue 3, 2012, 289–300

Grupo A

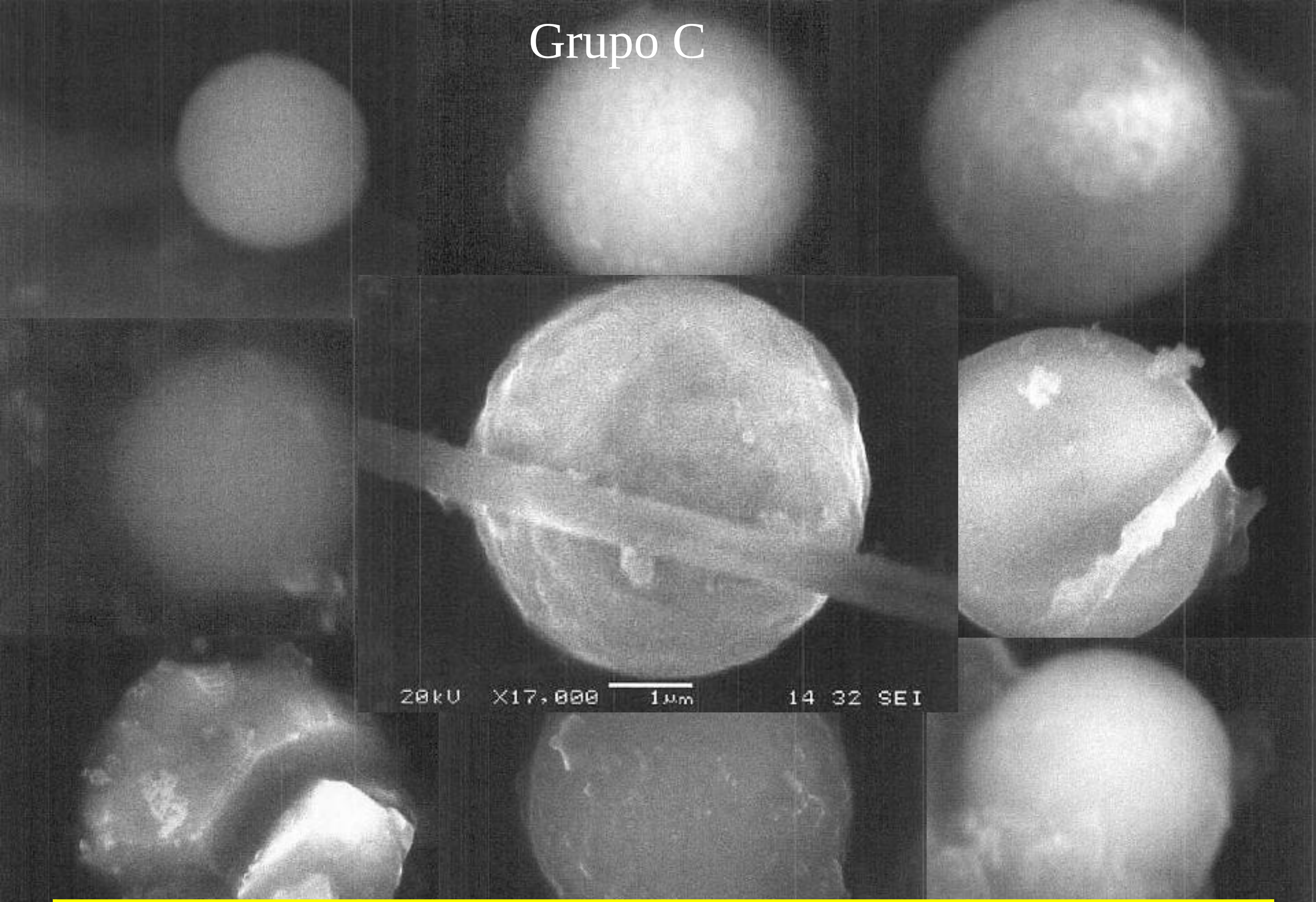


Grupo A **I**	Forma redondeada. Aspecto multiporoso	**C, O, S y V principalmente**	NE, SE, Centro, SO y NO

Grupo B

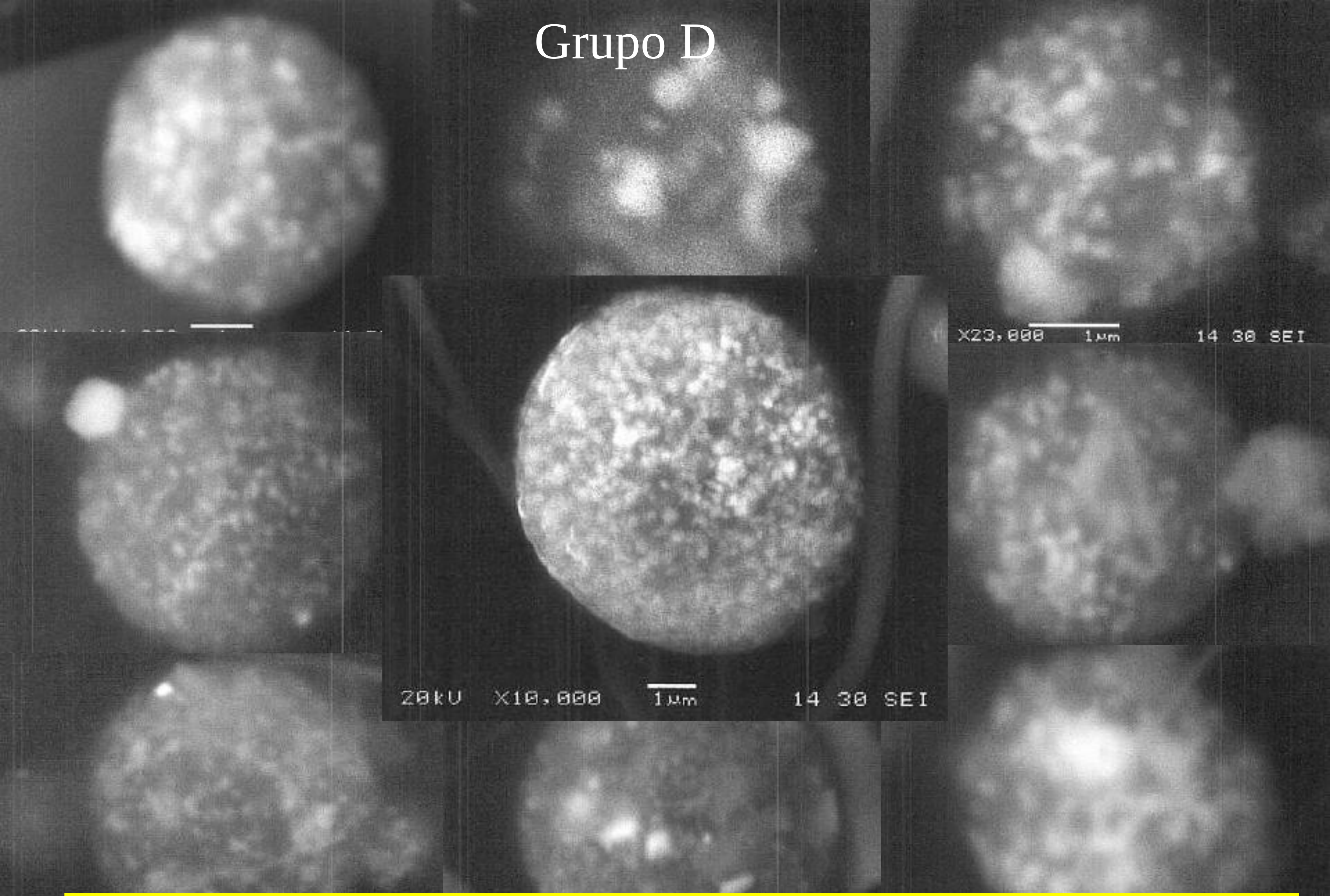
Grupo B **I**	Forma irregular. Aspecto de cristales y agujas	**C, O y alto contenido de S y Ca**	SO, NO, NE y SE

Grupo C



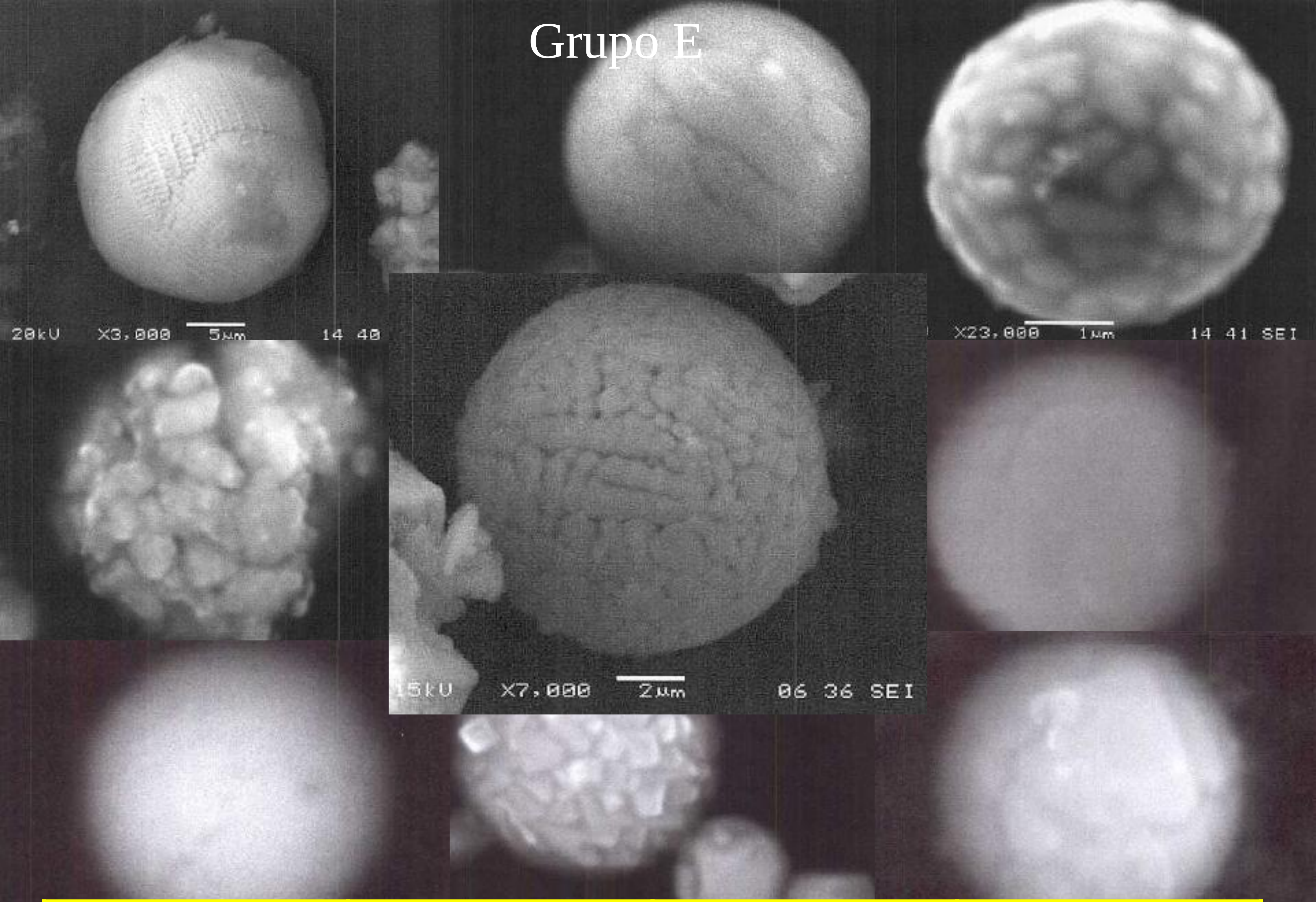
Grupo C **I, II y III**	Forma muy redondeada. Aspecto homogéneo	**C, O, Al, Si, P y Ca. Escaso contenido de Fe y Cu**	NE, NO y SE

Grupo D



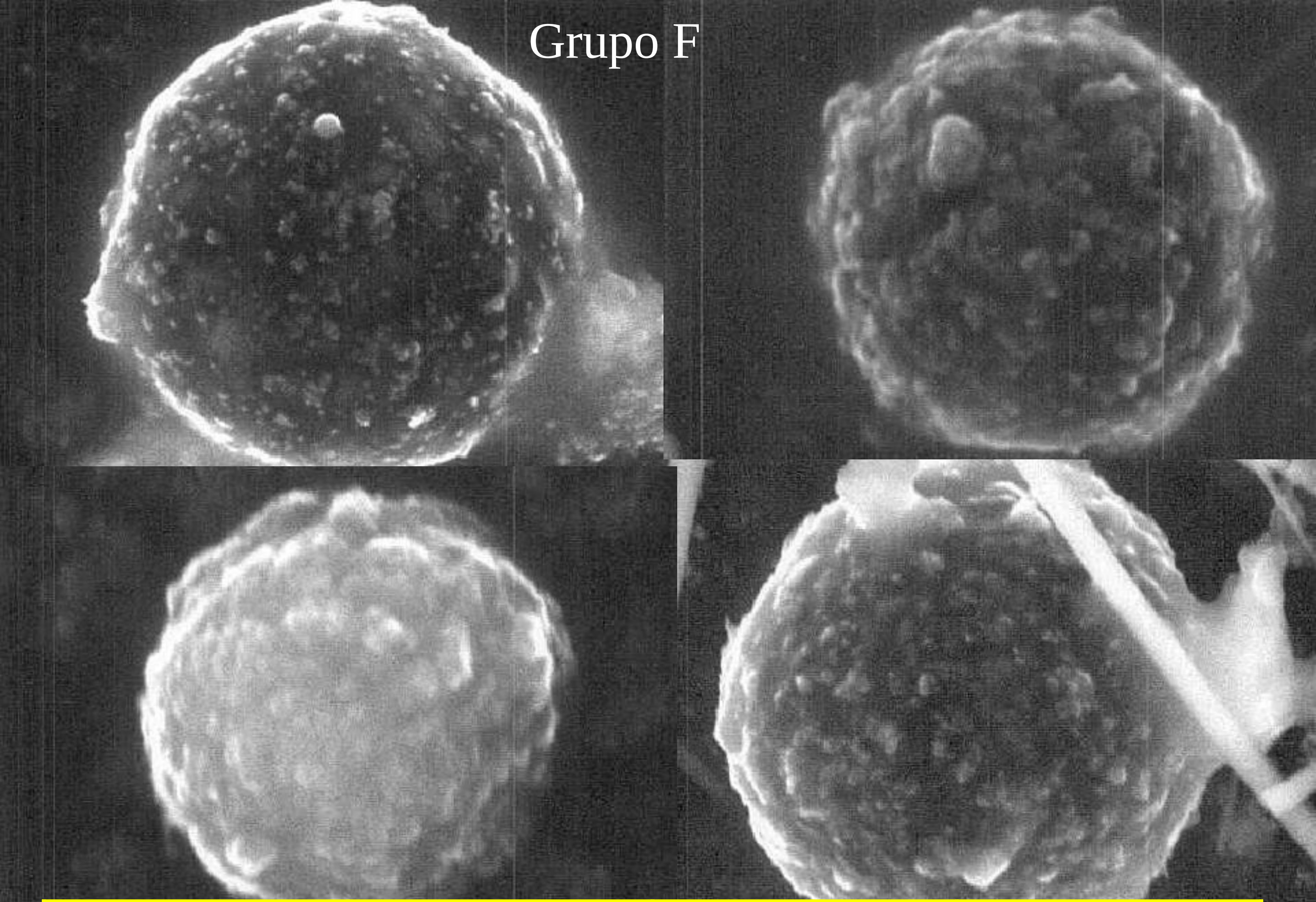
Grupo D **I y II**	Forma redondeada.Aspecto de matriz obscura y multitud de pequeñas nanopartículas muy brillantes en su interior	**C, O y Ti. Escaso contenido de Si, Al, Cu, Na, Mg, Ba y S**	NE, NO, SE y SO

Grupo E



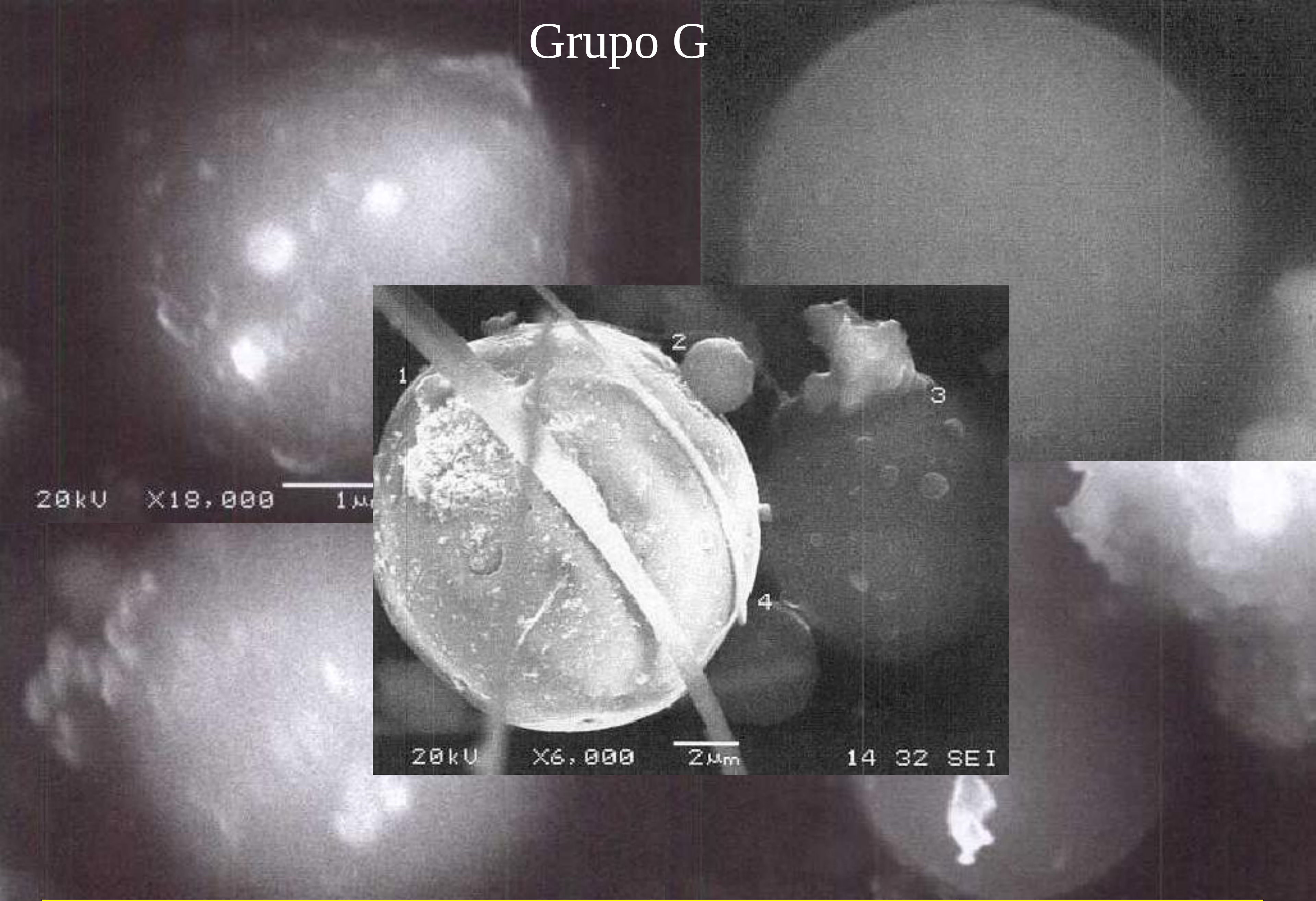
Grupo E **I**	Forma redondeada. Aspecto acordonado	**Alto contenido de Fe y O**	NE, NO y SO

Grupo F



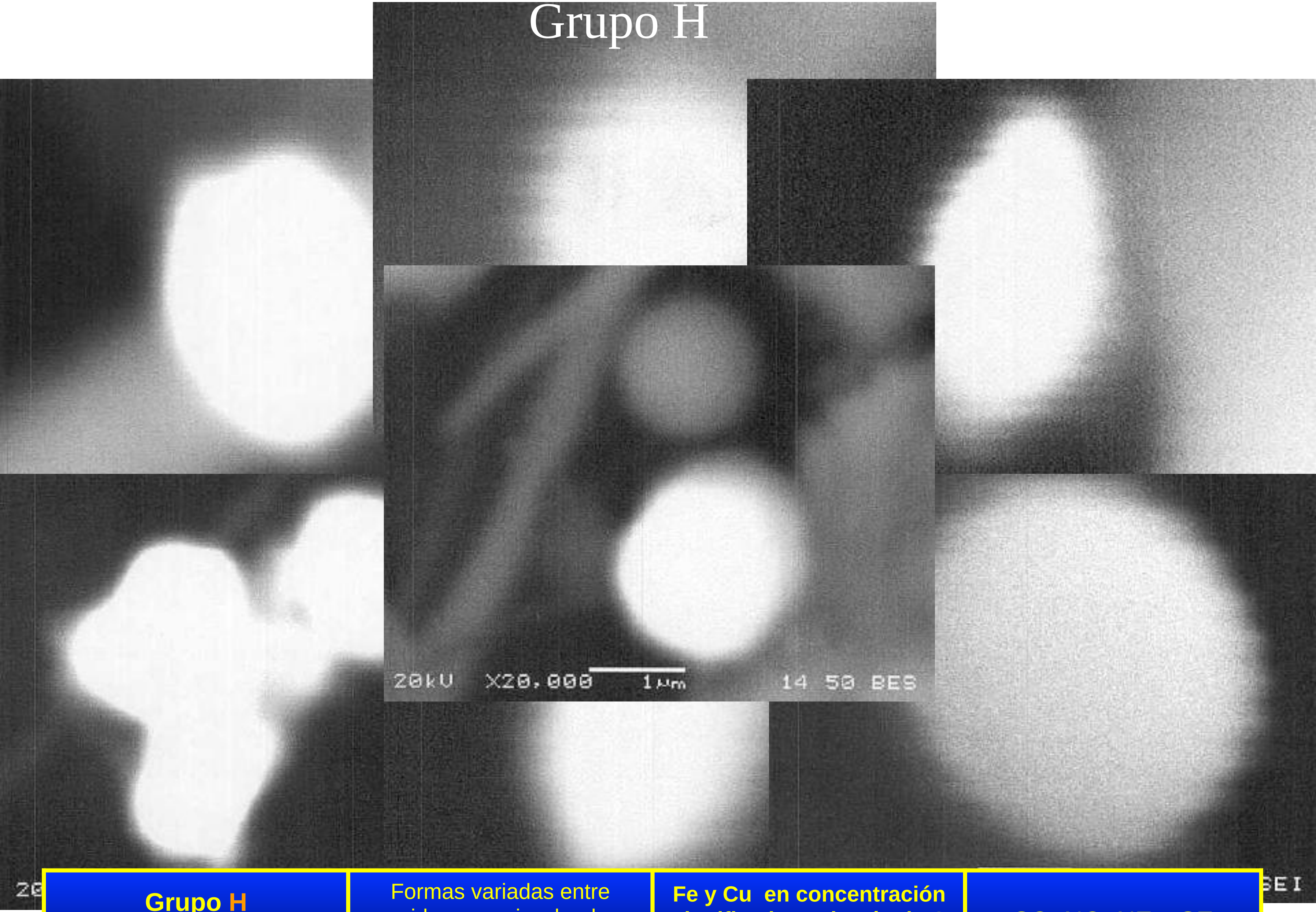
Grupo F **I**	Forma redondeada. Aspecto grumoso	**Alto contenido de C y O y escaso contenido de otros marcadores**	NE

Grupo G



Grupo G **I y II**	Forma muy redonda. Aspecto homogéneo y obscura	**Alto contenido de C y O y escaso contenido de otros marcadores**	NE, NO y SO

Grupo H

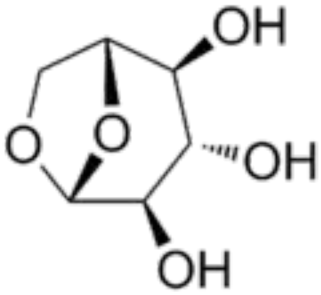


Grupo H **I, II y III**	Formas variadas entre ovoides y semirredondas. Aspecto muy brillante	**Fe y Cu en concentración significativa, además de C y O**	SO, NO, NE y SE

Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles

B.R.T. Simoneit!, J.J. Schauer, C.G. Nolte, D.R. Oros!,V.O. Elias, M.P. Fraser, W.F. Rogge, G.R. Cass

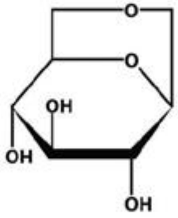
Atmospheric Environment 33 (1999) 173-182



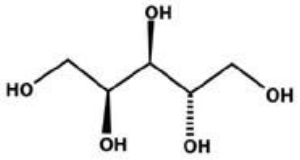
($C_6H_{10}O_5$)

Levoglucosan (1,6-anhydro-b-D-glucopyranose) is a major organic component emitted in fine smoke particulate matter from burning of biomass. It is generally accompanied by other monosaccharide derivatives and biomarker compounds such as aliphatic and oxygenated compounds and terpenoids from biomass waxes, resins, gums and other biopolymers. Levoglucosan with the associated biomarkers can be utilized as specific indicators for the presence of emissions from biomass burning in samples of atmospheric fine particulate matter. Levoglucosan is emitted at such high concentrations that it could be detected in aerosol particulate matter at considerable distances from the combustion sources.

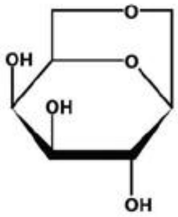
Sacáridos como Trazadores de Aerosoles Atmosféricos



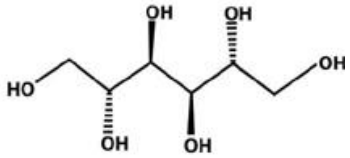
levoglucosan
(1,6-anhydro-beta-D-glucopyranose)



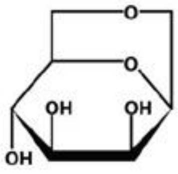
arabitol
((2R,4R)-pentane-1,2,3,4,5-pentol)



mannosan
(1,6-anhydro-beta-D-mannopyranose)



mannitol
((2R,3R,4R,5R)-hexane-1,2,3,4,5,6-hexol)



galactosan
(1,6-anhydro-beta-D-galactose)

Los monosacáridos anhídridos **levoglucosano** (1,6-anhydro-beta-D-glucopyranose) y en menor cantidad sus estereoisómeros **manosano** (1,6-anhydro-beta-D-mannopyranose) y **galactosano** (1,6-anhydrobeta-D-galactose) pueden ser determinados como productos de la degradación térmica de polisacáridos presentes en la biomasa.

Mientras que el Levoglucosano se origina de la pirólisis de la celulosa, manosano y galactosano se derivan de la hemicelulosa.

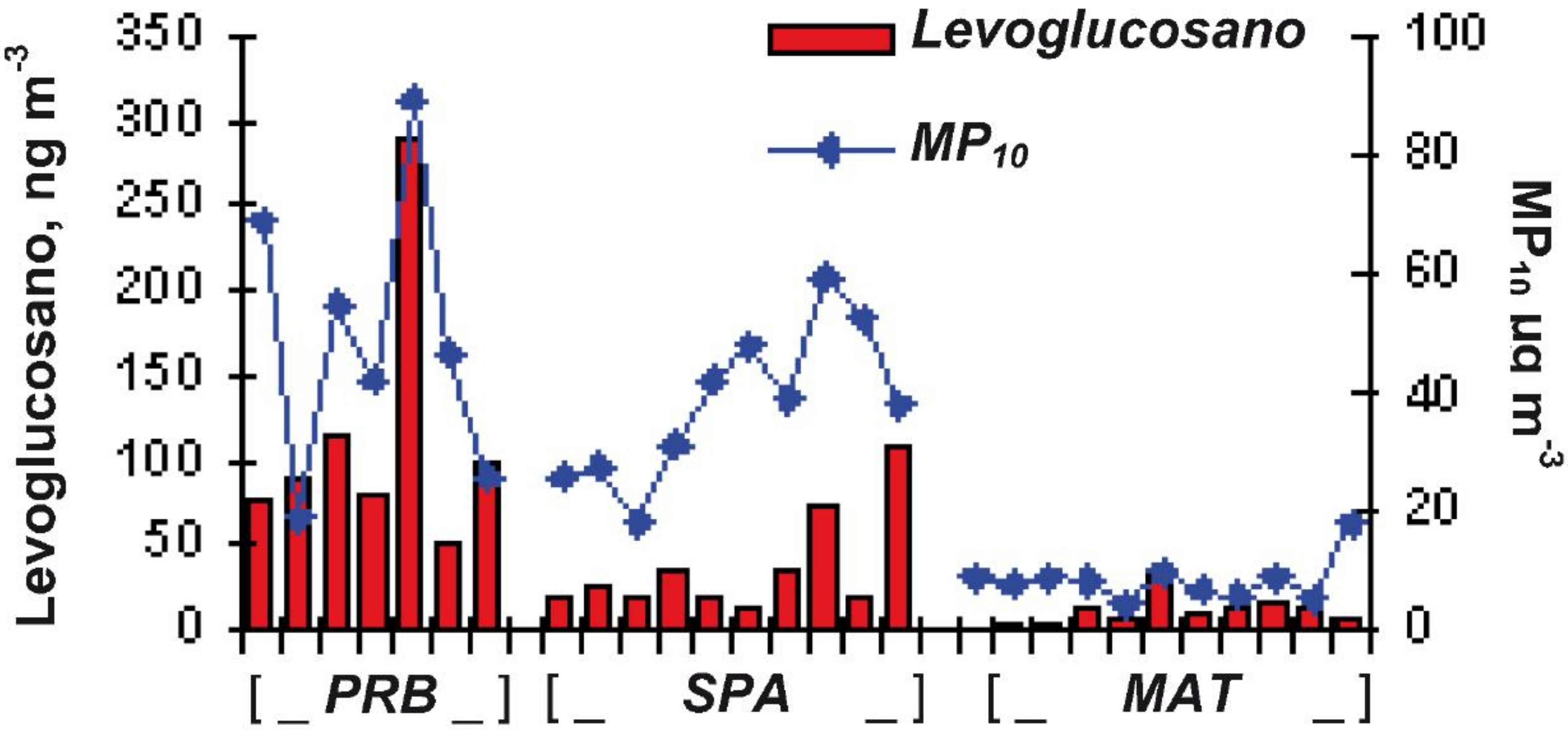
Los combustibles fósiles no liberan azucares anhídridos.

During the combustion of fossil fuels no anhydrosugars are released.

Levoglucosano reúne condiciones importantes como trazador: es abundante en el humo de madera, altamente específico de la fuente y con alta estabilidad en la atmósfera.

En tanto que arabitol y manitol son característicos de bacterias, hongos y líquenes.

Levoglucosano, um biomarcador da queima de biomassa – um estudo em três sítios do Estado de São Paulo

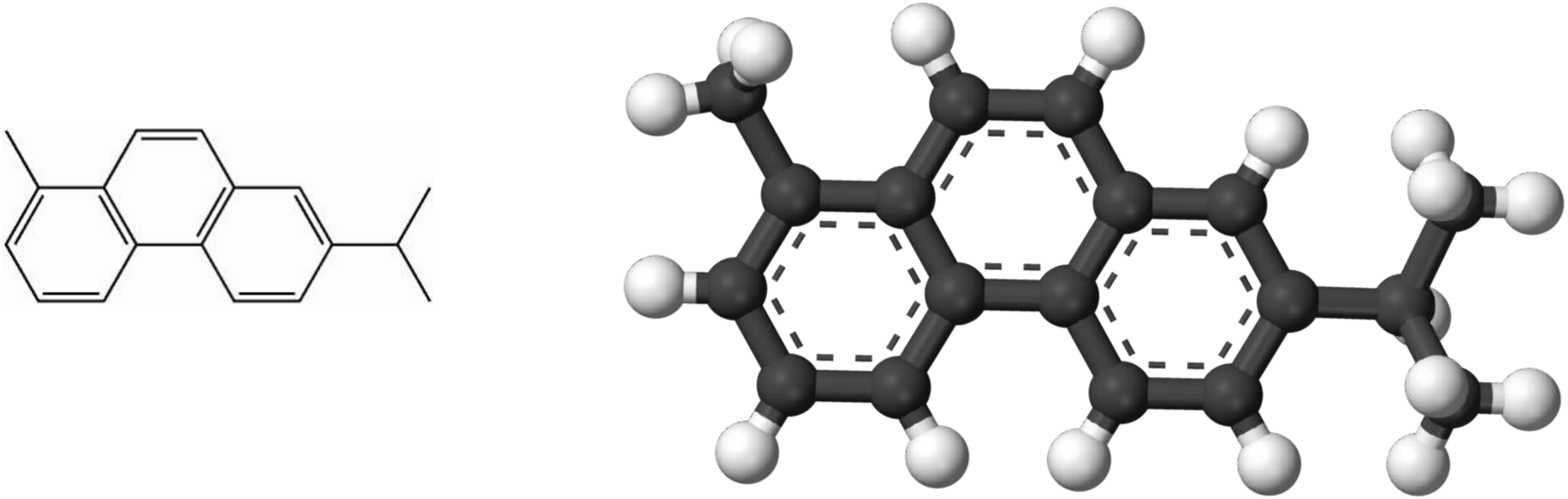


As amostragens do aerossol atmosférico ocorreram em três sítios (2007):
a) em uma região de queimadas: ESALQ/Piracicaba (PRB); b) em uma área tipicamente urbana: Cidade Universitária/ USP (SPA); c) em uma área florestal: Reserva Florestal de Santa Virgínia, Mata Atlântica (MAT).

Sociedade Brasileira de Química (SBQ)
32a Reunião Anual da Sociedade Brasileira de Química
Davi Z. Souza, Helena Lee, Oscar W. V. Bustillos, Pérola C. Vasconcellos

RETENENO: Biomarcador de Plantas Mayores

Metil isopropil fenantreno, $C_{18}H_{18}$, es un hidrocarburo aromático policíclico presente en el alquitrán de hulla y de ebullición a 360ºC.



La presencia de reteneno en el aire es un indicador de incendio forestal, siendo el principal producto de la pirólisis de coníferas.
También esta presente en efluentes de pulpa de madera y fábricas de papel.
Reteneno se deriva de la degradación específica de diterpenoides biologicamente producidos por los arbóles del tipo coníferas.

Oil and gas VOC emissions and chemistry

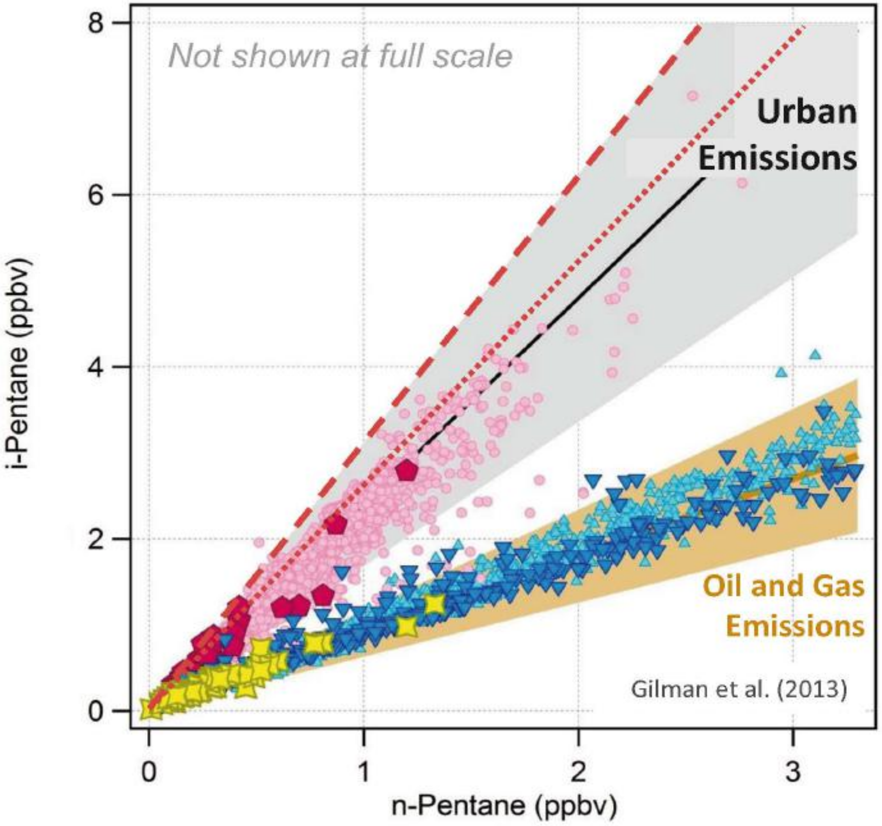
Emissions from oil and gas have a unique "source signature"

— Urban Ratio = 2.4 ± 20%
● Pasadena, CA 2010
⬟ 28 U.S. Cities *(Baker, 2008)*
- - Gasoline *(Schauer, 2002)*
····· Vehicle Exhaust *(Gentner, 2009)*

Urban emissions of VOCs are dominated by gasoline related sources (Warneke, 2013)

- i-Pentane is the most abundant hydrocarbon in gasoline

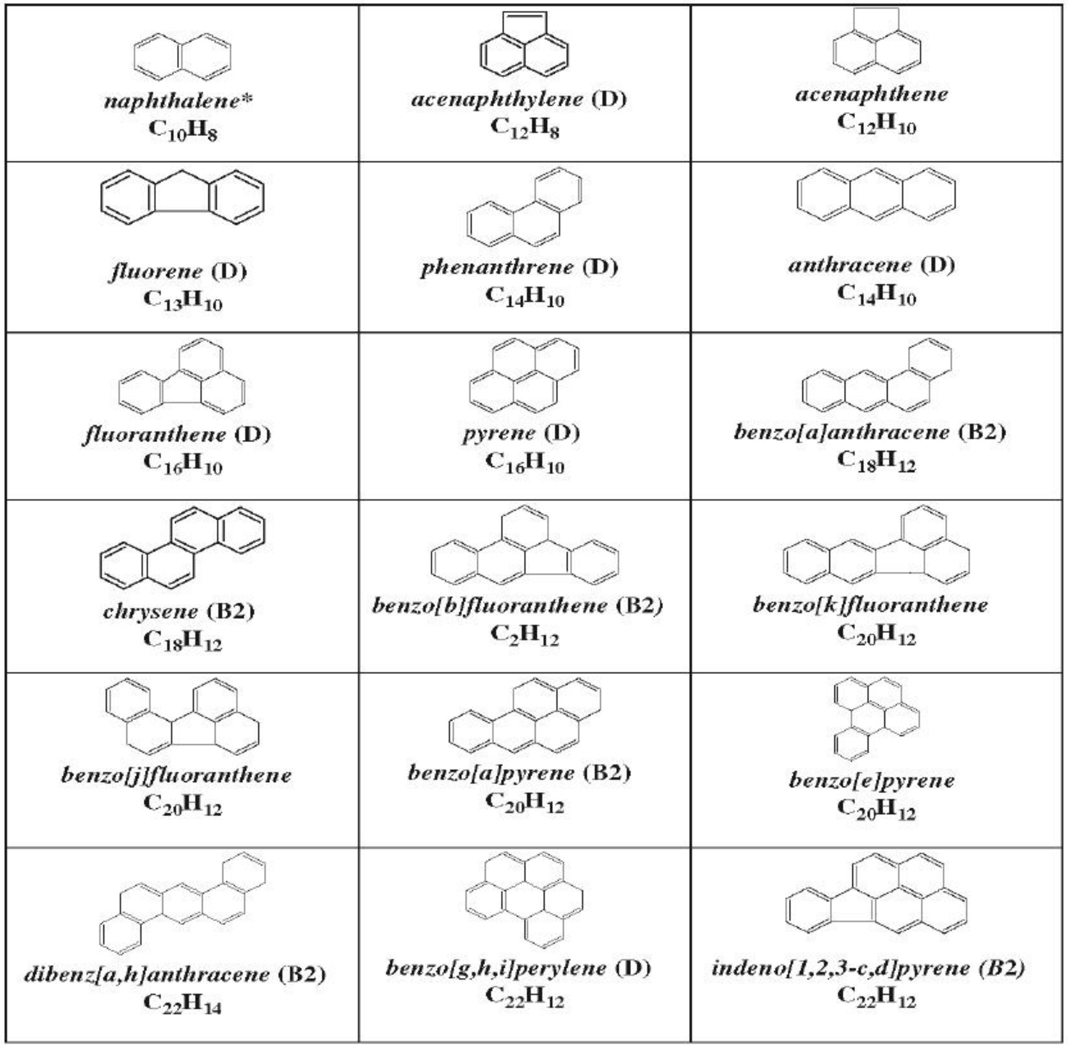
— Natural Gas Ratio = 0.88 ± 20%
▲ Uintah Basin, UT 2012
▼ Denver Basin, CO 2011
¤ Raw Natural Gas Composition
from Colo. Oil and Gas Conservation Comm. Report



Gilman et al. (2013)

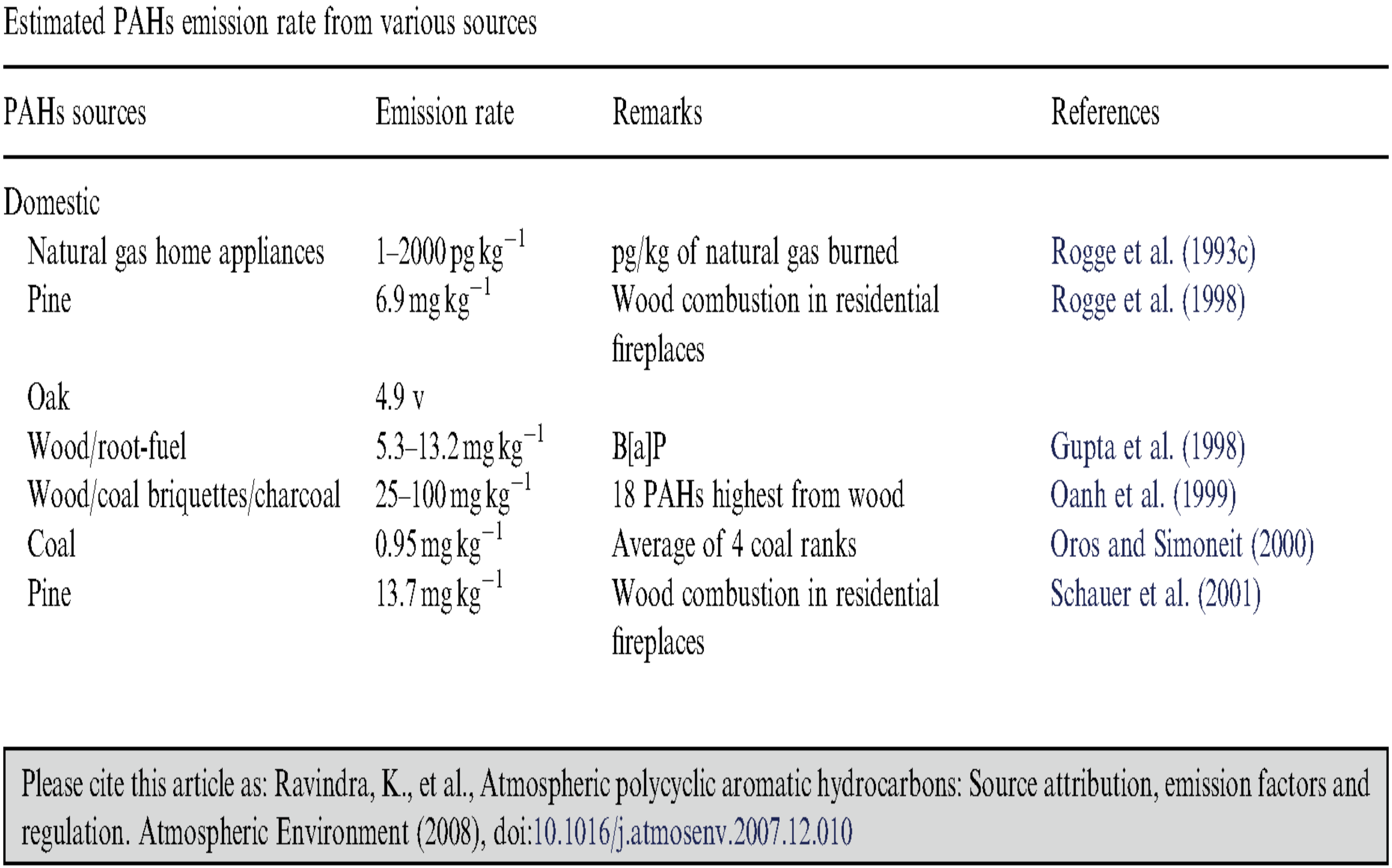
Emissions of volatile organic compounds (VOCs) from oil and gas can be clearly distinguished from other fossil fuel sources allowing for accurate source apportionment

HIDROCRBUROS AROMÁTICOS POLICICLICOS (PAHS)



_naphthalene_* $C_{10}H_8$	_acenaphthylene_ (D) $C_{12}H_8$	_acenaphthene_ $C_{12}H_{10}$
fluorene (D) $C_{13}H_{10}$	_phenanthrene_ (D) $C_{14}H_{10}$	_anthracene_ (D) $C_{14}H_{10}$
fluoranthene (D) $C_{16}H_{10}$	_pyrene_ (D) $C_{16}H_{10}$	_benzo[a]anthracene_ (B2) $C_{18}H_{12}$
chrysene (B2) $C_{18}H_{12}$	_benzo[b]fluoranthene_ (B2) C_2H_{12}	_benzo[k]fluoranthene_ $C_{20}H_{12}$
benzo[j]fluoranthene $C_{20}H_{12}$	_benzo[a]pyrene_ (B2) $C_{20}H_{12}$	_benzo[e]pyrene_ $C_{20}H_{12}$
dibenz[a,h]anthracene (B2) $C_{22}H_{14}$	_benzo[g,h,i]perylene_ (D) $C_{22}H_{12}$	_indeno[1,2,3-c,d]pyrene_ (B2) $C_{22}H_{12}$

Fig. 1. Priority listed PAHs. *Not included in priority list; D (not listed as to human carcinogenicity); B2 (probable human carcinogen).

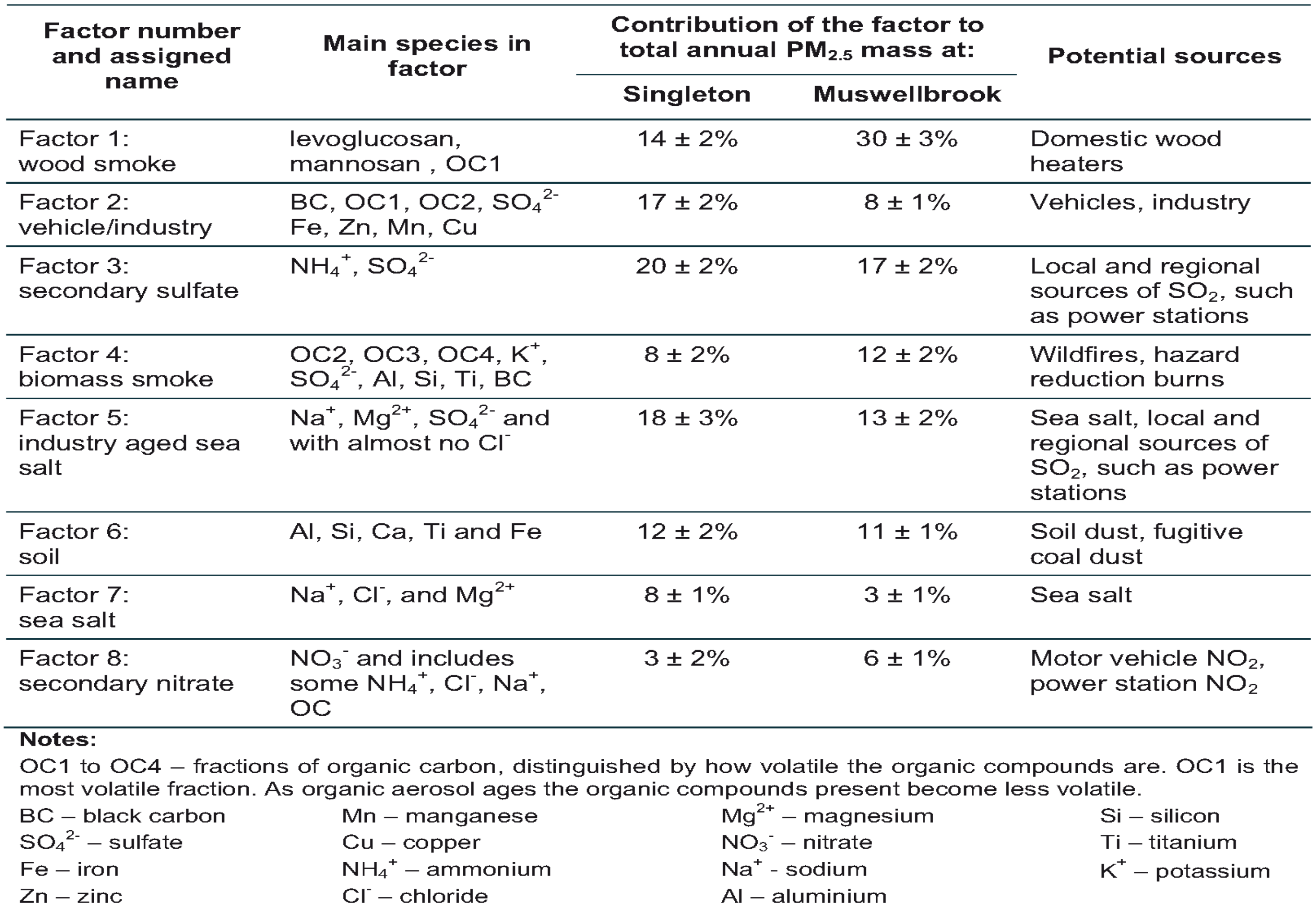


Estimated PAHs emission rate from various sources

PAHs sources	Emission rate	Remarks	References
Domestic			
Natural gas home appliances	1–2000 pg kg^{-1}	pg/kg of natural gas burned	Rogge et al. (1993c)
Pine	6.9 mg kg^{-1}	Wood combustion in residential fireplaces	Rogge et al. (1998)
Oak	4.9 v		
Wood/root-fuel	5.3–13.2 mg kg^{-1}	B[a]P	Gupta et al. (1998)
Wood/coal briquettes/charcoal	25–100 mg kg^{-1}	18 PAHs highest from wood	Oanh et al. (1999)
Coal	0.95 mg kg^{-1}	Average of 4 coal ranks	Oros and Simoneit (2000)
Pine	13.7 mg kg^{-1}	Wood combustion in residential fireplaces	Schauer et al. (2001)

Please cite this article as: Ravindra, K., et al., Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. Atmospheric Environment (2008), doi:10.1016/j.atmosenv.2007.12.010

Singleton and Muswellbrook at Upper Hunter Valley, Australia
Particle Characterisation Study
2012



Factor number and assigned name	Main species in factor	Contribution of the factor to total annual $PM_{2.5}$ mass at:		Potential sources
		Singleton	Muswellbrook	
Factor 1: wood smoke	levoglucosan, mannosan , OC1	14 ± 2%	30 ± 3%	Domestic wood heaters
Factor 2: vehicle/industry	BC, OC1, OC2, SO_4^{2-} Fe, Zn, Mn, Cu	17 ± 2%	8 ± 1%	Vehicles, industry
Factor 3: secondary sulfate	NH_4^+, SO_4^{2-}	20 ± 2%	17 ± 2%	Local and regional sources of SO_2, such as power stations
Factor 4: biomass smoke	OC2, OC3, OC4, K^+, SO_4^{2-}, Al, Si, Ti, BC	8 ± 2%	12 ± 2%	Wildfires, hazard reduction burns
Factor 5: industry aged sea salt	Na^+, Mg^{2+}, SO_4^{2-} and with almost no Cl^-	18 ± 3%	13 ± 2%	Sea salt, local and regional sources of SO_2, such as power stations
Factor 6: soil	Al, Si, Ca, Ti and Fe	12 ± 2%	11 ± 1%	Soil dust, fugitive coal dust
Factor 7: sea salt	Na^+, Cl^-, and Mg^{2+}	8 ± 1%	3 ± 1%	Sea salt
Factor 8: secondary nitrate	NO_3^- and includes some NH_4^+, Cl^-, Na^+, OC	3 ± 2%	6 ± 1%	Motor vehicle NO_2, power station NO_2

Notes:

OC1 to OC4 – fractions of organic carbon, distinguished by how volatile the organic compounds are. OC1 is the most volatile fraction. As organic aerosol ages the organic compounds present become less volatile.

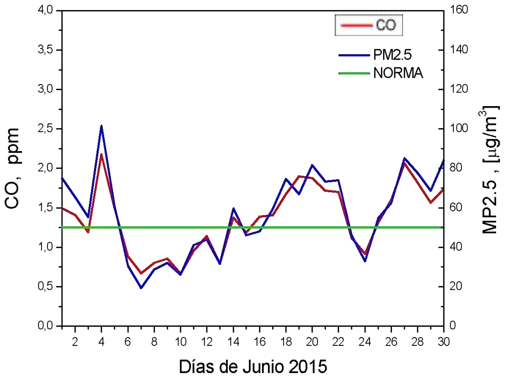
BC – black carbon
SO_4^{2-} – sulfate
Fe – iron
Zn – zinc
Mn – manganese
Cu – copper
NH_4^+ – ammonium
Cl^- – chloride
Mg^{2+} – magnesium
NO_3^- – nitrate
Na^+ - sodium
Al – aluminium
Si – silicon
Ti – titanium
K^+ – potassium

The chemical composition of all the samples was analysed using a mathematical technique called positive matrix factorisation (PMF) to identify factors contributing to the total PM2.5 concentration.

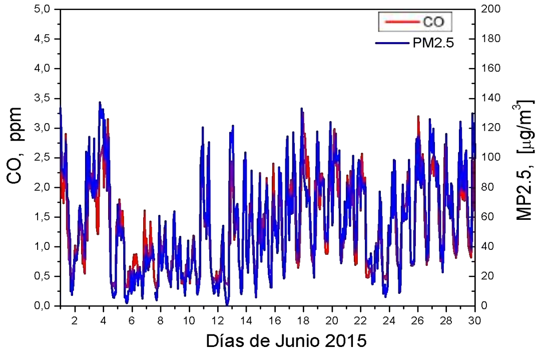
Contaminación por MP2.5 en la Provincia de Talagante durante Episodios Críticos de Junio de 2015 en Santiago

Gregorio P. Jara, Richard Toro, Manuel A. Leiva y Raúl G.E. Morales

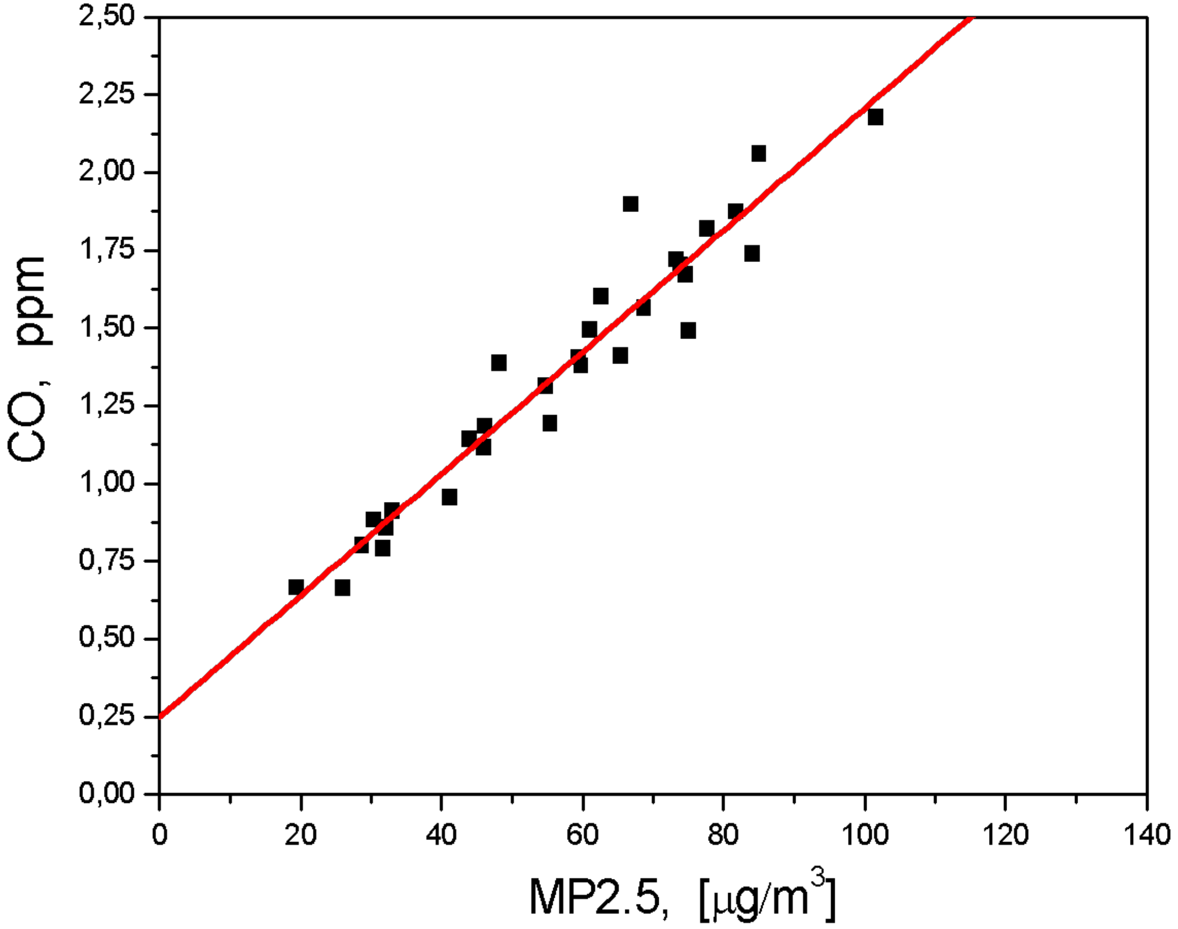
Talagante: CO y MP2.5 - Promedio diario



Talagante: CO y MP2.5 - Promedio horario



Talagante: MP2.5 vs CO - Promedio diario



DIOXINAS Y FURANOS

“Dioxin” is the term commonly given to a class of compounds known chemically as polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/F’s). As discussed below, there are other compounds beside PCDD/F’s that exhibit dioxin-like toxicity. Evidence suggests that human exposure to PCDD/F’s and dioxin-like compounds can lead to various forms of cancer and various developmental and endocrine-disruption effects.

There are 210 different chlorinated dioxin and furan molecules or “congeners.” Each different congener has its chlorines in different positions in the structure. The general structure of PCDD/F molecules is shown in the diagrams below; also, as examples, the specific congeners 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) are shown.

Structures of (left) polychlorinated-para-dioxins and (right) dibenzofurans.

It has been found that only the 17 PCDD/F congeners with chlorines in at least the 2,3,7,8 positions show evidence of dioxin-like toxicity. The toxicity of each congener can be expressed in terms of its estimated, approximate potency relative to that of the most toxic congener (2,3,7,8-tetrachlorodibenzo-*p*-dioxin) by multiplying by its estimated “Toxic Equivalency Factor” or TEF. Values of the TEF’s commonly used are given in Table 1 below. The overall PCDD/F toxic potency of a mixture of dioxin and furan congeners is often summarized by multiplying the amount of each congener by its TEF and then summing over all the congeners to get the total Toxic Equivalents (TEQ) in the mixture. The meaning of a result expressed as “TEQ” is that the total overall toxicity of the mixture is presumed to be equivalent to the stated amount of “pure” 2,3,7,8-TCDD.

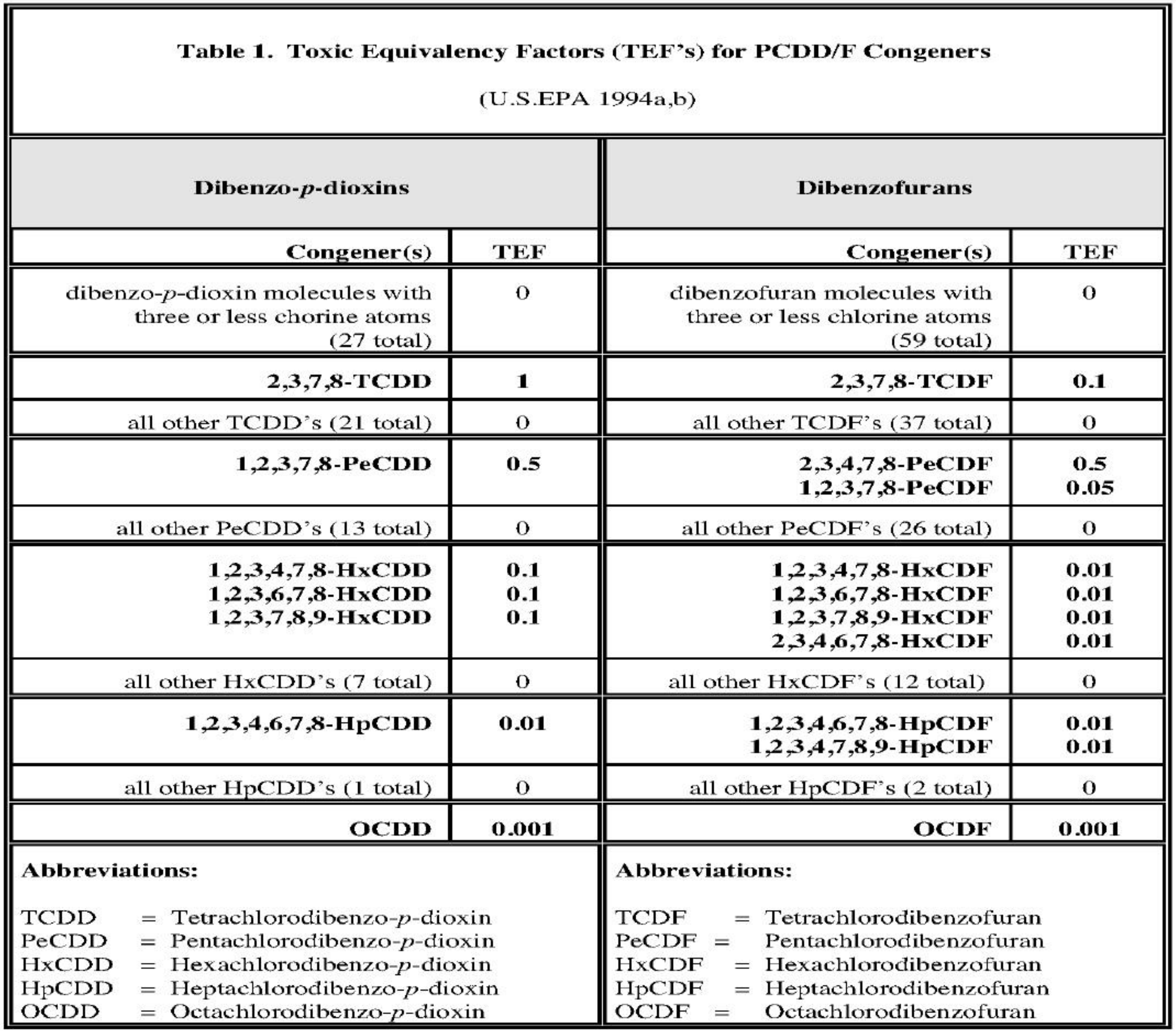


Table 1. Toxic Equivalency Factors (TEF's) for PCDD/F Congeners

(U.S.EPA 1994a,b)

Dibenzo-*p*-dioxins		**Dibenzofurans**	
Congener(s)	**TEF**	**Congener(s)**	**TEF**
dibenzo-*p*-dioxin molecules with three or less chorine atoms (27 total)	0	dibenzofuran molecules with three or less chlorine atoms (59 total)	0
2,3,7,8-TCDD	**1**	**2,3,7,8-TCDF**	**0.1**
all other TCDD's (21 total)	0	all other TCDF's (37 total)	0
1,2,3,7,8-PeCDD	**0.5**	**2,3,4,7,8-PeCDF** **1,2,3,7,8-PeCDF**	**0.5** **0.05**
all other PeCDD's (13 total)	0	all other PeCDF's (26 total)	0
1,2,3,4,7,8-HxCDD **1,2,3,6,7,8-HxCDD** **1,2,3,7,8,9-HxCDD**	**0.1** **0.1** **0.1**	**1,2,3,4,7,8-HxCDF** **1,2,3,6,7,8-HxCDF** **1,2,3,7,8,9-HxCDF** **2,3,4,6,7,8-HxCDF**	**0.01** **0.01** **0.01** **0.01**
all other HxCDD's (7 total)	0	all other HxCDF's (12 total)	0
1,2,3,4,6,7,8-HpCDD	**0.01**	**1,2,3,4,6,7,8-HpCDF** **1,2,3,4,7,8,9-HpCDF**	**0.01** **0.01**
all other HpCDD's (1 total)	0	all other HpCDF's (2 total)	0
OCDD	**0.001**	**OCDF**	**0.001**

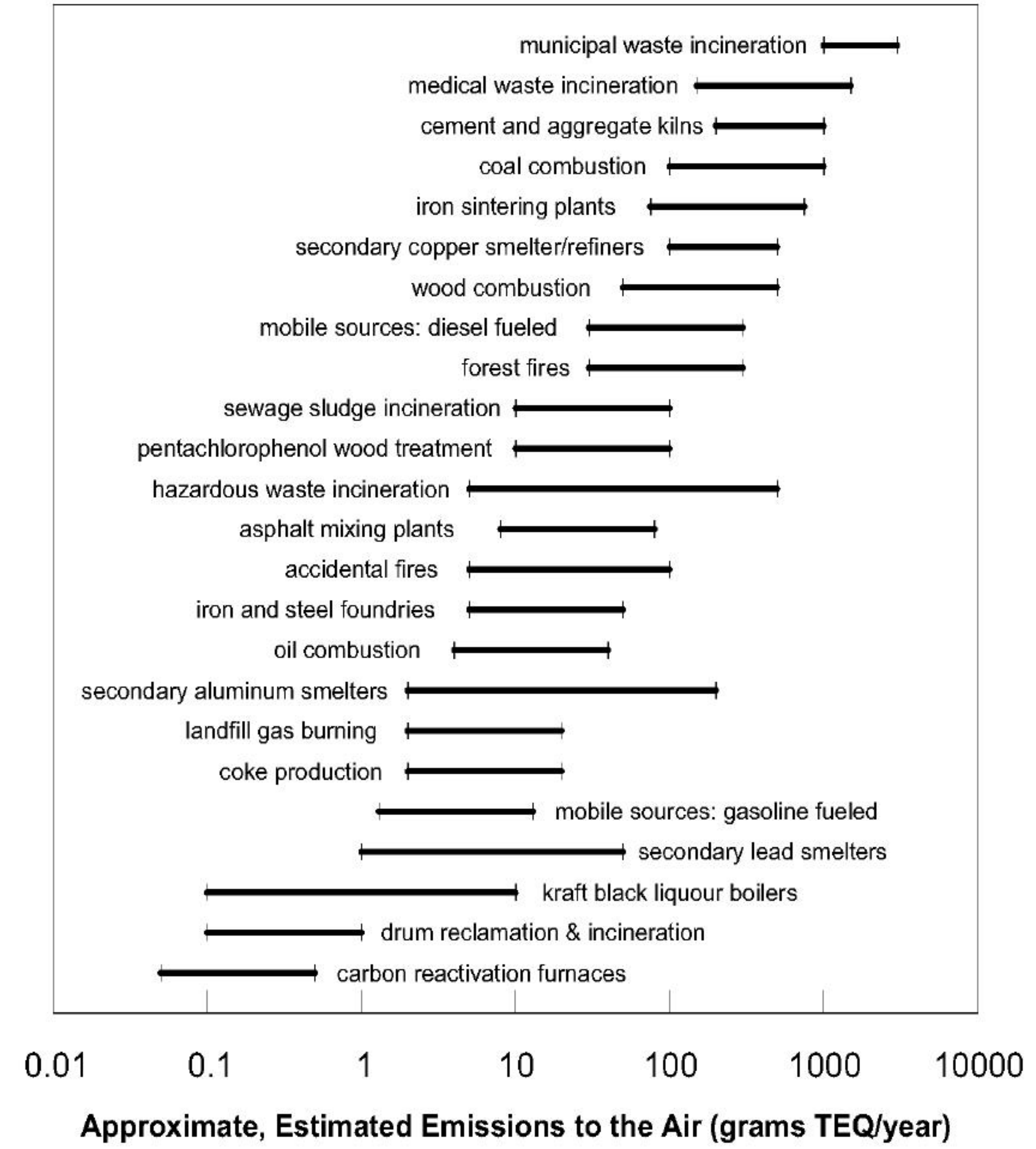
Abbreviations:

TCDD = Tetrachlorodibenzo-*p*-dioxin
PeCDD = Pentachlorodibenzo-*p*-dioxin
HxCDD = Hexachlorodibenzo-*p*-dioxin
HpCDD = Heptachlorodibenzo-*p*-dioxin
OCDD = Octachlorodibenzo-*p*-dioxin

Abbreviations:

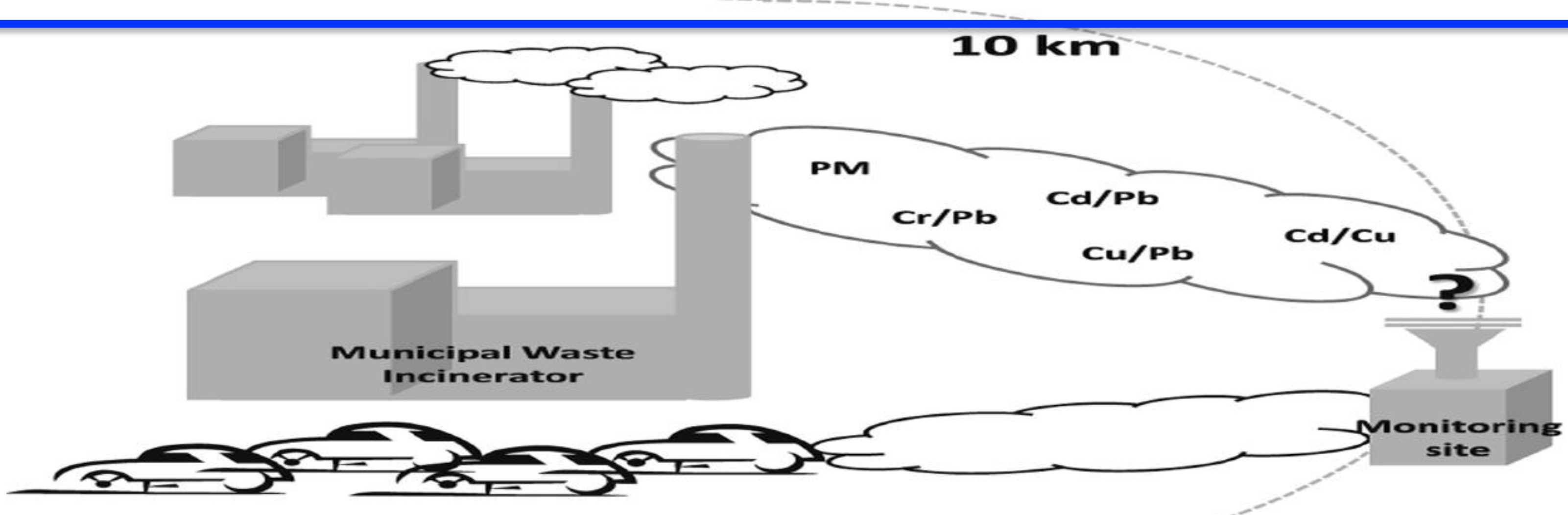
TCDF = Tetrachlorodibenzofuran
PeCDF = Pentachlorodibenzofuran
HxCDF = Hexachlorodibenzofuran
HpCDF = Heptachlorodibenzofuran
OCDF = Octachlorodibenzofuran

La formación de PCDD/F esta más favorecida en el rango de temperatura entre 300 y 450ºC.



"TEQ" = 2,3,7,8-TCDD Toxic Equivalents
The Indicated "Ranges" for Each Source Show the Approximate Uncertainty in the Emissions Estimate

PCDD/F congeneres tipo 6, 7 y 8 chloros se espera que estén asociados con pequeñas partículas de la atmósfera y tendrán vidas medias del orden de una semana. Fracciones significativas de los congéneres de las más tóxicas tetra y penta cloro dioxinas se espera que existan en fase vapor y en las partículas.



Atmospheric Environment, Volume 113, July 2015, Pages 177–186

Using metal ratios to detect emissions from municipal waste incinerators in ambient air pollution data

Anna Font[a, ,] , Kees de Hoogh[b, c, d], Maria Leal-Sanchez[d], Danielle C. Ashworth[e], Richard J.C. Brown[f], Anna L. Hansell[d, g], Gary W. Fuller[a]

This study aimed to fingerprint emissions from six municipal waste incinerators (MWIs) and then test if these fingerprint ratios could be found in ambient air samples.

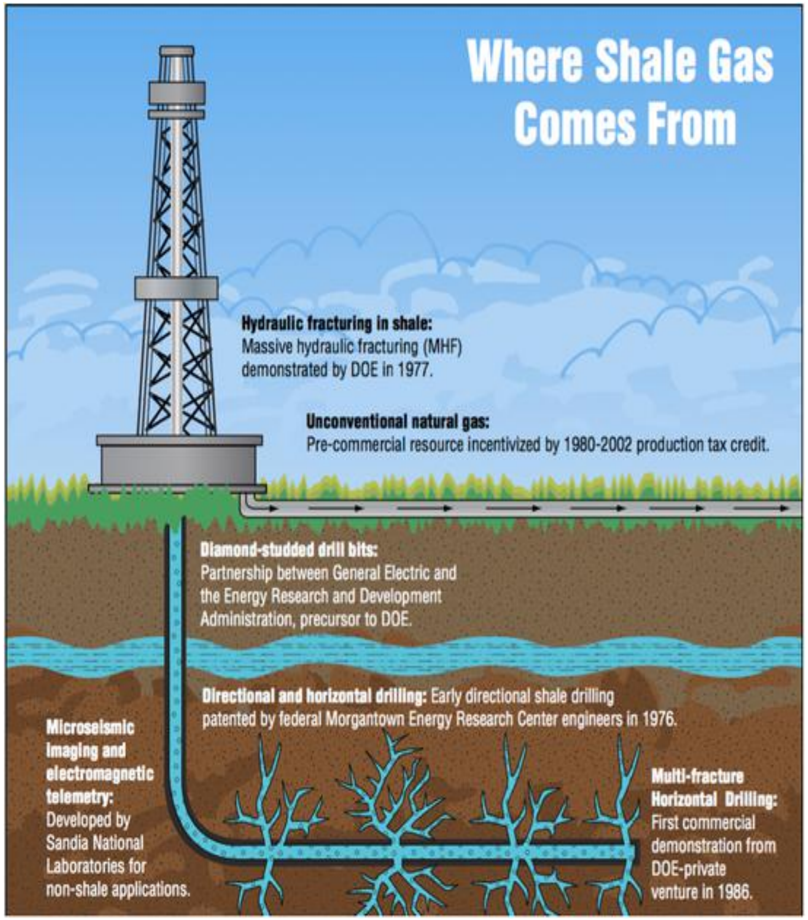
Stack emissions tests from MWIs comprised: As, Cd, Cr, Cu, Pb, Mn, Ni, V and Hg.

Those pairs of metals showing good correlation (R > 0.75) were taken as tracers of MWI emissions and ratios calculated: Cu/Pb; Cd/Pb; Cd/Cu and Cr/Pb

J Air Waste Manag Assoc. 2014 Jan;64(1):61-72.

An exploratory study of air emissions associated with shale gas development and production in the Barnett Shale.

Objectives of this exploratory study were to collect ambient air samples in residential areas within 61 m (200 feet) of shale gas extraction/production and determine whether a "fingerprint" of chemicals can be associated with shale gas activity.

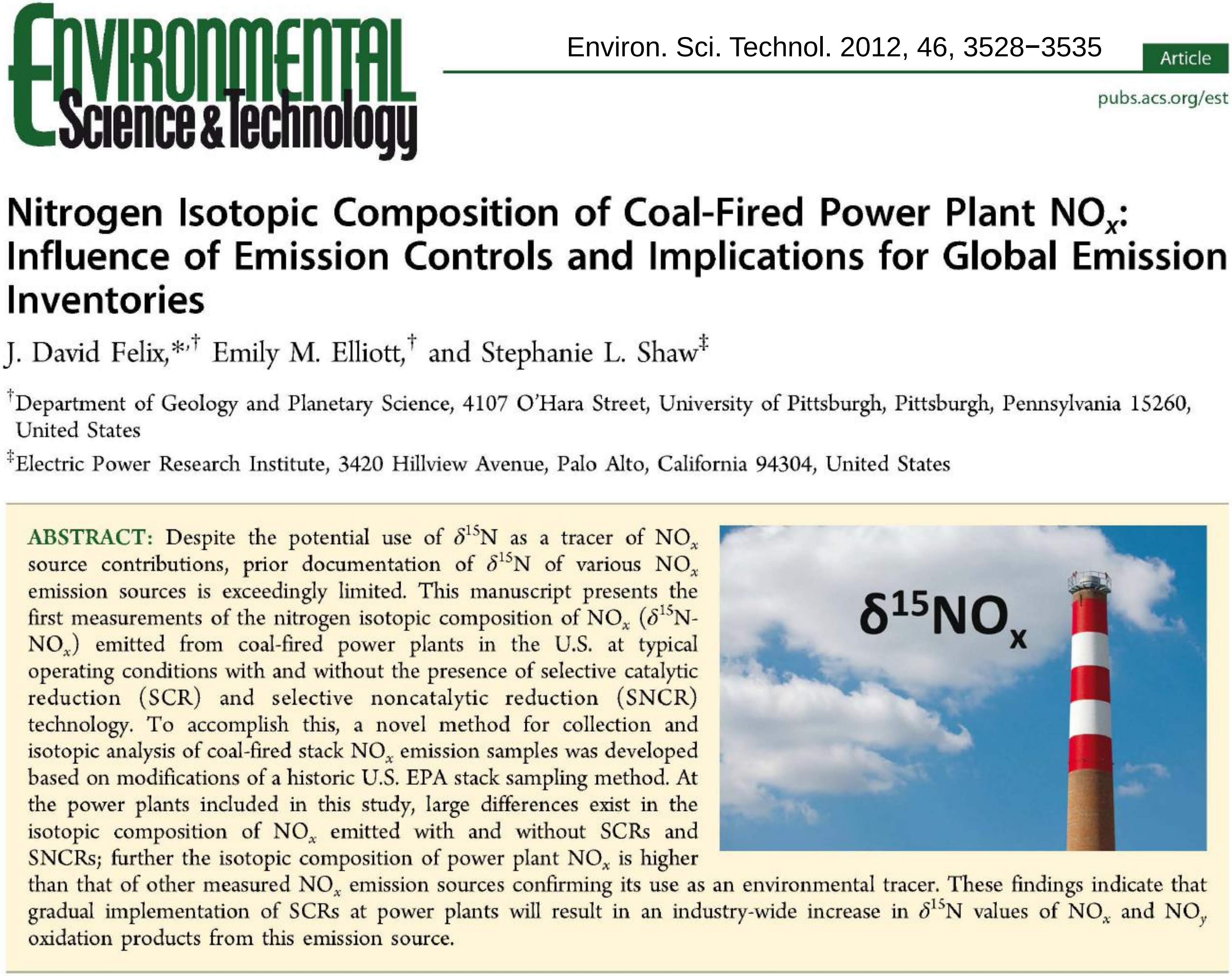


Most of the areas investigated had atmospheric methane concentrations considerably higher than reported urban background concentrations (1.8-2.0 ppm(v)).
Other chemical constituents were found to be correlated with presence of methane.

A principal components analysis (PCA) identified multivariate patterns of concentrations that potentially constitute signatures of emissions from different phases of operation at natural gas sites.

The first factor identified through the PCA proved most informative. Extreme negative values were strongly and statistically associated with the presence of compressors at sample sites.

The seven chemicals strongly associated with this factor (o-xylene, ethylbenzene, 1,2,4-trimethylbenzene, m- and p-xylene, 1,3,5-trimethylbenzene, toluene, and benzene) thus constitute a potential fingerprint of emissions associated with compression.



Environmental Science & Technology

Environ. Sci. Technol. 2012, 46, 3528−3535

Article

pubs.acs.org/est

Nitrogen Isotopic Composition of Coal-Fired Power Plant NO_x: Influence of Emission Controls and Implications for Global Emission Inventories

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ABSTRACT: Despite the potential use of $\delta^{15}N$ as a tracer of NO_x source contributions, prior documentation of $\delta^{15}N$ of various NO_x emission sources is exceedingly limited. This manuscript presents the first measurements of the nitrogen isotopic composition of NO_x ($\delta^{15}N$-NO_x) emitted from coal-fired power plants in the U.S. at typical operating conditions with and without the presence of selective catalytic reduction (SCR) and selective noncatalytic reduction (SNCR) technology. To accomplish this, a novel method for collection and isotopic analysis of coal-fired stack NO_x emission samples was developed based on modifications of a historic U.S. EPA stack sampling method. At the power plants included in this study, large differences exist in the isotopic composition of NO_x emitted with and without SCRs and SNCRs; further the isotopic composition of power plant NO_x is higher than that of other measured NO_x emission sources confirming its use as an environmental tracer. These findings indicate that gradual implementation of SCRs at power plants will result in an industry-wide increase in $\delta^{15}N$ values of NO_x and NO_y oxidation products from this emission source.

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GRACIAS POR SU ATENCION !!!