Engineered Nanoparticles in the Environment
Analysis, Occurrence and Impacts

19 - 20 October 2010
Koblenz, Germany

Nanomaterial residues in aquatic ecosystems

Damià Barceló, Marinella Farré, Josep Sanchís

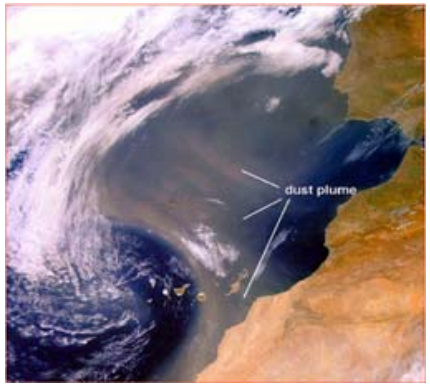
Outline

1. Introduction
2. Objectives
3. Analytical methodology
4. Analysis of real samples
5. Conclusions and future work

Introduction

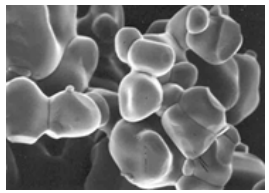
- Natural event
  - Volcanic ash
  - Forest fire
  - Dust
  - Mineral composites
  - Ferritin
- Incidental production of nanoparticles from human activity
  - Combustion subproducts
  - Kitchen
  - Sandblasting
  - Mining
  - Metallurgy
- Manufactured nanoparticles (Nanotechnology)

Introduction: Natural events



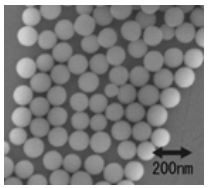
Airbone mineral dust

Ferrihydrite



Complex metal oxide NP: Bi_2CuO_4

Fullerenes



Silica NP

Lava spurts out of the site of a volcanic eruption at the Eyjafjallajökull volcano in Iceland on March 27, 2010

Introduction: Incidental events

- Combustion Products
- Car and plane brakes
- Sandblasting
- Mining
- Metallurgy
- Collapses and explosions

Introduction: Nanotechnology





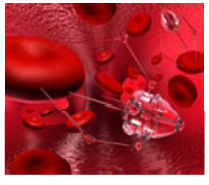


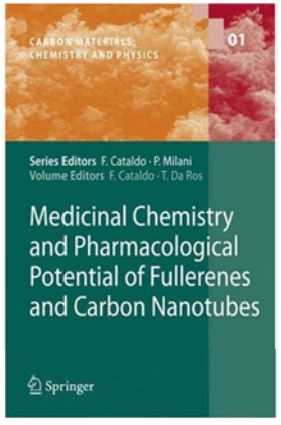


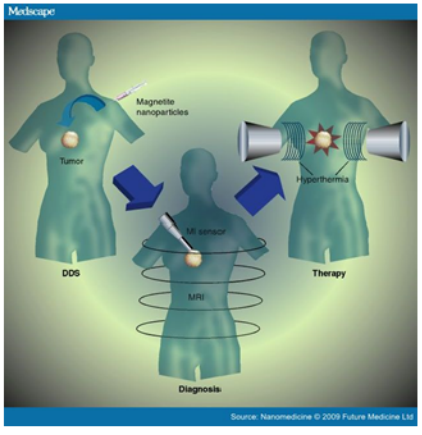








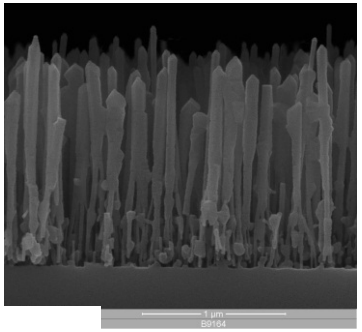


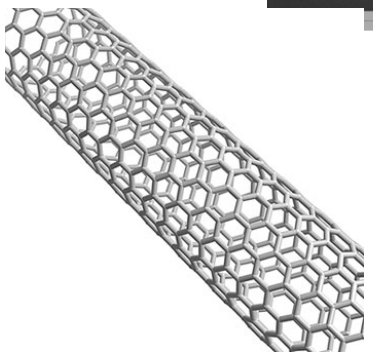


- Microelectronics
- Personal care products
- Pharmaceuticals and nano medical applications
- New materials
- Anti-odor or stain resistant textiles

Introduction

Studying medieval Damascus swords, researchers found that Medieval smiths used, maybe for the first, nanotechnology:
the steel of these blades embarks in its structure **cementite (iron carbide) nanowires**, and **carbon nanotubes**, that might explain the unusual hardness, sharpness and banding of the blade.





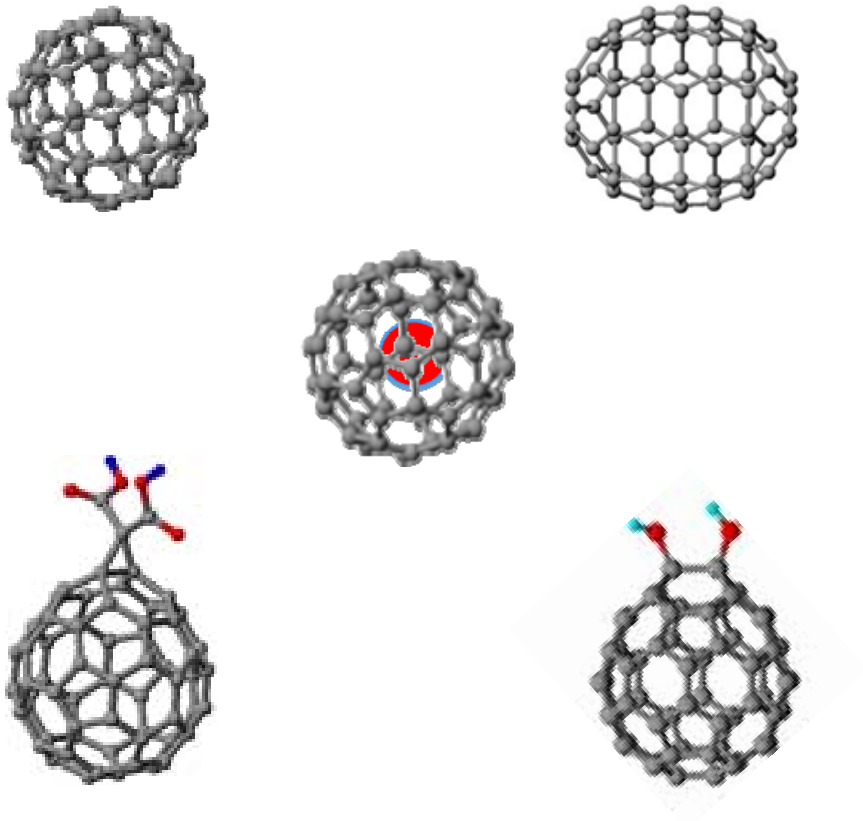
Reibold, Paufler, Levin, Kochman, Patzke & Meyer. 2006. Nature 444: 286

Introduction

- If organisms on earth have therefore clearly been exposed to nano-sized materials through evolution, so why are nanoparticles a cause of concern?

- Naturally occurring and manufactured NPs can be toxic depending on composition and shape. In addition, due to their large surface area NPs have great chemical and biological activity.
- The amounts of NPs have increased globally. Combustion processes in the last 200 years have released high amounts of NP to the environment. Now Nanotechnology is a new input.
- In addition, manufactured NPs might be more persistent because they can be stabilized by capping or fixing agents such as surfactants or organic matter

Introduction: Fullerenes



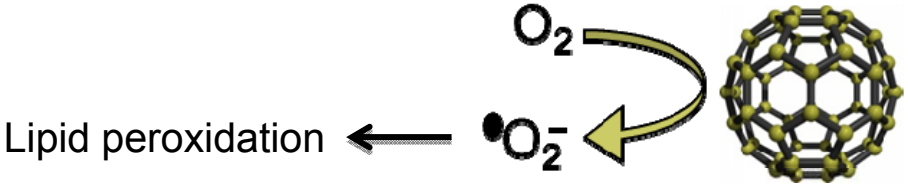
- Fullerenes are a family of carbon allotropes, in the form of a hollow sphere, ellipsoid, tube, or plane.
- Spherical fullerenes are also called buckyballs, and cylindrical ones are called carbon nanotubes or buckytubes.
- Sources: Natural, accidental, nanotechnology

Introduction: Fullerenes

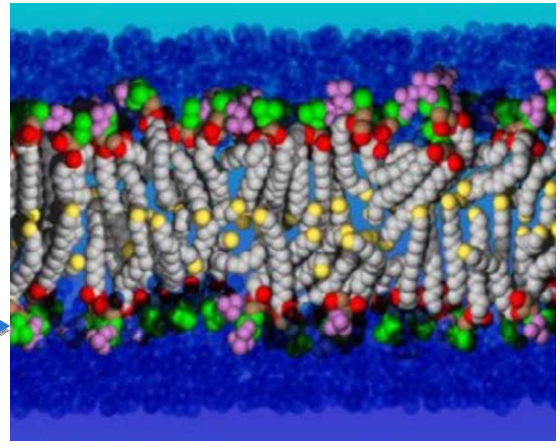
Basic nanomaterial properties relevant to toxicity

- Dose
- Size and shape
- Biopersistence
- Surface chemistry

Fullerenes have been related to cytotoxicity



Hydrophobic partitioning



Sayes et al., 2004;
Oberdorster, 2004

<u>Postulated mechanism</u>:
Hydrophobic attachment to / incorporation in cell membranes with redox catalysis of lipid peroxidation

Objectives

1

- **To develop analytical methods** suitable to assess the occurrence of **fullerenes** in environmental samples.

2

- **To investigate the presence of fullerenes in environmental samples**
  - **Waste water:** 42 effluent samples from 22 WWTPs subjected to the European Pollutant Released and Transfer Register (E-PRTR) regulation were investigated during 2 consecutive campaigns
  - **Freshwater:** The occurrence of Fullerenes was investigated in 62 freshwater samples from the Llobregat River
  - **Airborne:** The presence of fullerenes was investigated 40 samples of Mediterranean sea airborne particulate collected during 2 sampling campaigns carried out by the Oceanographic Research Ship *García del Cid*

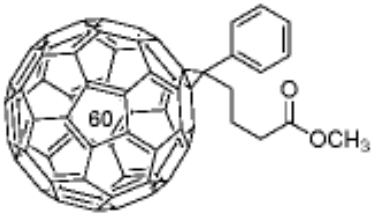
Target compounds

BUCKYBALLS

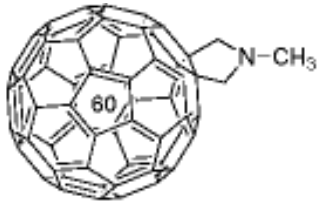
C_{60}

C_{70}

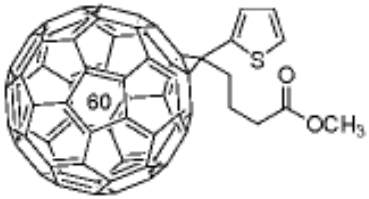
FULLERENE DERIVATIVES



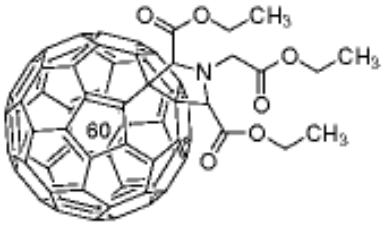
[6,6]-Phenyl C_{61} butyric Acid methyl ester (PCBM)



N-Methylfullero-pyrrolidine (MFP)



[6,6]-Thienyl C_{61} butyric acid methyl ester (ThPCB)



C_{60} Pyrrolidine tris-acid ethyl ester (PTAE)

Several applications in medicine, food industry and electronics.

Target compounds

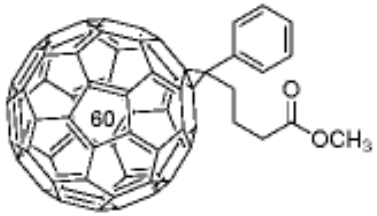
First studied compounds

BUCKYBALLS

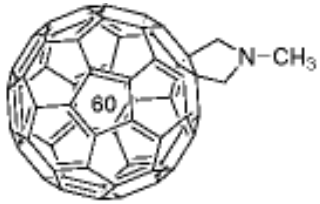
C_{60}

C_{70}

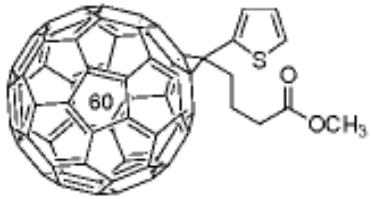
FULLERENE DERIVATIVES



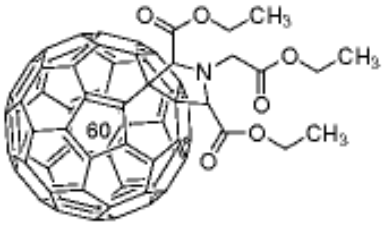
[6,6]-Phenyl C_{61} butyric Acid methyl ester (PCBM)



N-Methylfullero-pyrrolidine (MFP)



[6,6]-Thienyl C_{61} butyric acid methyl ester (ThPCB)



C_{60} Pyrrolidine tris-acid ethyl ester (PTAE)

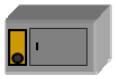
Several applications in medicine, food industry and electronics.

Analytical method

Extraction

100 ml Wastewater

Filtration (0.45 µm)x3



Dryness (3h 50 ºC)

Toluene extraction

Redisolution in 1mL
Toluene/Methanol (50/50)

LC

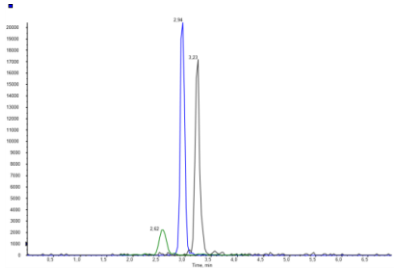
Purospher Star RP-18 endcapped column

Isocratic elution

Mobile phase toluene-methanol (1:1, v/v)

Flow-rate 0.4 mL/min flow rate

Injection volume 150µL



Detection

- MS/MS
- Electrospray ion (-) source

Surrogate:
20-30% ^{13}C enriched C_{60}

Internal standard:
20-30% ^{13}C enriched C_{70}

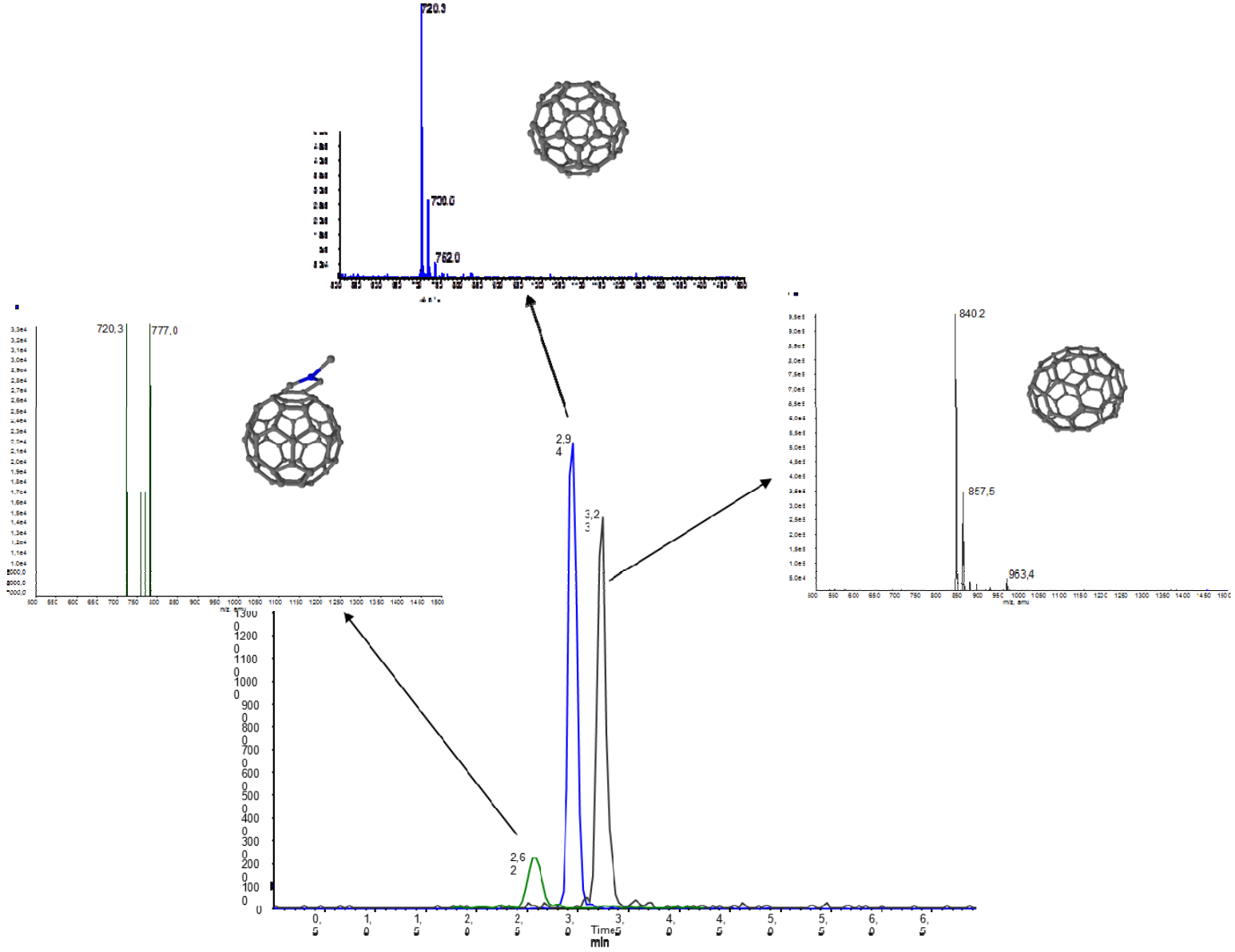
Journal of Hydrology, 383 (2010) 44-51
M. Farré, S. Pérez, K. Gajda-Schrantz, V. Osorio, L. Kantiani, A. Ginebreda, D. Barceló

Analytical method

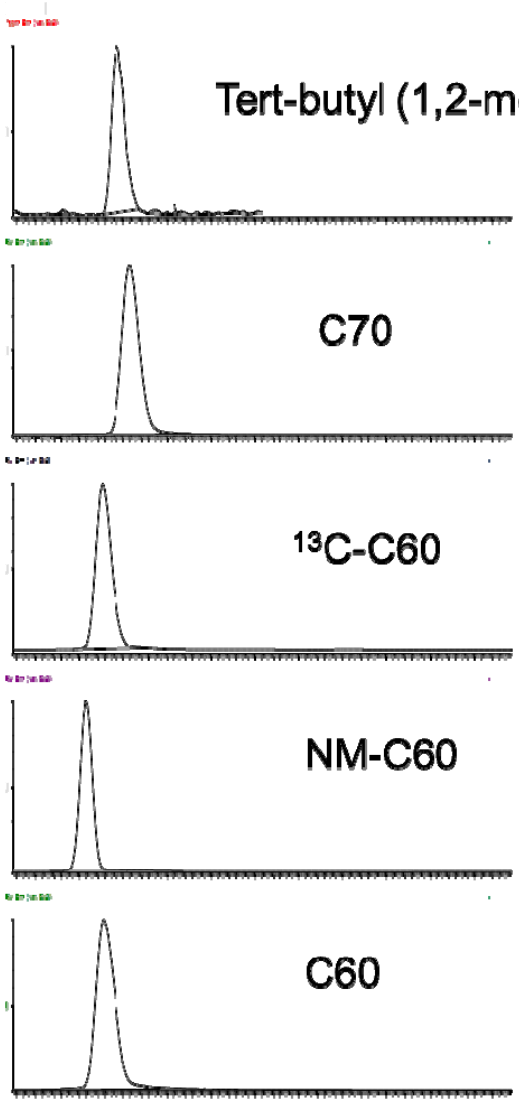
Compounds	Linearity (R^2)	IDL (pg inj.)	MDL (ng/L)			MLQ (ng/L)			Reproducibility % RSD (n=5)
			UPW	SW	WW	UPW	SW	WW	
Fullerene C60	0.9965	3	1	2	5	0.05	0.1	0.2	5
Fullerene C70	0.9969	7	3	5	8	0.1	0.13	0.5	6
N-Methyl fullero pyrrolidine	0.9957	11	10	12	20	0.3	0.4	1	9

Journal of Hydrology, *Volume 383, Issues 1-2, 15 March 2010, Pages 44-51*
Marinella Farré, Sandra Pérez, Krisztina Gajda-Schrantz, Victoria Osorio, Lina Kantiani, Antoni Ginebreda, Damià Barceló

Analytical method

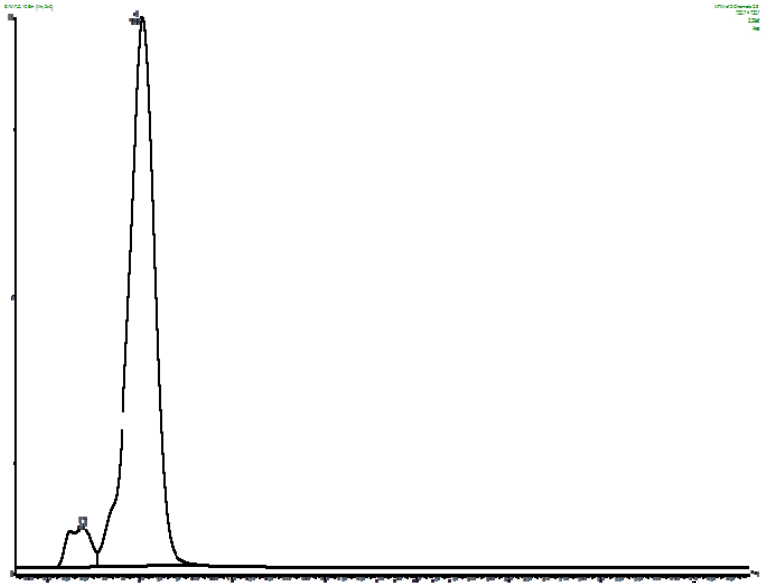


Analytical method

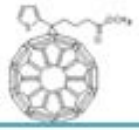


Phenomenex C_{12} Synergi Hydro-RP

(50 mm x 2 mm i.d., 4 µm, 80 Å)



Analytical method

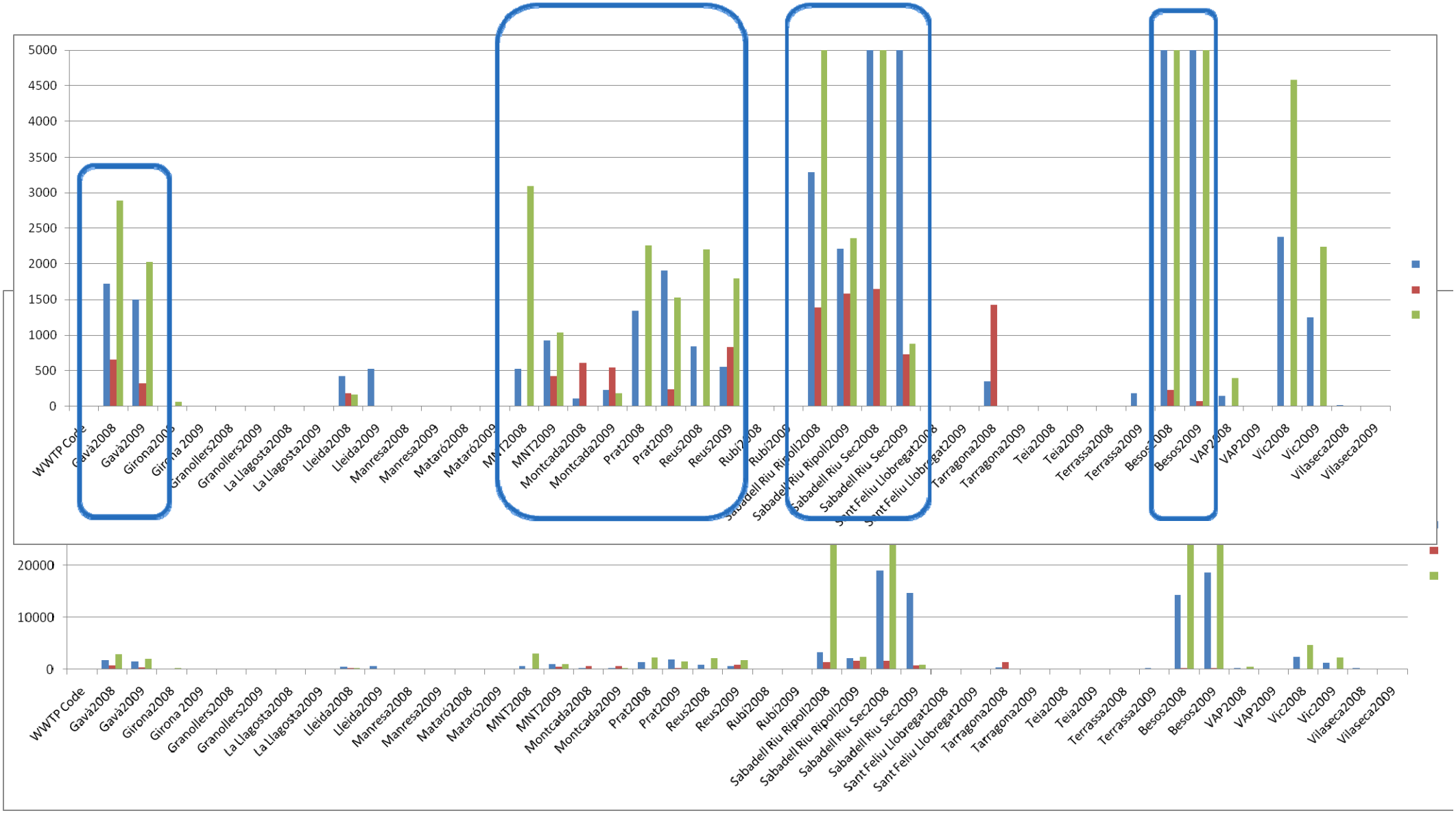
Compound	C60Fullerene	C70Fullerene	N-methylfullero pyrrolidine C60	[6,6]-Phenyl C61 butyric acid methyl ester	C60 Pyrrolidine tris-acid ethyl ester	[6,6]-Thienyl C61 butyric acid methyl ester
Structure						
Formula	C60	C70	C63H7N	C72H14O2	C72H19O6N	
Monoisotopic mass	720.6420	840.7490	777.7363	910.88	993.92	916,91
MRM transition	720.7 → 720.7	840.8 → 840.8	777.8 → 736.5 777.8 → 720.7	910.9 → 720.7 910.9 → 809	993.9 → 720.7 993.9 → 993.9	916,3 → 720,2 916,3 → 828,3

Analysis of Wastewater Treated Effluents

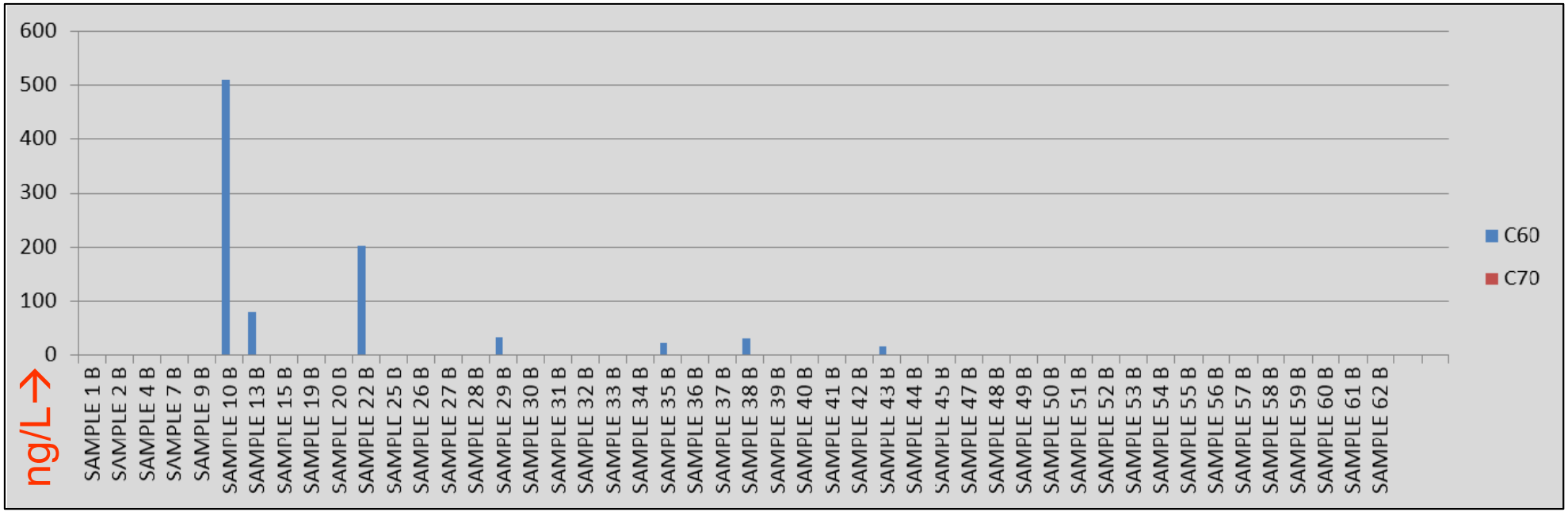
42 effluent from 22 WWTPs located in Catalonia (NE of Spain) receiving urban and industrial loads and subjected to the European Pollutant Released and Transfer Register (E-PRTR) regulation were investigated during 2 consecutive campaigns

Results in Wastewater

C70 Fullerene
C60 Fullerene
N-methyl fulleropyrrolidine

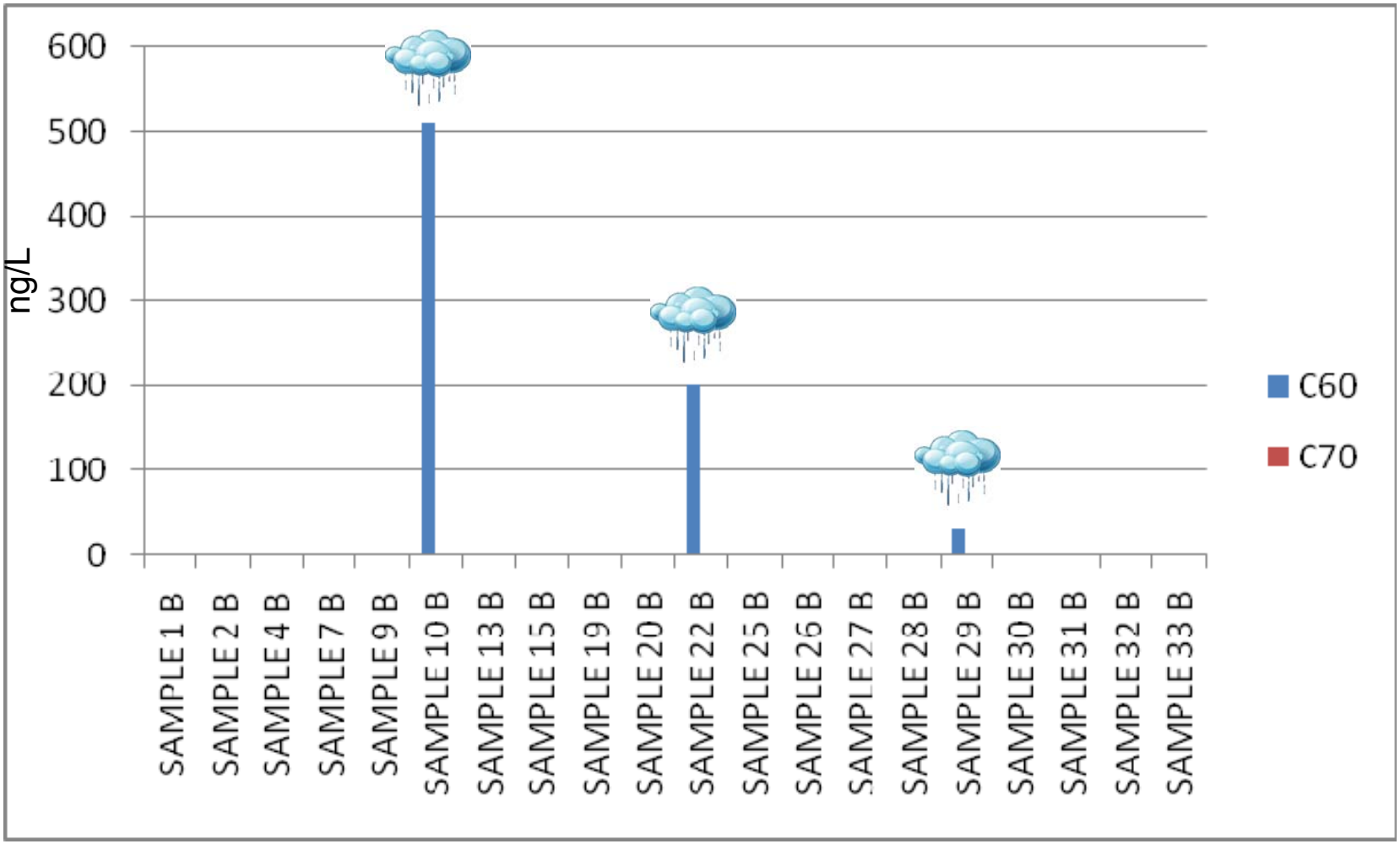


Freshwater: **The occurrence of Fullerenes was investigated in 62 freshwater samples from the Llobregat River**



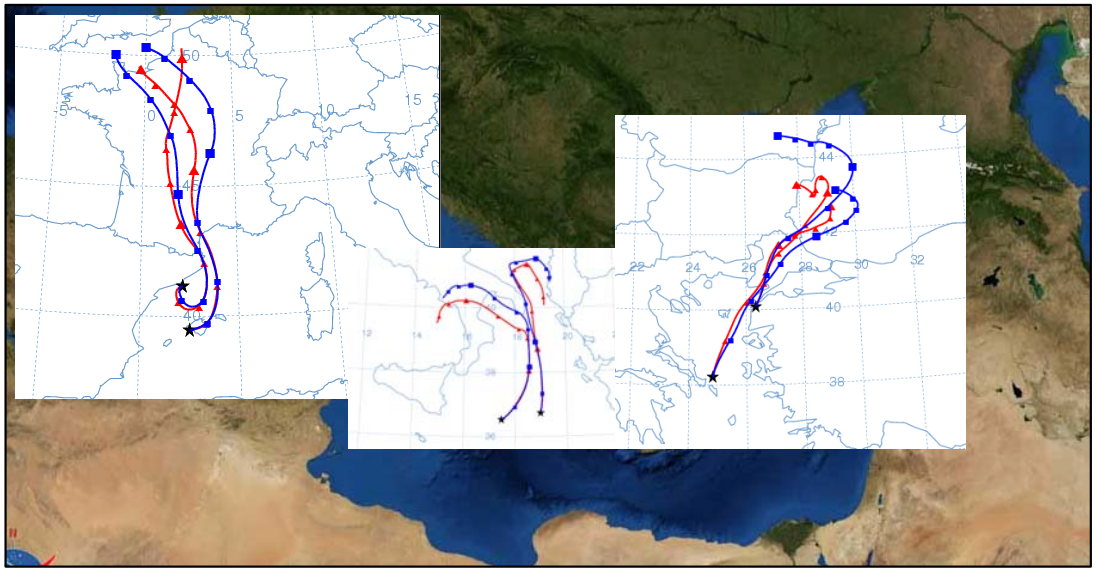
- 7 samples have quantificable concentrations of C_{60} fullerene
- C_{70} fullerene was detected in 77% of the samples but under LOQ
- The other fullerenes investigated here were not detected

Freshwater: **The occurrence of Fullerenes was investigated in 62 freshwater samples from the Llobregat River**



Airborne: **The occurrence of Fullerenes was investigated in 40 samples of marine airborne particulate matter**

>40 airborne particulate samples (200 ~1000 m^3) were collected in the Mediterranean Sea on board of the Oceanographic Research Ship “García del Cid”

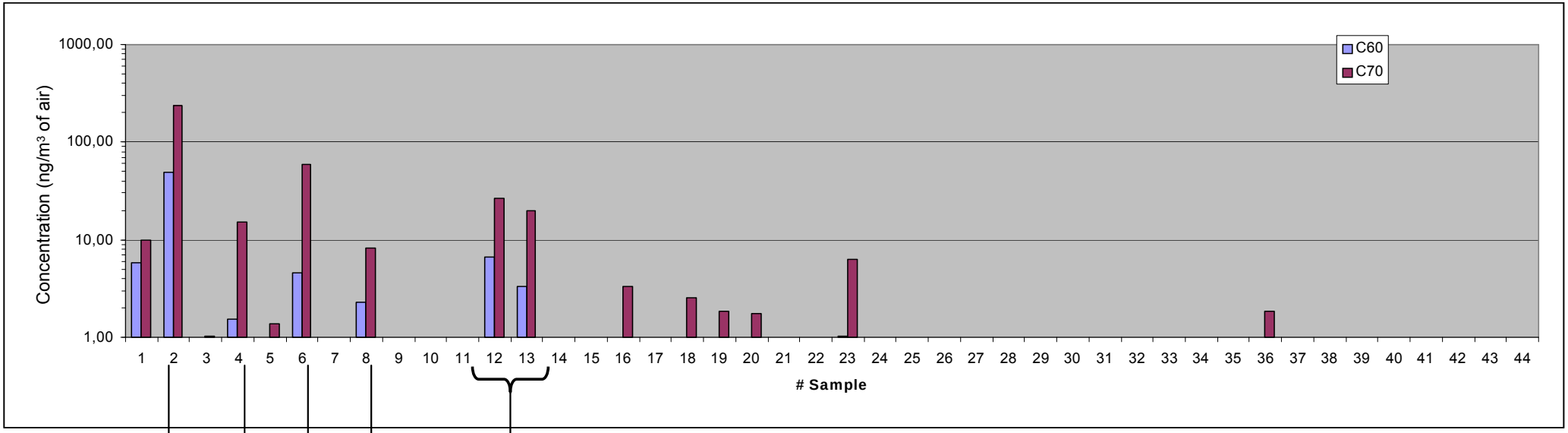


Metadata:

- Sample volume
- Sample total weight
- Sample TOC
- Sample procedence

The back-trajectories of every sampling point were modelled by means of HYSPLIT model (N.O.A.A. Air Resource Lab. Website)

Airborne: The occurrence of Fullerenes was investigated in 40 samples of marine airborne particulate matter



Zonguldak (Turkish Black Sea Coast)→ Intense coal mining activity

Athenes Basin, Greek Coast

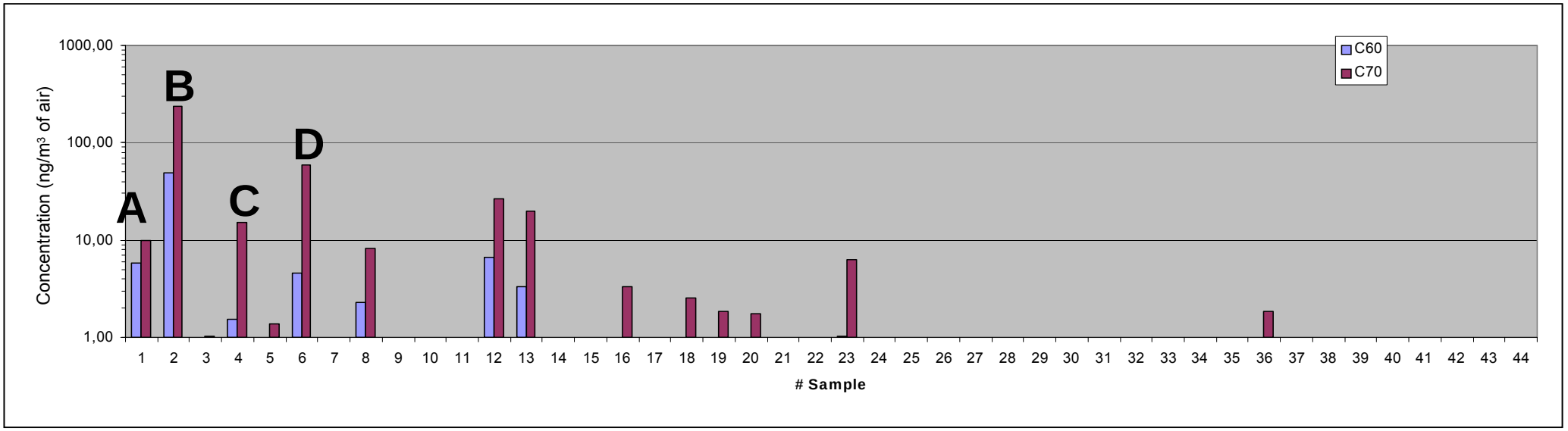
AZ-Zawiyah (Libia) → Intense petroliun industry activity

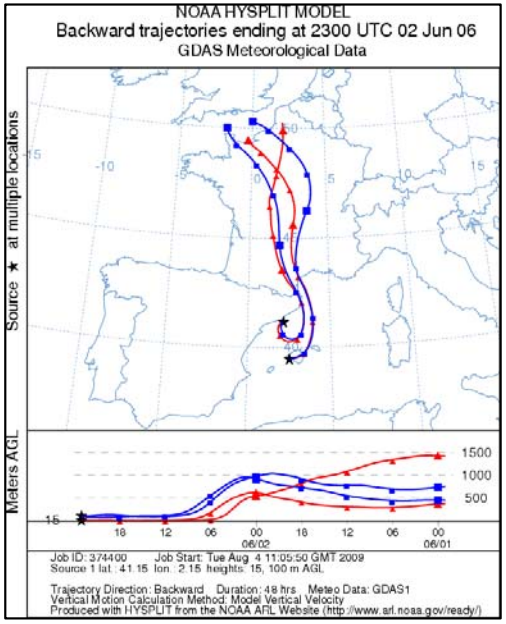
Tunisian Coast

BCN - Palma

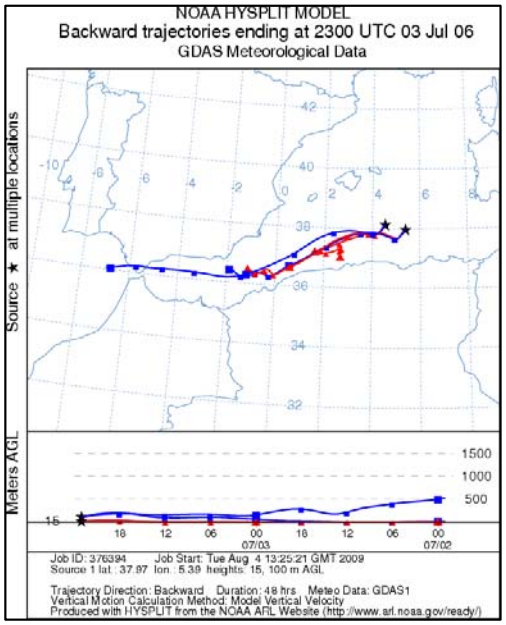
- Several aerosol samples exhibite values of fullerene at **pg/m³~ng/m³** of air levels
- The samples which had displaced over **highly populated** or **industrialized areas** exhibeted the highest levels of fullerenes.

Airborne:

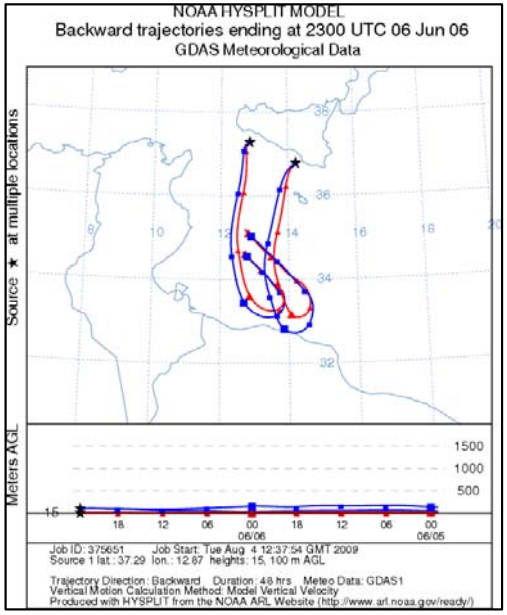




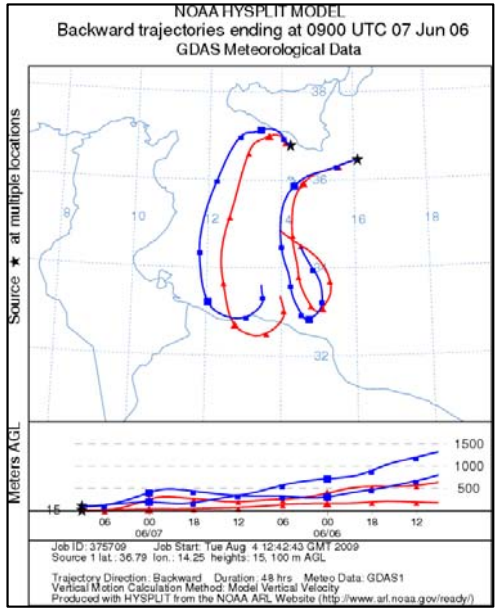
A



B

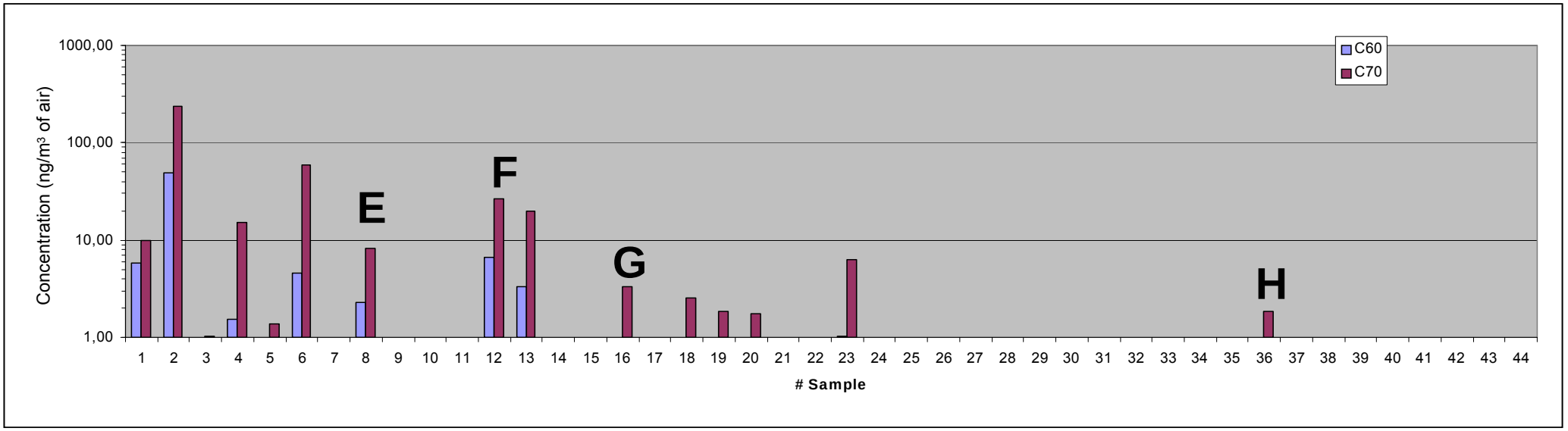


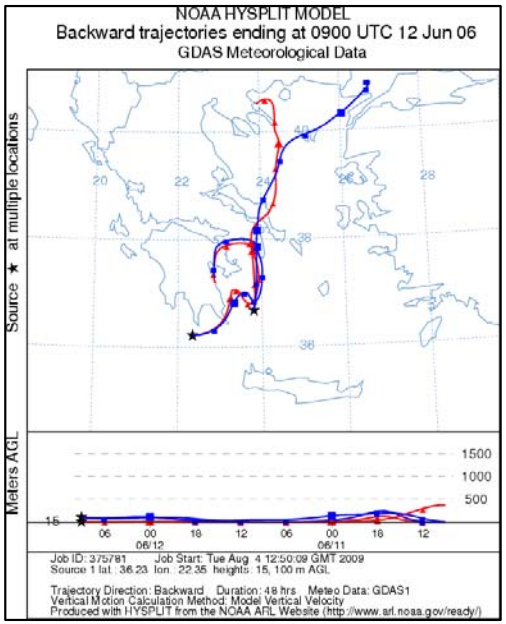
C



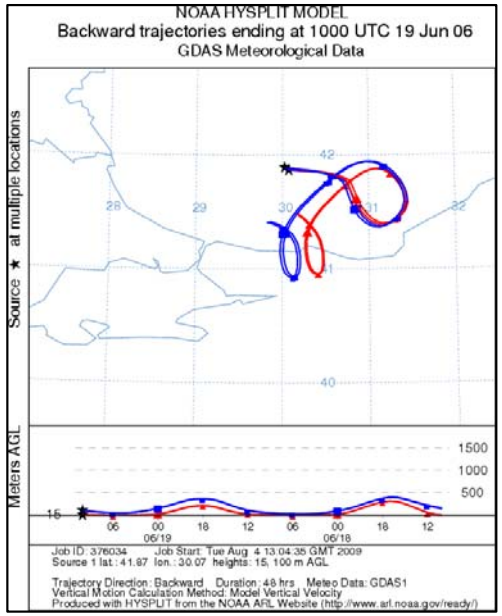
D

Airborne:

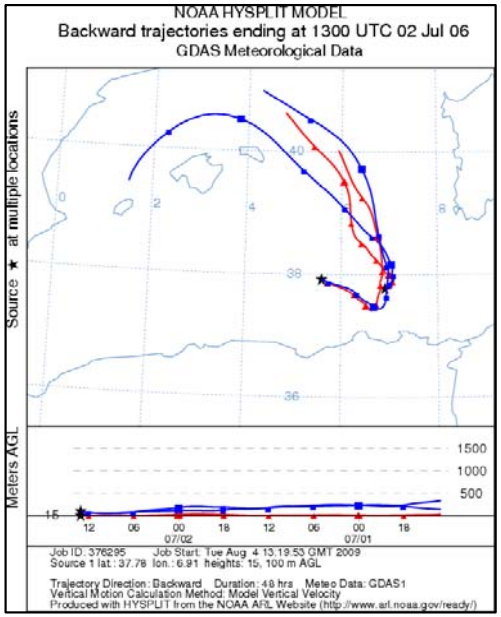




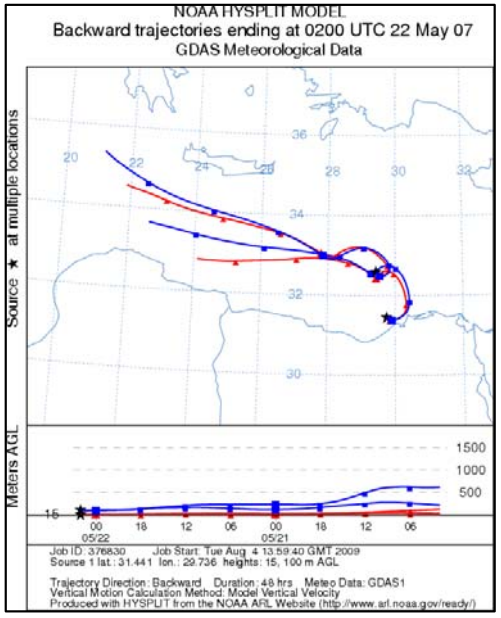
E



F

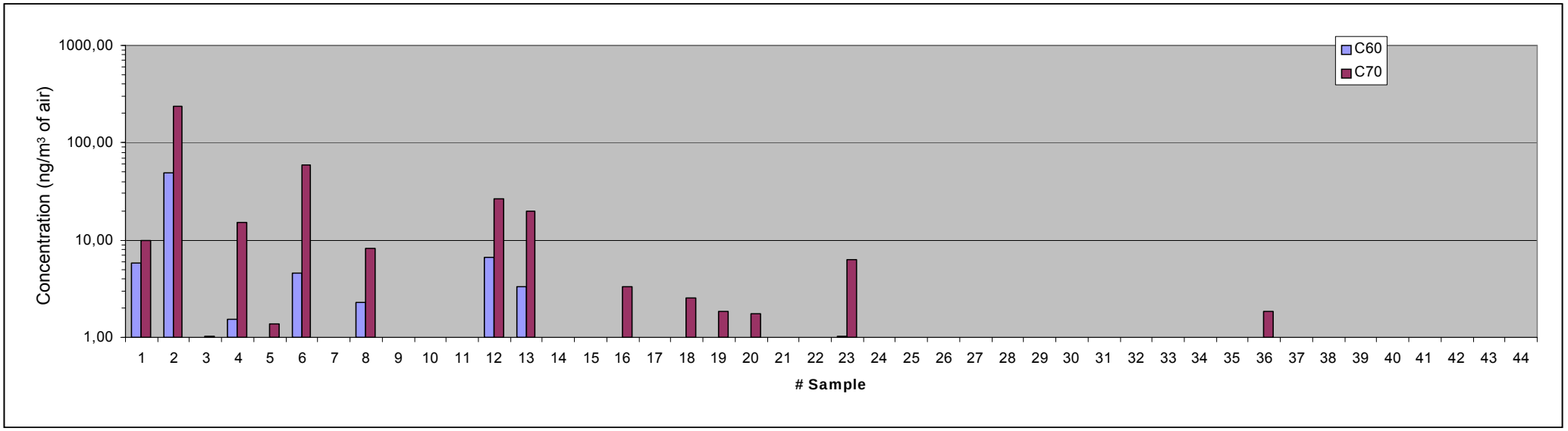


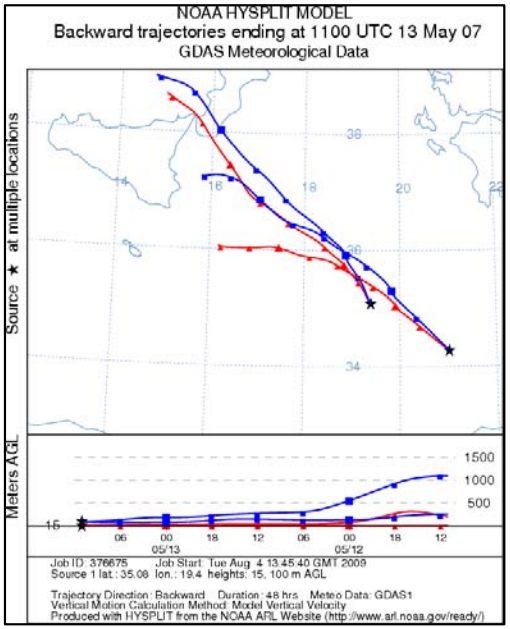
G

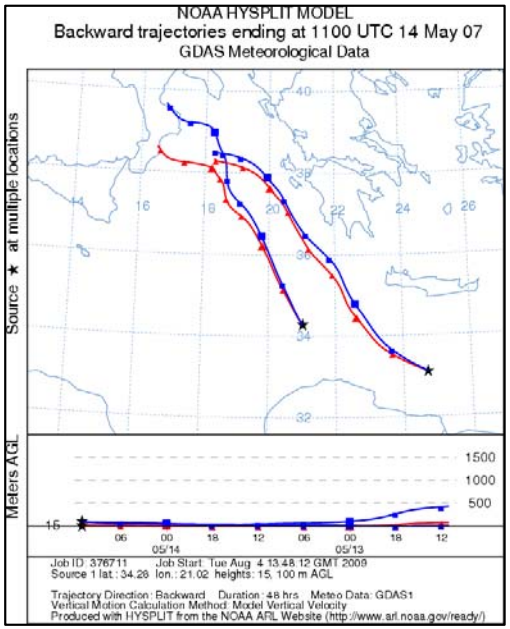


H

Airborne:







On the other hand, the **lowest levels** corresponded to air masses which had circulated over **large sea areas** during the last 48 h.

Conclusions I

- Different analytical approaches based on ultrasonic extraction or/and liquid-liquid extraction followed by LC-MS/MS were developed for the analysis of the fullerenes content in different environmental matrices,
  - Associated to suspended matter in water or wastewater
  - In water
  - In airborne particulate

The analytical methods were validated for different matrices presenting adequate limits of quantification

Conclusions II: Wastewater

- In wastewater the 65% of samples gave quantifiable concentrations for at least one of the compounds investigated.

- C_{60} fullerene was the most abundant one in wastewater, achieving maximum concentrations in the µg/L range.

- Nine of the samples showed concentrations at µg/L range

- Samples showing the highest concentrations were located in highly populated and industrialized areas, with a high traffic, or located near airports.

Conclusions III: Freshwater

- The presence of fullerenes was confirmed in freshwater from Llobregat River, but in a lower frequency, and in a lower concentration than in WW.

- The presence of fullerenes was higher in rainy days due to the increase of river flow, increase of turbulence, and resuspension of contaminants contained in sediment

- Accumulation in fresh water organisms should therefore be considered for future works

Conclusions IV: Airborne particulate

- Real samples present significant concentrations of C_{60} and C_{70} fullerenes.

- Fullerenes have been quantified in airborne particulate at concentrations of pg/m3 ~ ng/m3 air.

- C_{70} fullerene was the more frequent fullerene found in the airborne samples and also was the compound quantified at higher concentrations

- The more polluted samples were corresponding to those samples whose back trajectories indicated a high influence by industrial and human activity

ACKNOWLEDGEMENTS

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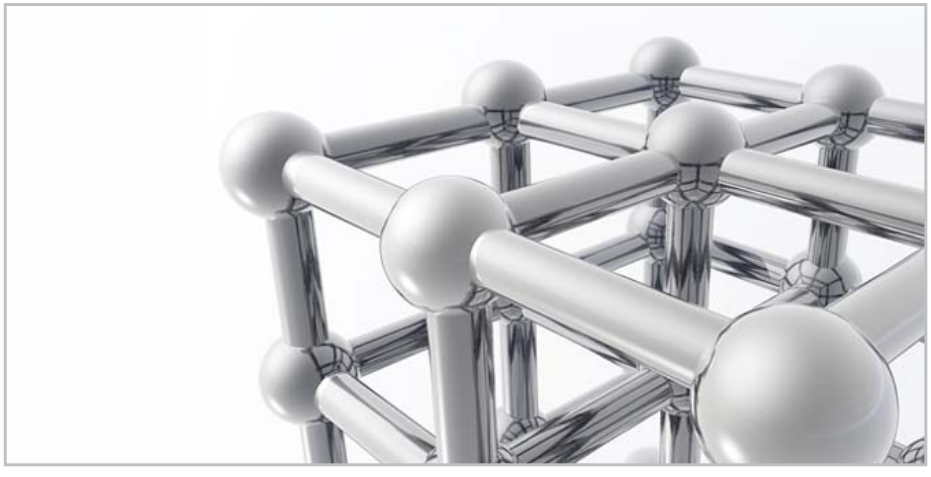

Thank you for you attention

Do You Have Any Questions?