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il futuro dei pneumatici fuori uso, oggi



Characterization of Tyre Recycled Rubber and Assessment of the Risks Associated with Dermal and Inhalation Exposure

Florence, October 28, 2016



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- Since 2011 – ELT management under an Extended Producer Responsibility scheme
- Management of 250.000 tonnes ELT/y
- Non for Profit
- (New) Business Development

BRIDGESTONE

Continental

DUNLOP
TIRES

GOODYEAR

MARANGONI

 **MICHELIN**

PIRELLI

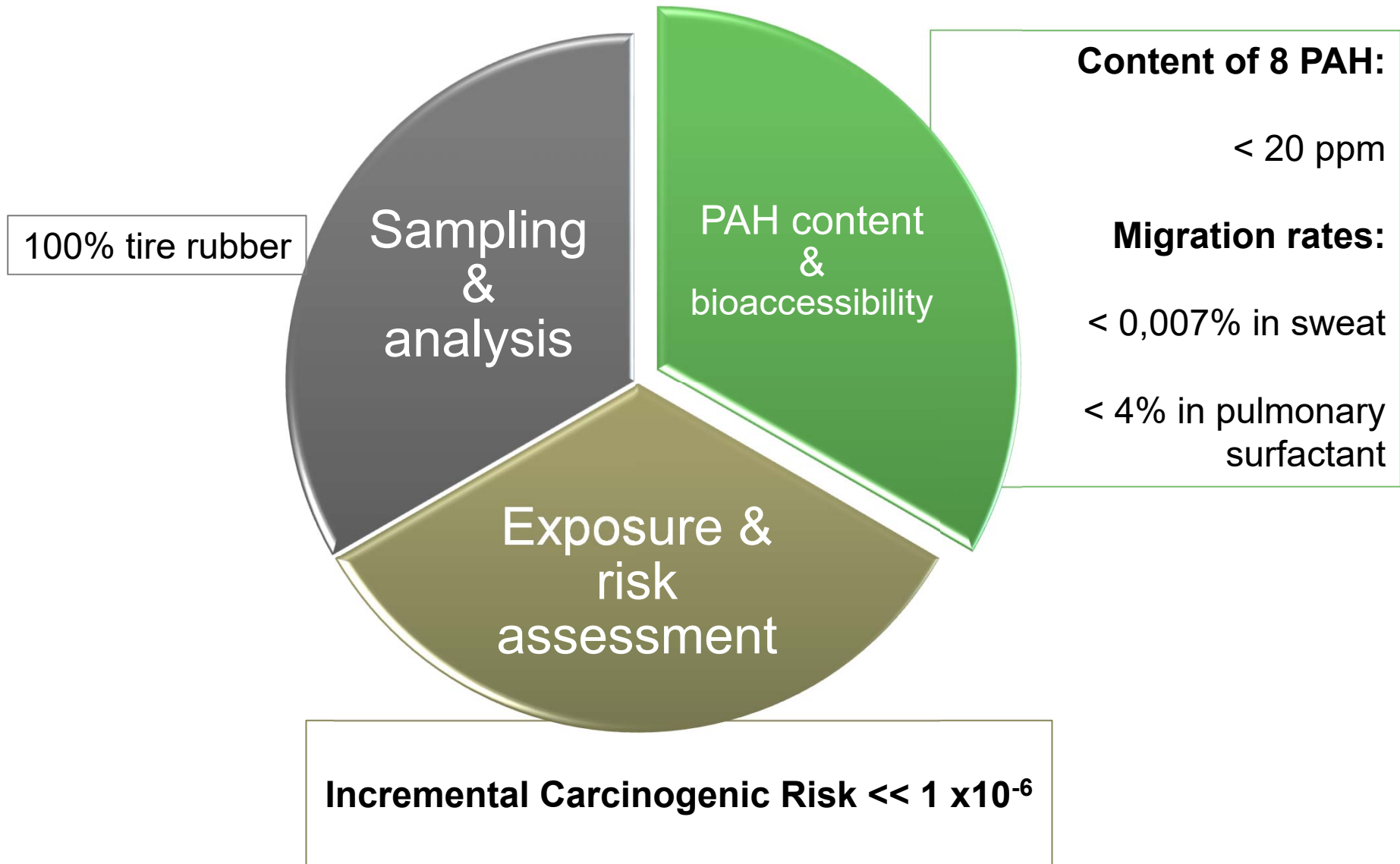
Besides collecting tires..



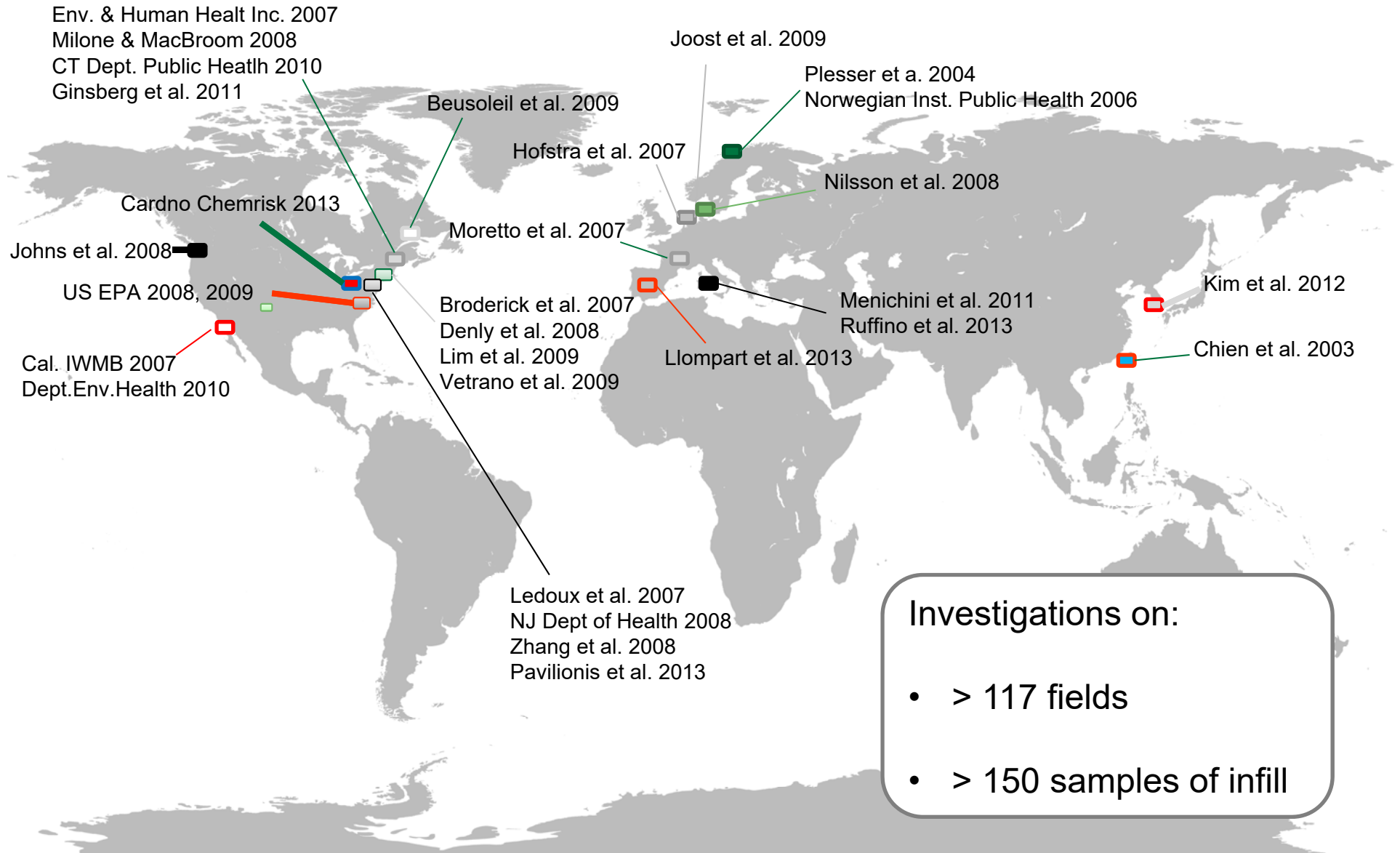
About the safety of rubber



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Literature review



Investigations on:

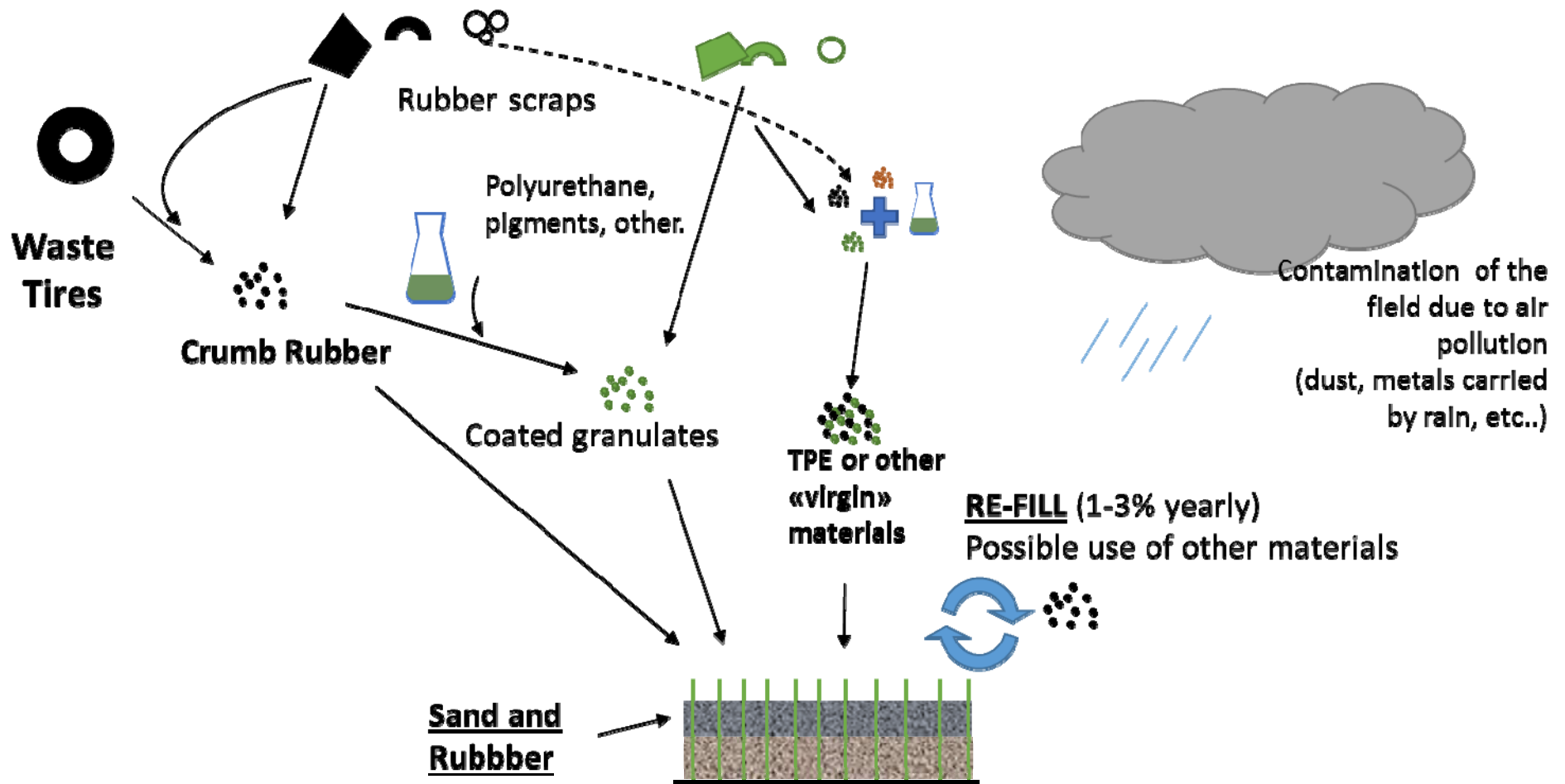
- > 117 fields
- > 150 samples of infill

Facts



- Most of the studies generically refer to «Tyre recycled rubber» but the origin of the infill is not thoroughly investigated
- Crumb rubber with high PAHs content was found sometime
- Bioavailability of the PAHs of vulcanized rubber is not fully investigated
- The incremental carcinogenic risk related to the use of ELT recycled rubber is negligible ($< 10^{-6}$)

What is «crumb rubber»?



Scientific partners



Isituto Farmacologico Mario Negri

www.marionegri.it

- *Determination of the PAH content*
- *Migration tests*
- *Risk assessment*



Waste and Chemicals

www.wasteandchemicals.eu

- *Exposure assessment*
- *Risk assessment*



Bureau Veritas

Witnessing - sampling



Cerisie

Characterization of the samples



Tun Abdul Razak Research Centre

Aromaticity Index (Hbay)



Biochemisches Institut für Umweltcarcinogene

-PAH content

Project outline



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Sampling and classification

PAH content and other analysis

PAH migration tests

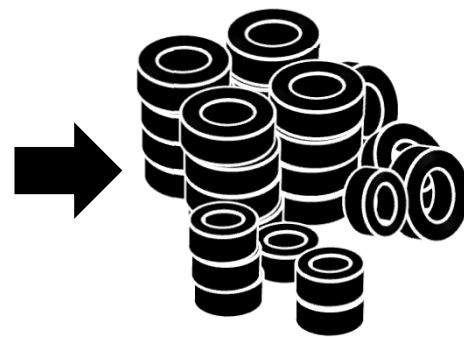
Exposure of workers and athletes

Risk assessment

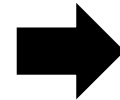
Representative samples of tire rubber



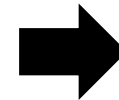
Waste tires
managed by
Ecopneus:
250.000
tonnes/y



Primary
sample
250 tonnes



Reduced sample
50 tonnes



25 increments
(400 g each) to
ensure the
representativeness
of the sample

Sampling and classification



- 5 Facilities involved
- 250 t ELT mixed and reduced to ca. 50 t
- 3.885 ELTs classified by age and origin
- Witnessing and chain of custody by Bureau Veritas
- 5 Laboratories involved (UK, DE, IT)



Sorting by age and «made in»



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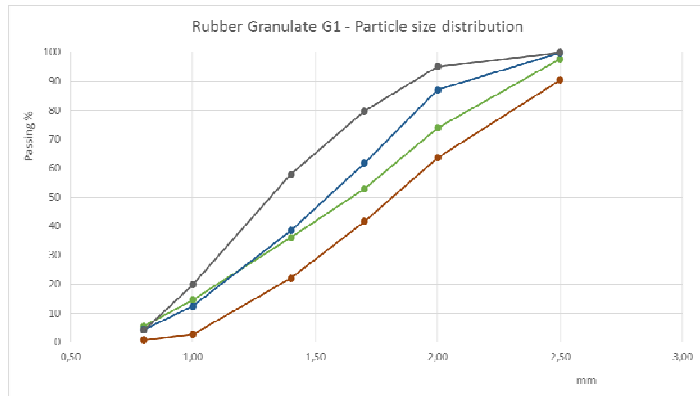
| | | | |
|--|--|---|--|
| <p>Before 2010 Made in EU</p> <p>«Ante-EU»</p> | <p>Before 2010 Non- EU</p> <p>«Ante-nonEU»</p> | <p>After 2010 Made in EU</p> <p>«Post-EU»</p> | <p>After 2010 Non-EU</p> <p>«Post-nonEU»</p> |
|--|--|---|--|



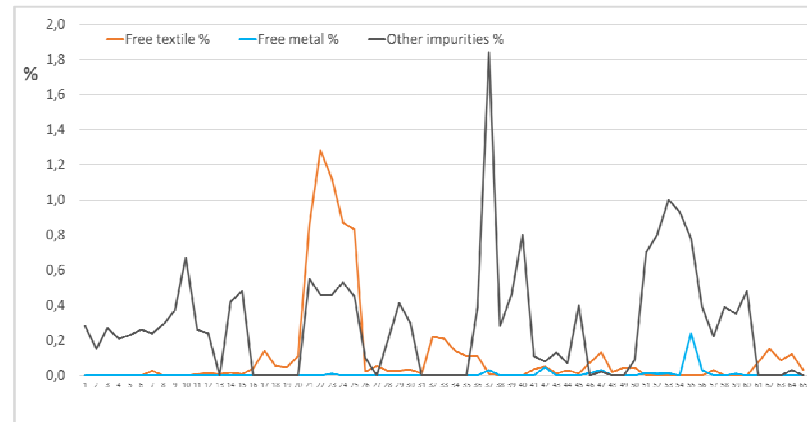
Characterization of 65 samples



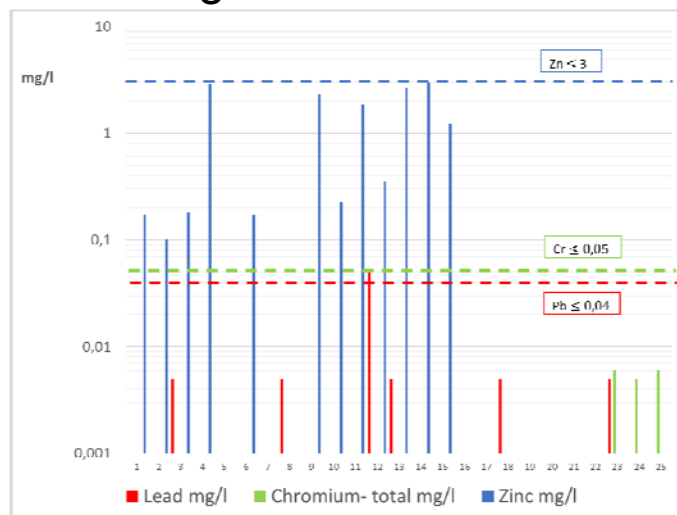
Particle size distribution



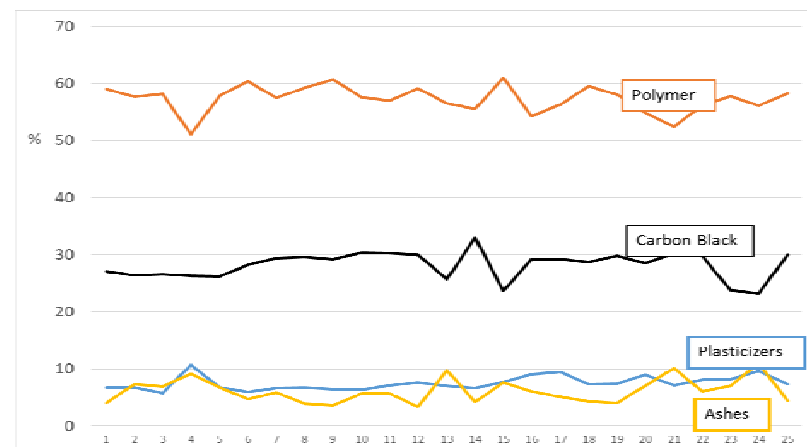
Metal, textile & other impurities



Leaching of metals



Thermogravimetric Analysis

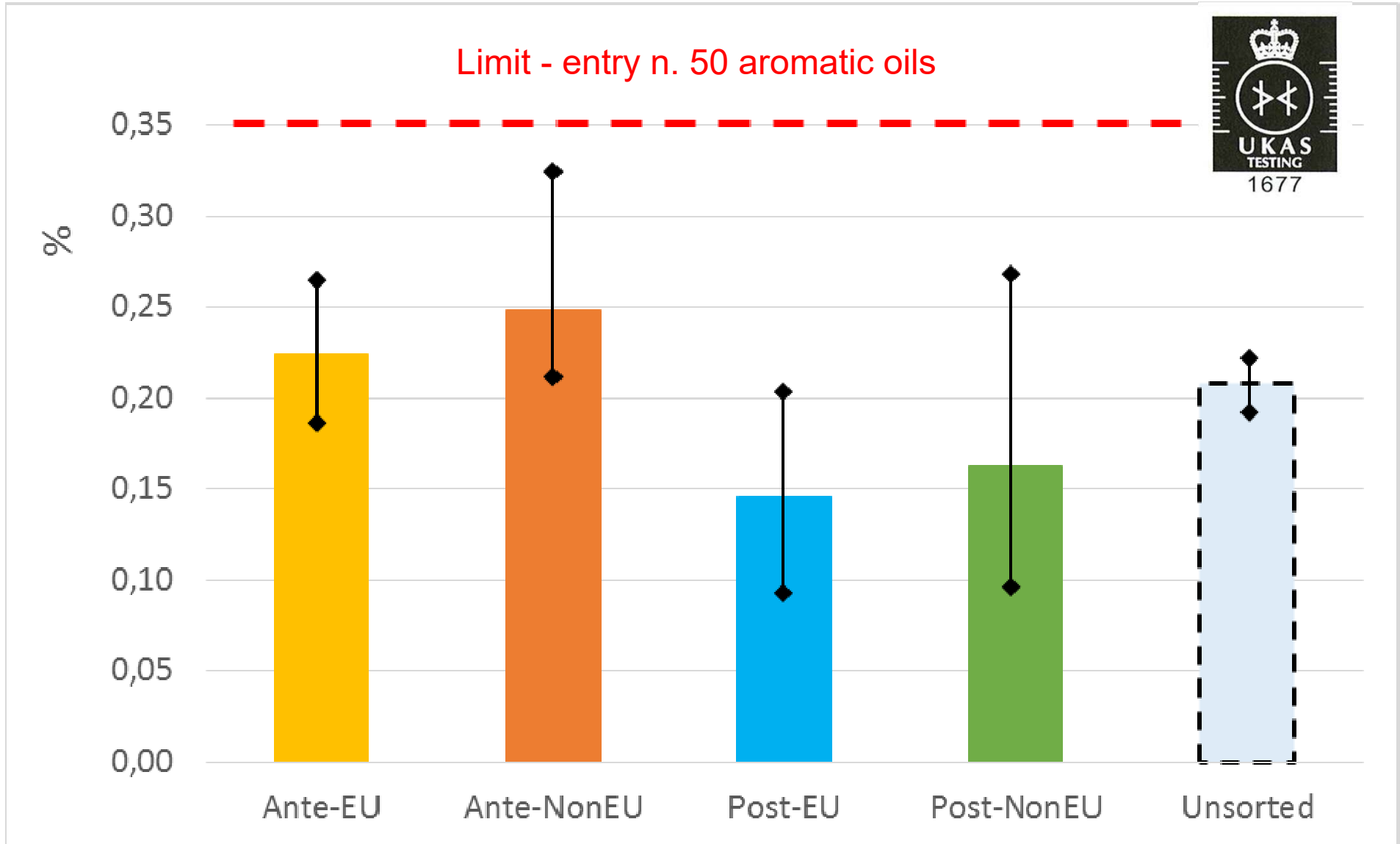




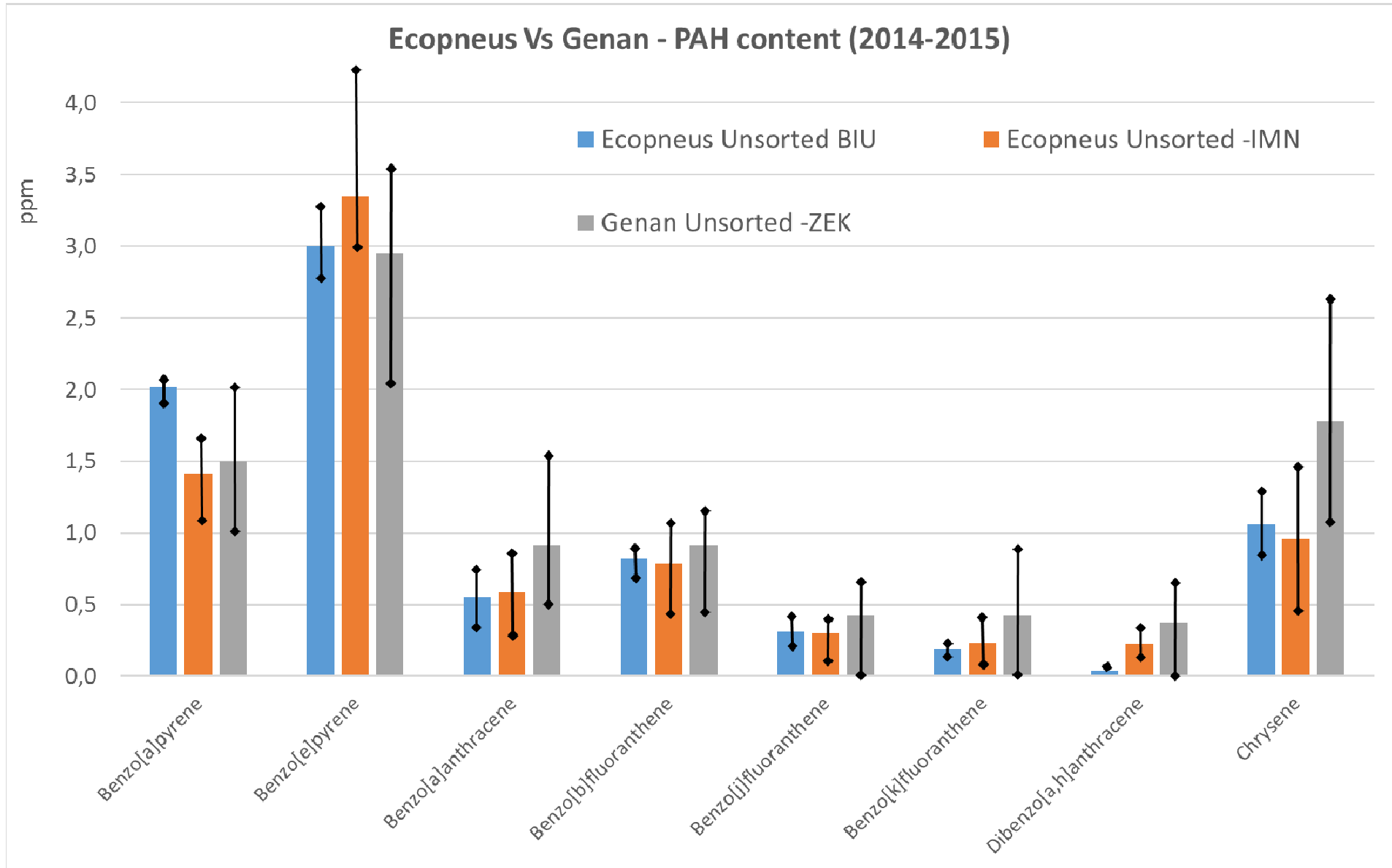
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Poly Aromatic Hydrocarbons - PAH

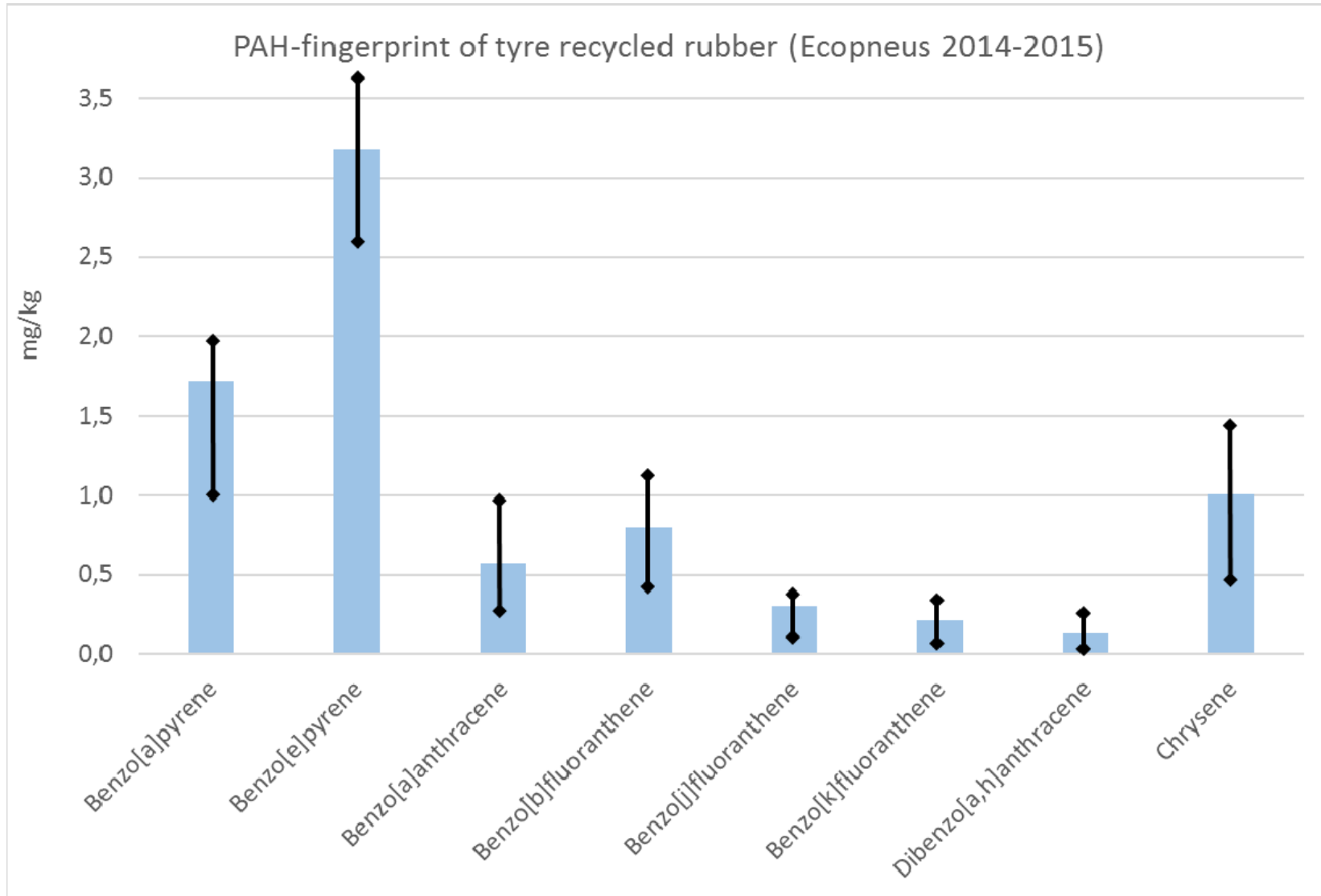
H-Bay – oil aromaticity (ISO-21461)



Comparison with central-European ELTs



PAH FINGERPRINT 2014-2015



Was it «tyre recycled rubber»?



Chemosphere 90 (2013) 423–431



Contents lists available at SciVerse ScienceDirect

Chemosphere

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



Hazardous

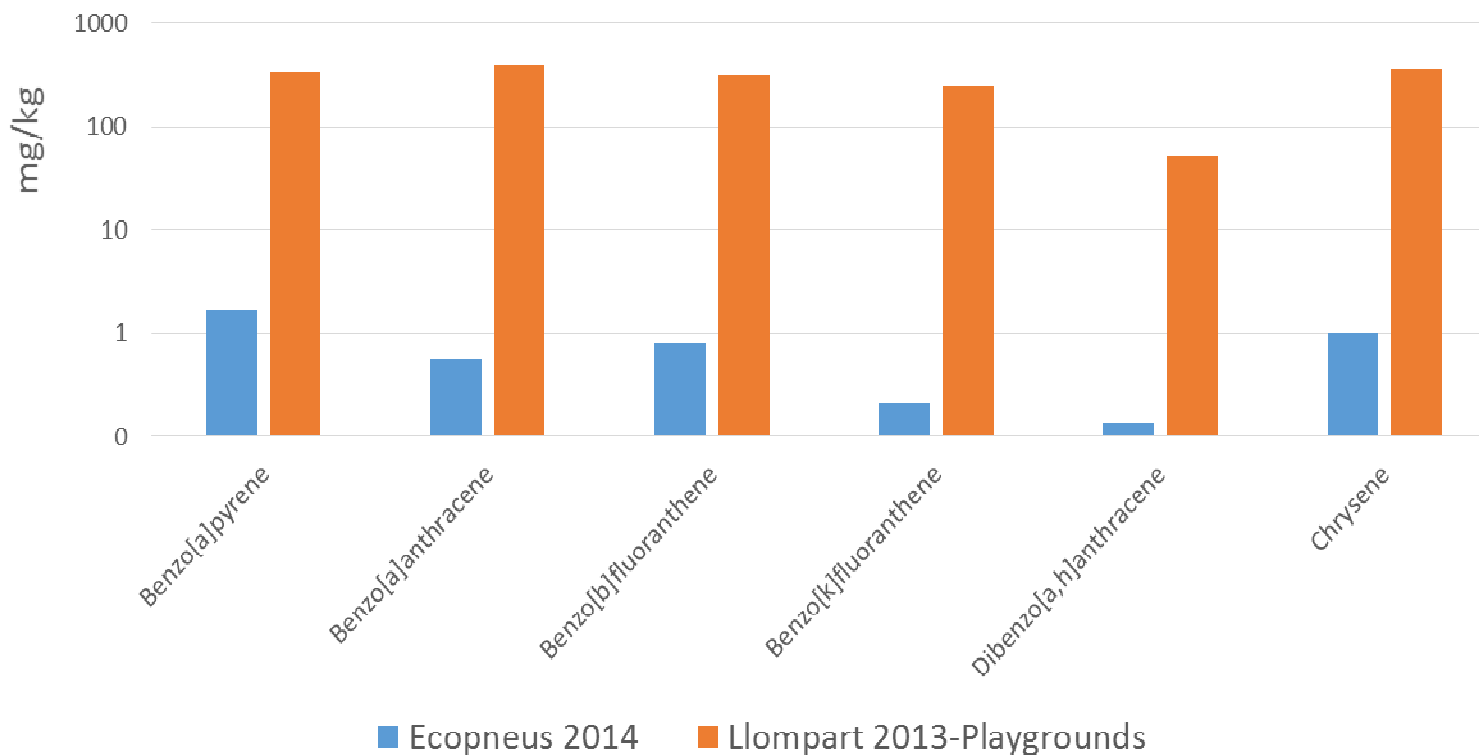
Maria Llompart
Thierry Dag

^aDepartamento de
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E-15080 A Coruña, S

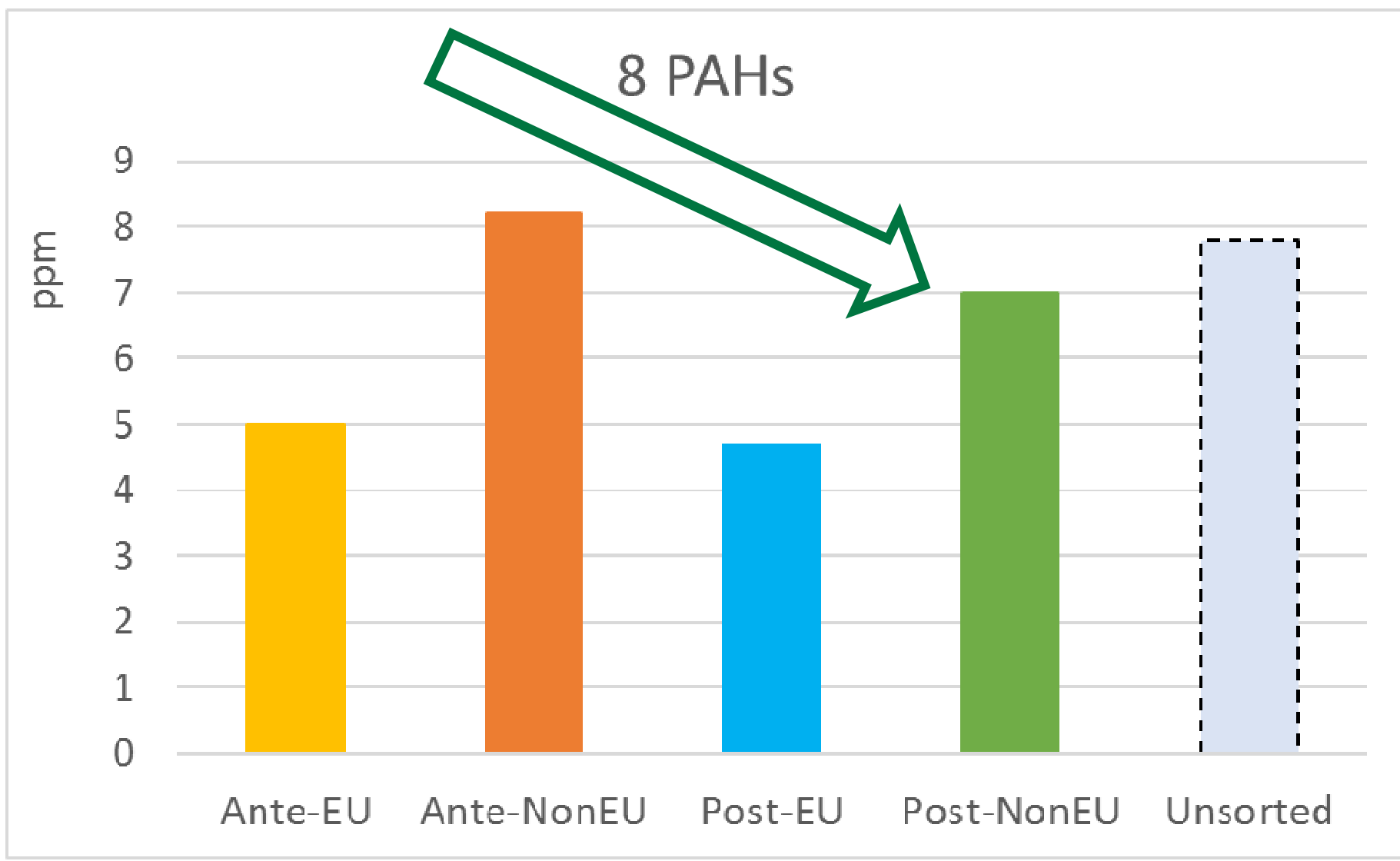
HIGHLIGHTS

- ▶ A large number of playgrounds analyzed have been analyzed.
- ▶ The occurrence of PAH compounds at the analyzed sites is confirmed.
- ▶ Thirty-one target analytes were analyzed by GC-MS/MS.
- ▶ Total PAH concentrations were remarkable. Concentrations must be highlighted.
- ▶ Target analytes were analyzed by headspace SPME-GC-MS/MS at room temperature.

Tyre recycled rubber Vs Unknown rubber



8 PAHs in ELTs of different age/origin



Migration rate and bio-availability



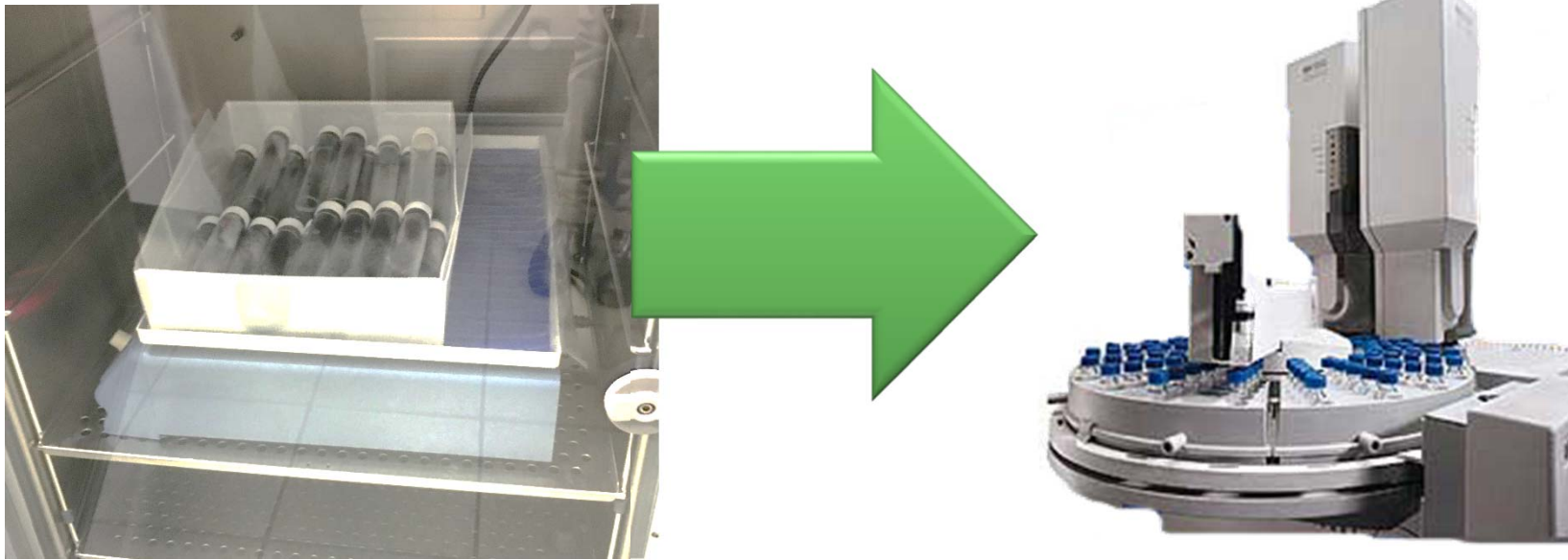
Artificial
sweat

- Dermal Contact

Pulmonary
Surfactant

- Inhalation

Migration in bio-fluids



MIGRATION IN ARTIFICIAL SWEAT < 0,007%

MIGRATION IN PULMONARY SURFACTANT < 4%

Migration Test in Artif. Sweat (EN 1810)



-24 h mixing @ 37°C instead of 1h

-5g rubber in 30 ml Artificial Sweat

-PAH in sweat close to the limit of detection <0,05 ng/g B(a)P



Migration < 0,007%

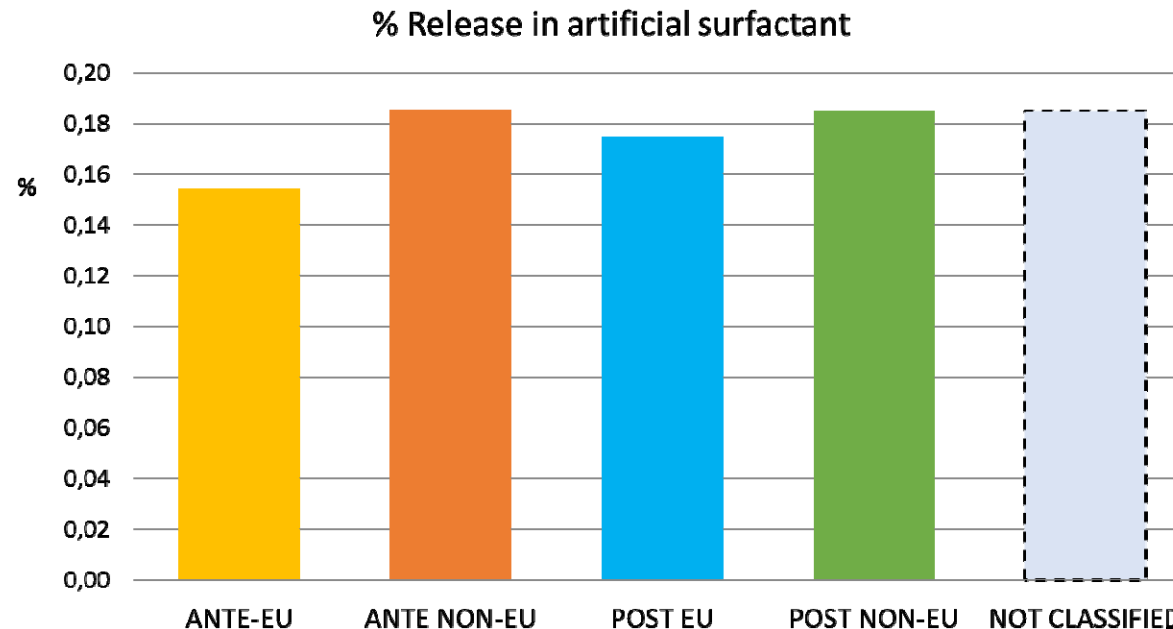
Migration Test in Pulmonary Surfactant



-24 h mixing @ 37°C

-5g rubber in 30 ml Pulmonary Surfactant (3 fluids)

1. 10 mM magnesium chloride, 150 mM sodium chloride, 4 mM potassium chloride, 1mM di-potassium phosphate, 5 mM sodium sulphate, 25 mM calcium chloride, 7 mM sodium acetate, 24 mM sodium bicarbonate, 3 mM sodium citrate) diluted 1:4, and **0.18% (w/v) 1,2-Dipalmitoyl-sn-glycero-3-phosphocholine**.
2. **Natural surfactant** (pig pulmonary surfactant)

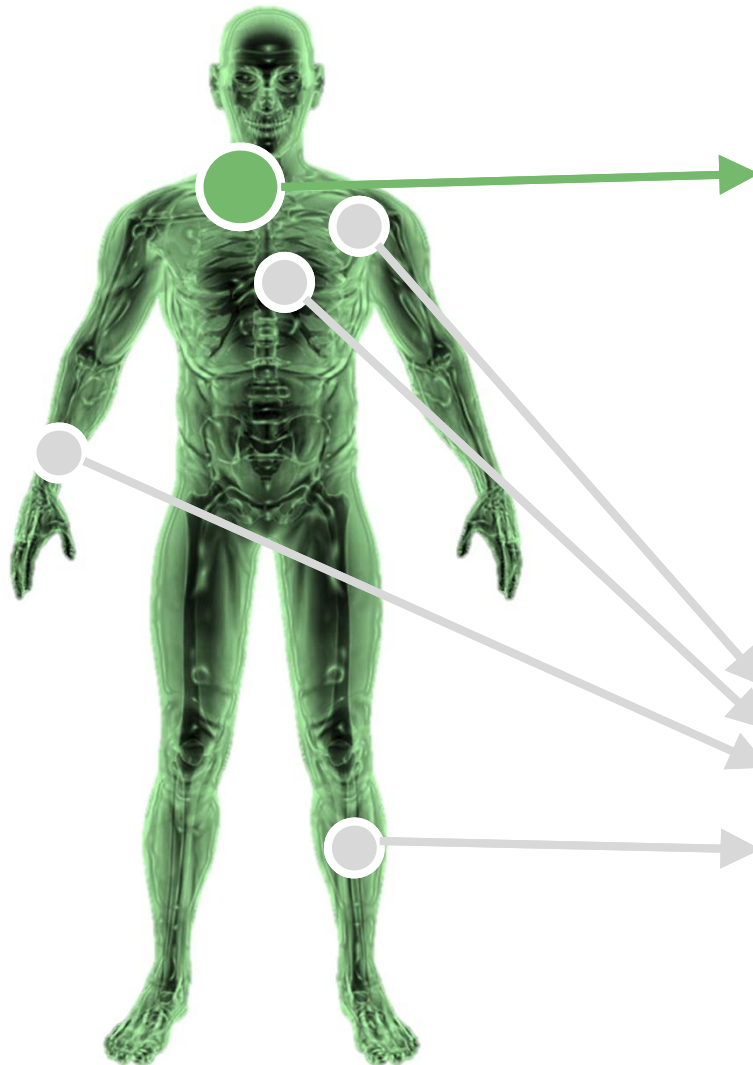




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Exposure assessment for workers and athletes.
PAH uptake.
Risk assessment.

Exposure assessment - method



Inhalation exposure

PAH - air

- Breathing zone sampling (NIOSH 5515)
- Quartz filters → 2 l/min

PAH – dust

- Respirable particles (NIOSH 0600)
- Glass filters → 1,7 l/m

Dermal exposure

- Dermal polypropilene patches
- particulate and gaseous PAH adsorption
- chest-shoulder-wrist-calf

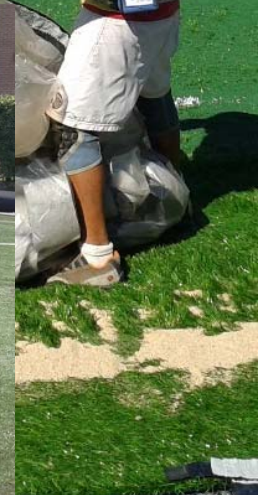
Monitored sites:



| # | Field | Date | Type* | Infill |
|----|----------------|-------|-------|--------|
| 1 | Trecella (MI) | 07/15 | I | SBR |
| 2 | | 11/15 | T | SBR |
| 3 | Roma | 09/15 | I | SBR |
| 4 | | 09/15 | I | SBR |
| 5 | San Salvo (CH) | 09/15 | I | Cork |
| 6 | Milano | 10/15 | I | SBR |
| 7 | | 10/15 | I | SBR |
| 8 | Trecella (MI) | 05/16 | T | SBR |
| 9 | | | T | Erba |
| 10 | Trecella (MI) | 05/16 | T | SBR |
| 11 | | | T | Grass |
| 12 | Roma (x2) | 06/16 | T | SBR |
| 13 | | 06/16 | T | Grass |



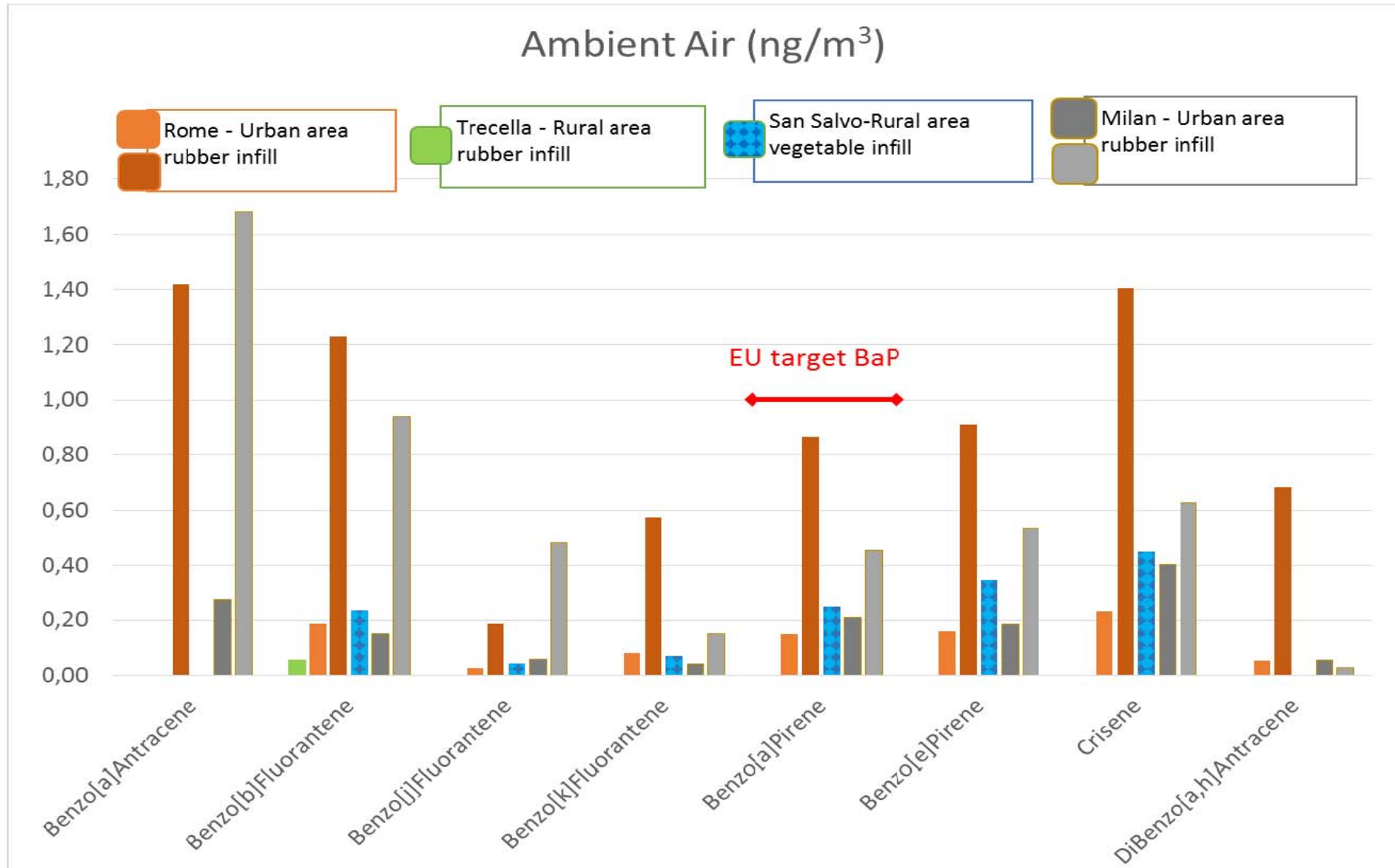
Workers exposure



Athletes exposure



Workers' exposure (Summer- Early Autumn)

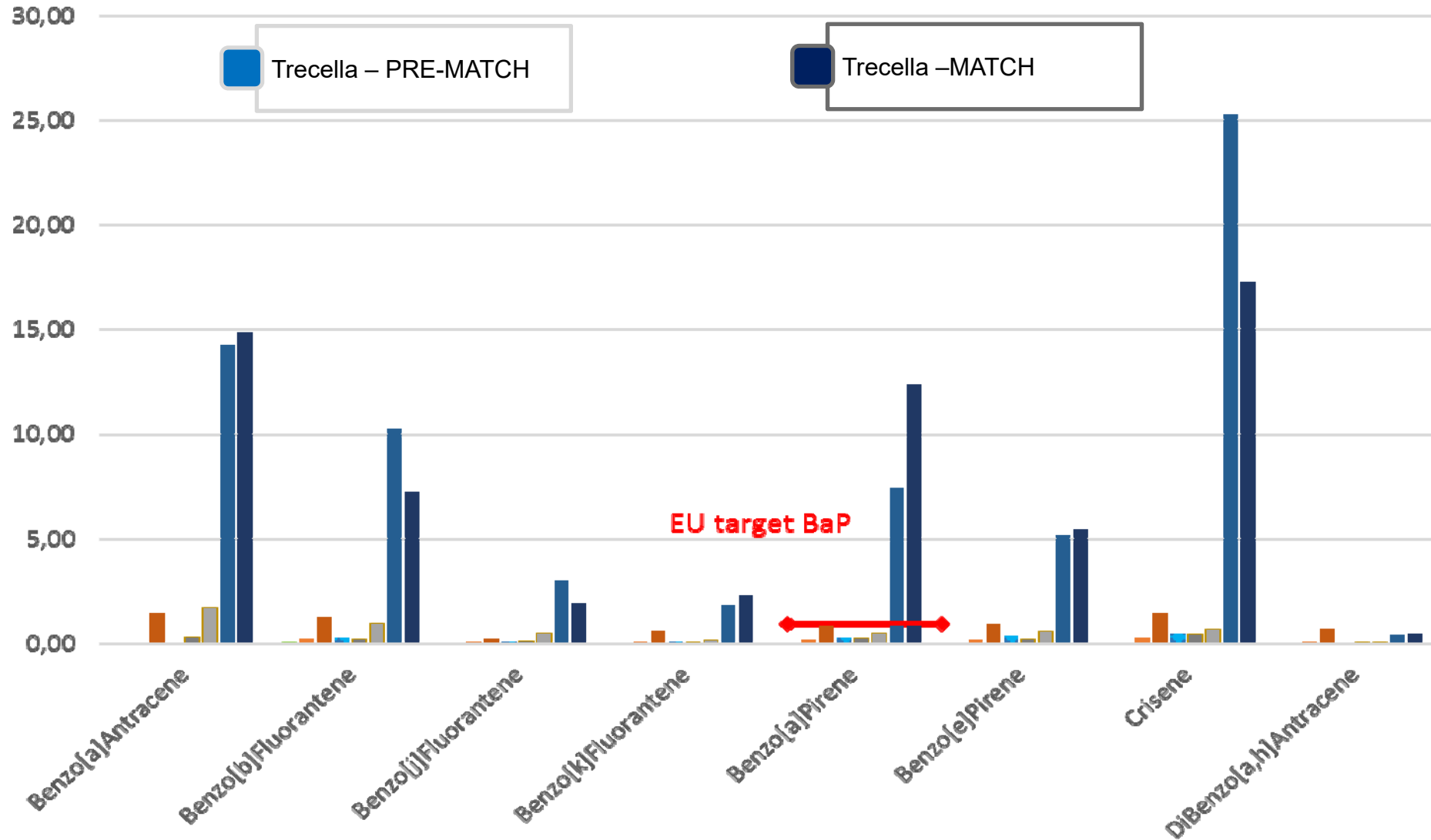




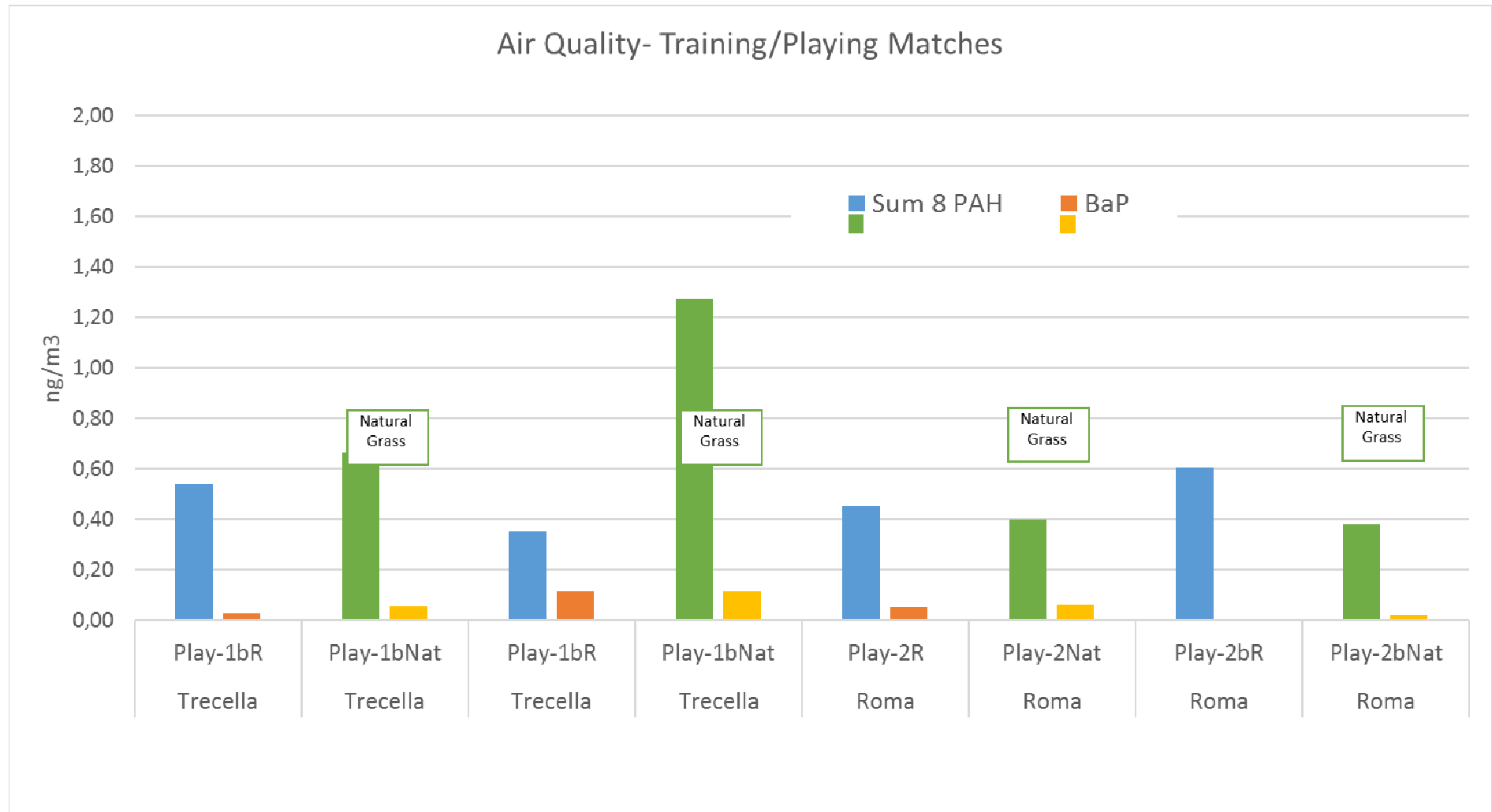
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Athletes' exposure (December)

Ambient Air (ng/m³)



Athletes' exposure (Late spring)

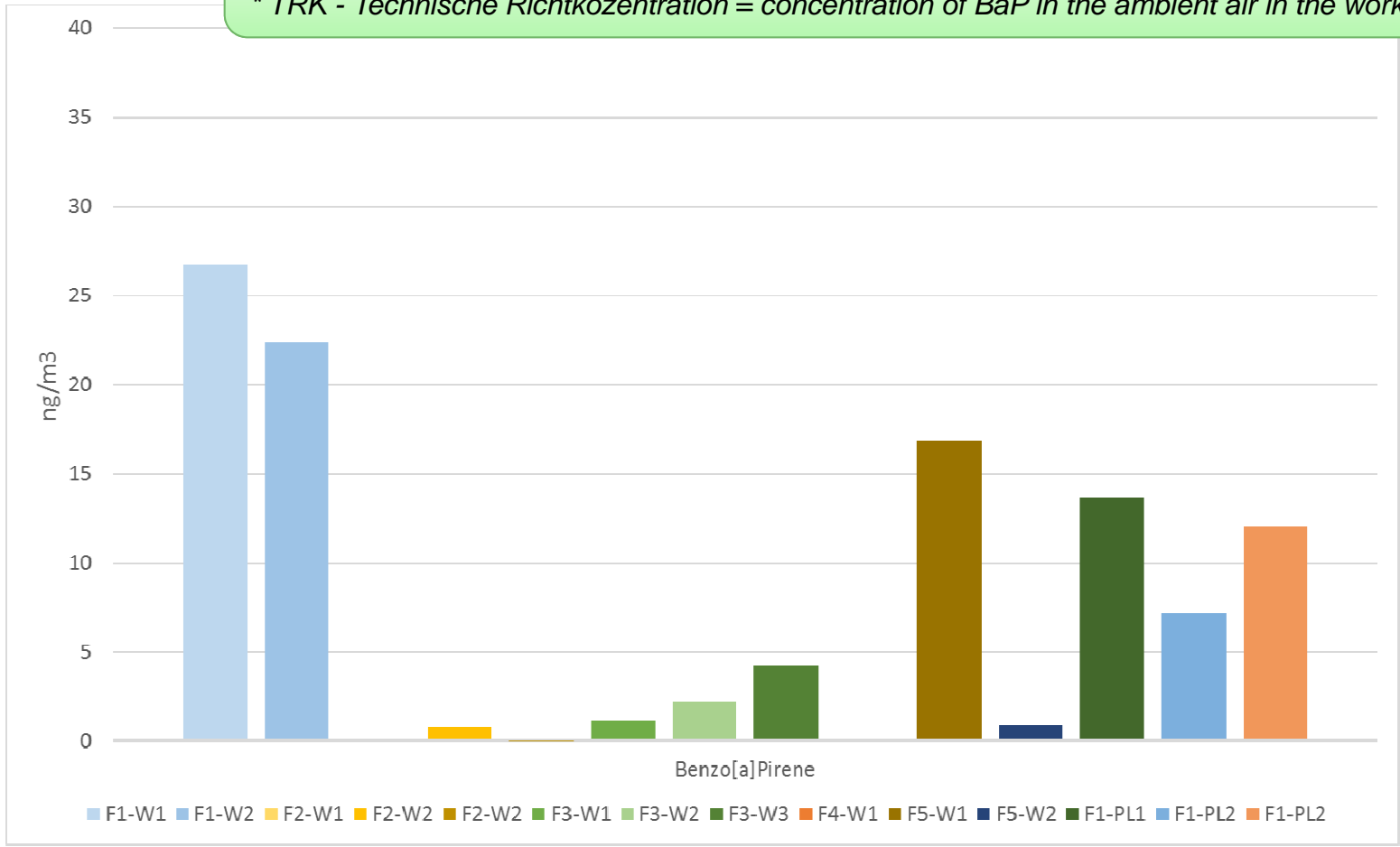


Inhalation exposure (ng/m³ - breathing zone)

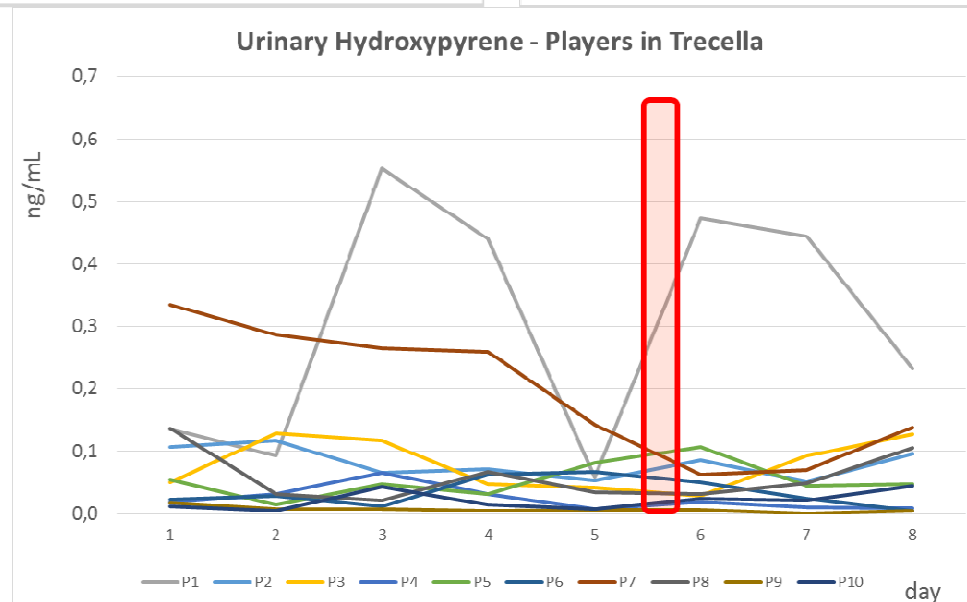
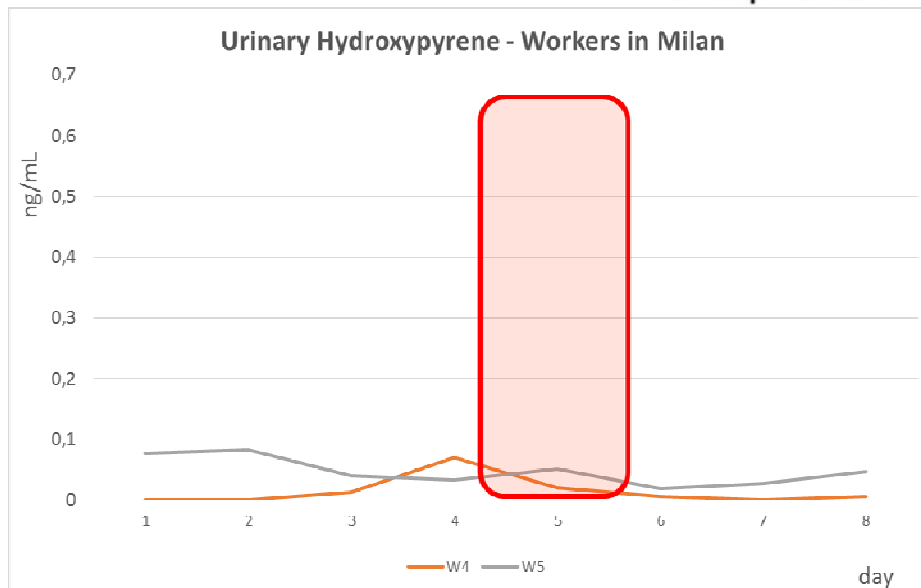
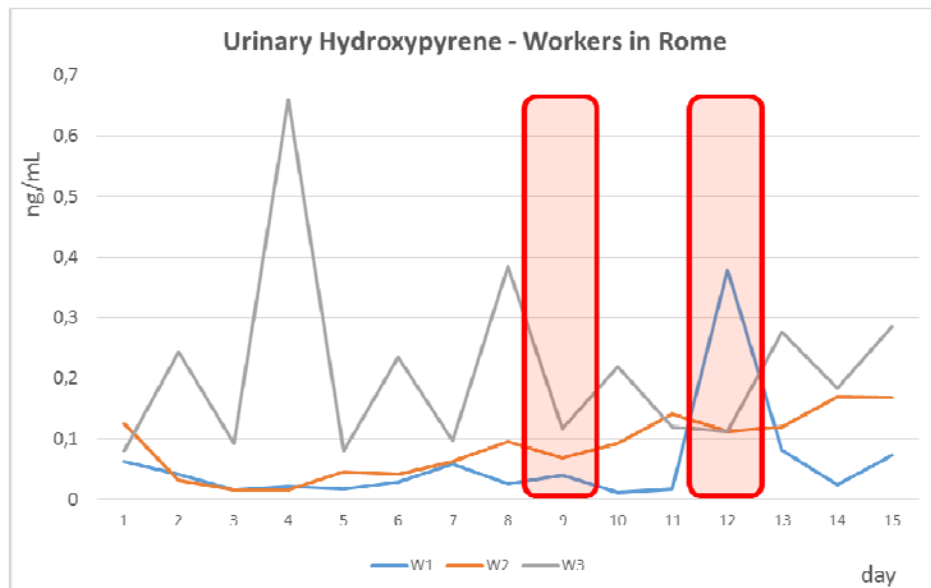


Occupational exposure limit BaP (German TRK*) = 2.000 ng/m³

** TRK - Technische Richtkonzentration = concentration of BaP in the ambient air in the workplace*



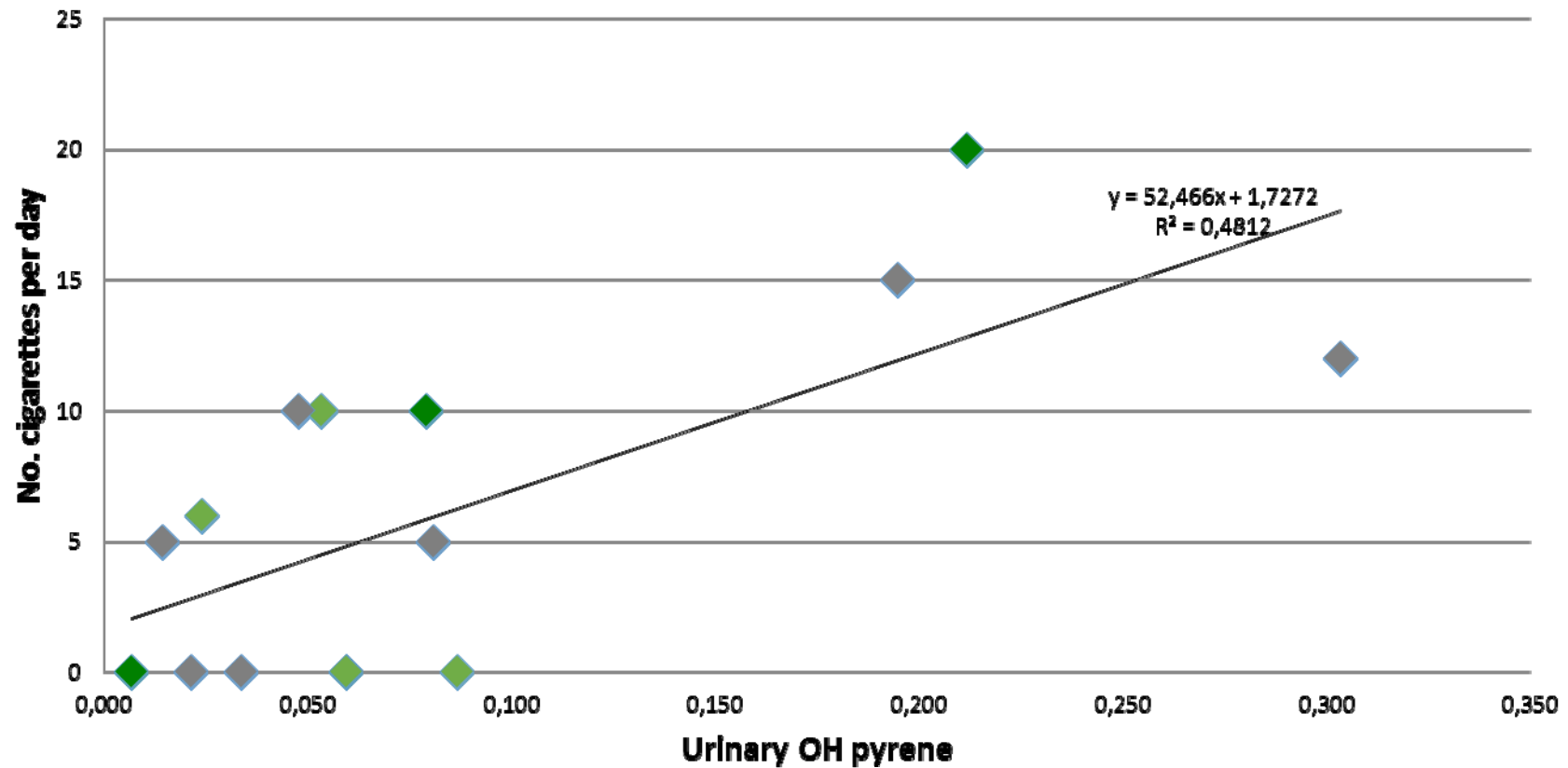
PAH uptake – Urinary Hydroxypyrene



PAH uptake and lifestyle



Urinary OH pyrene vs. cigarettes smoked

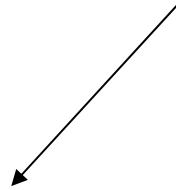


◆ Resident in rural area

◆ Resident in urban area

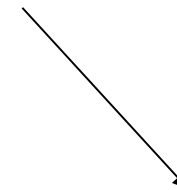
◆ Resident in sub-urban area

2 Risk assessments



WASTE AND CHEMICALS

- Based on experimental data
- Exposure values were measured on the fields
- Conservative approach regarding the bioavailability of PAH (1% dermal migration)



ISTITUTO MARIO NEGRI

- Based on average PM10 annual concentration
- 100% PM10 assumed to be ELT-rubber
- 100% bioavailability of PAH in rubber was considered (conservative approach)

Risk assessment



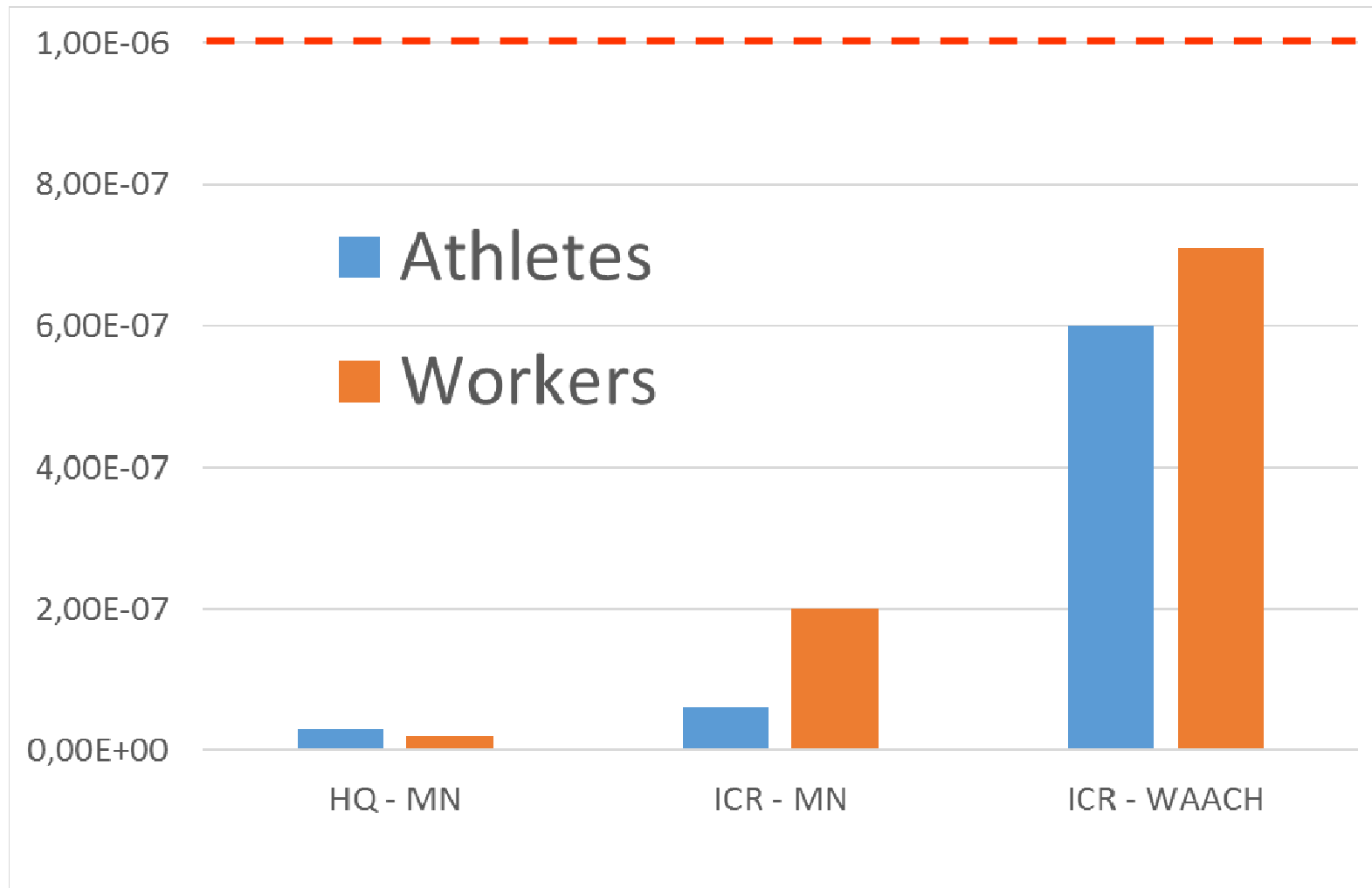
- Equation for inhalatory exposure:

$$R_I = SF_I \frac{(C_p + C_v) \times I_R \times HE \times EF \times ED}{BW \times AT \times 365}$$

- Equation for dermal exposure:

$$R_D = SF_d \frac{C_{pad} \times HE \times BF \times S \times EF \times ED}{ET \times BW \times AT \times 365}$$

Risk assessment



Conclusions



- The risk associated with the PAH exposure is negligible in fields infilled with tire rubber
- The PAH content in tire rubber is limited (< 20 ppm)
- The bioaccessibility of PAH in vulcanized rubber is limited
- The traceability of the infill material should not be given for granted in forthcoming surveys.



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Thank you for your attention.

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