Characterisation of PAHs in the ambient air of steelworks

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Overview

➢ Background

- *ERAMAC project*
- *Cokemaking and iron ore sintering*
- *Overview of sampling and analytical methods*

➢ Emissions inventory

- *Fugitive and stationary emissions of PAHs in cokemaking*
- *Sinter plant main stack PAH emissions in the UK*

➢ Ambient air studies

- *Long-term PAH monitoring campaign at a Corus Coke Plant*

ERAMAC

Objectives

'Emissions, Reduction through Analysis, Modelling and Control'

Research Fund for Coal and Steel (RFCS-CR-03001)

1. Develop sampling and analytical methods for the measurement emissions of organic pollutants such as VOCs (volatile organic compounds : e.g. benzene, toluene, xylenes) and SVOCs (semi-volatile organic compounds : PAHs, benzo [a] pyrene) from cokemaking and iron ore sintering plants.

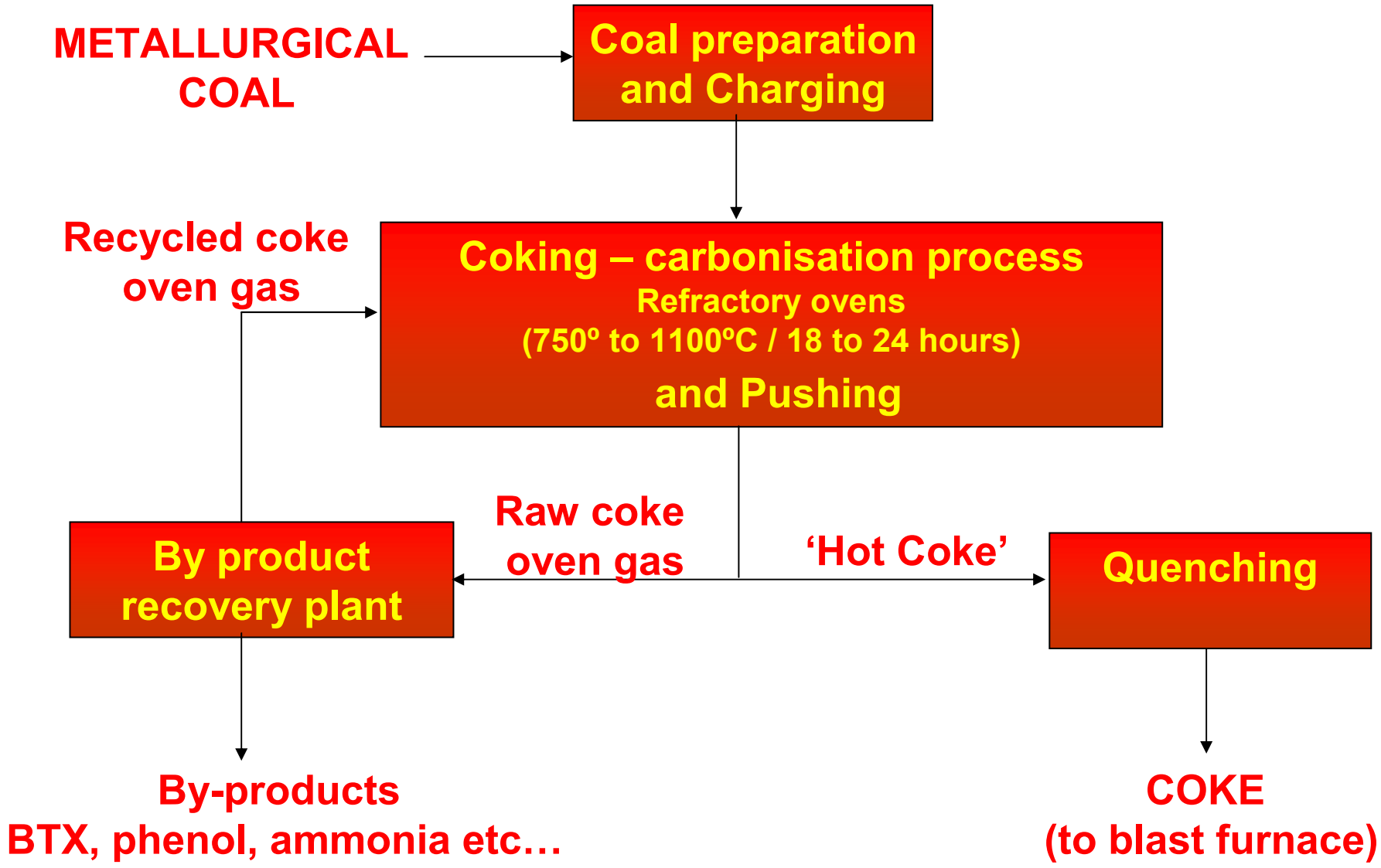
2. Apply these methods to obtain an emissions inventory of these organic pollutants and to identify the priorities for pollution control.

3. Undertake measurement of these species in the ambient air and, using mathematical models, apportion the sources to iron and steel-making processes.

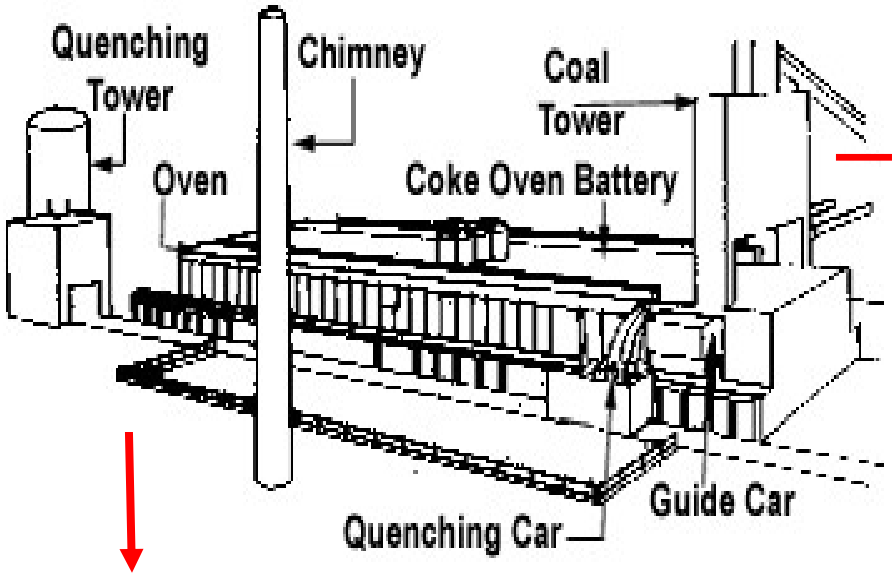
Ciaparra et al., 2009. Atmospheric Environment 43, 2070-2079.
Aries et al., 2007, The Year Book of the Coke Oven Managers Association, 136-197.

Cokemaking

By-product recovery coke ovens



Coke oven batteries

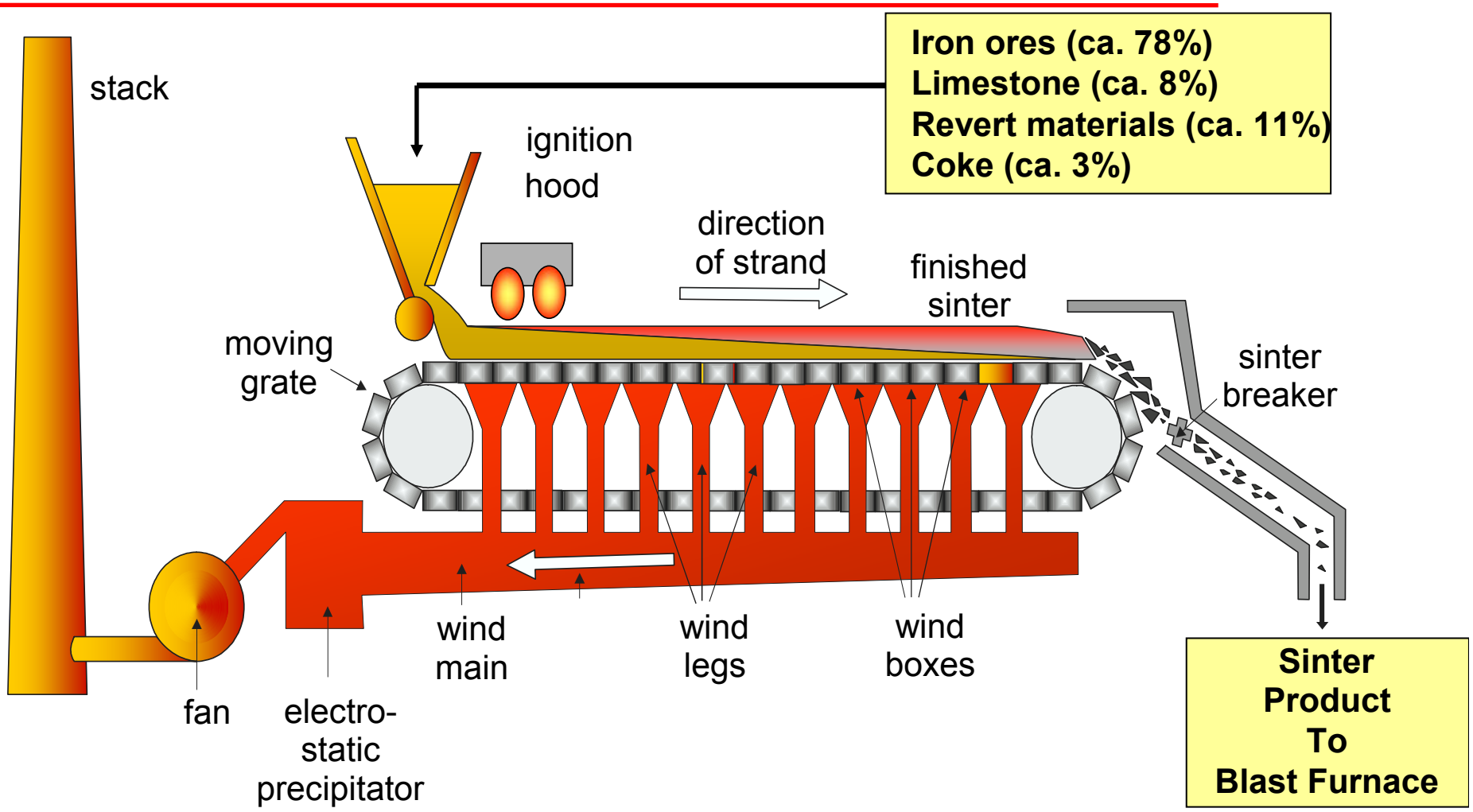


‘Ram Side’ of the battery: Coal side

‘Coke side’ of the battery after pushing

Refractory oven during coking

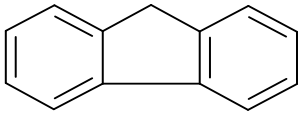
Iron ore sintering process



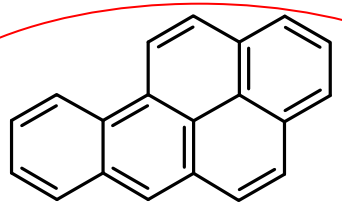
Polycyclic Aromatic Hydrocarbons (PAHs)

US EPA 16 Polycyclic Aromatic Hydrocarbons (PAHs)

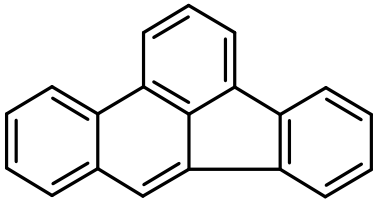
Naphthalene
Fluorene
Acenaphthene
Acenaphthylene
Anthracene
Phenanthrene
Chrysene
Pyrene
Fluoranthene
Benzo (a) anthracene
Benzo (b) and (k) fluoranthene
Benzo (a) pyrene
Indeno (1,2,3-cd) pyrene
Dibenzo (a,h) anthracene
Benzo (g,h,i) perylene



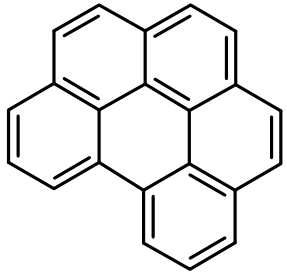
Fluorene



Benzo (a) pyrene B[a]P



Benzo (b) fluoranthene



Benzo (g,h,i) perylene

Fourth 'Daughter' Directive of the Air Quality Framework (96/62/EC)

The commission proposed a target value of 1.0 ng.m^{-3}, annual mean, for B[a]P in the ambient air. The target value should be attained by the 1st of January 2010.

Sampling methods

Door emissions

Charging hole lid emissions

For stationary sources, (underfiring stack and sinter plant stacks), samples were collected isokinetically following US EPA method 23.

For ambient air monitoring, high volume samplers equipped with PUFs and filters (Total Suspended Particles) were used . They were operated for 24 hours at a flow rate of 0.2 m^3 / min (ca. 290 m^3)

PAHs

Sample preparation and analysis

EMISSION or AMBIENT AIR SAMPLES

DIONEX ASE 200 extraction (DCM / 150ºC)

Basic Alumina Chromatography
Activity Grade I
200°C / 16h

***1) n*-hexane (30 ml)**
2) *n*-hexane / DCM (80 / 20) (5 ml)

DCM (30 ml)

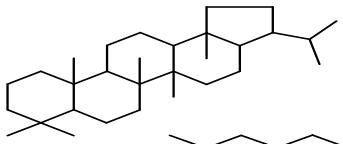
Aliphatic Fraction 1

Aromatic Fraction 2

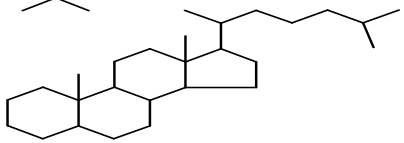
Aliphatic, branched and cyclic saturated hydrocarbons :

***n*-alkanes**

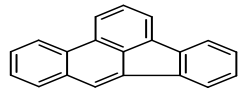
Hopanes



Steranes



PAHs



GC/MS analysis

Emission factors, annual mass releases

Door fugitive emissions in other European coke plants

	Annual mass releases (kg / year)	**Emission factors** (mg / t of coke)	Klein, 1990 (mg / t of coke)	**ERAMAC, 2006 European coke plant** (mg / t of coke)	Eisenhut, 1990 (mg / t of coke)
Total PAHs **Range** **Mean**	**1338 - 2731** **1580**	**2247 - 4585** **2653**	**83** (6 m door, new plant) **28** (7 m door, new plant) **3760** (4,5 m doors ; 20 to 30 years old plant)	**5400**	**9** (new plant) **3709** (20 to 30 years old plant)
B[a]P **Range** **Mean**	**6.6 - 114** **59**	**11 - 190** **100**	**10** (6 m door, new plant) **2.7** (7 m door, new plant) **180** (4,5 m doors ; 20 to 30 years old plant)	**90**	**56** (Rigid hammer knife sealing)

- *Klein, F, 1990. Recherche communautaire sur la pollution par les HAPs en cokerie Information days organised by the commission of the European communities.*
- *Eisenhut, 1990. Coking plant environment in West Germany. Coke making International, Vol 1, 74 - 77.*

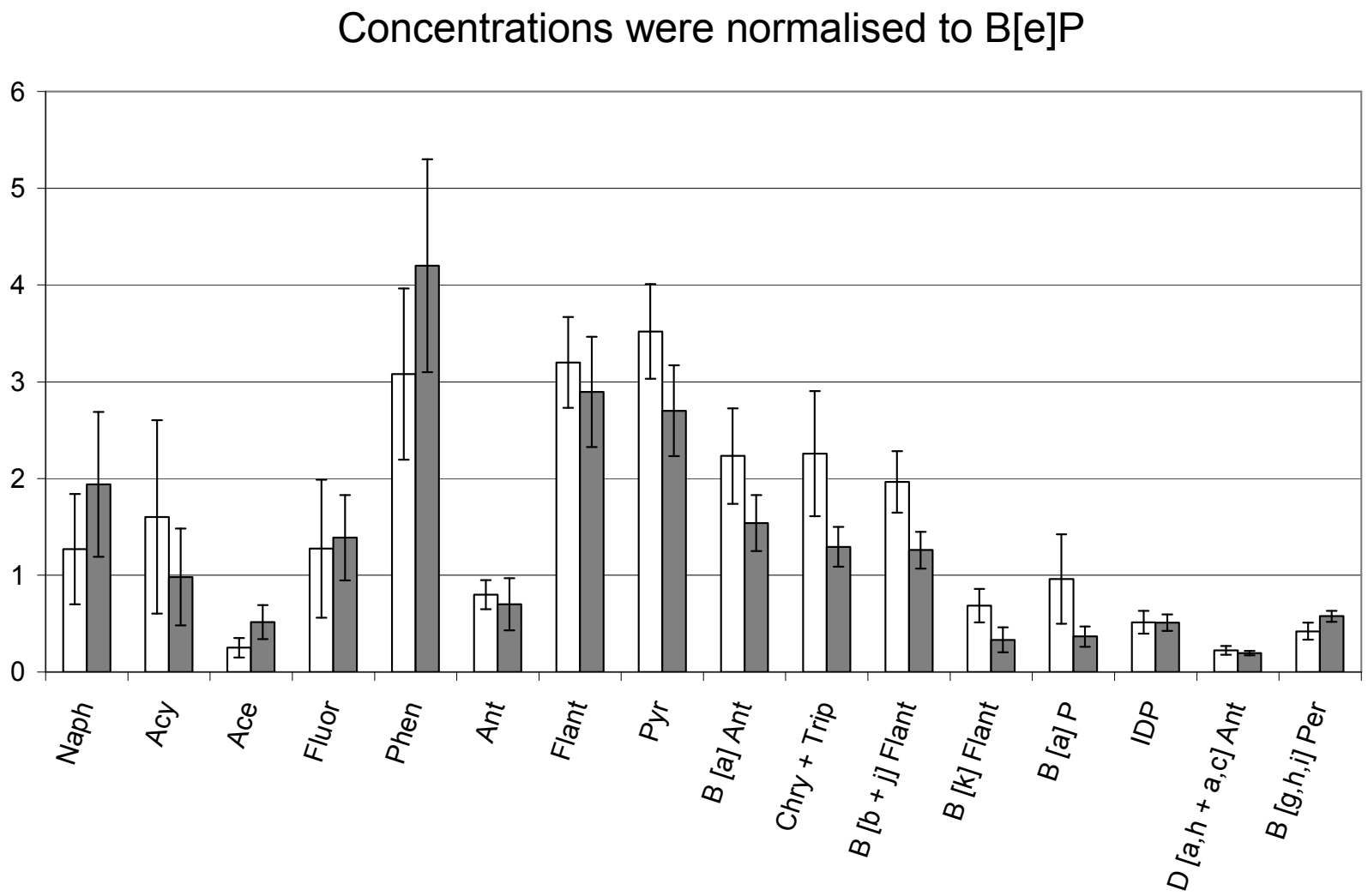
B[a]P emissions inventory for sintering

Typical UK sinter production per plant : ca. 4,5 million tonnes per annum
Typical stack emission flow rate : ca. 300 Nm^3 / s

Sinter Plant	A	B	C
Mean stack emission concentration (µg / Nm^3)	2.5 (n = 77)	1.1 (n = 89)	1.8 (n = 24)
Estimated annual mass releases (kg / annum) Mean	25	11	18
Emission factors (mg / t sinter) Mean	4.5	4.3	2.4

PAH emission profiles

Coke oven fugitive door vs. sinter plant main stack emissions

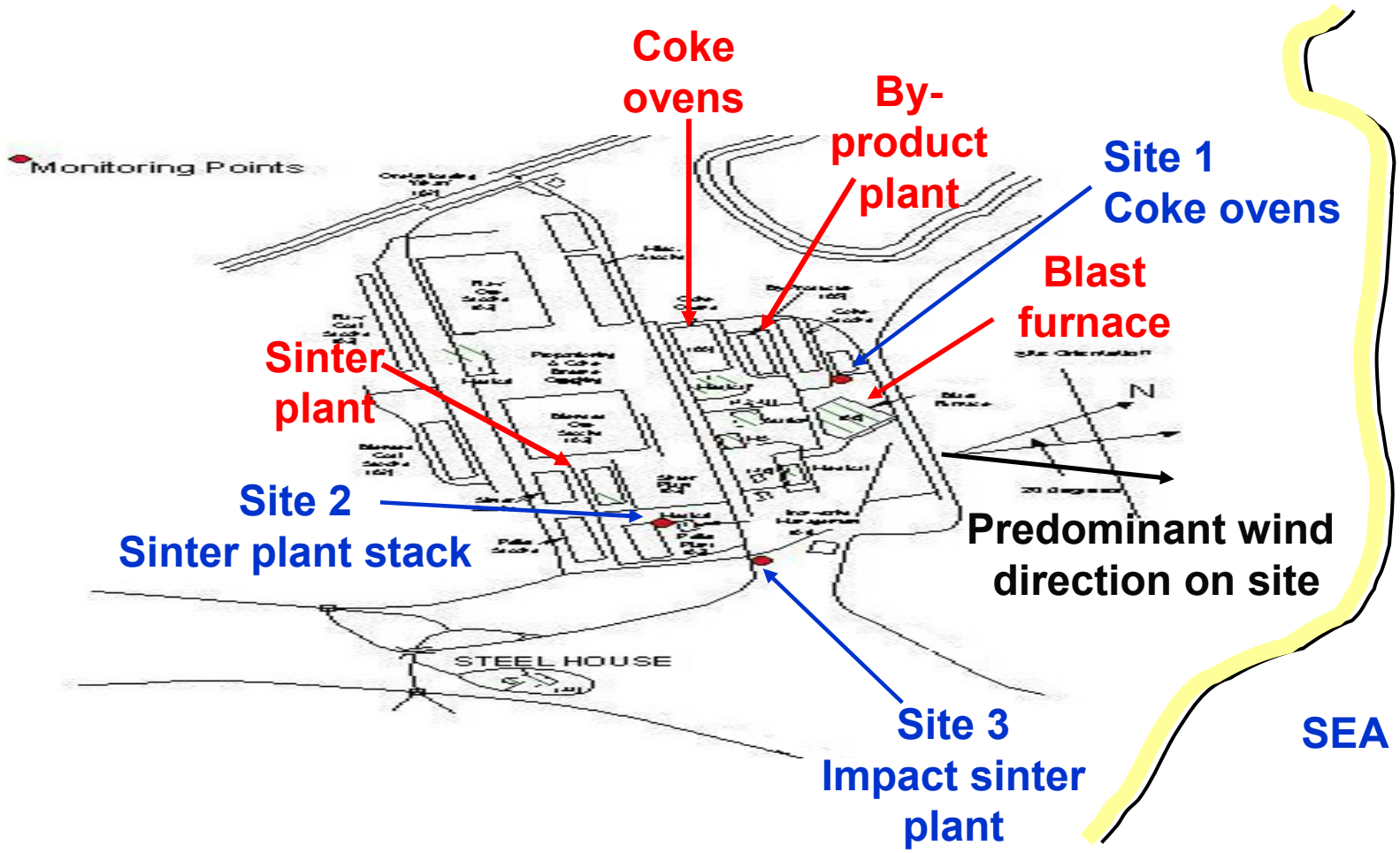


Ambient air studies

- ***PAH monitoring campaign at a Corus Steelworks***

PAH ambient air monitoring

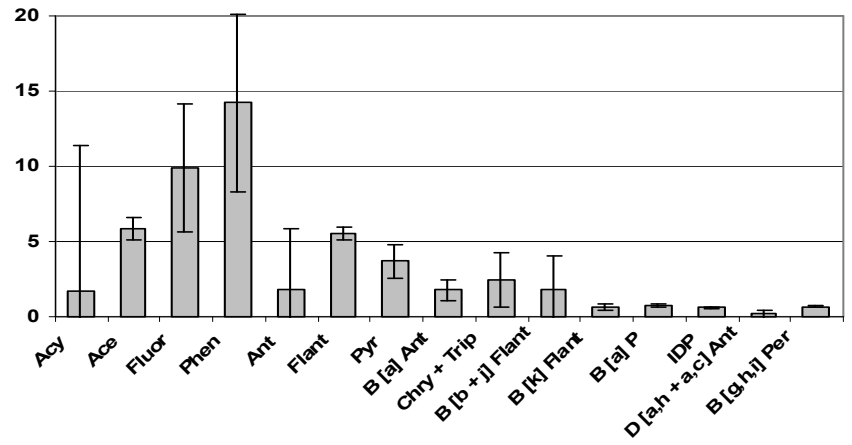
28-day sampling campaign at a Corus Steelworks



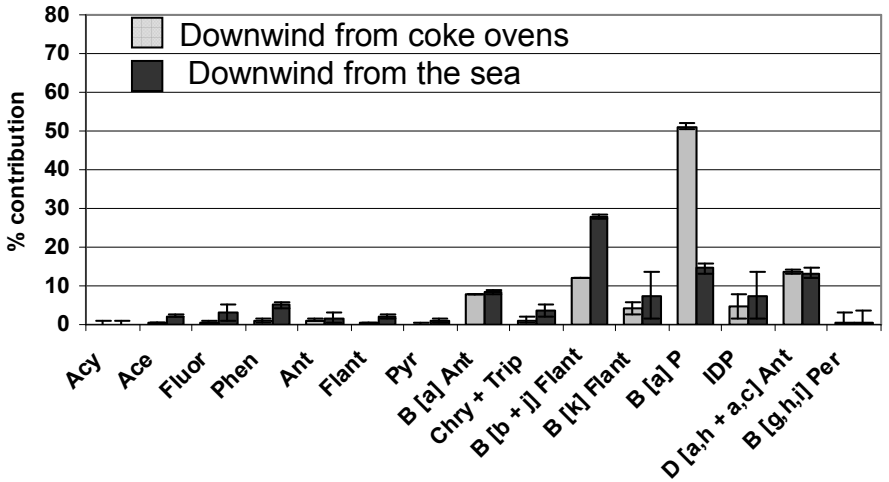
- Samples were collected using High volume Samplers (0.2 m^3/min ; 24 h)
- Weather data

PAH ambient air profiles downwind from the sinter plant

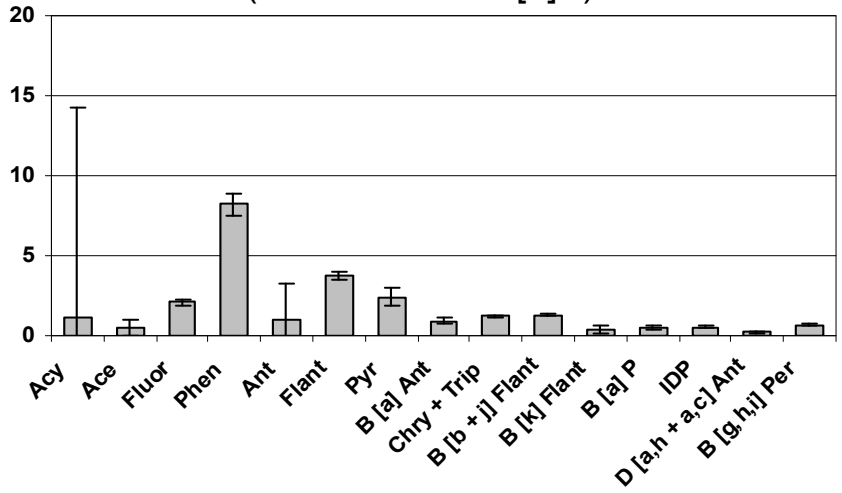
Sampling site downwind from the sinter plant
PAH ambient air profile



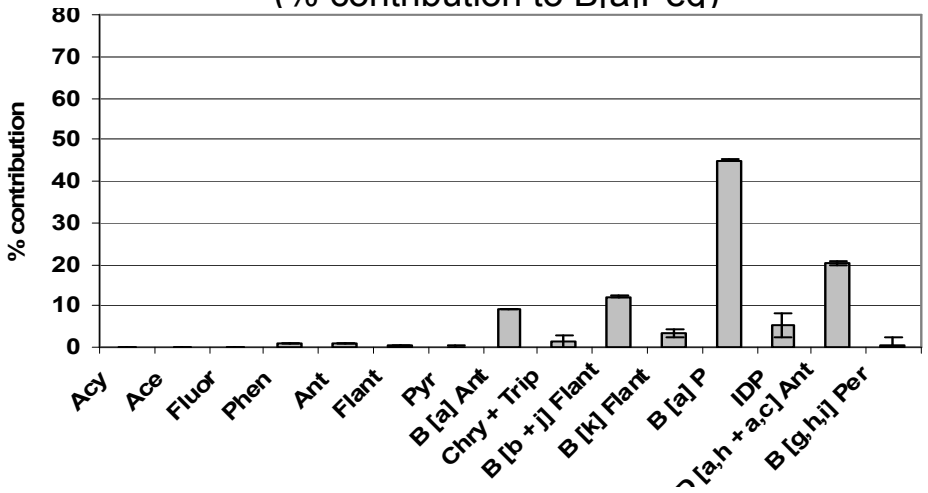
Sampling site downwind from the sinter plant
PAH ambient air profile function of wind direction



Sinter plant emissions – PAH profile
(normalised to B[e]P)

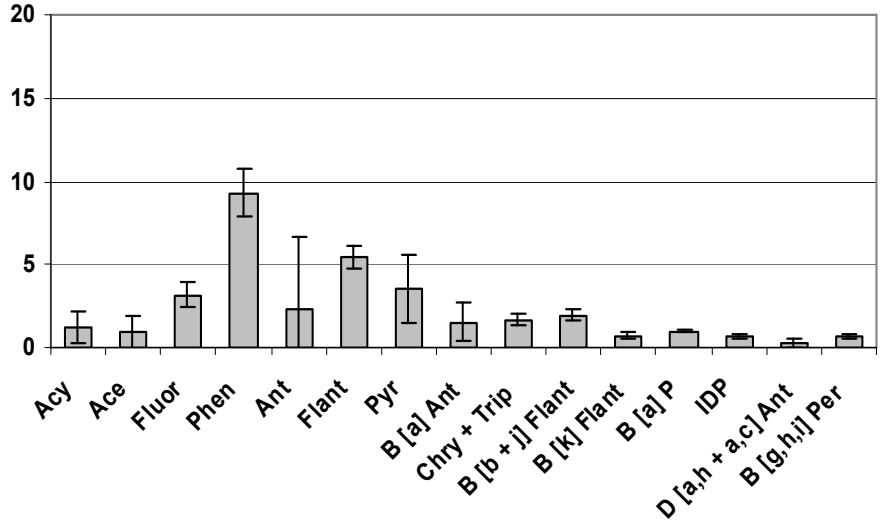


Sinter plant emissions – PAH profile
(% contribution to B[a]Peq)

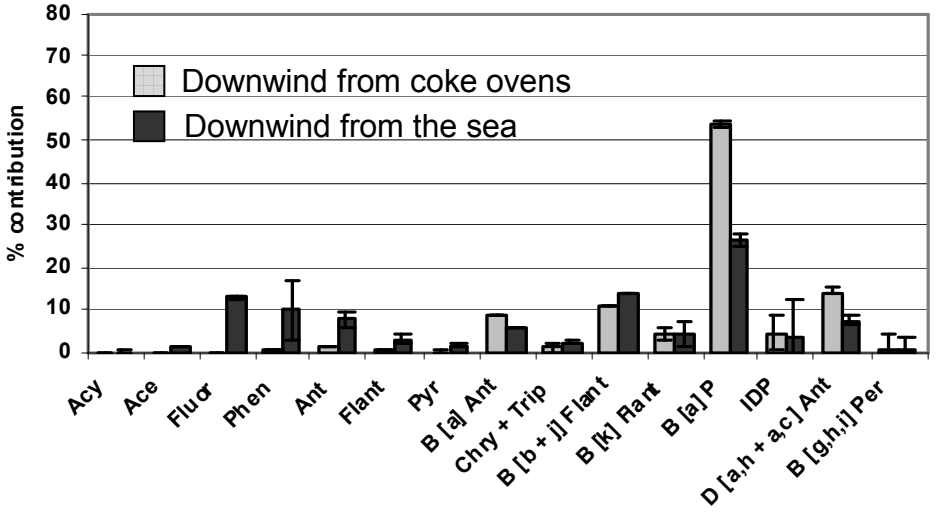


PAH ambient air profiles downwind from the coke ovens

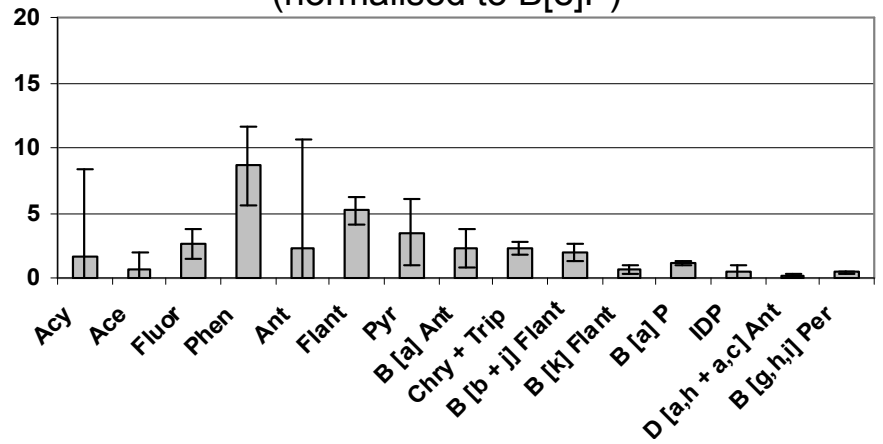
Sampling site downwind from the coke ovens
PAH ambient air profile



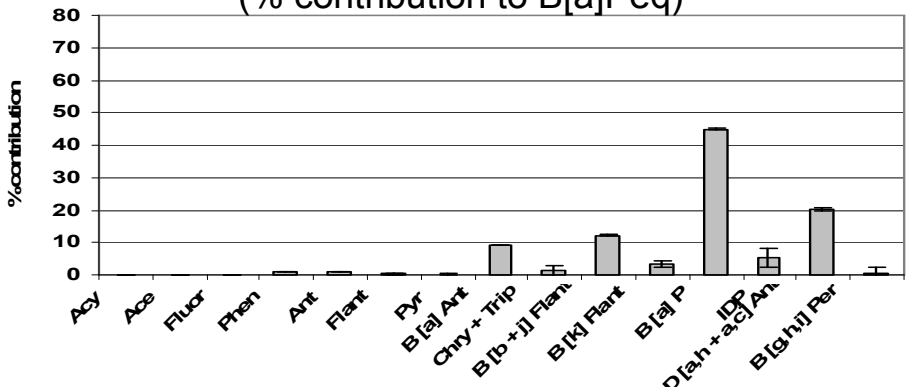
Sampling site downwind from the coke ovens
PAH ambient air profile function of wind direction



Coke oven fugitive emissions – PAH profile
(normalised to B[e]P)



Coke oven fugitive emissions – PAH profile
(% contribution to B[a]Peq)



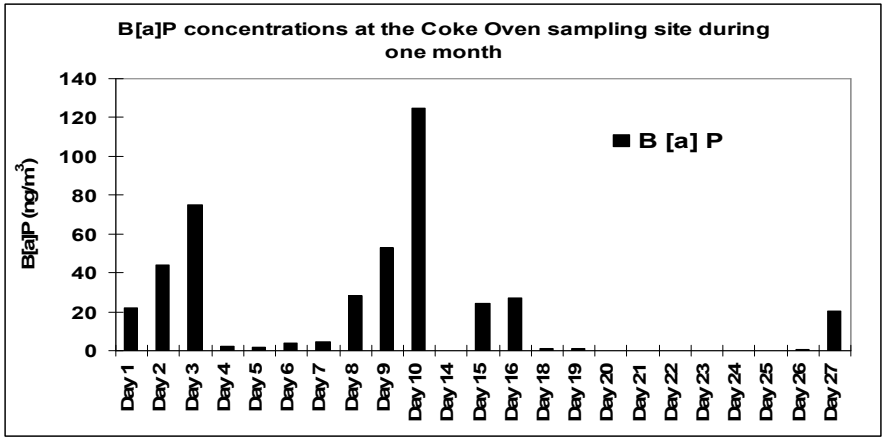
PAH ambient air monitoring

Evolution of B[a]P concentrations

Coke ovens

B[a]P mean (1 month) = 19 ng / m^3

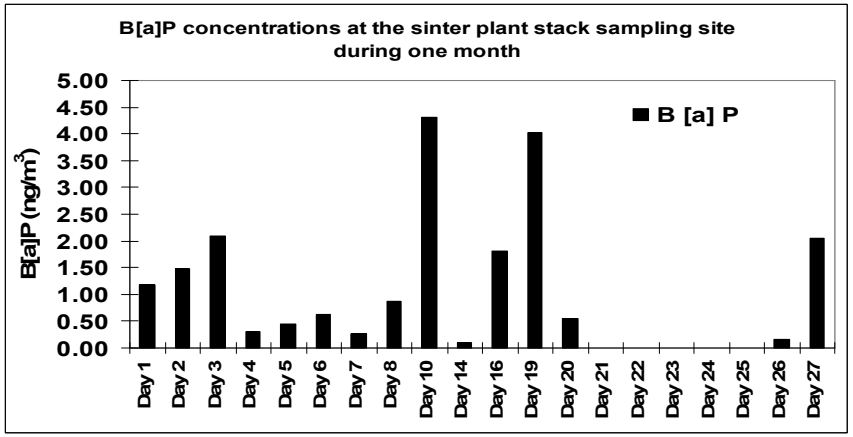
Range = 0.05 to 125 ng / m^3



Sinter plant stack

B[a]P mean (1 month) = 1.02 ng / m^3

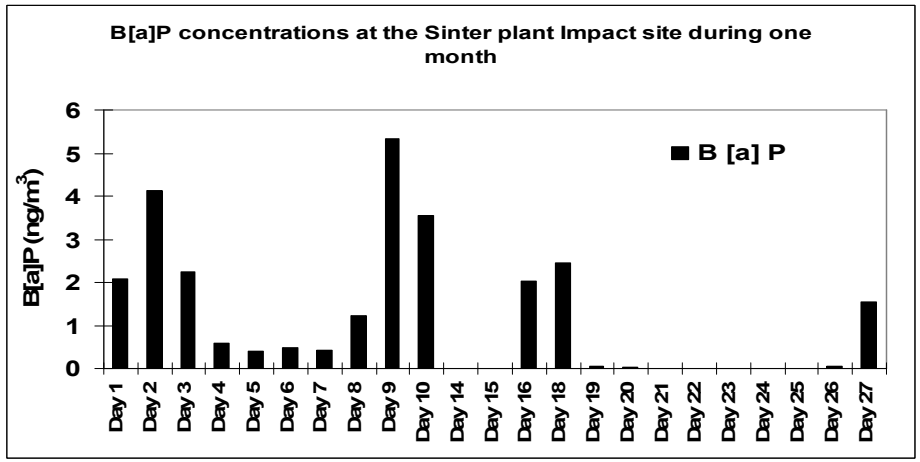
Range = 0.02 to 4.3 ng / m^3



Impact sinter plant

B[a]P mean (1 month) = 1.2 ng / m^3

Range = 0.03 to 5.3 ng / m^3



Conclusions

- Emissions inventory for coke making operations by Corus showed that the main source of PAHs (B[a]P) was associated with fugitive emissions from coke oven doors.

  Door emissions (59 kg / year) > underfiring emissions (0.273 kg / year) > lid emissions (0.08 kg / year)

- Emissions inventory for the three UK sinter plants operated by Corus showed that the B[a]P releases from UK sinter plants were significantly lower than the releases from cokemaking operations.

- A comparative study was carried out between the PAH profiles from iron ore sintering emissions and fugitive door emissions in cokemaking. It showed that there were very little differences between both PAH profiles.

- An ambient air monitoring campaign was carried out at a Corus steelworks to study the impact of cokemaking and sintering operations in the local ambient air quality. Running monthly concentrations of B[a]P were typically above the air quality standard limits in the direct vicinity of the coke ovens, but within the limits downwind to the sinter plant. At this site, the nearest housing is situated upwind from the coke ovens and more than 1 km away from the batteries, so the impact of coke oven batteries upon the ambient air quality is expected to be low.

Acknowledgements

- European commission : Research Programme of the Research Fund for Coal and Steel (Project ERAMAC : Emissions Reduction through Analysis, Modelling and Control)
- Dave Darlow & Tim Evans (Birmingham University)
- Amanda Horne, Steve Baker & Neil Schofield (Corus RD&T)