

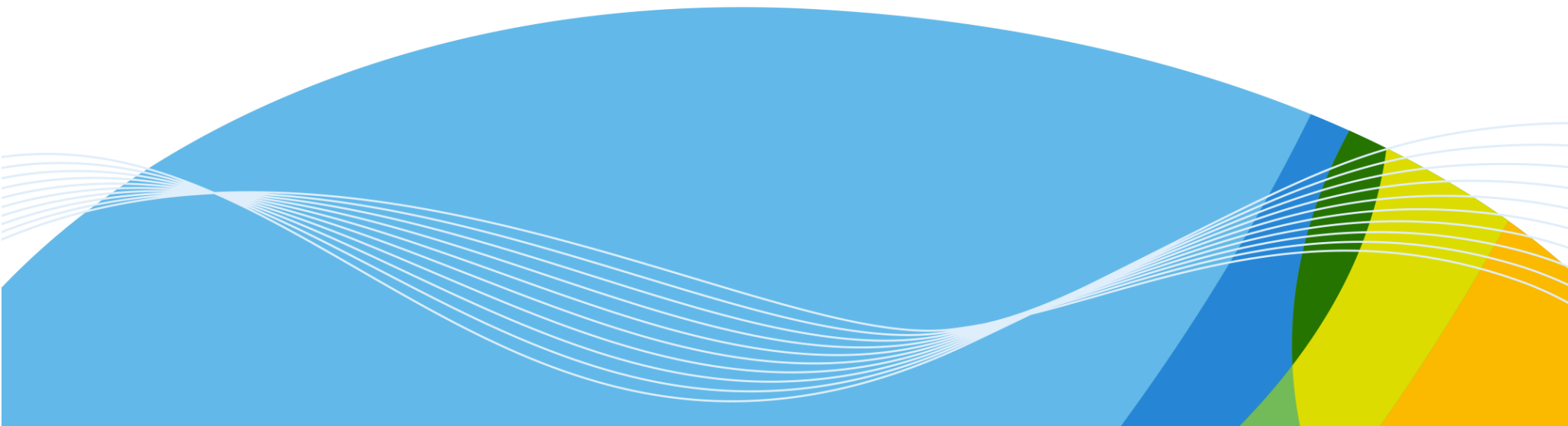


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PAH pitoisuudet Suomessa ja Raahen PAH pitoisuudet - Miten tulkitseen tuloksia?

Mika Vestenius, Ilmatieteen laitos

Ilmanlaadun mittaajatapaaminen 10-11.4.2018





sisälllys

- Yleistä PAHeista ja bentso(a)pyreenistä
- PM10-bentso(a)pyreenimittaukset Suomessa
- b(a)p
 - tausta-alueilla
 - Helsingissä
 - Euroopassa



Polysykliset aromaattiset hiilivedyt (PAH-yhdisteet)

- Karsinogeenisia yhdisteitä
- kaikkialla maapallolla
- Muodostuvat orgaanisen aineen epätäydellisen palamisen seurauksena
- Antropogeenisia lähteitä: Liikenne, fossiilisten polttoaineiden poltto energiantuotannossa, biomassan poltto, teollisuus...
- Luonnollisia lähteitä: metsäpalot, tulivuoren purkaukset





Bentso(a)pyreeni

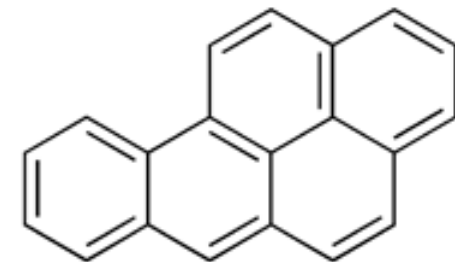
-EU-direktiivi edellyttää jäsenmaiden seuraavan PAH-yhdisteiden pitoisuuksia Ilmassa PM10-fraktiosta.

-*Bentso(a)pyreeni (BaP)* on PAH-yhdisteiden aiheuttaman syöpäriskin merkkiaine, jolle EU on asettanut raja-arvot.

Bentso(a)pyreenin lisäksi täytyy seurata myös bentso(a)antraseenin, bentso(b)fluoranteenin, bentso(j) fluoranteenin, bentso(k) fluoranteenin, indeno(1,2,3-cd)pyreenin ja dibentso(a,h)antraseenin konsentraatiota ilmassa.

Taulukko 1: bentso(a)pyreenin raja-arvot aerosolissa tausta-alueilla

Bentso(a)pyreeni	ng/m ³
Raja-arvo	1
Ylempi arviointikynnys	0,6
Alempi arviointikynnys	0,4



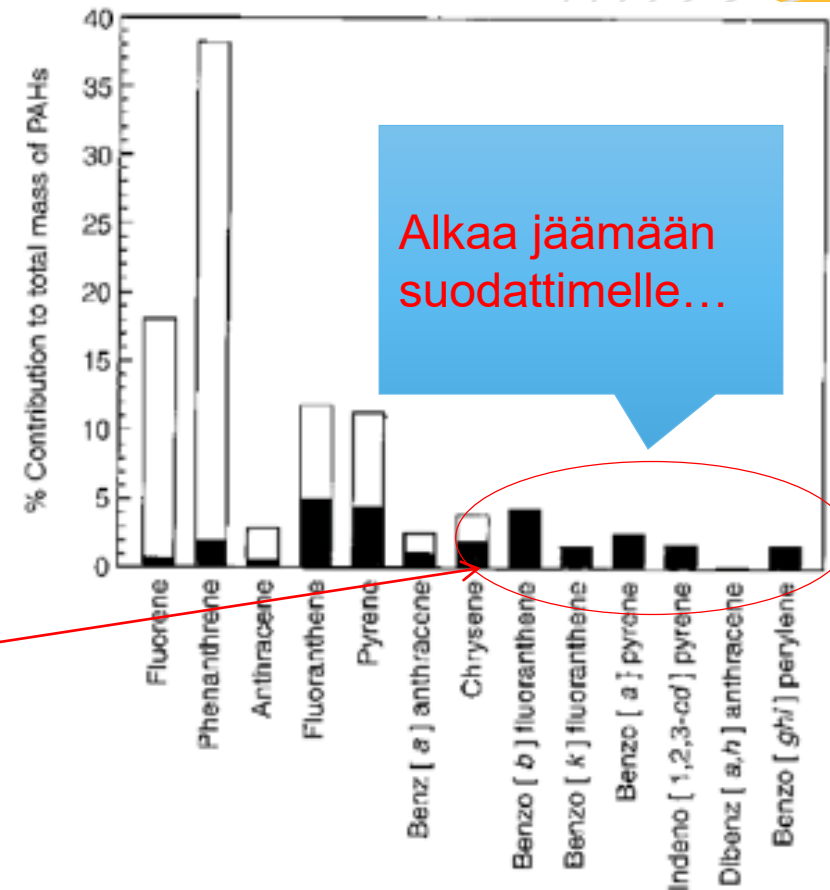


PAHien kaasu-hiukkasjakaumasta

TABLE 13.18 Partitioning Estimation for Selected PAHs Based on Data Collected in Osaka, Japan, Assuming a Total Aerosol Mass of $100 \mu\text{g m}^{-3}$

Compound	$\log p^\circ$ (Torr) at 20°C	A_p (K)	$K_p(20^\circ\text{C})$	c_{aer}/c_g
Fluorene	-2.72	—	4.8×10^{-6}	0.00048
Phenanthrene	-3.50	4124	3.1×10^{-5}	0.0031
Anthracene	-3.53	4124	3.3×10^{-5}	0.0033
Fluoranthene	-4.54	4412	3.6×10^{-4}	0.0036
Pyrene	-4.73	4451	5.6×10^{-4}	0.056
Benzo[a]fluorene	-5.24	4549	1.9×10^{-3}	0.19
Benzo[b]fluorene	-5.22	4549	1.8×10^{-3}	0.18
Benz[a]anthracene	-6.02	4836	0.012	1.2
Chrysene	-6.06	4836	0.013	1.3
Triphenylene	-6.06	4836	0.013	1.3
Benzo[b]fluoranthene	-7.12	5180	0.16	16
Benzo[k]fluoranthene	-7.13	5180	0.17	17
Benzo[a]pyrene	-7.33	5301	0.27	27
Benzo[e]pyrene	-7.37	5301	0.29	29

Source: Pankow and Bidleman (1992).



Average mass percent contributions (gas + particle phase of 13 PAHs collected in urban air from Chicago in Feb/March 1995. (From Harner and Bidleman, 1998)

lähde: Seinfeld and Pandis, Atmospheric Chemistry and Physics (1998)



Entäpä OXY/NITRO-PAHit?

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Sources and atmospheric chemistry of oxy- and nitro-PAHs in the ambient air of Grenoble (France)



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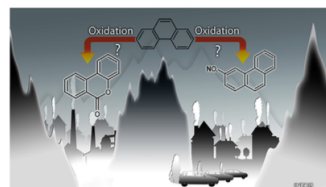
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HIGHLIGHTS

- PACs measured over a year together with an extended aerosol chemical characterization.
- Cold period was affected by primary emissions especially from residential heating.
- The highest (2 + 3)-NFlt/1-NP ratio was surprisingly observed during the winter period.
- Different secondary processes involved during the severe PM pollution events observed.
- Marker of PAH oxidation identified based on field observations and literature data.

GRAPHICAL ABSTRACT



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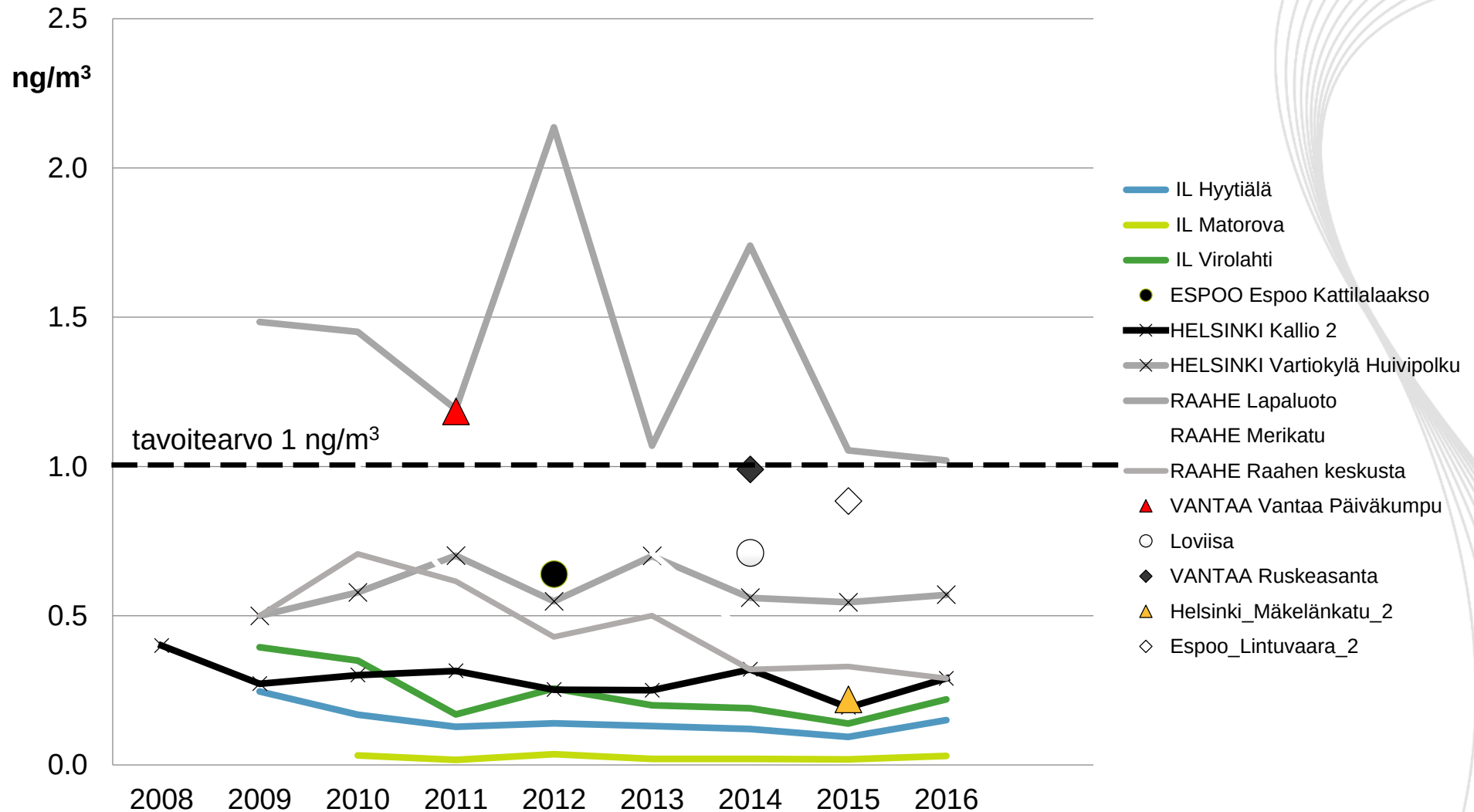
Reactivity

ABSTRACT

Total individual concentrations (in both gaseous and particulate phases) of 80 polycyclic aromatic compounds (PACs) including 32 nitro-PAHs, 27 oxy-PAHs (polycyclic aromatic hydrocarbons) and 21 parent PAHs have been investigated over a year in the ambient air of Grenoble (France) together with an extended aerosol chemical characterization. The results indicated that their concentrations were strongly affected by primary emissions in cold period, especially from residential heating (i.e. biomass burning). Besides, secondary processes occurred in summer but also in cold period under specific conditions such as during long thermal inversion layer periods and severe PM pollution events. Different secondary processes were involved during both PM pollution events observed in March–April and in December 2013. During the first one, long range transport of air masses, nitrate chemistry and secondary nitro-PAH formation seemed linked. During the second one, the accumulation of primary pollutants over several consecutive days enhanced secondary chemical processes notably highlighted by the dramatic increase of oxy-PAH concentrations. The study of the time trends of ratios of individual nitro- or oxy-PAHs to parent PAHs, in combination with key primary or secondary aerosol species and literature data, allowed the identification of potential molecular markers of PAH oxidation. Finally, 6H-dibenzo[b,d]pyran-6-one, biphenyl-2,2'-dicarboxaldehyde and 3-nitrophenanthrene have been selected to be the best candidates as markers of PAH oxidation processes in ambient air.

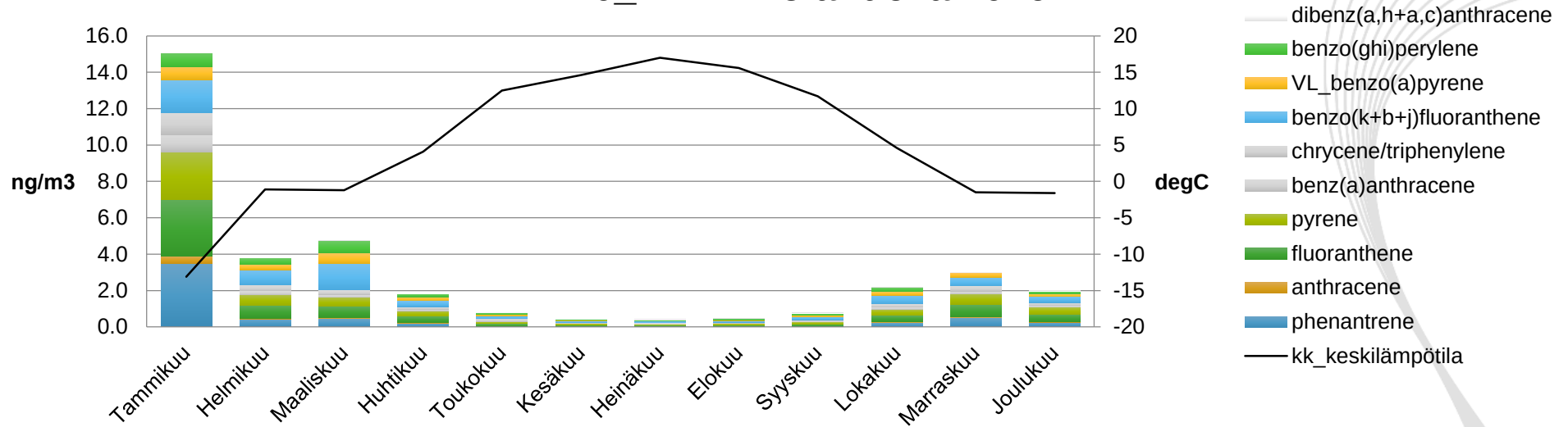
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PM10-bentso(a)pyreenimittaukset Suomessa v.2008-2016

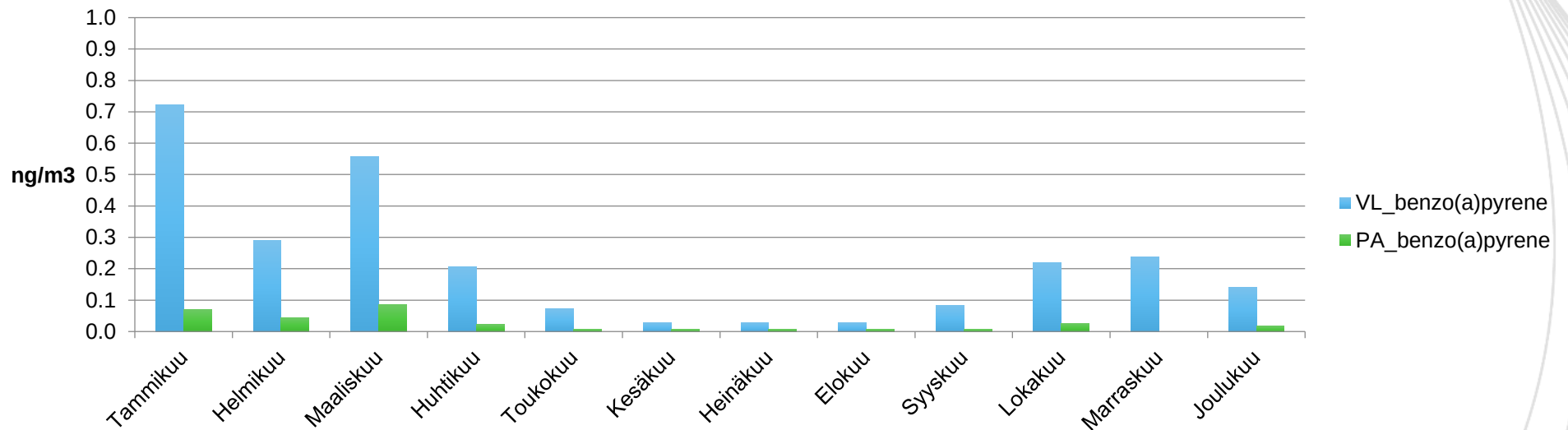




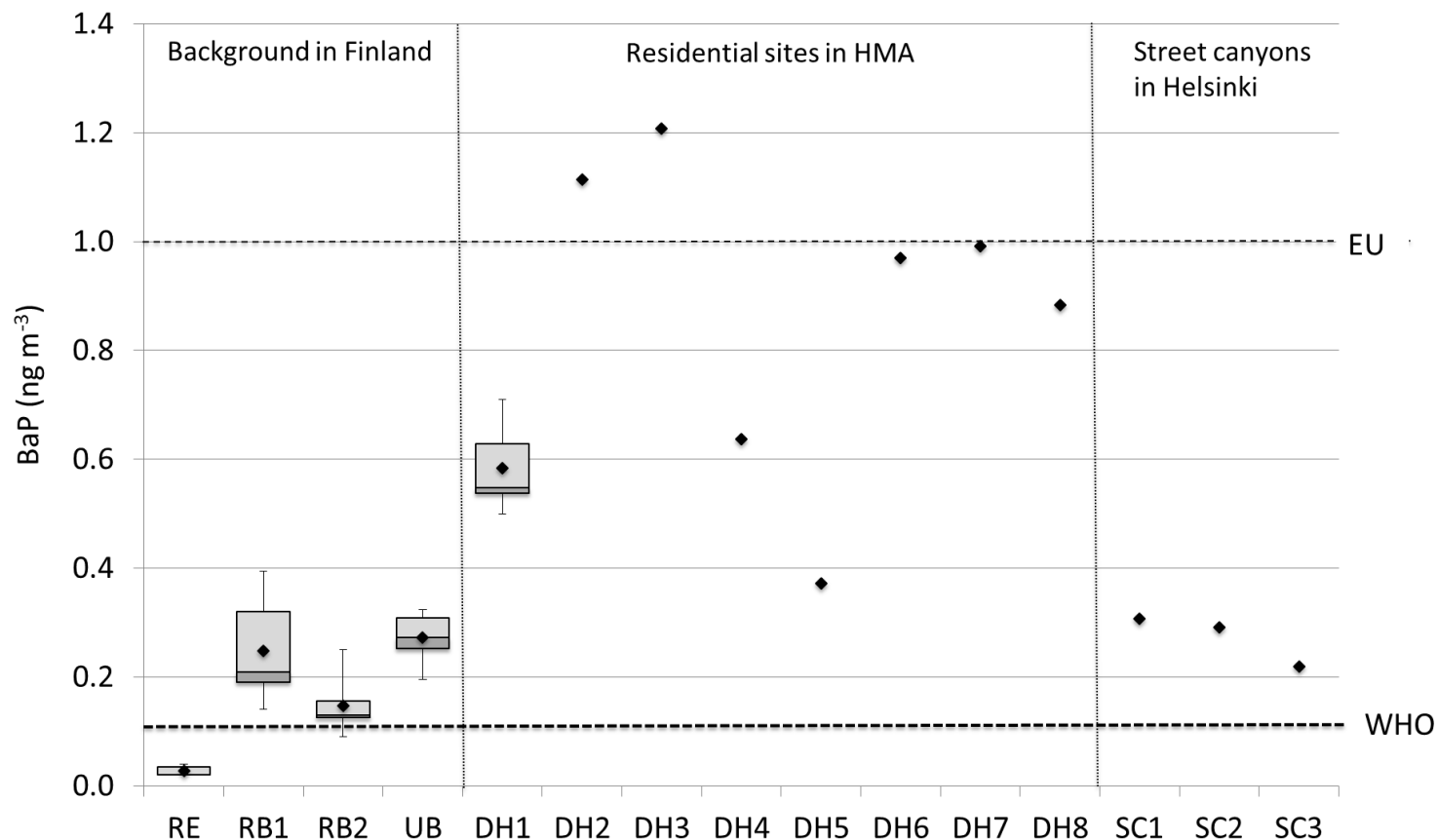
PM10_PAH Virolahdella 2016



PM10_b(a)p Virolahdella ja Pallaksella 2016



Measured annual means of BaP concentrations (ng m⁻³) at different stations in Finland in 2007-2015



Classification of site	Code	Name of site	Sampling year(s)	BaP (ng m ⁻³)	PM _{2.5} (μg m ⁻³)	NO _x (μg m ⁻³)
Detached-house area 1	DH1	Vartiokylä	2009–2015	0.6 (0.08)	7.5	21
Detached-house area 2	DH2	Itä-Hakkila	2008	1.1	–	–
Detached-house area 3	DH3	Päiväkumpu	2011	1.2	10.4	21
Detached-house area 4	DH4	Kattilalaakso	2012	0.6	8.2	18
Detached-house area 5	DH5	Kauniainen	2013	0.4	7.1	13
Detached-house area 6	DH6	Tapanila	2013	1.0	8.8	22
Detached-house area 7	DH7	Ruskeasanta	2014	1.0	10.8	19
Detached-house area 8	DH8	Lintuvaara	2015	0.9	7.1	14
Street canyon 1	SC1	Unioninkatu	2007	0.3	–	76
Street canyon 2	SC2	Töölöntulli	2010	0.3	13.0	166
Street canyon 3	SC3	Mäkeläkatu	2015	0.2	8.0	108
Urban background	UB	Kallio	2007–2015	0.3 (0.04)	7.8	28
Rural background 1	RB1	Virolahti	2007–2015	0.2 (0.1)	6.1	5.1
Rural background 2	RB2	Hyytiälä	2009–2015	0.1 (0.05)	–	2.2
Remote background	RE	Pallas	2009–2015	0.03 (0.01)	3.7*	1.0

* Only for years 2011, 2012, 2014 and 2015.

Hellén, H., Kangas, L., Kousa, A., Vestenius, M., Teinilä, K., Karppinen, A., Kukkonen, J., and Niemi, J. V., 2017. Evaluation of the impact of wood combustion on benzo[a]pyrene (BaP) concentrations; ambient measurements and dispersion modeling in Helsinki, Finland, Atmos. Chem. Phys., 17, 3475-3487, doi:10.5194/acp-17-3475-2017.



Mitatut b(a)p kuukausikeskiarvot ja lauantaipäivien b(a)p keskiarvot Helsingin Tapanilassa vuonna 2013

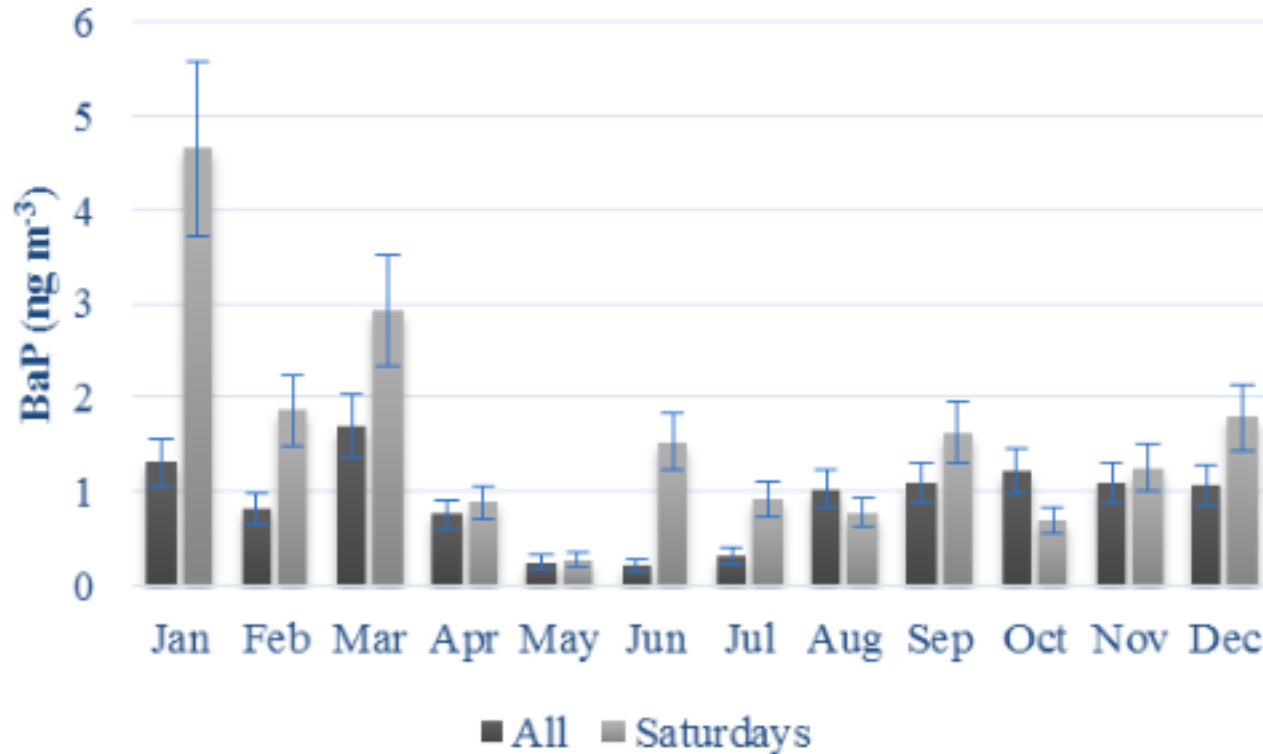
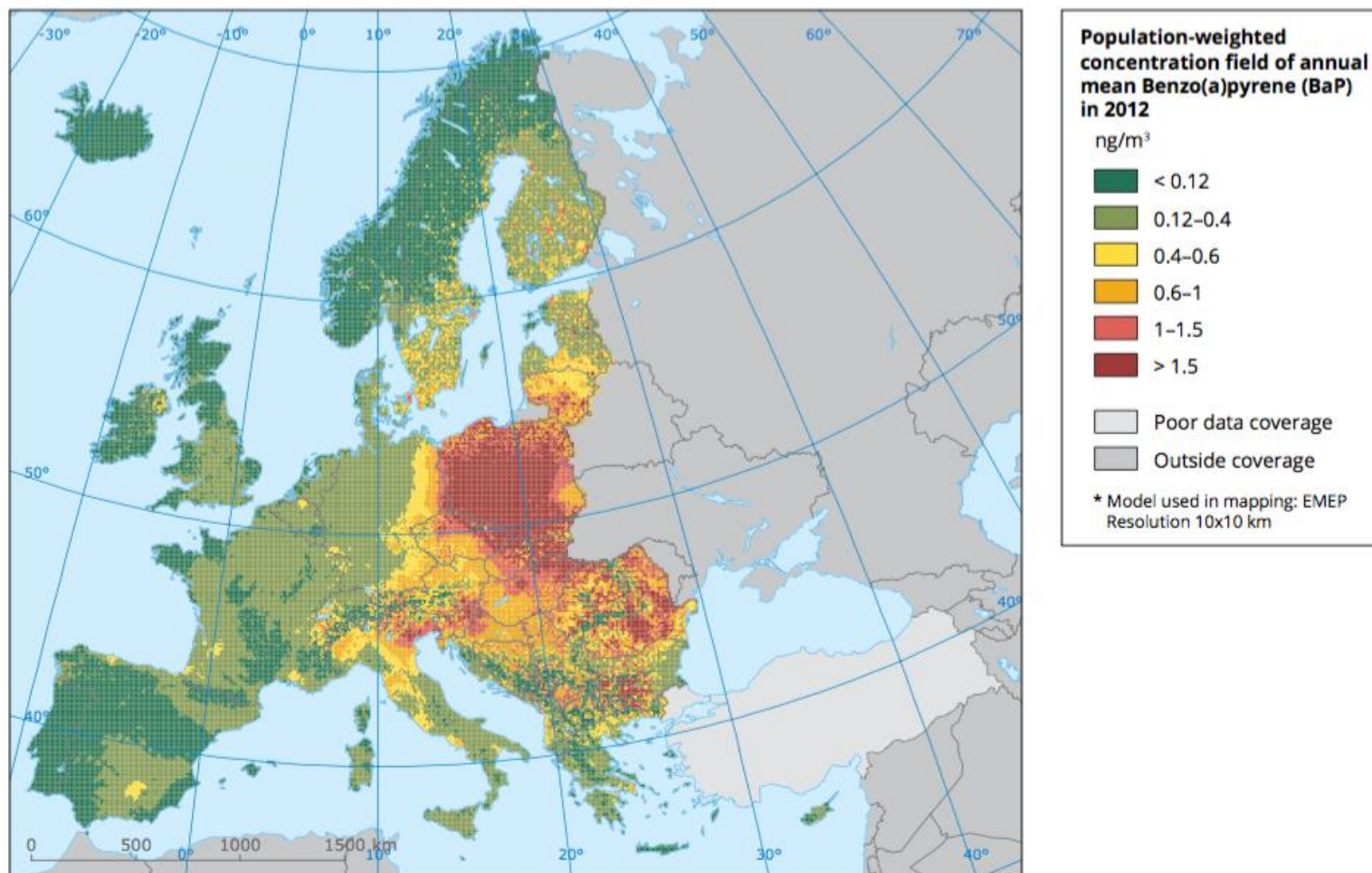


Figure 5. Monthly mean BaP concentrations together with monthly mean concentrations on Saturdays at the detached-house area around the measurement site DH6 in Helsinki in 2013. Error bars show the measurement uncertainty.

Hellén, H., Kangas, L., Kousa, A., Vestenius, M., Teinilä, K., Karppinen, A., Kukkonen, J., and Niemi, J. V., 2017. Evaluation of the impact of wood combustion on benzo[a]pyrene (BaP) concentrations; ambient measurements and dispersion modeling in Helsinki, Finland, Atmos. Chem. Phys., 17, 3475-3487, doi:10.5194/acp-17-3475-2017.



Map 10.1 Population-weighted concentration field of annual mean BaP in 2012



Notes: Dark-green areas correspond to concentrations under the estimated reference level (0.12 ng/m³). Dark-red areas correspond to concentrations exceeding the 2004 AQ Directive target value of 1 ng/m³.

Source: ETC/ACM, 2015b.

Year: 2

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Air quality statistics

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Air quality statistics

Year: **2016** | Pollutant: **Benzo(a)pyrene (BaP)** | Statistics: **Annual mean**

Year

2016

Pollutant

Benzo(a)pyrene (BaP)

Statistics

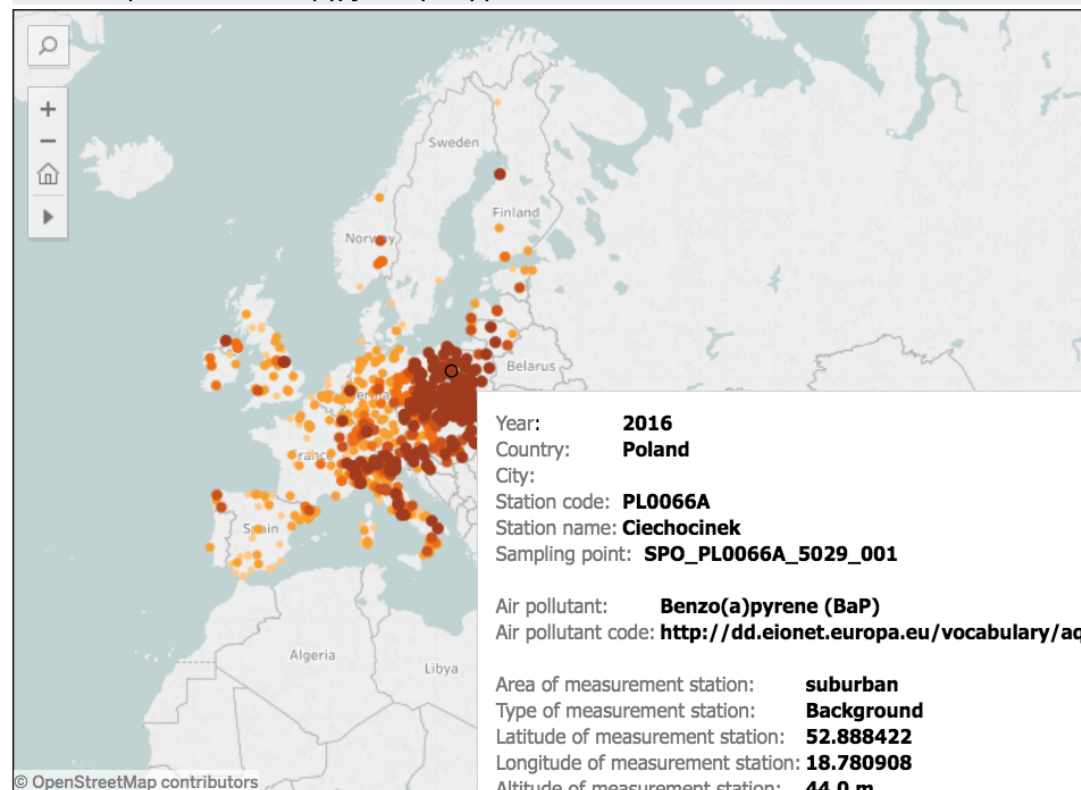
Annual mean

Country

(All)

Type of station

(All)



Year: **2016**
Country: **Poland**
City:
Station code: **PL0066A**
Station name: **Ciechocinek**
Sampling point: **SPO_PL0066A_5029_001**

Air pollutant: **Benzo(a)pyrene (BaP)**
Air pollutant code: <http://dd.eionet.europa.eu/vocabulary/eq/pollutant/5029>

Area of measurement station: **suburban**
Type of measurement station: **Background**
Latitude of measurement station: **52.888422**
Longitude of measurement station: **18.780908**
Altitude of measurement station: **44.0 m**

Air pollution level: **3.56 ng/m3**
Data aggregation process: **Annual mean (P1Y)**

17.65

1.0 - ng/m3 .
0.6 - 1.0 ng/m3 .
0.4 - 0.6 ng/m3 .
0.1 - 0.4 ng/m3 .
0.0 - 0.1 ng/m3 .



Table ES.1 Percentage of the urban population in the EU-28 exposed to air pollutant concentrations above certain EU and WHO reference concentrations (2012–2014)

Pollutant	EU reference value ^(a)	Exposure estimate (%)	WHO AQG ^(a)	Exposure estimate (%)
PM _{2.5}	Year (25)	8–12	Year (10)	85–91
PM ₁₀	Day (50)	16–21	Year (20)	50–63
O ₃	8-hour (120)	8–17	8-hour (100)	96–98
NO ₂	Year (40)	7–9	Year (40)	7–9
BaP	Year (1)	20–24	Year (0.12) (RL)	88–91
SO ₂	Day (125)	< 1	Day (20)	35–49

Key:	< 5 %	5–50 %	50–75 %	> 75 %
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Notes: ^(a) In µg/m³; except BaP, in ng/m³.

The reference concentrations include EU limit or target values, WHO air-quality guidelines (AQGs) and estimated reference levels (RLs).

For some pollutants, EU legislation allows a limited number of exceedances. This aspect is considered in the compilation of exposure in relation to EU air-quality limit and target values.

The comparison is made for the most stringent EU limit or target values set for the protection of human health. For PM₁₀, the most stringent limit value is for 24-hour mean concentration, and for NO₂ it is the annual mean limit value.

The estimated exposure range refers to a recent 3-year period (2012–2014) and includes variations attributable to meteorology, as dispersion and atmospheric conditions differ from year to year.

As the WHO has not set AQGs for BaP, the reference level in the table was estimated assuming WHO unit risk for lung cancer for PAH mixtures, and an acceptable risk of additional lifetime cancer risk of approximately 1 in 100 000.

Sources: EEA, 2016f.



Kiitos!

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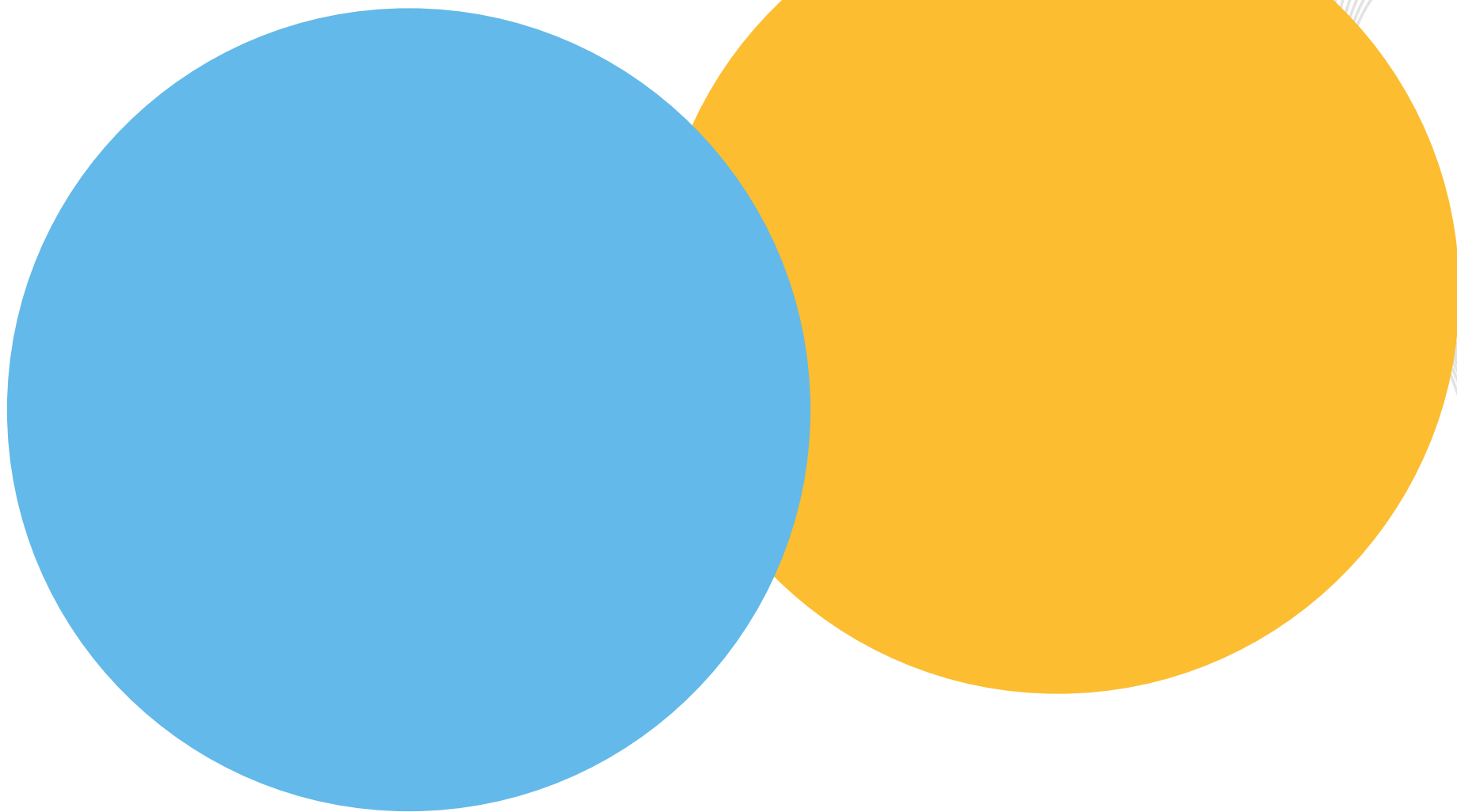




OXY/NITROPA Hs?

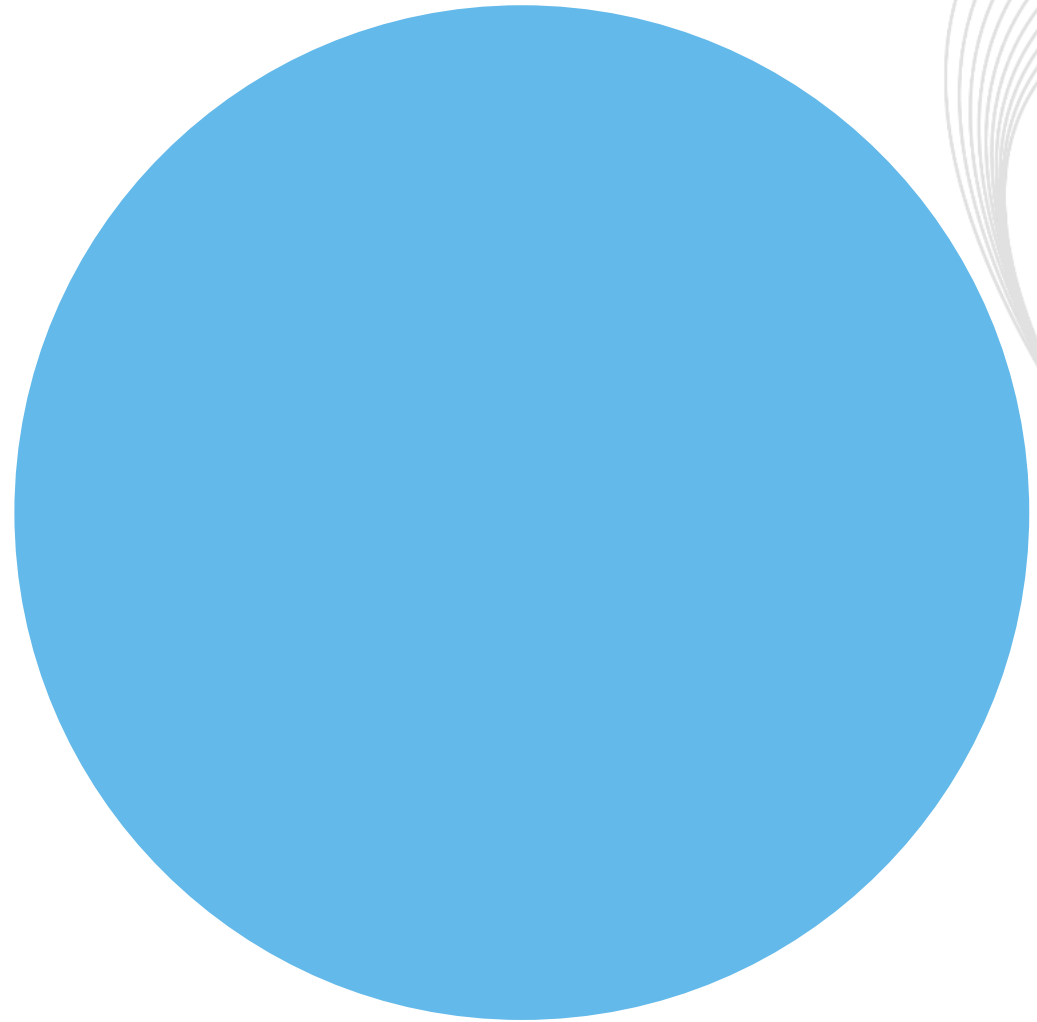




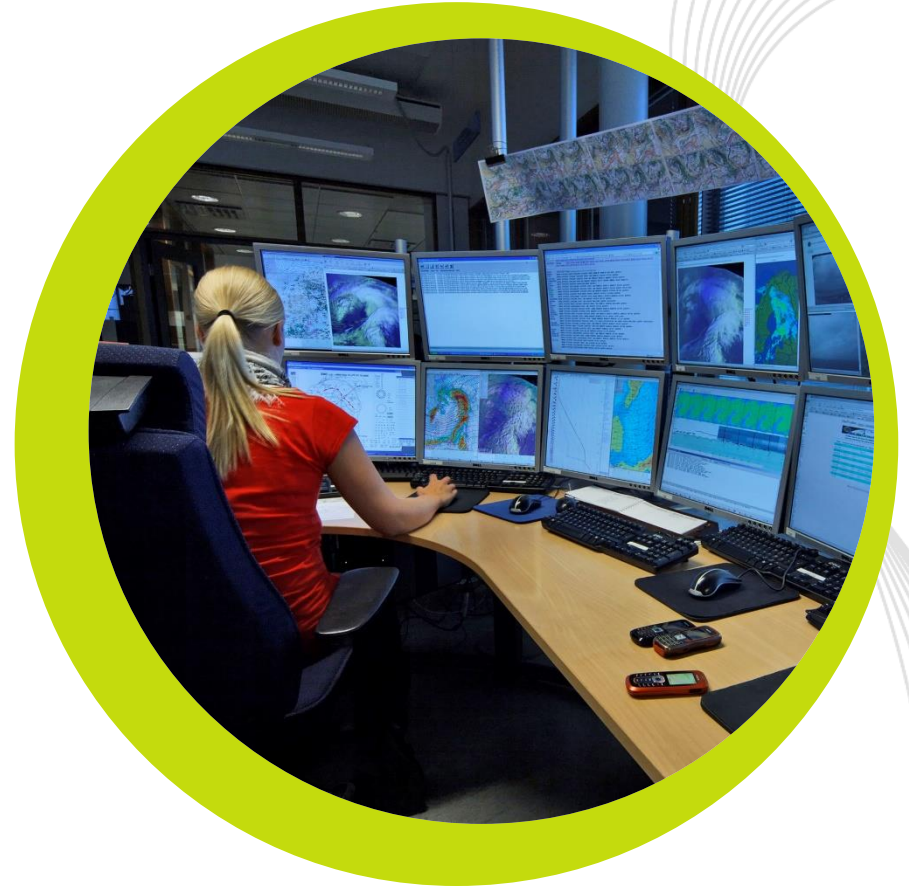














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