300 YEARS OF ORGANIC POLLUTION RECORDED IN AN URBAN SPELEOTHEM (PARIS, FRANCE)

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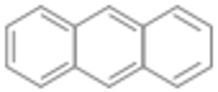
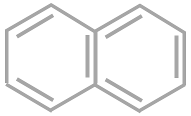
- Organic Pollution

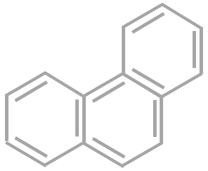
Polycyclic Aromatic Hydrocarbons (PAH)



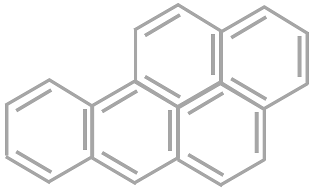
Anthracene
C4H10



Naphtalene
$CH_{10}H_8$



Phenanthrene
$CH_{14}H_{10}$



Benzo[a]pyrene
$CH_{20}H_{12}$

Toxicity

TOXIC FOR HUMAN AND ENVIRONMENT

- Mutagenic
- Carcinogenic
- Teratogenic

> over 100 different chemicals
> 16 PAH to the list of "priority pollutants" of the U.S – EPA

Persistent Organic Pollutants (POP)

Molecules composed of benzene aromatic rings, classified according to the number of rings :

- Light Molecular Weight: < 4 rings
- Heavy Molecular Weight : ≥ 4 rings

Mostly produced by **incomplete combustion** of organic matter

Sources

Forest fires

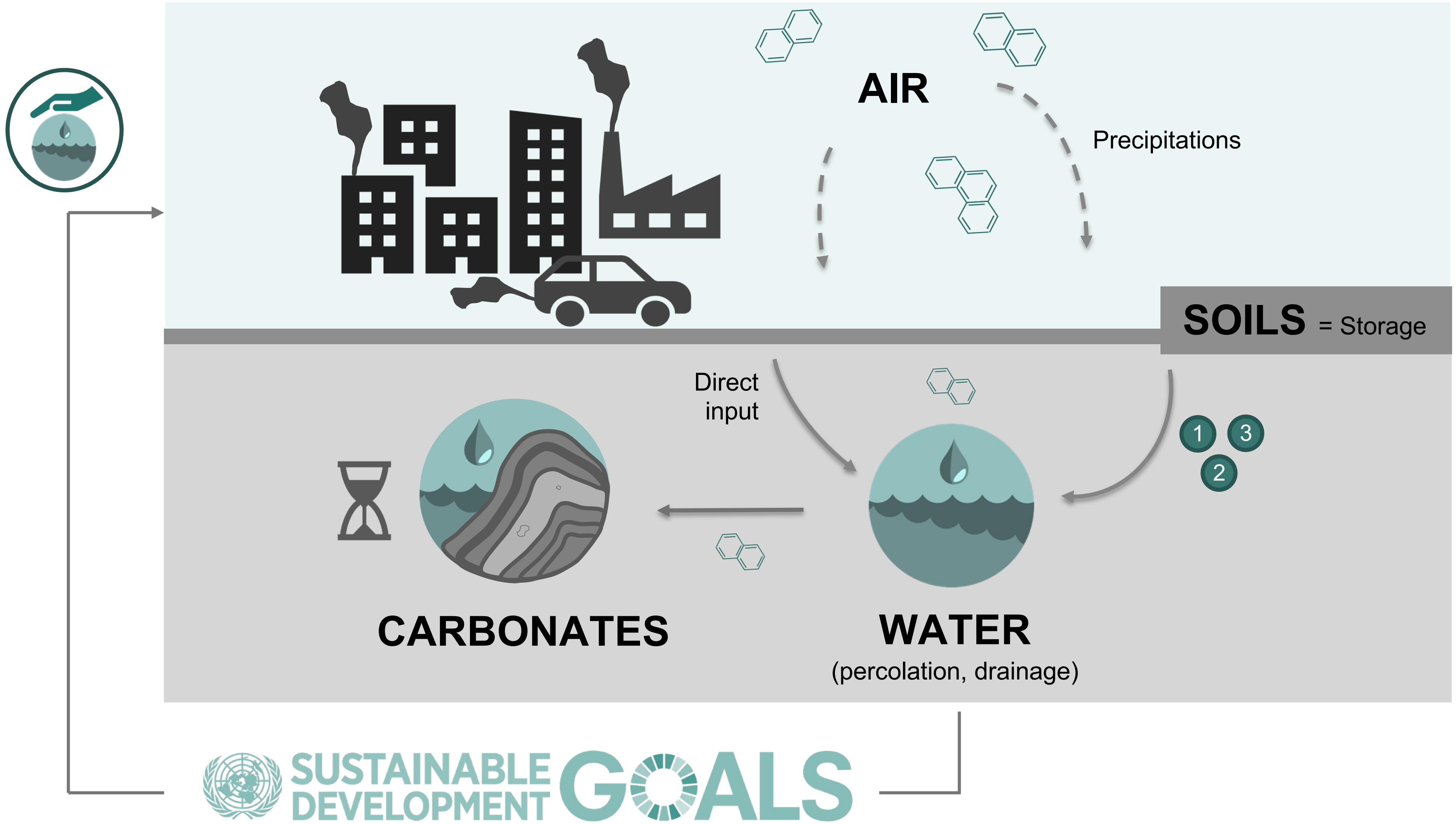
Volcanoes

Organic TRACER of anthropic activity

Traffic

Heating

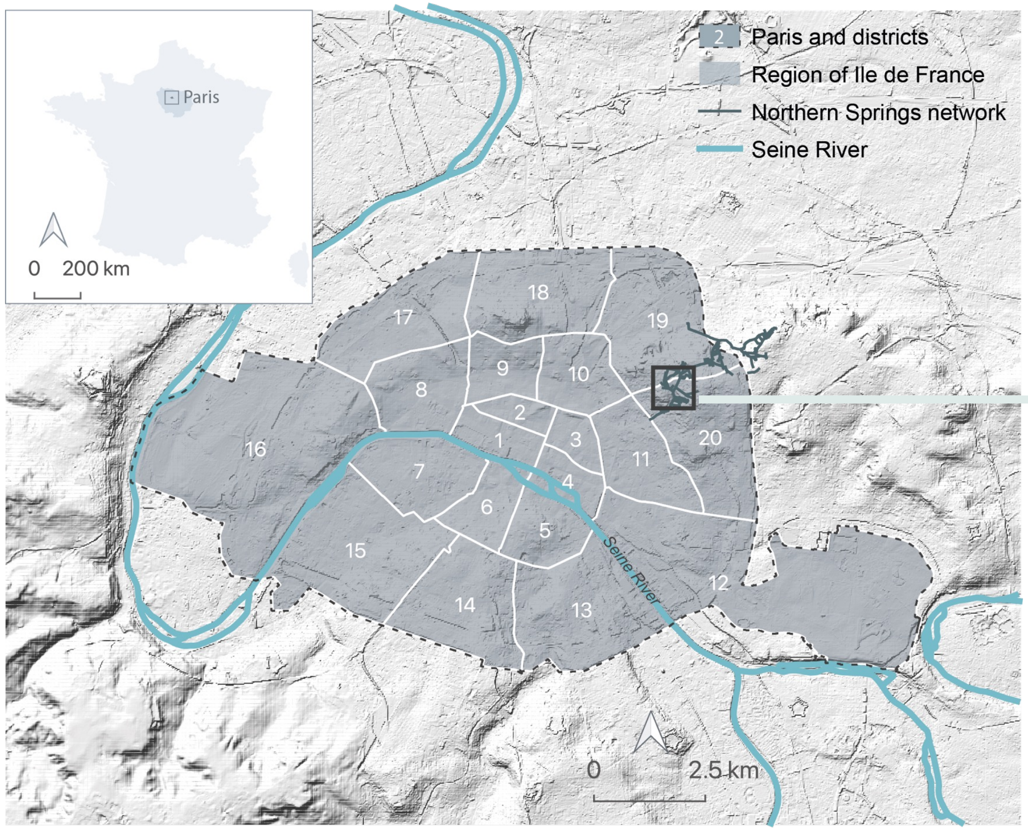
Industries



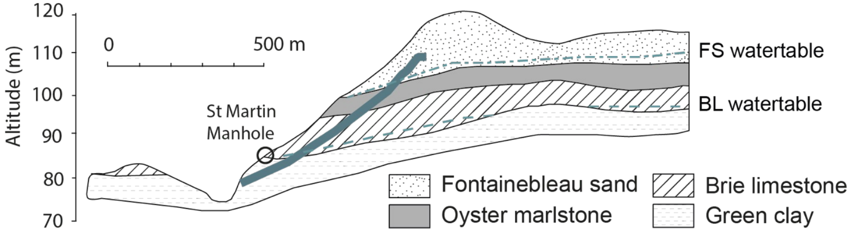
Transport assumptions

1. Direct atmospheric signal
2. DOM transport
3. Organic/Inorganic Particulate transport (erosion, remobilisation…)

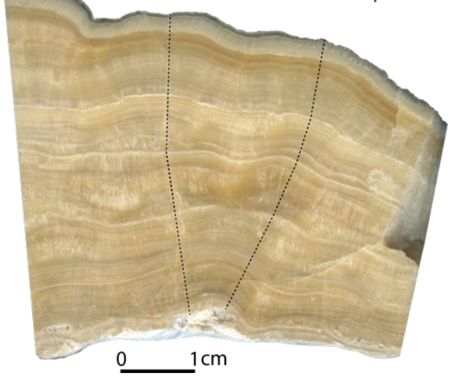
- Study site - Belleville Aqueduct

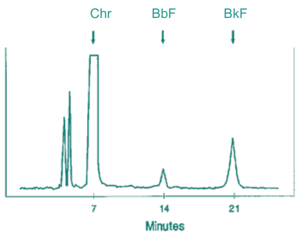


Garagnon et al., 2023, in prep.



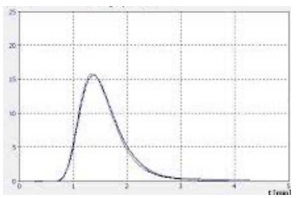
BEL2 sample





PAH

Characterization and quantification of PAH (HPLC Fluo)

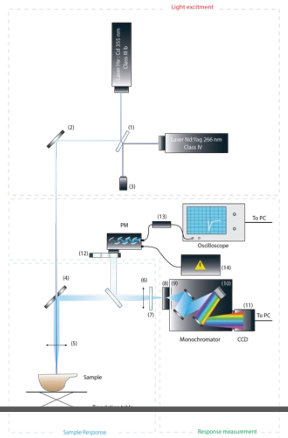


Non purgeable organic carbon (TOC analyser)

NPOC

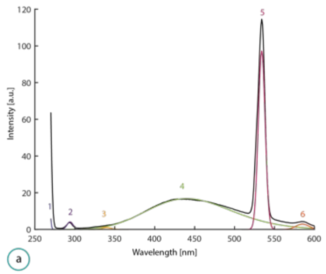
UV SPF

Solid phase UV Fluorescence (SPF) – high resolution (50 μm)

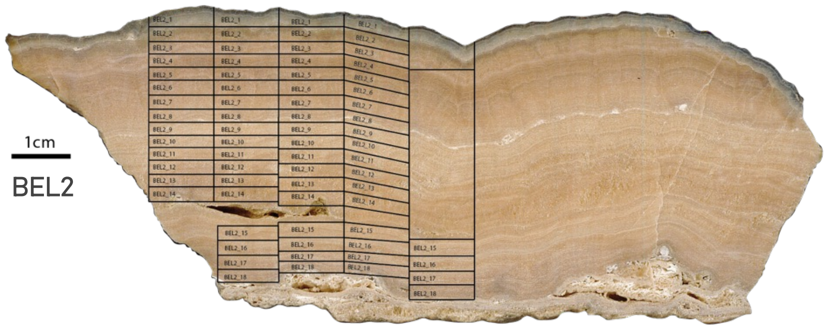


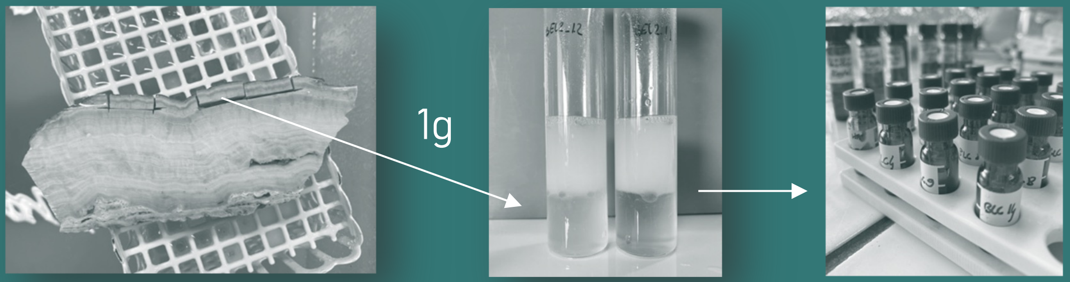
Liquide Phase UV Fluorescence (LPF)

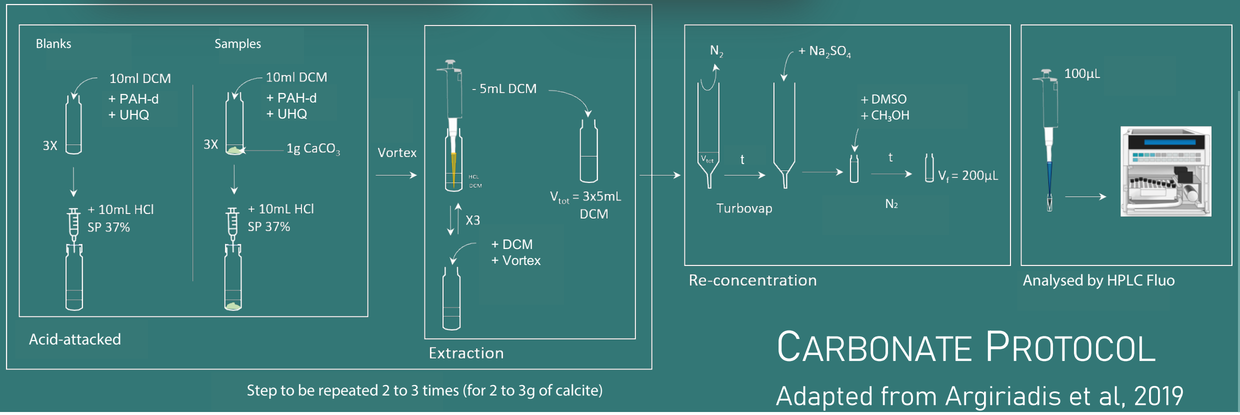
UV LPF



- PAH EXTRACTION PROTOCOL







Carbonate Protocol

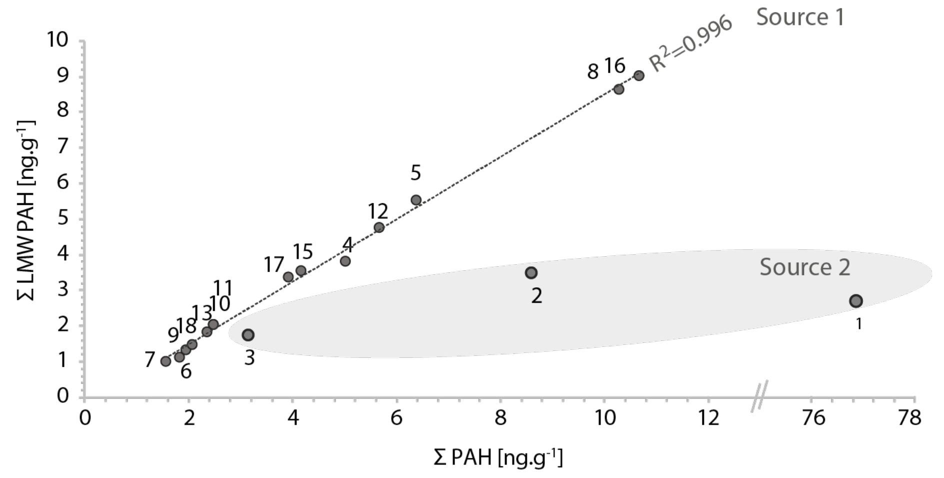
Adapted from Argiriadis et al, 2019

HAP	LOD [ng/g]	LOQ [ng/g]
Naphtalene	0,13	0,31
Acenaphtene	0,09	0,23
Fluorene	0,59	1,19
Phenanthrene	0,19	0,36
Anthracene	0,27	0,64
Fluoranthene	0,20	0,39
Pyrene	0,34	0,64
Benzo[a]Anthracene	0,13	0,32
Chrysene	0,19	0,41
Benzo[b]Fluoranthene	0,21	0,45
Benso[k]Fluoranthene	0,22	0,48
Benzo[a]Pyrene	0,49	0,96
Benzo[ghi]Perylene	0,13	0,31
Dibenzo[ah]Anthracene	0,22	0,51
Indeno-Pyrene	0,09	0,23

Results of Limits of Detection (LOD), Limits of Quantification (LOQ) for each PAH

- Temporal variations in PAH

- PAH present for 300 years
- 5 increase phases in total PAH of which only one is related to an increase in HMW PAH.
- Very significant increase in PAH concentration (x7) over the recent period (1995-2011 +/- 15 years AD)
- Omnipresence of Phenanthrene
- Trend of increasing proportion of HMW PAH and in particular Benzo[b]fluoranthene and Benzo[ghi]Perylene since 1800.
- From 1960, change of source, emergence of Benzo[a]Pyrene and Indeno-Pyrene.



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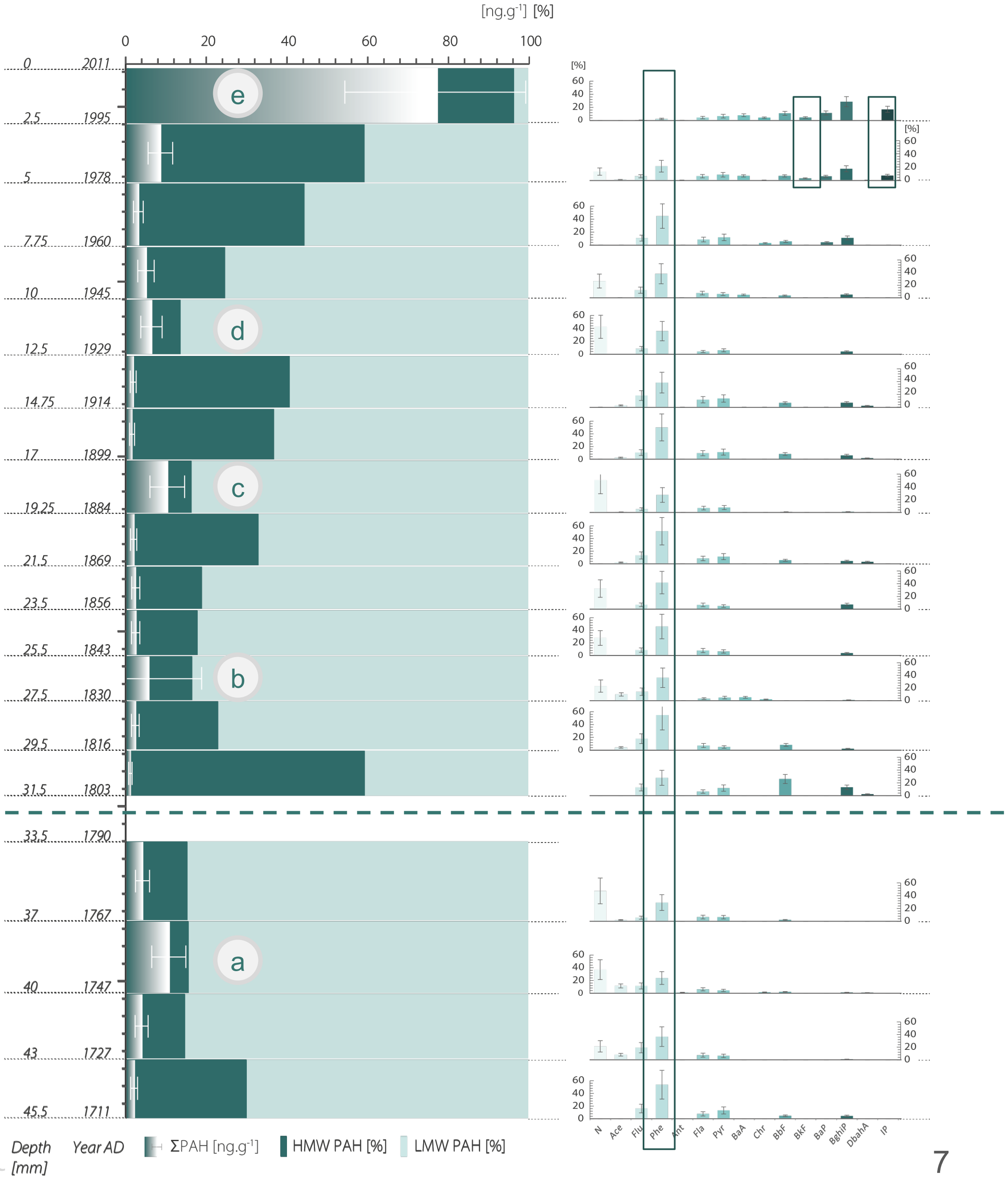
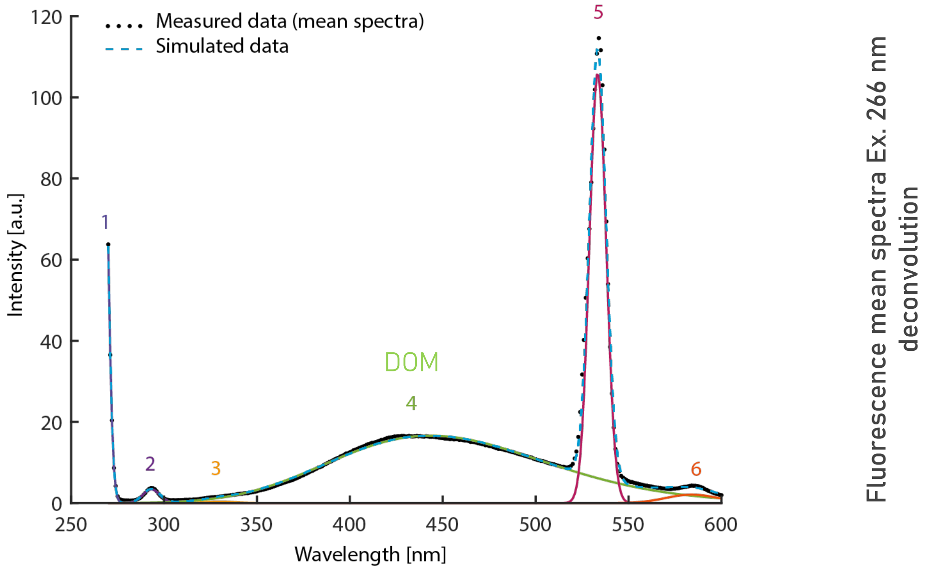
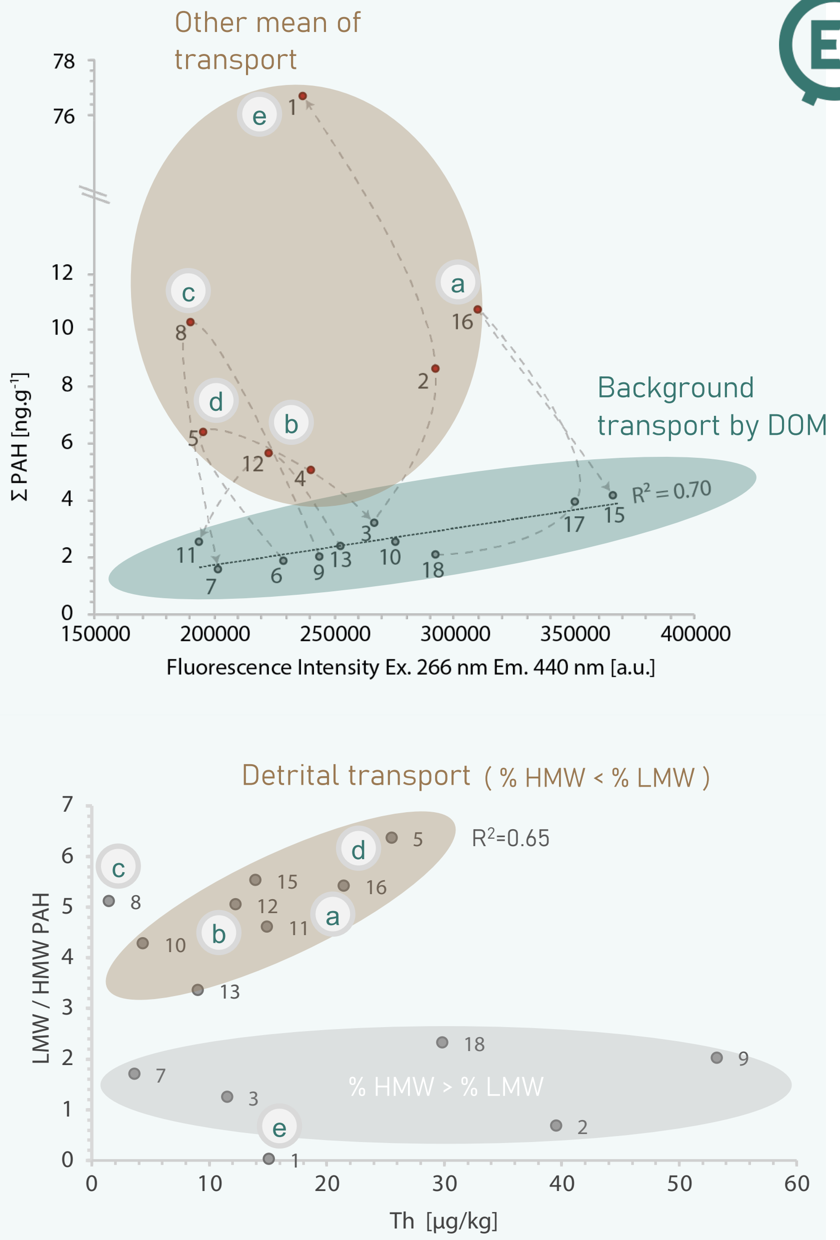


Comparison of PAH data with LPF data.

- Evidence of background transport by the DOM
- PAH peaks not related to this mode of transport
- Most of the peaks enriched in LMW PAH (a, b, d) can be explained by detrital transport (comparison with Th data (Pons-Branchu et al., 2015))





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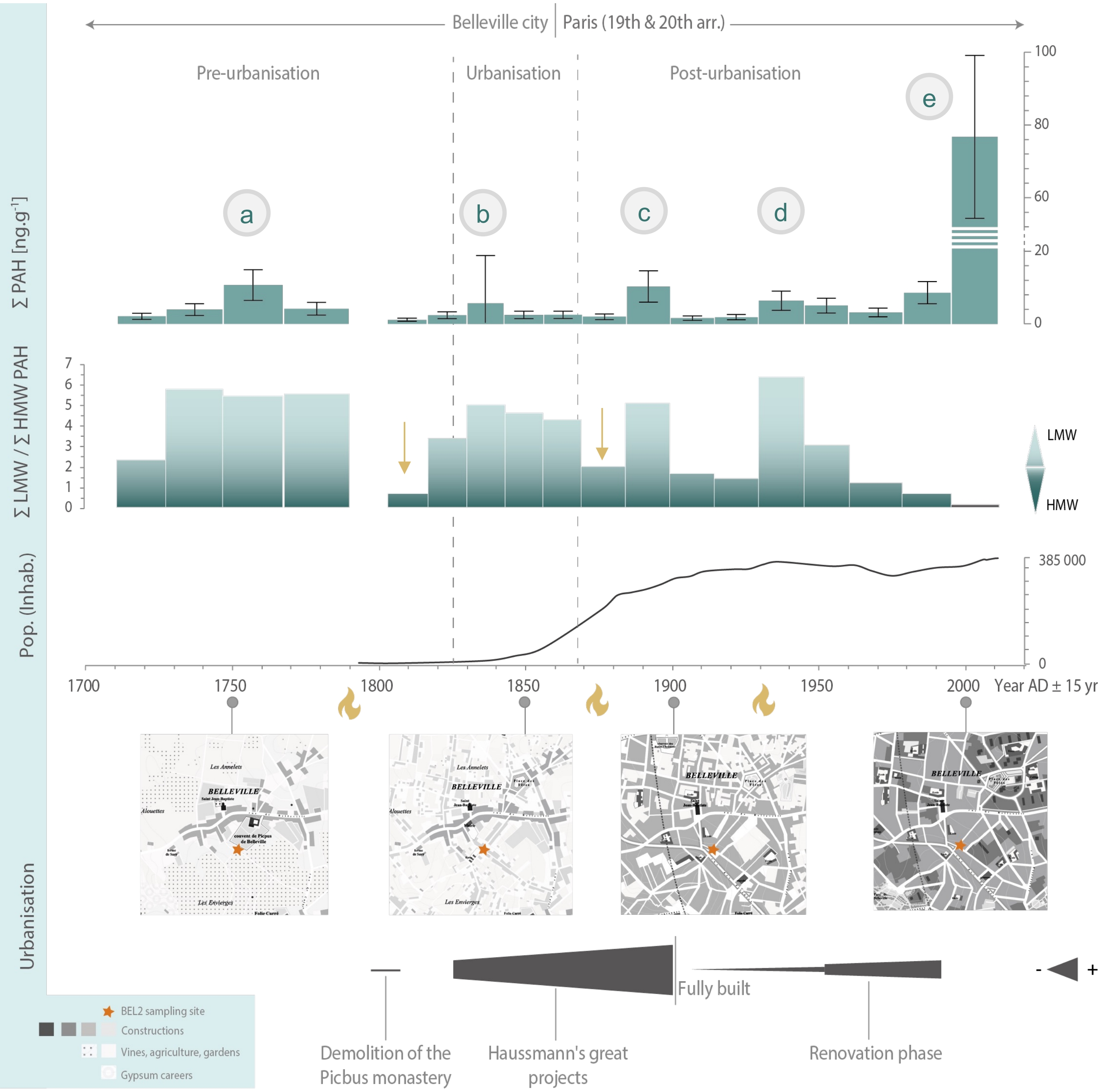
– Link with urbanisation

- Since 1850s, increasing trend in HMW PAH in line with increasing urbanisation and demography

- From 1960 to 2011 ± 15 yr AD completely urbanised but major increase in PAH and mostly in HMW PAH :
  - ⇢ Increase in vehicle traffic
  - ⇢ Historic paving stones are replaced by asphalt
  - ⇢ Urban streets washout

- Some lines of inquiry to refine : contribution from urban sludge spreading during the agricultural period; fires; remobilisation during the demolition of a monastery above….



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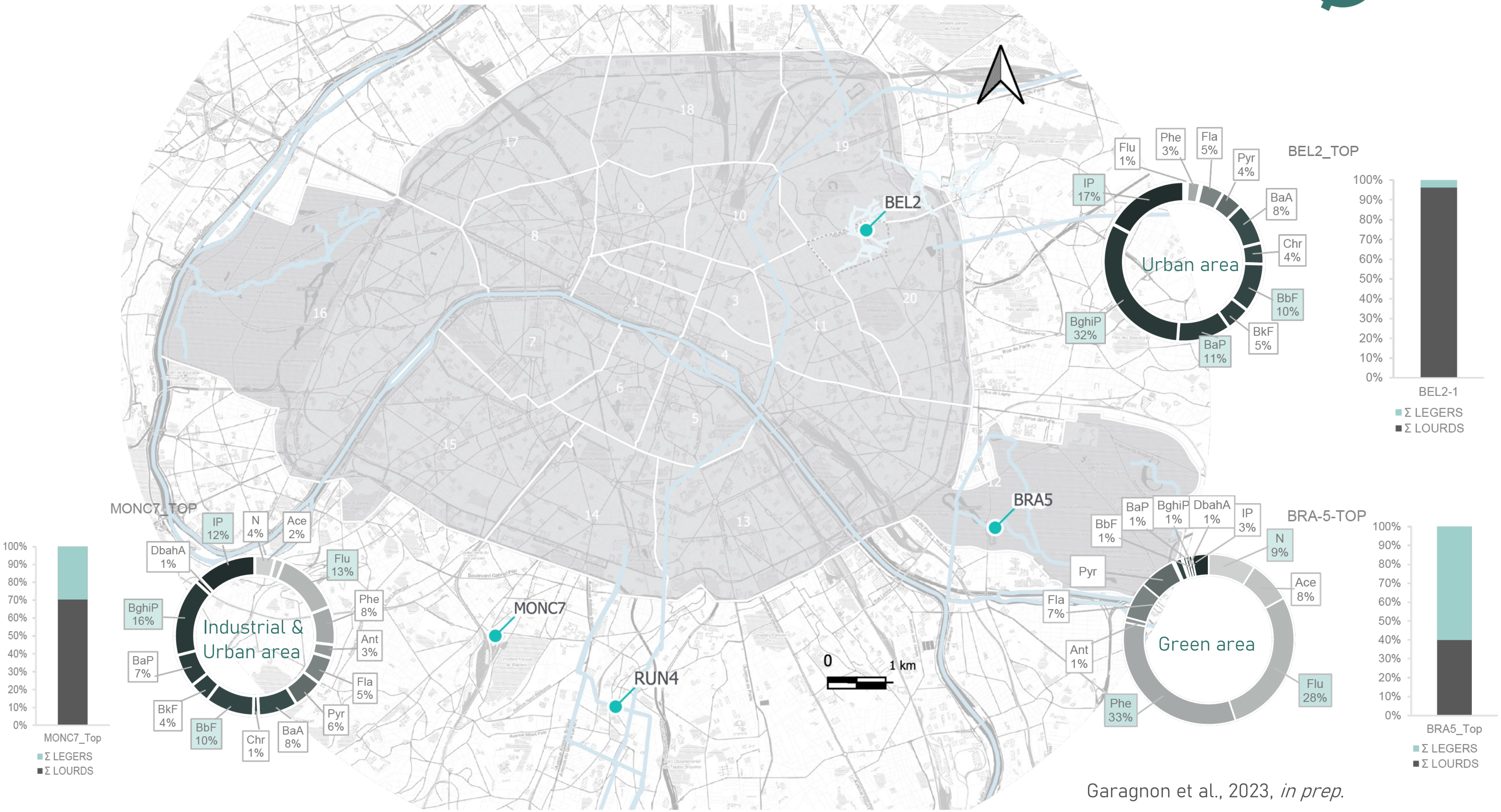
- SPATIAL VARIABILITY



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- TAKE HOME MESSAGES

- **Speleothems** are archives that allow to trace the water quality over time

- **Methods** from natural speleothems **not directly usable** on urban speleothems (transport conditions **not only related to OM/detrital)**

- Evidence of PAH in sub-surface water for 300 years

- **Major increase in total PAH** over the last few years

- **A change in source since 1960s** ± 15 years AD with emergence of Benzo[a]Pyrene, one of the most toxic and carcinogenic PAH

- Soil sealing seems to facilitate HMW PAH transport.

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- SUPPLEMENTARY – TIME CALIBRATION

Dating realised on BEL2 by Pons-Branchu with U/Th and laminae counting published in Pons-Branshu et al, 2014.

REF axis = 45.5 mm/300 laminae = 0.152 mm/yr

ERR = ± 15 yr

TC/TN/LPF samples	Depth	Depth Ref	Age
BEL2-0	0,5	0,5	2008
BEL2-1	2,5	1,75	1999
BEL2-2	4,5	3,5	1988
BEL2-3	7,5	7	1965
BEL2-4	9,75	8,5	1955
BEL2-5	12,75	11	1938
BEL2-6	15,25	13,5	1922
BEL2-7	17,5	16	1906
BEL2-8	19,5	19	1886
BEL2-9	21,5	20,5	1876
BEL2-10	24	22,5	1863
BEL2-11	26,25	24,5	1849
BEL2-12	28	26,5	1836
BEL2-13	30,75	28,5	1823
BEL2-15	35,5	35	1780
BEL2-16	39	38,5	1757
BEL2-16b	39	38,5	1757
BEL2-17	42	42	1734
BEL2-18	44,5	45	1714

TE samples	Depth	Depth Ref	Age published	Age reset from ref axe
BEL2-1	1	1,5	2004	2001
BEL2-2	4,5	3,5	1981	1988
BEL2-3	8,5	7	1954	1965
BEL2-4	12,75	11	1925	1938
BEL2-5	14,75	16	1911	1906
BEL2-15	15	19	1910	1886
BEL2-6	18,25	20,5	1888	1876
BEL2-7	20,5	22,5	1872	1863
BEL2-8	24,5	24,5	1845	1849
BEL2-9	26,5	26,5	1832	1836
BEL2-10	30	28,5	1808	1823
BEL2-12	37,5	35	1757	1780
			2011	2011
BEL2-13	40,5	38,5	1737	1757
				2011
BEL2-14	44,5	45	1710	1714

PAH samples	Top depth ref	Bottom depth ref	Top age	Bottom age	Mean Depth	Mean Age
BEL2-1	0	2,5	2011	1995	1,25	2003
BEL2-2	2,5	5	1995	1978	3,75	1986
BEL2-3	5	7,75	1978	1960	6,375	1969
BEL2-4	7,75	10	1960	1945	8,875	1952
BEL2-5	10	12,5	1945	1929	11,25	1937
BEL2-6	12,5	14,75	1929	1914	13,625	1921
BEL2-7	14,75	17	1914	1899	15,875	1906
BEL2-8	17	19,25	1899	1884	18,125	1891
BEL2-9	19,25	21,5	1884	1869	20,375	1877
BEL2-10	21,5	23,5	1869	1856	22,5	1863
BEL2-11	23,5	25,5	1856	1843	24,5	1849
BEL2-12	25,5	27,5	1843	1830	26,5	1836
BEL2-13	27,5	29,5	1830	1816	28,5	1823
BEL2-14	29,5	31,5	1816	1803	30,5	1810
BEL2-15	33,5	37	1790	1767	35,25	1779
BEL2-16	37	40	1767	1747	38,5	1757
BEL2-17	40	43	1747	1727	41,5	1737
BEL2-18	43	45,5	1727	1711	44,25	1719

(Pons-Branchu et al, 2014)

□ PAH
○ TC/TN/LPF
◯ TE

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