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Spatial and temporal distribution of polycyclic aromatic hydrocarbons in marine sediments from the Canadian Arctic Archipelago

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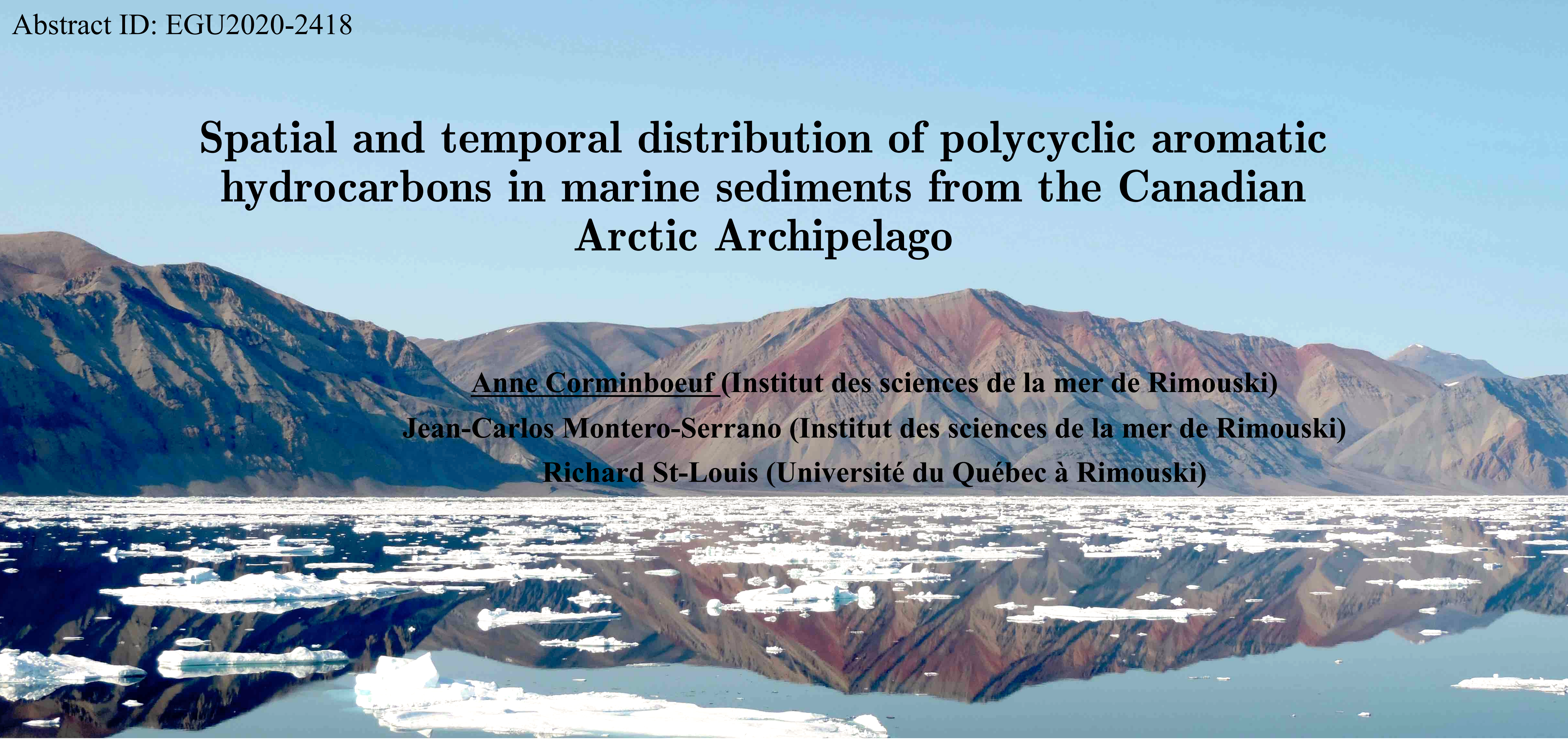

EGU2020 OS1.11 Changes in the Arctic Ocean, sea ice and subarctic seas systems: Observations, Models and Perspectives

Warning

This is a M. Sc. curently in progress at UQAR-ISMER (Canada).
The data presented here are not yet published.
If you intend to use any data/scheme/figure of this presentation, please ask the corresponding authors before:

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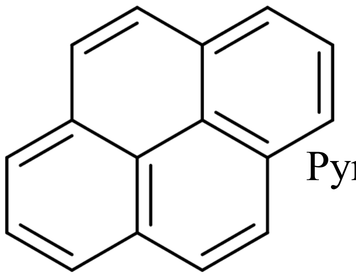
Thank you and have a good presentation!

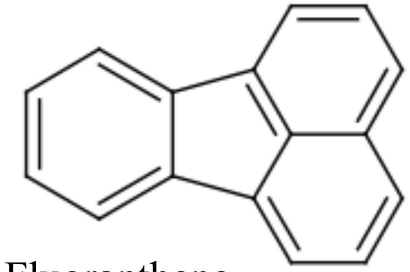
1. Context

- The Arctic is undergoing major changes: ⇧ of temperature and ⇩ of the sea ice coverage of ~12 % per decade (Lindsey and Scott, 2019).
- Anthropogenic activities are expected to increase in the future years and they are source emissions of many compounds such as polycyclic aromatic hydrocarbons (PAHs).
- There is a knowledge gap regarding to PAHs concentration and sources in sediments for all the Canadian Arctic Archipelago, except the Beaufort Sea and the North Baffin Bay, which have already been studied (Yunker *et al.*, 1996; Foster *et al.,* 2015).

PAHs →
- Two origins →
  - Petrogenic (rock weathering, oils seeps)
  - Pyrogenic (by-product of any combustion)
- Dispersed together with terrigenous particles by wind, sea ice and ocean circulation
- Carcinogenic potential during metabolism ⚠



Pyrene



Fluoranthene

↳ Among this class of componds, USEPA have identified 16 PAHs of great concern due to their potential toxicity.

2. Objectives

Objective #1

Characterize PAHs concentration

▶ In marine surface sediments

Objective #2

Compare with historical tendencies

▶ Box corer sediment samples

Objective # 3

Assess the origin of PAHs

▶ Diagnostic ratio

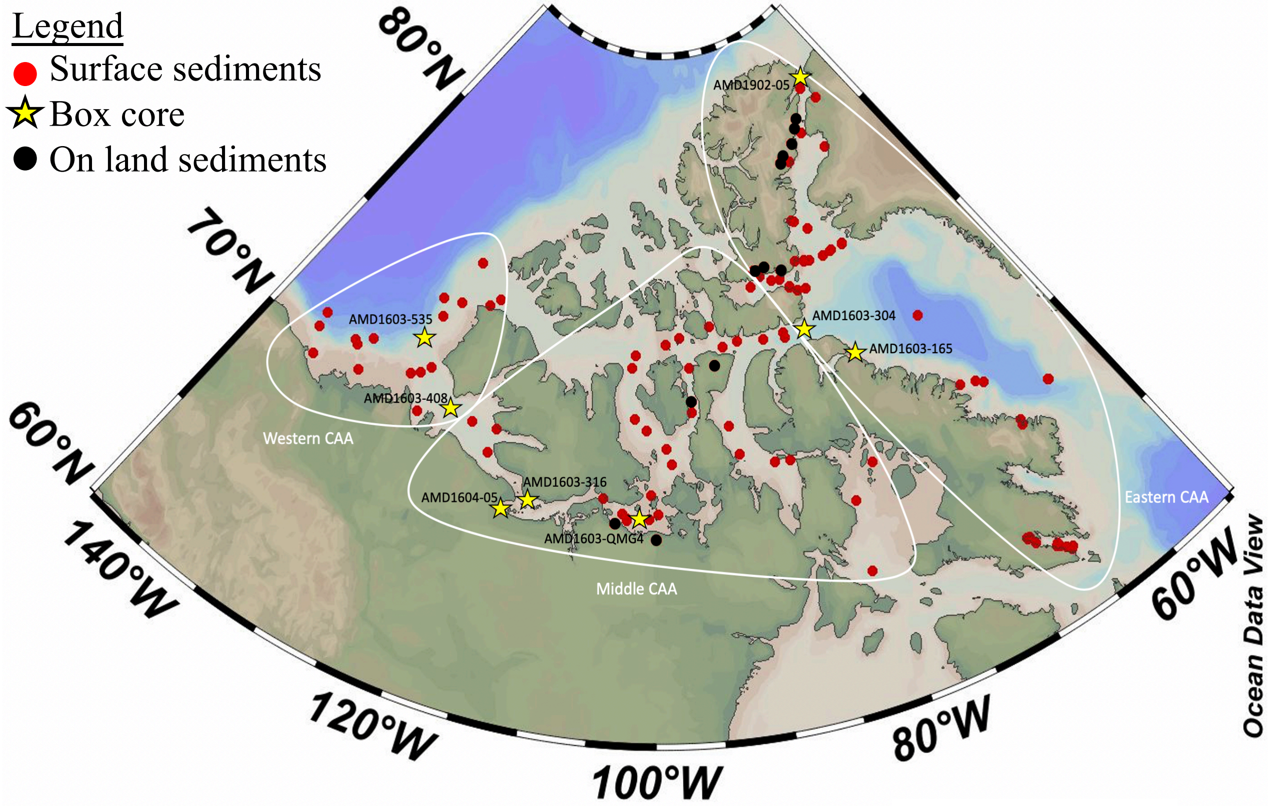
$$\frac{\text{Fluoranthene}}{\text{Fluoranthene} + \text{Pyrene}}$$

▶ Reference state

▶ **Before** a significant increase of anthropogenic activities within the Canadian Arctic Archipelago

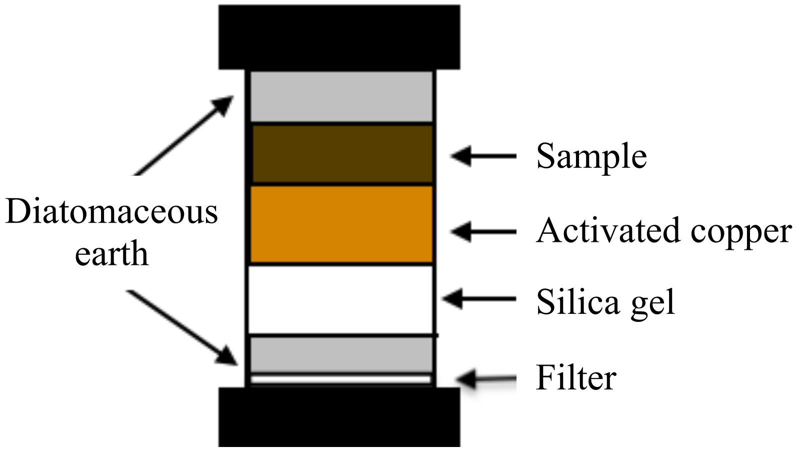
3. Sampling and methods

Sampling was performed with the box corer onboard the Canadian icebreaker *CCGS Amundsen* during the 2016, 2017, 2018 and 2019 ArcticNet's summer expeditions.



PAHs extraction on the <150 µm is performed with a one-step accelerated solvant extraction (ASE Dionex 200) following the method developped by Choi *et al.* (2014).

PAHs are quantified using gas-chromatography coupled to a mass spectrometer (GC-MS) and 23 PAHs are quantified, including the 16 priority PAHs of the USEPA. The analysis of standard reference material SRM-1944 (n=19) had a recovery of 29 – 131% for the concerned PAHs. Those recoveries were similar to those obtained by Choi *et al.* (2014).



Packing of the extraction cell, adapted from Choi *et al.*, (2014).

4. Results – Sums of the 16 priority PAHs in surface sediments

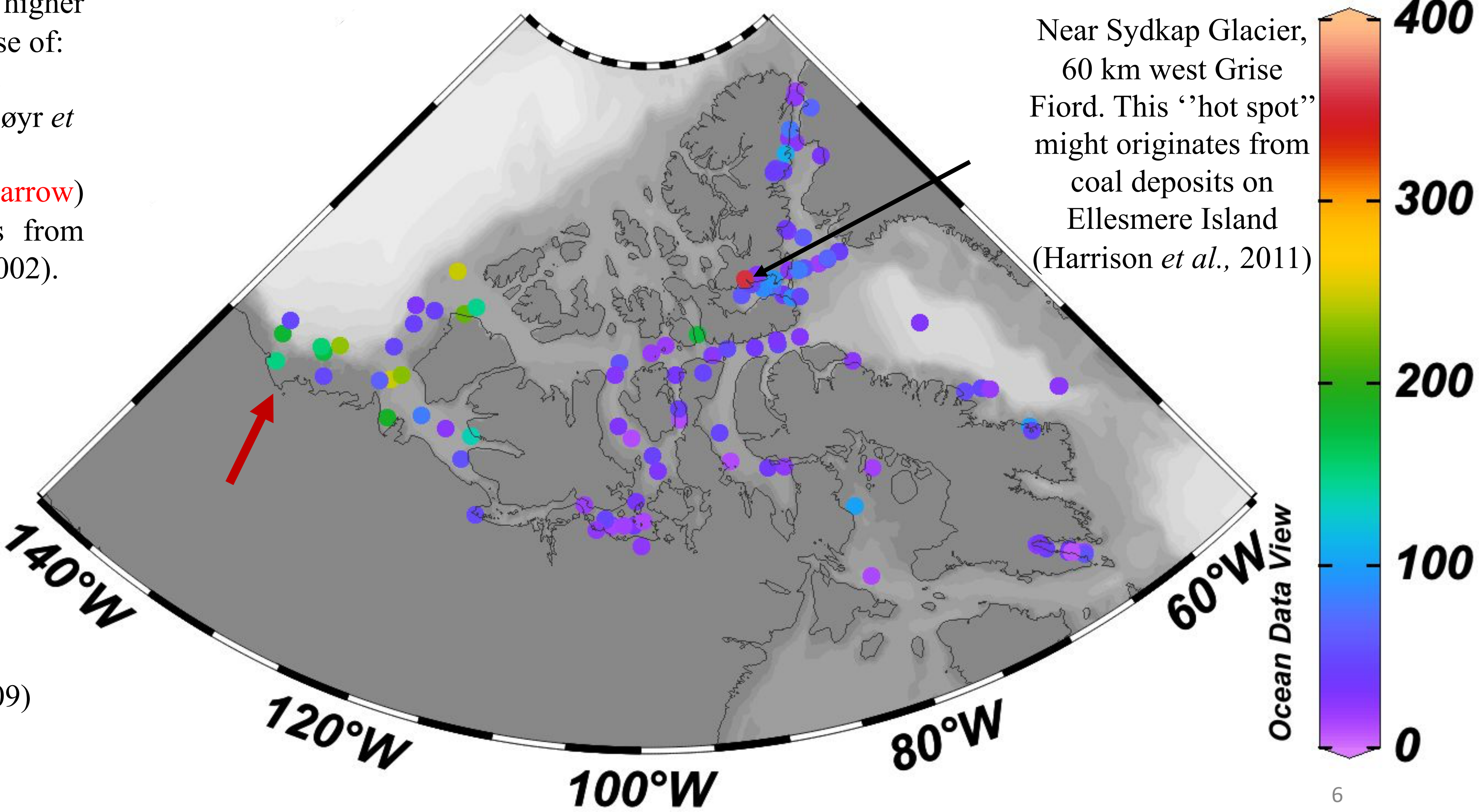
Western CAA shows higher concentrations likely because of:
1. Underwater hydrocarbons reserves in this area (Klungsøyr *et al.*, 2010)
2. Mackenzie River (red arrow) discharge containing PAHs from weathering (Yunker *et al.*, 2002).

Middle and eastern CAA show low concentrations similar to other Arctic regions with little to no anthropogenic influence:

Kara Sea: ND – 100 ng/g (Sericano *et al.*, 2001)

Svalbard coastal sediments: 25 – 38 ng/g (Jiao et al., 2009)

Concentration (Σ_{16}PAHs ng/g, dw)



Near Sydkap Glacier, 60 km west Grise Fiord. This ''hot spot'' might originates from coal deposits on Ellesmere Island (Harrison *et al.*, 2011)

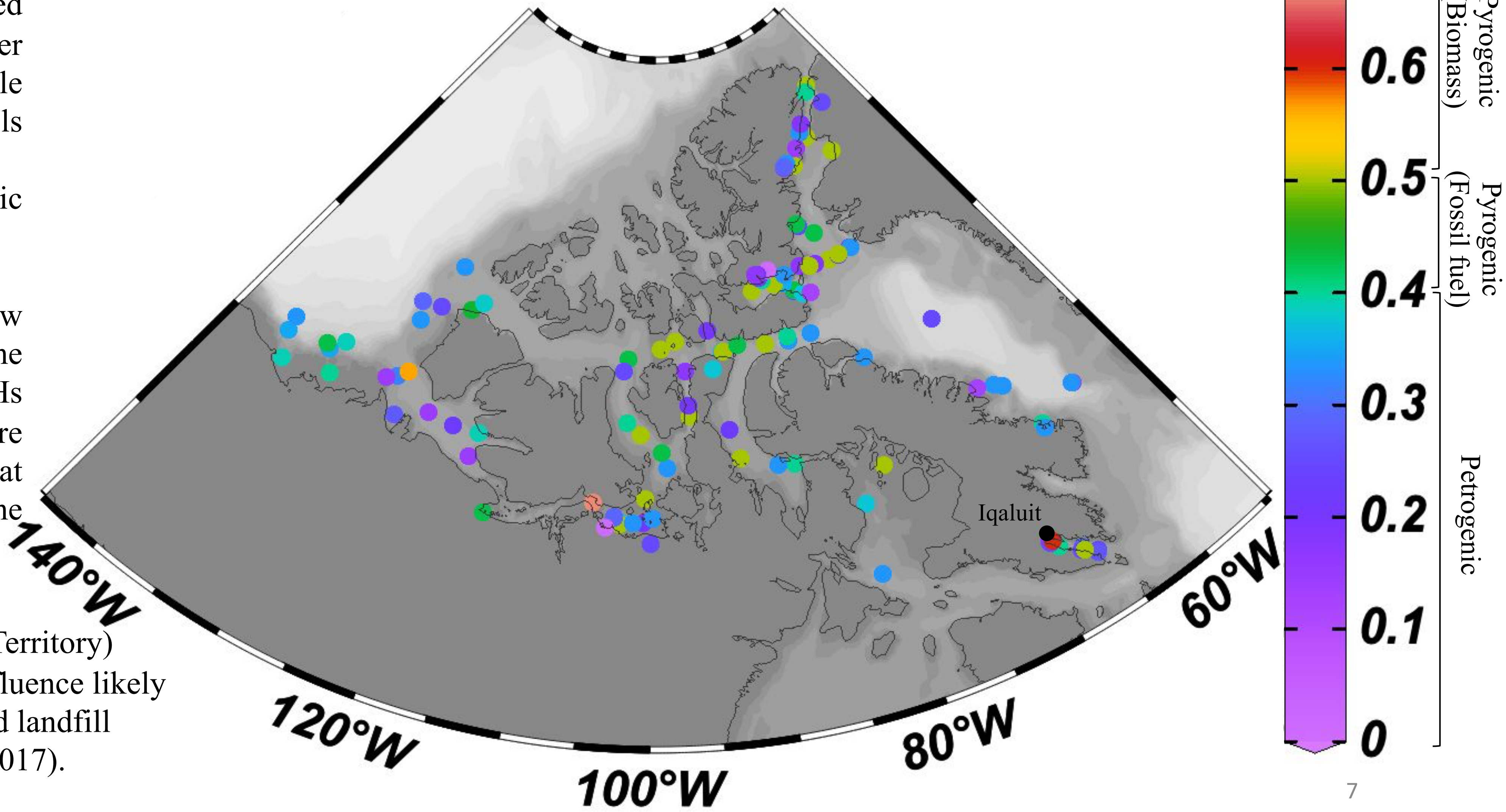
4. Results – Contemporary sources of PAHs

Western CAA shows mixed profile: the Mackenzie River delivers petrogenic PAHs while anthropogenic activities (oils explorations/exploitations) contribute to a pyrogenic influence (Yunker *et al.*, 2002).

Middle and eastern CAA show petrogenic PAHs (likely from the natural background) and PAHs on the ratio boundary of 0.5 are likely from forest fire events that became more frequent over the last decades.

Iqaluit (capital of the Nunavut Territory) shows a local anthropogenic influence likely due to electricity production and landfill fires (Government of Canada, 2017).

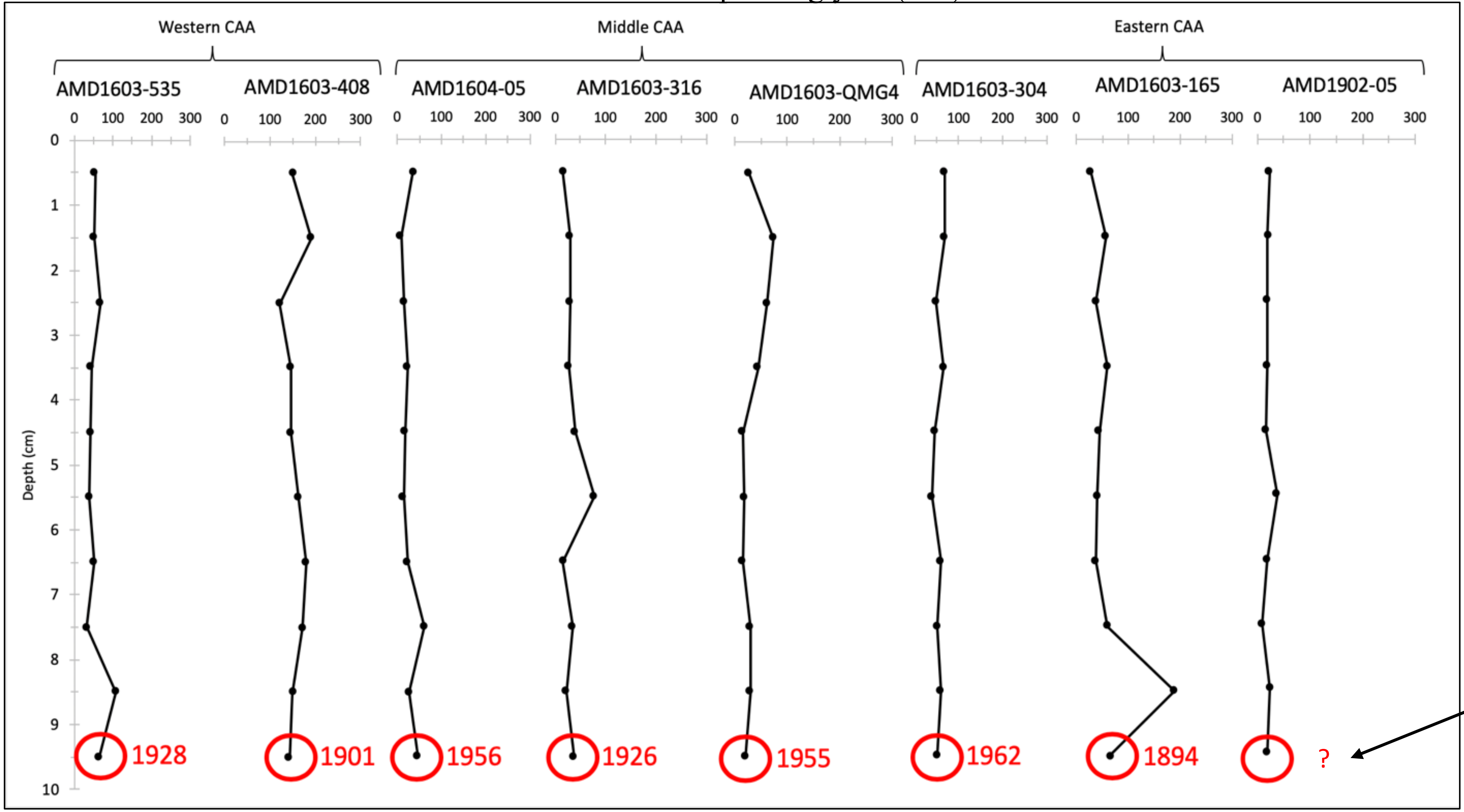
Diagnostic ratio of Fluoranthene/(Fluoranthene+Pyrene) in surface sediments



4. Results – Inputs of PAHs over the last century

Concentration (Σ_{16}PAHs ng/g, dw) in sediments from 0 to 10 cm

Red number indicates de corresponding year (AD) of the 10th cm

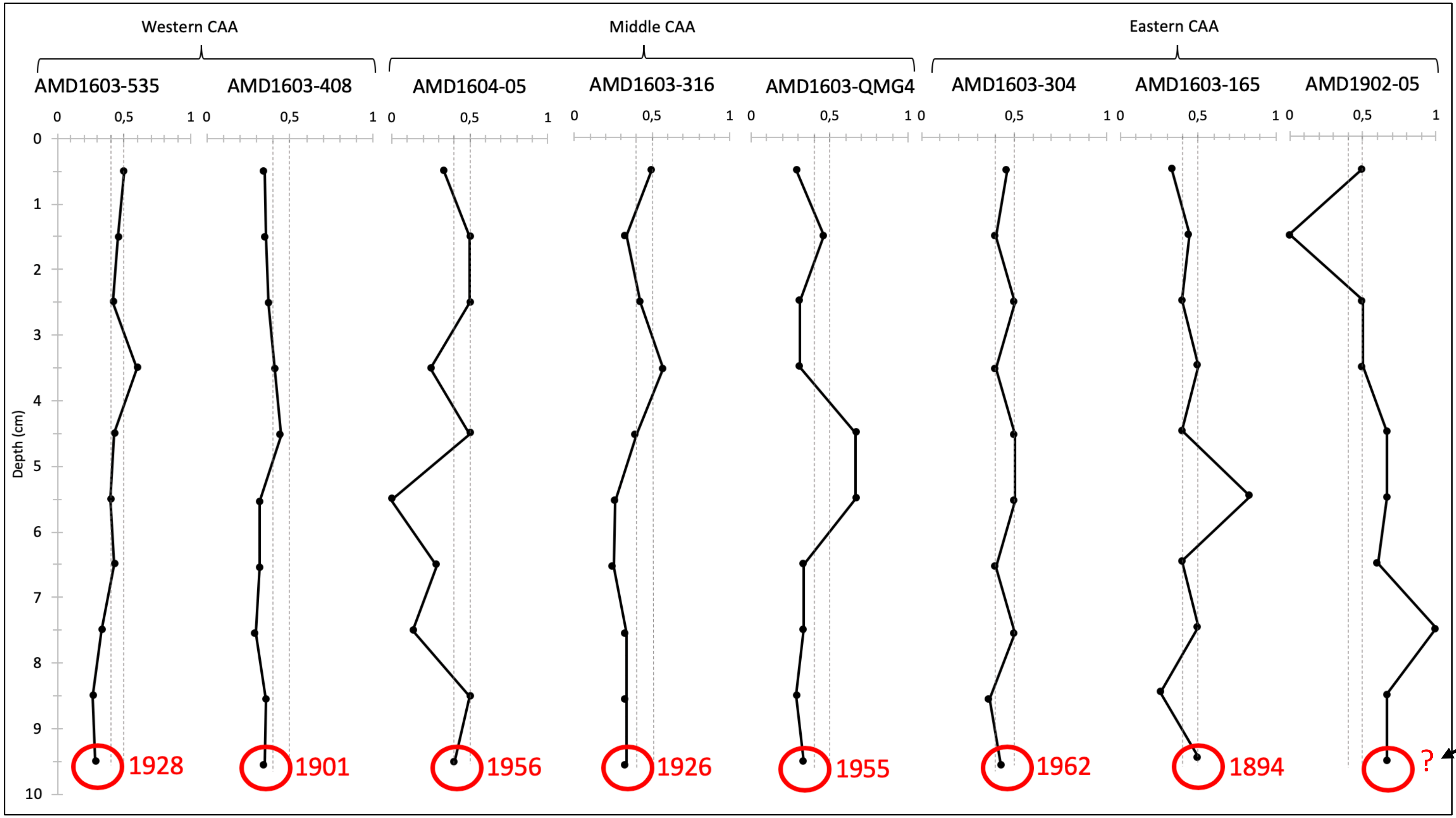


Dating in progress

4. Results – Sources of PAHs over the last century

Fla/(Fla+Pyr) ratio from 0 to 10 cm

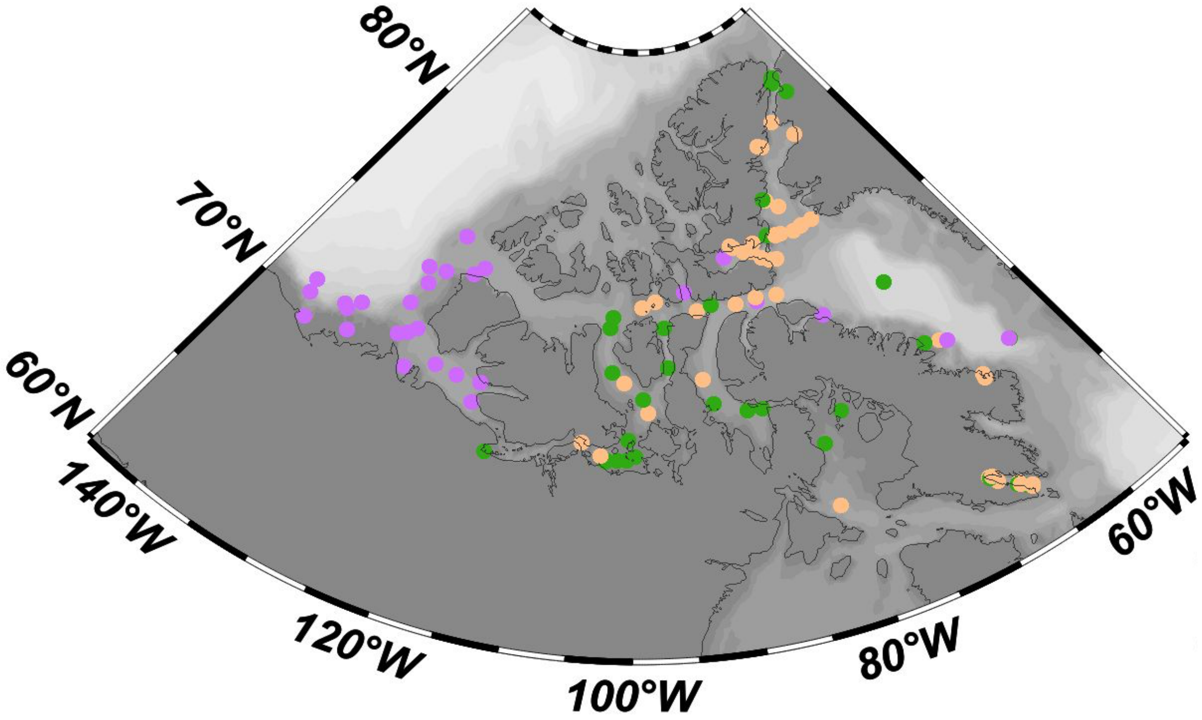
Dashed lines indicate ratio boundaries of 0.4 and 0.5



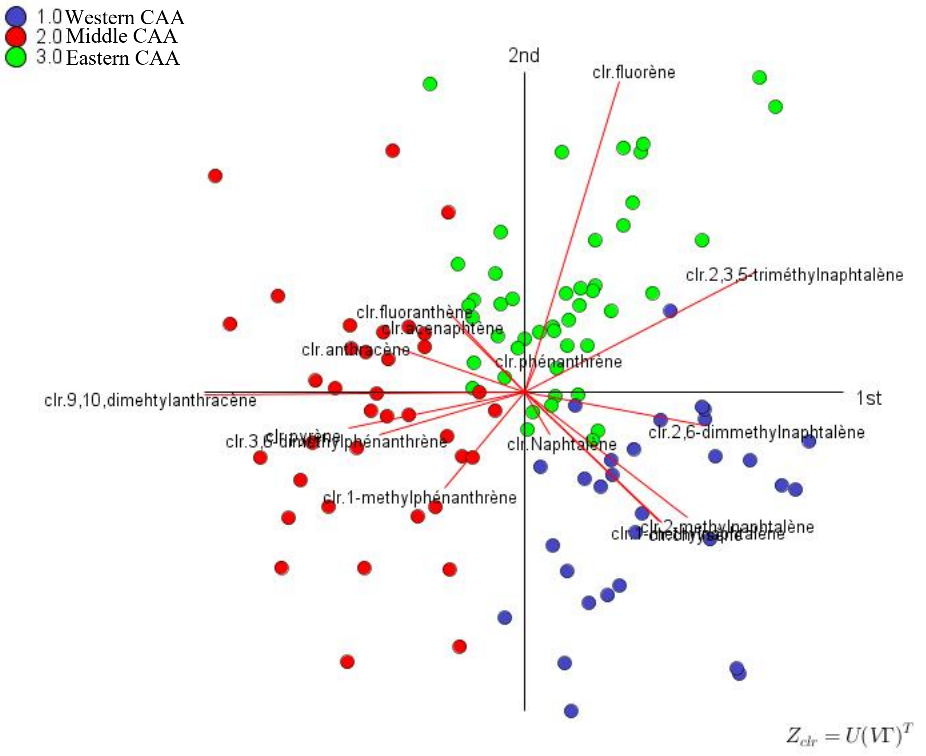
Dating in progress

4. Results – Statistical analysis

Map illustrating the cluster analysis, with n=3 as the optimal number of clusters



Principal component analysis (PCA)



Alkyl-PAH: generally derived from petrogenic PAHs (Yunker and Macdonald, 1995)
Parent PAH: more associated to combustion processes (Yunker and Macdonald, 1995)

4. Results - Interpretation

Inputs over time

When looking to Σ_{16}PAHs (ng/g, dw) over time, inputs seem relatively constant. No value exceed the maximum of 247 ng/g obtained for surface sediments and they are therefore all within the general values for surface sediments from the CAA.

Sources of PAHs over time

Diagnostic ratios show constant sources over time, mainly in the petrogenic signature (below 0.4).
Cores from the middle and the eastern archipelago have ratios in the fossil fuel burning signature (between 0.4 and 0.5). The influence of forest fire events might contributes to drag the ratio from the petrogenic side to the pyrogenic one. Bias from degradation of fluoranthene (less stable than pyrene) leads to decreasing values when going down-core.
AMD1902-02 shows a different pattern: increasing ratio while going downcore. The sample was taken at the deepest location in Robertson Channel, where the sedimentation rate is very slow. Sediments are therefore oldest than others from the CAA (Jennings *et al.,* 2011).

Statistical analysis

Cluster analysis confirms that the western archipelago is different from the middle and the eastern archipelago.
Principal component analysis confirms that the western archipelago has mainly petrogenic PAHs and that the middle and eastern archipalgo have a mixed PAHs profile from both petrogenic and pyrogenic from biomass burning.

5. Conclusions

- PAHs in marine and on land sediments from the Canadian Arctic Archipelago are present in **low concentrations** and are comparable to other pristine Arctic regions.

- They are mainly from **petrogenic origin**, with some pyrogenic origin from biomass burning, likely from long-range atmospheric transport of emissions from forest fires events.

- Therefore, they are mainly from **natural sources**.

- Regarding to the risk contamination of marine fauna by PAHs, the Canadian Arctic Archipelago undergoes **very little anthropogenic influence**.

This study provides a strong baseline record of compounds of great interest (PAHs) in sediments from the Canadian Arctic Archipelago before a significant increase of the anthropogenic activities that are likely to occur within the next decades.

To better document the actual baseline and this increase of activities, other compounds could be analyzed: analysis of metals of interest (i.e. Pb, Cd and Hg) could be performed and combined with the use of enrichment factors, for example.

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