



# Pb isotope ratios measurements using ICP-QQQ

## Applications to environmental materials to assess pollution source terms

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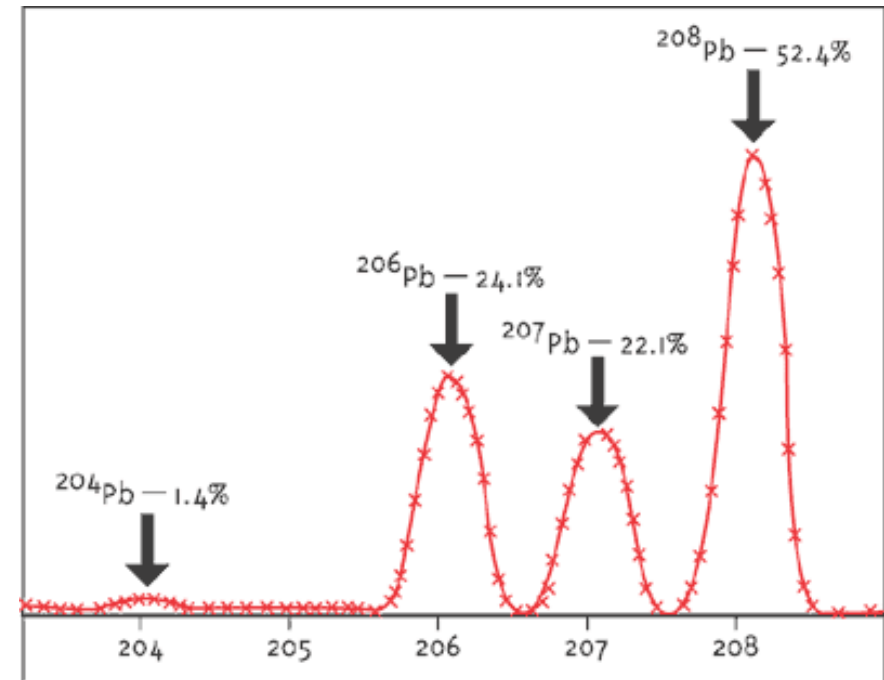
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# Applications of precise Pb isotope ratio measurements

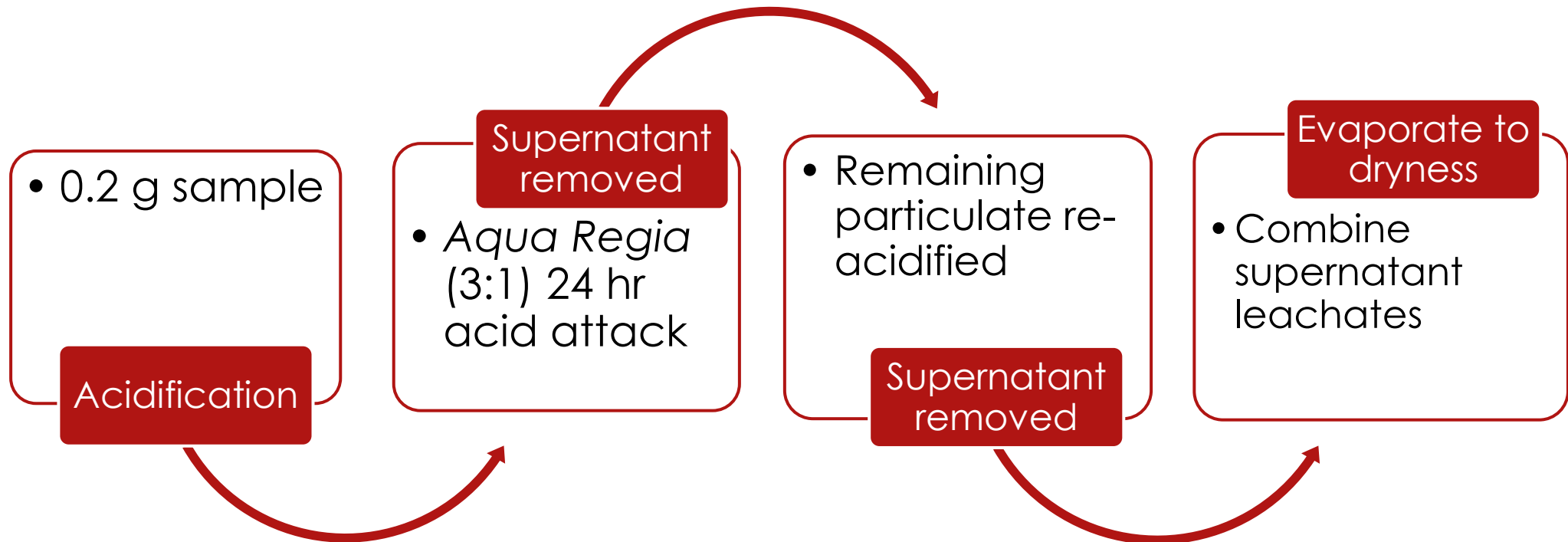
- ▶ Pb has 4 major stable isotopes
- ▶ 204 is primordial
- ▶ 206, 207 and 208 are Radiogenic
- ▶ 206, 207 are formed from  $^{238}\text{U}$ ,  $^{235}\text{U}$  decay while
- ▶ 208 is from  $^{232}\text{Th}$  decay
  
- ▶ Environmental studies commonly use 206/207 ratio to identify different Pb sources in samples
- ▶ In the UK, Australian, Canadian and US ores were used in leaded petrol which have significantly different isotopic ratios from UK lead ores
  
- ▶ 206/204 : Normally less precisely measured due to the low abundance of 204 isotope and possible isobaric interference from mercury ( $^{204}\text{Hg}$ )



# High precision measurements

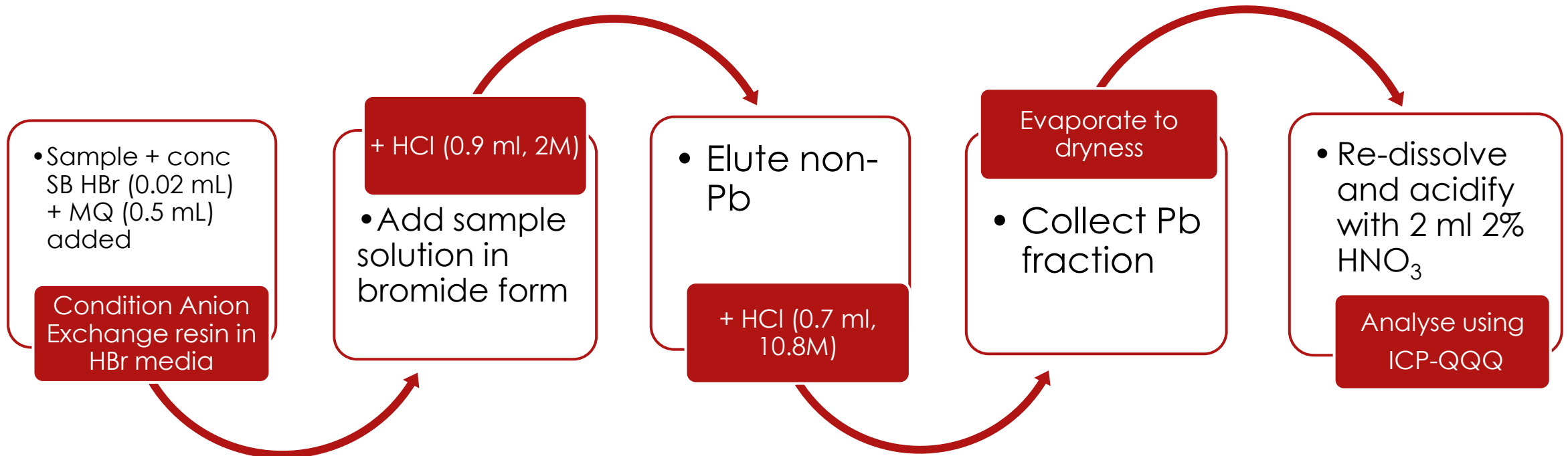
- ▶ MC-ICPMS (Thermo Neptune)
  - ▶ Double Pb spike (Taylor *et al.*, 2017)
    - ▶ Accurately measure the instrumental mass fractionation of Pb isotopes
    - ▶ Pair of artificially enhanced isotopes. Compare spiked vs unspiked to calculate the fractionation
    - ▶ Often hampered by significant interferences from laboratories and procedural blanks
  - ▶ Thallium spiking
    - ▶ Non-isobaric mass fractionation through the use of another element (Tl)
  - ▶ Bracketing
    - ▶ Externally correct fractionation bias
    - ▶ Can be used in tandem with other methods (double spike and Tl spiking)
- ▶ How effective is the Agilent ICP-QQQ-MS for Pb isotope ratio measurements?

# Sample Acid Leaching Methodology



All reagents are sub-boiled and stored in PFA bottles  
All handling is carried out in two small purpose-designed HEPA cabinets  
All containers are acid washed with sub-boiled acids

# Pb Extraction – anion exchange chromatography



# Clean lab conditions



State-of-the-art  
NOCS clean labs  
Class 100 - 1000;  
Cost 600k Euros

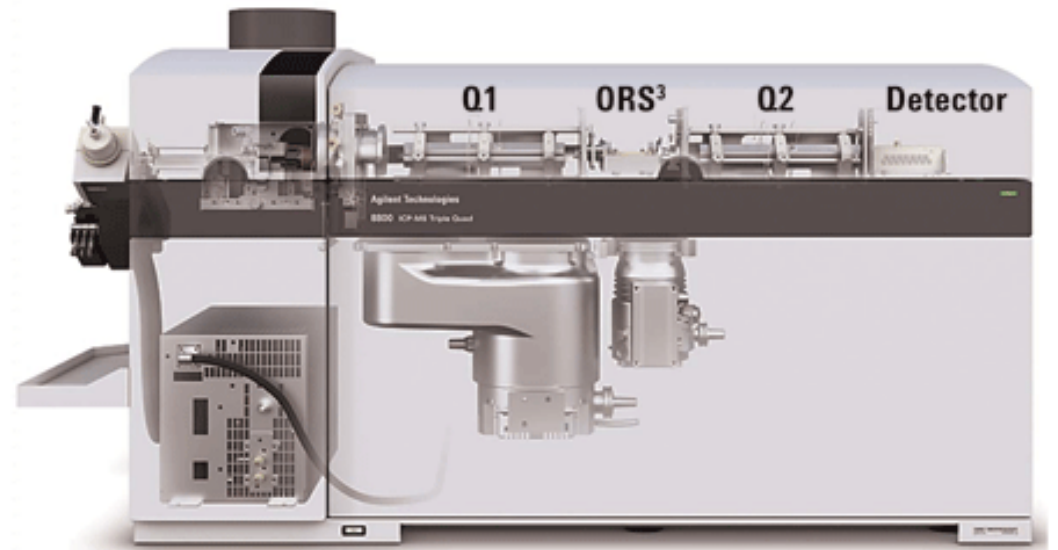


GAU-designed HEPA  
cabinets that proved  
highly effective at  
contamination control;  
Cost 1.2k Euros

# ICP-QQQ-MS

## Benefits

- ▶ MS/MS
- ▶ good abundance sensitivity
- ▶  $\text{NH}_3$  can be used to suppress isobaric Hg 204
- ▶ **Conditions for analysis assessed and chosen**
  - ▶ Free aspiration
  - ▶ SQ
  - ▶ No gas
  - ▶ Sample bracketing with NIST-981 Pb ISO standard
  - ▶ 10 ppb solution analysis
  - ▶ Replicate, maximum sweeps/replicate, maximum integration





# Locations of sediment cores investigated

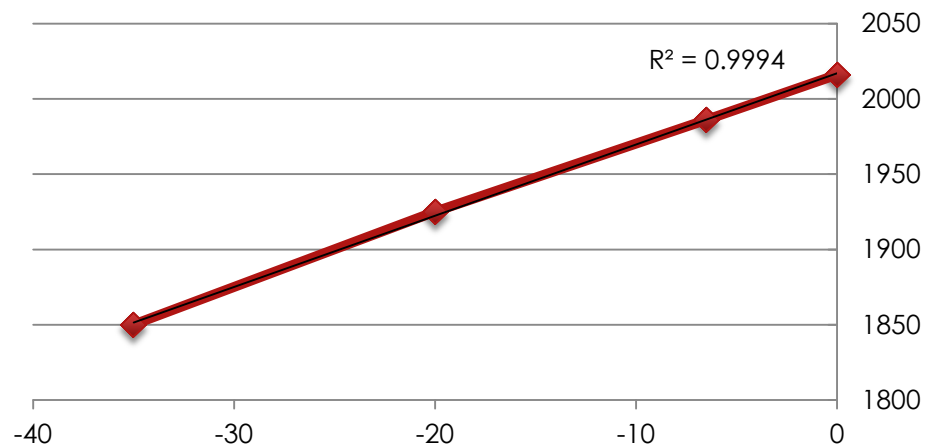
- ▶ **Windermere, largest English lake NW England**
  - ▶ 0.5 m lake sediment core
  - ▶ Important tourist facility since 1850s – leisure linked to rising affluence linked to Industrial Revolution
  - ▶ Inside a National Park
- ▶ **Hythe salt marsh, Southampton Water, England**
  - ▶ 0.8 m estuarine sediment core
  - ▶ Industrial port area since Victorian Era
  - ▶ The main build-up location for D-Day during WW2 naval operations
- ▶ **Dating** –  $^{137}\text{Cs}$  allowed conversion of core depth to age



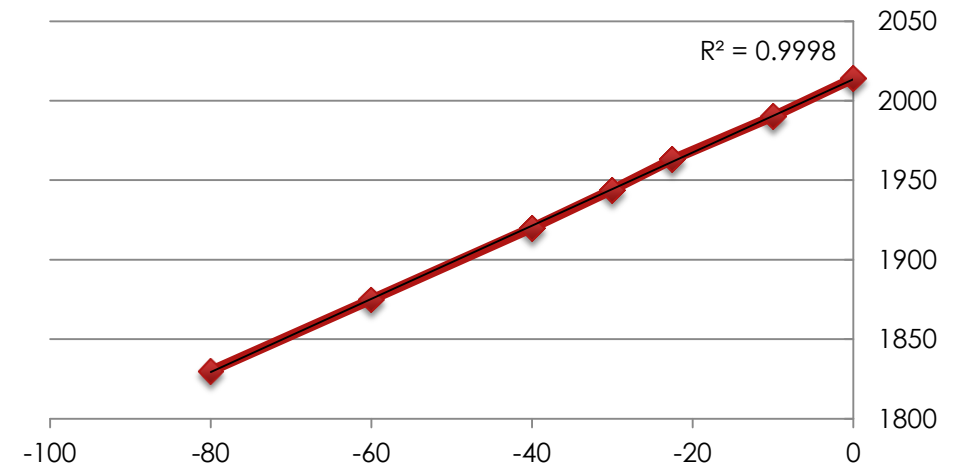
# Age vs Depth Models for Windermere and Hythe cores

Based on Cs-137, Pb-210 and other known historical geochemical indicators

Windermere Age vs Depth Model



Hythe Age vs Depth Model

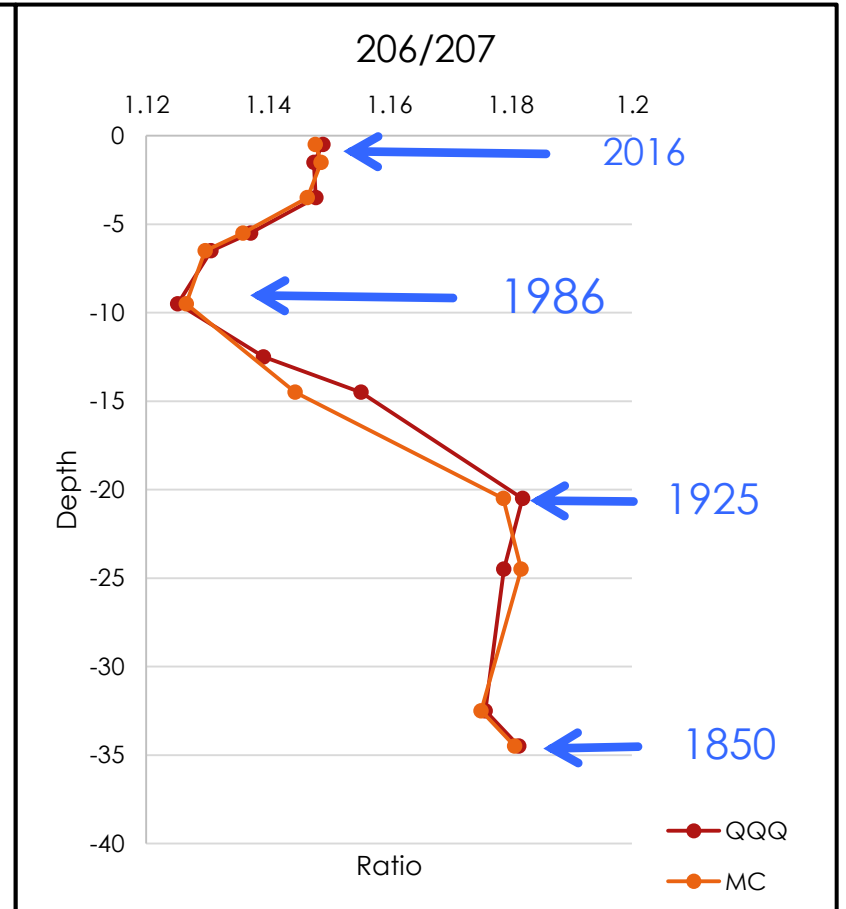
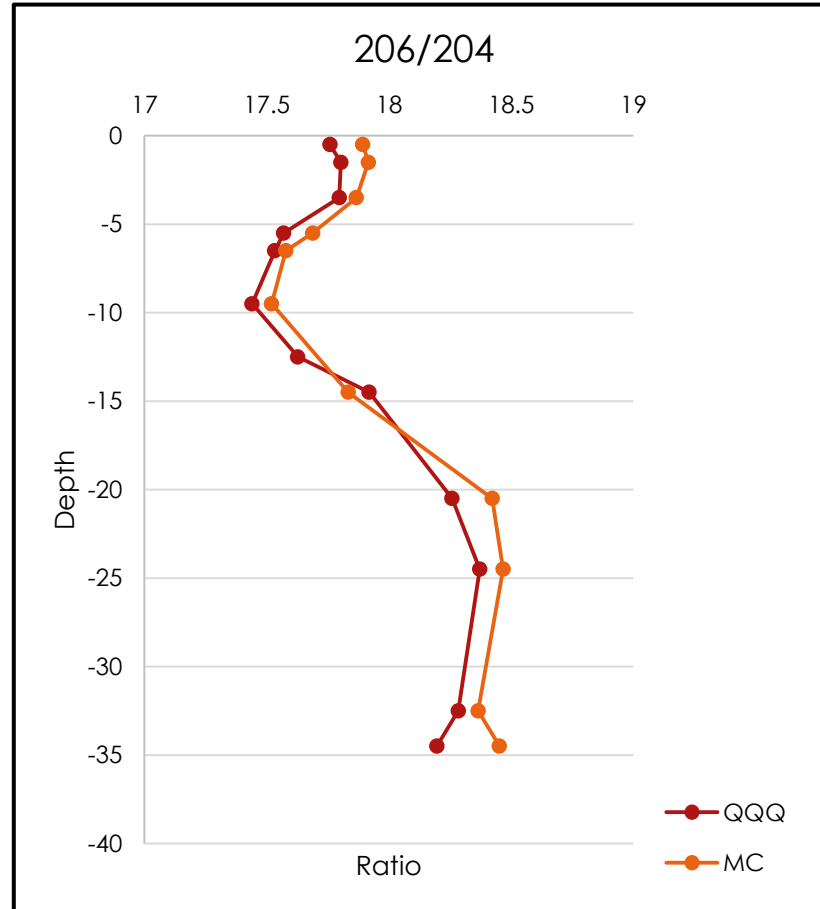


- ▶ Introduction of leaded petrol in the UK was ~1925
- ▶ 1986 : 50% reduction in Pb added to leaded petrol in the UK

# Multi-collector vs ICP-QQQ

## Windermere lake sediment core profile

Dates inferred from Cs-137 and other geochemical changes



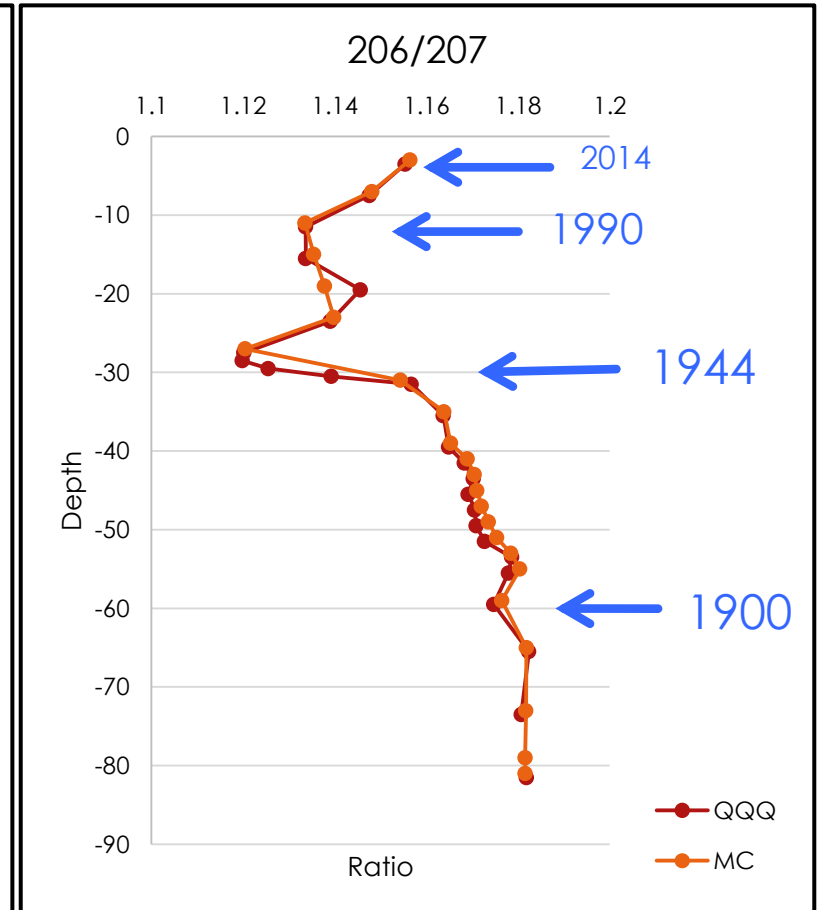
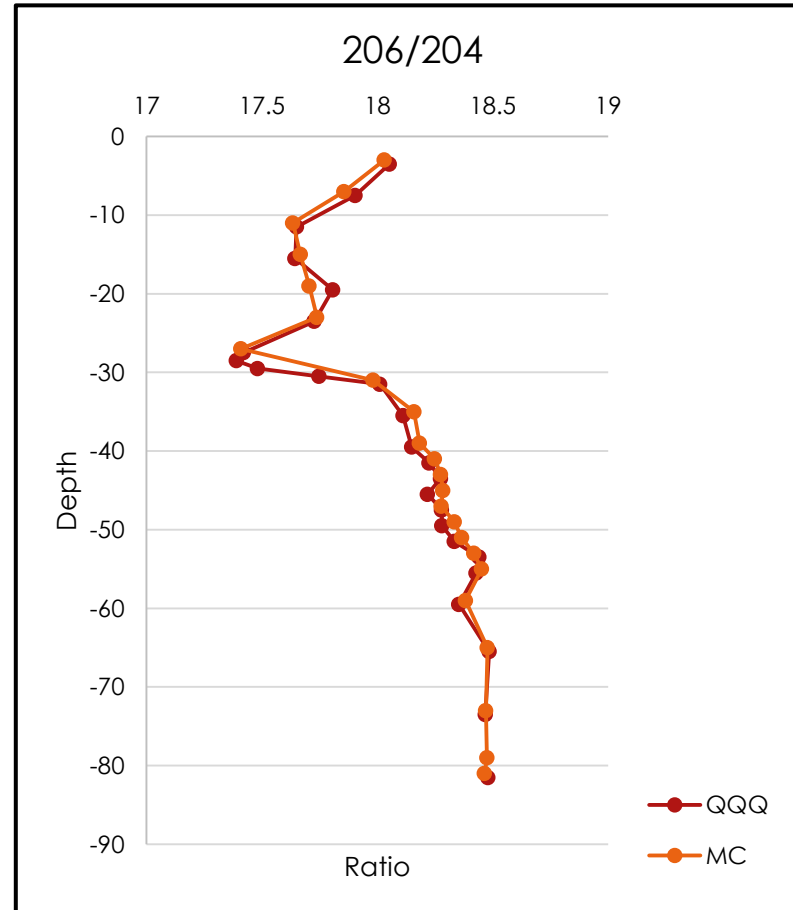
# Multi-collector vs ICP-QQQ

## Hythe saltmarsh sediment core profile

Dates inferred from Cs-137



Landing Craft Assault in Southampton Water, 3 June 1944



# Summary

MS Mode	Instrument Precision (% RSD) 206/207	Instrument Precision (% RSD) 206/204	References
SQ	1-2%	~2-4%	Walder and Furuta 1993, Mukal et al., 1993,
TIMS	0.009	0.0260	Galer and Abouchami 1998 , Thirlwall 2002, Kuritani and Nakamura 2003, Amelin and Davis 2006, Hoernle et al., 2011
MC	0.003	0.007	Thirlwall 2002, Baker et al., 2004, Makishima et al., 2007, Makishima and Nakamura 2010,
TOF	0.099	0.854	Tian et al., 2000, Baker et al., 2004,
<b>QQQ (SQ)</b>	<b>0.185</b>	<b>0.134</b>	This work
QQQ (MS/MS)	0.254	0.563	This work

# Conclusion

- ▶ Agilent 8800 well-suited for determination of environmentally-useful Pb isotope variations
- ▶ Best precision is obtained using a high efficiency chemical purification
- ▶ No need for MS/MS as the improved sensitivity outweighs abundance sensitivity
- ▶ No need for NH<sub>3</sub> reaction gas to reduce <sup>204</sup>Hg as chemical separation removes Hg
- ▶ 8800 SQ mode was used as it produces the highest sensitivity
- ▶ Mass bias correction carried out using sample bracketing (using NIST 981)
- ▶ Results show very good consistency with the 'gold standard' ultra-high precision MC-ICPMS
- ▶ 8800 Pb isotope data are of research quality for environmental forensic and related studies

# Thank you for listening

## ▶ Acknowledgements

- ▶ GAU-Radioanalytical for provision of geochemical facilities and for co-funding the PhD
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- ▶ Agilent for a travel bursary to attend the Riso conference
- ▶ MSci collaborators (Alex Hatley and Callum Slade) who contributed to the Pb chemical separation

