

You've got to be Kelping Me! Determination of ^{129}I / ^{127}I in Kelp Samples using ICP-MS/MS

Nausheen Sadiq and Hakan Gürleyük

Proper thyroid function is crucial to the regulation of hormones, growth, and development. Iodine is an element that is essential to proper thyroid function. Many foods are naturally rich in iodine, kelp being one of them. ^{129}I is produced by the fission of uranium atoms during the operation of nuclear reactors and by plutonium (or uranium) in the detonation of nuclear weapons. Therefore, the concentration of ^{129}I and the ratio of ^{129}I to ^{127}I changes significantly depending upon the geographic region (10^{-11} to 10^{-2}). Accelerator mass spectrometry and instrumental neutron activation analysis are the most common analytical techniques for the determination of ^{129}I / ^{127}I , yet ICP-MS/MS offers certain advantages over these techniques.

Several samples of kelp were collected from local stores in Seattle, USA covering a range of source locations from China, Iceland, Japan, Korea, and the USA. Concentrations of iodine in these samples ranged from 58-5600 mg/kg. The ICP-MS/MS instrument was optimized to achieve the highest signal for iodine while keeping the ^{129}I background at the minimum. At the optimal conditions, different iodide and iodate standards obtained from the USA consistently provided $^{129}\text{I}/^{127}\text{I}$ between 7×10^{-11} and 2×10^{-10} . Due to the high sensitivity of the ICP-MS/MS instrument, $^{129}\text{I} / ^{127}\text{I}$ as low as 10^{-11} can be measured in sample solutions containing as little as 20 ppm iodine in only 10 minutes. Lower concentrations of iodine in some kelp samples required preconcentration before analysis. A method was developed in order to convert over 90% of the iodine in the kelp samples into the form of iodide. This allowed for these samples to be coupled to an ion chromatography system which was used for the on-line preconcentration of iodine. Results from different kelp samples are presented along with a discussion of challenges related to obtaining accurate $^{129}\text{I}/^{127}\text{I}$ using different ICP-MS technologies.



You've Got to be Helping Me!

Iodine 129 in Various Kelp Samples
Nausheen Sadiq and Hakan Gürleyük

The Importance of Iodine

- Iodine is essential for the proper functioning of the thyroid
- A lack of iodine in the body can lead to goiter
 - This can cause developmental delays in children as well as several other health problems in adults
- Many foods can be consumed that have high levels of iodine
 - Salt commonly contains iodine

Analyzing Iodine with ICPMS

- ICP-MS is the most widely used analytical technique for iodine analysis [1]
- Iodine ($I_{2(g)}$) is volatile and can be analyzed in more stable forms such as Iodide (I^-) and Iodate (IO_3^-)
 - A basic medium is preferential over acidic to stabilize iodide and iodate
- Iodine analysis has been conducted using a dynamic reaction cell (DRC)
- BAL has access to 10 instrument = FUN!

[1] Moreda-Pineiro, A. et al. (2011) **26**, 2107-2152.

Why Kelp?

- Kelp is a type of seaweed that is readily being consumed in various forms
 - Powder
 - Sheets
 - Sushi
- Previous studies have shown ranges between 1 and 12000 mg/kg of I in Kelp often surpassing the daily suggested intake of 150 mg/kg [2]

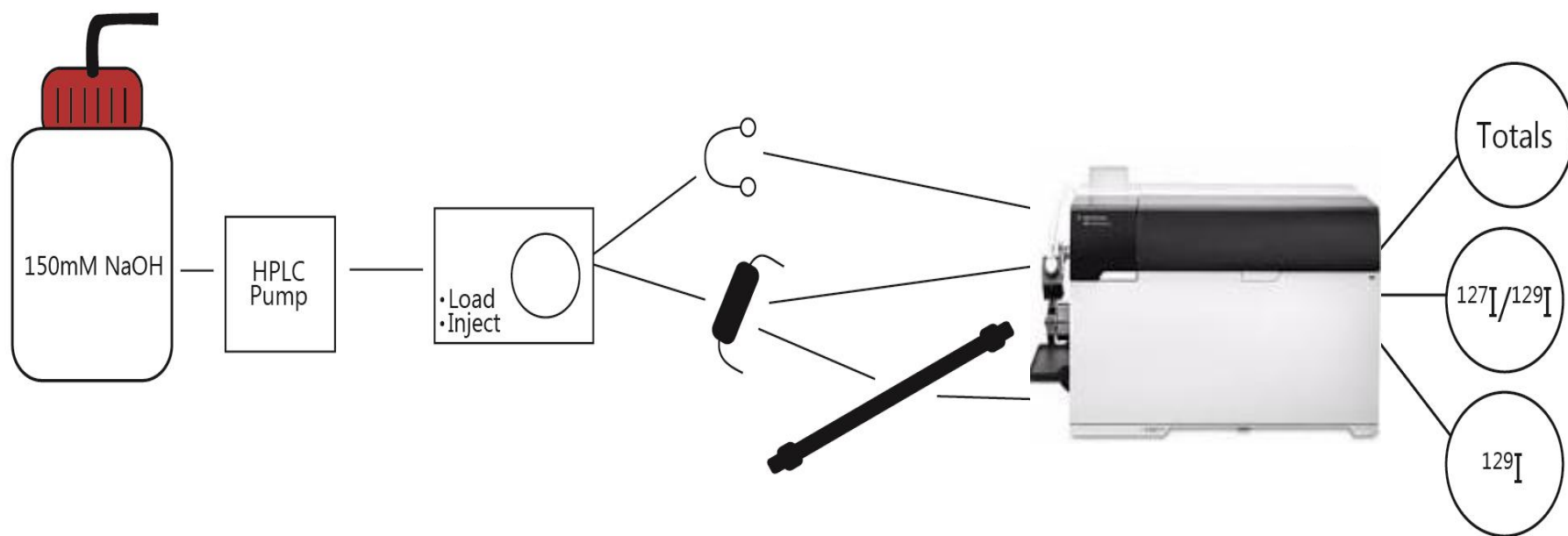


[2] Dietary Reference Intakes (DRIs), Food and Nutrition Board, National Academics (www.nap.edu)

#Goals

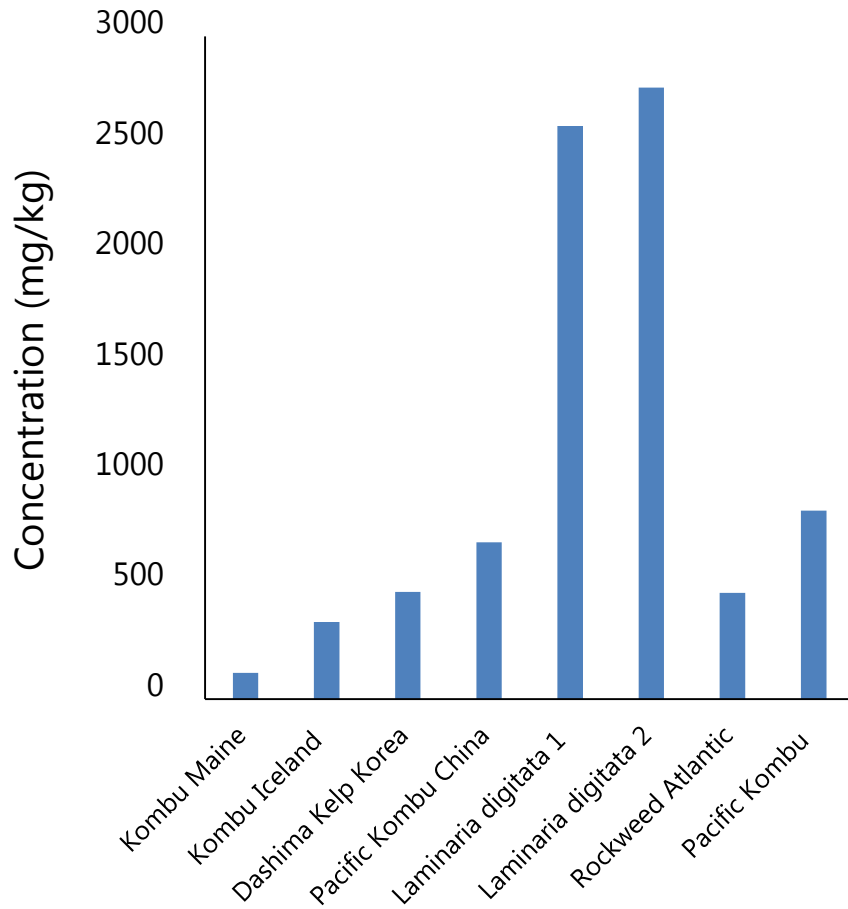
1. Totals analysis – using DRC and QQQ
 - What is in our samples?
2. Iodide vs total I
 - Does form matter?
3. $^{129}\text{I}/^{127}\text{I}$
 - Optimization is essential!
4. ^{129}I
 - How low can we go?
 - Is this an indicator for sample location?

Experimental Setup

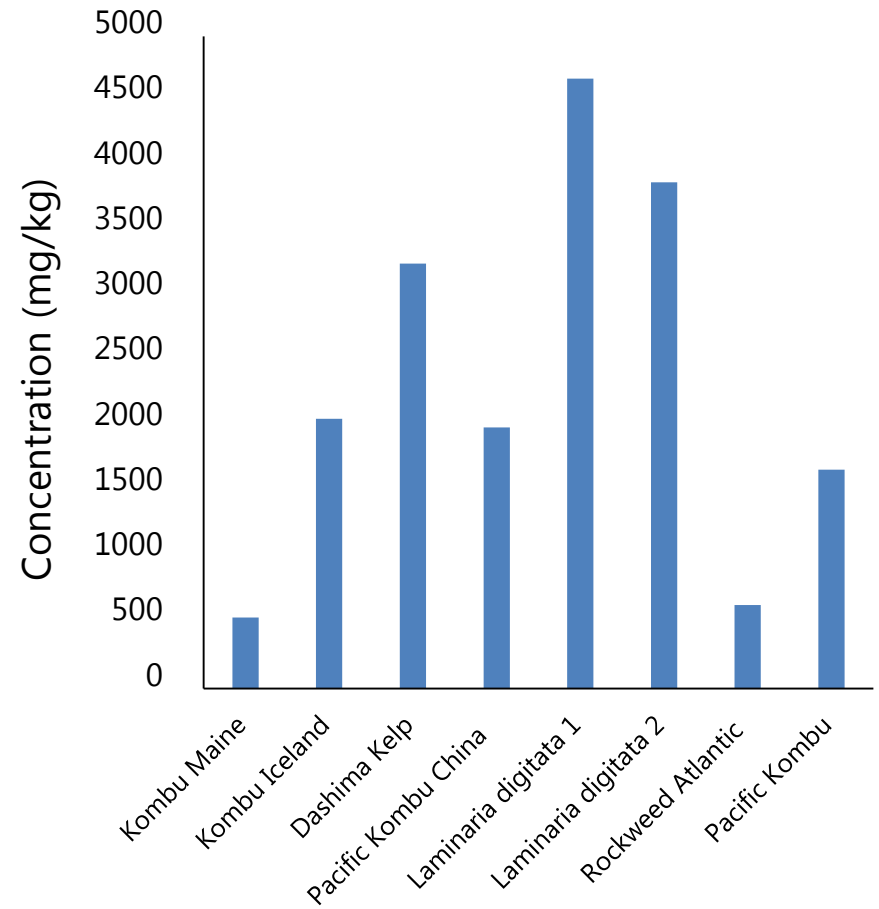


TMAH Extraction Results

16 Hour Cold Digest



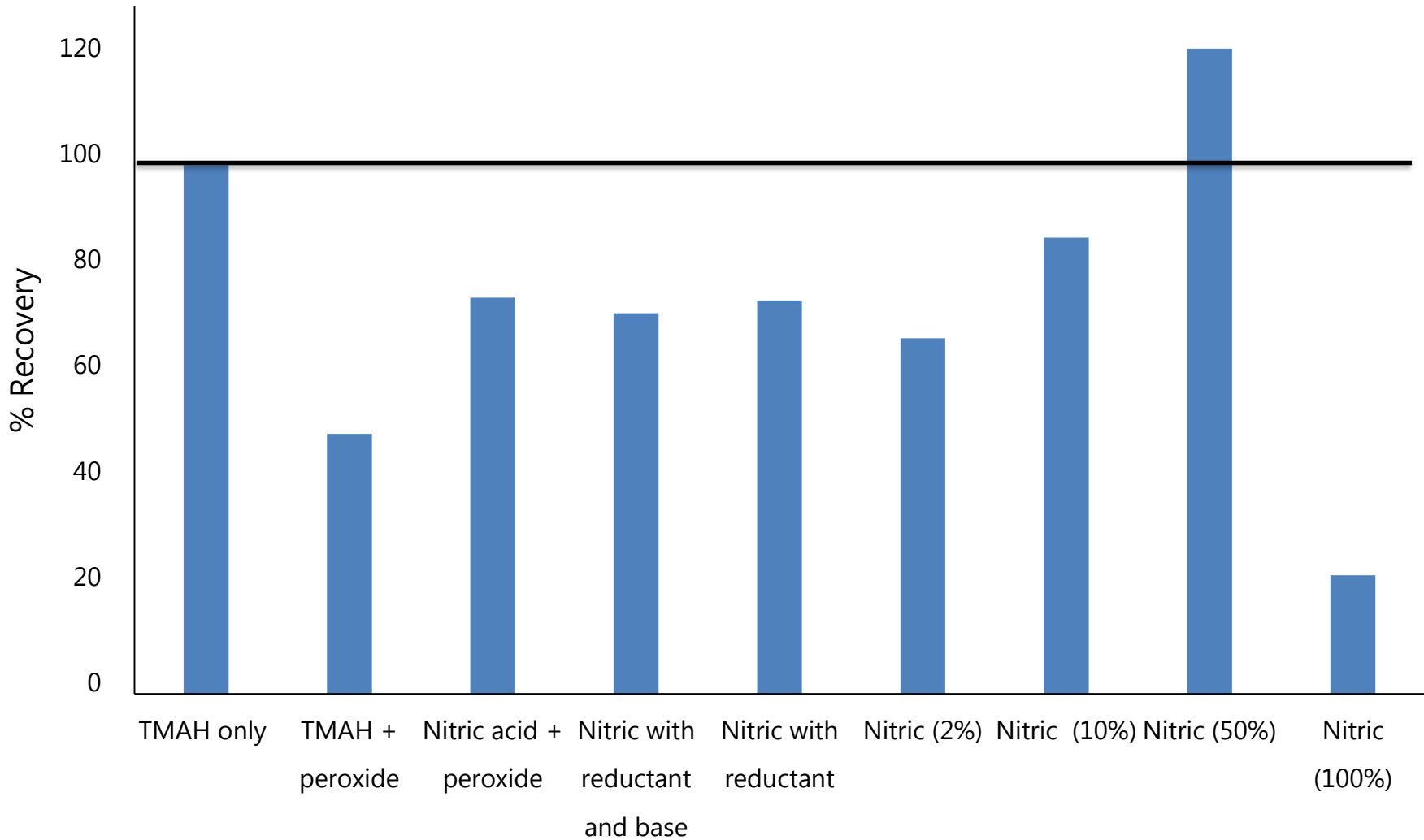
MW TMAH Digest



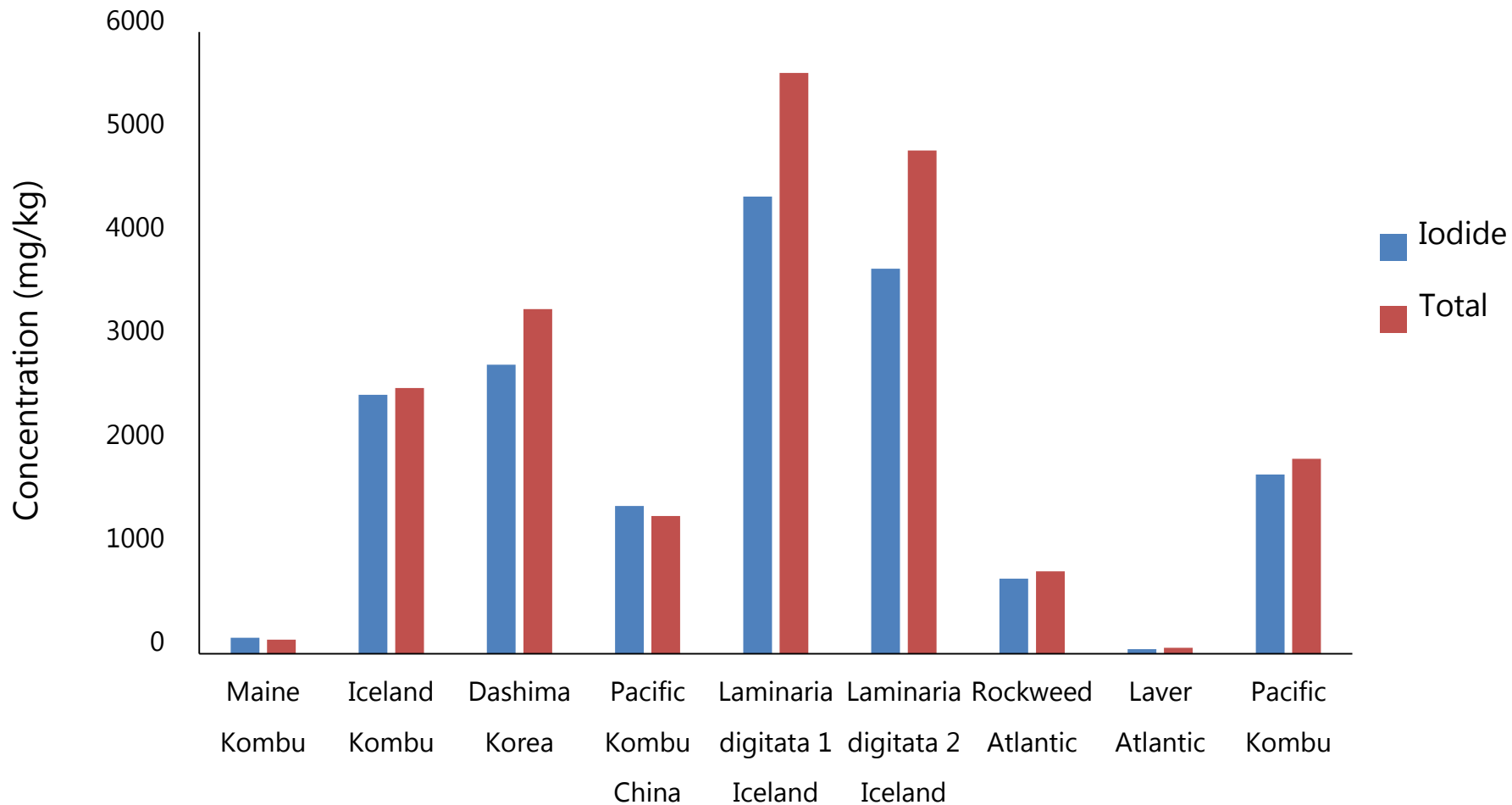
Does Form Really Matter?

- Speciation analysis of TMAH digest showed majority of I in organic forms
- Several methods were tested in order to breakdown I from organic bonds
- Conversion to a single and stable form will allow for enhanced sensitivity
- An anion exchange column with a high capacity for iodide could allow for the high signal required for this form of analysis

Kelp Digestion Analysis



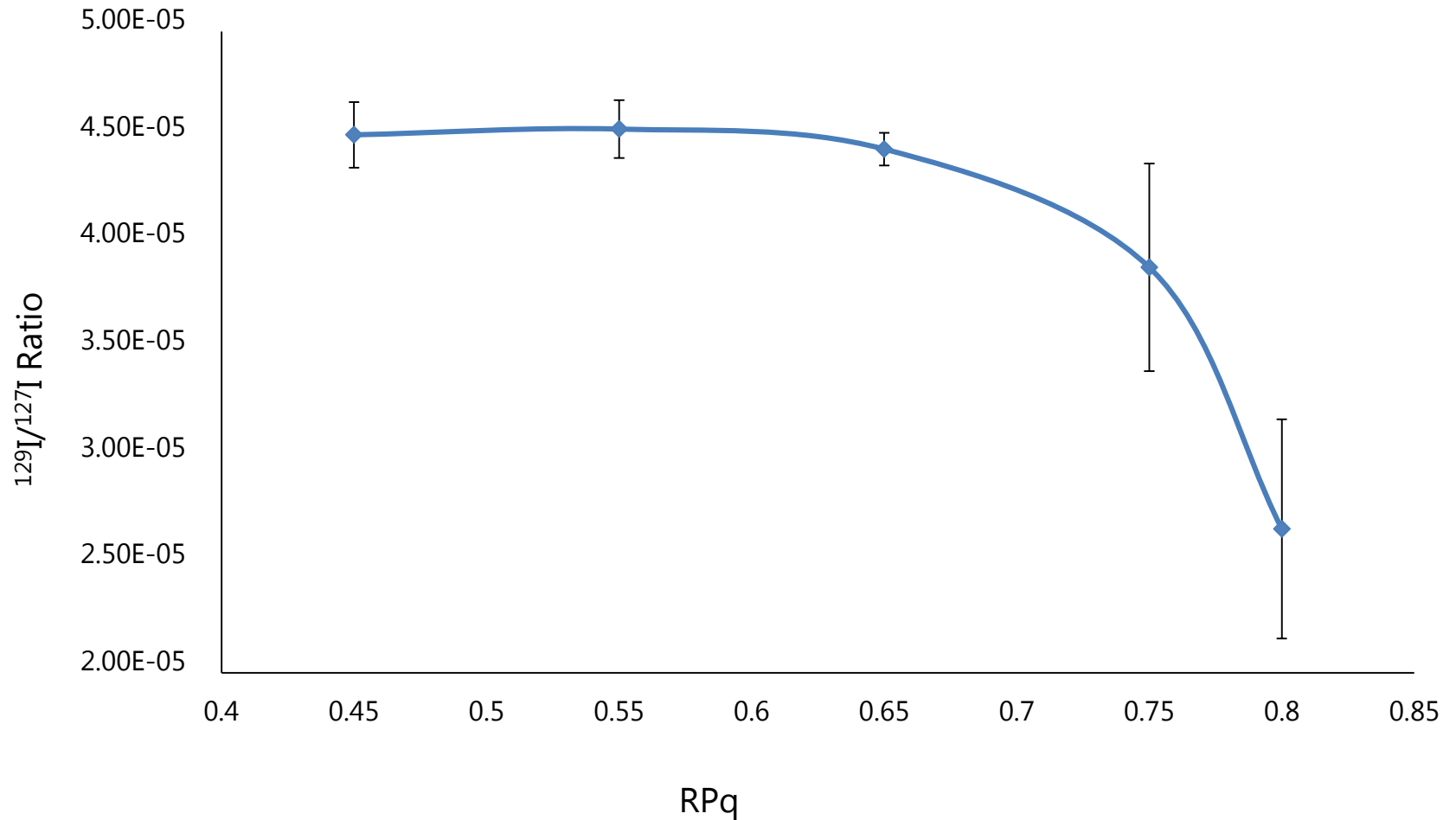
Iodide vs total I



Isotope Ratios and ^{129}I

- Isotope ratios can be a great insight into geographical location of samples
- Past studies have shown the importance of ^{129}I analysis in areas after nuclear power plant explosions
- To correctly study isotope ratios, high sensitivity and low background are critical
- DRC allows for RPq optimization
- When using QQQ, axial acceleration provides the equivalent parameter

DRC Isotope Ratio Optimization



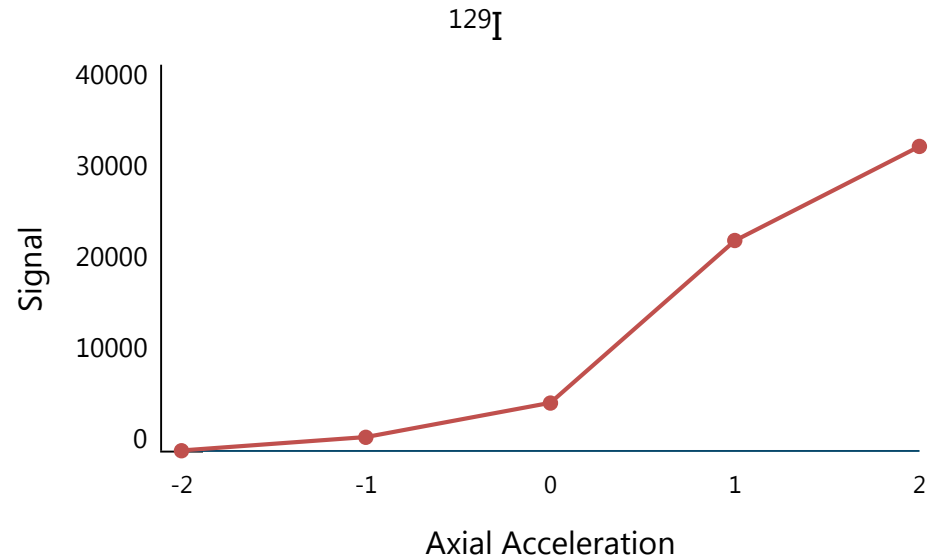
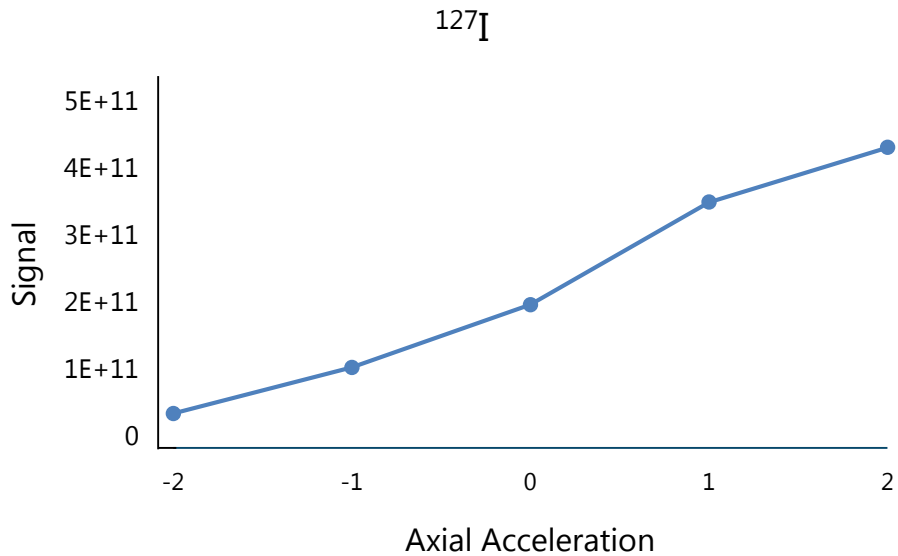
Isotope Ratio Optimization

- Several parameters can be optimized in order to enhance sensitivity while keeping background signal low
- AFT, He gas flow, O₂ gas flow have been focused on
 - Diluents and flow rate were also compared and optimized

Optimization Parameters

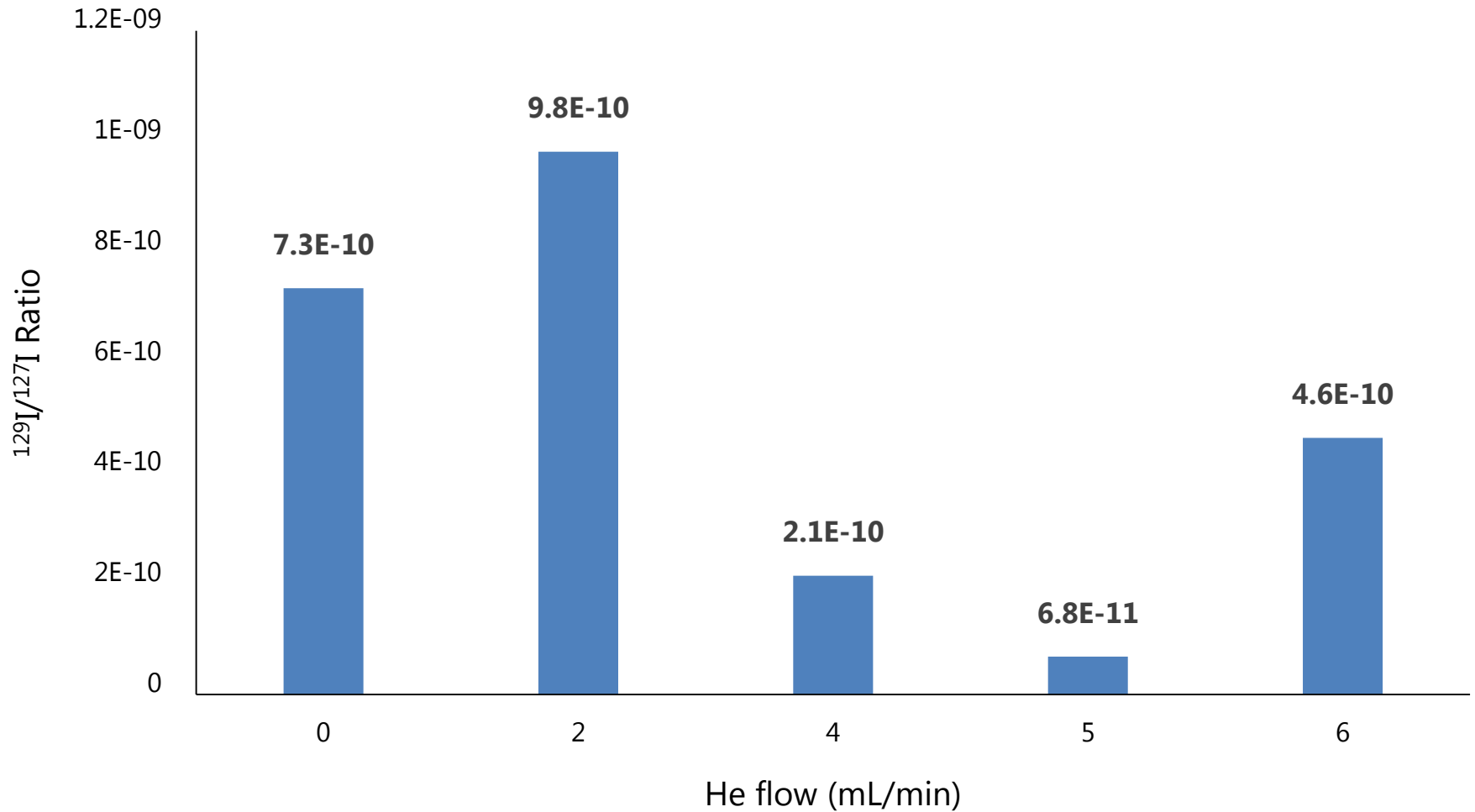
- Axial Field Technology (AFT)
 - Range: -2 to +2
- He Gas
 - Range: 0 to 6 mL/min
- Oxygen Gas
 - Range: 80 to 100%

Axial Field Technology (AFT)

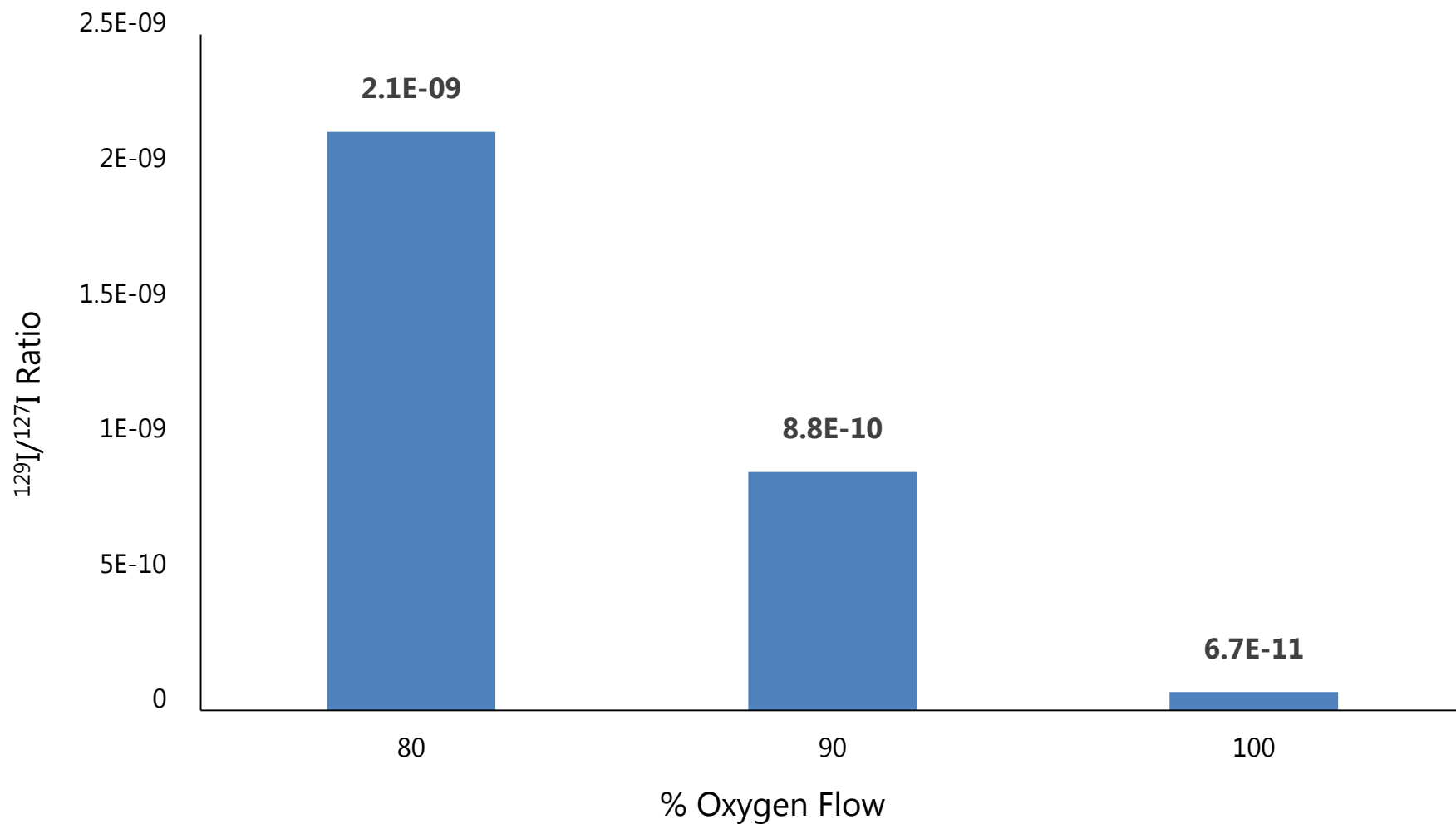


- As sensitivity increases for ^{127}I (left), background signal for ^{129}I increases as well (right)

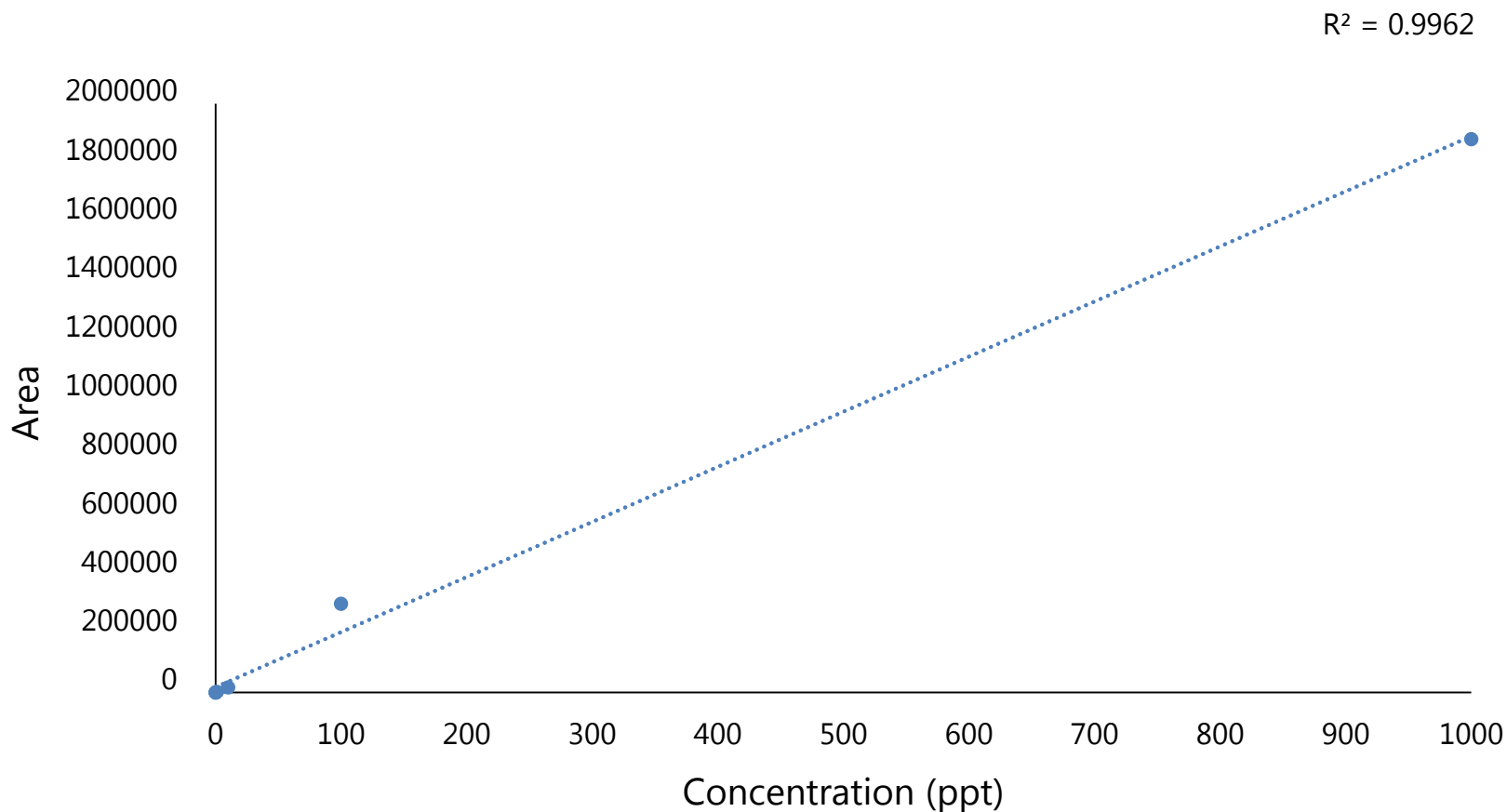
He Gas Flow



O₂ Gas Flow



How low can we go?

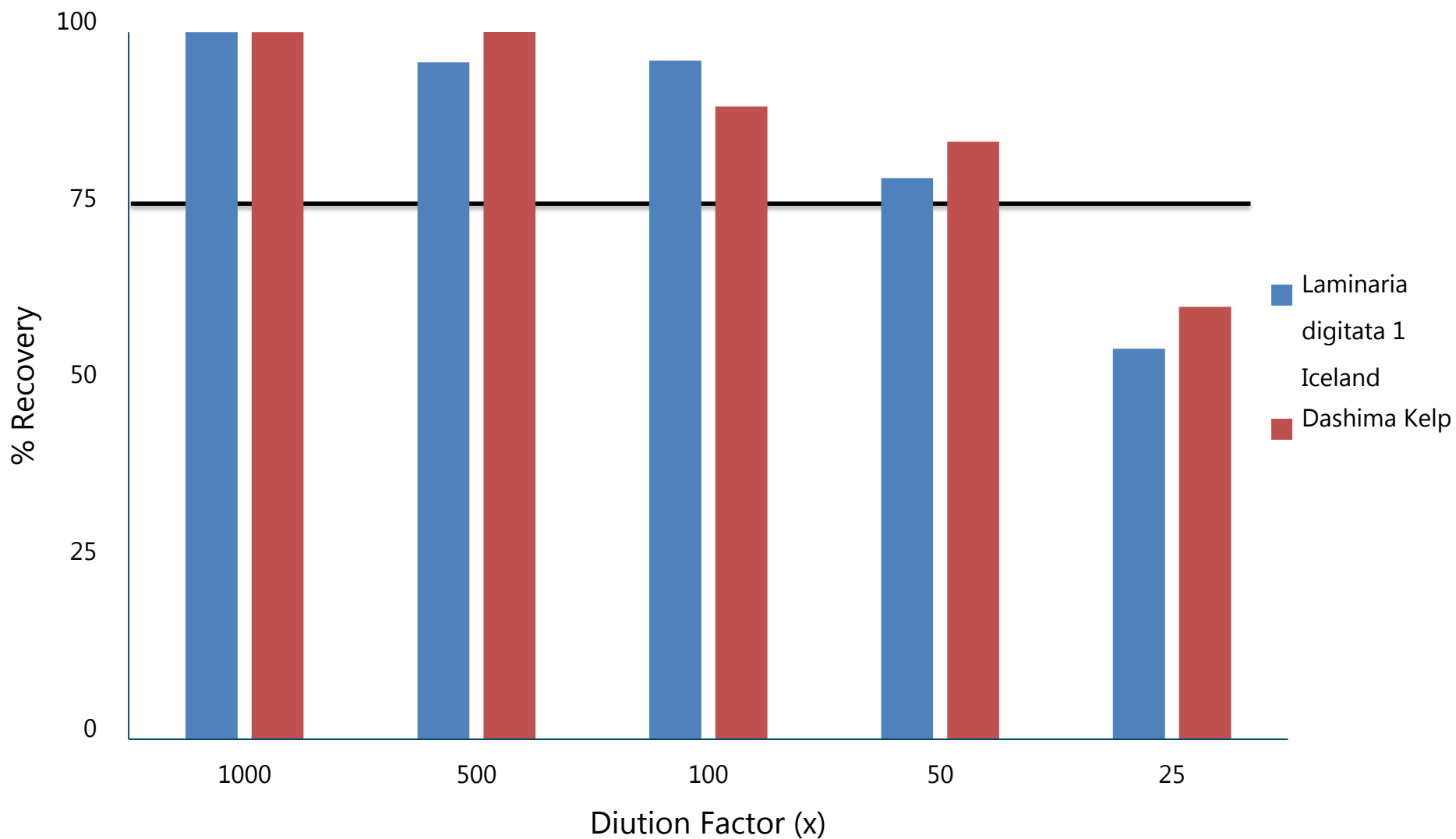


- Calibration curve ranges from 10 ppq to 1 ppb

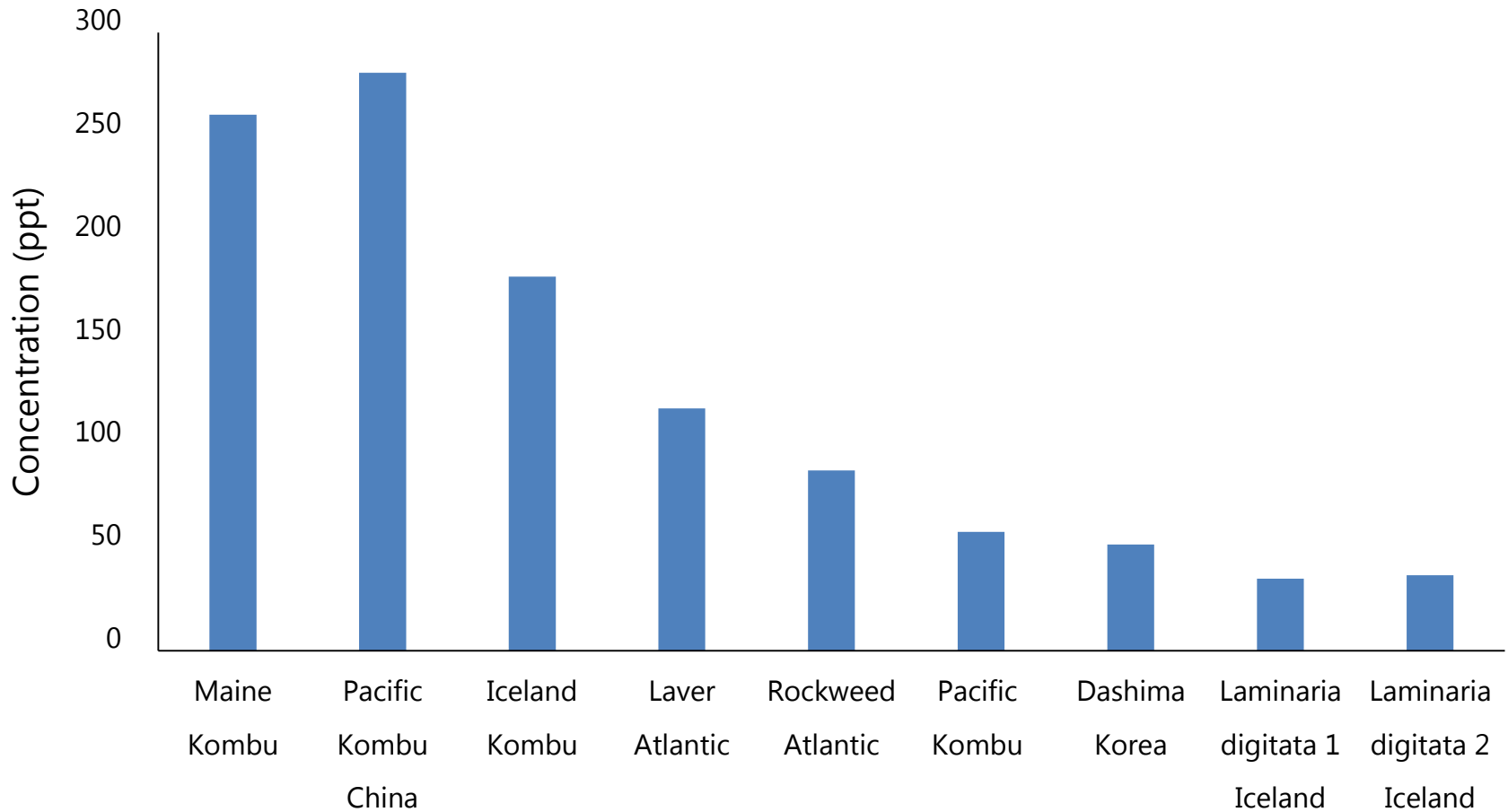
^{129}I in Kelp

- Test sample at various dilutions while running ^{129}I spike
- Test at what dilution the matrix effects drop ^{129}I recoveries outside 75-125% recovery
- 1000x, 500x, 100x, 50x and 25x were tested for two samples with high levels of ^{127}I
- The goal is to introduce the highest concentration of sample with the least amount of matrix effects

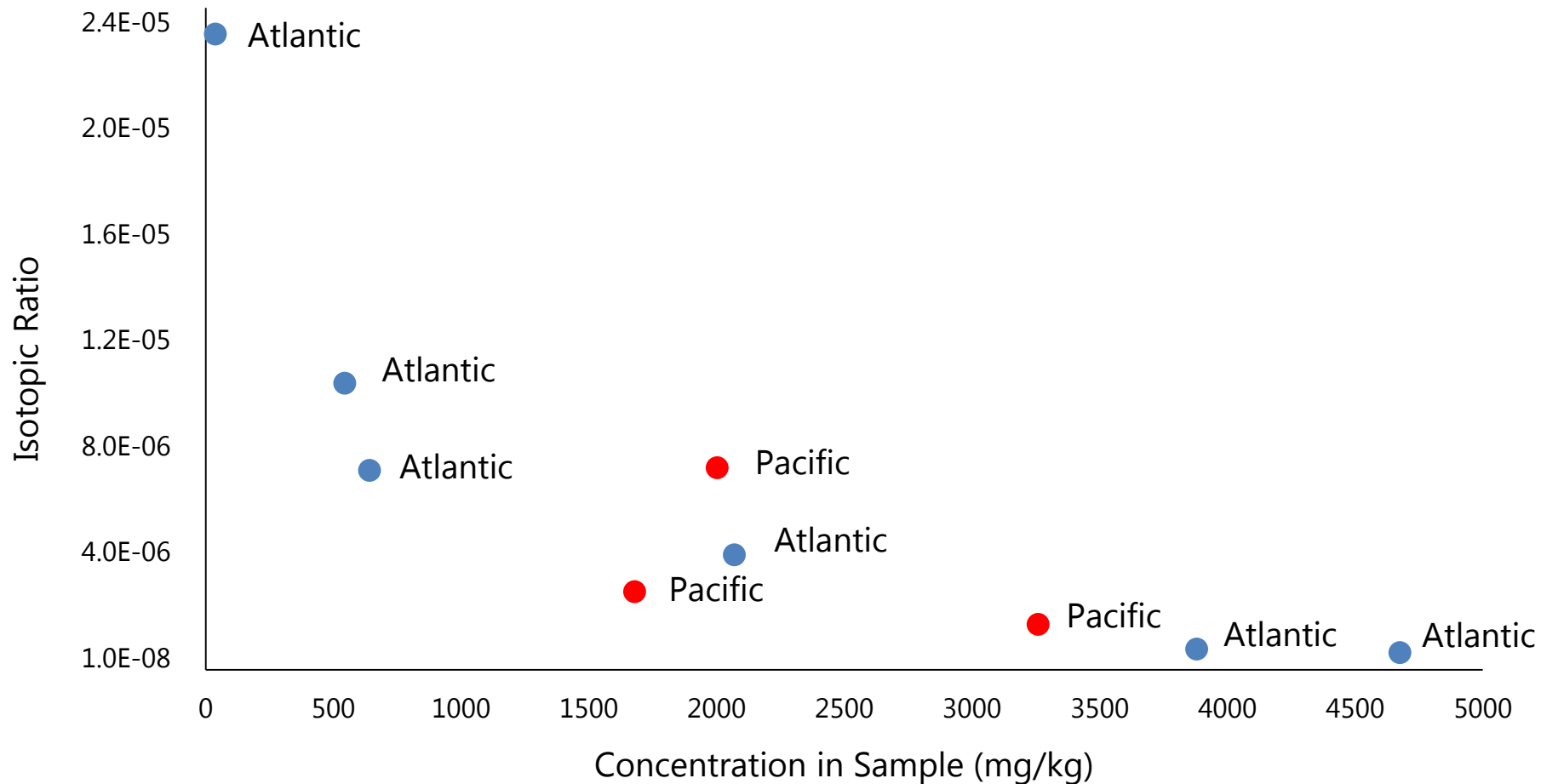
Matrix Effects on ^{129}I



^{129}I in Kelp Samples



Isotopic Ratios in Kelp



Conclusions

- We were able to successfully conduct isotope ratio analysis of I using an Agilent 8900 QQQ
- The Agilent QQQ was seen to be beneficial to remove interferences
- Isotope ratios could get down to 10^{-11} with 100 ppm I standards
- ^{129}I calibration can go to ppq levels

Future Work

- Increase the number of samples studied from varying locations from around the world
- Use mass profiler for source identification considering factors such as species, concentration and isotope ratio

Questions?

