Stable isotope deltas: Natures own traceability system for verifying food authenticity

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Food Fraud - Definition

- The UK Food Standards Agency states food fraud has occurred "..when food is deliberately placed on the market, for financial gain, with the intention of deceiving the consumer".
- The Overarching EC requirements intended to ensure consumers are not misled are the Food Labelling Directive 2000/13, Article 2, which requires that food labelling must not mislead the purchaser to a material degree, particularly:
    - (i) as to the characteristics of the foodstuff and, in particular, as to its nature, identity, properties, composition, quantity, durability, origin or provenance, method of manufacture or production.

High profile examples...

Tests take buzz out of manuka

Jonathan Leake
Science Editor

MANUKA honey, an increasingly popular yet costly health supplement, is at the centre of an international food fraud investigation amid evidence that much of it is fake.

The Food Standards Agency (FSA) has issued a nationwide alert to all trading standards departments asking them to watch out for honey that has been labelled as manuka but is derived from other sources.

Manuka honey, which sells for up to £45 for a 500g jar, has been praised by sports stars and celebrities such as Katherine Jenkins, the classical singer, Scarlett Johansson, the actress, and Novak Djokovic, the world No 1 tennis player.

Tests carried out by the Food and Environment Research Agency (Fera), the scientific arm of Defra, the environment and food ministry, along with overseas studies suggest that much of the honey labelled as manuka has nothing to set it apart from ordinary honey — except the price.

Research by the main honey producers' organisation in New Zealand — from where almost all the world's manuka honey comes — revealed that 1,700 tons of manuka are produced there each year, compared with the estimated 1,800 tons of "manuka" honey sold in the UK alone. As much as 10,000 tons are sold worldwide, suggesting widespread fraud.

John Rawcliffe of the Unique Manuka Factor Honey Association (UMFHA), which represents New Zealand's producers, said: "There is potentially huge fraud. There are higher and ever-increasing volumes of honey labelled as manuka that are not manuka. More manuka is sold in the UK alone than the total actually produced. The same applies to China, America and so on."

Manuka users: Novak Djokovic

Scarlett Johansson

Manuka honey is produced by bees whose hives are placed near flowering wild manuka bushes that grow mostly on New Zealand's North Island. Until 1981, when a New Zealand scientist found it had powerful anti-microbial properties, it was classed as a low-grade honey and used in cattle feed.

In October 2011 Fera tested five brands of manuka honey sold in the UK. Only one showed the "non-peroxide" anti-microbial activity that is unique to genuine manuka honey. In further tests of 23 manuka-labelled honeys, 11 failed the non-peroxide test.

The UMFHA commissioned more tests in 2012 and also this year in Britain, China and Singapore. Of 73 samples tested, 41 showed no non-peroxide activity. Separate tests in Hong Kong found that of 55 manuka honeys sampled, 14 had been adulterated with syrup.

The FSA said all trading standards authorities had been "asked to make sure anyone selling manuka honey is aware that they must fully comply with the law".

Sterilised manuka has been shown to help skin to heal when used in wound dressings. However, there is no clinical evidence that eating manuka honey aids health.

Despite this it has enjoyed soaring popularity — and sales — thanks to clever marketing and its use by celebrities. For example, Jenkins says it helps to prepare her throat for performances and Djokovic praises manuka honey in Serve to Win, his book about his diet. Johansson says she uses manuka beauty products on her skin, so she may benefit — if the honey is genuine manuka.

The success of manuka means New Zealand honey farmers now use helicopters to seek out clumps of the bushes and, when they are found, drop hives alongside them. With 1,800 beekeepers operating 100,000 hives there is intense competition for the best spots.

Since other plants grow with manuka and bees forage on them, too, there is no knowing how pure manuka honey really is. Such problems provide opportunities for fraudsters and undermine public trust in genuine producers.

Patrick Robinson, chairman of the British Honey Importers and Packers Association and operations director at Rowse Honey, the UK's largest honey producer, said: "Consumers' confidence in the authenticity was a concern. "Every batch of our honey is tested and labelled properly," he said.

Critics claim that labelling is another area where the industry is letting consumers down. The absence of agreed standards means there are at least four complex systems for describing manuka's anti-microbial potency.

Holland & Barrett, the health food chain, stocks a variety of manuka honeys, each with different ways of describing the supposed anti-microbial potency.

For example, a 500g jar of Manuka Doctor honey priced at £22.55 is labelled as "12+ active", described as a measure of the "naturally occurring peroxide activity". A 500g jar of Manuka Pharm honey costing more than £30 was labelled as "30+ total activity", also described as a measure of peroxide activity.

Separately, however, a 250g jar of Pure Gold honey costing £12.69 was labelled as "active 12+", described as "a measure of the total phenol activity". None of the three products provided a measure for the non-peroxide activity unique to manuka.

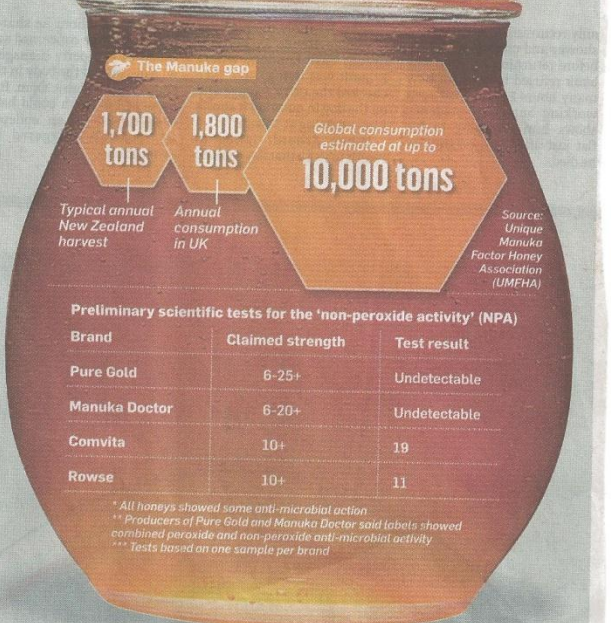
Holland & Barrett said the

LEW ROBERTSON/ LAUREN BURKE

Most honeys have an antibacterial action known as their 'peroxide activity'

Genuine manuka honey, almost all of which comes from NZ, has a unique, additional antimicrobial action, known as its 'non-peroxide activity'

A bee collecting pollen from manuka flowers



Preliminary scientific tests for the 'non-peroxide activity' (NPA)

Brand	Claimed strength	Test result
Pure Gold	6-25+	Undetectable
Manuka Doctor	6-20+	Undetectable
Comvita	10+	19
Rowse	10+	11

* All honeys showed some anti-microbial action
** Producers of Pure Gold and Manuka Doctor said labels showed combined peroxide and non-peroxide anti-microbial activity
*** Tests based on one sample per brand

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Information Delivered by IRMS

Precise Isotope Ratios of:

Element	Minor Isotope	Natural Abundance [%]
• Hydrogen	^{2}H	0.01557
• Carbon	^{13}C	1.11140
• Nitrogen	^{15}N	0.36630
• Oxygen	^{18}O	0.20004
• Sulfur	^{34}S	4.21500

This is where the information is

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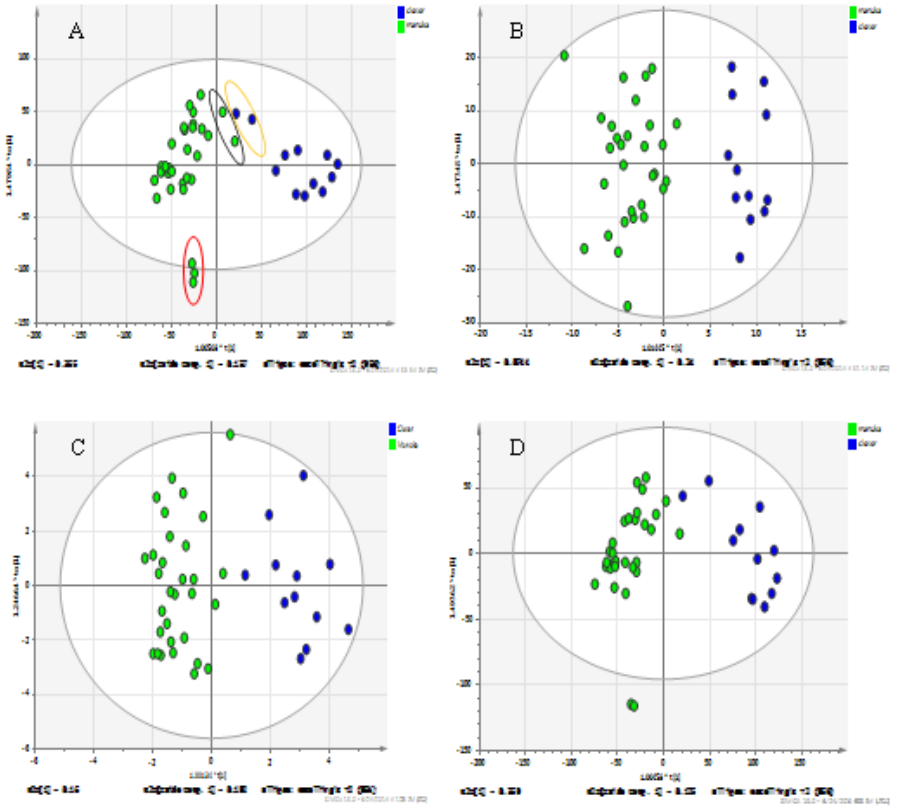
Forensic Isotope Ratio Mass Spectrometry (FIRMS)

- Isotope fingerprinting
- Conventional chemical analysis – identification and quantification.
- IRMS - determine relationships or pathways
- **Isotopic composition is unique to the origin and history of the substance**

Batch Testing

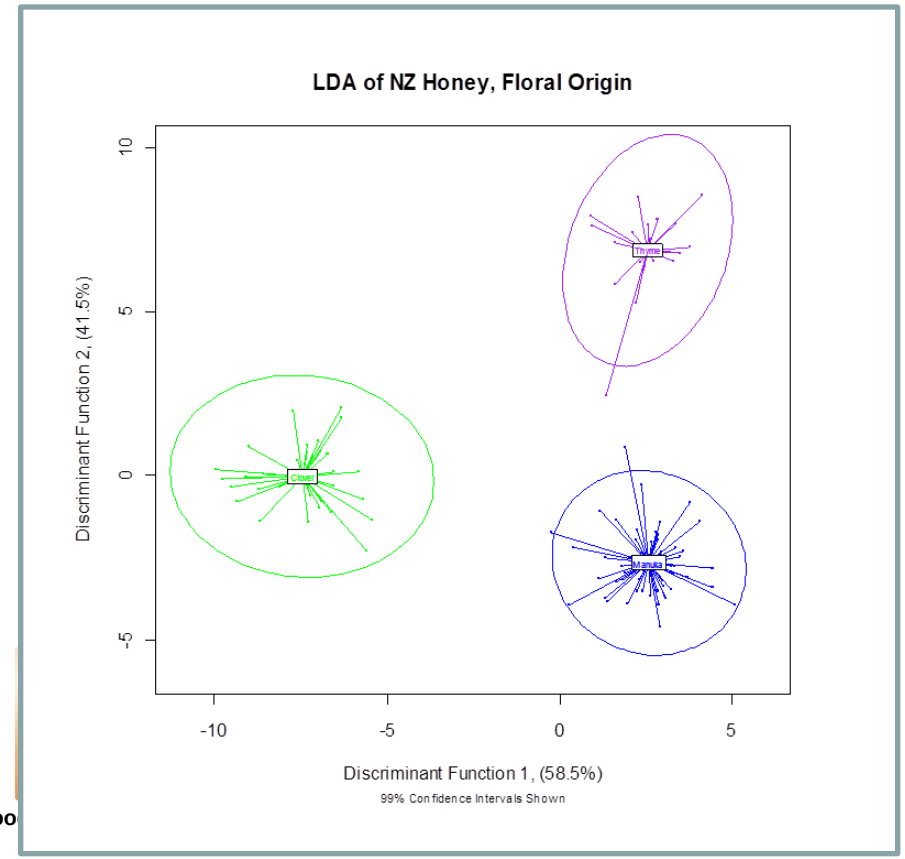
- Collect authentic samples
- Measure number of parameters (e.g. stable isotopes, trace elements, metabolites)
- Define specifications using multivariate analysis



Batch Testing

Pro's

- Can be very robust



Con's

- Expensive to collect the authentic samples/data
- Need to sample variability
- Only applicable to samples related to the training set
- Need for seasonal resampling
- Not predictive
- High level of analytical expertise

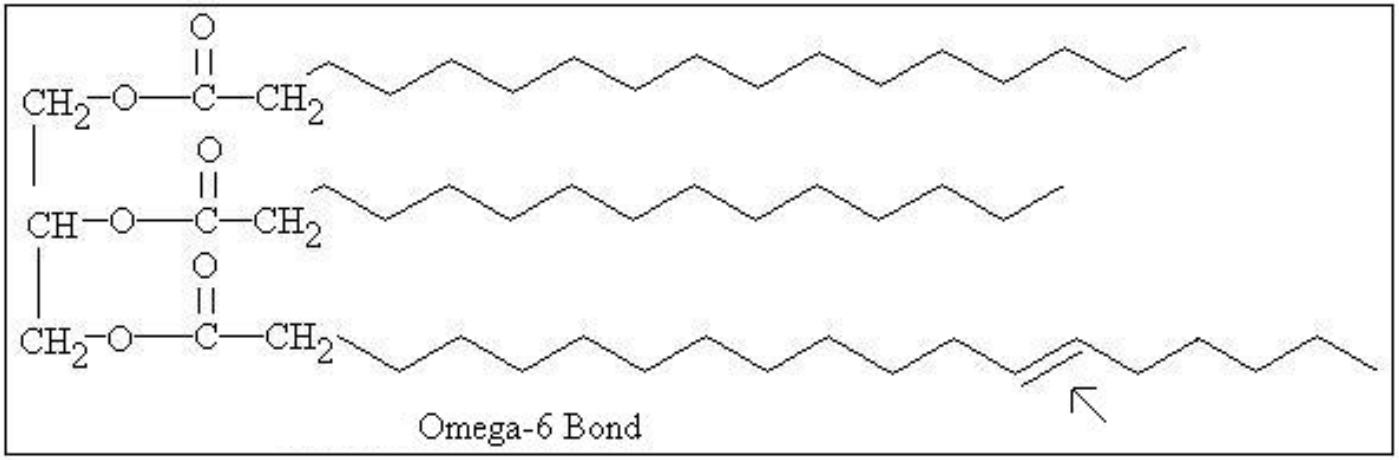
New Zealand Dairy Milk

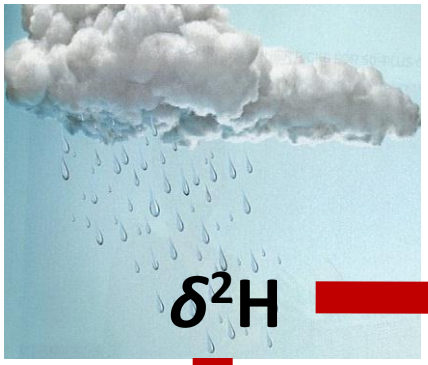
- New Zealand is capable of drying 40 million liters quality milk on a daily basis

- A good target for fraud
  - Globally known for it's quality
  - Used as an ingredient in sensitive products (e.g. infant formula)
  - Significant amount of milk powder traded on spot market

Milk composition

- 88% water
- 5% carbohydrates
- 3% protein
- ~1% minerals
- 3% fat (98% triglyceride)





δ^2H, $\delta^{13}C$, $\delta^{15}N$

δ^2H, $\delta^{13}C$, $\delta^{15}N$

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Location of dryers

- Milk powder collected from each dryer during November
- Milk originated from dairy farms within a 50 km radius of the dryer
- Samples collected as anhydrous milk powder

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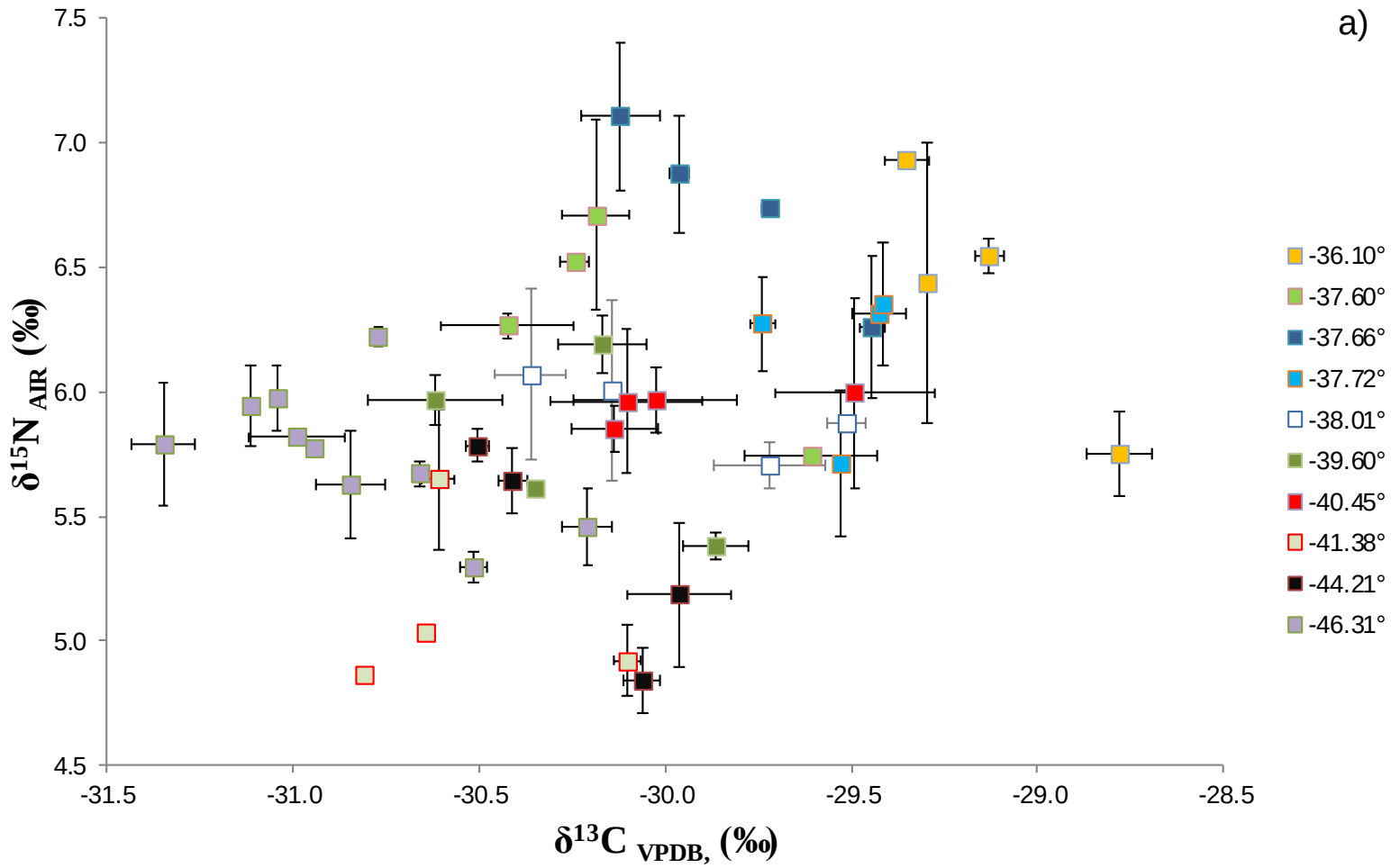

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Ehteshamrad E., et al., 2013. *Journal of Agricultural and Food Chemistry*, http://dx.doi.org/10.1021/jf4024883

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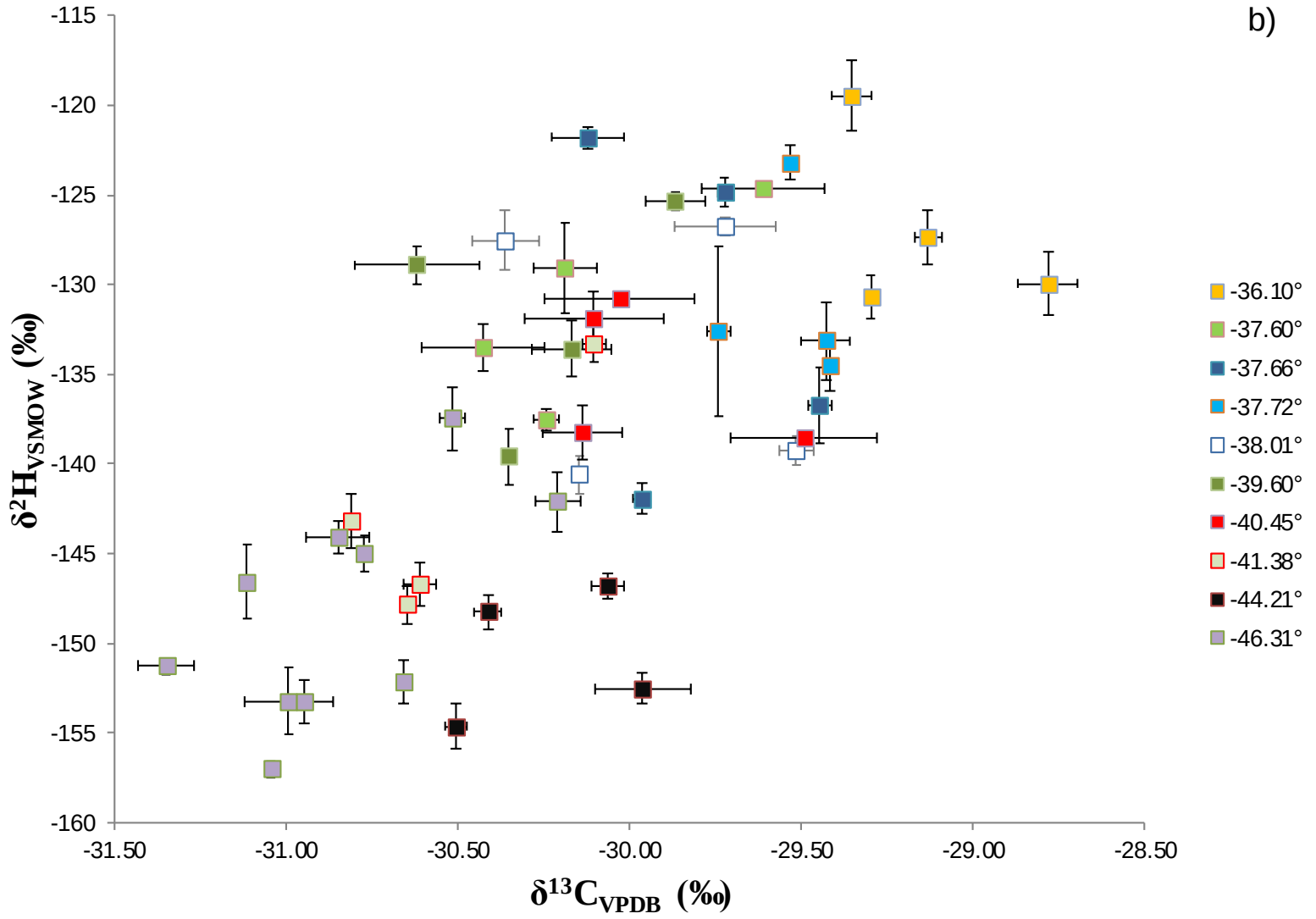

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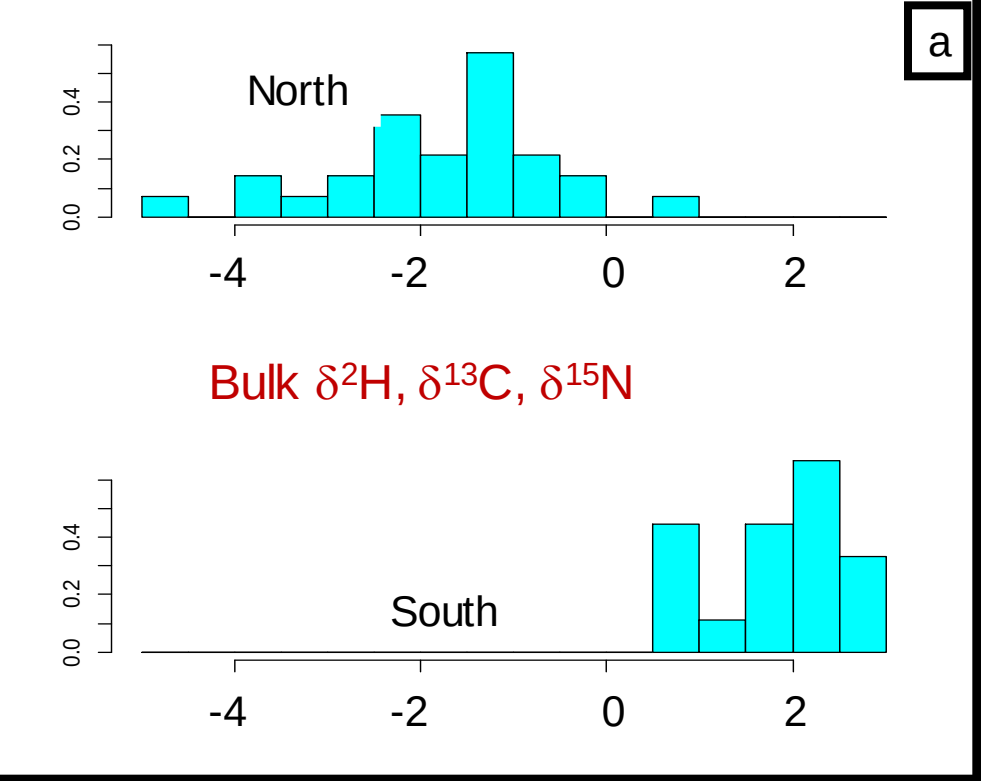
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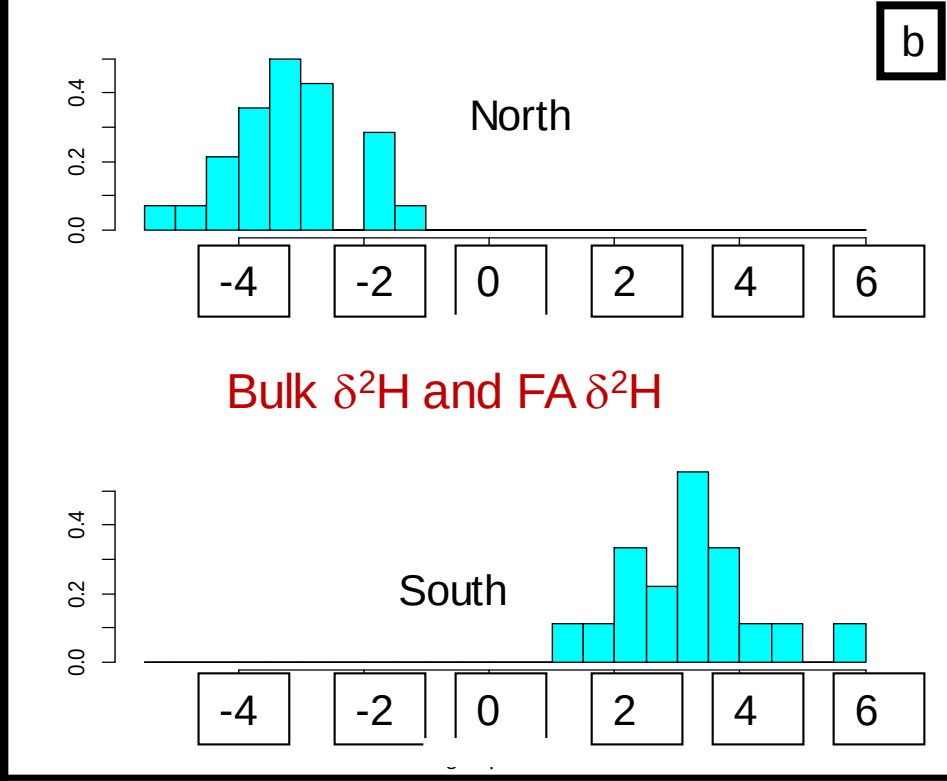
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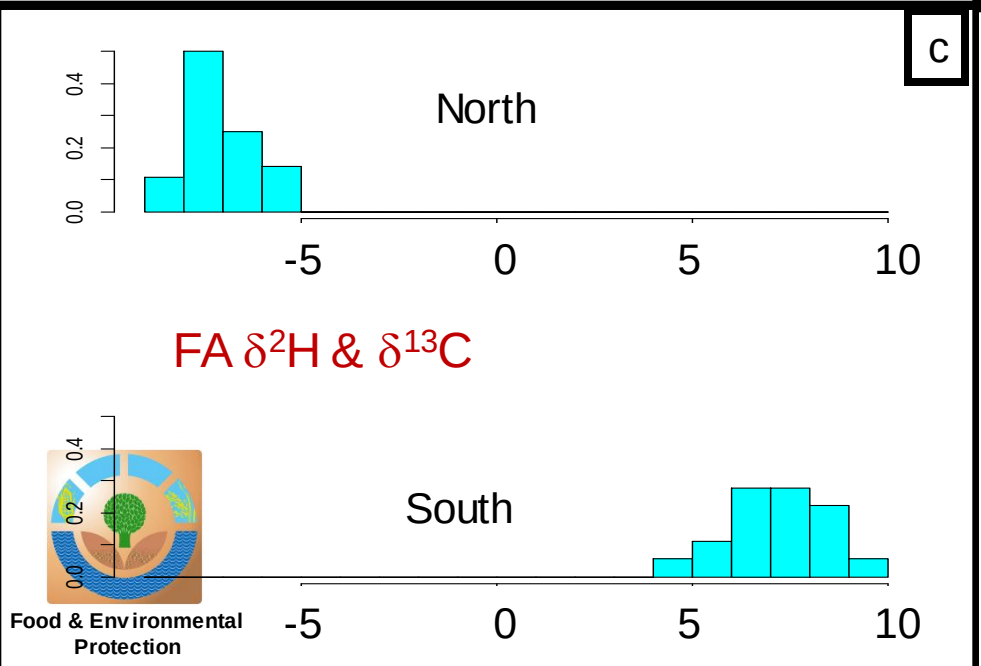
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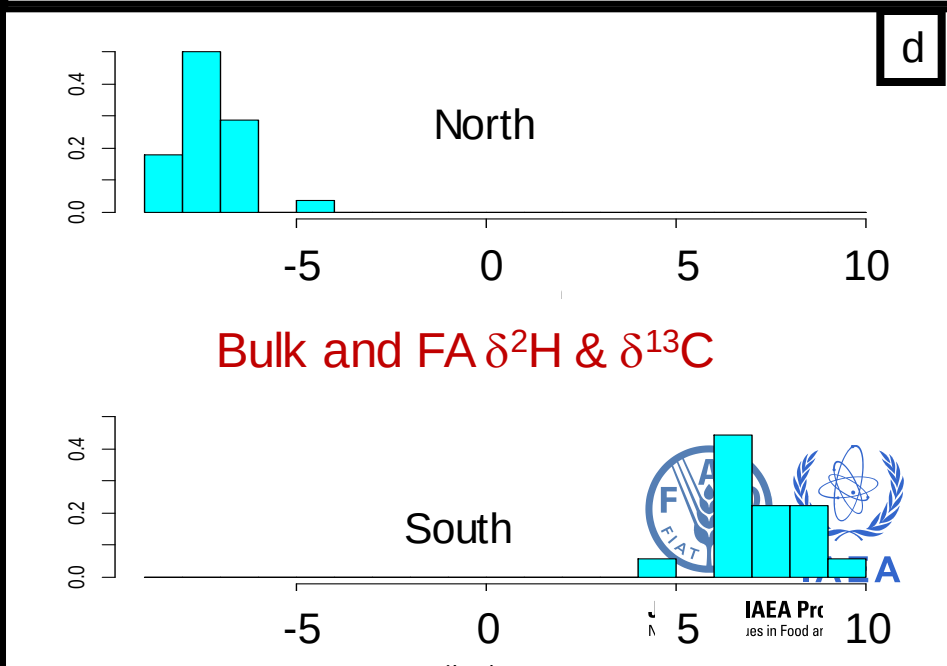
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Barriers to Entry

Despite many studies that demonstrate its usefulness, there has been very limited uptake of this technology to date. The reasons for this include:

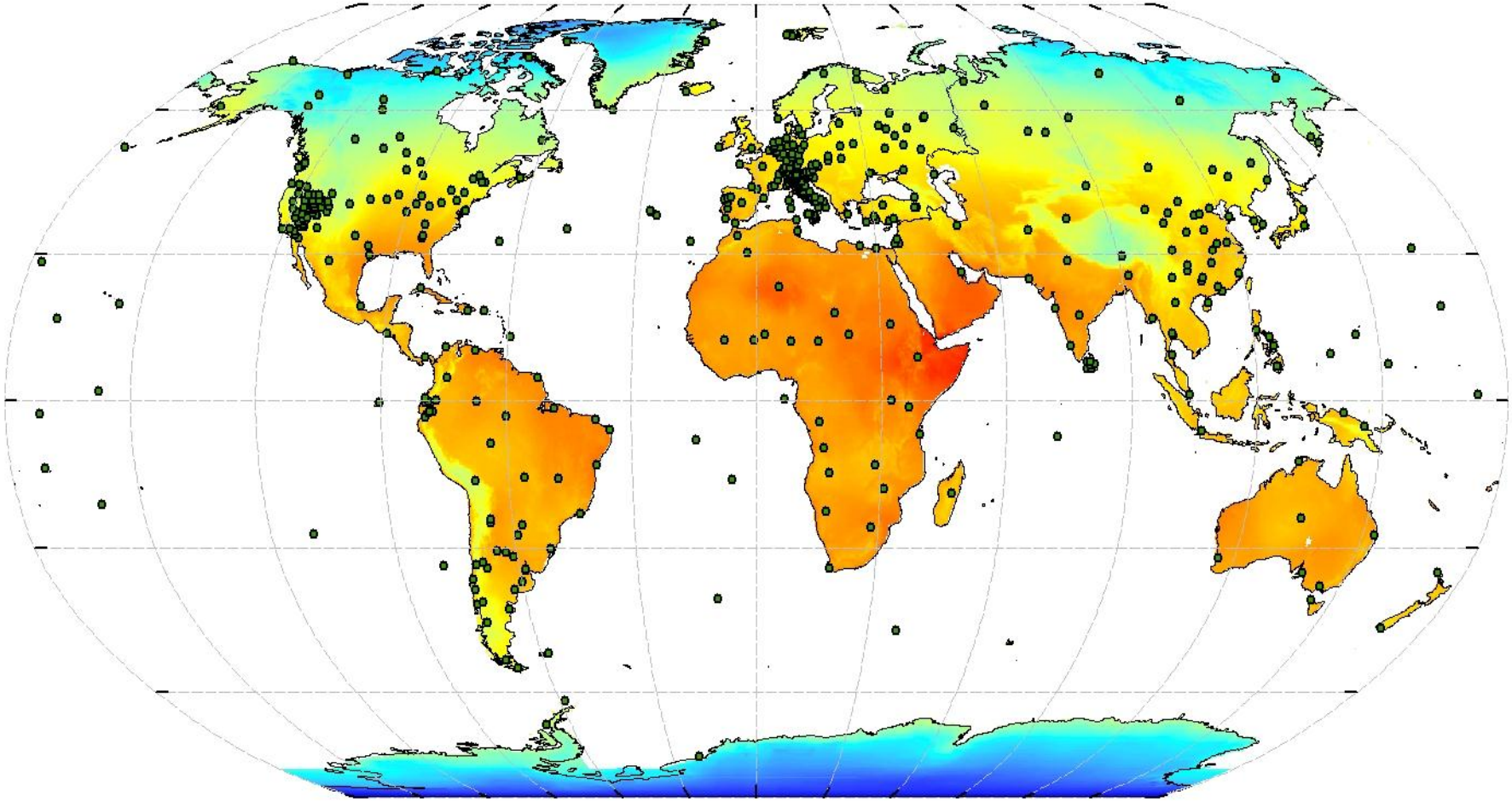
- The high cost to entry (background information)
- The interpretation of the data and the level of certainty attainable (accessible multi-variate and spatial data analysis tools)
- Awareness (acceptance)
- The bespoke nature of the technology requires a high level of expertise for implementation

An alternative approach

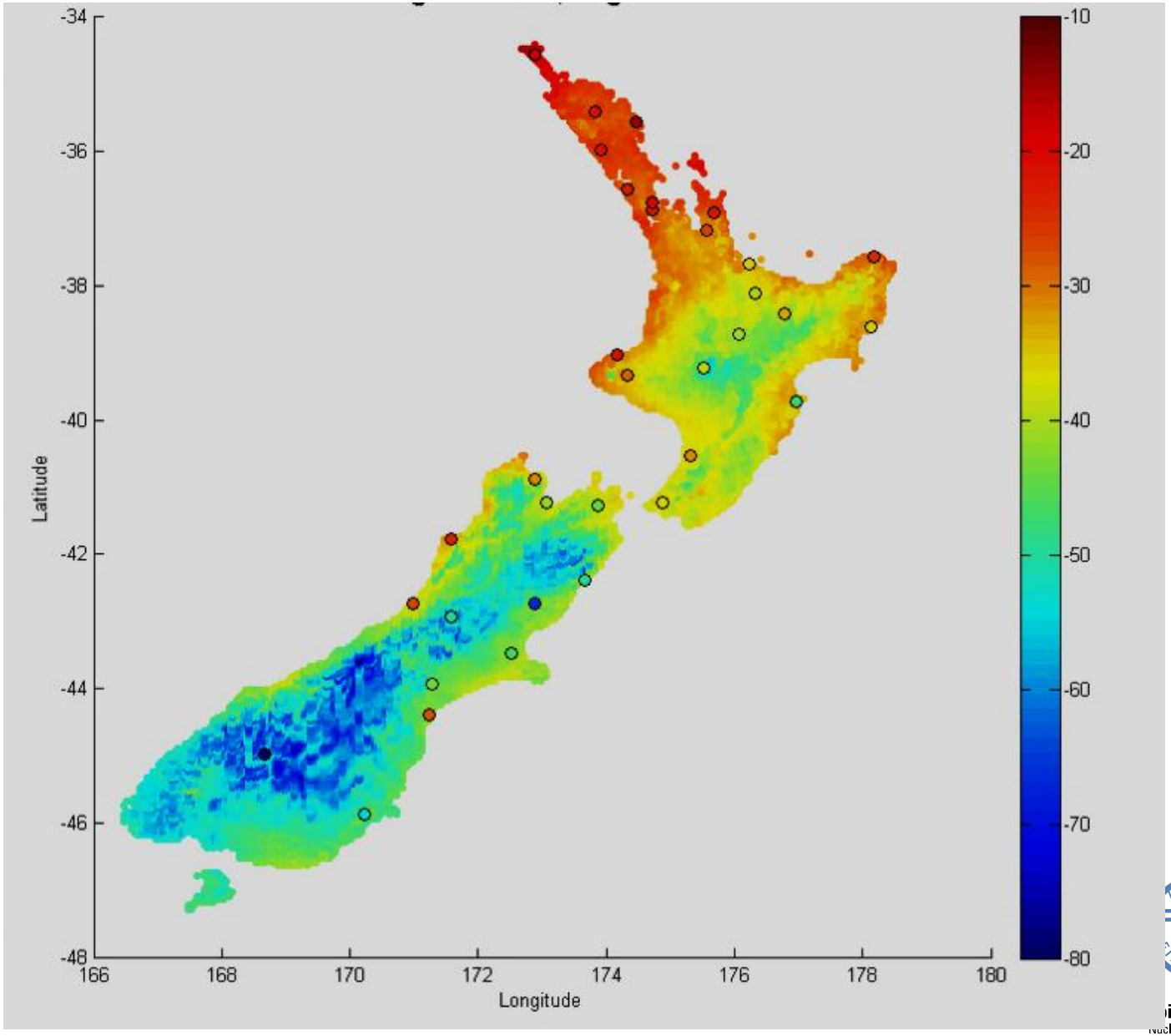
Geospatial modeling

- Make use of regional patterns in geochemical data
- Determine transfer functions
- Create models/ maps of patterns in food compositon
- Ground-truth with authentic samples

Global Patterns



New Zealand Rainfall δ^2H



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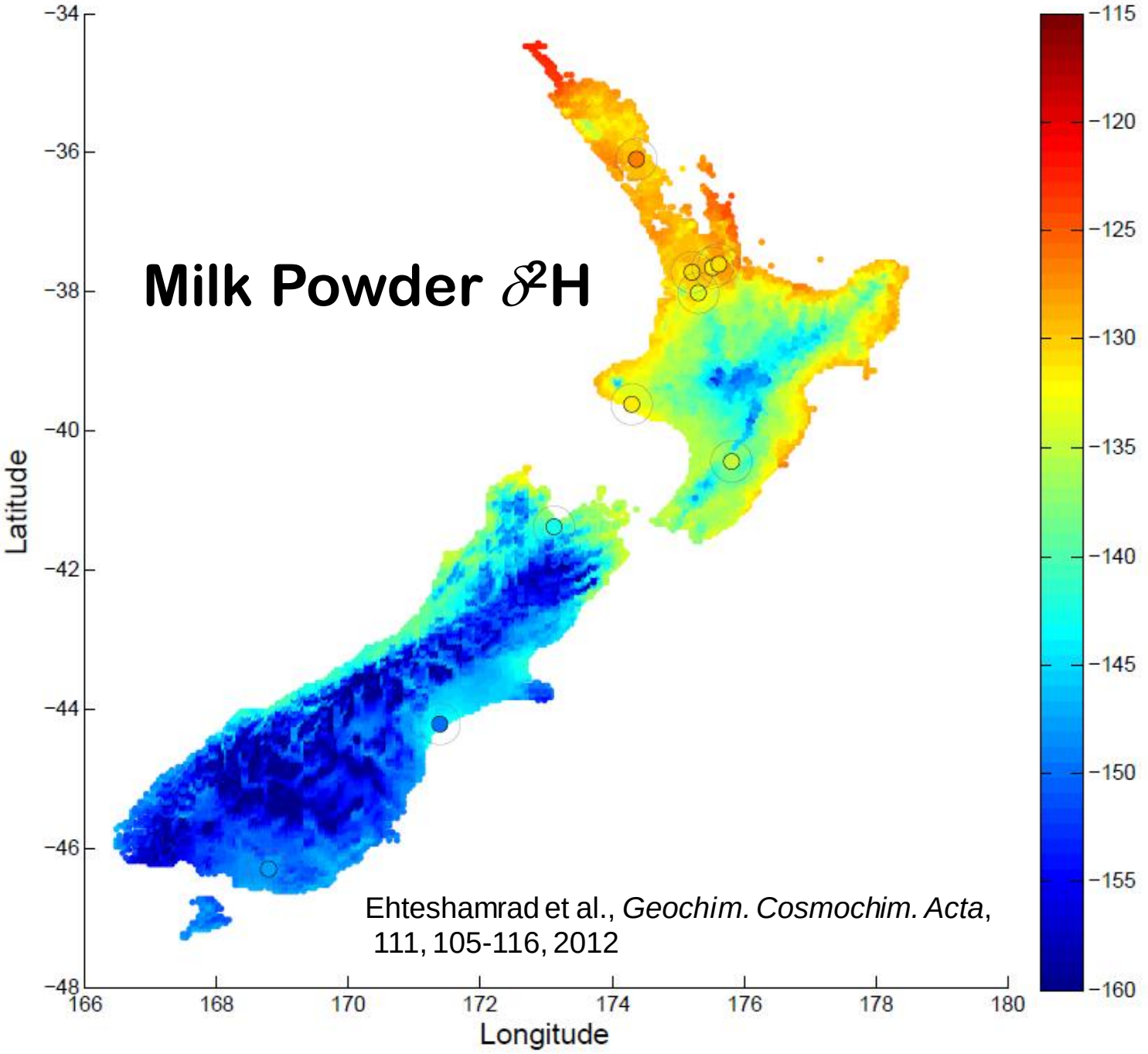
Milk Powder δ^2H



Ehteshamrad et al., *Geochim. Cosmochim. Acta*, 111, 105-116, 2012

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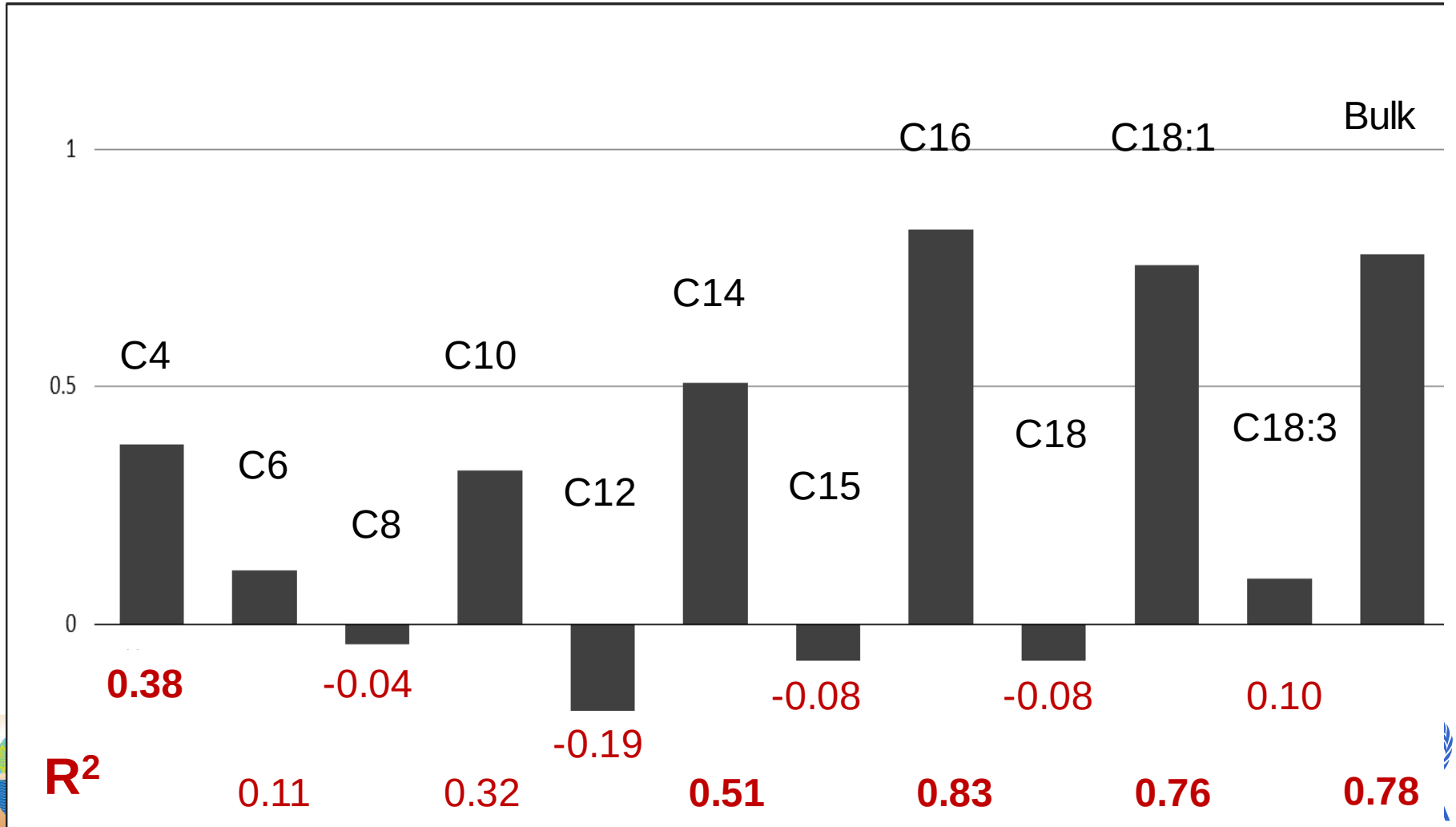
Correlation With Rainfall Model



Conclusions

- Hydrogen isotope ratio analysis of milk is a potential tool to identify origin of milk products
- The δ^2H values of butyric, myristic, palmitic and oleic acid enabled discrimination of the region of origin for >90% of milk samples.
- These measurements convey reliable isotopic information that can be used to verify origin, provided appropriate authentic-region reference samples are available.

Considerations

- Reliable discrimination between different countries and regional production can be achieved (**but not always**).
- Technique is most easily applied against a Country of origin labelling claim (COOL). The general question where is this food from is much harder to answer.
- As with all statistical techniques the method does not permit definitive proof – it can only confirm its possible origin at a specified level of confidence and spatial specificity of the method.
- The reflection of the local climate and geological signal is complex. Modelling the relationships requires a thorough understanding of the mechanisms behind the geographical variation of the isotope patterns in food.
- Isotope mapping as a predictive tool is in its infancy but will play an increasing role in food forensics and other areas of science that require the determination of provenance over coming years.