

Food Authentication by Chemical Profiling



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PREFACE

This booklet was written to summarise the intentions, results and possible applications of the inorganic chemical profiling work done within the TRACE project. The focus of this work was to develop predictive modelling of food commodities based on chemical properties in relation to geographical and geological source areas.

The following food commodities were included in the investigation: mineral water, wheat, olive oil, honey, chicken, lamb and beef. In addition, to measure transfer of geographical and geological properties from source areas to food, surface water and topsoil and subsoil samples were collected and measured.



Disclaimer

The information reflects the author's views; the European Commission is not liable for any use of the information contained therein.

INTRODUCTION

What is the implication of food fraud, and how does it affect us?

Some examples:

- Non-organic meat, fruit and vegetables sold as organic
- Meat unfit for human consumption is sold
- Meat sold as 'lean' when the fat content equals that of 'normal' meat
- Providing the wrong geographical origin to pretend the product comes from a desirable area
- Battery farm eggs sold as free-range
- Dying olive oil green to make it resemble virgin olive oil
- Diluting olive oil with cheaper oil
- Replace famous brand alcohol products with counterfeit versions, which could contain dangerously high levels of methanol
- Watering down spirits



The aims of the work presented here:

- Make consumers aware of the issues of food fraud
- Provide confidence in the authenticity of European food to consumers
- Improve food traceability along entire fork to farm pathway
- Develop cost effective analytical methods that enable the verification of the geographical origin of food
- Develop the ability to predict food chemistry of food of known origin
- Provide assurance to importers and exporters that it will not be possible for fraudulent reproductions of their food products to be distributed
- Assist in national and international monitoring and tracking of products for law-enforcement purposes



TECHNICAL OVERVIEW

Food Specification Maps – What is it and how can we use it?

The **classical approach** to food authentication:

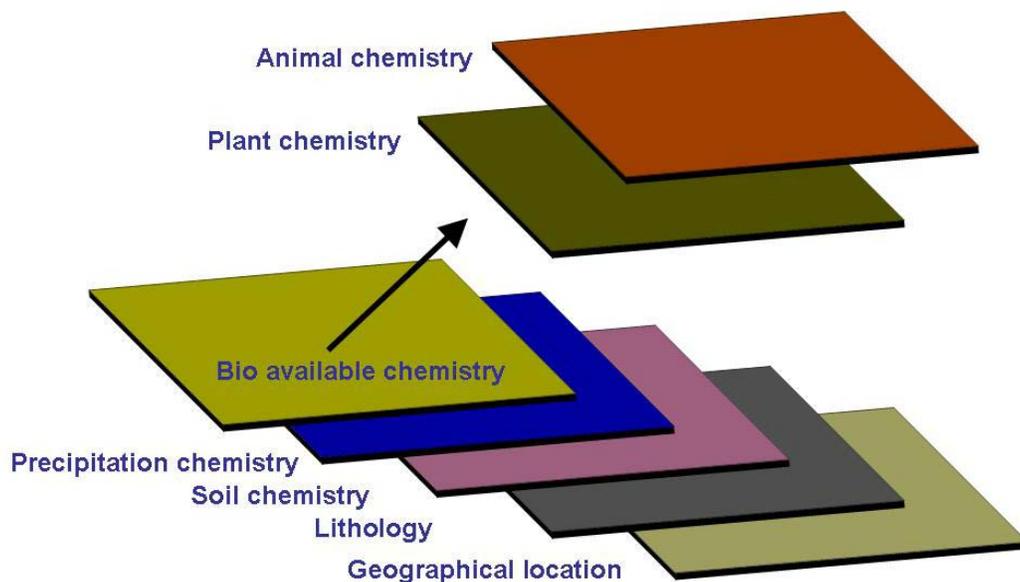
Construct a **database** by collecting and analysing food from as many production areas as possible. Then we know the specific chemical properties of these products from these areas.

The disadvantages of this approach include:

- The properties might change with changes in weather or climate conditions, or agricultural practices, and so have to be updated regularly;
- We have to make sure that the variation within an area is reflected in the samples collected, so a large enough number of samples should be included;
- We can't make any conclusions on areas not included in the data base, or on commodities not included in the data base – they could be similar or different to samples already included in the database;
- This whole process is intensive and expensive.

The construction of a database for food products is only truly effective if there are only a small number of known producers of a commodity.

An alternative approach is to determine how chemical properties are transferred between components or layers in a source region, and then from the source region to a food commodity.

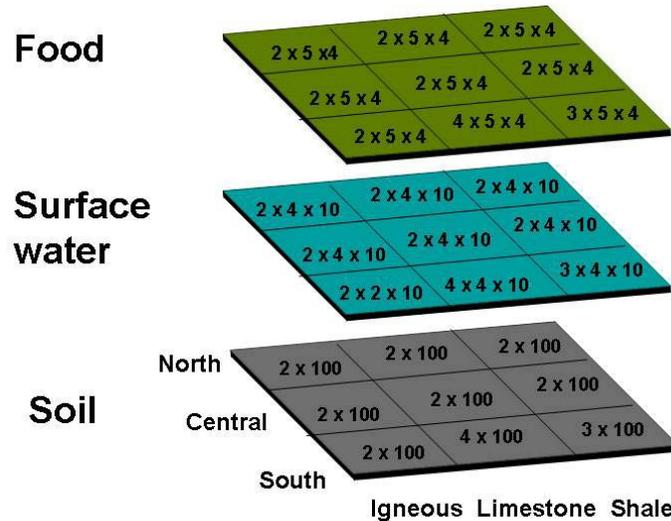


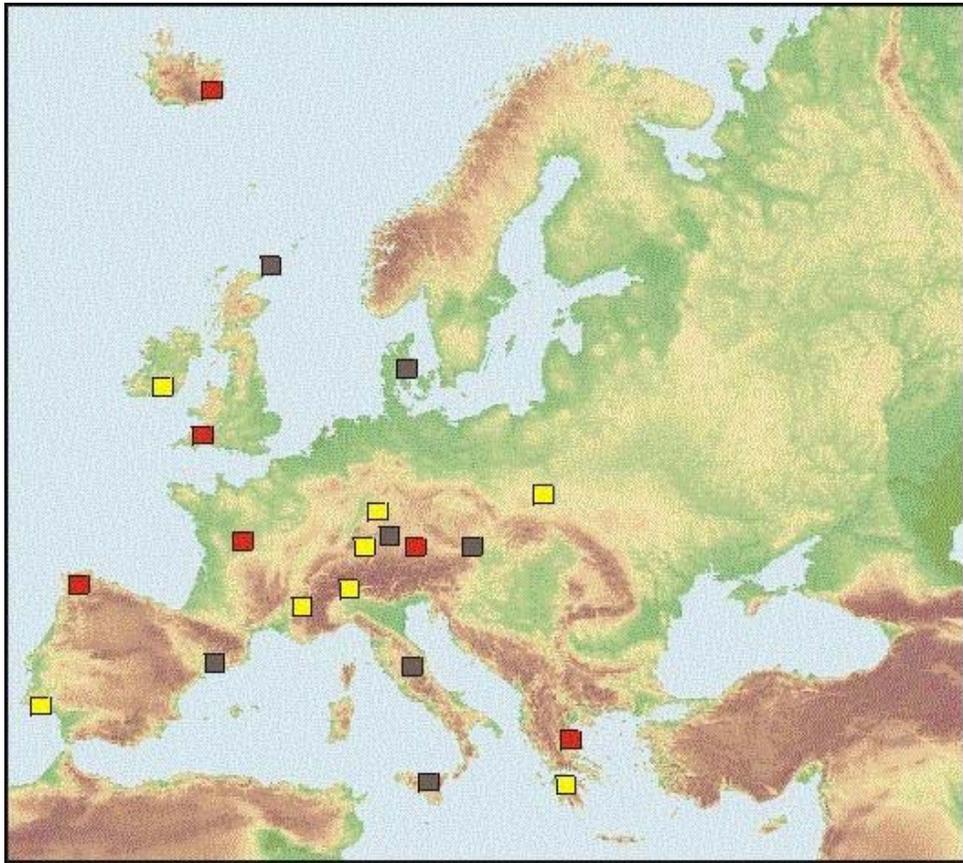
If we understand how this happens, we can predict what the chemical property in a food product should be, based on the chemical properties of the claimed source region.

Experimental Design and Sampling

Sampling was planned according to a **Latin cube design**. **21 test areas** were selected across Europe. These areas were chosen to represent different types of **climate** (north to south) and **geology** (three main classes).

Latin cube design



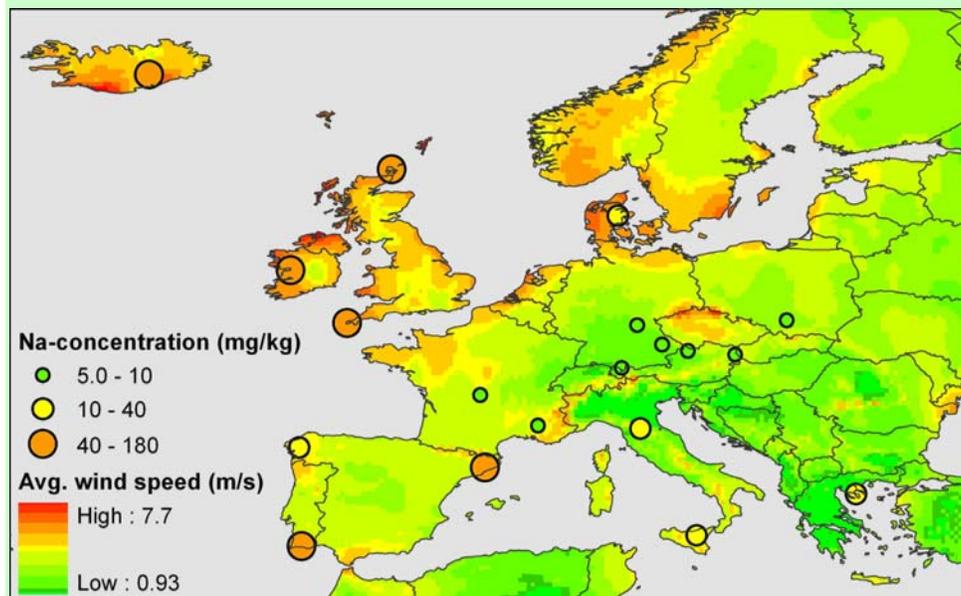


Soil and surface water, wheat, honey, olive oil, chicken, lamb and beef samples were collected from these sites over a period of two years. A selection of the soil and all surface water samples was collected from the same locations over three follow-up seasons to establish variability over time. Sub-surface soil samples were collected for a sub-set of soil samples to establish depth-related variability, as these samples would retain more properties of the underlying bedrock geology. Food commodities were collected from the same locations over two years to establish time related variability. Mineral water samples were not collected according to the experimental design, but simply as many samples

from as many locations as possible were included. Between 500 and 2100 samples were collected for each commodity.



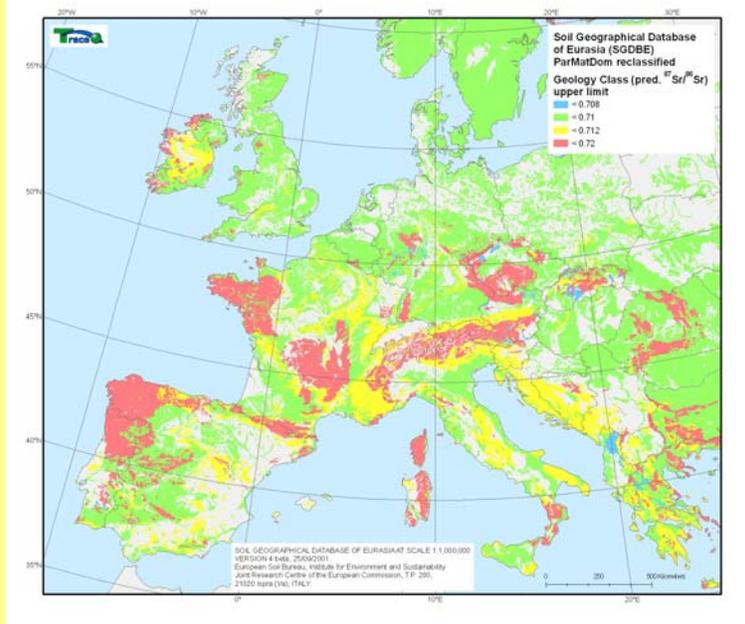
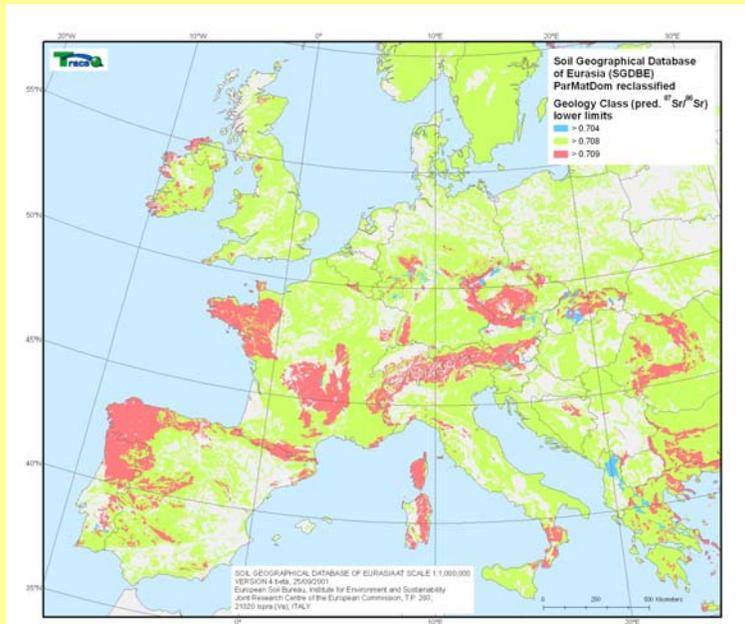
On the map below the sodium (Na) concentration measured in wheat samples from 19 of the test areas are shown. Large circles indicate high sodium concentrations. It is most likely that the high sodium concentration in wheat samples from areas close to the coast is due to a sea-spray effect, because sea-water has a high sodium concentration. This is not always the case – in some coastal areas, where the wind direction is predominantly away from the coast, the wind speed is low, or where a physical barrier such as height above sea level intervenes, the effect is less visible. However, in all cases wheat from areas far inland contain comparably low sodium concentrations. High sodium concentration in wheat is therefore an indication of a coastal origin for the wheat.



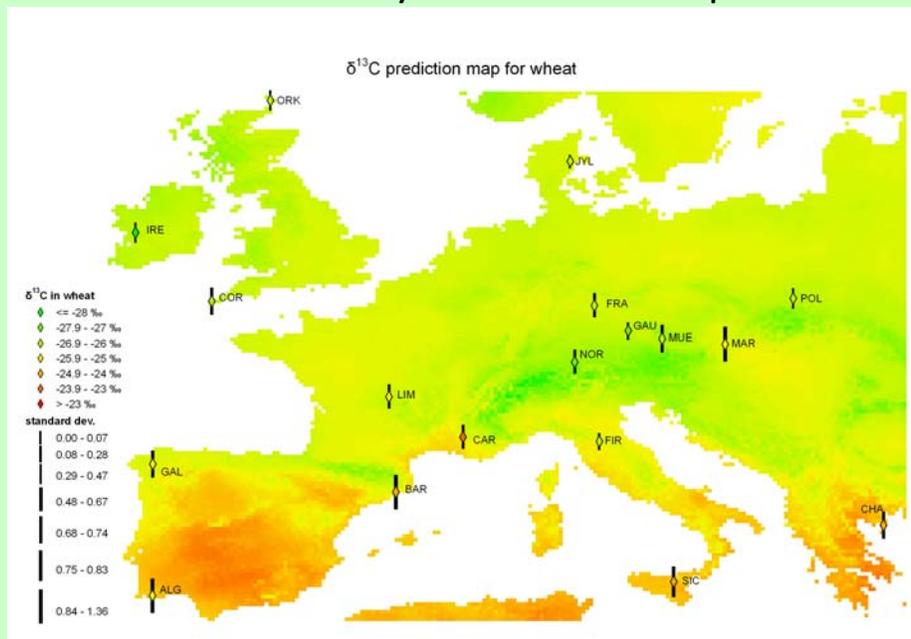
On the following two maps the predicted strontium isotope ratios of honeys are shown. These maps were prepared using knowledge and measurement results of underlying rocks and soils, and measurements of honey samples collected from our test sites. The colours on the first map



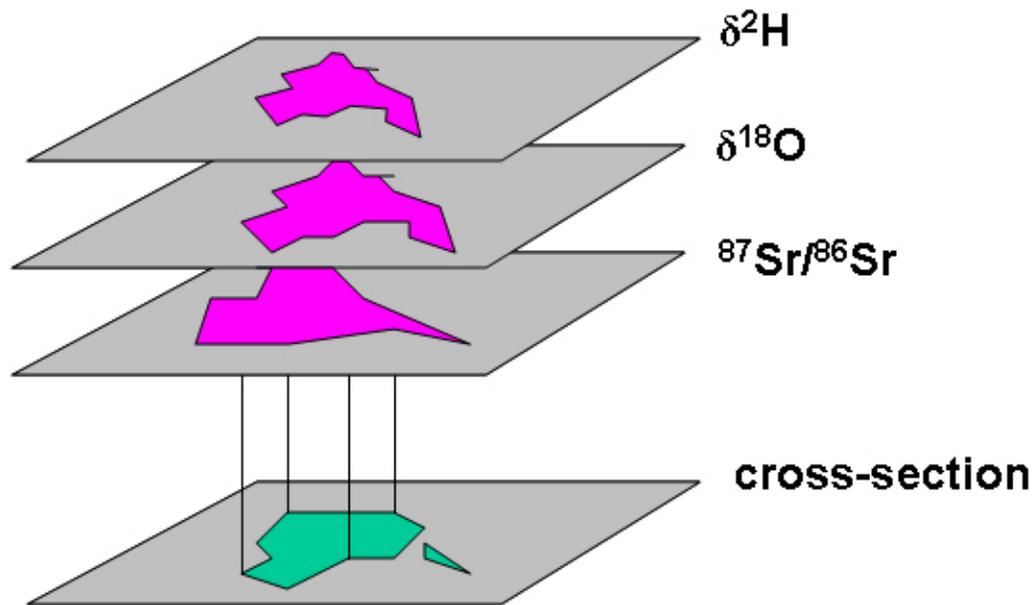
indicate the lowest possible strontium isotope ratio that could be expected in honeys from those regions. The second map shows the highest possible strontium isotope ratios expected. So an interval for strontium isotope ratios in honey from any location in Europe can be determined from these maps.



The measured carbon isotope ratios in wheat samples from 18 of our test sites are indicated on the map below. The colour of the diamonds indicates the interval into which the $\delta^{13}\text{C}$ isotope ratio values measured for samples from each site falls. The sizes of the vertical lines indicate the extent of internal variation from each site. This information was combined with factors calculated from climatic conditions during the growing season of the wheat. The back-ground colours on the map indicate the carbon isotope ratio that we predict to measure in wheat samples that were produced across Europe. Therefore, by combining the results of isotopic measurements in actual wheat samples with knowledge of climate conditions across Europe, it is now possible to estimate the carbon isotope ratio of wheat from any location in Europe.



One chemical property might be very similar over a large source area or areas. If we combine knowledge of many different chemical properties, each determined by different local conditions, we will be able to obtain a greater ability to distinguish between different production areas.



Here we see that if we combine information of three characteristic properties, the cross-section – where all requirements are satisfied – is smaller than any of the other areas.

These expected, or predicted, properties can be represented on a map, which is called a food specification map. The combined knowledge of different independent properties can be combined into a prediction model.

Techniques and instrumentation

Various types of instruments were used to measure a selection of inorganic chemical parameters:

- Isotope Ratio Mass Spectrometry (IRMS)
- Inductively Coupled Plasma Mass Spectrometry (ICPMS)
- Multi-Collector ICPMS (MC-ICPMS)
- Thermal Ionisation Mass Spectrometry (TIMS)

Light isotope fractionation - Isotope Ratio Mass Spectrometry (IRMS)



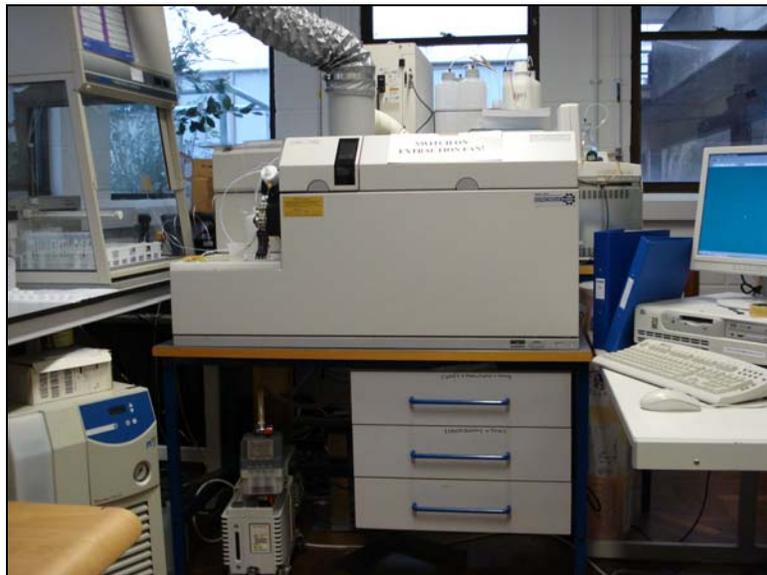
This technique was used to measure **isotope ratios** of the elements **H, O, C, N** and **S**. Isotopes are two different versions of the same element, one being heavier than the other. The isotopes of the elements listed here are separated by natural processes such

as evaporation and precipitation and metabolic processes in plants and animals.

These ratios give the following information:

- Isotope ratios of O and H – climate indicator
- Isotopes of C – climate indicator; level in the food chain
- Isotopes of N – organic food/agricultural practices; level in the food chain
- Isotopes of S – geological indicator

Trace Element Quantification - Inductively Coupled Plasma Mass Spectrometry (ICPMS)



The **concentrations of elements** can be determined by ICPMS, by comparing unknown concentrations to quantified standard concentrations. Many elements in the same solution can be analysed, and in this

investigation a total of 31 elements were measured in all sample types.

The type of information that can be obtained from Trace Element Concentrations:

- Geologically related fractionation – Li, B, Mg, K, Ca, Mn, Ga, Se, Rb, Sr, Cs, Rare Earth Elements (La, Ce, Nd, Sm, Eu, Yb, Lu), Tl
- Agriculturally related discrimination – Al, Se
- Human activities – Al, C, Ni, Cu, Zn, Mo, Cd, Ba, Tl, Pb
- Geographically related fractionation – Na

Sr isotope ratios - Multi-Collector ICPMS (MC-ICPMS) and Thermal Ionisation Mass Spectrometry (TIMS)



Multi-Collector ICPMS



Thermal Ionisation Mass Spectrometry

Both these techniques were used to measure the ratio between two isotopes of the element Strontium (Sr). The **Sr ratio** is directly related to the **geological** material incorporated in water or food stuff. Different types of geological formations have distinct, but not always unique, Sr isotope ratios, so if these ratios are measured in food products, they can be related to one or more types of geological formations.



Summary

In this project we attempted to combine measured chemical parameters with knowledge of local geographical and geological conditions to be able to predict the expected composition of food from known origins. The aim is to be able to predict various chemical properties based simply on knowledge of the production area of a food product. If the chemical properties measured in the food do not comply with the specified values, the claimed origin of the food is most likely false.



APPLICATIONS

Industry

In a modern marketplace where **consumers** are **aware** of the impact of food and components of food products on **human and environmental health**, it is an **advantage** for the producer to claim **verification of the authenticity** of the components in his products.

For example a baker who can prove the **organic** origin of the wheat used in his bakery will find loyal support from a certain group of consumers, willing to pay for this attribute. **Consistent quality** could also be guaranteed if ingredients are consistent.



Fruit or vegetable products **produced locally** have a **low carbon footprint**, popular to environmentally

aware consumers, so that if claims of local origin could be verified it would have an **increased value** to these consumers.



Other fruit and vegetable commodities might have increased value because it was produced in a desirable or famous production area, such as kiwi fruit from New Zealand.

In order to back up claims of authenticity, producers/importers were in the past forced to rely on paper traceability. This procedure is however not infallible, and can be surpassed by the clever swindler, or simply through mistakes. By using the type of techniques investigated here, it could now be possible to back up claims of production origin and location through independent analytical proof.

Olive Oil Authentication

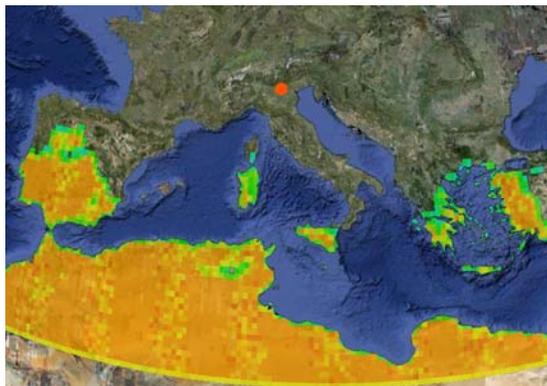
Olive oil is a commodity for which high value is attached to the region of origin. Certain regions, particularly Italian, are more popular, and as a result higher prices can be asked for these oils. Oils from other regions, or even other types of oils, are often fraudulently sold as Italian. Such exploitation can damage the reputation of the authentic product, and cause losses to the producer, exporter and importer.



Thanks to some of the knowledge obtained in this project, we can combine measurement results of oxygen and carbon isotope ratios of olive oils to be able to estimate the origin. If we have an olive oil which according to the labelling come from Valpolicella in the province of Verona in Northern Italy, the predicted specifications are for $\delta^{13}\text{C}$ carbon -31.2 to -29.6

per mill and for $\delta^{18}\text{O}$ oxygen 19.0 to 24.2 per mill. If we analyse the olive oil and the results show a $\delta^{18}\text{O}$ oxygen isotope ratio of 25.6 per mill and a $\delta^{13}\text{C}$ carbon isotope ratio of -28.1 per mill, we know the claimed origin to be false.

The red dot on the map shows the claimed origin of the oil, and the coloured areas the most likely source regions – the warmer colours being more likely than the cool colours.



Consumer

Food products are often sold with the claimed benefit of being either healthy, organically and/or ethically produced or being from an established source region, in response to consumer demands. Meat and alcohol are the most common sources of food fraud – both are high value products with high profit margins, but both pose great health risks (www.which.co.uk).



Due to the increased value associated with such products false claims for production procedures and source regions of food commodities are becoming more common, and when exposed are well publicised. The Italian olive oil scandal is an example (see 'Italian Police crack down on olive oil fraud'; The Telegraph, 5 March 2008, www.telegraph.co.uk). Such cases have made consumers more aware of the importance of ascertaining claims of origin. In cases of intentional food fraud paper traceability could easily be falsified, and is therefore unreliable. An independent traceability technique could be implemented routinely to ascertain authenticity of food production claims, particularly if the associated cost is low.

Mineral water authentication

The mineral water market is a case in point where the consumer has frequently been misled in terms of origin claims. How can we believe what it says on the bottle?

Using information obtained from the analytical work done in this project, we can now predict a combination of chemical factors that we expect to see in mineral water from specific source areas in Europe. The isotopes of oxygen, hydrogen and strontium in mineral water can be compared against the model developed in this project, allowing us to identify the most likely areas in Europe where this water could have originated from. More importantly, we can determine areas where the water could definitely not have originated from.

We can test a bottle of water claiming to come from the French Alps, promoted for its purity through natural filtering processes. If we measure a $\delta^{18}\text{O}$ oxygen value of -4.2 per mill, a $\delta^2\text{H}$ hydrogen value of -26.1 per mill and a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.710 , we can incorporate the values into our model to obtain the most likely source regions - shown by the colours on the map, the warmer colours indicating the most likely sources. The claimed origin in the French Alps, indicated by the red dot, was most likely not the source for this water.



Law enforcement

For various legal aspects it is extremely useful to test claims of origin. In cases where unhealthy or contaminated meat products are distributed and causes health risks, it is important to find the source to contain further damage.

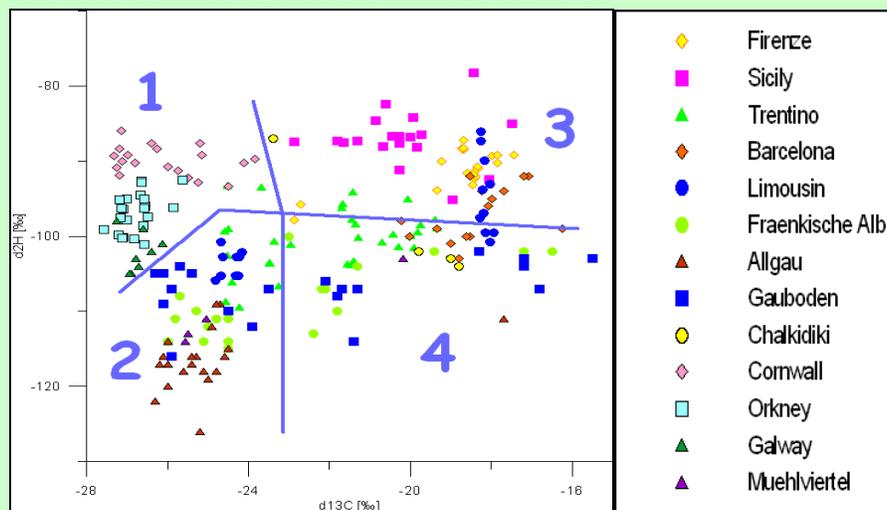


Knowingly claiming a false origin for food products is fraud, and should be identified and stopped. Paper trails of food products can be falsified by experienced criminals, or errors could be introduced unintentionally, leading to incorrect information on products. Therefore, an independent verification technique would be a practical and valuable contribution to the food record process. The chemical authentication techniques described here could provide such an independent tool.

Beef Provenancing

Isotope ratios of carbon and hydrogen measured in individual beef samples from 13 of the test areas in this study are presented on the graph below. Groups of samples from the different types of areas can be separated from each other to varying degrees with the use of only these two chemical properties.

The samples in Group 1 come from western European regions with low altitude and minimal use of maize as feed, exposed to the Atlantic Ocean. Group 2 samples come from mostly high altitude continental areas with no influence from the sea, and limited use of maize as cattle feed. Group 3 samples come from Mediterranean areas exposed to the Mediterranean Sea, using a moderate to intense amount of maize as cattle feed. The samples in Group 4 originate from continental regions with limited influence from the sea, and moderate to intense use of maize as feed.



This graph was prepared using only two chemical parameters. If we combine this information with additional discriminating chemical parameters, the model will become more successful at differentiating between samples from different types of source regions.

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URL:

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Information on food fraud:

www.thisismoney.uk

www.which.co.uk

INDEX

Authentication technique – a means to determine whether claimed properties of a product is true, such as the production region, or the cultivation method

Chemical profiling – measuring a variety of chemical properties of a product, and combining this information to obtain a characteristic collection of properties

Food fraud – when untrue information is provided regarding the production process or area of food products

Food specification model – a collection of characteristic chemical properties of a certain type of food product is combined and related to natural phenomena, to be able to predict food composition when the source area is known

Isotope ratio – Some elements have more than one variant, where some versions are heavier due to additional particles included in the atom nucleus. These light and heavy versions of elements are naturally fractionated by geological, atmospheric and biological processes.

Paper traceability/Paper trail – a paper or electronic history of a product