PRESENTATION

Session: **Cotton Quality and Testing**

Title: **Textile-Tracker: Where is my T-shirt from? Testing the influence of textile processing on stable isotope signatures in cotton**

Speaker: **Karin Ratovo,** Hochschule Niederrhein, Germany **Markus Boner**, Agroisolab GmbH, Germany

Presentations are available in the conference archive: https://baumwollboerse.de/en/competencies/international-cotton-conference/speeches/

Conference Organization

Faserinstitut Bremen e.V., Bremen, Germany. E-Mail: conference@faserinstitut.de
Bremer Baumwollboerse, Bremen, Germany. E-Mail: info@baumwollboerse.de

Textile-Tracker

Where is my T-shirt from?

Testing the influence of textile processing on stable isotope signatures in cotton

29.09.2022 – 2 pm (CET)

Where is my T-shirt from?

Sponsored by:

sponsored by DBU Deutsche Bundesstiftung Umwelt www.dbu.de

Partners:

FTB (Hochschule Niederrhein)
- **Processing of Cotton**

Agroisolab GmbH
- **Analytics**

WWF Germany
- **Advisory**

Maybe, but…
that must be verified with controlled produced textiles

One Year Project

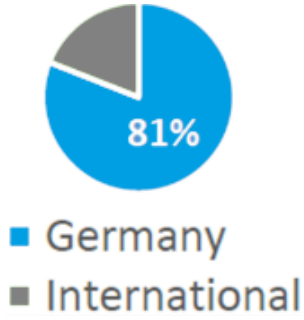
Hochschule Niederrhein
University of Applied Sciences

Hochschule Niederrhein

// around 14,283 students
// 2 locations (Krefeld and Mönchengladbach)
// 10 faculties

Department for Textile and Clothing Technology

// students in total	1,955
// PhD candidates	19
// B. Sc. (2019)	234
// M. Sc. (2019)	81
// professors	33
// employees	64 (30 members of research staff)
// labs & pilot plants	32



Hochschule Niederrhein
University of Applied Sciences

Research Institute for Textile and Clothing (FTB)

- Facts and Figures

// founded in 2009
// professors 23 (head: Prof. Dr. Maike Rabe)
// researchers 31 (textile engineers, chemists...)
// assistants 33 (student and scientific)
// inventions 12 (2 patents)

→ Realisation of publicly funded (18) and private (2) research projects all along the textile chain.

Research Institute for Textile and Clothing (FTB)

Textile Production Chain

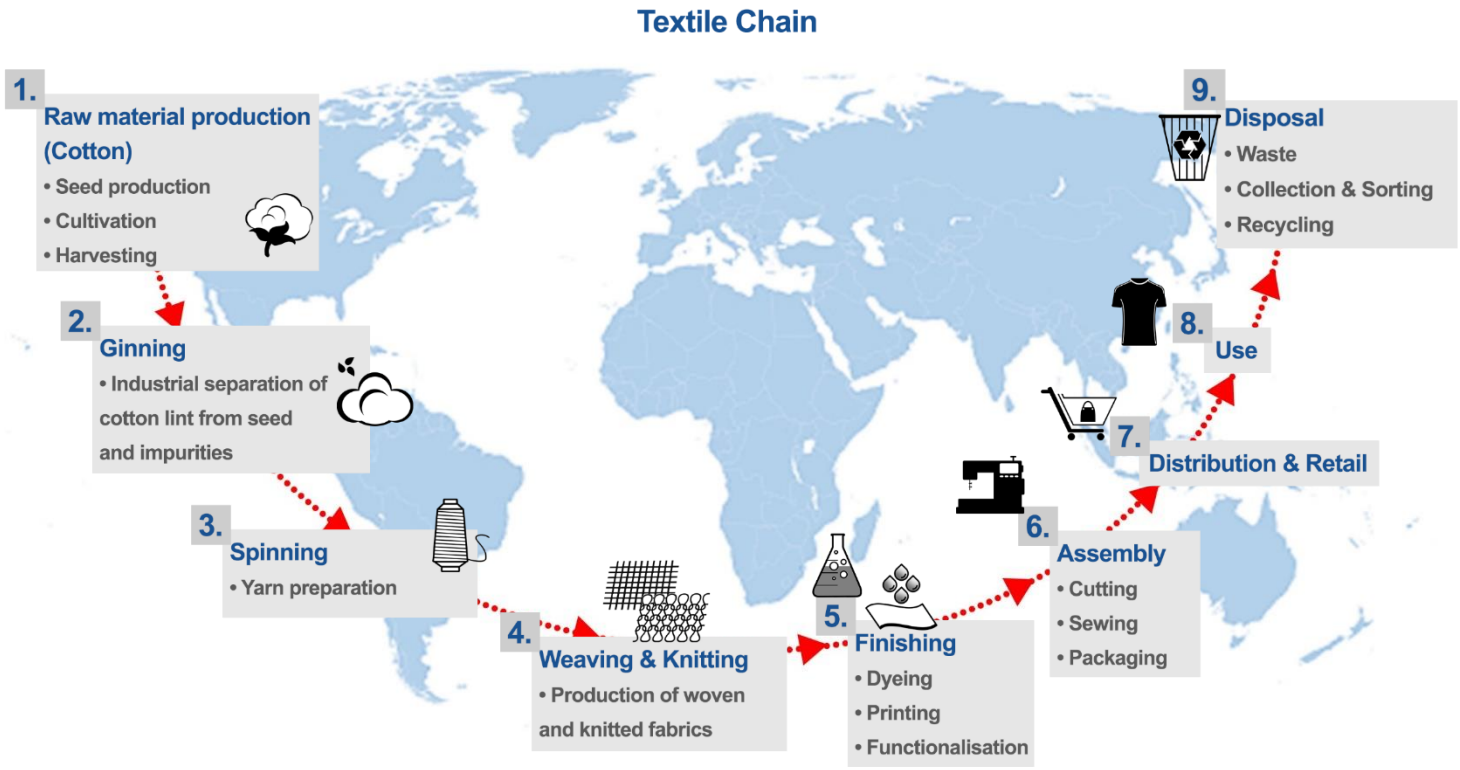
- **Fibre processing**
  - // secondary spinning (rotor-, air-, ring-, friction-)
  - // non-woven production (needle-punched)

- **Fabric production**
  - // weaving (narrow-, wide-, jacquard-)
  - // knitting (warp and weft / circular and flat)

- **Finishing**
  - // dyeing and finishing of yarns and fabrics
  - // coating, plasma technology, laser technology, digital printin embroidery
  - // lab-scale up to production scale

- **Production of apparel and technical products**
  - // analogue and digital product development process (VirLab: 3D scanning, simulation)
  - // cutting, sewing, welding, fusing technology, embroidery

Textile Processing along the Cotton Textile Chain



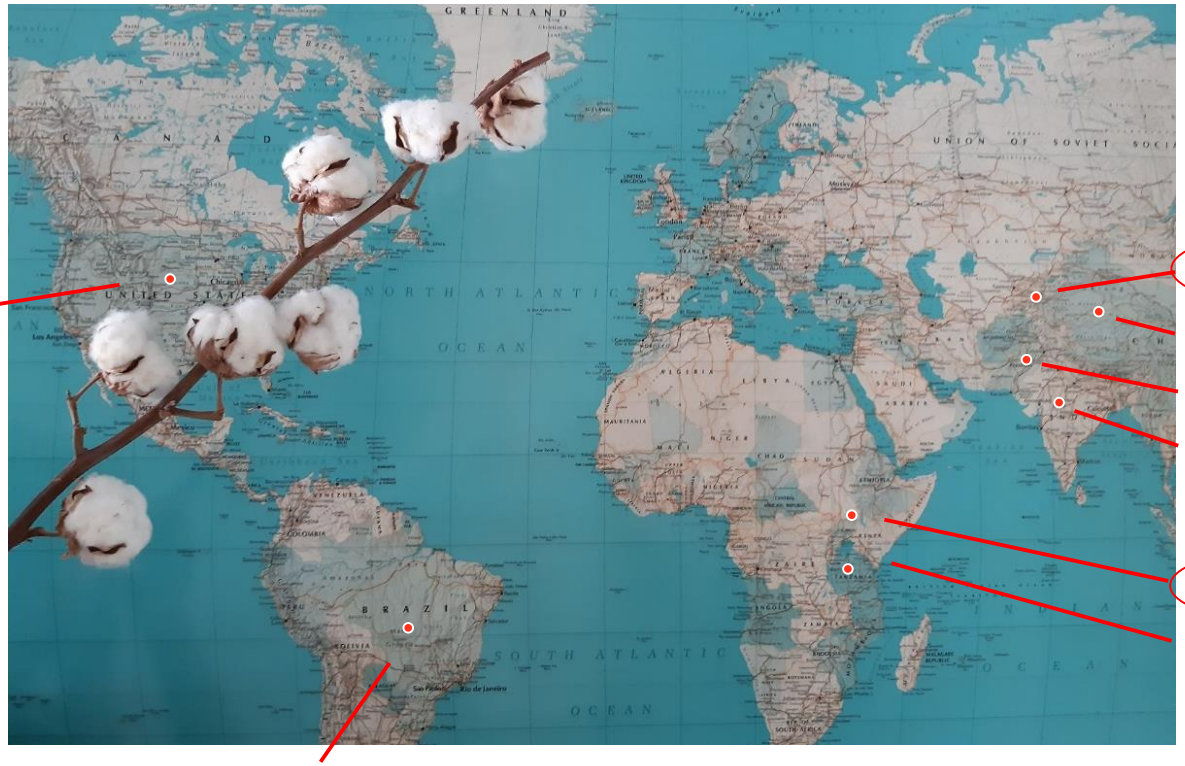
Selection of Cotton Samples

Selection of regiospecific cotton samples (3-5)

- regular cotton
- organic cotton (oc)

Selection of batches per region

- different samples of one harvesting season
- different years



Textile Processing – Mechanical Processes

Spinning Processes

Cotton Fibre

Sliver

Knitting yarn (paraffined)

- ✓ Uganda (UG) 2009, 2016, 2018, 2019, 2020
- ✓ Kirgyzstan (KG) 2019, 2020

⇩

- ✓ Uganda (UG) 2009, 2016, 2019
- ✓ Kirgyzstan (KG) 2019, 2020

Textile Processing – Mechanical Processes

Rotorspinning Process

Sliver

Knitting yarn (paraffined)

Textile Processing – Mechanical Processes

Knitting Process

Knitting yarn (paraffined)

Knitted tube (raw fabric)

Textile Processing – Chemical Processes

Pretreatments

Knitted tube (raw fabric)

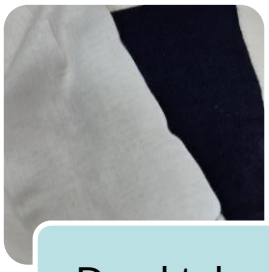
- ✓ **Scouring** (surfactants, diluted alkali)
- ✓ **Boil off process** (NaOH 0.1 %)
- ✓ **Bleaching** (NaOH 0.05 % / hydrogen peroxide)

- ✓ **Mercerisation process** (NaOH 26 %)

Textile Processing – Chemical Processes

Dyeing Process

Knitted tube (pretreated fabric)



Dyed tube (dyed fabric)

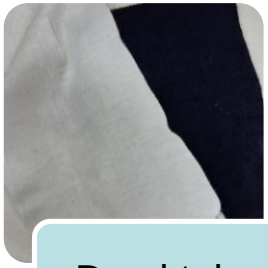
✓ **Reactive dye, black**

→ **Dye fixation: < 5 mass %**

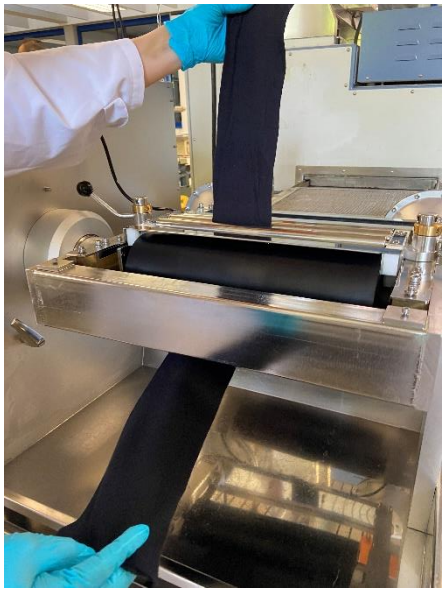
using alkali (soda Na_2CO_3)

Textile Processing – Chemical Processes

Different Finishes



Dyed tube
(dyed fabric)



Finish	Mass proportion of chemicals on textile
Easy-care finish (modified dihydroxyethylene urea)	5.3 %
Hydrophobic treatment (highly branched polymers in a carbon matrix)	1.0 %
Flame retardant finish (inorganic phosphorus-nitrogen compound)	13.8 %
Permanent flame retardant finish (reactive organic phosphorus compound / phosphoric acid)	11.6 %
Pigment print (colour pigments mixed with compound of polyurethane hand dispersion, thickener and additives)	22.8 %

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Textile Processing – Chemical Processes

Let´s start Analytics…

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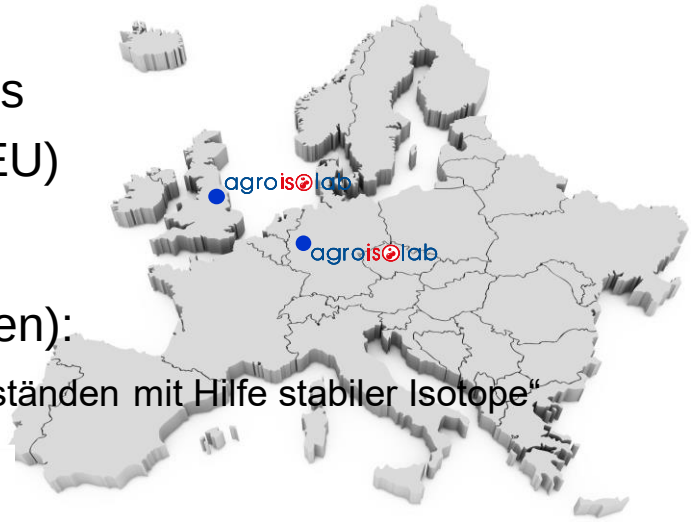
2021 More than 150 different databases
- Agricultural, chemical products, commodities
- 12 Isotopic mass spectrometer (biggest in EU)
- ICP-MS, DART-TOF Profiling



2008 Winner of the innovation award (region Aachen):
„Aktive Markierung von Lebensmitteln und Bedarfsgegenständen mit Hilfe stabiler Isotope“

2006 Accredition of the laboratory

DAkkS
Deutsche
Akkreditierungsstelle
D-PL-14370-01-00

2003 Best Practice Award, NRW

2002 Technology Award of the Research Centre Juelich

2002 Collaboration Award of NRW

2002 Founding of Agroisolab GmbH (spin off from the Research Centre Juelich)

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Our core competences.

- **Origin:** Verification of the geographic origin of goods, e.g. food, drinks, commodities, timber and cotton / textiles (2022)
- **Adulteration:** Detection of adulterants in food and drink products (e.g. sugar, water addition)
- **Organic Farming:** Verification of consistency with organic farming methods
- **Authenticity:** Verification of synthetic and natural compounds (e.g. vanillin)
- **Biobased carbon:** Quantification of the percentage of biobased / fossil carbon in e.g. bioplastics, fuel, stack gas
- **Active System:** Marker systems (stable isotopes)
- **Research:** Project development e.g.

  new tracking tools: Ukraine grain project
  (UK funded: Detection of the stolen grain in the global market)

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Agroisolab.
Our core competences

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- **Authenticity:** Verification
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- **Research:** Project develo

new tracking tools: Ukraine grai
(UK funded: Detection of the stolen grain in the global market)

REUTERS

UK HELPING ENSURE STOLEN UKRAINIAN GRAIN DOES NOT MAKE IT TO MARKET - MINISTER

6/27/2022

Listen to article 2 minutes

LONDON, June 27 (Reuters) - Britain is providing technology to ensure that any wheat stolen from Ukraine by Russia does not make it to the global market, Britain's environment minister George Eustice said on Monday.

Russia's Feb. 24 invasion of Ukraine and blockade of its Black Sea ports has prevented the country, traditionally one of the world's top food producers, from exporting much of the more than 20 million tonnes of grain stored in its silos.

Last week Turkey said it was investigating claims that Ukrainian grain had been stolen by Russia and shipped to countries including Turkey, but added the probes had not found any stolen shipments so far.

Russia has previously denied allegations that it has stolen Ukrainian grain.

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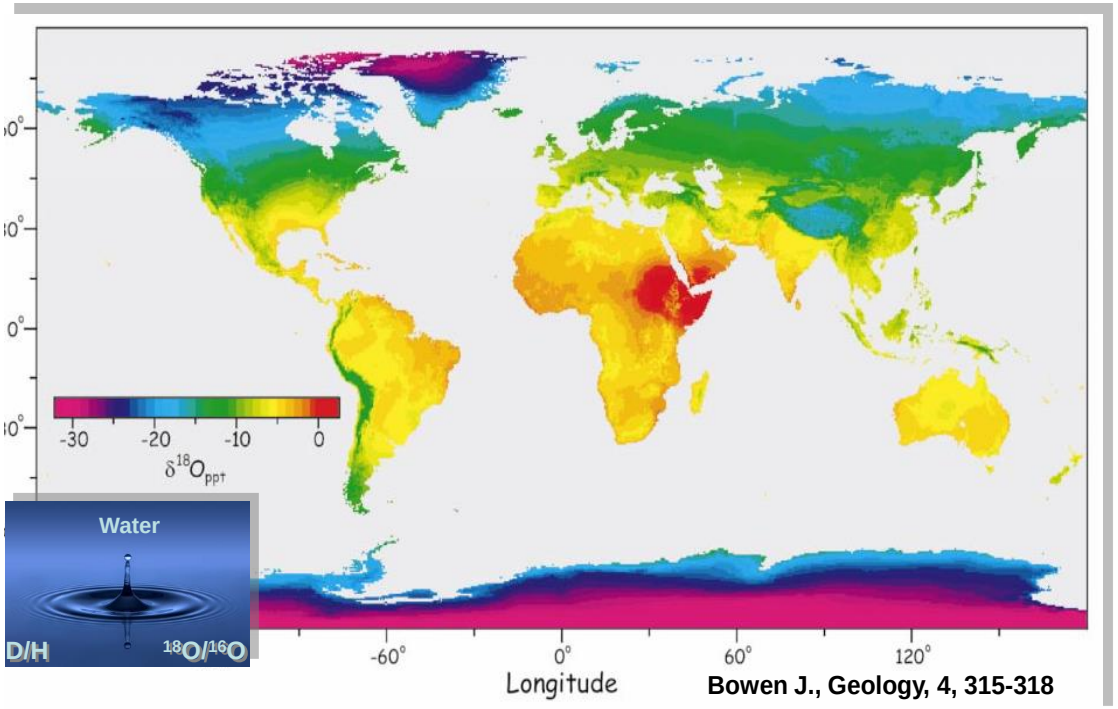
Our analytic tools.

Stable isotopes in Elements

- **Heavy variants of the elements**
- **Not radioactive**
- Found in all nature, but very little
- Different distribution and pattern
- -> Perfect physical tracking tool



Bowen J., Geology, 4, 315-318

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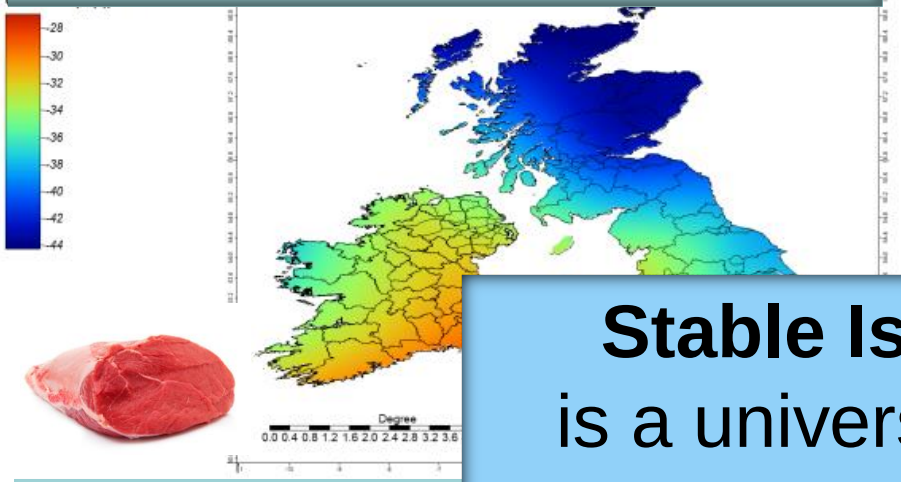
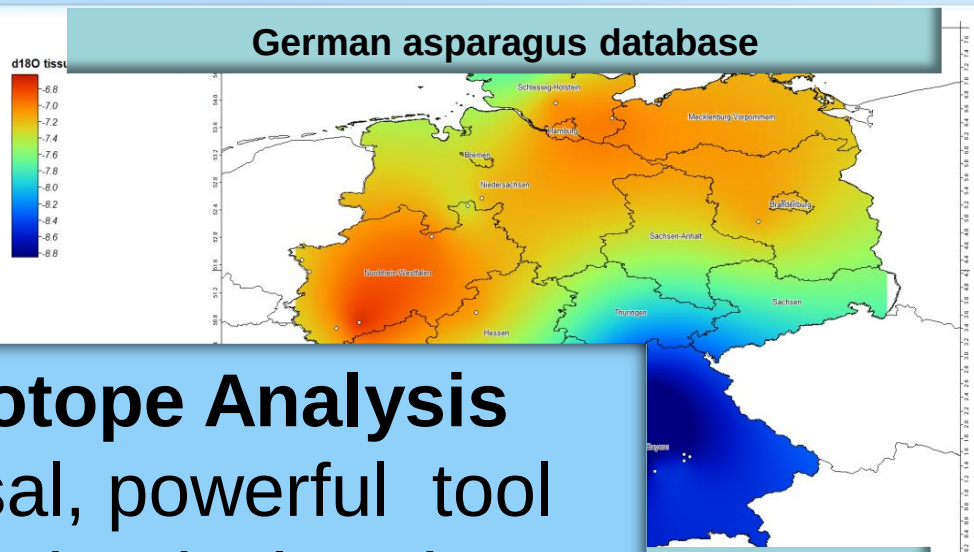
Example: Isotopic water signatures in various products

Pork database of the British pig industry

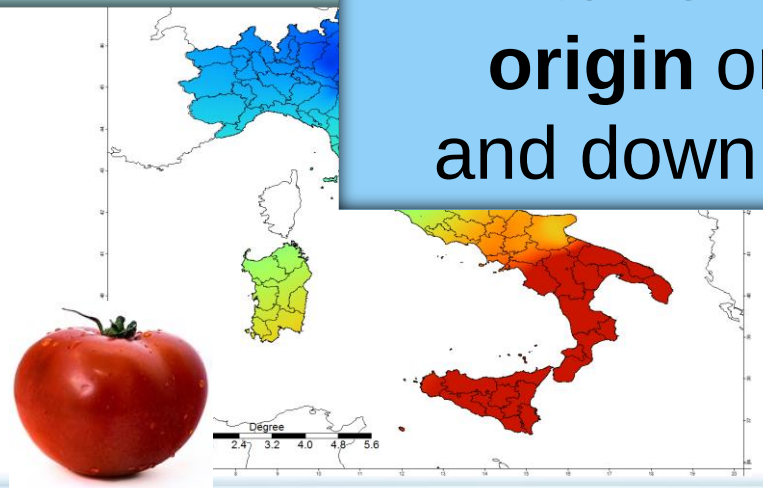


German asparagus database



Stable Isotope Analysis
is a universal, powerful tool
to verify the declared
origin on **country scale**
and down to **the field level.**

Italian tomato databas



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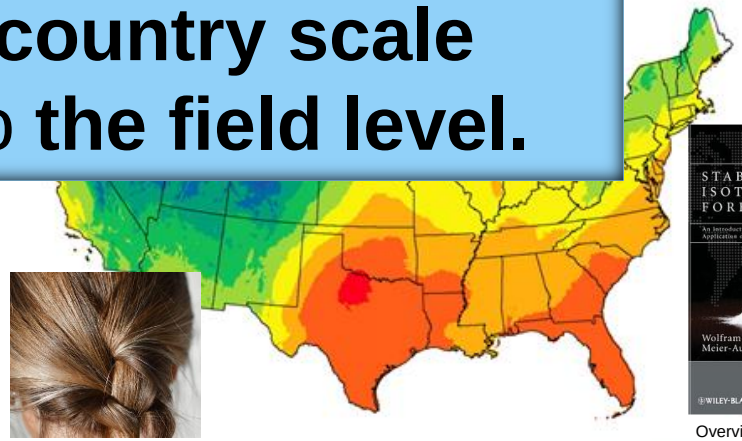

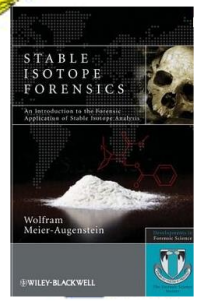

Overview:
W. Meier-Augenstein,2010

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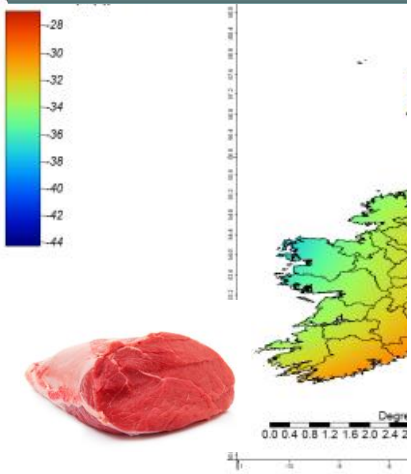
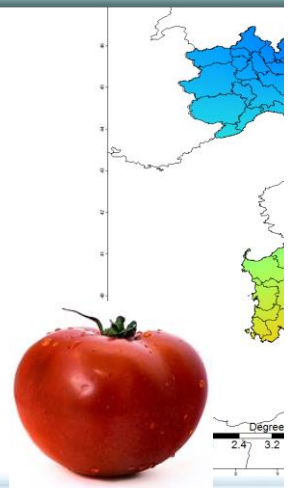
Example: Isotopic

Pork database of t



Italian tomato datab



Trends in Food Science & Technology 61 (2017) 176–187

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journal homepage: http://www.journals.elsevier.com/trends-in-food-science-and-technology

Review

Stable isotope techniques for verifying the declared geographical origin of food in legal cases

Federica Camin [a, *], Markus Boner [b], Luana Bontempo [a], Carsten Fauhl-Hassek [c], Simon D. Kelly [d], Janet Riedl [c], Andreas Rossmann [e]

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[b] Agroisolab GmbH, Prof. Rehm Str. 6, D-52428, Jülich, Germany
[c] Department Safety in the Food Chain, BfR – Federal Institute for Risk Assessment, Max-Dohrn-Straße 8-10, D-10589, Berlin, Germany
[d] Food and Environmental Protection Laboratory, Joint FAO/IAEA Division of Nuclear Techniques in Food and Agriculture, Department of Nuclear Sciences and Applications, International Atomic Energy Agency, Vienna International Centre, PO Box 100, 1400, Vienna, Austria
[e] Isolab GmbH, Laboratorium für Stabile Isotope, Woelkestrasse 9/l, 85301, Schweitenkirchen, Germany

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Keywords:
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PGI
Legal cases
Fraud
Mislabeling

ABSTRACT

Background: Consumers are increasingly interested in the provenance of the foods and European laws require protection against the mislabelling of premium foods. Methods for testing authenticity require robust analytical techniques that can be utilised by the various regulatory authorities. Of the many techniques, the most widely-used method is stable isotope ratio analysis.
Scope and approach: Focus is on the use of stable isotope ratios of H, C, N, O, S and Sr for verifying the geographical origin of food, cross-referencing it with examples of legal cases. State of the art including rules for building an authentic sample reference database (commonly called databank) and for interpreting the results obtained in actual cases is described. The overall objective is to provide stakeholders and competent authorities dealing with fraud, with a best-practice guide for its use.
Key findings and conclusions: Stable isotope ratios can differentiate foods on the basis of their geographical origin and, especially for light elements, can be measured reliably in routine work in different matrices and compared successfully between different laboratories. Examples of legal applications are grape products, orange juices, olive oil, cheese, butter, caviar. Sometimes, the cases are not brought directly to the court, but before further verifications (e.g. paper traceability, forensic accounting) are conducted. The system can satisfy the court when a robust databank of authentic samples exists, the methods used are officially recognized, validated and accredited, and the expert demonstrates that the conclusions are sufficiently robust and reliable to stand up to the required level of proof.

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Stable isotopes – Principle to track the origin

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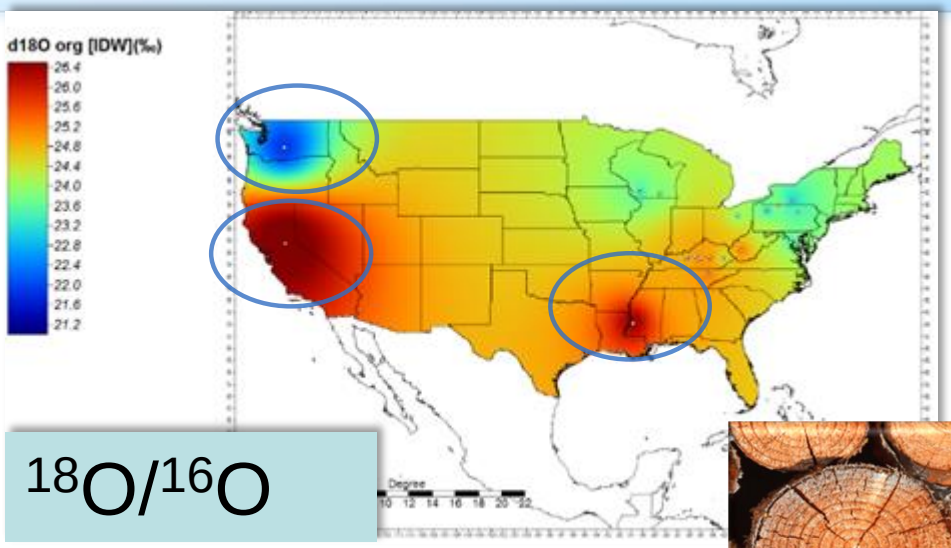
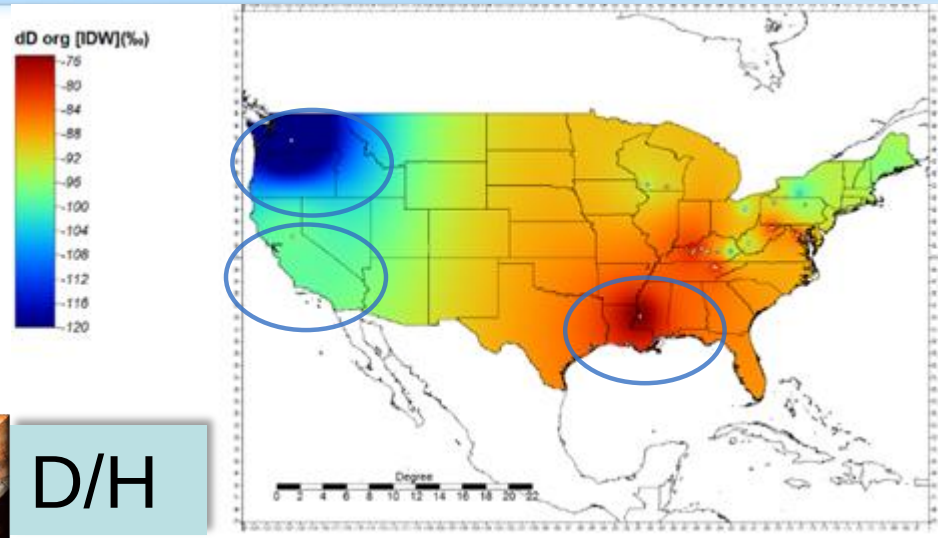
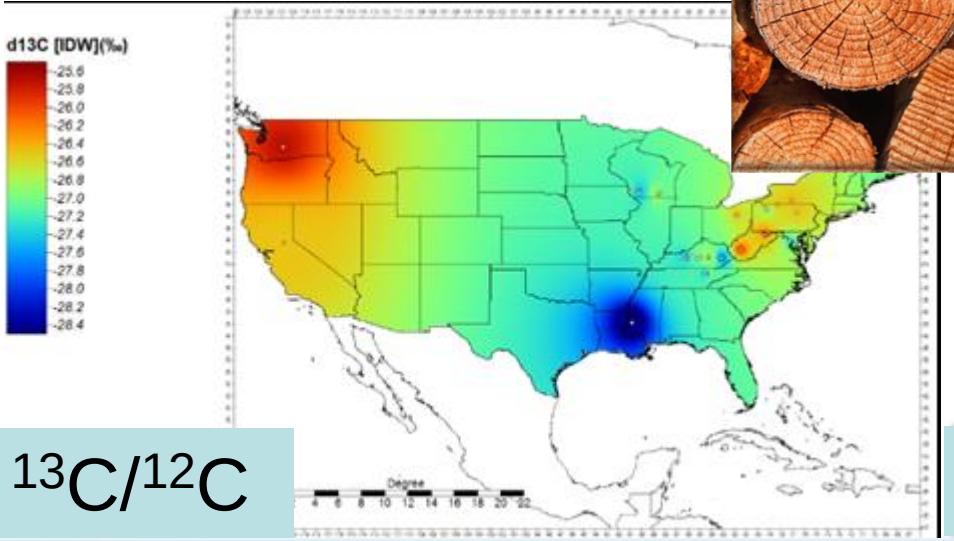
Current overview of the stable isotopic signatures in USA (oak)



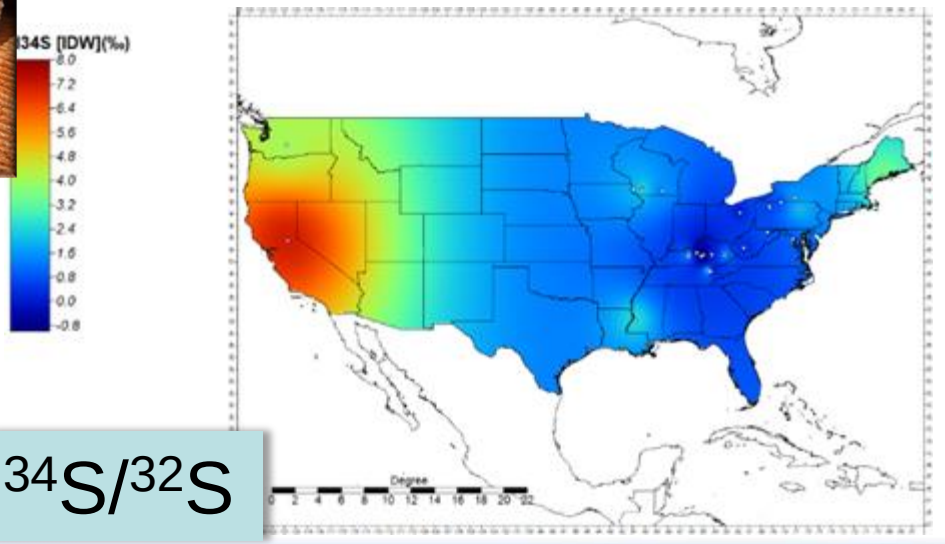
$^{18}O/^{16}O$



D/H



$^{13}C/^{12}C$



$^{34}S/^{32}S$

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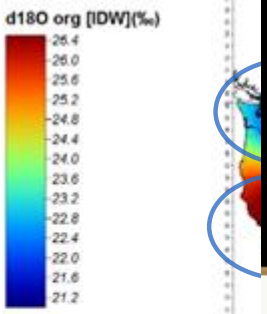
Current overview of the stable isotopic signatures in USA (oak)



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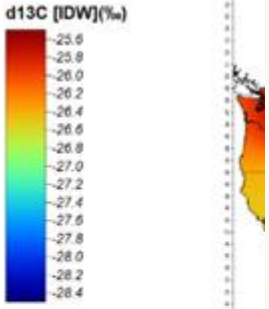

$^{13}C/^{12}C$

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JUSTICE NEWS

Department of Justice

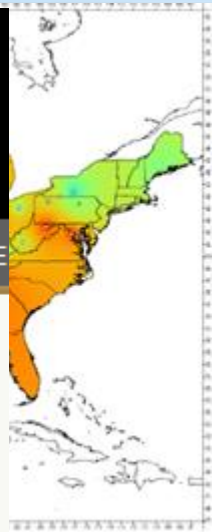
Office of Public Affairs

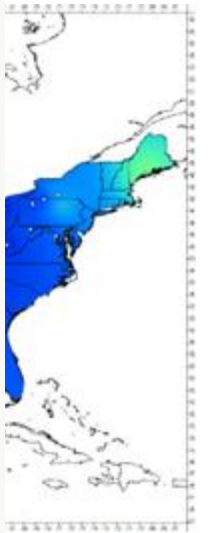
FOR IMMEDIATE RELEASE — Monday, February 1, 2016

Lumber Liquidators Inc. Sentenced for Illegal Importation of Hardwood and Related Environmental Crimes

Virginia Hardwood Flooring Company to Pay $13 Million, Largest Lacey Act Penalty Ever

Virginia-based hardwood flooring retailer Lumber Liquidators Inc. was sentenced today in federal court in Norfolk, Virginia, and will pay more than $13 million in criminal fines, community service and forfeited assets related to its illegal importation of hardwood flooring, much of which was manufactured in China from timber that had been illegally logged in far eastern Russia, in the habitat of the last remaining Siberian tigers and Amur leopards in the world, announced the Department of Justice.





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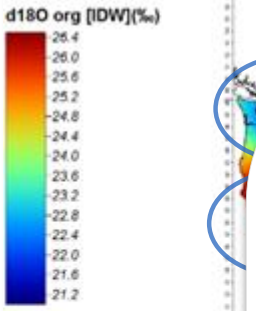
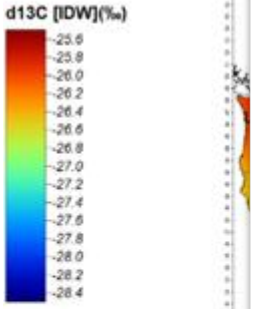


$^{18}O/^{16}C$



$^{13}C/^{12}C$

EUROPEAN
COMMISSION

Brussels, 12.2.2016
C(2016) 755 final

COMMISSION NOTICE

of 12.2.2016

GUIDANCE DOCUMENT

FOR THE EU TIMBER REGULATION

The higher the risk of corruption in a specific case, the more it is necessary to get additional evidence to mitigate the risk of illegal timber entering the EU market. Examples of such additional evidence may include third-party-verified schemes (see section 6 of this guidance document), independent or self-conducted audits, or timber tracking technologies (e.g. with genetic markers or stable isotopes).

Russia, in the habitat of the last remaining Siberian tigers and Amur leopards in the world, announced the Department of Justice.

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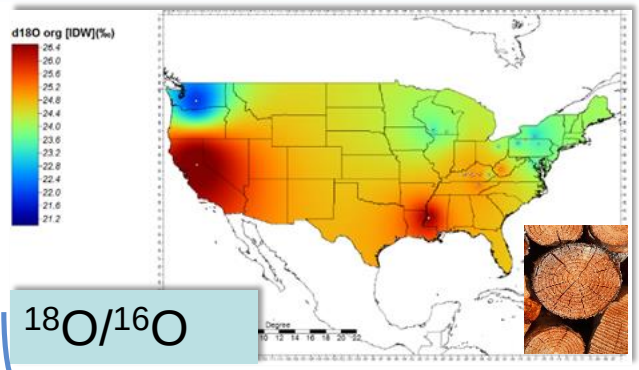
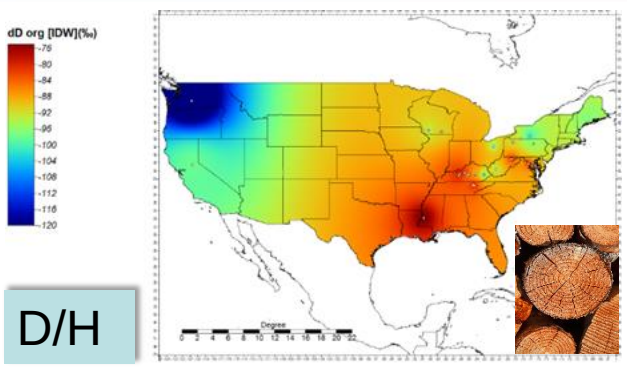
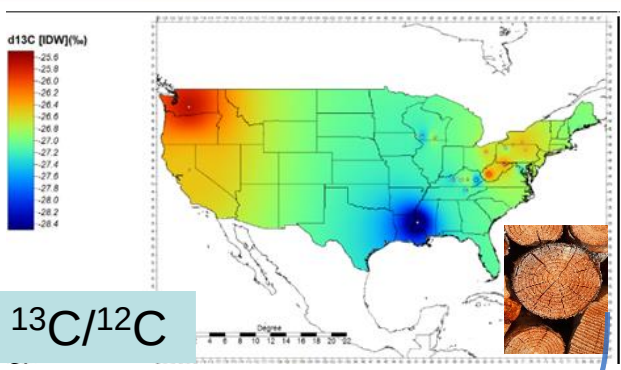
Main principle; stable isotopes signatures in cellulose



$^{18}O/^{16}O$

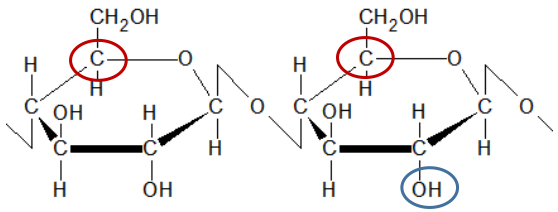


D/H



$^{13}C/^{12}C$

Carbohydrates = hydrated coal,
e.g. **cellulose**



Memory of the water and climate

Main component of cotton

The basis for determining the origin is available

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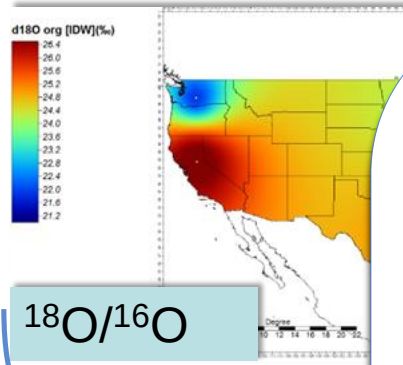
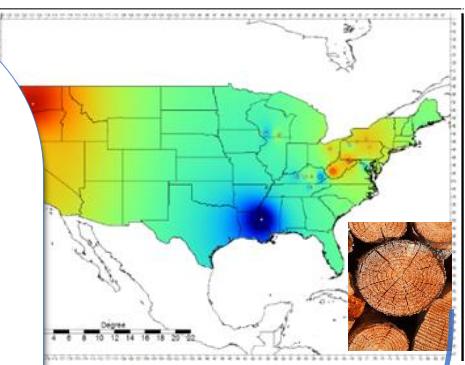
Main principle; stable isotopes signatures in cellulose

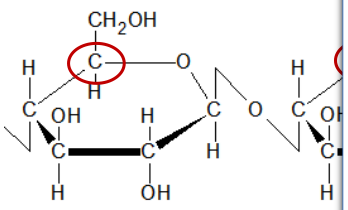


$^{18}O/^{16}O$

Is the determination of origin still possible in cotton and textiles?



Carbohydrates = hydra
e.g. **cellulose**



Memory of the wate

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Proof of Concept: May 2021 -> June 2022

US ban on imports from China's Xinjiang region takes effect

21-06-2022. BBC, By Annabelle Liang

Why is analytical proof of origin important ?

- - It creates independent (analytical) transparency in the market and therefore the company brand is protected.

- - Typical risk e.g.
  - ❖ Undesirable exploitation of the environment
  - ❖ Undesirable forced labor (China Xinjiang)

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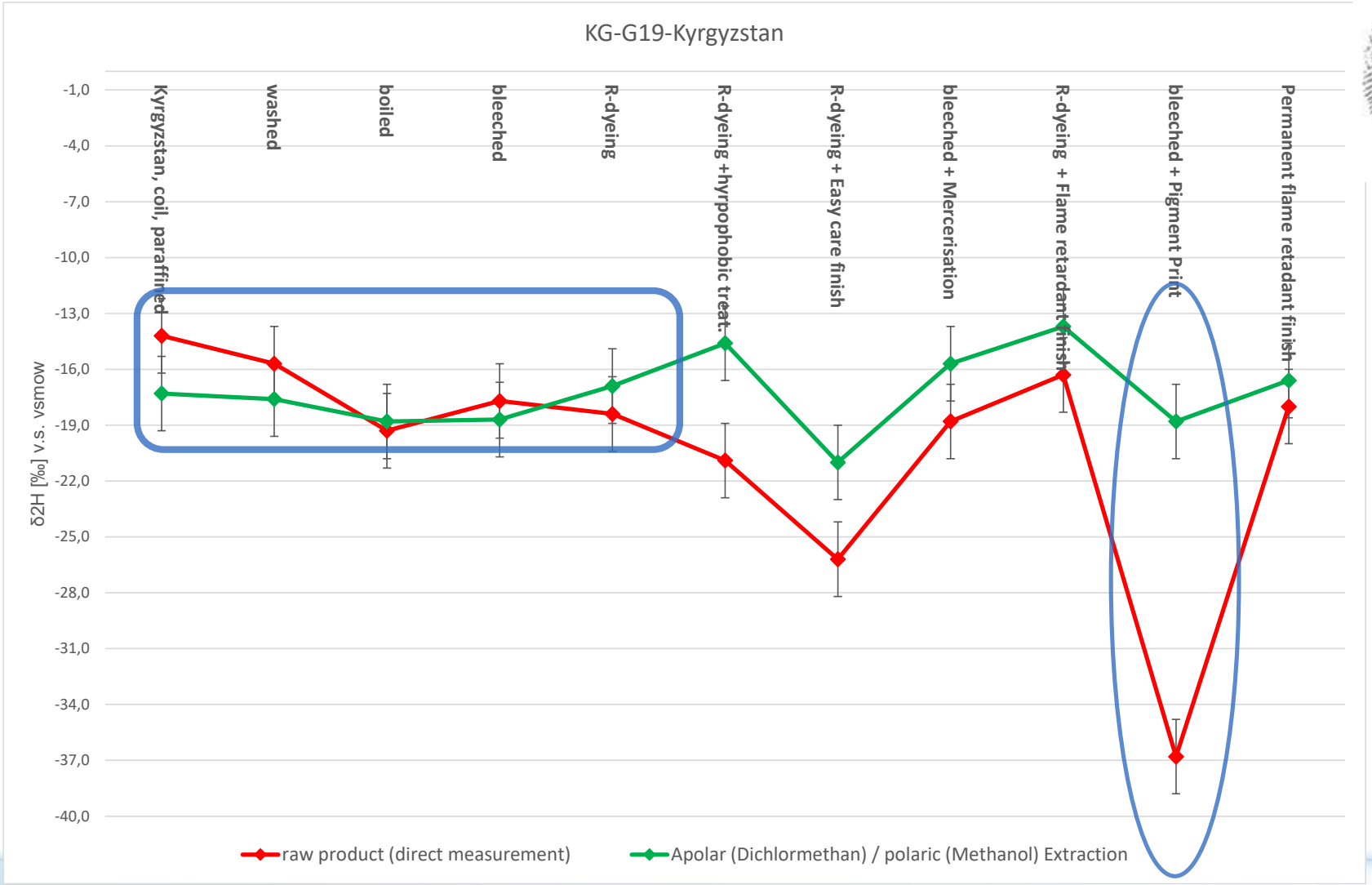
Influence of the different processing stages on the isotope pattern in the cotton.



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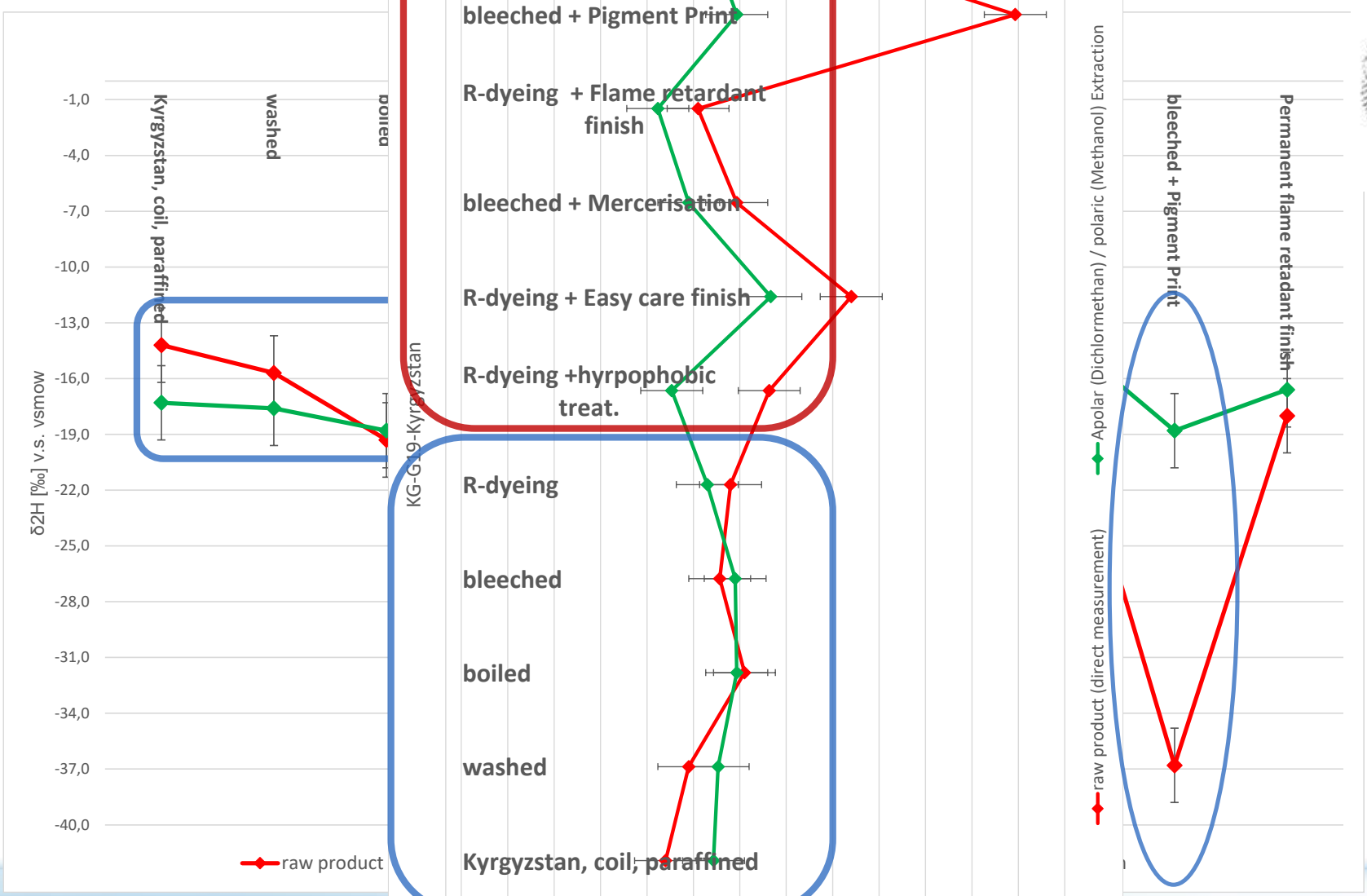
Influence of the differe ttern in the cotton.



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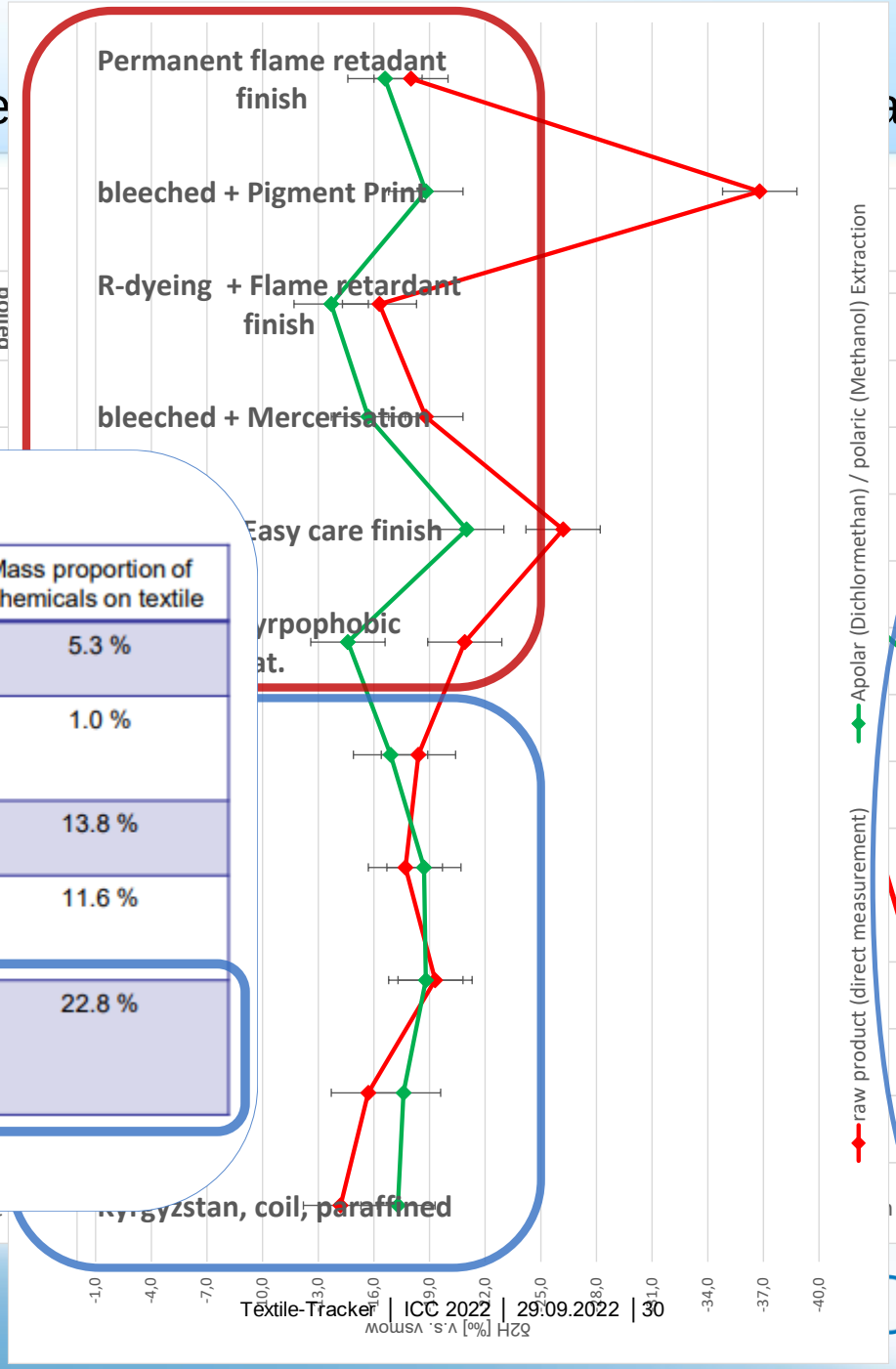
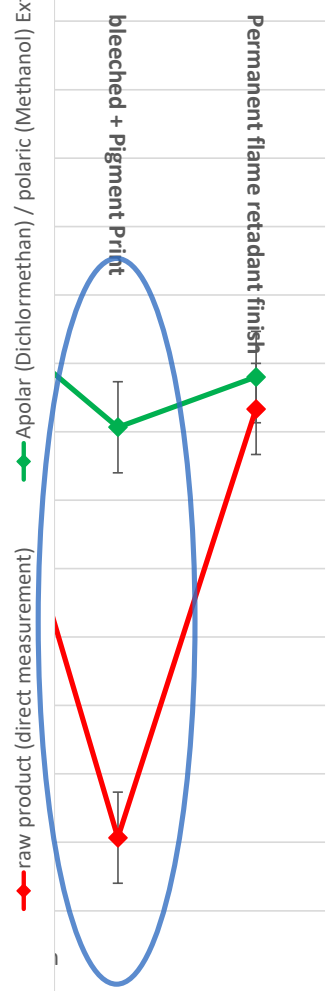


Finish	Mass proportion of chemicals on textile
Easy-care finish (modified dihydroxyethylene urea)	5.3 %
Hydrophobic treatment (highly branched polymers in a carbon matrix)	1.0 %
Flame retardant finish (inorganic phosphorus-nitrogen compound)	13.8 %
Permanent flame retardant finish (reactive organic phosphorus compound / phosphoric acid)	11.6 %
Pigment print (colour pigments mixed with compound of polyurethane hand dispersion, thickener and additives)	22.8 %



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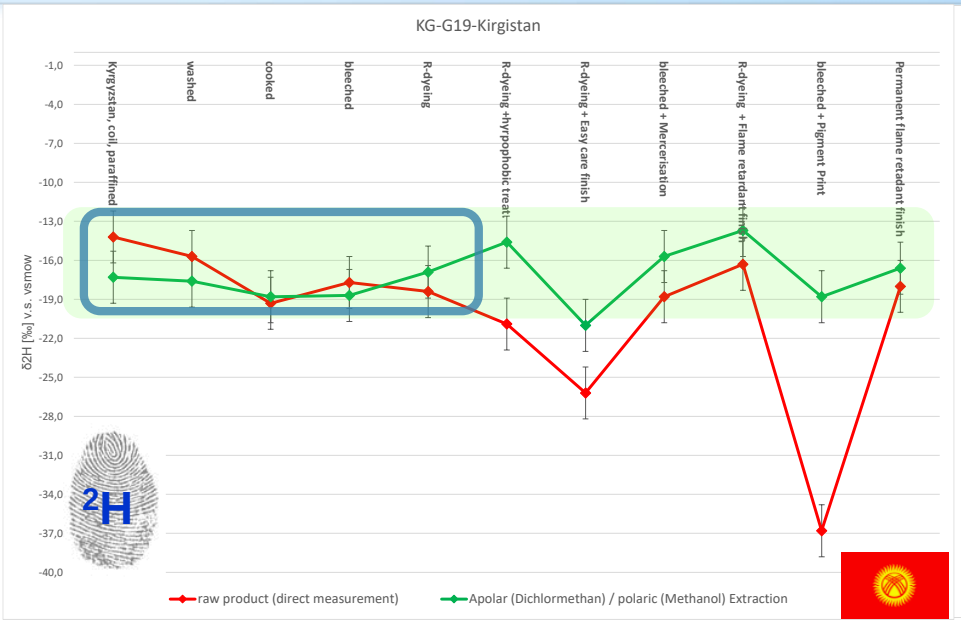
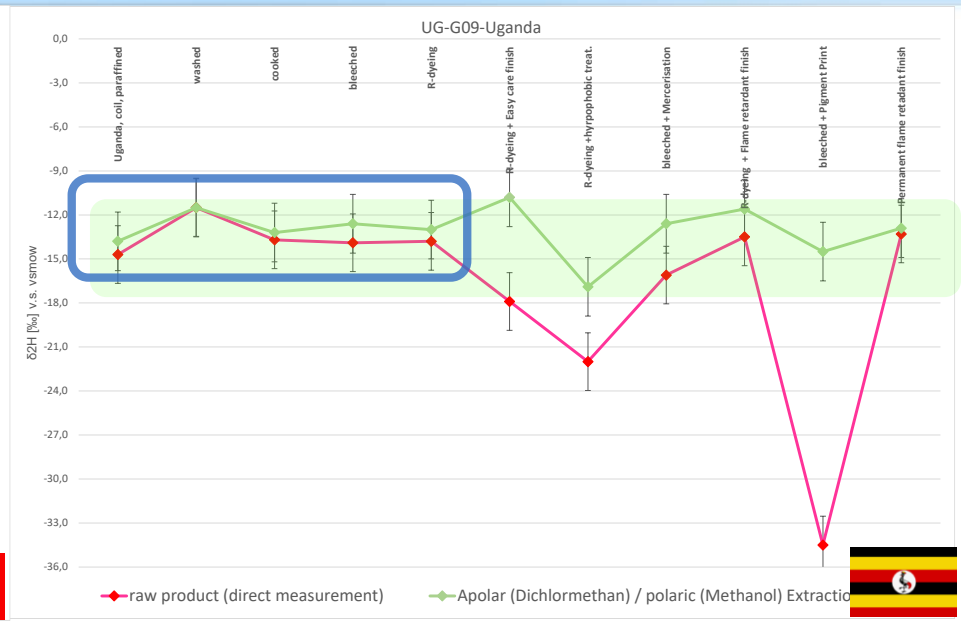
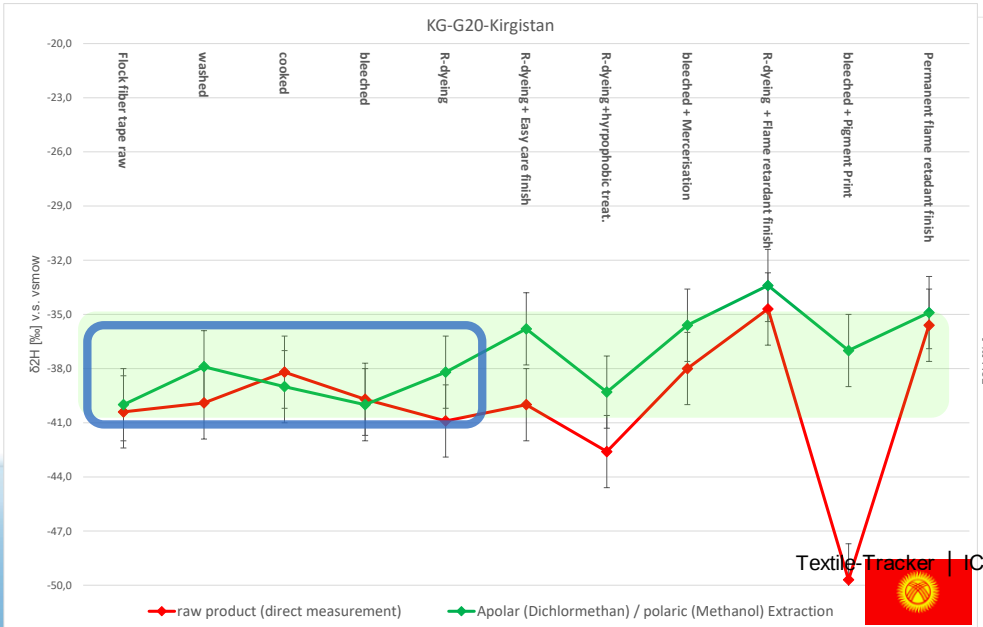
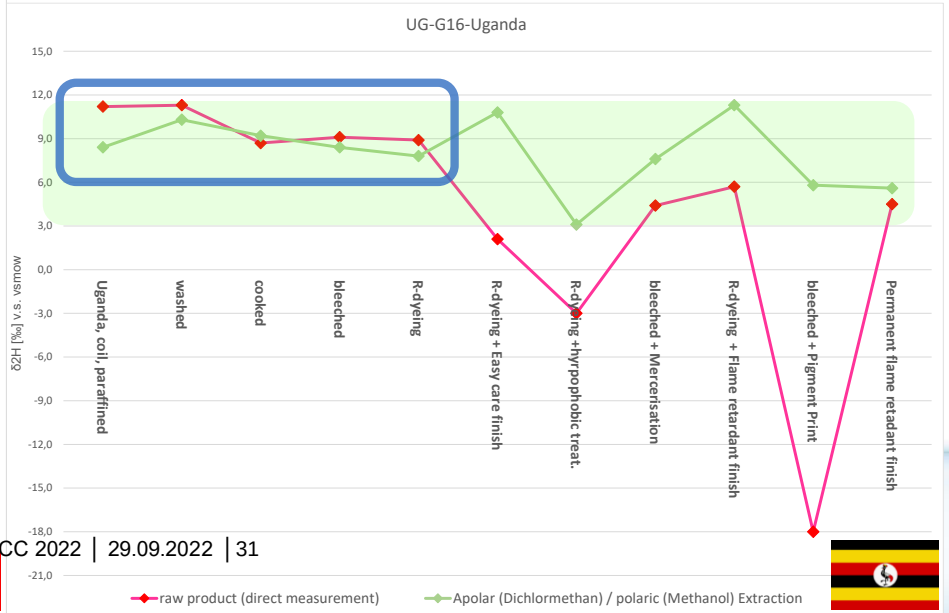
Influence of the different processing stages on the isotope pattern of Hydrogen.









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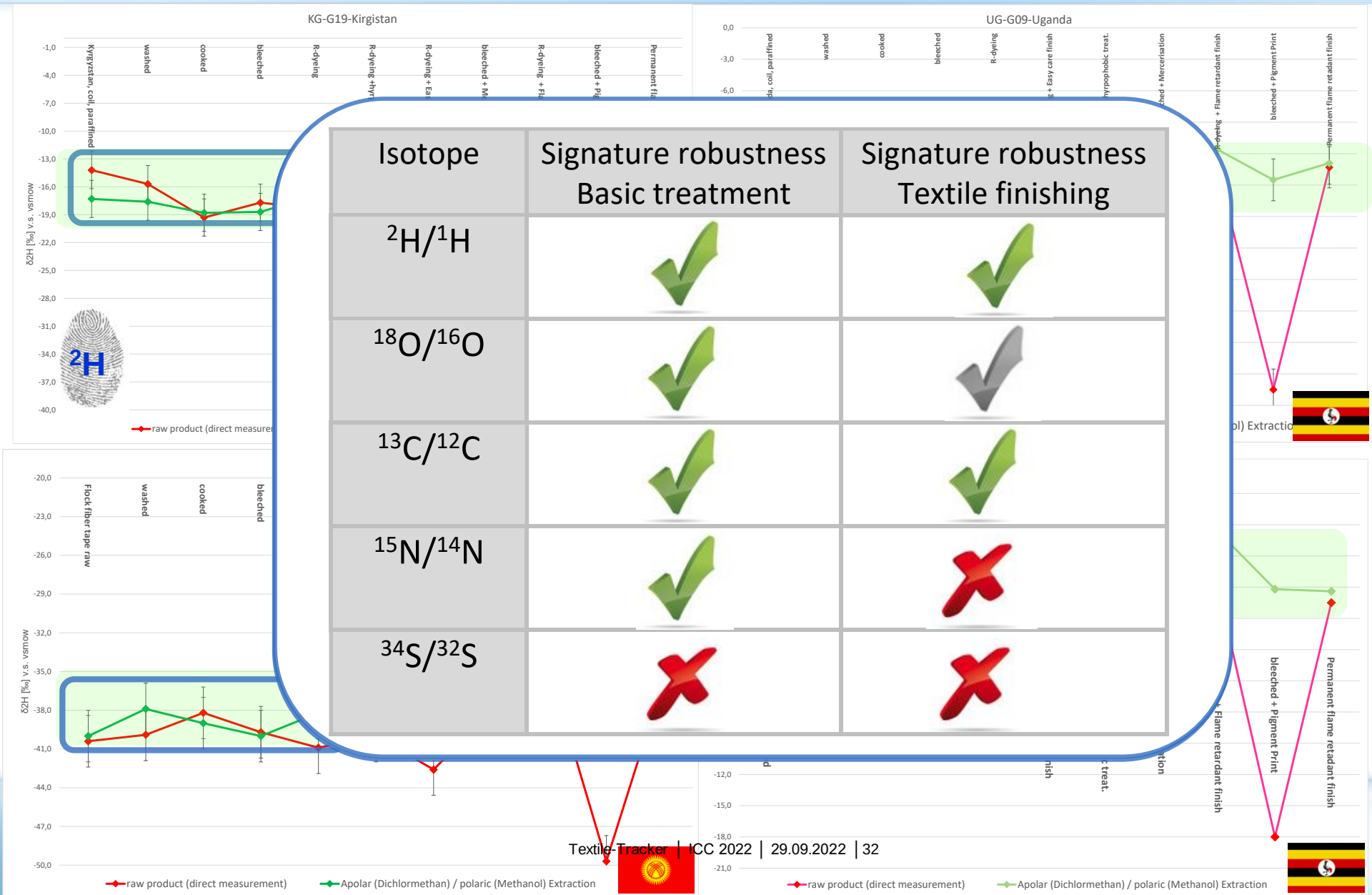

Isotope	Signature robustness Basic treatment	Signature robustness Textile finishing
$^{2}H/^{1}H$	✓	✓
$^{18}O/^{16}O$	✓	✓
$^{13}C/^{12}C$	✓	✓
$^{15}N/^{14}N$	✓	✗
$^{34}S/^{32}S$	✗	✗

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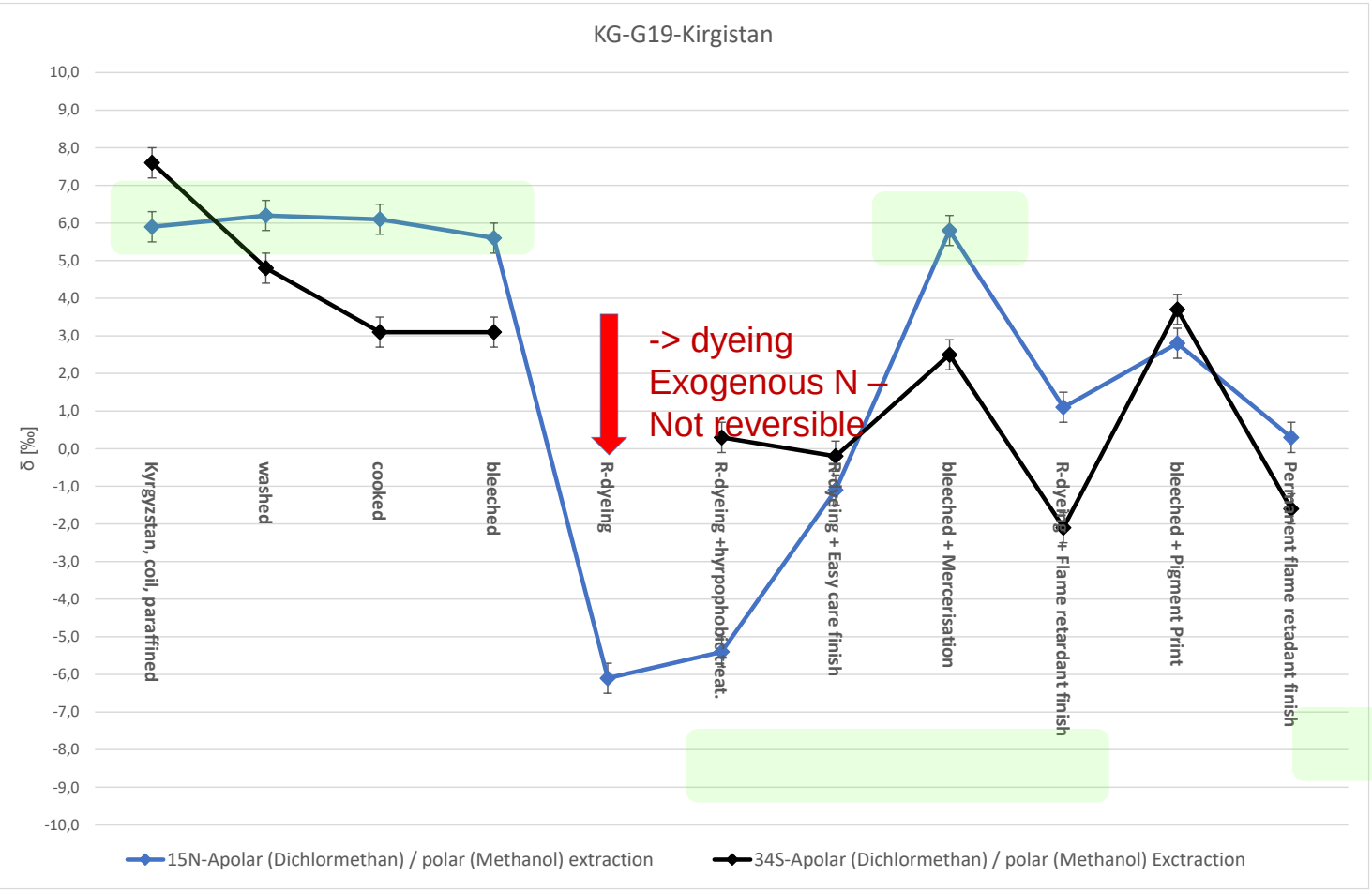
Influence of the different processing stages on the isotope pattern of nitrogen and sulfur



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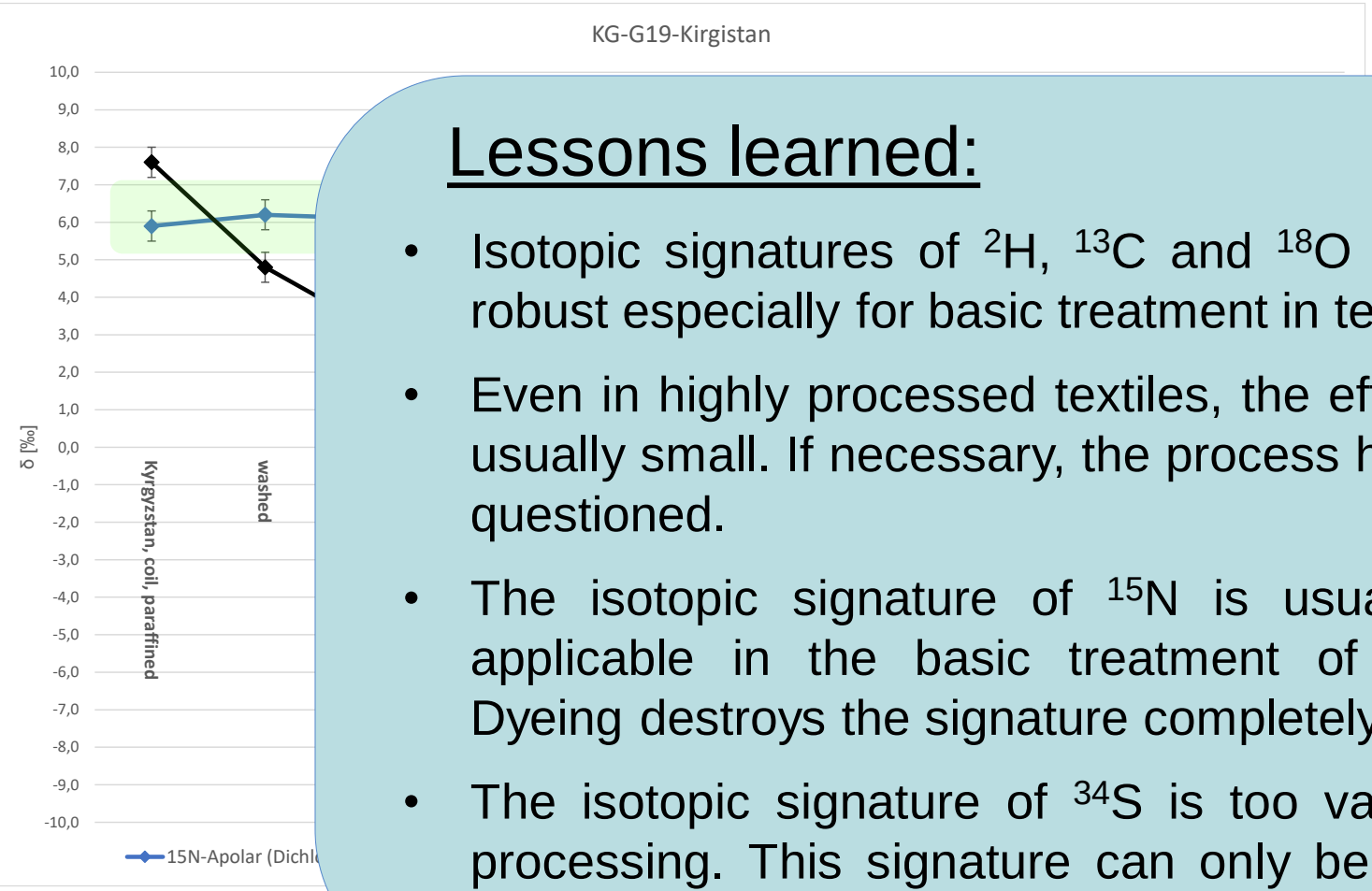
Influence of the different processing stages on the isotope pattern of nitrogen and sulfur



Lessons learned:

- Isotopic signatures of ^{2}H, ^{13}C and ^{18}O are very robust especially for basic treatment in textiles.
- Even in highly processed textiles, the effects are usually small. If necessary, the process has to be questioned.
- The isotopic signature of ^{15}N is usually only applicable in the basic treatment of textiles. Dyeing destroys the signature completely.
- The isotopic signature of ^{34}S is too variable in processing. This signature can only be used in unprocessed cotton.

N

12 largest cotton producing countries in the world

	Country	Production (Tons)
	India	6,188,000
	China	6,178,318
	United States of America	3,593,000
	Pakistan	2,374,481
	Brazil	1,412,227
	Uzbekistan	1,106,700
	Australia	885,100
	Turkey	846,000
	Argentina	327,000
	Greece	308,000
	Mexico	302,000
	Burkina Faso	265,500

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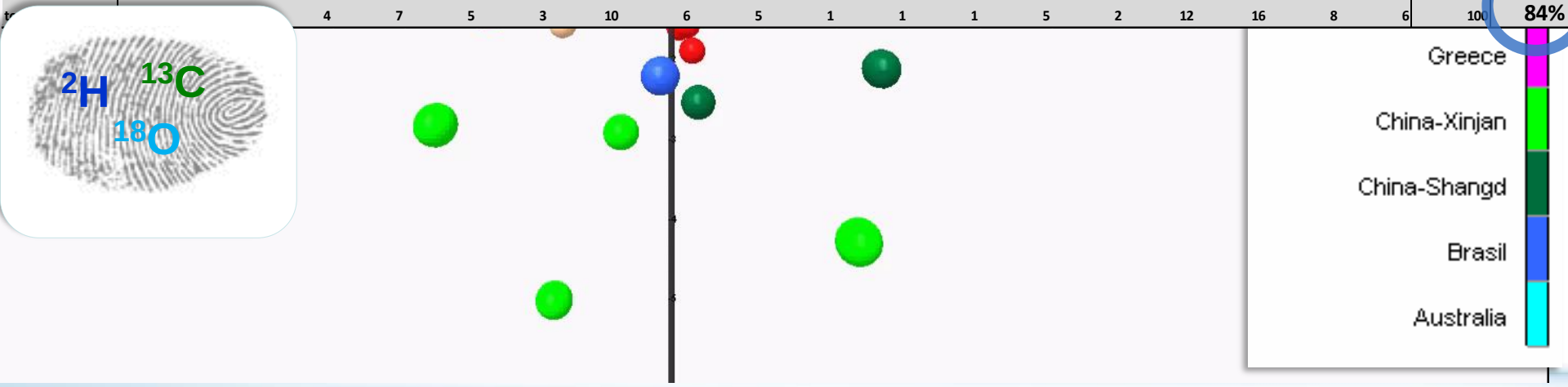
Discriminate Analysis (DA) of reference samples of various origins

from \ to	Australia	Brasil	China-Shangdong	China-Xinjang	Egypt	Greece	India	Kasachstan	Kyrgyzstan	Mali	Peru	Sudan	Tansania	Tschad	Turkey	USA	Uganda	Uzbekistan	Total	% correct
Australia	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3	100%
Brasil	0	5	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	6	83%
China-Shangdc	0	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4	100%
China-Xinjang	0	0	0	6	0	0	1	0	0	0	0	0	0	0	0	0	0	0	7	86%
Egypt	0	0	0	0	5	0	0	0	0	0	0	0	0	0	0	0	0	0	5	100%
Greece	0	0	0	0	0	3	0	0	0	0	0	0	0	0	1	0	0	0	4	75%
India	0	0	0	0	0	0	6	0	0	0	0	0	0	1	0	0	0	0	7	86%
Kasachstan	0	0	0	0	0	0	0	4	0	0	0	0	0	0	0	0	0	0	4	100%
Kyrgyzstan	0	0	0	0	0	0	0	0	4	0	0	0	1	0	0	0	0	0	5	80%
Mali	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	1	0	0	2	50%
Peru	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	1	100%
Sudan	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	1	100%
Tansania	0	0	0	0	0	0	2	0	0	0	0	0	2	0	0	1	1	0	6	33%
Tschad	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1	100%
Turkey	0	0	0	0	0	0	1	0	0	0	0	0	1	0	11	0	0	0	13	85%
USA	0	0	0	0	0	0	0	2	0	0	0	0	0	0	0	14	0	0	16	88%
Uganda	0	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	7	0	9	78%
Uzbekistan	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	6	6	100%
t			4	7	5	3	10	6	5	1	1	1	5	2	12	16	8	6	100	84%



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The final aim….the global database

Further step:
Creation of an international open database to analyse the origin of **cotton** and **textiles**.

More than 10 years to get:

WORLD FOREST ID

Using science to take deforestation off the shopping list

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The final aim….the global database

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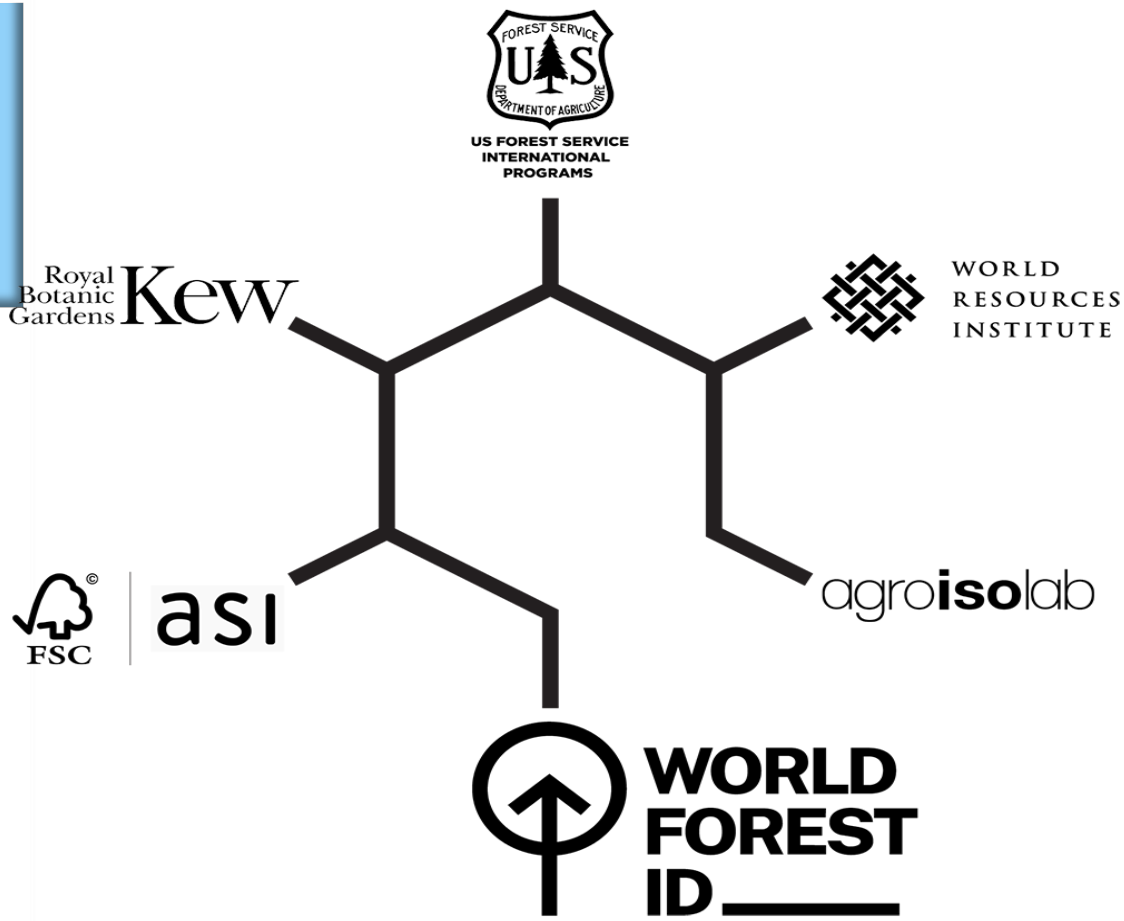
Creation of an international open database to analyse the origin of **cotton** and **textiles**.



More than 10 years to get:

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Why is stable isotope method currently the leading universal standard method to verify the origin?

	Stable Isotopes	Genetic
Robustness	The stable isotope information is available in the elements or in the main components of the product of cotton / textiles -> cellulose ➔ very robust information ➔ no processing effects (^{2}H, ^{13}C, ^{18}O)	The genetic information is available but only as an add on component in cotton. Processing (e.g. drying, washing, boiling) destroys the genetic information in cotton / textiles.
information	The stable isotope information reflects the conditions of the location (hydrology, climate, geology).	The genetic information is only an indirect origin information, i.e. which variety is used or which population drifts exist (Nature). ➔ no direct origin information

Issues:

Mixtures are still the greatest challenge in analytics and will never be completely solved. As a rule, only the predominant origin (> 80 %) will be testable.

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However…,
Any data (e.g. isotopic, genetic, trace elements) matters and might be important for origin check.

So let´s start collecting data…

Thank you very much for your attention

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