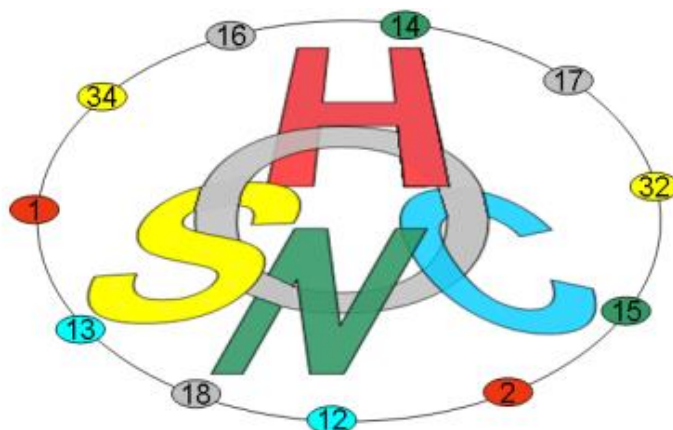


The 1st Isotope Ratio MS DAY



May 9-11, 2016

Fondazione Edmund Mach

S. Michele all'Adige (Trento, Italy)

BOOK OF ABSTRACTS

**PROCEEDINGS OF THE
1st ISOTOPE RATIO MS DAY**

May 9-11, 2016
Fondazione Edmund Mach

Federica Camin
Editor

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FOREWORD

Isotope ratio mass spectrometry (IRMS) is gaining a lot of interest with many applications in different fields, ranging from food (traceability, authentication,), medicine, ecology, hydrology, environment, cultural heritage to geosciences.

The 1st IRMS Day inaugurates a new series of workshops dedicated to the applications of isotope ratio mass spectrometry to the different fields. It's aimed to bring together a wide community of scientists working in the stable isotope area to encourage communication across disciplines and dealing with similar issues.

Organized in plenary lectures, keynotes, oral and poster communications, the 1st IRMS Day is a good opportunity to link industrial needs and academic knowledge and to promote meeting, discussion and cooperation among scientists coming from public and private institutions, universities and industries to define the state of the art, instrumentation, methodologies, applications and innovations in the isotope ratio mass spectrometry field.

We would like to thank many partners who contributed in the organization: sponsors, various supporting Institutions, patronages and the Province of Trento.

Our highest gratitude to all involved in the organization of this workshop.

On behalf of the Scientific and Organising Committees

Federica Camin, Gianluca Giorgi.

SCIENTIFIC PROGRAMME

Monday, May 9

1:00 p.m. – 2:30 p.m.	Registration and poster installation
2:30 p.m.– 3:00 p.m.	Welcome and opening ceremony
	Session 1: FOOD
	Chairpersons: Luigi Dallai, Paola Iacumin
3:00 p.m. – 3:30 p.m.	PL1: Working group stable isotope analytics of GDCh and its role with regard to food authentication in Germany <i>Andreas Rossmann</i> Isolab, Germany
3:30 p.m. – 3:45 p.m.	OR1: The influence of climate variability on chemical composition of European wines: a regional scale study (Italy and Slovenia) <i>Fabio Paolo Polo</i> Ca' Foscari University, Venezia, Italy
3:45 p.m. – 4:00 p.m.	OR2: Isotope ratio mass spectrometry in combination with chemometrics for the characterization of the geographical origin and the agronomical practice of table grape <i>Grazia Casiello</i> University of Bari “Aldo Moro”, Bari, Italy
4:00 p.m. – 4:15 p.m.	OR3: Characterization of Mozzarella di Bufala Campana and farm production technique using C, N and O stable isotopes analysis: preliminary results <i>Simona Altieri</i> Second University of Naples, Napoli, Italy
4:15 p.m. – 4:45 p.m.	Poster session & coffee break
4:45 p.m. – 5:05 p.m.	KN1: State of the art Isotope Ratio Mass Spectrometry (IRMS) applied to food traceability <i>Lionnel Mounier</i> Thermo Fisher Scientific, Coutaboeuf, France
5:05 p.m. – 5:20 p.m.	OR4: Using GC/c/IRMS analysis to improve food traceability <i>Mauro Paolini</i> Fondaz. E.Mach, S. Michele all'Adige (TN), Italy
5:20 p.m. – 6:00 p.m.	COSTITUZIONE DEL GRUPPO IRMS ITALIANO
6:00 p.m.	End of session
6:00 p.m. – 7:00 p.m.	Cocktail offered by Thermo Fischer Scientific

Tuesday, May 10

8:30 a.m. – 9:00 a.m.	Registration
	Session 2: ISOSCAPES
	Chairpersons: Enrico Brugnoli, Federica Camin
9:00 a.m. – 9:30 a.m.	<p>PL2: Transforming rainwater isoscape patterns into effective applications for migratory wildlife conservation <i>Len Wassenaar</i> IAEA, Wien, Austria</p>
9:30 a.m.– 9:45 a.m.	<p>OR5: <i>The geographical origin of birds migrating through Alps: a stable isotope approach (δ^2H)</i> <i>Alessandro Franzoi</i> Fondaz. E.Mach, S. Michele all'Adige (TN), Italy</p>
9:45 a.m. – 10:00 a.m.	<p>OR6: <i>Spatial- and spatio-temporal analysis of stable isotopes ratios in biogeochemical processes</i> <i>Marco Ciolfi</i> CNR Institute of Agro-Environmental and Forest Biology Porano, Italy</p>
10:00 a.m.– 10:15 a.m.	<p>OR7: <i>Olive ripening and cultivar effects on carbon stable isotope compositions of n-alkanes and fatty acids in extra-virgin olive oils</i> <i>Silvia Portarena</i> CNR Institute of Agro-Environmental and Forest Biology Porano, Italy</p>
10:15 a.m. – 11:00 a.m.	Coffee break and poster session
	Session 3: WATER
	Chairperson: Len Wassenaar
11:00 a.m. – 11:20 a.m.	<p>KN2: <i>Reconstructing Antarctic climate over the last 2000 years by means of isotopic profiles</i> <i>Barbara Stenni</i> Università Ca' Foscari Venezia, Italy</p>
11:20 a.m. – 11:35 a.m.	<p>OR8: <i>Oxygen and hydrogen stable isotope content in daily-collected precipitation samples at Dome C, East Antarctica</i> <i>Giuliano Dreossi</i> Università Ca' Foscari Venezia, Italy</p>

11:35 a.m. – 11:50 p.m.	OR9: <i>The “ISONITRATE Italy” project: exploring nitrate sources in polluted aquifers of the Po river alluvial plain (North Italy) by means of isotopic techniques</i> <i>Luisa Stellato</i> Seconda Università degli Studi di Napoli, Italy
11:50 p.m. – 12:05 p.m.	OR10: <i>CNS stable isotopes in the Adige river waters: insights on natural and anthropogenic components</i> <i>Chiara Marchina</i> Scuola Superiore S. Anna, Pisa, Italy
12:30 p.m. – 2:00 p.m.	Lunch
	Session 4: ENVIRONMENT
	Chairpersons: C. Lubritto, Barbara Stenni
2:00 p.m. – 2:20 p.m.	KN3: <i>Simultaneous determination of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in CO_2 involved in leaf gas-exchange processes by means of isotope ratio infrared spectrometry (IRIS - Delta Raytm)</i> <i>Marco Lauteri</i> National Research Council, Porano, Italy
2:20 p.m. – 2:35 p.m.	OR11: <i>A multiparametric approach to study the forest ecosystem responses to environment</i> <i>Martina Pollastrini</i> University of Florence, Italy
2:35 p.m. – 2:50 p.m.	OR12: <i>Applications of carbon and nitrogen stable isotopes analyses in environmental studies</i> <i>Federico Rampazzo</i> ISPRA STS Chioggia, Italy
2:50 p.m. – 3:05 p.m.	OR13: <i>Long-term warming affects ^{13}C and ^{15}N allocation in a field-grown Mediterranean shrub <i>Cistus Monspeliensis</i></i> <i>Olga Gavrichkova</i> National Research Council, Porano, Italy

3:05 p.m. – 3:20 p.m.	OR14: <i>Thermally based isotopic speciation of carbon pools in environmental matrices</i> <i>Claudio Natali</i> University of Ferrara, Italy
3:20 p.m. – 3:40 p.m.	KN4: <i>Preliminary results from a microvolume, dynamically heated analytical column for preconcentration and separation of simple gases prior to stable isotopic analysis</i> <i>Filip Volders</i> Elementar analysensysteme, Hanau, Germany
3:40 p.m. – 4:20 p.m.	Coffee break and poster session
	Session 5: SOIL
	Chairperson: F. Grassa, F. Marzaioli
4:20 p.m. – 4:35 p.m.	OR15: <i>Elucidating the fate of applied nitrogen fertilizer in rice paddy soils by means of bulk and compound-specific stable isotope $\delta^{15}N$ techniques</i> <i>Daniel Said-Pullicino</i> University of Turin, Italy
4:35 p.m. – 4:50 p.m.	OR16: <i>Belowground carbon allocation patterns as determined by the in-growth soil core ^{13}C technique across different ecosystem types</i> <i>Mirco Rodeghiero</i> Fondaz. E. Mach, S. Michele all'Adige (TN), Italy
4:50 p.m. – 5:05 p.m.	OR17: <i>Carbon allocation and partitioning in mountain grassland ecosystems during drought stress and recovery</i> <i>Angela Augusti</i> CNR, Porano, Italy
5:05 p.m. – 5:25 p.m.	OR18: <i>Use of stable isotopes in agricultural sciences</i> <i>Federica Tamburini</i> ETH, Zurich, Switzerland
5:25 p.m.	End of session
6:30 p.m.	Guided tour of the Muse museum and social dinner

Wednesday, May 11

	Session 6: DOPING AND ARCHAEOOMETRY
	Chairpersons: Andreas Rossmann
9:15 a.m. – 9:35 a.m.	<p>KN5: <i>Detection of pseudo-endogenous steroids In doping control analyses by GC/c/IRMS</i> <i>Xavier de La Torre</i> Laboratorio Antidoping Federazione Medico Sportiva Italiana, Roma, Italy</p>
9:35 a.m. – 9:55 a.m.	<p>KN6: <i>Carbon and oxygen isotope data of carbonates and of structural carbonate of bioapatite: what are their meaning and possible use?</i> <i>Paola Iacumin</i> University of Parma, Italy</p>
9:55 a.m. – 10:10 a.m.	<p>OR19: <i>A multiproxy approach to study dietary habit in different historical contexts</i> <i>Paola Ricci</i> Second University of Naples, Italy</p>
10:10 a.m. – 10:25 a.m.	<p>OR20: <i>¹⁴C mortar dating: selection of uncontaminated binder fractions by using stable carbon isotope analysis</i> <i>Anna Addis</i> University of Padova, Italy</p>
10:25 a.m. – 11:00 a.m.	Coffee break and poster session
	Session 7: NEW TECHNIQUES
	Chairperson: Xavier de La Torre
11:00 a.m. – 11:20 a.m.	<p>KN7: <i>High efficiency multidimensional gas chromatography coupled to isotope ratio mass spectrometry and quadrupole mass spectrometry simultaneous detection</i> <i>Daniilo Sciarrone</i> University of Messina, Italy</p>

11:20 a.m. – 11:35 a.m.	OR21: <i>Comparison of isotopic ratio mass spectrometry (IRMS), non-dispersive infrared spectroscopy (NIRS) and infrared spectroscopy for the isotopic composition analysis of food</i> <i>Concetta Pironti</i> University of Salerno, Italy
11:35 a.m. – 12:15 p.m.	Round table: stable isotopes: state-of-the-art, innovation & perspectives
12:15 p.m.	Closing remarks and arrivederci!

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ORAL COMMUNICATIONS

PL1 - Working group stable isotope analytics of GDCh and its role with regard to food authentication in Germany

Andreas Rossmann^{1,2}

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² Lehrstuhl für Grünlandlehre, Technische Universität München, 85350 Freising-Weihenstephan, Germany

The working group stable isotope analytics (AG (Arbeitsgruppe) Stabilisotopenanalytik) of GDCh (Gesellschaft Deutscher Chemiker e.V., subgroup “Food Chemistry” (Lebensmittelchemische Gesellschaft)) was founded in July 2001 on an initiative of GDCh working group fruit juice analytics. Members are from universities, from public control laboratories, from industry and from commercial laboratories. Currently there are 16 active and 11 corresponding members of this working group, which meet usually twice a year. Work conducted until now includes publication of scientific statements (“Positionspapiere”) about questions dealing with application of stable isotope analyses in food control, eg regarding differentiation of products from conventional and organic production, application of oxygen isotope analysis of water, control of meat geographical origin, or testing of vanilla flavor authenticity, and respective data evaluation. Inter laboratory method testing of carbon isotope determination in vanillin prepared from flavored milk products, of oxygen isotope analysis of water from wine and of ethanol from fermented juices had been organized. A small proficiency testing system is maintained with 4-6 rounds per year, using water samples and relevant components from natural substances, and considering all bio elements’ (HCNOS) stable isotope results. The working group runs its own database about single strength apple juices, and a database of other food products investigated by its members (eg asparagus, fruits, vegetables). Currently a database of milk and milk products is being planned for, and calibration of common and suitable inter laboratory reference materials is performed. The working group has already initiated several events for exchange of knowledge and professional development, sometimes together with other working groups of GDCh (eg AG fruit juice analytics, AG flavor analytics).

OR1 - The influence of climate variability on chemical composition of European wines: a regional scale study (Italy and Slovenia)

Fabio Paolo Polo¹, Giulio Cozzi², Nives Ogrinc³, Clara Turetta², Carlo Barbante²

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Climate change is having an increasing influence on vine phenology and grape composition, affecting vinifications, wine chemistry and the quality of productions. Wine grape cultivation provides a good test case for measuring indirect impacts mediated by changes in agriculture, because viticulture is sensitive to climate and is concentrated in Mediterranean climate regions that are global biodiversity hotspots. Moreover, on a regional level and on a shorter time scale, the seasonal weather conditions modify the quality of yields determining the final properties of wine. In the present research, we studied wines from Italy and Slovenia with the purpose of differentiating them by the different vintages (from 2009 to 2012), which are supposed to be influenced by temperature and rain during each year's growing season. Specific chemical techniques were used, in particular mass spectrometry (ICP-MS) and isotopic mass spectrometry (IRMS), both of which are usually employed to detect wine adulterations and to establish the geographical provenance of wines. In particular, we investigated the relationship between macro- and micro-elements, Rare Earth Elements and stable isotopes [$\delta^{13}\text{C}$, $\delta^{18}\text{O}$, (D/H)I, (D/H)II]. The datasets were examined via statistical techniques to show their relation to weather conditions as well as their mutual connection. Italian and Slovenian wines were distinguished, with the exception of few samples, by both TEs and REEs results. This separation, due to different elemental compositions, may be justified as being part of two distinct environmental and geographical belongings (terroir) but also to the processes of wine production, from the harvest to the bottling, which have certainly interfered and characterized the products. In the case of Italian wines the weather conditions were evidenced with an important separation of stable isotopes which they confirmed to be very sensitive. Regarding Slovenian wines, the studied regions were characterized of three very different environments, and the elemental measurements resulted very useful. However, it was not possible to separate the different wine regions using elemental composition while the vintages were clearly evidenced. The results of this work were not able to confirm the mass spectrometry and the isotopic mass spectrometry to be useful to distinguish a wine for a specific region while they were able to separate vintages growth in different weather conditions. In conclusion of the work we can furthermore suggest from our data that weather conditions showed to have more influence in the chemical composition of wines than the environmental contribution. Moreover, the more is different a year in terms of weather conditions, the more the techniques of analysis can show the separation of the wines made in that year. However, has been not possible distinguish vintages produced in years of similar weather conditions.

OR2 - Isotope ratio mass spectrometry in combination with chemometrics for the characterization of the geographical origin and the agronomical practice of table grape

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The aim of this study was to evaluate the usefulness of isotopic ratios (i.e. $^2\text{H}/^1\text{H}$, $^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$, and $^{18}\text{O}/^{16}\text{O}$) in combination with appropriate statistical techniques, as possible markers, to discriminate the agronomical practice (conventional vs. organic farming) or the place of production of table grape samples of cv. Italia and cv. Red globe, respectively.

In order to quantitatively evaluate which of the isotopic variables were more discriminating, a t-test was carried out highlighting statistically significant differences ($p \leq 0.05$) only for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotopic ratios both for the geographical origin and for the farming method. A Principal Component Analysis (PCA) showed no good separation of samples according to their geographical area and agronomical practice therefore, for classification aims, a supervised approaches were carried out. In particular, General Discriminant Analyses (GDA) were used giving prediction abilities of 75.0% and 92.2% for the farming and origin discrimination, respectively.

OR3 - Characterization of Mozzarella di Bufala Campana and farm production technique using C, N and O stable isotopes analysis: preliminary results

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The traceability of PDO (Protected Denomination of Origin) products is increasingly in importance to guarantee both producers and consumers. The certification of the geographical origin of these foodstuffs is essential to assure the authenticity and quality of itself. Multi-element stable isotopes analysis is nowadays affirmed as a valuable technique to discriminate the origin area of foods, providing a univocal characterization useful against possible counterfeiting.

The Mozzarella di Bufala Campana is a typical dairy product of South Italy, made exclusively using milk of buffaloes living in the specific regions designated for the production. Carbon isotopes can give information about the animal's diet. Nitrogen signal can depend on the isotopic composition of plants consumed and of the original soil, including agriculture practice as fertilization. Instead, oxygen isotopic ratios of Mozzarella should reflect the signal of the water used by animals.

The objectives of this project, financed by LR5 law of Campania Region, are:

- i. characterization of the raw material used and the farm making process, by means of isotopic analysis on fodder, milk and Mozzarella collected in the agricultural company of the territory of the Caserta and Salerno provinces (approved PDO production areas);
- ii. comparison of isotopic measurement performed on samples coming from several brands of Mozzarella directly from selling points.

Carbon, Nitrogen and Oxygen stable isotopes ratios were measured on the lyophilized samples. Moreover, other analyses (NMR, trace elements, etc.) will be realized and processed in a common statistical framework.

Preliminary results showed a differentiation of samples in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signals. Nitrogen isotopic ratios were less discriminating.

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KN1 - State of the art Isotope Ratio Mass Spectrometry (IRMS) applied to food traceability

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Keywords: food authenticity, isotope fingerprinting, isotopic ratio mass spectrometry

Several analytical methods, including chromatography, spectroscopy or mass spectrometry, can reveal adulterations or can enable to track the origin of substances. Isotope Ratio Mass Spectrometry (IRMS) is a particularly efficient technique when it becomes necessary to distinguish between the sources (what from) and between the origins (where from). The isotope ratio fingerprinting is based on the analysis of small isotopic differences in compounds in order to determine the relative isotopic abundances of elements such as C, N, O, H and S contained in the material. The measured isotopic differences are originating from the physical and biochemical isotope fractionation occurring in nature, they are providing information about the source, the origin, and the naturalness of substances. Based on isotopic ratios it is possible to collect information about the geographical, the chemical or the botanical origin of substances and isotopic ratios can enable the differentiation between natural and synthetic products.

The purpose of the presentation is to explore and to illustrate the state of the art in Isotope Ratio Mass Spectrometry to characterize the origin and the naturalness of food products.

Recent advances in instrumentation and in applications will be highlighted.

OR4 - Using GC/c/IRMS analysis to improve food traceability

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Bulk analysis of the stable isotope ratios of carbon, nitrogen, sulphur, oxygen and hydrogen in food samples is a common tool for assessing origin and/or food fraud. Many studies have shown that bulk isotope analysis of agricultural products is able to distinguish between organic and conventional agriculture systems and to separate the geographical areas from which food originates.

In the last few years methods aimed at compound specific stable isotope analysis using gas chromatography-isotope ratio mass spectrometry (GC/IRMS) have been developed in many research areas. The ability to separate compounds and then determine the isotopic ratio of each of them represents a significant advance in isotopic analysis, obtaining a more in-depth understanding.

In different studies we proved the accuracy of the information obtained by applying compound specific analysis in comparison to bulk analysis. Compound groups such as amino acids and fatty acids can help to provide further detailed information on physiological pathways and local conditions (soil and water availability) and can therefore add further information.

$\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ determination of single amino acids after N-acetylisopropyl derivatisation was used to discriminate between conventional and organic wheat grown using synthetic nitrogen fertilisers and animal manure or green manure from nitrogen-fixing legumes respectively. The results demonstrated that the $\delta^{13}\text{C}$ of glutamic acid and glutamine in particular, but also the combination of the $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ of 10 amino acids (alanine, aspartate, glutamate, glycine, isoleucine, leucine, phenylalanine, proline, threonine and valine), can significantly improve discrimination between conventional and organic wheat (Paolini et al., 2015).

The $\delta^{15}\text{N}$ of wine proline has been shown to be an additional isotopic marker for tracing the geographical origin of wine. Indeed, measurement of the variability of nitrogen isotopic values along the wine production chain has shown that the $\delta^{15}\text{N}$ value of proline is very close to the $\delta^{15}\text{N}$ value of the growing soil (Paolini et al., 2016).

Finally the $\delta^{13}\text{C}$ of palmitic, stearic, oleic and linoleic acids after ethanol transesterification of oil triglycerides, considerably improved geographical differentiation between European and non-European extra-virgin olive oil.

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PL2 - Transforming rainwater isoscape patterns into effective applications for migratory wildlife conservation

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Critical to the effective conservation of migratory species is the ability to quantitatively connect vast, often remote, geographical regions used by individuals or populations during their annual life cycle. Traditional approaches to determine migratory connectivity over larger geospatial scales have rely on spatially-biased observation and mark & recovery methods – which are for the most part unsuccessful.

The linkage of known and modeled rainwater isotopic distribution patterns across the globe, and the robust translation of these so-called precipitation “isoscape” patterns into biosphere components (e.g. soils, plants, organisms) offers an unbiased alternative approach to tracking migratory linkages. Organisms moving between isotopically distinct biomes carry in their tissue intrinsic spatial isotopic information about the previous feeding location. Knowing *a priori* the global or regional spatial patterns of various stable isotopes in the landscape (ecological isoscapes) allows us to infer geographical region of origin of migrating animals.

This presentation will provide a review of the progress made in isotope assays and approaches (primarily $\delta^2\text{H}$) aimed at unraveling migration linkages in migratory animals (e.g. examples of birds and insects will be illustrated), as well as insights into the underpinning precipitation isoscape models that ecologist are often not familiar with, and elaboration on analytical challenges for measuring $\delta^2\text{H}$ in organic materials and tissues. Awareness of assumptions and pitfalls at all steps are key to conducting successfully isoscape studies. The isoscape approach has been most successful with hydrogen isotopes owing to highly predictable global spatial isotopic patterns, but other isotopic tracers are increasingly being used. Combining GIS and geo-statistical tools, “Isoscapes” represents an increasingly powerful tool for wildlife migration research, with obvious applications into other disciplines like forensics and food authenticity research.

OR5 - The geographical origin of birds migrating through Alps: a stable isotope approach ($\delta^2\text{H}$)

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Every year hundreds of thousands of European birds travel through Europe to reach their wintering areas after the breeding season. Geographical barriers such as seas, deserts or high mountain chains force migrating birds into constrained flyways that oblige populations of different geographical origin to aggregate and follow the ecological corridors they find along their journeys (Cox 2010). The Alps represent an ecological barrier for many bird species that migrate from central and northern breeding latitudes to southern wintering destinations, such as the Mediterranean basin or trans-Saharan Africa. To cross this barrier, birds and especially small Passerines are obliged to follow the geographical morphology of the alpine valleys and use ecological bottle-necks such as mountain passes in order to change valleys and continue their journey to the south (Bruderer and Jenni 1990). The majority of small songbirds migrate through the Alps between August and November, with two peaks in terms of abundance, the first in August for trans-Saharan species and the second in October for intra-Palearctic species. Since 1996 ISPRA and CNI (Centro Nazionale di Inanellamento – Italian Bird-ringing Centre) have conducted activities to monitor bird migration through the Alps ('Progetto Alpi', coordinated by MUSE in Trento and ISPRA). The project involves several ringing stations that work simultaneously between August and November from east to west across the Italian Alps (Pedrini et al. 2008, 2012). The project aims to understand the trends and timing involved in the migration of several songbirds. Hence, it becomes crucial to know the geographical origin of populations using the Italian alpine migratory corridor. In this study the $\delta^2\text{H}$ values measured in feathers sampled at the 'Bocca di Caset' ringing station (province of Trentino) from two passerines, the European robin *Erithacus rubecula* and the pied flycatcher *Ficedula hypoleuca* are presented. The known 'local feather/precipitation $\delta^2\text{H}$ ' regression was used to transform the $\delta^2\text{H}$ measured in feathers into values comparable with the mean-annual isoscape for the $\delta^2\text{H}$ of European precipitation water (Hobson et al. 2004, Bowen et al. 2005). The data obtained were subsequently used to calculate assignment, using IsoMAP to produce probability surfaces of geographical assignment (Bowen et al. 2014). The obtained areas of origin were further trimmed using prior information provided by a recovery dataset and the known breeding range of the species.

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OR6 - Spatial- and spatio-temporal analysis of stable isotopes ratios in biogeochemical processes

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From a geostatistical point of view, both time and space variability characterise many subjects of interest of Earth and environmental sciences. Datasets often include such spatial- and temporal variability and while some established tools exist for spatial interpolation and time series analysis, mixing these techniques calls for compromise: researchers are often forced to choose which is the main source of variation, neglecting the other (Cressie 1990, Cressie and Wikle 2011). We developed Timescape, a simple algorithm, which can be used in many fields of environmental sciences when both time and space variability must be considered on equal grounds.

Stable isotopes of Hydrogen, Oxygen, Carbon and Nitrogen are involved in biogeochemical cycles (West et al. 2010) and their concentration varies within the substrates depending on the environmental processes. Isotopic fractionation occurs in every reaction and it is a well-known tracer of the biochemical details involved.

Analysing the isotopic variability from both a time and space point of view highlights the patterns of change of the concentration values and allows the researchers to find a possible relationship between the sample values and the time and place of collection. As some studies relating the site of production to the isotopic content of food commodities suggest, finding an isotopic signature of such commodities could be of great help in contrasting the frauds related to a pretended geographical origin (Camin et al. 2010a, Camin et al. 2010b, Chiocchini et al. 2016, Portarena et al. 2014, 2015, van der Veer 2013, West et al. 2007).

We present as first case study, a “flat” space-only interpolation of Carbon stable isotopes concentrations for the Ogliarola campana olive cultivar; this is a regular **Isoscape** (West et al. 2010). Isoscapes (short for **I**sotopic **l**andscape) are thematic GIS raster layers, which relate the stable isotopes ratios values δnX with the space coordinates. Stable isotopes bring a lot of information about the environment where the olives growth took place (soil $\delta^{15}N$ and $\delta^{13}C$) and precipitation waters (δ^2H and $\delta^{18}O$) so they can be used to relate a final consumer product to the actual zone of production.

Regular Isoscapes, however, do not capture the temporal variability of the isotopic datasets. The GIS standard procedure delivers a stack of Isoscapes, one per each relevant time or time interval. This can be acceptable if the dataset consistency (number of samples) allows the interpolation of such many layers but this is not always the case. Furthermore, the samples could have been collected sparsely both in time and in space, or could be the result of the merging of different research projects. This was the main goal in the development of the **Timescape** Algorithm which produces, in a broad sense, a time-aware three-dimensional extension of regular Isoscapes, relating the dependent δ^nX ratio variable to the independent space and time coordinates.

Two geostatistical software tools have been developed based on the Timescape algorithm: **TimescapeGlobal**, which uses geographical coordinates and **TimescapeLocal**, which uses projected coordinates. The global version has already been published as free software with the open license GNU GPLv3.0 (the whole package is available at <https://sourceforge.net/projects/timescapeglobal/>). The local version is currently under development, some results in the field of stable isotopes modelling have been obtained with an older, unpublished version, available upon request to the authors.

The second case study shows the interpolation over space and time of the mycorrhizal $\delta^{15}\text{N}$ derived from a host-mycorrhiza symbiosis study in Umbria (Gavrichkova et al. 2016). The ^{15}N fractionation between mycorrhiza and host trees occurred all along the sampling period (about three months), thus requiring some kind of correction in order to compare $\delta^{15}\text{N}$ data from different days of collection. Also space variability of mycorrhiza, trees and soil $\delta^{15}\text{N}$ had to be taken into account. Although less critical from the point of view of fractionation, also $\delta^{13}\text{C}$ has been taken into account for mycorrhiza and host plants. A development version of **TimescapeLocal** has been used to produce spacetime distribution models of $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ in order to find the maximum probability of symbiosis.

Ordinary flat Isoscapes have been computed too, from $\delta^{15}\text{N}$ of soil, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of leaves and $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of pine stumps. The soil $\delta^{15}\text{N}$ Isoscape was used as a statistical bias to be subtracted from mycorrhizal $\delta^{15}\text{N}$ in order to correct the mycorrhizal Nitrogen according to the actual soil substrate.

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OR7 - Olive ripening and cultivar effects on carbon stable isotope compositions of *n*-alkanes and fatty acids in extra-virgin olive oils

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The valuable market of extra virgin olive oil (EVOO) requires authentication of geographic origin and variety. Stable isotope analysis of bulk olive oils has been used previously for authentication purposes (Iacumin et al. 2009, Camin et al. 2010a, Camin et al. 2010b, Portarena et al., 2014, Chiocchini et al, 2016). The bulk isotope composition of olive oil represents an average of a relatively large number of isotopically heterogeneous compounds, whose relative proportions may vary among different cultivars and environments (Mihailova et al, 2015). Therefore, variations in isotopic ratios at the bulk level may be influenced by a change in stomatal conductance and/or by a modification in the biochemical composition of oil.

Establishing the links between biochemical and physiological responses of different cultivars of olive trees (*Olea europaea* L.) under various climatic conditions is an important issue for identifying the authenticity and geographical location of olive oils (Portarena et al., 2015). For example, comparing the EVOO's isotopic compositions among varieties with different metabolism (e.g., oil accumulation pattern) may mask the isotopic differences resulting from climate gradients among oil producing regions. Studying isotopic compositions of individual components in EVOO, however, is more suited to traceability studies, particularly when investigating those organic compounds (sterols, aliphatic alcohols, glycerol, fatty acids, *n*-alkanes) with direct link to environmental factors or sensitive to the biosynthesis stages (Portarena & Brugnoli 2016).

To our knowledge, no published studies on combined carbon isotope ratios ($\delta^{13}\text{C}$) analyses of fatty acids (FAs) and *n*-alkanes in olive oils are currently available. In this project, bulk oil $\delta^{13}\text{C}$ as well as *n*-alkane (*n*-C₂₉, *n*-C₃₁, *n*-C₃₃) and FAs (16:0, 18:0, 18:1, 18:2) $\delta^{13}\text{C}$ values have been determined to investigate the link between ¹³C/¹²C composition of the components and environmental conditions during oil accumulation. In particular, 80 monovarietal EVOO samples were analyzed, representing 4 cultivars in a comparative field and 5 ripening stages. The $\delta^{13}\text{C}$ values of *n*-C₃₃ alkane varied among the studied varieties and showed phenological sensitivity, appearing as a useful tool for studying inter-varietal differences in olives.

The $\delta^{13}\text{C}$ of FAs were mainly influenced by ripening stage, without significant effects of the cultivar. Therefore, the environmental conditions mostly determined the $\delta^{13}\text{C}$ value of FAs during oil accumulation. Thus, combining the bulk $\delta^{13}\text{C}$ and those of specific compounds, such as *n*-alkanes and FAs, could provide a better knowledge of EVOO biosynthesis as well as a powerful tool to detect possible adulterations characterizing both the variety and the geographical origin EVOOs.

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KN2 - Reconstructing antarctic climate over the last 2000 years by means of isotopic profiles

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Due to the limited temporal and spatial distribution of direct (instrumental) climate records, paleoclimate reconstructions are essential if we want to distinguish the natural versus anthropogenic induced climate changes over the most recent part of our current interglacial period, allowing us to place the recent trends in a long-term context. Different natural archives can be used for this purpose such as tree rings, pollen, corals, lake and marine sediments, glacier ice, speleothems, being characterized by different temporal resolution, spanning from seasonal to decadal scale, and based on different type of calibrated temperature proxies.

High-latitudes are particularly interesting places to document natural climate variability since: (1) every component of the climate system interacts in these regions in a still poorly-constrained and non-linear way; (2) changes are amplified compared to low latitude environments; (3) Antarctica and its surrounding are characterized by a strong regional variability. However, the meteorological observations in Antarctica, a continent one and a half the size of Europe, started only during the 1957-58 International Geophysical Year with most of the stations along the coast and only some (e.g., South Pole, Vostok) in the interior. For this reasons Antarctica offers a unique opportunity to fill this spatial and temporal gap by interpreting the isotopic profiles obtained from the ice cores and allowing to reconstruct the climate of the past at different temporal scales from centuries to glacial-interglacial cycles.

Paleotemperature reconstructions from Antarctica mainly rely on water stable isotope records from ice cores. The key factor controlling this proxy has been mainly related to temperature variations; however, this is not always straight forward and other processes acting on different spatial and temporal scales may influence the calibration between water stable isotopes and temperature. These processes can include precipitation-weighting of recorded air temperature, post-depositional movement and loss of snow, and ice flow and elevation effects. Early efforts to reconstruct the continental-scale temperature history of Antarctica over the past 2000 years indicated that at the continent-scale Antarctica is the only land region where the long-term cooling trend of the last 2000 years has not yet been reversed by recent significant warming (PAGES 2k Consortium, 2013). However, this Antarctic temperature reconstruction has large uncertainties and masks important regional-scale features of Antarctica's climate evolution over the last 2000 years. Here using a greatly expanded paleoclimate database and new reconstruction methodologies we present the initial results obtained from the Antarctica2k working group in the framework of the PAGES 2k initiative aiming to reconstruct the climate of the past 2000 years at both global and continental scales. This will include the compilation of ice core isotope records over seven distinct climatic regions: the Antarctic Peninsula, the West Antarctic Ice Sheet, the East Antarctic Plateau, and four coastal domains of East Antarctica.

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OR8 – Oxygen and hydrogen stable isotope content in daily-collected precipitation samples at Dome C, East Antarctica

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The oxygen and hydrogen stable isotope content of the Antarctic ice cores provides integrated tracers of the atmospheric water cycle and local climate, allowing to obtain exceptional past climate records. Low accumulation sites of the East Antarctic plateau provide the oldest ice core records, with the record-breaking EPICA Dome C drilling covering the last eight climate cycles. However, the isotope-temperature relationship, commonly used to derive the temperature, may be characterized by significant geographical and temporal variations. Moreover, post-depositional effects may further complicate the climate interpretation. A continuous series of precipitation data is needed in order to gain a better understanding of the factors affecting the water stable isotopes in Antarctic precipitation at a specific site. In this study, we use the first and so-far only multi-year series of daily precipitation sampling and isotope measurements from the French-Italian Concordia Station, located at Dome C in East Antarctica (75°06'S 123°21'E; elevation: 3233 m a.s.l.; mean annual temperature: -54.5°C; snow accumulation rate: 25 kg m⁻² yr⁻¹), where the oldest deep Antarctic ice core has been retrieved. Surface air temperature data have been provided by the US automatic weather station (AWS), placed 1.5 km away from the base, while tropospheric temperature profiles are obtained by means of a radiosonde, launched once per day by the IPEV/Italian Antarctic Meteorological Observatory. The new dataset also enables us for the first time to study the isotope-temperature relationship distinguishing between different types of precipitation, namely diamond dust, hoar frost and snowfall, identified by the observations carried out by the winter-over personnel collecting the snow samples. Here we present the complete data series of water stable isotopes ($\delta^{18}\text{O}$, δD and deuterium excess) in precipitation at Dome C spanning the time period from 2008 to 2014, in the framework of the PNRA PRE-REC project.

OR9 - The “ISONITRATE Italy” project: exploring nitrate sources in polluted aquifers of the Po river alluvial plain (North Italy) by means of isotopic techniques

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Shallow aquifers worldwide are often contaminated by NO₃⁻ leached from soils exploited by intensive agriculture or from leaks of the sewage system in densely populated areas, becoming a risk for both drinking water and surface water bodies health.

The development of remediation plans for polluted areas and effective policies to protect water quality require the identification of the sources and the understanding of processes influencing NO₃⁻ concentration in water bodies.

The Italian Ministry of Agriculture, Food and Forestry (MIPAAF) in collaboration with the Institute for Environmental Protection and Research (ISPRA) promoted a study to identify nitrate contamination sources by means of the application of isotope techniques in five Regions of the Po River basin, following the ISONITRATE model developed in France by the French Geological Survey (BRGM, Bureau de Recherches Géologiques et Minières).

The apportionment of nitrate contamination sources in shallow groundwater (GW) has been evaluated by means of an integrated approach measuring nitrogen and oxygen isotopic ratios of dissolved nitrate ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) and isotopic ratios of boron ($\delta^{11}\text{B}$) monthly. Samples of GW, surface water (SW), soil, potential nitrate sources (i.e., synthetic and organic fertilizers, sewage, etc.) in six reference sites with a documented history from the point of view of nitrate contamination (i.e., natural, single source, multiple sources, denitrification site) were collected and analyzed over a period of 6 months. The isotopic data have been integrated with hydrogeological, hydrochemical, chemo-physical and pedologic data in order to characterize the studied systems. A mass balance mixing model was applied to soil extracts before and after manure or mineral fertilizers treatment to evaluate the isotope fractionation correction factors of the NO₃⁻ sources (mineral and manure) in order to accurately determine the isotopic signals of nitrate sources in the vulnerable water bodies.

Finally, a multiple sources mixing model based on a Bayesian stable isotope mixing model, SIAR, (Parnell et al., 2010) tested in the six reference sites, has been applied to 84 threatened zones, where over long term series NO₃⁻ concentration resulted above 40 mg L⁻¹, in order to determine the probability distribution of the relative contribution of each source in the considered GW and SW.

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OR10 - CNS stable isotopes in the Adige river waters: insights on natural and anthropogenic components

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Previous investigation by Natali et al. (2016) indicated that the Adige river waters display a common Ca-HCO₃ hydrochemical facies, reflecting a natural (geogenic) signature related to the weathering processes of the rocks outcropping in the basin; on the other hand nitrate increased in the last decades reflecting the growing of anthropogenic inputs. To crosscheck these statements 18 water samples have been collected along the riverine profile in May 2015 in order to analyze the isotopic compositions of Carbon, Nitrogen and Sulphur.

These isotope analyses were performed in the laboratories of the Helmholtz-Zentrum für Umweltforschung (UFZ) Leipzig/Halle (Germany). Isotope analyses of carbon and associated oxygen were carried out on dissolved inorganic component (DIC) using the method described by Atekwana and Krishnamurthy (1998). Isotope analyses of sulphur and associated oxygen were carried out on sulphate recovered using the method described by Knöller et al. (2005). Isotope analyses of nitrogen and associated oxygen were carried out on dissolved inorganic nitrogen (DIN) using the bacteria denitrification method described by Sigman et al (2001) and Casciotti et al (2002). This method involved the use of bacteria to transform NO₃ in N₂O. Isotope measurements were performed using a Delta V plus mass spectrometer (Electron with a Gasbench II, Thermo Electron GmbH).

The $\delta^{13}\text{CDIC}$ isotopic composition varies regularly along the riverine profile between -4.5‰ and -9.5‰. Analogously, the $\delta^{34}\text{S}_{\text{SO}_4}$ isotopic composition varies regularly along the riverine profile between +4.4‰ and +11.4‰. On the other hand $\delta^{15}\text{N}_{\text{NO}_3}$ isotopic composition varies between +3.9‰ and +10.5‰ with a more irregular pattern along the riverine profile.

Isotopic data have been compared with another important riverine system in the same season, the Po river, described in Marchina et al. 2016 to highlight potential analogies or difference of the two Alpine rivers. Coherently with what observed in the Po River, carbon and Sulphur isotopic compositions reflect a geogenic signature, whereas the nitrogen isotopic composition are influenced by local effects related to anthropogenic contributions.

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KN3 - Simultaneous determination of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in CO_2 involved in leaf gas-exchange processes by means of isotope ratio infrared spectrometry (IRIS - Delta Raytm)

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The analysis of stable isotope ratios of light elements is normally used for various applications in a number of disciplines like geochemistry, physiology, ecology, paleontology, climatology, criminology, ornithology and others. Pioneering studies by geochemists formerly highlighted peculiarity of carbon isotopes distributions in natural compartments, enclosing plant materials (Nier & Gulbransen, 1939). It is now a long lasting frame that the study of stable isotope fractionations of carbon and oxygen in plants tissues and metabolites provides insights into the photosynthetic metabolism (Wickman, 1952; Bender, 1968; O'Leary, 1981; Farquhar et al., 1982; 1983; 1984; 1989; Evans et al., 1986; Brugnoli and Farquhar, 2000). For instance, perspectives in studying WUE in natural systems are allowed by stable isotope techniques and, particularly, by analysing carbon stable isotope composition ($\delta^{13}\text{C}$) recorded in tissues of C3 plants. A negative relationship between carbon isotope discrimination (Δ) and intrinsic water use efficiency has been widely tested (Farquhar et al., 1989; Brugnoli et al., 1997; Brugnoli and Farquhar, in press). The depletion of the heavy isotope ^{13}C in plant tissues with respect to its abundance in the atmospheric CO_2 , is directly related to the ratio of intercellular to atmospheric CO_2 molar fraction (C_i/C_a); this ratio represents the equilibrium between the availability and the requirement of CO_2 at the leaf level, that is the set point for gas exchange activity (see Ehleringer, 1993). Since C_i/C_a is negatively related with WUE, a mechanistic negative relationship between Δ and WUE conseques. According to this theory, carbon isotope discrimination analysis allows an assimilation weighted estimation of both C_i/C_a and intrinsic WUE integrated over different time scales, depending on which tissues or metabolites are analysed. The analysis of samples representative of the entire dry matter furnishes an evaluation of WUE integrated over the whole plant life. Instantaneous information is given by analysis on line with gas exchange measurements (Evans et al., 1986; von Caemmerer and Evans, 1991), whilst a picture of a few days is associated to the isotopic analysis of newly fixed carbon in metabolites such as leaf soluble sugars or starch (Brugnoli et al., 1988; Lauteri et al., 1993; Scartazza et al., 1998).

Due to physical and climatic factors, different water resources are characterized by different isotopic signatures for both $^{18}\text{O}/^{16}\text{O}$ and D/H ratios (Craig, 1961; Dansgaard, 1964). Xylem water usually reflects the isotopic compositions of water used by plant species (Dawson, 1993, 1995; Dawson and Ehleringer, 1998; Dawson et al., 2002). Hence, stable isotopes are considered a powerful tool to investigate water relations. Especially, oxygen isotopic composition of xylem water results always in accordance with the water source used by plants and provides fundamental information in tracing the depth of root systems and the functional links between vegetation and different water sources.

The broad application of stable isotopes in physiological and ecophysiological studies have led to many new insights on the processes that control primary productivity and efficiency of resource use by plants (Dawson et al., 2002). As already shown, carbon stable isotopes have

provided a powerful tool for analysing constraints on photosynthesis and water-use efficiency of C_3 plants (reviews by Farquhar et al., 1989; Brugnoli and Farquhar, 2000). More recently, the availability of new analytical techniques has increased the interest in using $^{18}\text{O}/^{16}\text{O}$ and D/H ratios both as tracers of the movement of water along the soil-plant-atmosphere continuum (SPAC) and as integrative indicators of microclimatic conditions and physiological processes related to water use by plants. Leaf water is generally enriched in the heavier isotopes with respect to xylem water because of transpiration while xylem water reflects the isotopic signature of soil water taken up by plants. The extent of the enrichment of leaf water relative to soil water depends on both atmospheric conditions and stomatal regulation of water loss. Particularly, leaf isotope enrichment is affected by leaf and air vapour pressures, which are dependent on leaf and air temperatures, the fraction of evaporating water to source water and their mixing to compose the bulk leaf water, the isotopic composition of atmospheric water vapour and the stomatal and boundary layer resistances to water vapour diffusion. Farquhar and Lloyd (1993) have modelled the leaf water enrichment during transpiration after Craig and Gordon (1965) model of evaporative enrichment from a free water body (e.g. lake). It should be noted here that the isotope fractionation occurs in a precise pool of the leaf water called evaporating water; this is the fraction of leaf water at the sites of transpiration. In contrast, bulk leaf water is all of the water pools present in the leaf. The enrichment of leaf water that occurs during transpiration above the source (input) water value ($\Delta^{18}\text{O}_e$) equals: $\Delta^{18}\text{O}_e = \varepsilon^* + \varepsilon_k + (\Delta^{18}\text{O}_v - \varepsilon_k) e_a/e_i$, where ε^* is the equilibrium fractionation between liquid and vapour, ε_k is the kinetic fractionation factor when vapour diffuses through stomata and leaf boundary layer to the atmosphere, $\Delta^{18}\text{O}_v$ is the isotopic enrichment of atmospheric water vapour relative to source water, e_a/e_i is the ratio of ambient to intercellular vapour pressures (\approx relative humidity). The variation in the oxygen isotope compositions of soil, xylem and leaf water and vapour surrounding the leaf has the potential to be a relevant signal of plant-environment interactions and adaptive processes. It is also worth noting that the oxygen isotopic composition of evaporative water is at a certain extent reflected on that of the CO_2 molecule. Indeed, the molecule is isotopically labelled when entering the water solution of the mesophyll cell from the intercellular air spaces, a process facilitated by the enzymatic activity of carbonic anhydrase (Cernusak et al., 2004).

Important insights on the above mentioned processes are typically gained by coupling a leaf gas-exchange system and an isotope ratio mass spectrometer (IRMS). Air samples ingoing and outgoing the leaf cuvette are respectively collected or diverted to the IRMS. The discrimination occurring during the leaf gas exchange and affecting the ^{13}C and ^{18}O abundances in the CO_2 molecules can be then calculated. In recent years, new instruments have been developed, based on absorption of electromagnetic radiation. Such tools allow to measure isotope ratios of different atomic species in real time. Furthermore, their reduced size and weight allow to perform experiments in field conditions.

Main objective of this work was to test the reliability of results obtained by coupling an isotope ratio infrared spectrometer (IRIS; Delta RayTM, Thermofisher) with a laboratory gas-exchange open system. To achieve the purpose, leaves of several plant species differing in life form (herbaceous and trees) and photosynthetic metabolism (C_3 , C_4 and CAM) were subjected to a range of controlled environmental conditions in the leaf cuvette by manipulating humidity, temperature and CO_2 concentration. Particular attention in C_3 plants was spent in estimating the mesophyll conductance to CO_2 transfer to the carboxylation sites into the chloroplasts, by adopting the on-line discrimination technique (Evans, 1986).

OR11 - A multiparametric approach to study the forest ecosystem responses to environment

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Forest ecosystems are subjected to numerous environmental constraints, both abiotic (edaphic and climatic limitations) and biotic (competition and facilitation processes between tree species, pest and pathogen attacks). To understand the mechanisms of plant's response to environmental factors, a multiparametric approach has been developed in order to improve the informative potential of methods commonly applied in ecological researches and, at the same time, to design an effective cost-benefit surveys. In this presentation we report an experience concerning the application of foliar $\delta^{13}\text{C}$ as part of the 'leaf traits analysis' in forest tree species. This approach was adopted to study the responses of forest trees in mixed forests and in relation to environmental factors, within the 7FP project FunDivEUROPE. Foliar $\delta^{13}\text{C}$ is a key parameter for exploring carbon sequestration and strategies for an efficient water use of plants under water stress conditions. Its combination with other plant functional traits, that are indicators of climatic stress, drought, air and soil pollution, light use, competition, plant nutritional status, health plant condition (i.e. specific leaf area, leaf C and N content, chlorophyll *a* fluorescence parameters) is a powerful tool to analyse on the whole and in-depth the physiological processes involved in the plant responses to environment. This presentation provides examples about the informative potential of foliar $\delta^{13}\text{C}$, in combination with other plant traits, in the assessment of the cause and consequences of crown defoliation on tree health in a mixed forests in Tuscany. Moreover are provided examples about the application of foliar $\delta^{13}\text{C}$ as supporting parameter in a study on the taxonomic and ecological meaning of the chlorophyll *a* fluorescence signature of tree species. These examples point out the effectiveness and powerful of the combined analysis of functional plant traits, included foliar $\delta^{13}\text{C}$, in the ecological research, improving significantly the informative potential of the (field) surveys.

OR12 - Applications of carbon and nitrogen stable isotopes analyses in environmental studies

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Stable isotopes are now commonly used in environmental studies, in particular to: identify different sources (autochthonous-allochthonous), infer processes (bacteria degradation, nitrification-denitrification), estimate rates (soil carbon turnover), determine proportional inputs (percent contribution of a particular prey item to a predator's diet), and confirm, reject, or constrain models derived from the use of other techniques.

In this study stable isotopes analyses were applied in order to achieve different environmental goals. A first approach was developed to estimate different organic contributes (allochthonous input as urban treated and untreated wastewater) to the particulate matter (POM) of Venice Lagoon. In fact the amount of POM in transitional environments is composed by the contributions of different sources: allochthonous sources (i.e. marine, riverine-terrestrial runoff and anthropic inputs as untreated and treated sewages) and autochthonous sources that principally derive from primary production (i.e. phytoplankton, macroalgae). The understanding of the nature and the origin of POM can provide interesting insights about the occurrence of natural processes and anthropogenic pressures in both the lagoon itself and drainage basin. In the framework of a more extensive program aimed at the classification of the ecological and chemical status of the Venice lagoon in accordance with the Water Framework Directive (WFD, Directive, 2000/60/CE), POM were collected at 28 stations in the Venice lagoon and its isotopic signatures were elaborated using a mixing model equations (Berto et al., 2013).

The results showed a prevalence of allochthonous sources (82%) over autochthonous in all lagoon stations. The contribution of terrestrial/riverine POM was maximum during the most raining period (November, 51%), whereas in summer, when Venice tourism pressure is highest, the sewage percentage prevailed (47%) This study evidence that, even stable isotopes analyses are not mentioned among the instruments adopted by WFD for the environmental status evaluation, there are good perspectives for their use as additional parameters for the accomplishment of WFD in transitional and coastal-marine environment.

A second purpose of our research was a first preliminary characterization of different plastic polymers and their degradation processes once discharged in marine environment, a severe and upcoming issue, considering that their production is rising exponentially in the last years also due to their massive use in developing and emerging economies: global plastic production in 2012 rose to 288 million tones, a 2.8% increase compared to 2011, with Asian countries covering the 44.6 of the global plastic material production in 2012 (Plastics Europe, 2013). Unfortunately, the unique properties of plastic (durability, asepsis, light weight and low cost) support its massive use leading to severe complications in term of environmental policy. In fact there is no agreed time that plastic takes to degrade, but it could be estimated from hundreds to thousands of years. Most types of plastic can be broken into smaller fragments, which then

produce so-called ‘microplastics’, which could potentially be easily absorbed by marine organism (Andrady, 2011). Microplastics are particularly difficult to monitor and they may also have more influential impacts than larger plastics, considering also the recent discovery of possible health and environmental effects, such as the impacts of the chemicals contained in plastics (bisphenol a, phtalathes and brominated flam retardant) (Talness et al., 2009). Recently, some attempts at plastic classification by optical methods (NIR, Raman spectroscopy, FT-IR) were made, while the use of stable isotopic analysis has not yet been applied for this purpose. Our preliminary results showed an interesting differentiation among different plastic polymers, in particular carbon isotopes ratios allow to distinguish between recycled vs raw polyethylene and between petroleum vs plant derived polymers. Furthermore a study case focused on high density polyethylene subjected to degradation process in the marine environment seems to indicate a depletion of ^{13}C isotope. Considering the low amount of material needed to perform the isotopic analysis, the low time consuming of the method and no limitation due to the color of the material (with respect to Raman spectroscopy), a future perspective will be to identify the composition of plastic debris collected from the stomach contents of different marine organisms.

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OR13 - Long-term warming affects ^{13}C and ^{15}N allocation in a field-grown mediterranean shrub *Cistus Monspeliensis*

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The greenhouse gas emissions continue unabated, projecting rapid changes in the global climate. During the 20th century the global temperatures have raised by 0.6°C. A further increase of 0.3 to 0.7°C is projected for the period 2016–2035 (IPCC 2013). Long term field manipulation experiments, which mimic expected changes in future air temperatures and water regimes, could give realistic picture on the response of different aspects of ecosystem C cycle to changing climate. Temperature was manipulated for 10 years in a Mediterranean shrubland of Porto Conte (Italy). Reflective curtains spanned over the vegetation at night decreased the loss of IR radiation from plots, resulting in the increase of average air and soil temperature by approximately 1°C. Passive night time warming reflects global heating patterns where major increases are registered in night minimum temperatures rather than in day maximums. We took an advantage of this experimental set-up to study changes in allocation patterns of C between pools and fluxes in *Cistus monspeliensis* shrub – a dominant species within the experimental site. For this purposes we labeled control and warmed plots in ^{13}C enriched atmosphere and studied the distribution of labeled assimilates between numerous pools and fluxes. To better explain C allocation patterns a particular attention was given to interactions with plant N availability which was evaluated by labeling of soil with $\text{N}^{15}\text{-enriched KNO}_3$.

Higher enrichment was found in non-soluble leaf sugar fraction under Warming. This additional C was however just temporary stored in reserves rather than stabilized in the cell walls and was further utilized to fuel metabolic processes. By the end of the chasing period more C was allocated to leaves in Control plots. Shoot respiration resulted to be a considerable sink for newly assimilated C especially in warming plots where 40% of recovered ^{13}C was allocated to this flux immediately after the labeling. Tissues N content explained patterns of root-derived respiration, which was more enriched in Control plots. Lower N availability here strengthen the sink capacity of roots for C in confront to leaves. Higher root-derived respiration rate in Control was therefore a result of higher substrate availability. Changes in soil water content determined patterns of tissue's N. Highly mobile components of soil N pool were lost with rain water runoff. However, our data indicate that N losses should be promptly counterbalanced by increased N mineralization under Warming resulting in higher tissues N content when meteorological conditions of the site are stable.

Higher allocation of C to shoot respiration coupled to lower amount of C remaining in biomass constrains C sequestration capacity of plants under Warming. For a positive C balance, which is observed by a long-term monitoring survey in this site, gain of C should exceed its losses, therefore we predict higher assimilation rates in Warming plots over the season. Longer

growing season and reduction of the frost days in Warming plots should add to the Cistus productivity success.

OR14 - Thermally based isotopic speciation of carbon pools in environmental matrices

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In the last years several authors applied the thermal speciation techniques to different environmental matrices such as biological material (Boyle et al., 2004; Pallasser et al., 2013) and soils/sediments (Hsieh and Bugna 2008; Bisutti et al. 2007; Leifeld 2007), in order to identify the different carbon pools. The abovementioned methods have been improved by coupling the elemental content with the carbon isotope analysis, which represents a powerful tool for the discrimination of the distinct carbon pools in heterogeneous environmental materials (Lopez-Capel et al. 2006; Manning et al. 2005, 2008).

Elemental and isotopic analyses of carbon in environmental matrices usually highlight multiple pools of different composition and $^{13}\text{C}/^{12}\text{C}$ ($\delta^{13}\text{C}$ ‰) isotopic ratio. Interpretation necessarily needs the characterization of the diverse end-members that usually are constituted by inorganic and organic components. In this view, we developed a routine protocol based on coupling of elemental and isotopic analyses that is able to discriminate the inorganic (IC) and organic (OC) contributions to the total carbon (TC) content. The procedure is only based on thermal destabilization of the different carbon pools and has been successfully applied on different environmental matrices (rocks, soils, and biological samples) with a mean C elemental and isotopic recoveries of 99.5 % (SD= 1.3 %) and 0.2‰ (SD=0.2‰), respectively. The thermally based speciation (TBS) leads us to define precise isotopic end-members, which are unaffected by any chemical treatment of the sample, to be used for accurate mass balance calculation that represents a powerful tool to quantify the distinct carbon pools. The paper critically evaluates the method explaining the potentials and the current limits of the proposed analytical protocol.

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KN4 - Preliminary results from a microvolume, dynamically heated analytical column for preconcentration and separation of simple gases prior to stable isotopic analysis

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Stable isotope applications that call for preconcentration (i.e. greenhouse gas measurements, small carbonate samples, etc.) universally call for cryogenic fluids such as liquid nitrogen, dry ice slurries, or expensive external recirculation chillers. This adds significant complexity, first and foremost in the requirements to store and handle such dangerous materials. A second layer of complexity is the instrument itself – with mechanisms to physically move either coolant around the trap, or move a trap in or out of the coolant. Not to mention design requirements for hardware that can safely isolate the fluid from other sensitive areas. In an effort to simplify the isotopic analysis of gases requiring preconcentration, we have developed a new separation technology, UltiTrap™ (patent pending), which leverage's the proprietary Advanced Purge & Trap (APT) Technology employed in elemental analysers from Elementar Analysensysteme GmbH products. UltiTrap™ has been specially developed as a micro volume, dynamically heated GC separation column. The introduction of solid-state cooling technology enables sub-zero temperatures without cryogenics or refrigerants, eliminates all moving parts, and increases analytical longevity due to no boiling losses of coolant . This new technology makes it possible for the system to be deployed as both a focussing device and as a gas separation device. Initial data on synthetic gas mixtures (CO₂/CH₄/N₂O in air), and real-world applications including long-term room air, solid carbonates and a comparison between carbonated waters of different origins show excellent agreement with previous technologies.

OR15 - Elucidating the fate of applied nitrogen fertilizer in rice paddy soils by means of bulk and compound-specific stable isotope $\delta^{15}\text{N}$ techniques

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Intensive high-yield agriculture is dependent on the addition of fertilizers. About 60% of global nitrogen (N) fertilizer is used for producing the world's three major cereals: rice, wheat and maize (Ladha et al. 2005). However, more than 50% of the applied N is generally not assimilated by plants, and is a potential source of environmental pollution. Nitrogen-use efficiency in agricultural cropping systems may be increased by better matching temporal and spatial N supply with plant demand, but obtaining this requires a thorough comprehension of the fate of applied N.

The biogeochemical cycling of N in rice paddies is perhaps one of the most complex systems in agriculture, making N the most yield-limiting and difficult nutrient to manage in lowland rice cropping systems worldwide. Although N supply drives productivity, poor N fertilizer-use efficiency (30–40% recovery of applied N) is characteristic of irrigated rice systems (Cassman et al. 2002). This is mainly due to the particular irrigation water management practices adopted in rice fields that involve the intermittence of flooded and drained conditions during the cropping season. The consequent frequent changes in soil redox conditions strongly affect biotic and abiotic processes involved in the immobilization/release of applied N as well as N losses from soil to atmospheric and hydrological compartments, with important consequences on N availability for the crop (Fig. 1). Moreover, crop residue management practices, such as straw incorporation often further confound these processes.

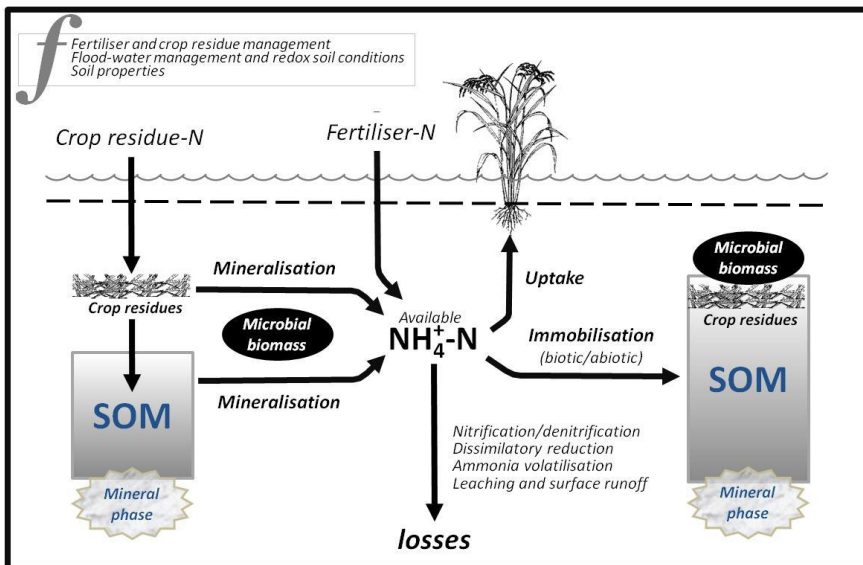


Fig. 1: Soil processes controlling N availability in rice paddy soils (SOM, soil organic matter)

Most of our current knowledge of the biogeochemical cycling of N as a function of soil redox conditions and crop residue incorporation obtained from the study of flooded rice systems contains contrasting evidence regarding the principal factors controlling the availability of applied N. However, the development and adoption of stable-isotope techniques have contributed extensively to our understanding of the key processes involved.

In our research, bulk stable-isotope $\delta^{15}\text{N}$ analyses (EA-IRMS) combined to soil extraction (KCl and HF:HCl), micro-diffusion and fractionation (aggregate-size and density fractionation) techniques enabled the evaluation of the distribution of applied ^{15}N between available and immobilized forms, as well as provided important insights into the major mechanisms involved in N immobilization (Cucu et al. 2014).

Although more time consuming with respect to bulk analysis, coupling the analysis for molecular markers with compound-specific stable-isotope $\delta^{15}\text{N}$ determinations (GC-C-IRMS) proved to be an essential tool for following the involvement of applied N in biotic processes. In our case, we developed and utilized a method for the compound-specific $\delta^{15}\text{N}$ analysis of amino sugars, important constituents of microbial cell walls (Amelung, 2001). This approach not only enabled to differentiate between old (soil-inherent) and new (tracer-derived) markers, but allowed for the evaluation of microbial utilization of applied N (Said-Pullicino et al. 2014).

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OR16 - Belowground carbon allocation patterns as determined by the in-growth. Soil core ¹³C technique across different ecosystem types

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Belowground carbon inputs, in particular rhizodeposition, are a key component of the global carbon cycle and yet their accurate quantification remains a major challenge. In the present paper, the in-growth soil cores-¹³C method was used to quantify net root carbon input (root-derived C). Four different ecosystem types (forest, alpine grassland, apple orchard and vineyard) in northern Italy, characterized by C₃ vegetation with a broad range of aboveground net primary production (ANPP; 155–770 gC m⁻² y⁻¹) were investigated. Cores, filled with soil of a known C₄ isotopic signature were inserted at each site for twelve months. After extraction, root-derived C was quantified by applying a mass balance equation. Gross primary production (GPP) was determined by eddy covariance whereas ANPP was quantified using a biometric approach. NPP partitioning among sites differed, with fruit production dominating at agricultural sites. At these sites, belowground C inputs were dominated by rhizodeposits, likely due to relatively high root turnover. In natural ecosystems (forest and grassland) fine root production dominated belowground net primary production (BNPP) likely due to higher root growth determined by low phosphorus availability. Root derived C represented a significant contribution to BNPP varying from 40 to 60%. Our results underline the fact that failure to account for rhizodeposits may lead to a significant underestimation of BNPP.

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OR17 - Carbon allocation and partitioning in mountain grassland ecosystems during drought stress and recovery

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Future climate scenarios suggest not only an increase in atmospheric CO₂ concentration and air temperature, but also more frequent and severe extremes events, such as heat waves and severe drought. Moreover, more frequent drought events are forecasted in the early season, like in May and June (IPCC, 2013). Although the effect of drought on carbon assimilation and on biomass production is quite well established, it is not completely clear which is the effect of drought on the belowground C allocation and partitioning in the atmosphere-plant-soil continuum in particular in the recovery phase. On the other hands, how C allocation and partitioning is a potentially important mechanism for building up resistance against water limitation and recovery should be addressed. At the same time, other concerns exist about the balance of C between atmosphere and biosphere (vegetation and soil) during the peak of drought and the following rehydration, this with the aim to understand if resistance and resilience mechanisms are differing. We have focused on these issues in mountain grassland ecosystems with different land managements and with different species composition. This because resistance and resilience of grassland communities may depend on management, plant strategies, functional composition.

In a first study, we examined the response of two differently managed grasslands, a traditionally more intensive managed hay meadow and a completely unmanaged (less intensive managed) abandoned area. In a second study, we used planted mesocosms, differing in their relative composition of 6 local grass and forb species, to examine the effect of functional evenness on drought resistance and resilience.

The destiny of newly assimilated C into the plant-rizosphere continuum under a period of severe drought and following rehydration has been studied by two ¹³CO₂ pulse labelling, the first during peak drought and the second during the rehydration phase. We followed the kinetics of ¹³C incorporation in above- and below-ground bulk plant material as well as in non-structural carbohydrates, soil extractable organic C, soil microbial C, marker lipids for soil microbes and CO₂ respired from roots, up to 5 days succeeding each labelling.

Results from the first study show that ¹³C incorporated in bulk phytomass material, non-structural carbohydrates and in soil microbial communities seems to indicate, as expected, a drought-altered kinetics of aboveground ¹³C incorporation and its allocation to storage pools as well as to the belowground (Bahn et al. 2013; Hasibeder et al., 2014). A lower incorporation of ¹³C in the total phytomass in drought compared to control was shown in hay meadow, while for abandoned plots the effect of drought was less evident, showing for this grassland higher resistance to drought. The kinetics of ¹³C incorporation in sucrose seems not to be affected during drought, while a decrease of ¹³C allocation in storage carbohydrates, such as starch and fructans, is evident both in shoot and in roots. This shows that the main metabolism and translocation towards non-autotrophic organs is preserved compared to storage metabolism. Indeed, in root respired CO₂ a peak of new C is evident 24 hours after the labelling corresponding to a peak of ¹³C incorporation in root sucrose. During

rehydration, the ^{13}C incorporation both in bulk material and in non-structural carbohydrates shows control values, showing a complete recovery of the metabolic machinery from water deficiency. While we do not have enough data points to show the kinetics of ^{13}C evolved from roots as CO_2 during drought labelling, we can show that in the recovery phase, the ^{13}C evolved from roots is comparable in control and drought plots, with a tendentially higher value in roots for hay meadow plots showing higher resilience to drought stress. Regarding the microbial biomass (examined by chloroform fumigation extraction; Malik et al., 2013), tracer dynamics generally reflect the root ^{13}C enrichment and consequently show a more pronounced effect of drought in meadow treatments. Conclusions on the resistance and resilience capacity of grassland ecosystem managed in a different ways (regular cutting versus no cutting events), namely, higher resistance to drought for abandoned grassland and at the same time higher resilience for meadow possibly explained with their higher frequency to perturbation.

Results from the second experiment, in which species composition (grass versus forb) were different, are still preliminary, although they show similar drought effects. For root respiration, the results seem to confirm the decrease due to the drought treatment both on root respiration rates and on ^{13}C evolved from root respired CO_2 and the complete recovery during the rehydration. However, it will be interesting to see how differences in functional diversity may contribute to the effects found in the first experiment.

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OR18 - Use of stable isotopes in agricultural sciences

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Stable isotopes have always been a preferred tool to study nutritional status of plant and soils in agricultural sciences. Nitrogen has been since long used to determine the importance of nitrogen fixation from the atmosphere, or to calculate the recovery of fertilizer nitrogen by the use of ^{15}N enriched tracers and isotopic dilution techniques.

Beside nitrogen, the group of Plant Nutrition of the ETH Zurich is working with carbon and sulfur isotopes in soils and plants. In addition to these more conventional isotopes, we are also studying oxygen isotopes associated to phosphorus in phosphate. Indeed, one of the main goals of the group is to gather a better understanding of the cycle of these important nutrients to optimize crop nutrition and nutrient utilisation.

The challenges presented by this task encompass low concentrations of some of the studied nutrients, long purification procedure to obtain clean samples to analyse for isotopic analysis, and the use of highly enriched tracers applied to incubation or field experiments to be able to observe the recovery of the isotope in the system compartments.

In this contribution, we will present some case studies together with the analytical and practical challenges we faced during sample preparation and isotope analysis.

KN5 - Detection of pseudo-endogenous steroids in doping control analyses by GC/c/IRMS

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The confirmation of the abuse of androgenic anabolic steroids (AAS) and glucocorticosteroids (GCS) by the athletes is based on mass spectrometric techniques. For "pseudo-endogenous" steroids (i.e. the same chemical structure of those endogenously produced in humans), the use of isotope ratio mass spectrometry (GC/C/IRMS) is mandatory. To obtain accurate and reliable results ($\delta^{13}\text{C}$ values) the urinary extracts must be of adequate purity. Liquid chromatography (HPLC) has demonstrated to be the best approach to purify a large number of target steroids from urinary samples. In some occasions, a double purification, using columns of different polarities, may be required.

The utility of IRMS in sports testing is based on the fact that androgens of synthetic origin present an isotopic fractionation ($\delta^{13}\text{C} < -27\%$), linked to the phytosteroids used for their production, compared to the endogenously produced in humans ($\delta^{13}\text{C}$ from -19 to -26%). To improve the robustness of the method, the delta values of the target steroids are compared with the values of compounds not altered by the exogenous administration, used as endogenous reference compounds (ERCs).

The presence of some AAS metabolites in urine samples (i.e 19-norandrosterone or 5β -androst-1-en-17 β -ol-3-one) can also be the result of some specific physiological (in vivo) conditions or of an unusual ex-vivo formation. Also in those cases, the confirmation of the origin of such compounds is mandatory before a result can be released.

For the analyses of all the compounds of interest, it has not been necessary to add a derivatization step prior to the GC/C/IRMS analysis, avoiding potential discrimination or isotopic dilution.

The effectiveness of the approach here proposed has been demonstrated by the analysis of samples collected after controlled administrations of AAS and GCS.

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KN6 - Carbon and oxygen isotope data of carbonates and of structural carbonate of bioapatite: what are their meaning and possible use?

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Carbon and oxygen isotope ratios, expressed as δ values, of carbonate minerals and bioapatite, are rapidly obtained using of the Finnigan GasBench II automatic sampling connected to a spectrometer by measuring the δ values of gaseous CO₂ released from the carbonate group by H₃PO₄ acid dissolution. Considering the “acid” fractionation factors $\alpha_{\text{gas,m}/\text{C}_3\text{.m}}$ and $\alpha_{\text{gas,RF}/\text{C}_3\text{.RF}}$, where m = generic CO₃²⁻-bearing mineral, C₃ = CO₃²⁻ group of mineral m, gas = CO₂, RF = pure calcite laboratory standard, the following general equation may be obtained:

$$\delta_{\text{C}_3\text{.m(PDB)}} + 1 = K (\delta_{\text{C}_3\text{.RF (PDB)}} + 1) \frac{\delta_{\text{gas.m(L)}+1}}{\delta_{\text{gas.RF(L)}+1}} \quad (1)$$

where L is the working laboratory reference gas (CO₂), and $K = \alpha_{\text{gas,RF}/\text{C}_3\text{.RF}}/\alpha_{\text{gas,m}/\text{C}_3\text{.m}}$. Taking into account the GasBench modality of sample storage and the very low pH of the H₃PO₄ acid solution, we can reasonably assume that all carbon is transferred to the gaseous phase as CO₂. In this case is $K = 1$, equation (1) becomes $^{13}\delta_{\text{C}_3\text{.m(PDB)}} + 1 = (^{13}\delta_{\text{C}_3\text{.RF (PDB)}} + 1)$

and the $^{13}\delta_{\text{C}_3\text{.m(PDB)}}$ true value may be calculated. This is not the general case for oxygen because only two oxygen atoms form gaseous CO₂. In this case fractionation between acid solution and overlying gaseous phase occurs depending on temperature, %H₃PO₄ of the acid solution used for mineral dissolution, and the structural and chemical features of the mineral. In general only a “conventional” value

$$(^{18}\delta_{\text{C}_3\text{.m(PDB)}} + 1)^* = (^{18}\delta_{\text{C}_3\text{.m(PDB)}} + 1) / K = (^{18}\delta_{\text{C}_3\text{.RF (PDB)}} + 1) \frac{^{18}\delta_{\text{gas.m(L)}+1}}{^{18}\delta_{\text{gas.RF(L)}+1}} \quad (2)$$

may be obtained. The true value $(^{18}\delta_{\text{C}_3\text{.m(PDB)}} + 1)$ will be rigorously calculated only for pure calcite (m = RF) or for some other carbonates in the case their $^{18}\alpha_{\text{gas,m}/\text{C}_3\text{.m}}$ is known, in addition to $^{18}\alpha_{\text{gas,RF}}$. Unfortunately, for bioapatite(ap), $^{18}\alpha_{\text{gas,ap}/\text{C}_3\text{.ap}}$ is not known and thus only the conventional value $^{18}\delta_{\text{C}_3\text{.ap(PDB)}}^*$ may be calculated. Since the values $^{18}\delta_{\text{gas.ap(L)}}$ and mainly $^{18}\delta_{\text{gas-RF(L)}}$ are strongly dependent on temperature and on %H₃PO₄, rigorous inter-laboratory comparison of routine $^{18}\delta_{\text{C}_3\text{.m(PDB)}}^*$ data is impossible. This could be possible only in the case all the laboratories dispose of the same bioapatite reference material (AP); actually, in this case, since ap and AP have the same chemical composition, is $K = 1$ and equation (2) becomes

$$(^{18}\delta_{\text{C}_3\text{.ap(PDB)}} + 1)\# = \frac{^{18}\delta_{\text{C}_3\text{.ap(PDB)}} + 1}{^{18}\delta_{\text{C}_3\text{.AP (PDB)}} + 1} = \frac{^{18}\delta_{\text{gas.ap(L)}+1}}{^{18}\delta_{\text{gas.AP(L)}+1}}$$

where $^{18}\delta_{\text{C}_3\text{.ap(PDB)}}\#$ is an universal conventional value.

However, in spite of these limitations, comparison between oxygen isotopes of the phosphate group and the obtained oxygen conventional values for the carbonate group of bioapatite produced in the same laboratory may be used to have indication on diagenetic variation of bioapatite $\delta^{13}\text{C}$, and thus to verify if these values may be used for reconstruction of palaeo-diet and environmental conditions.

OR19 - A multiproxy approach to study dietary habit in different historical contexts

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For several years now, the study of human osteological remains has been able to take advantage of chemical-physical methods, to study the dietary habits of ancient populations through isotopic mass spectrometry, based on the measurement of the isotopic ratios of carbon and nitrogen, which are absorbed by humans through their diet. These isotopic markers permit to examine the diet models in the last few years of life of the individuals, through isotopic analysis of collagen, highlighting the use of a particular type of food or whole diet among different sites, social classes or groups.

Therefore, paleodietary reconstructions by means of stable isotope analysis have become a well-established technique for strengthening the investigation of food supply and subsistence strategies, both at the individual and community level. Moreover, the use of stable isotopes of oxygen and strontium allow us to study the phenomena of migration between populations.

In this paper, we present the results of a multiproxy approach used in paleodiet studies recently conducted by the IRMS group of the Department of Environmental, Biological and Pharmaceutical Science and Technologies of the Second University of Naples, in various archaeological site and for different historical periods.

In detail will be presented the results coming from studies concerning isotopic analysis of the diets of populations of the past, that will be compared and analyzed with historical sources and archaeological data, techniques of husbandry, analysis of charred plant remains, palaeopathological studies, preservation of organic residues in ceramic vessels used for the production, preparation, storage and consumption of food.

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OR20 – ¹⁴C mortar dating: selection of uncontaminated binder fractions by stable carbon isotope analysis

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Mortar binders harden through the absorption of atmospheric CO₂ by calcium hydroxide, incorporating the 14-carbon signature of the setting time (Lindross et al. 2007, Nawrocka et al. 2005, Baxter and Walton 1970). In order to date a mortar, the carbon of the binder must be separated from other sources of ¹⁴C, such as geologic limestone, recrystallized calcite and non-carbonate C-bearing phases. Such sources could contaminate the primary 14-carbon signature of the mortars invalidating the dating process. In order to separate and purify the binder, several approaches have been proposed, among which the Cryo2Sonic purification method (Marzaioli et al. 2011) is one of the most reliable. During recent years, this method has been improved and optimized (Secco et al 2014), involving an initial minero-petrographic characterization of the mortars followed by the Cryo2Sonic protocol for separating purified binder fractions. At the end of the Cryo2Sonic procedure, isotopic and mineralogical characterizations of the separated fractions are performed in order to evaluate the purification level of the obtained fractions. In particular, stable carbon isotope analysis are used as an effective and fast tool to differentiate the anthropogenic calcite of the binder versus any contamination (van Strydonck et al. 1989, Dotsika et al. 2009, Kosednar-Legenstein et al 2008, Marzaioli et al. 2011, Addis et al. 2015). The improvements of the Cryo2Sonic method were tested on the mortars of the religious complex of Lomello (Pavia) in Northern Italy, constituted by the baptistery of San Giovanni and the church of Santa Maria Maggiore. The complex was built during different construction phases, from early Roman to Late Medieval time, employing different types of mortars, from cocchiopesto to lean mortars. The minero-petrographic characterization of the mortars showed the presence of calcium carbonates into the cocchiopesto matrix of the baptistery mortars and as aggregates into the lean mortars of the internal walls of the church. The separation procedure allowed to obtain binder fractions richer in 14-carbon of the construction time, giving an excellent correspondence between radiocarbon dates and the archaeological records. The radiocarbon dates measured from the separated fractions were also compared with those resulting from the measurements of lime lumps and charcoal fragments extracted from the same samples. The comparison between lime lumps, charcoal residues and purified binders indicated that the latter are the most reliable materials to be dated.

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KN7 - High efficiency multidimensional gas chromatography coupled to isotope ratio mass spectrometry and quadrupole mass spectrometry simultaneous detection

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Isotope Ratio Mass Spectrometry (IRMS) is commonly recognized to be able to provide information about the geographical, chemical, and biological origins of substances. The ability to determine the source of substances stems from the relative isotopic abundances of the elements which comprise the material. By performing a separation prior to isotope ratio analysis, hyphenated techniques such as GC-C-IRMS, can provide isotopic analysis of a complex mixture, thereby providing additional information and higher discriminatory power. Since its introduction, the use of this analytical approach was not widespread due to a series of drawbacks related to chromatographic and isotopic issues. In fact, dead volumes due to the typical instrumental setup, requiring the combustion of the components followed by a drying step, often limit the separation efficiency, driving to an increased band broadening and peak asymmetry producing peak coelutions, thus falsify the measurements. Moreover, the reduced chromatographic performance increases the gas chromatographic isotope effect (or inverse isotopic effect) that generates GC peak not isotopically consistent because composed of lighter isotopes (¹²C, ¹H and ¹⁶O) that elute after the isotopomers containing heavier organic compounds because of their higher volatility. The present research deals with the development of an MDGC-MS/IRMS prototype characterized by the improved resolution capability of the heart-cut mode, exploiting two different GC stationary phases, and the simultaneous qMS and IRMS detection of the 2D chromatographic bands. The IRMS system was optimized in terms of dead volumes enabling to overcome the extra-column band broadening effect that usually affects the commercial systems. Different applications on food and flavour and fragrance samples are reported showing the enhanced performances of the prototype described.

OR21 - Comparison of Isotopic Ratio Mass Spectrometry (IRMS), Non-Dispersive Infrared Spectroscopy (NDIRS) and infrared spectroscopy for the isotopic composition analysis of food

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Stable isotope analysis has gained increasing interest in the study of the geographic origin of food products giving the possibility for testing food authenticity, quality and typicality.

The technique for $\delta^{13}\text{C}$ analysis must be highly accurate and sensitive.

Moreover it has been recognized as an important technique for the investigation of food adulterations, falsifications and fraud, and for the traceability of animal-derived food products including cheese, milk and butter. In 2000 the EU mentioned traceability as one of the basic principles of consumer protection .

The stable carbon isotopic data are expressed in delta as the per mill deviations of the isotope ratio of a sample relative to standard (Peedee belemite limestone PDB)

$$\delta^{13}\text{C} = [(R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}] \times 10^3$$

where $R = {}^{13}\text{C}/{}^{12}\text{C}$.

Generally the isotopic measurements are carried out analyzing the carbon dioxide obtained by converting the carbon of the sample. The first technique used for highly accuracy determinations of $\delta^{13}\text{C}$ analysis of food was the the Isotopic Ratio Mass Spectrometry (IRMS). Afterwards, several methods for isotopic analysis have been reported as LARA (Laser-Assisted Ratio Analyzer), OGE (Optogalvanic Effect), NDIRS (Non-Dispersive Infrared Spectroscopy) and traditional IR. In such scenario, great interest is based on the development of new analytical methodologies, accurate and inexpensive, in order to increase the choice of the analyst.

The objective of this work was to assess the agreement and the reliability of FTIR and NDIRS techniques for the measurement of stable carbon isotope ratio of food sample, in comparison to IRMS. The $\delta^{13}\text{C}$ was determined on samples of oil, durum, cocoa, pasta and sugar analyzing the samples by means of IRMS, NDIRS and FTIR.

For analysis the samples were reduced to carbon dioxide. The samples were combusted in pure oxygen at $T=1000^\circ\text{C}$. Carbon dioxide gas was collected in an impringer filled with 100 mL of $\text{Ba}(\text{OH})_2$ 0.3 M. This reaction started with a flash and carried on by itself. Carbon dioxide reacted with $\text{Ba}(\text{OH})_2$ and it was quantitatively converted in BaCO_3 . Before analysis, barium carbonate was washed with H_2O and dried under vacuum at 120°C for 1 hour. For NDIRS analysis 100 mg carbonate were introduced into a 10 mL glass flask, that was evacuated, and 2.5 mL of orthophosphoric acid was syringed to produce carbon dioxide. CO_2 gas produced was collected in a specific aluminum bag. For FTIR analysis 500 mg of BaCO_3 was introduced into a 10-ml glass flask with aPS (atactic polystyrene) film linked under the cap. The flask was evacuated and adsorbed CO_2 was released by acidification with 2.5 mL of orthophosphoric acid. The polymeric film was left for 2 hours at room temperature into CO_2 gas and then promptly introduced into the FTIR spectrometer.

Amorphous aPS film, with a thickness of 100-160 μm , was obtained by casting from 1.5% aPS chloroform solutions at room temperature.

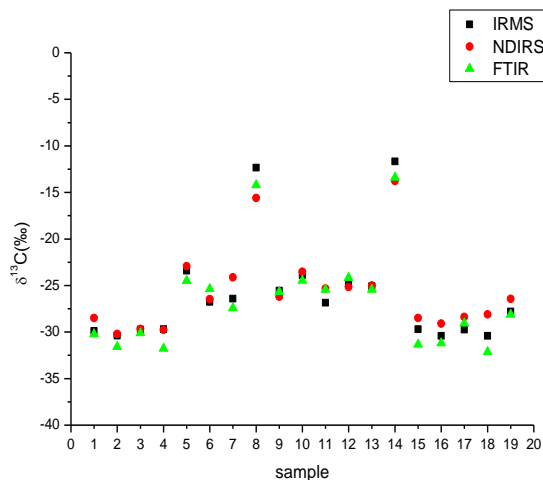


Figure 1. Correlation of the delta values obtained by means of IRMS, NDIRS and FTIR.

Results show a strong correlation between the three methods was demonstrated by regression analysis performed to compare IRMS, NDIRS and IR (Figure 1.). A significant correlation ($r = 0.983$) was obtained between NDIRS and IRMS techniques. A similar significant correlation ($r = 0.981$) between the methods was observed for IRMS and IR and for NDIRS and IR ($r = 0.953$).

Although our intention was not to provide information about the geographical origin of food or to evidence any falsification or fraud, the examination of different products in terms of variety, composition and chemical nature, demonstrated that these methods can enhance the choice of techniques useful for the analysis of isotopic composition of food.

The advantage of using NDIRS or FTIR as an alternative to IRMS in measuring $\delta^{13}\text{C}$ values is principally related to the lower cost with respect to IRMS, the rapidity of the analysis and the fact that the equipment does not require well-trained operator.

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POSTER COMMUNICATIONS

P1 - Strontium isotopic ratio in agricultural products: research gaps and future investigations for its use in geographical traceability

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A geographical indication (GI) is a widely known mark that relates a product to its specific district of origin and production process, attesting an intrinsic quality and authenticity. Furthermore, it is a useful tool to promote and protect rural economy. Therefore, GI is an added value that has acquired the status of guarantee not only for producers but also for consumers. However, due to its large use, GI is exposed to misuse and counterfeiting, thus several efforts have been made to detect and fight this fraud in the last decades. Among the analytical tools available, the use of the strontium isotope ratio ($^{87}\text{Sr}/^{86}\text{Sr}$) is gaining increasing importance in the field of geographical traceability, since it is related to the geological features of the district in which agricultural products are grown. Moreover, several studies reinforced this connection proving that strontium keeps unaltered its original isotopic fingerprint up to the end product, even after processing, with no isotopic fractionation. One of the most important processes through which this element is transferred in the soil-plant system is root uptake. Strontium shows some common chemical features with calcium (Ca) since they are both alkaline earth elements. For this reason, they are absorbed together by organisms, even if from a biological point of view calcium is required as an essential mineral with physiological role while strontium is not. Several investigations conducted so far have examined the potential of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, for instance comparing the fruit with its parent material or agrifood from different areas. Nevertheless, knowledge gaps are still present and until now few works have investigated the influence of the strontium concentration and isotopic composition of irrigation water and fertilizers used in agriculture on the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of end products.

The aim of the current contribution is to focus the attention on the strontium uptake in fruit trees, particularly to identify the major source from which this element is absorbed.

We selected apple orchards as case study, considering that apple is one of the most valuable produce in South Tyrol, with an acreage of about 18 500 ha. Moreover, apples from South Tyrol have been certified with the “protected geographical indication” (PGI) sign since 2005.

This work serves as a background for a PhD project focused on the isotopic characterization of agricultural food products. The comprehension of the process of strontium uptake is fundamental to acquire a better knowledge of the absorption of strontium in the soil-plant system, and will allow further investigations, in addition to strengthening the use of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio as a geographical tracer.

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P2 - Analysis of the differences in water use strategies of three Mediterranean shrubs in Sardinia (Italy), through tree-rings C and O stable isotopes ratios

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In Mediterranean-type climates, drought has been recognized as the main factor limiting plant species growth and distribution. To face this issue, plants have developed different ecophysiological mechanisms, as limiting the water loss by means of stomatal control. In this study we assessed the inter-annual changes of the intrinsic water use efficiency (WUEi) of three co-occurring Mediterranean shrubs, sampled at Capo Caccia site (Sardinia), two broad-leaved evergreen (*Pistacia lentiscus* and *Phillyrea angustifolia*) and one needle-like-leaved evergreen (*Juniperus phoenicea*), by means of tree-rings $\delta^{13}\text{C}$ analysis. In addition, the $\delta^{18}\text{O}$ helped to better explain the role of the stomatal conductance.

The sampled species resulted to have very different WUEi: in particular, *Juniperus phoenicea* seemed to be the most vulnerable to the increasing temperature and dry periods, while the other two species appeared to be more tolerant to drought due to a more efficient stomatal control. Our study increases the knowledge concerning the strategies of Mediterranean species to survive under water stress.

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P3 - Effect of fruit removal on photosynthetic characteristics and carbon isotope composition in olive leaves

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The cultivation of olive, one of the most economically valuable species in the Mediterranean countries, is highly encouraged because of its limited water requirement in areas, which are subjected to prolonged summer drought (Chartzoulakis et al., 1992). Olive trees may experience considerable water stress during the summer, when drought periods often occur at high temperatures and light levels (Angelopoulos et al., 1996). Many anatomical features and physiological mechanisms of olive trees are clear adaptations to drought conditions and allow some degree of control over water loss (Fernández et al., 1997). In olive trees, photosynthetic products are exported from leaves to the fruits to fulfil the metabolic requirements for oil synthesis (Sánchez & Harwood, 2002). Fruit removal was investigated to define how fruit growth interferes with the autotrophic processes of the olive plant. This information could be used for assuring a correct balance between source and sink and to develop and improve management practices such as irrigation.

Carbon stable isotopes provide a powerful tool for analysing constraints on photosynthesis and water-use efficiency of C3 plants (Farquhar et al., 1989; Brugnoli & Farquhar, 2000). This approach is based on the isotope fractionations occurring at the molecules of CO₂ entering and diffusing through the leaf and at enzymatic level (kinetic isotope effect) during assimilation of CO₂. The well-established relationship between the carbon isotope discrimination ($\Delta^{13}\text{C}$) and the ratio between the intercellular and the atmospheric concentration of CO₂ (c_i/c_a) (Farquhar et al., 1982) can be used to gain information on the photosynthetic behaviour of plant species.

On 6 out of 12 olive trees (cultivar Arbequina) 3 years old, inflorescences were removed just before flowering (de-fructified trees) in May 2014. In 2015, half of not-de-fructified and half of de-fructified trees in 2014 were de-fructified. During summer 2015, the 4 different kinds of trees obtained by applying de-fructification were analysed, namely trees de-fructified both 2014 and 2015, trees de-fructified in 2014 and not de-fructified in 2015 and vice versa and trees never de-fructified. Photosynthetic capacity at leaf level, as well leaf characteristics and ¹³C and ¹⁵N isotope composition were analysed.

Preliminary results, obtained during the maturation period of fruits in 2015, showed a clear difference in photosynthetic capacity of de-fructified trees compared to the not-de-fructified ones. When analysed at ambient CO₂ concentration, the de-fructified trees showed around 50% lower CO₂ assimilation compared to the not-de-fructified ones. These results were explained either with the lower stomatal conductance and the lower performance of the enzyme RuBisCo of de-fructified trees compared to the not-de-fructified ones. Interestingly, the stable isotope composition of carbon was related to the assimilation rate, confirming a lower isotope fractionation associated to lower assimilation. These results show a lower carbon investment in olive leaves when an important sink, such as the fruit is missing. This seems to be regulated both at stomatal and enzymatic levels, showing a high regulation at metabolic level, and it opens the way for the improvement of agricultural practices such as irrigation. Further

investigation are needed, in particular to validate the obtained results, also using different levels of fruit removal. This should be done with the aim of improving water use efficiency and, at the same time, by considering the effects on fruit and oil production and quality.

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P4 - Site-scale isotopic variations along a river course help localize drainage basin influence on river food webs

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In human-impacted rivers, nutrient pollution has the potential to disrupt biodiversity organisation and ecosystem functioning, prompting calls for effective monitoring and management. Pollutants, together with natural variations, can modify the isotopic signature of aquatic organisms. Accordingly, we explored the potential of isotopic variations as an indicator of drainage basin influences on river food webs. We assessed stable N and C isotopes within six food webs along a river affected by multiple pollution sources. CORINE land cover maps and Digital Elevation Models (DEMs) were also applied to understand the impact on surface waters of anthropogenic pressures affecting the catchment. N isotopic signatures of taxa fell in association with ammonium inputs from agriculture, indicating that nitrogen pollution was related to synthetic fertilizers. Isotopic variations were consistent across trophic levels, highlighting site-specific communities and identifying taxa exposed to pollutants. This allowed us to locate point sources of disturbance, suggesting that food web structure plays a key role in pollutant compartmentalisation along the river. Thematic maps and DEMs helped understand how the anthropogenic impact on river biota is mediated by hydro-geomorphology. Thus, the integration of site-scale analyses of stable isotopes and land use represents a promising research pathway for explorative nutrient pollution monitoring in human-impacted rivers.

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P5 - Fermentation and re-fermentation process: effects on isotopic parameters in sweet wines

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Aim of this study is to assess the relationship between isotopic ratios of extracted ethanol and fermentable sugar contained in sweet wines, which are commonly produced by stopping fermentation, both naturally or induced, in such way to leave unfermented sugars. As well as suggested by the biosynthetic pathway in plants, if residual sugar and ethanol have the same origin, it is reasonable that the isotopic parameters should be the same for both compounds.

Several sweet wines have been analyzed, and $\delta^{13}\text{C}$, $(\text{D}/\text{H})_{\text{I}}$, and $(\text{D}/\text{H})_{\text{II}}$ parameters have been collected after extraction of ethanol with a distillation process. The undistilled residue, containing non volatile compounds and residual sugars, has been added of yeasts and re-fermented in order to take out with a second distillation the resulting ethanol. The results were compared each other and they were interesting. In a systematic way, the $\delta^{13}\text{C}$ and the $(\text{D}/\text{H})_{\text{I}}$ have been showed higher value for residual sugars than the ethanol obtained with the first distillation.

The same results have been observed when Eurofins samples of the FIT Proficiency Testing Scheme for sweet wines in the years 2009-2015 have been taken into account.

One of the main fraudulent practices in sweet wine production is the undeclared exogenous sugar addition to enhance alcoholic strength and/or to give softness and sweet taste. In sweet wines, both alcohol and sugar content are obtained from grape sugar. In fraudulent sugaring practices, the parameters evaluation of stable isotopes carbon, hydrogen, and oxygen could not provide sufficient information when the official methods are applied only on the distilled ethanol. If the investigation range will cover the unconverted residual sugars, the possibility to detect illicit sugar employment could be controlled in an more efficient way.

P6 - Isotope Ratio Mass Spectrometry in combination with chemometrics for the characterization of the geographical origin of sweet cherries

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Sweet cherries from two Italian regions, Apulia and Emilia Romagna, were analysed using isotope ratio mass spectrometry (IRMS), in combination with statistical techniques, with the aim of distinguishing them according to their geographic origin. Preliminary exploratory overviews were performed and then linear discriminant analyses (LDA) were used for classification. The LDA results in terms of recognition and cross-validated prediction abilities were 94.9% and 91.0%, respectively. In order to validate the final results, the model was tested using an external set of samples with excellent results (94.1%).

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P7 - Carbon and oxygen isoscapes for geographical traceability of Italian extra virgin olive oils

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The authentication and verification of the geographical origin of food commodities are important topics in the food sector. Several authors have successfully exploited stable isotope techniques in the characterization, authenticity and traceability of olive oils (Angerosa et al., 1999; Iacumin et al. 2009; Camin et al. 2010a; Camin et al; 2010b, Portarena et al. 2014; Portarena et al., 2015). Nevertheless, no previous studies on extra virgin olive oil (EVOO) traceability have accounted for the spatial component as an independent variable in determination of isotopic signatures.

Methods for verifying the geographical origin of food based on a geospatial modelling approach have been developed recently (West et al., 2010; van der Veer, 2013) and, to date only a few studies have been published (West et al., 2007). Previously West and collaborators merged the terms “isotopes” and “landscapes” into “isoscapes”, thus defining the geospatial predictive power of stable isotopes, such as those of C, H, O and N involved in biogeochemical processes (West et al., 2010). Such processes produce isotopic fractionations that depend on the geographical location and spatial transport, and determine the spatial variability in the isotopic composition of materials (Bowen et al., 2009). More recently, van der Veer (2013) extended the geospatial model concept to multiple sets of suitable geographical markers (e.g., isotopes of heavy elements, organic compounds, trace elements) in order to better confine the area of possible origin. The general assumption in geospatial modeling for food provenance assessment is that the commodity of interest comes from one or more confined production areas, thus reflecting the peculiar isotopic composition of the provenance. These assumptions are met by some products, such as wine, honey, meat or EVOO, which are all characterized by the intrinsic identity of the areas of origin.

We followed a geospatial approach, combining stable isotope analysis with the use of GIS (Geographical Information System) technology and spatial analysis to develop geospatial models for the isotopic composition of Italian EVOOs. This study shows the spatial variability in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of 387 samples of EVOO collected in nine Italian regions, from 2009 to 2011, previously analysed by Portarena et al. (2014). EVOOs' $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values were related to GIS layers of source water $\delta^{18}\text{O}$ and climate data (mean monthly temperature and precipitation, altitude, xerothermic index) to evaluate the impact of the most significant large-scale drivers for the isotopic composition of Italian EVOOs. We used a hybrid procedure based on the spatial relationship between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values and the geo-climatic variables (ancillary variables) of the production areas. Ordinary Least Squares (OLS) analysis allowed us to quantify the positive correlation between EVOO $\delta^{18}\text{O}$ values and $\delta^{18}\text{O}$ of long-term average of annual precipitation. We found a positive correlation among $\delta^{18}\text{O}$ of EVOOs and annual mean temperature, mean temperature of the warmest months, mean precipitations of the spring quarter and the xerothermic index. No significant correlation exists between $\delta^{13}\text{C}$ values and the ancillary variables considered in 2009 EVOOs. Values of $\delta^{13}\text{C}$ for 2010 and 2011 samples show positive correlation with annual mean temperature, mean temperature of the warmest months,

and the xerothermic index. In the same years, negative correlations were observed with annual mean precipitation, and mean precipitation of both the spring and summer quarters. We derived $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ annual isoscapes of Italian EVOOs by joining regression techniques and geostatistical interpolation (Kriging). A direct estimate of the model variance is also provided.

The annual prediction maps of EVOO $\delta^{18}\text{O}$ largely reflect the isotopic composition of precipitation water, while the spatial pattern of the xerothermic index may explain the slight latitudinal gradient of EVOOs' $\delta^{18}\text{O}$. A clear distinction exists between $\delta^{13}\text{C}$ for EVOOs produced in the northern regions and those from the other Italian regions for each year of production, which reflects the different local climatic conditions.

Carbon and oxygen isoscapes identified EVOOs from four distinct areas: north, south-central Tyrrhenian, central Adriatic and islands, highlighting a zonation for the spatial patterns of the expected isotopic signatures. The geospatial approach appears promising in defining a protocol for the analysis of EVOOs' isotopic composition, to control and certify their origin and prevent food fraud.

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P8 - Diet reconstruction of the Po valley people from neolithic to the early bronze age by stable isotopes

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Stable isotope analyses of mammal fossil remains represent a well established method for gathering dietary and environmental information from ancient peoples in archaeological sites. It's possible to measure the isotope abundance of several elements in skeletal remains, for example: carbon, nitrogen and oxygen isotopic composition from organic (collagen) and inorganic (apatite) fractions of mammal bones and teeth.

Carbon stable isotopes help to distinguish between diet based on C₃ and C₄ plants because the distribution of two groups of plants is bimodal with no overlap between them. The nitrogen isotope ratios primarily reflect the trophic level of the individual; moreover it allows understanding if there is fish consumption.

For this case study, a large group of individuals from different localities in the Po Plain were considered, in order to reconstruct the palaeo-diet. They date from the Neolithic to the Early Bronze Age. In detail, the bones and teeth belonging to 134 individuals from Neolithic age (VBQ culture), 9 from Eneolithic and 23 from Early Bronze age were analyzed, for a total of 359 samples. In addition, 16 skeletal fragments (bones and teeth) belonging to 7 individuals found in the Arene Candide Cave (Liguria) were considered for comparison.

The $\delta^{13}\text{C}_{(V-PDB)}$ measured on collagen and apatite of skeletal remains indicate that the diet of these individuals was essentially terrestrial composed of C₃ plants and of a certain amount of proteins from animals which ate the same type of vegetation. This element is confirmed by the fact that the $\delta^{15}\text{N}$ values of the humans are enriched by about 3‰ compared to the $\delta^{15}\text{N}$ values of animal fragments found in the same sites.

For the individuals from the Early Bronze Age, the enrichment in the nitrogen isotopic composition would suggest increased consumption of fish, presumably of fresh water. This hypothesis may be true also for the individuals of the other groups, although in much lower quantities.

In many cases, it was possible to measure for the same individual three skeletal remains: bone, first and second molar. It allows to make assessments on nutritional changes during the different phases of the human life. Moreover, the high number of children has allowed establishing that the breastfeeding was prolonged in time, even for a few years.

Another interesting element is the fact that, for all sites in the Po Plain, the bone apatite is systematically enriched in ¹³C than tooth enamel. It is known that normally the opposite condition occurs in the collagen of the first molar, which starts to mineralize before birth, retaining information of early years of life that are influenced by breastfeeding. A possible explanation could be related to the different mechanism of formation of teeth and bones.

P9 - Effects of different zeolite amendments on plants C-N isotopic compositions

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The application of organic and inorganic amendments has been recognized as a valuable technique for increasing soil physic-chemical properties (Colombani et al., 2014). Among them, zeolites are known to be well suitable in a wide range of agricultural applications because of their high cation exchange capacity that allow a controlled retention/release of water and nutrients (e.g. NH_4^+) (Reháková et al., 2004).

The main aims of this study were to verify if natural zeolites amendments can increase the uptake of N from chemical fertilizers and if the N transfer from NH_4 -enriched zeolites to plants really occurs. The elemental and isotopic composition of plants grown with no zeolite addition and plants grown on soils amended with natural and NH_4 -enriched zeolites (the latter obtained after mixing with pig-slurry) were compared for two cultivation cycles. It is well known that plants $\delta^{15}\text{N}$ (of leaves, stems or grains) can reflect with a good approximation the isotopic ratio of the N source in the soil, thus, plants grown under conventional farming systems (using chemical fertilizers) and plants grown under organic farming (using animal manure and slurry) can be often easily discriminated (Choi et al., 2003).

The experimentation was carried out during 2014 (Maize) and 2015 (Wheat) cultivation cycles in the ZeoLIFE experimental field (Codigoro, Ferrara, Italy), which was properly parceled and amended with natural and NH_4 -enriched zeolites. Plants and the relative rhizospheric soils were sampled before the harvest and subdivided in stems and grains. The elemental and isotopic C-N compositions have been determined by an Elementar Vario Micro Cube Elemental Analyzer in line with an ISOPRIME 100 IRMS.

Results showed that plants grown on plots amended with natural zeolites had significantly lower $\delta^{15}\text{N}$ with respect to plants grown on unamended soils. Considering that the employed chemical fertilizers (Urea and NH_4NO_3) have a slight negative $\delta^{15}\text{N}$, it is highly possible that natural zeolites have adsorbed part of NH_4^+ ions formed after Urea and NH_4NO_3 hydrolysis because of their very high CEC and ammonium affinity. The retention of these ions probably allowed plants to uptake higher amounts of N from this specific source, resulting in a lower $\delta^{15}\text{N}$ of plant tissues with respects to plant grown on the unamended soil.

On the other hand, plants grown on NH_4 -enriched zeolites registered a higher $\delta^{15}\text{N}$, approaching that of the pig slurry employed for enriching the zeolites, confirming that this material can constitute a N pool for plants at least for two cultivation cycles.

The distinct agricultural practices seem to be reflected in the plant physiology, as recorded by the carbon discrimination factor ($\Delta^{13}\text{C}$) which generally increases in plots amended with natural zeolites indicating better water/nutrient conditions (Lasa et al., 2011)

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P10 - Nature and origin of millennial-scale climate variability in the mid-latitude north Atlantic ocean from foraminiferal $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$

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Since the pioneering efforts of Emiliani (1955) and Shackleton (1967), oxygen and carbon isotopic records derived from measurements of fossil foraminiferal shells have played a pivotal role in palaeoceanography, addressing a large range of questions regarding the evolution and history of the ocean and climate.

For any given species of foraminifera, variations in the $\delta^{18}\text{O}$ of its calcite test reflect some combination of a thermodynamic component (surface or deep-water temperature) and a water $\delta^{18}\text{O}$ component, the latter of which combines a global glacioeustatic signal with local hydrographic effects due to changes in the T - $\delta^{18}\text{O}$ signature of deep-water bathing the core site (Elderfield et al., 2012). The discovery that the foraminiferal $\delta^{18}\text{O}$ signal reflects fluctuations in global ice volume started the widespread use of $\delta^{18}\text{O}$ in global stratigraphic correlations (Shackleton and Opdyke, 1973). ‘Stacking’ a great number of $\delta^{18}\text{O}$ records in various ways to develop a global curve for comparison with models of astronomically forced ice volume fluctuations has allowed to establish detailed age control for marine records around the world (Imbrie et al., 1984; Prell et al., 1986, Lisiecki and Raymo, 2005). In this way, oxygen isotope stratigraphy has become not only a global correlation tool, but also a very powerful dating tool, particularly in regard to long-term Milankovitch-scale climate variability.

In this study, special emphasis is placed on the use of stable oxygen and carbon isotopes from foraminiferal shells in order to document millennial-scale climate variability and determine its cause. Over the past years, these observations have been largely restricted to the last glacial cycle because of the lack of high sedimentation rate records with known continuity that extend beyond the last glacial cycle, and because of the difficulty of placing the isotope records on an accurate time scale beyond the range of radiocarbon dating and the Greenland ice core record. Here we examine the record of climatic conditions beyond the last glacial cycle, from Marine Isotope Stages 24 to 16 (c. 920-650 ka), using high-resolution stable isotope records from benthic and planktonic foraminifera from a sedimentary sequence recovered in the North Atlantic (Integrated Ocean Drilling Program Expedition 306, Site U1313), in order to assess millennial-scale changes in sea-surface and deep-water conditions, the dynamics of thermohaline deep-water circulation and ice sheet-ocean interactions. We demonstrate the presence of interactions between orbital and suborbital components of climate variability, and show that insolation changes, forced by variations in Earth orbital geometry, are of fundamental importance in regulating the timing and amplitude of millennial scale climate variability (Ferretti et al., 2015). On a broader perspective, our results suggest that the variables measured by proxies are replicated in cycles apparently paced by orbital changes, suggesting the climate

system is to a significant extent understandable and deterministic, being contingent upon both forcing and previous history.

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P11 - Stable isotope ratios of H, C, and O in Italian citrus juices

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The stable isotope ratios (SIR) of C, H, and O have been intensively used in fruit juices quality control for the practices prohibited by European legislation in juices (sugar addition, watering down of concentrated juice and substitution of cheaper fruits instead of citrus). In this work $(D/H)_I$, $(D/H)_{II}$ and $\delta^{13}C_{\text{ethanol}}$, $\delta^{18}O_{\text{vegetalwater}}$, we considered Italian citrus juices samples officially collected by the Ministry of Agricultural and Forestry Policies from 2013 to 2015. The range of variability in genuine Italian citrus juice samples is presented here, along with the relationships between SIRs and their compliance with the limits suggested by AIJN.

Data showed in the present work represent an upgrade of a previous paper in which stable isotopic parameters of authentic citrus were collected for the harvests 1998-2012. Stable isotopic ratios have been obtained from Isotopic Ratio Mass Spectrometry (IRMS) and Site-Specific Natural Isotope Fractionation-Nuclear Magnetic Resonance (SNIF-NMR).

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P12 - The trophic ecology of migratory birds as shown by stable isotope ratios

($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{34}\text{S}$)

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In the last thirty years, the trophic ecology of animals has increasingly been studied using the stable isotope ratios approach (Boecklen et al. 2011). Generally, the ratios of carbon, nitrogen and sulphur isotopes have been used to reconstruct food chains and describe the trophic niches of animals within ecosystems (Post 2002, McCutchan et al. 2003, Bearhop et al. 2004). Moreover, isotopic ratios in animal tissues ultimately reflect diet, and the isotopic composition of diet reflects the biogeochemical characteristics of growth environments/habitats. Finally, the isotopic signature of environment may show spatial patterns, both on a local and continental scale (Hobson 2005, West et al. 2010). Thus the isotopic variability of carbon, nitrogen and sulphur in different species is related to the species' physiology and trophic niche, depending on the isotopic landscape in which the tissues grew (Hobson and Wassenaar 2008). In this study, we measured carbon, nitrogen and sulphur isotope ratios in the feathers of 48 species of European Passerines. More than 800 birds were captured and banded at a ringing station set up in an alpine pass in the province of Trentino ('Bocca di Caset', Progetto Alpi, Pedrini et al. 2008, 2012) during post-breeding migration (August-October, migration from northern breeding quarters to southern wintering areas) in 2010, 2011, 2012 and 2013. All the individuals were juveniles, namely born in the year of sampling, and the feathers were sampled from the nest-grown moulting generation (Jenni and Winkler 1994). Hence the isotopic values of each individual were related to the diet brought to it by its parents. We classified species according to the type of habitat used during the breeding season (open land, grasslands, wetlands, open woodland and forests), migratory phenology (trans-Saharan, intra-Paleartic, irruptive species) and the feeding habits of the species (strictly insectivorous - mainly adult insects, strictly insectivorous - mainly larvae, granivorous, omnivorous - insects and seeds) (del Hoyo et al. 2004-2011). A preliminary graphic overview of the results obtained is shown here.

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P13 - Geochemical and isotopic characterization of discharge waters from the Piz Boe´ active rock glacier, dolomites, eastern Italian Alps

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Rock glaciers are debris-covered mixtures of rock and ice common in many alpine and arctic regions and represent the most widespread periglacial phenomena on the Earth. Beside the importance as striking geomorphological forms, rock glaciers also contain significant amount of ice preserved from ablation by several meters of debris. While the kinematics and thermodynamics of rock glaciers have been extensively studied in the past decades, only little information is available on the hydrological regime and the geochemical characteristics of active rock glaciers.

Here we present the preliminary results of the Piz Boe´ hydrological system, an active “ice-cored” rock glacier from the Dolomites (2900 m a.s.l.), North-Eastern Italian Alps. Gaging stations have been installed to measure continuously the discharge of two streams, which drain surface and melting waters from the hydrological basin. Electrical conductivity (EC) has also been measured continuously by specific dataloggers, submerged into the spring waters. A complete hydrological station was also installed on the shallow lake just downstream the rock glacier to monitor air temperature, liquid precipitation, barometric pressure, water depth and temperature and EC. Water samples from the springs and the shallow lake have been collected weekly from the second half of June to the first half of October, starting from 2011. Snow and rain samples have also been collected from snowpits and through rain collectors respectively. All the samples have been analyzed for water stable isotopes as well as for a large suite of chemicals such as pH, major ions, nutrients, trace elements and rare earth elements.

Strong diurnal variations characterize both the discharge and the geochemical and isotopic features of the springs until the seasonal snow is completely melted (second half of August). Water precipitation from rainfall summer events is quickly released from the rock glacier within a few hours causing sharp peaks in discharge and severe decrease in EC and trace elements concentration.

After the snow-melting period the discharge rapidly decrease with less evident diurnal fluctuations. The concentrations of all the chemical parameters increase reaching a maximum at the end of August. In this period an increasing in the heavy metals (Pb, Zn, Cu, Cd) content is also evident with values that greatly differ with the local geo-chemical characteristics. Also the $\delta^{18}\text{O}$ shows seasonal variations becoming less negative.

The geochemical and isotopic features suggest that the hydrological budget of this rock glacier is mainly influenced by water from snow-melting, rainfall and, to a lesser extent, from rock glacier ice melting. On the other hand, this seems to strongly impact the geochemical features of surface waters at the end of summer. Further studies are required to determine more precisely the amount of water released from the rock glacier and how these phenomena could impact the water resource, both from a quantitative and qualitative point of view.

P14 - Precision, accuracy and repeatability of sulfur determination in several matrices by elemental analysis

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The importance of Sulfur determination has grown dramatically in recent years in many application fields (geological, agronomy, petrochemistry, environmental, food etc.) and many of the classical methods are now no longer suitable for routine analysis. As the demand for improved sample throughput, reduction of operational costs and minimization of human errors is becoming every day more notable, it is very important apply a simple and automatic technique which allows the fast analysis with excellent reproducibility.

Analytical instruments based on the combustion of samples improve the reliability of the data available, without the use of hazardous chemicals.

The FLASH 2000 Analyzer, based on the dynamic flash combustion of the sample, copes effortlessly with the wide array of laboratory requirements such as accuracy, reproducibility and high sample throughput.

This paper presents data of Sulfur determination in different matrices to show the high quality of the results obtained.

P15 - Carbon sequestration and distribution in soil aggregate fractions under miscanthus and giant reed in the Mediterranean area

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In this study, we assessed the carbon (C) distribution within soil aggregates, Macroaggregates (Macro), microaggregates (micro), silt and clay (s+c), through three soil depths, after 9 years of land conversion from two annual crops, continuous wheat and maize/wheat rotation, to Miscanthus and giant reed, respectively. ¹³C natural abundance analysis was combined with physical fractionation to trace the fate of the new C derived from Miscanthus and giant reed in aggregate fractions. Macro always represented the highest proportion of soil and highest amount of C. In Miscanthus, the amount of C decreased from 0-0.15 to 0.3-0.6 m soil layer, while the C storage capacity of micro and s+c increased with depth. In giant reed, the distribution of soil fractions and the associated C were more uniform in all layers. The new C derived from perennial species was mainly concentrated in the upper layer in Macro under Miscanthus, while it was more evenly distributed in the three layers and fractions under giant reed. Irrespective of fractions, in Miscanthus plantation the great C accumulation derived from both new C directly entering the soil and old C preserved from mineralization. Conversely, in the giant reed plantation C accumulation only derived from the new C component. These patterns reflect the different structure of the root apparatus of the two perennial species, mainly concentrated in the upper layer that of Miscanthus, more evenly distributed in soil profile that of giant reed. This is perceived to be responsible for different mechanisms of C storage and turnover.

P16 - Fate of N in soil amended with ¹⁵N-labeled residues of winter cereals combined with an organic n fertilizer

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In organic farming winter cereals, as cover crops, provide nutrients, when they return to soil as crop residues. The fate of N deriving from two decomposing ¹⁵N-labelled winter cereals, with or without the supply of an organic N fertilizer, was studied in a field experiment. The stabilization of residues N in soil aggregates and the portion lost from the system were also evaluated. Barley or triticale residues were incubated alone or with hydrolyzed leather (L) in mesocosms over one year. The residues derived N was measured in soil and in soil aggregate size fractions > 250 µm (macroaggregates, Macro); 53-250 µm (microaggregates, micro); < 53 µm (silt and clay, s+c) obtained by wet sieving. Barley degradation (77 % of the initial amount) was faster than triticale degradation (55 %). The L slowed down the barley degradation (72 %) and speeded that of triticale (64 %). Greater amount of residues N was in Macro and micro than in s+c. The presence of L reduced the residues N stabilized in the finest fractions. The losses of barley N were reduced by the L addition, those from triticale were increased. The fate of residues N was affected by the L application that influenced the residues mineralization, the stabilization and the losses of their derived N.

P17 - Stable isotope signatures of fluids emitted from “Macalube di Aragona” mud volcanoes (Sicily, Italy)

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Mud volcanoes (MVs) are geologic structures representing important natural emissions of water, oil and gaseous hydrocarbons from buried sediments. Waters associated to MVs are brackish or brines having variable chemical and isotopic composition, depending on their origin (mainly seawater) and the post-deposition processes they have undergone. Gas composition is mainly dominated by methane (>90%) being biogenic, thermogenic or mixed in origin.

In Sicily, there are many examples of MVs which are mainly located within the Apennine accretionary wedge and on the offshore shelf of southern Sicily. The most active onshore MVs areas are that of “Macalube di Aragona” close to the city of Agrigento and that of Terrapelata, close to the city of Caltanissetta.

In this paper we reported the main isotopic signatures of waters and gas expelled from the “Macalube di Aragona” mud volcanoes area (Sicily, Italy) with the aim to identify the origin of the emitted fluids.

Previous studies (Grassa et al., 2006) on chemistry of water emitted from “Macalube di Aragona” have highlighted that:

- i) Na and Cl are the dominant dissolved components;
- ii) salinity is about 60-70% lower than seawater;
- iii) all the ionic ratios are modified with respect to seawater;
- iv) alkalinity (up to 63.6 mMol l⁻¹) and B contents (up to 17.2 mMol l⁻¹) are relatively high.

“Macalube di Aragona” mud volcanoes mainly emit hydrocarbons (CH₄ > 85% Vol and C₂H₆ up to 2% Vol.), with nitrogen and CO₂ contents generally not exceeding 10% Vol. C₂+alkanes and noble gas (Ar and He) are present at levels of hundreds or tens of ppm. In the past, some temporal variations has been recorded only in the chemical composition of the emitted gas while water chemistry remained almost stable.

Then, some questions arose out of the interpretation of the water chemistry and data: which is the origin (marine, meteoric, connate, or “secondary”) of the waters associated with mud volcanoes? Does such peculiar chemical composition reflect secondary post-genetic processes? Are the hydrocarbons thermogenic, biogenic or mixed in origin?

Therefore, we analyzed stable isotope (H, O, C and B) composition of the expelled waters. Waters result depleted in deuterium (around -15‰ vs. V-SMOW) and strongly enriched in 18-oxygen (around +8‰ vs. V-SMOW) with respect to seawater; the dissolved inorganic carbon (($\delta^{13}\text{C}_{\text{TDIC}}$) shows unusual positive signature (up to +24.6‰ vs. V-PDB); Boron isotope ratios straddle the $\delta^{11}\text{B}$ values in seawater (+39.5‰ vs NIST 951) ranging from +36.7 to +41.3‰.

Based on the stable isotope signatures and water chemistry, we propose that waters entrapped into sediments during deposition and having original composition similar to seawater, were strongly altered during diagenesis of clay minerals. Freshening of pore water is likely due to mixing with deep-seated fluids. On the basis of the δD and $\delta^{18}\text{O}$ values and the Cl content, we have identified these deep fluids to be originated by means the dehydration of smectite and its subsequent transformation into illite. Other diagenetic processes (alteration of organic matter,

precipitation of authigenic carbonate, anaerobic oxidation of methane) led to strong modification in salinity and ionic ratios as well.

B isotope signature and B enrichments in the fluids are also consistent with the rising of mature deep-seated fluids released during late stage of diagenesis of clay minerals toward surface along the main thrust faults

As regards the origin of unusual positive $\delta^{13}\text{C}_{\text{TDC}}$ values coupled with high alkalinity values has been interpreted as due to bacteria mediation (Grossman et al., 1989 and Martini et al., 1998). Alternatively, the dissolution of an “ultraheavy” CO_2 with $\delta^{13}\text{C}$ values from +10 to +16‰ vs V-PDB with a not well-defined origin in the deep crust/upper mantle has been inferred for Caucasian MVs (Kopf et al. 2003) also linked to methane generation, as proposed by Whiticar (1999).

At “Macalube di Aragona” MVs, the $\delta^{13}\text{C}_{\text{CO}_2}$ values range between -2.5‰ and +12.7‰ vs V-PDB and show a marked inverse correlation with CO_2 contents. Higher CO_2 contents (around 3% Vol) correspond to more negative $\delta^{13}\text{C}_{\text{CO}_2}$ values, while positive $\delta^{13}\text{C}_{\text{CO}_2}$ values are associated with CO_2 concentration around 1% Vol. Such a behavior seems to indicate a shallow secondary methanogenesis will produce CH_4 at the expense of CO_2 thus leading to the residual CO_2 enriched in ^{13}C isotopes.

$\delta\text{D}_{\text{CH}_4}$ and $\delta^{13}\text{C}_{\text{CH}_4}$ values range from -152 to -188 ‰ vs V-SMOW and from -44 to -54.0‰ vs V-PDB respectively. By plotting the samples in the CD diagram (Schoell 1980), the hydrocarbon gases emitted from “Macalube di Aragona” fall in an intermediate position between the field relative to thermogenic gas and that one relative to biogenic gas. This trend could be the result of a mixing between a prevailing thermogenic methane and a biogenically derived methane or the effect an isotope fractionation due to post-generation process. Under geological conditions, hydrocarbon production from low permeability reservoirs and/or migration towards surface are thought to produce isotope fractionation resulting in a more negative isotope composition of the gas with respect to the pristine isotope composition at source.

By coupling the carbon isotopes of methane and carbon dioxide and plotting the data on the $\delta^{13}\text{C}_{\text{CO}_2}$ vs. $\delta^{13}\text{C}_{\text{CH}_4}$ diagram proposed by Gutsalo e Plotnikov (1981) and it appears that gases emitted from “Macalube di Aragona” MVs are thermogenic in origin and they have modified their isotope signature as a consequence of secondary post-generation process.

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P18 - Stable isotope ratio analysis for authentication of red yeast rice

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Red Yeast Rice is a non-prescription dietary supplement used in traditional Chinese medicine and obtained from rice fermented with the yeast *Monascus purpureus* (*Aspergillaceae* family). Depending on the fermentation conditions, the products may contain monacolins, pigments and citrinin as secondary metabolites. The pharmacological compound Monacolin K is a naturally occurring hypocholesterolemic statin used to prevent cardiovascular diseases. The homologous prescription biosynthetic statin, lovastatin, cultured with *Aspergillus terreus* under patented and carefully controlled conditions, is not distinguishable from monacolin K. There is therefore a suspicion that RYR products are spiked with lovastatin, without declaration.

As reported by different authors the application of Stable Isotope Ratio Analysis represents a fast and simple tool to control whether or not a sample is of natural origin. We therefore collected around 10 samples of red yeast rice powder, and 10 samples of synthetic lovastatin. Monacolin K was isolated from rice by preparative HPLC and together with lovastatin, was subjected to the analysis of the isotopic ratio of C using an Isotope Ratio Mass Spectrometry interfaced with an Elemental Analyser. We found that the $^{13}\text{C}/^{12}\text{C}$ is able to clearly distinguish lovastatin (-17.3‰) from monacolin K (-29.8‰). In order to have an overall picture of the market we also investigated the authenticity of 20 samples of commercial products containing Red Yeast Rice.

P19 - Reconstructing climate changes from ombrotrophic peatlands using stable isotopes

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In studies about climate reconstruction, stable isotopes signatures are extremely valuable proxies. In the particular case of peat bogs, where the only source of water is precipitation, bog plants register isotope ratios as a function of precipitation (Bilali et al., 2013).

Oxygen isotope ratios are typically measured from cellulose extracted from peat, and it has been demonstrated that they are well correlated with various climatic parameters, in particular with temperature and relative humidity (Chambers et al., 2012). For hydrogen isotopes, measurements are usually performed on leaf-wax biomarkers such as n-alkanes or n-fatty acids: leaf waxes of vascular plants from aquatic environments are widely used to reconstruct the hydrogen isotopic composition of precipitation, and recently started to be applied also to peat samples (Nichols et al., 2006). Carbon isotopes in peat can be measured from cellulose, leaf-wax compounds and from non-extracted bulk samples (Chambers et al., 2012).

Although paleoclimatic data from these proxies are becoming extremely important, the interpretation of the isotopic composition in peat in terms of environmental changes is complicated by several factors, which include: the varying time resolution due to unevenly spaced dates and growth rates, species-specific differences, partially unknown biochemical pathways in plant tissues, and signal preservation in decomposed peat. Because of these factors, stable isotope records from peat sequences must be used and compared in a wider framework with other proxy-data (Tillman et al., 2010).

The aim of our study is to reconstruct environmental and climate changes that characterized the last 2000 years in two peat bogs sampled in the Dolomites (Cadore Area, Belluno province). We will performed oxygen, hydrogen and carbon isotopes analyses from different component of the peat and we will compare these data with all the geochemical, biological and physical data already collected from these samples.

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P20 - $\delta^{18}\text{O}$ and deuterium excess records from the GV7 ice core (Oates coast, East Antarctica)

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Here we present an overview of the GV7 drilling project along with the $\delta^{18}\text{O}$ and deuterium excess records obtained from a snow pit (4 m), two shallow firn cores (5.6 m and 12 m long respectively) and at the main drilling (low-resolution 60 cm-samples) which reached a depth of 245 m ice. This core was drilled at a near coastal site in East Antarctica, during the 2013-2014 Italian Antarctic Expedition. The project, funded by PNRA with KOPRI cooperation, represents a contribution to the IPICS theme "The 2k Array". The drilling site (GV7, 70°41'S, 158°52'E; elevation 1950 m, T = -31.8°C), located on the ice divide extending from the Oates Coast to Talos Dome, is characterized by a relatively high snow accumulation rate (240 mm w.eq. during the last 150 years). Previously, a 55 m-length firn core was retrieved in the same area. The obtained data, combined in a multicore-approach, will be used to produce a stacked climate record of the past centuries with at least an annual resolution.

A preliminary age scale was built using a snow accumulation rate of 237 mm w.eq. for the upper part of the core and two stratigraphic markers represented by the bottom age (1855 CE) of the previous core and a tephra layer found at 183 m dated 1254 ± 2 CE. The low-resolution $\delta^{18}\text{O}$ profile indicates a cooling trend over the last millennium, while the deuterium excess record shows an abrupt increase between 1400 and 1450 CE, which suggests an atmospheric circulation change.

P21 - Methionine incorporation into the breast muscle of broiler chickens at the final fase

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Stable isotopes are widely applied for study of muscle protein metabolism, including measurement of synthesis and breakdown rates of labeled compounds. The muscle is in a constant state of turnover. These enriched compounds, such as amino acids, are introduced to trace the element fates in the organism, delineate functional pathways and are used in a variety of kinetic studies. The aim of the study was to assess the rate of labeled methionine incorporation into the breast muscle of broilers aged 36-42 d-old. A total of 51 one-d-old male Cobb broiler chickens, with an initial body weight (BW) of 2.4 ± 0.06 kg, were housed (12 birds/m² density) after selection by weight. The diet was formulated based on corn and soybean meal. A dosage of 29 μmol of L-[¹³C₁]methionine/kg BW/h was used, administered orally within 6 h (99 atom% ¹³C, Cambridge Isotope Laboratories, Inc.) to promote tissue enrichment. At 0 (control), 0.5, 1, 2, 3, 4, 5, 6, 8, 10, 12, 16, 20, 24, 48, 72 and 96 h after initial dosing, were slaughtered 3 birds per time-point, and collected breast muscle samples, which have undergone lyophilization and milling processes. Carbon isotopic analysis was obtained using a mass spectrometer. Second-order polynomial fit was used to determine the maximum incorporation point, and analyzed by first-order exponential equation $[\delta^{13}\text{C}_{(t)} = \delta^{13}\text{C}_{(i)} + [\delta^{13}\text{C}_{(i)} - \delta^{13}\text{C}_{(f)}]e^{-kt}]$, obtained using the statistic software Minitab[®] 16. Maximum enrichment occurred 17.2 h after oral administration of enriched solution, and resulted in the equation: $\delta^{13}\text{C} = -18.07 - 2.37e^{-0.1801t}$ ($r^2=0.94$), with half-life $[T = \ln 2/k]$ of 3.8 h, representing the velocity of methionine incorporation into embedded tissue. Thus, the time required for 50% of orally-administered labeled methionine to be metabolized is approximately 3.8 h at this dose and age of bird.

P22 - $^{87}\text{Sr}/^{86}\text{Sr}$ TIMS analyses in the food chain of white wines and their use as geological fingerprint for tracing their geographic provenance

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The radiogenic isotopic compositions of inorganic heavy elements such as Sr, Nd and Pb of food chain may constitute a reliable geographic fingerprint being their isotopic ratios inherited by the geological substratum of the territory of production. The Sr isotope composition of geo-materials (i.e., rocks and soils) is largely variable, and it depends upon the age of the rocks and their nature (e.g., genesis, composition).

In the last years a high precision analytical procedure was developed for determining $^{87}\text{Sr}/^{86}\text{Sr}$ of labile fraction in soils and of grape juices, must, and wines at comparable uncertainty level of geological isotope. This permitted direct comparison between the products of agriculture food-chain and the isotope geology baseline of a geographic area (Boari et al., 2008; Braschi et al., 2013; Marchionni et al., 2013). In addition the possibility of Sr-isotope variation during wine-making process in red and white wines was also investigated analyzing yeast and other additives used (Tescione et al., 2015; Marchionni et al., 2016).

Replicate isotope analyses on Red “Aglianico Beneventano” wine from bottled samples of the same winery and vintage year provided consistency for the analytical protocol defined. As a matter of fact, 31 replicate Sr isotope analyses the same mean, median, and mode value of 0.708439 with 2 standard deviations (2σ) of 1.7×10^{-5} . A Sr-isotope value that is overlapping the geological substratum of the vineyard (Marchionni et al., 2013).

No $^{87}\text{Sr}/^{86}\text{Sr}$ variation was observed through the complete food chain of Red wines from the labile fraction of soil, to grape, musts and wine, suggesting that wine-making process has no effect on the isotope ratio of heavy elements differentiation (e.g., Marchionni et al., 2016). In addition no significant variability in the Sr isotope composition was observed in bottled wines from different vintage years (Boari et al., 2008; Braschi et al., 2013; Marchionni et al., 2013) suggesting that $^{87}\text{Sr}/^{86}\text{Sr}$ in wines can be considered a robust tracer for defining the “terroir” of Red wines and to constrain their geographic area of provenance, as also confirmed by other recent studies (e.g., Mercurio et al., 2014, Durante et al., 2015).

On the other hand, large discrepancies between $^{87}\text{Sr}/^{86}\text{Sr}$ of white wines and those of the geological substrata of their vineyards was observed, possibly due to yeast and other geologic additives used to stabilize and clarify the final product (e.g., Wolff-Boenisch et al., 1998; Marchionni et al., 2013; Petrini et al., 2015). With this in mind a complete isotopic study through the entire food chain of several white wines has been performed to investigate the possible variations of $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio during the winemaking process and Sr isotope relationships between white wines and the geological substratum of production vineyard.

Samples of grape, grape juice, must and wine of different cultivar varieties used for white wines production and vintage years, coming from one single winery, were collected and analyzed from 2013 to 2015. The same was done with yeast and bentonite used during wine-making process: the sampling campaign concerned every step of the production before and after the

treatment with the additives. The bedrock and the overlying soil of the substrata of the vineyards were also sampled and analyzed for comparison with the final product.

The obtained results clearly show that the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios is regular through all the winemaking process also for white wines and with values comparable to those of the labile fraction of the soil on which the vineyards are grown and farmed. Our data confirm the robustness of Sr-isotope in studies for defining terroirs and geographic provenance of both red and white wines.

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P23 - The potentiality of the stable isotope analyses in the discrimination between human and climate forcing: the study case of Arslantepe (Turkey)

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In semi-arid regions the socio-economic development of ancient societies was strongly linked to the crop management evolution (Wilkinson 1997). Despite attempts to link archaeological evidences to local palaeoclimatic data, the role of environmental conditions in past agricultural production has been rarely recognised (Riehl 2009). The stable carbon isotope analysis on fossil plant remains contributes to understand crop management and palaeoclimate fluctuations because water availability is the primary factor controlling C isotope variability in plants (Farquhar et al. 1989; Hartman and Danin 2010). Carbon isotope data ($\Delta 13C$), performed on charred grains of emmer (*Triticum dicoccon*) and barley (*Hordeum vulgare*) and on charcoals of juniper (*Juniperus*) and deciduous oaks (*Quercus*), constitute the basis of a new ongoing study from the archaeological site (Arslantepe, Turkey). The published isotopic record dates from 4300 BC to 2000 years BC and evidenced the potentiality of this approach in particular for the plant macroremains (Masi et al. 2013a-b, 2014). New samples have been added extending the record in time (about one millennium back), increasing the number of analysed taxa (*Triticum aestivum/durum*, wheat) and enclosing the N isotope composition in the investigation. New AMS radiocarbon dates have been carried out from the same plant remains. The aim was improving the chronology, the palaeoenvironmental reconstruction and the knowledge of agricultural practices.

Up to now, more than 100 cereal grains taken down in chronological sequence have been measured in two replicates (CIRCE - Center for Isotopic Research on the Cultural and Environmental heritage; Dip. di Matematica e Fisica, Seconda Università di Napoli, Caserta, IT) after ABA (acid-basic-acid) pre-treatment. This is the first time that isotopic analyses have been carried out on a single archaeological sequence spanning more than 2,000 years.

$^{13}C/^{12}C$ ratio reflects seasonal fluctuations in moisture conditions during crop growing (Aguilera et al. 2012; Ferrio et al. 2003; Fiorentino et al. 2008; Masi et al. 2014; Riehl 2012). The different isotopic behaviour of the cereal crops suggests that they grew under different water regimes. While wheat shows some similarities with emmer, the signal of barley seems to be directly linked to climatic fluctuations. In particular a drought event is recorded in the second half of the 3th millennium BC when a clearly different management system was adopted for barley and emmer. The latter was sustained by water supply, whereas barley was rain-fed due to its aridity resistance. Data interpretation is improved comparing the results with the available isotope data from wood remains and other regional palaeoclimatic records (Roberts et al. 2001, 2008; Bar-Matthews and Ayalon 2011; Wick et al. 2003).

The N isotope composition analysis is still in progress and will contribute to better understand the complex relation between agricultural systems and ancient societies and their resilience to climate changes.

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P24 - $\delta^{18}\text{O}$ and δD in water vapor and precipitation for a coastal lagoon

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Stable isotopes of hydrogen and oxygen give an important contribution in tracing waters through the water cycle. Following the pioneering studies of Craig (1961) and Dansgaard (1964) many applications of stable isotopes have been found in hydrology to examine the path of water, from evaporation to precipitation, and of course for atmospheric transport. To date, the isotopic composition of precipitation was deeply studied but uncertainties still exist on the dynamics of stable isotopes in water vapor due to the lack of data. In this study we present one year of observations of water vapor and precipitation for a lagoon at mid-latitudes (Venice, northern Italy). Samples have been collected with cryogenic trapping (once a week, for water vapor) and rain gauges (on monthly and event basis). Liquid samples have been analyzed with a Picarro L1102-I and results are reported against VSMOW. $\delta^{18}\text{O}$ and δD in water vapor and precipitation show seasonal patterns with outliers linked to air parcel origin. In fact, samples of water vapor collected delayed by few days with the same air temperature, show differences in terms of $\delta^{18}\text{O}$ up to 3 ‰. The linear relationship between δD and $\delta^{18}\text{O}$ in rain and water vapor samples has been examined and compared with the Global Meteoric Water Line (GMWL). The resulting Local Meteoric Water Line (LMWL) has lower slope and intercept than GMWL. Rain samples which have been slightly evaporated (probably between the cloud base and the ground level) fit a different line, namely an evaporation line. Samples of rain and water vapor show two distinct modal values on the LMWL, since the resulting distribution is the composition of two log-normal distributions. The per-mil differences between the modal values are close to enrichment factors of water estimated from average air temperature. Therefore, some paired samples of water vapor and precipitation have been collected at the same time during rainfall. Results show that rain and vapor are near the isotopic equilibrium, just considering air temperature measured at ground level. Finally, the sampling on event basis during occasional and discontinuous precipitation events allows to identify the rainout effect, which leads to lightening the water during a rainfall. Throughout a discontinuous rain, $\delta^{18}\text{O}$ and δD show variations up to 7 ‰ and 60 ‰, respectively. Since the amount of precipitation of separate events is a crucial parameter to consider, in this work we also estimate the $\delta^{18}\text{O}$ and δD of monthly precipitation from single rain events.

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P25 - Results of official controls by isotope ratio mass spectrometry of $\delta^{13}\text{C}$ in honey

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Following the scandal of horse meat not declared in meat products from different animals, the European Commission adopted the Recommendation C1558 of 12 March 2015 on the establishment of a coordinated plan of control to be implemented in the Member States, to detect any fraudulent practices regarding the marketing of certain foods in areas particularly at risk, including honey.

According with such provisions, 2237 honey samples were collected all over the European territory, at different stages along the production and marketing chain.

The controls carried out, by this central inspectorate, on 110 samples collected all over the Italian territory verified different types of honey and their origin. Irregular samples were found to be 9% of total samples.

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