Workshop A.I.S.E.T.O.V 2019

TRACEABILITY OF PROTECTED GEOGRAPHICAL INDICATION (PGI) SORRENTO LEMON BY CHEMOMETRIC ANALYSIS OF THE SOIL AND JUICE MINERAL COMPOSITION

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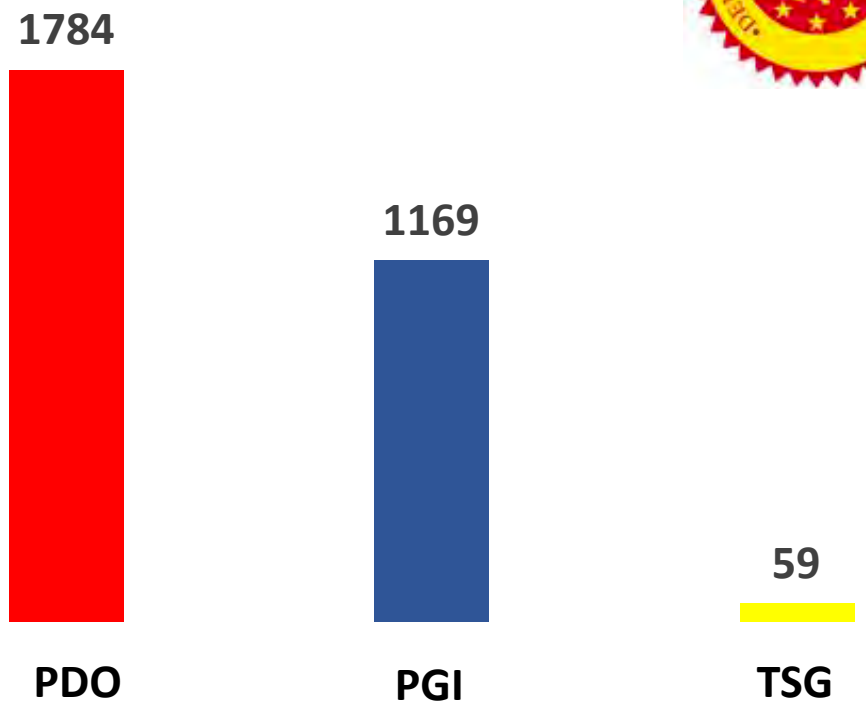
What is Traceability and Why is Important?

Strong connection that binds the food to its territory of origin

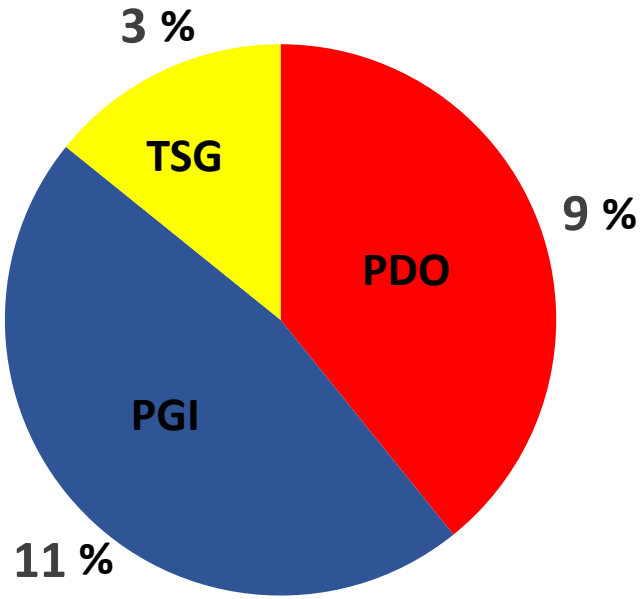
<u>For consumers</u>:

- **more guarantees;**
- **increased food safety;**

Overview of European and Italian High-Quality Food Products



European High-Quality Food Products



Italian High-Quality Food Products

QUALIVITA
Fondazione per la protezione e la valorizzazione dei prodotti DOP IGP STG

FOOD FRAUDS IN ITALY

In 2018, 17,500 tons of irregular agro-food products have been seized for a commercial value of over 21.8 million euros.

Analytical techniques for authentication and determination of the geographical origin of foods

Techniqaes	Sensitivity	Simplicity	Time analysis	Costs	Reported applications	Compounds	Identification/profiling
MS							
IRMS	+	+/–	+/–	–	+	Various	i + p
ICP-MS	+	+/–	+	–	+	Elements	i + p
PTR-MS	+	+	+	–	–	Volatile	p
GC-MS	+	+	+/–	–	+	(Semi) volatile	i + p
Spectroscopy							
NMR	–	+/–	+/–	–	–	Various	i + p
IR	+/–	+	+	+	+	Various	p
Fluorescence	+	+	+	+	–	Various	p
Atomic	+/–	+/–	+/–	+/–	+	Elements	i + p
Separation							
HPLC	+/–	+	+/–	+	+	Various	p
GC	+	+	+/–	+	+	(Semi) volatile	p
CE	–	+	+/–	+	–	Various	p
Other							
Sensor technol.	–	+	+	+/–	+/–	Volatile	p
PCR	+	+/–	+/–	+	–	DNA	i + p
Sensory analys.	+/–	+/–	–	–	–	Various	p

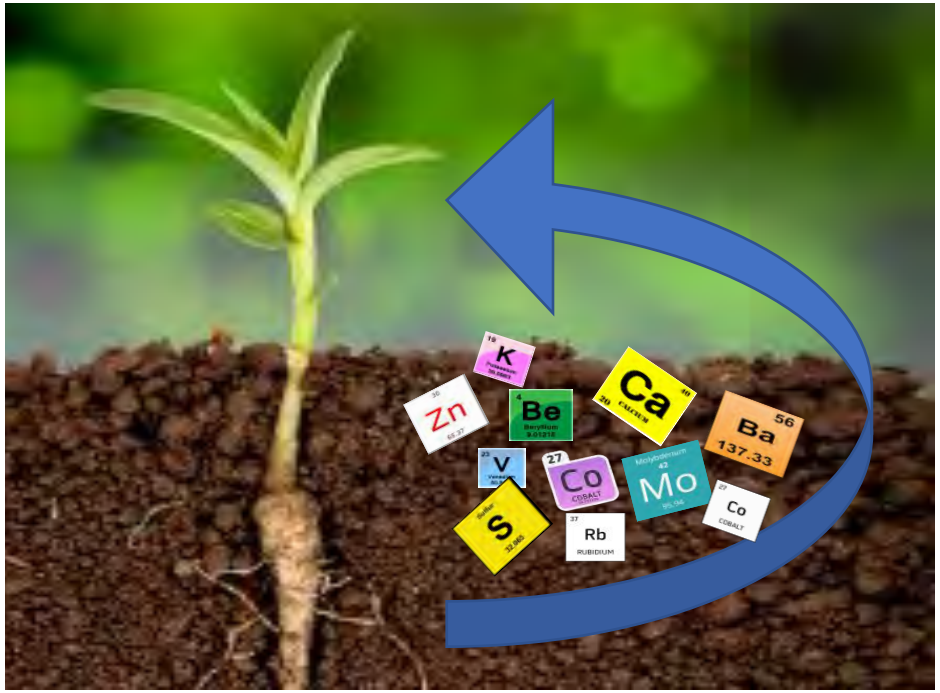
Favourable (+), moderate (+/-), unfavourable (-)

(Luykx et al., 2008).

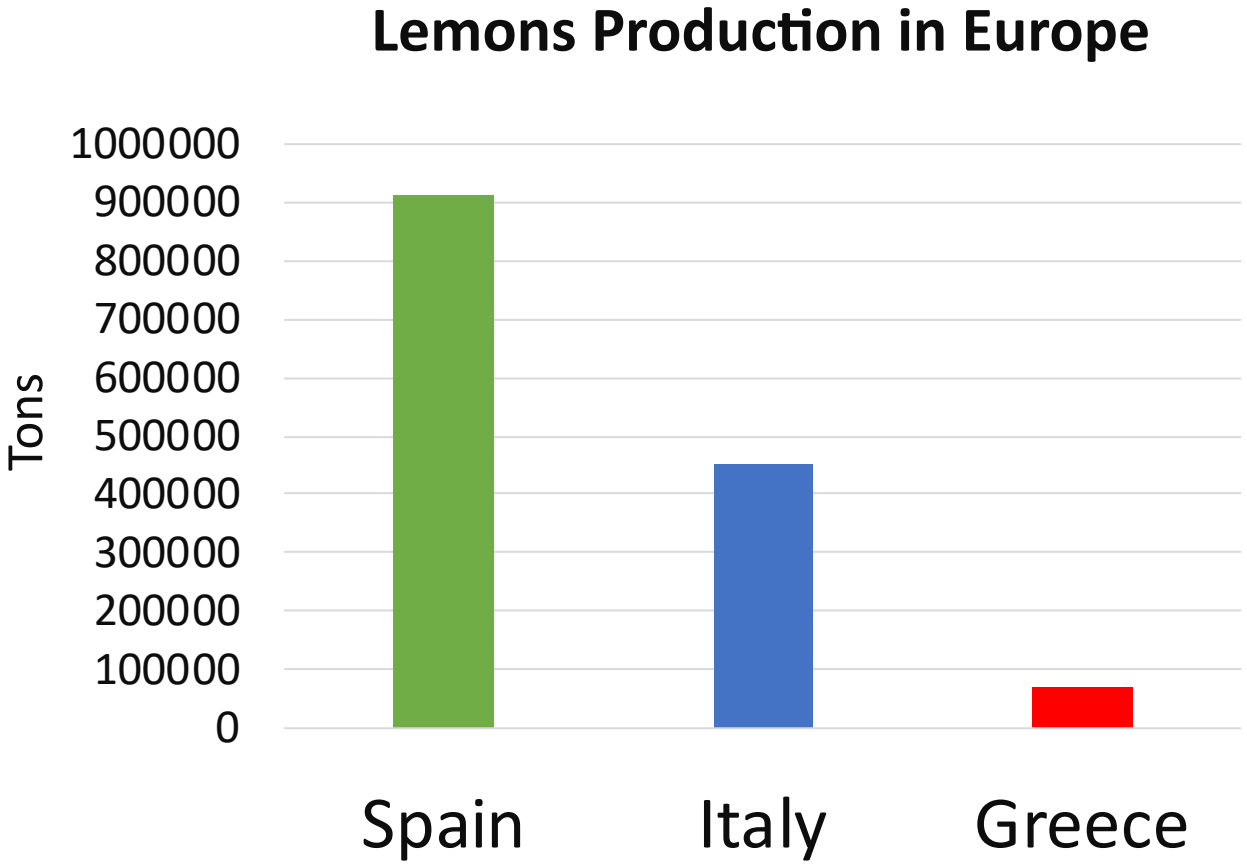
Elements in Soils and Plants

Soils formed in different geographic areas (different soil, different environment) are different for mineral and geochemical composition

The bioavailability of inorganic elements in soil and the chemical composition of a crop is greatly affected by soil properties, such as pH, moisture, organic matter and clay, as well as plant requirements



Lemon Fruits Production



1092 tons

1860 tons

Italy is the second largest lemon fruit producer in the Europe on a cultivated surface of 23,000 ha

Frauds

LIMONI DI SORRENTO DALL'ARGENTINA!

Sorrento news TeleStreet Arcobaleno

Gio, 04/10/2012 - 23:46

a cura di Pasquale Davide

Natale, scattano i sequestri delle derrate alimentari

la Città
QUOTIDIANO DI SALERNO E PROVINCIA

Nel mirino di Nas e Nac prodotti dolciari scaduti da anni e frutta secca avariata Al mercato ittico pesce di provenienza ignota e in Costiera olio con falsi limoni Igp

di Gianni Giannattasio

24 dicembre 2014

#NATALE 2014 #ALIMENTI #SEQUESTRI

As most part of high quality products, they are affected by a lot of frauds

Aims of the work

- **Discriminate** Limone di Sorrento samples multi-element fingerprinting that come from PGI area to lemon that come from two different cultivation area of Campania region.
- **Compare** multi-element fingerprinting of lemon with bioavailable element contents in the cultivation soil
- **Protect** Limone di Sorrento from frauds with lemons of other geographical origin.

Limone di Sorrento

STUDY AREA AND SAMPLING

- **39** full ripening lemon fruits, cv "Ovale di Sorrento, (from Jan. to Mar. 2018)

- **4** different sampling sites:
  - Limone di Sorrento **PGI area**
    - **Massa Lubrense (MS)**
    - **Piano di Sorrento (PZ)**
  - Limone di Sorrento **NO-PGI area**
    - **Portici (PORT)**
    - **Eboli (EBO).**

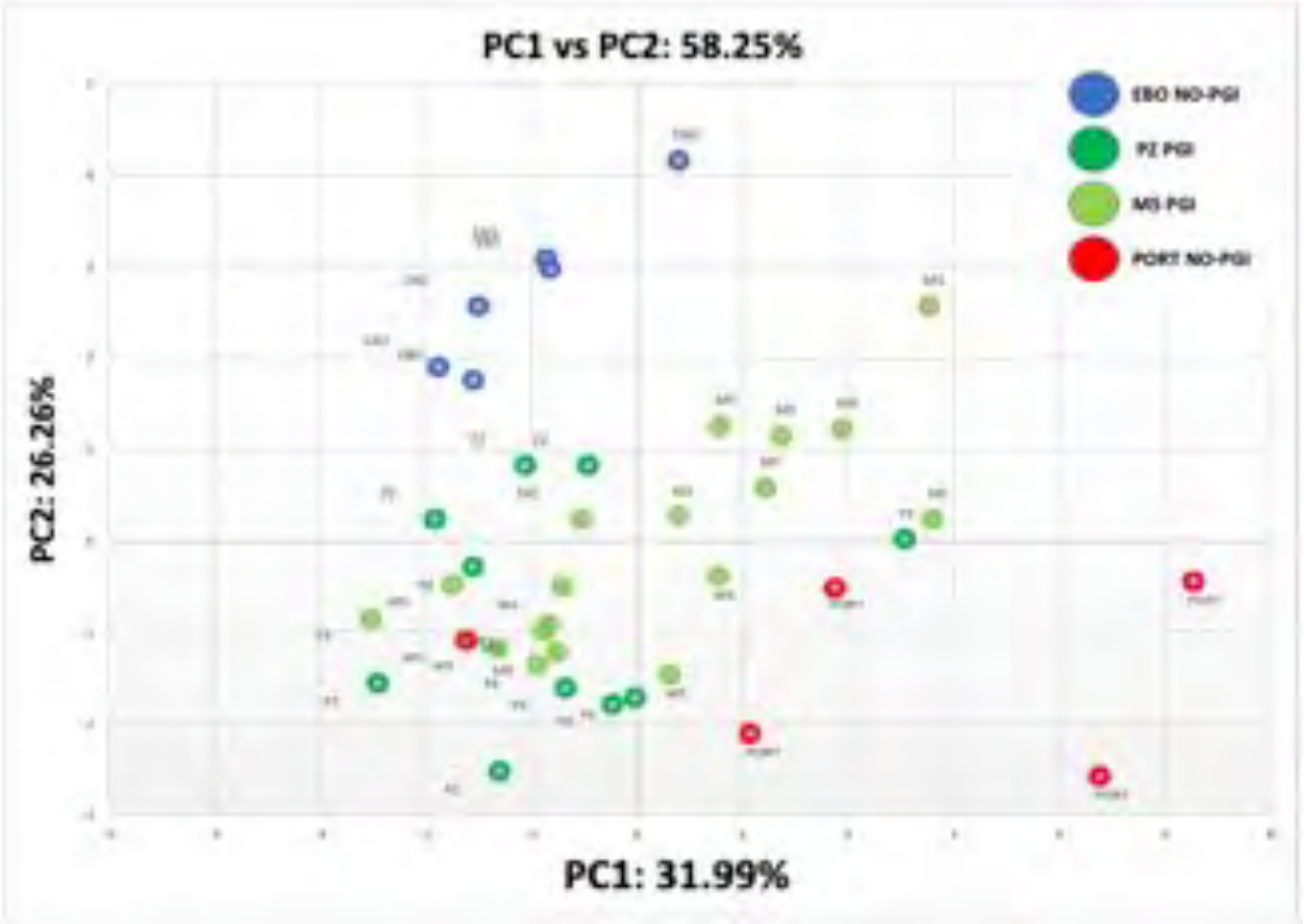
- Two depths of soil sampling
  - **top soils**, 0-20 cm
  - **sub soils**, 40-50 cm

MULTI-ELEMENT ANALYSES

- **Lemon Juices** were mineralized by acid digestion (5 mL HNO_3 , 2 ml H_2O_2) in microwave.
- **Potentially bioavailable elements in soils** were extracted by EDTA 0.05 M with 1:10 soil/solution ratio.

	LEMON JUICES (µg/kg)									SOILS (mg/kg)							
	PGI						NO-PGI			PGI				NO-PGI			
	MS (n=16)			PZ(n=12)			PORT (n=5)			EBO (n=6)			MS (n=4)		PZ(n=6)		PORT (n=2)		EBO (n=3)	
Elements	mean		±SD	mean		±SD	mean		±SD	mean		±SD	Top soil	Sub soil	Top soil	Sub soil	Top soil	Sub soil	Top soil	Sub soil
Ti	9.69	ab	2.98	9.51	ab	3.72	13.63	b	7.37	6.82	a	0.41	9.63	5.63	7.57	5.37	2.16	1.53	6.56	5.01
V	0.33	ab	0.18	0.45	a	0.32	0.63	a	0.33	0.36	a	0.07	1.63	1.82	1.48	1.53	1.16	1.13	9.46	8.01
Fe	207.71	c	27.27	193.29	b	59.02	359.68	b	120.48	73.02	a	8.47	143.81	72.13	188.79	119.70	76.92	61.83	123.57	94.65
Mn	108.06	a	42.88	145.51	a	35.89	106.75	a	44.06	95.95	a	14.59	85.76	55.56	33.36	13.82	18.30	23.36	416.21	326.17
Co	0.49	a	0.23	0.34	a	0.17	0.78	b	0.24	1.38	b	0.15	0.37	0.27	0.15	0.10	0.07	0.07	2.94	2.14
Cu	293.30	a	63.90	245.20	a	45.58	319.05	a	48.12	271.77	a	47.06	76.03	19.10	117.96	49.61	26.32	22.40	22.63	6.76
Zn	430.26	c	80.96	376.84	ab	84.09	499.94	bc	97.27	270.85	a	30.27	15.61	4.45	25.29	10.08	2.14	1.44	1.93	0.72
Se	1.47	a	0.62	1.31	a	0.34	1.99	a	0.24	1.68	a	0.72	0.15	0.14	0.12	0.12	0.08	0.06	0.34	0.31
Rb	1299.20	bc	329.69	890.77	a	132.14	1099.37	ab	271.49	1627.82	c	157.06	0.94	1.03	1.14	1.28	0.71	0.78	0.18	0.25
Sr	238.98	b	49.79	164.78	ab	65.36	160.89	a	61.78	139.95	a	34.14	33.00	29.61	24.71	27.28	15.15	16.69	19.82	18.34
Mo	7.96	a	4.45	7.76	a	4.56	15.80	b	4.82	9.82	ab	4.21	0.02	0.02	0.03	0.02	0.02	0.02	0.08	0.08
Ba	63.95	b	18.17	69.91	b	32.85	30.03	b	16.12	84.16	a	17.95	36.06	59.83	21.53	54.66	17.13	29.50	25.27	128.44

LEMON JUICES



	Principal Component		
	PC1	PC2	PC3
Ti	**0.46**	-0.10	0.01
Fe	**0.38**	**-0.39**	-0.07
Co	0.12	**0.46**	**-0.43**
Cu	0.30	0.19	0.25
Zn	**0.40**	-0.31	0.13
Se	0.35	0.22	-0.23
Rb	0.14	**0.50**	-0.06
Sr	0.28	0.14	**0.62**
Mo	**0.39**	-0.01	-0.39
Ba	0.04	**0.41**	0.38
Total Variance %	**32.0**	**26.3**	**13,1**
Cumulative Variance %	**32.0**	**58.2**	**71.3**

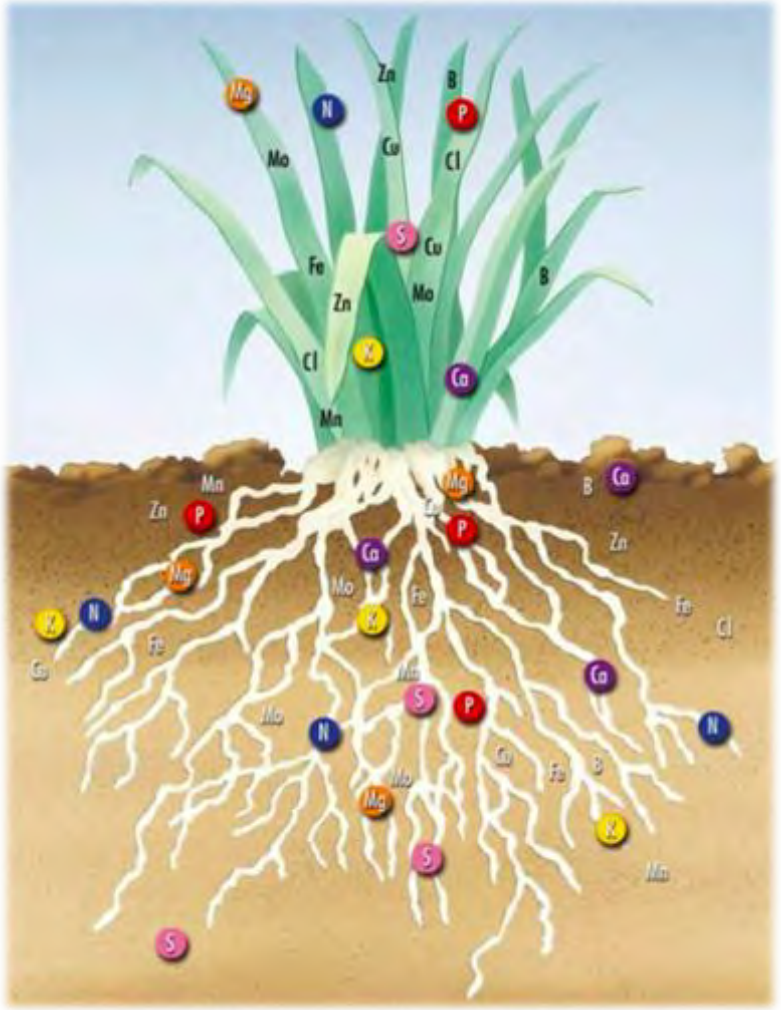
KMO test = 0.593;
Bartlett sphericity test, p <0.001

LEMON vs SOIL RELATIONSHIPS

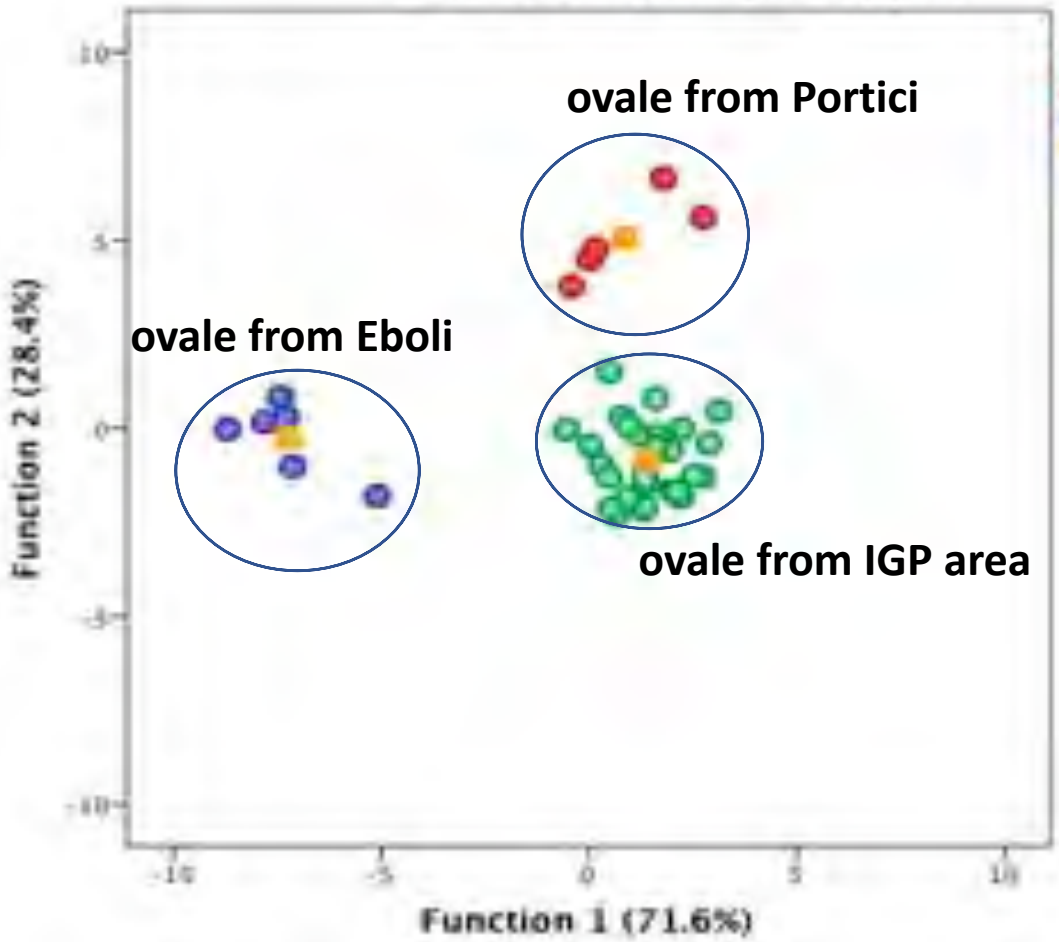
Person Correlation Analysis

	Fe	Co	Rb	Sr	Ba
Top Soil (0-20cm)	-0.360	0.800	-0.551	0.563	0.436
Sub Soil (40-50cm)	ns	0.799	-0.499	0.380	0.471

ns not significant



×LINEAR DISCRIMINANT ANALYSIS (LDA)



Structure Matrix		
	Function	
	F1	F2
Co	**-0.492**	0.232
Rb	**-0.192**	-0.031
Sr	**0.116**	0.114
Fe	0.305	**-0.514**
Mo	-0.031	**0.300**
Ba	-0.106	**-0.247**
Zn	0.209	**0.212**
Ti	0.099	**0.191**
Se	-0.048	0.183
Cu	0.011	0.137

- **Based on the 10 elements**
- **100% of correct classification**
- **The model was cross-validated with satisfactory results.**

(100% of correct reclassification).

λ Wilks 0.017
p-values <0.0001

CONCLUDING REMARKS

- The results confirm multi-element fingerprinting as a valid indicator of agri-food geographical provenience. Indeed, multi-element fingerprinting was able to discriminate the “Limone di Sorrento” from lemons of the same cultivar coming from NO-PGI areas.

- The results showed a relationship between the multi-element fingerprinting of the soil and the lemon.

- This suggests that the technique might be used to protect “Limone di Sorrento” by frauds.

Future investigations including a more significant number of cases are necessary to confirm these promising preliminary results

On going activities

- More samples and farms
- Samples from different years
- Samples at different maturation stages
- Analysis of Sr isotopic ratio ($^{87}Sr/^{86}Sr$) in Soil (Bioavailable content) and lemon
- Analysis of essential oils in lemon peels (GC-MS and PTR-MS)


Thanks for your attention