

CHARACTERIZATION OF SLOVENIAN MILK AND DAIRY PRODUCTS USING ELEMENTAL COMPOSITION AND STABLE ISOTOPES



Institut
"Jožef Stefan"
Ljubljana, Slovenija

Nives Ogrinc, Doris Potočnik, Darja Mazej, Marijan Nečemer, David Heath

Jožef Stefan Institute, Jamova 39, 1000 Ljubljana

The development and application of analytical tools for the verification of geographical origin, production origin and species origin of food products is one of the main topics in food science. The presented work uses stable isotope ratios and elemental composition to determine the regional provenance of milk and dairy products. The first database of authentic Slovenian cow, sheep and goat milk and cheese has been established. The database includes isotope values ($\delta^{18}\text{O}$ values and $\delta^2\text{H}$) in milk, the isotopic composition of carbon and nitrogen in casein ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) and the elemental composition from four different geographical regions in Slovenia: the Alps, the Dinaric Alps, the Pannonian Plain and the Mediterranean.

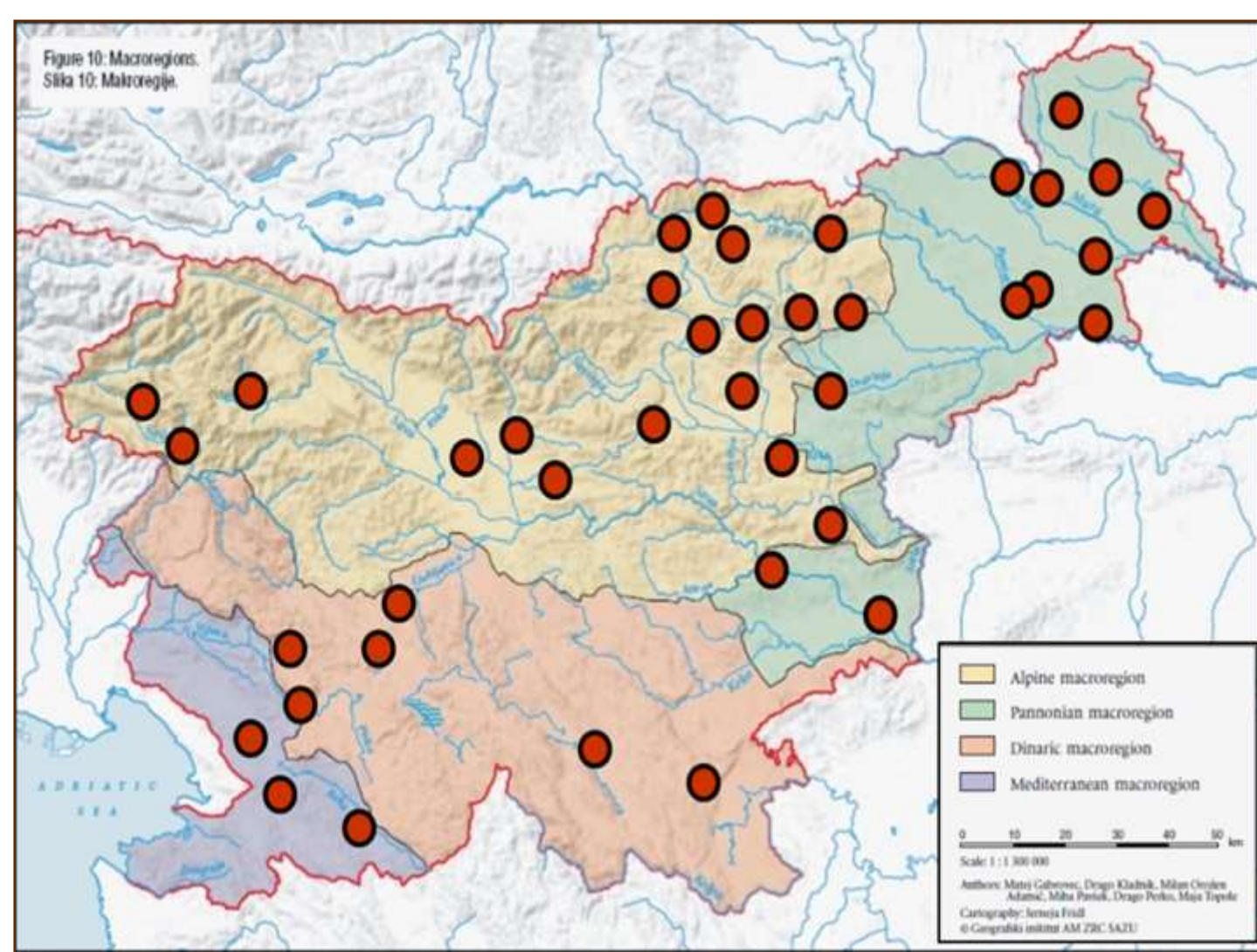
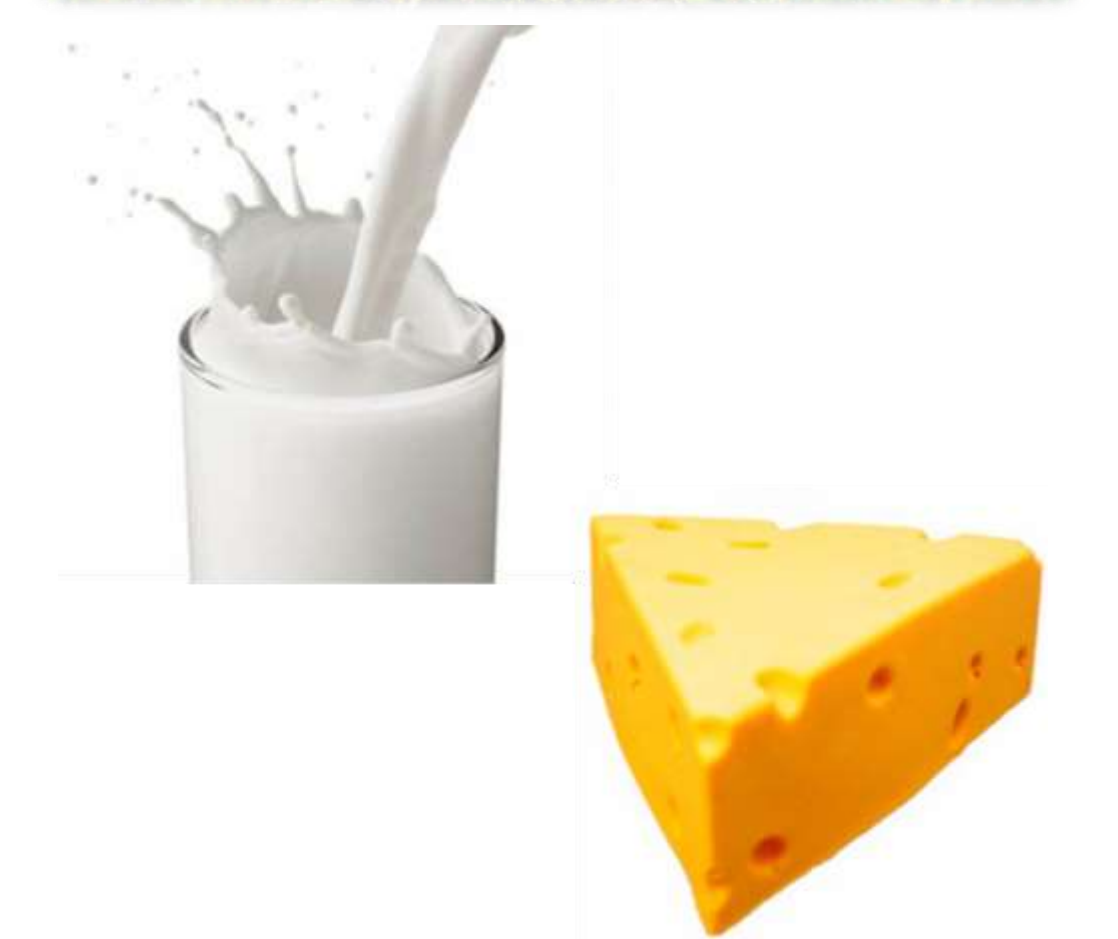


Figure 1: Sampling location

SAMPLING:

- 43 samples of authentic cow milk, twice per year (summer, winter), from different geographical regions (Mediterranean, Pannonia, Dinaric and Alpine) in Slovenia
- $\delta^{13}\text{C}$ monthly for $\delta^{18}\text{O}$ measurement
- $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in casein in summer and winter
- 75 samples of authentic sheep and goat milk (summer), cheese



ANALYTICAL METHOD:

- determination of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ directly in milk with IsoPrime MultiFlow Bio equilibration unit (GV Instruments)
- determination of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in casein using EA – IRMS
- determination of macro- and micro-elements (P, S, Cl, K, Ca, Zn, Br, Rb, Sr) on freeze-dried samples by X-ray fluorescence spectrometry (XRF)
- determination of trace elements (Mn, Fe, Cu, As, Se, Cd, Pb) using two preparation steps:
 - 1) microwave digestion with nitric acid and hydrogen peroxide
 - 2) dilution with an ammonia, EDTA and Triton X-100 solution

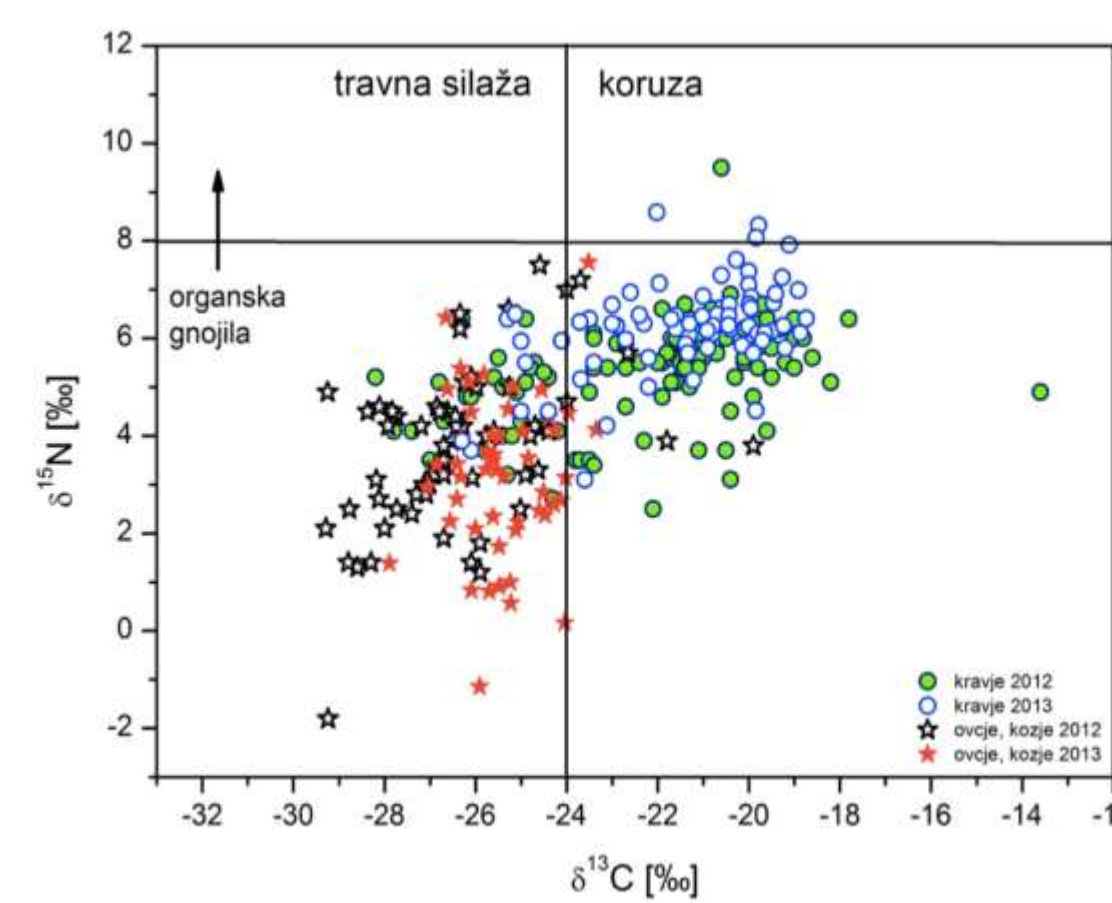


Figure 2: Stable isotopic composition of carbon and nitrogen in casein. $\delta^{13}\text{C}$ values, which are higher than -24‰ indicated a higher content of maize in the diet. $\delta^{15}\text{N}$ values higher than 6‰ suggests the use of organic fertilizers in food production or in pasture fertilization.

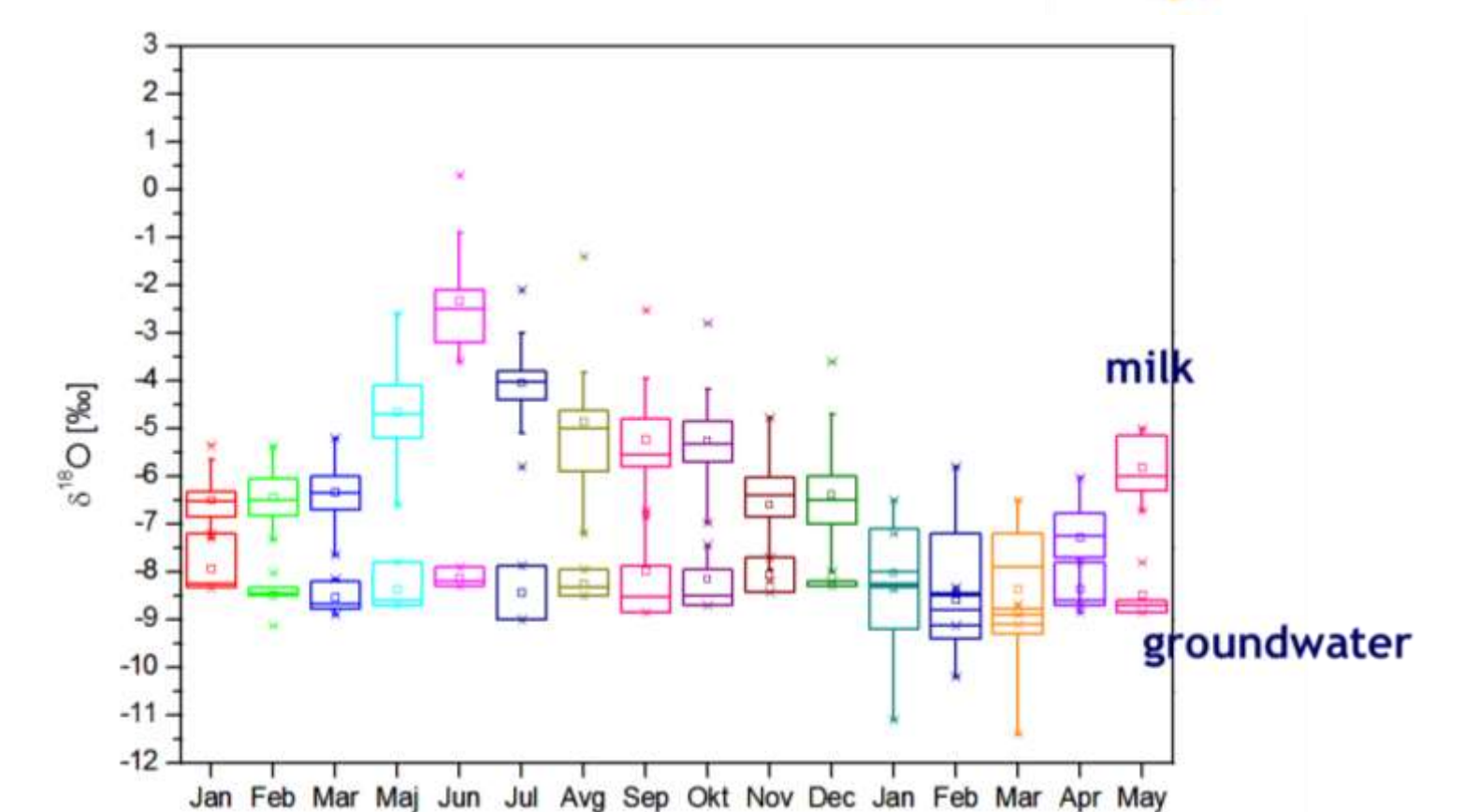
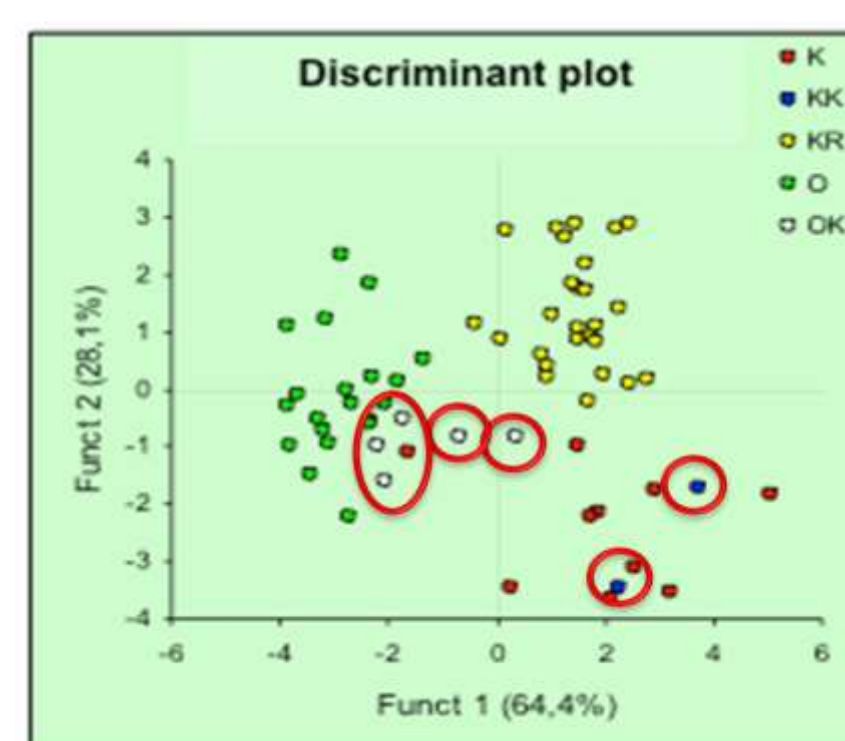


Figure 3: The isotopic composition of oxygen in milk is on average higher by 2‰ than the composition in groundwater, which is the results of the cow's metabolism and eating habits.

GEOGRAPHICAL ORIGIN:

- The isotopic composition of dairy products reflects the dietary regime and the metabolism of the milk producing animals.
- Climatic condition such as temperature and humidity are known to affect the $\delta^{13}\text{C}$ isotopic values in plants from different regions due to the effects of evapotranspiration and photosynthesis.

COW, SHEEP and GOAT MILK and CHEESE

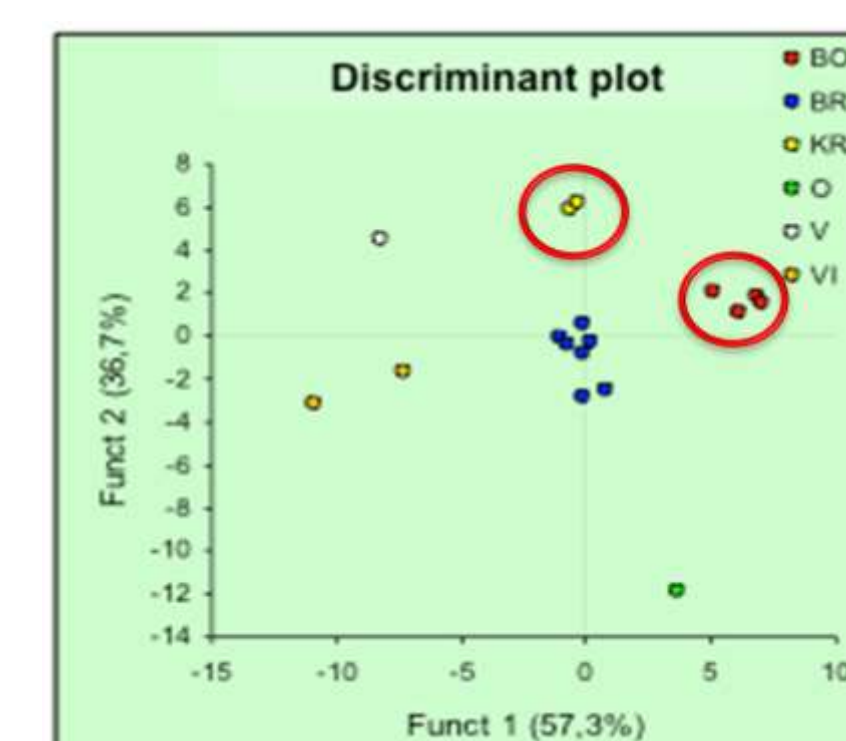


cow (KR), goat (K), sheep (O)
goat-cow (KK), sheep-cow (OK)

Type of milk	% of corrects classification
cow	100
sheep	95
goat	80
together	95.2

F1: K, $\delta^{15}\text{N}$, Br, Ca
F2: Zn, S, P, Ca

Figure 4: Classification of milk samples according to type. Based on stable isotope composition and elemental content it is possible to differentiate between cow, sheep and goat milk.

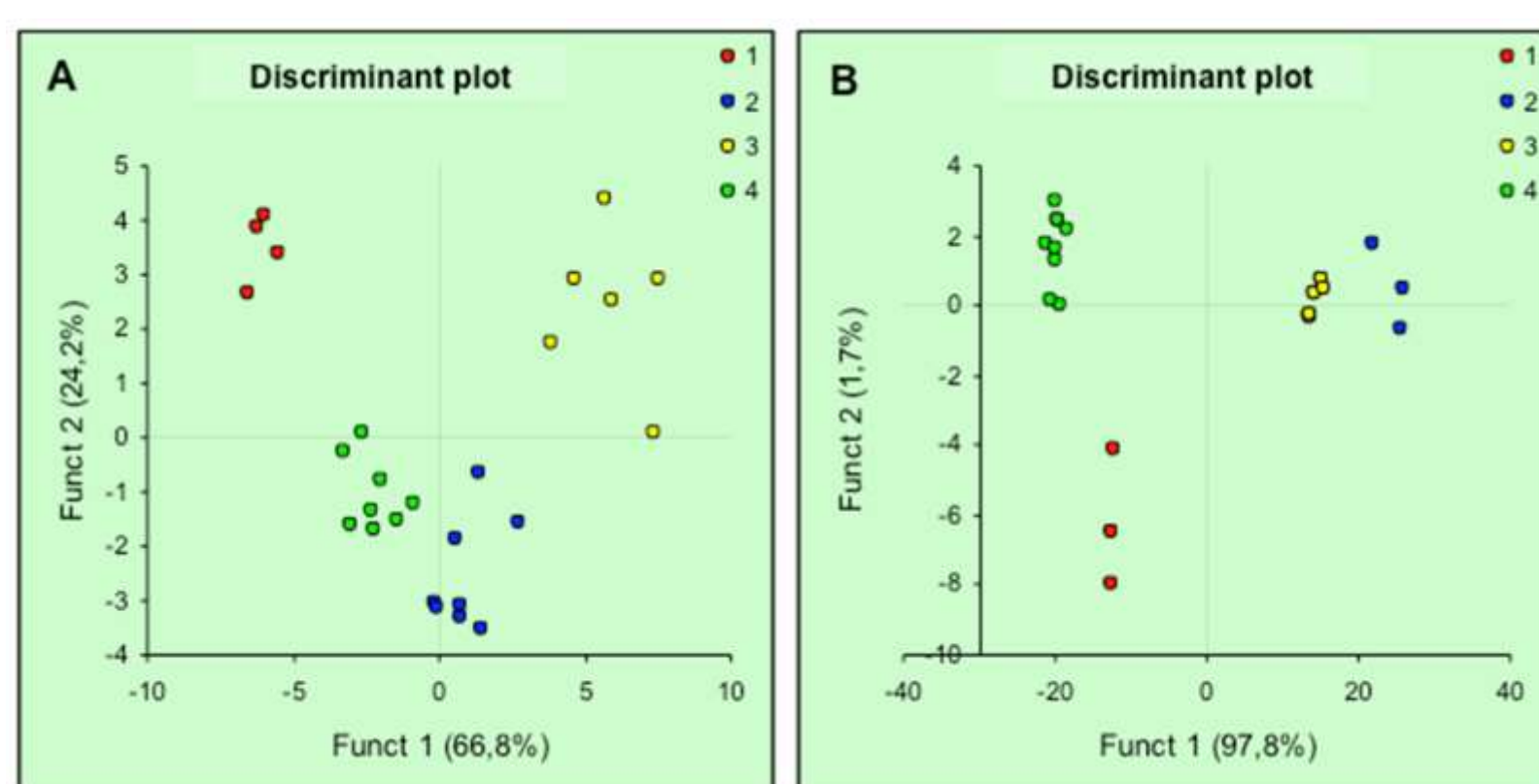


F1: K, $\delta^{13}\text{C}$, Mn, S, Cl in P

Figure 5: Geographical differentiation of Slovenian cheeses based on stable isotope composition and elemental composition. The most significant variables were K, $\delta^{13}\text{C}$, Mn, S, Cl and P.



BO – Bovec
BR – Notranjska
KRA – Kras;
O – Central
V – Dolenjska
VI – Vipava



June 2012
F1: Cl, Zn, K, Ca and $\delta^{13}\text{C}_c$

December 2012
F1: K, Cl, S, P, Mn, $\delta^{15}\text{N}_c$

Figure 6: Stable isotopes in combination with elemental composition is the most appropriate method for verifying the declared geographical origin. In summer the most significant variables were Cl, Ca, Zn, K and $\delta^{13}\text{C}$ during summer, while in winter Cl, K, P, S, Mn and $\delta^{15}\text{N}$ were more significant.



This research represents a part of the ERA Chair ISO-FOOD for isotope techniques in food quality, safety and traceability. ISO-FOOD will enable the fusion of multidisciplinary knowledge and ideas for target-oriented research divided into three pillar themes (Food Authenticity, Food Traceability and Food Safety) and two horizontal themes (Metrological Support and Knowledge Repository).

ACKNOWLEDGEMENTS:

The work was performed within the project V4-1108 entitled "The use of specific methods for determination and prevention of adulteration of milk and dairy products" financially supported by the Slovenian Research Agency and the Ministry of Agriculture and the Environment. We thank Ljubljanske mlekarne, d.d., Pomurske mlekarne, d.d., Mlekarna Vipava d.d., Mlekarna Planika predelava mleka d.o.o. and Mlekarna Celeia for supplying cow milk samples and Kmetijski gozdarski zavod Nova Gorica for supplying goat and sheep milk.