Distribuzione dell'arsenico nei suoli agricoli e nelle acque in Italia nell'ambito delle attività dell'EuroGeoSurvey Geochemistry Expert Group

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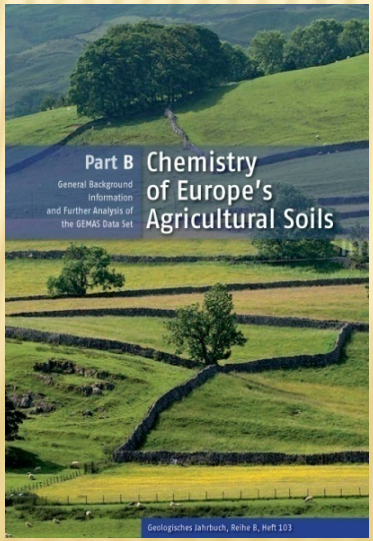
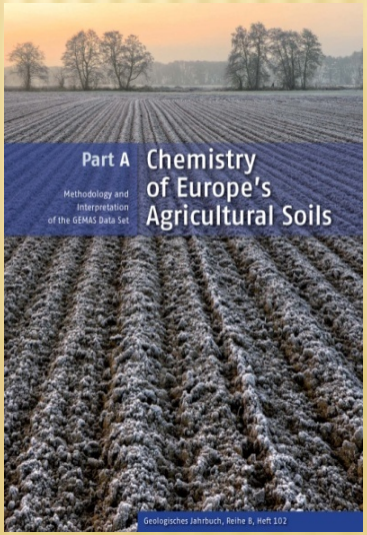
The GEMAS project has produced high quality exposure data for chemical elements across Europe, harmonised with respect to:

(1) land-use (agricultural soil, 0-20 cm and grazing land soil, 0-10 cm);
(2) spatial scale (homogeneous sampling density: 1 site/2500 km^2 (grid of 50 x 50 km) – described in the public available field manual;
(3) sample preparation (<2 mm grain size);
(4) analytical methodology: Aqua regia extractable (ICP-MS 53 elements), total (XRF, 41 elements) and mobile metal ion (MMI®, 55 elements) concentrations, lead isotope ratios, pH (0.01M $CaCl_2$), total Organic Carbon, Total Carbon, Total Sulphur, Effective Cation Exchange Capacity (eCEC at pH of the soil, silver thiurea method), mid-infra red (MIR) spectra, Texture (sand, silt, clay) and Partitioning coefficients (kD-values) for selected elements.

The GEMAS project data sets are made available to the general public with the release of the book “Chemistry of Europe’s agricultural soils”. Quality control of all analytical results is documented in three publicl available reports.

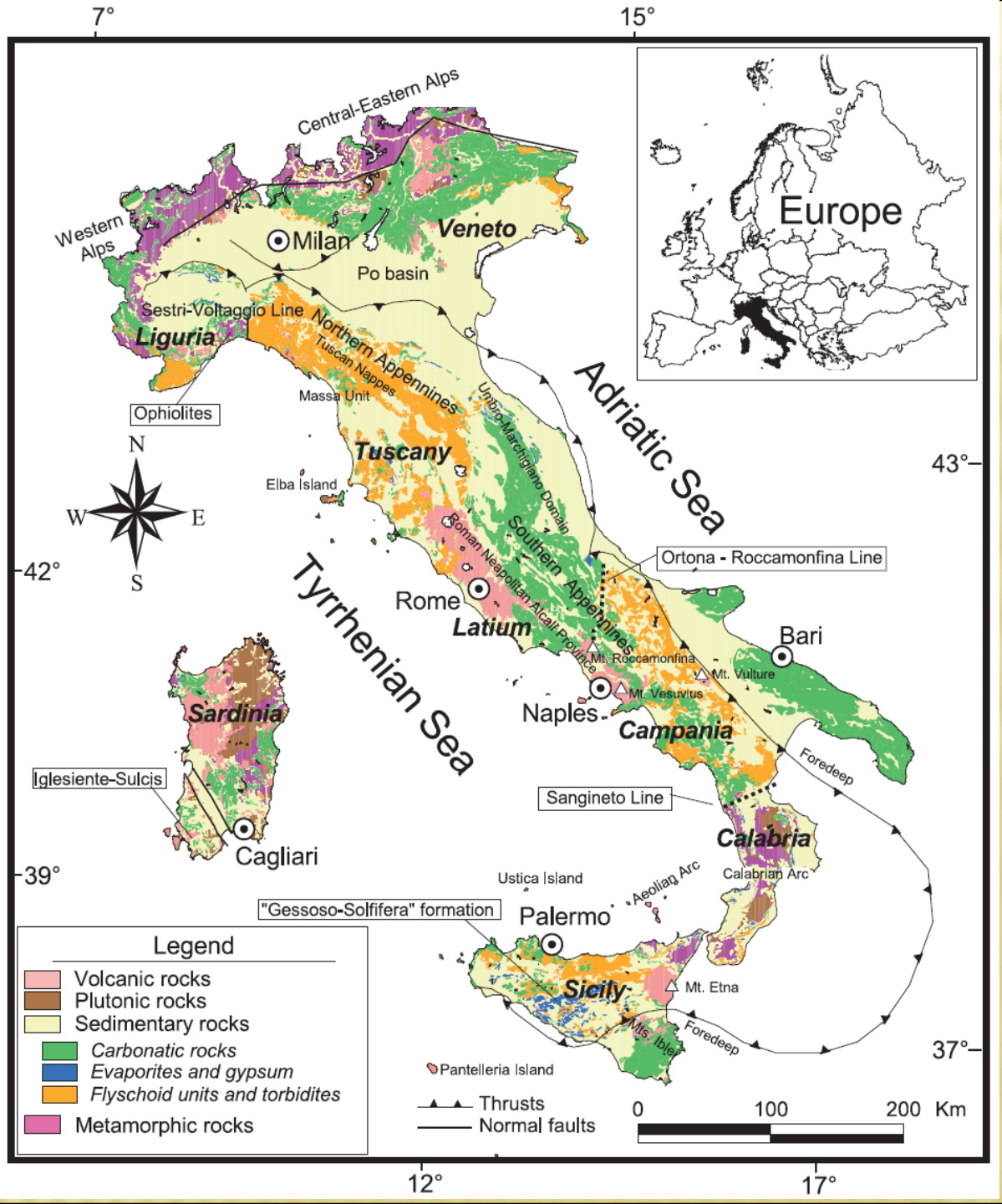




Italian grid

121 samples of agricultural soil (0-20 cm) and 121 samples of grazing land soil (0-10 cm) were collected in Italy at an average sample density of 1 site/2500 km^2

The aim of this work is to define background/baseline chemical element values on a national scale, which will help state decision makers to define trigger and action limits at a local scale, bearing in mind the complex spatial variability of Italian geology.

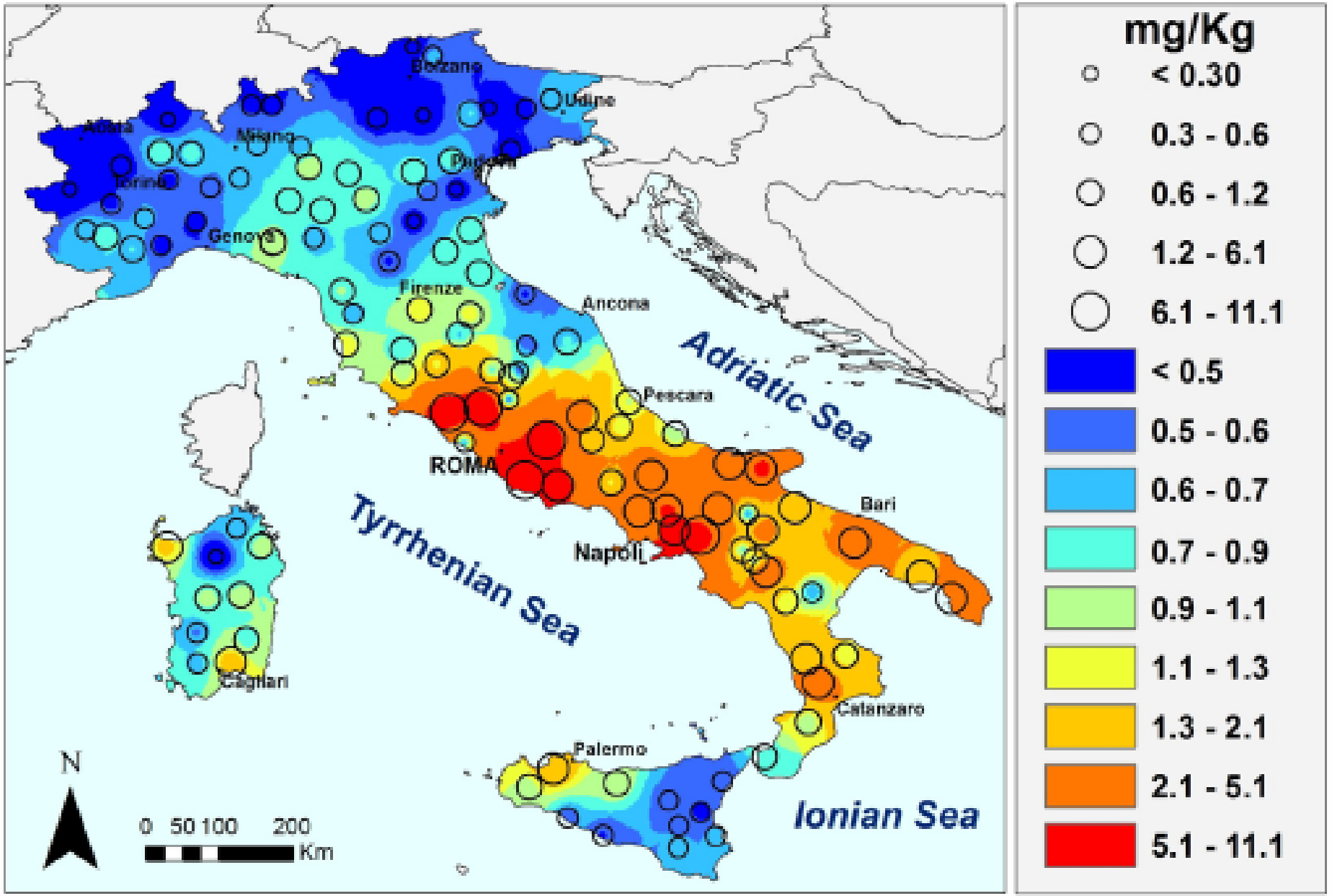


In Italy, especially in southern Italy, the problem of agricultural soil contamination is very actual, so mapping element distribution allows direct appraisal of the variability of these elements in an area and enables rapid identification of areas that may contain excessive concentrations of potentially harmful elements. This is an essential information for site and subsequent risk assessment

Several works, conducted in Italy at a local scale, have shown that anomalous concentrations of some elements (such as Be, Sn, As, Tl, V), exceeding the legislative limits, are completely natural. The lack of knowledge of these scientific works by the authorities responsible for environmental monitoring is causing, especially in South Italy, an overestimation of the contaminated areas extent.

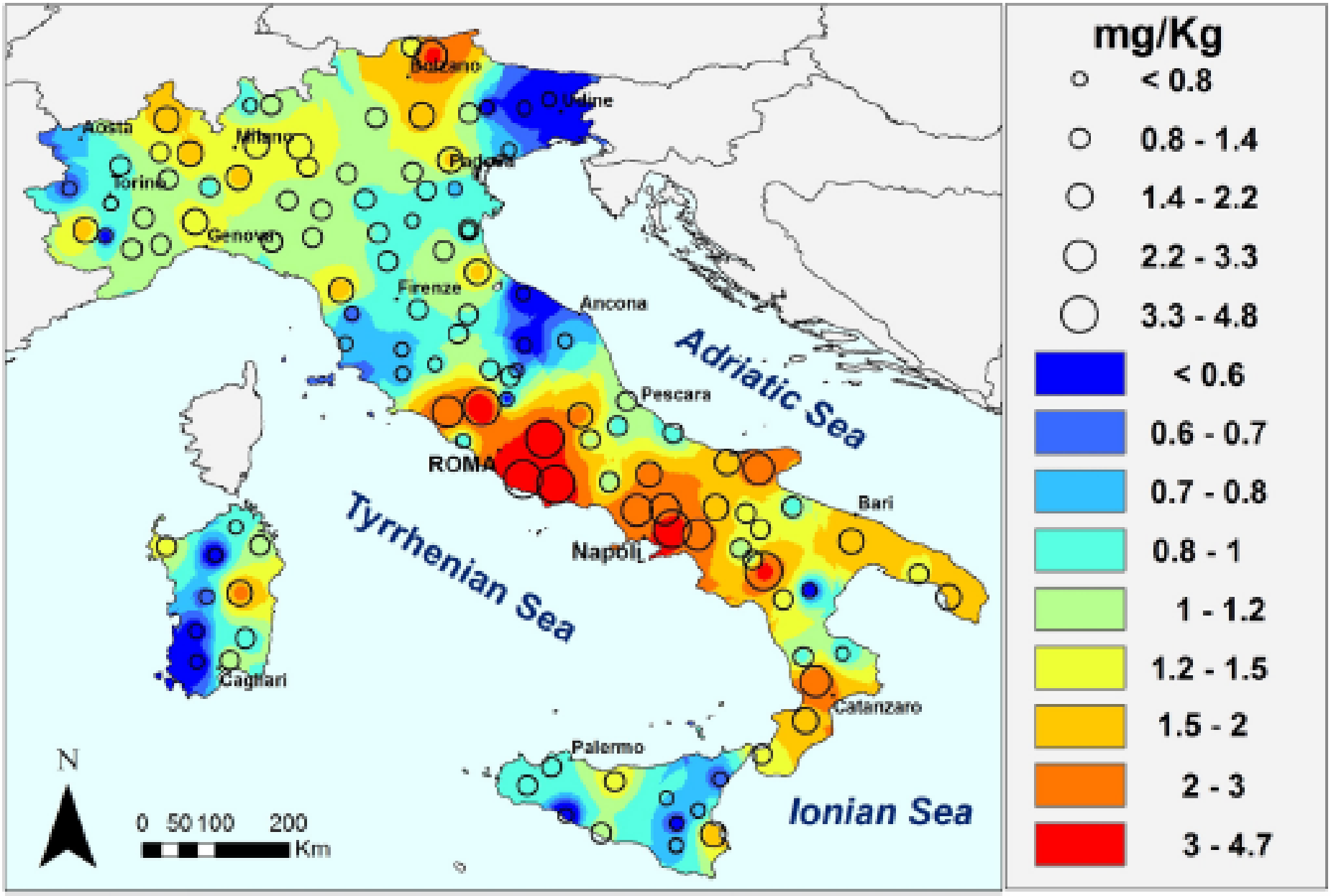
Beryllium (Be)

Agricultural soil (0-20 cm)
Aqua regia/ICP-MS



Tin (Sn)

Agricultural soil (0-20 cm)
Aqua regia/ICP-MS

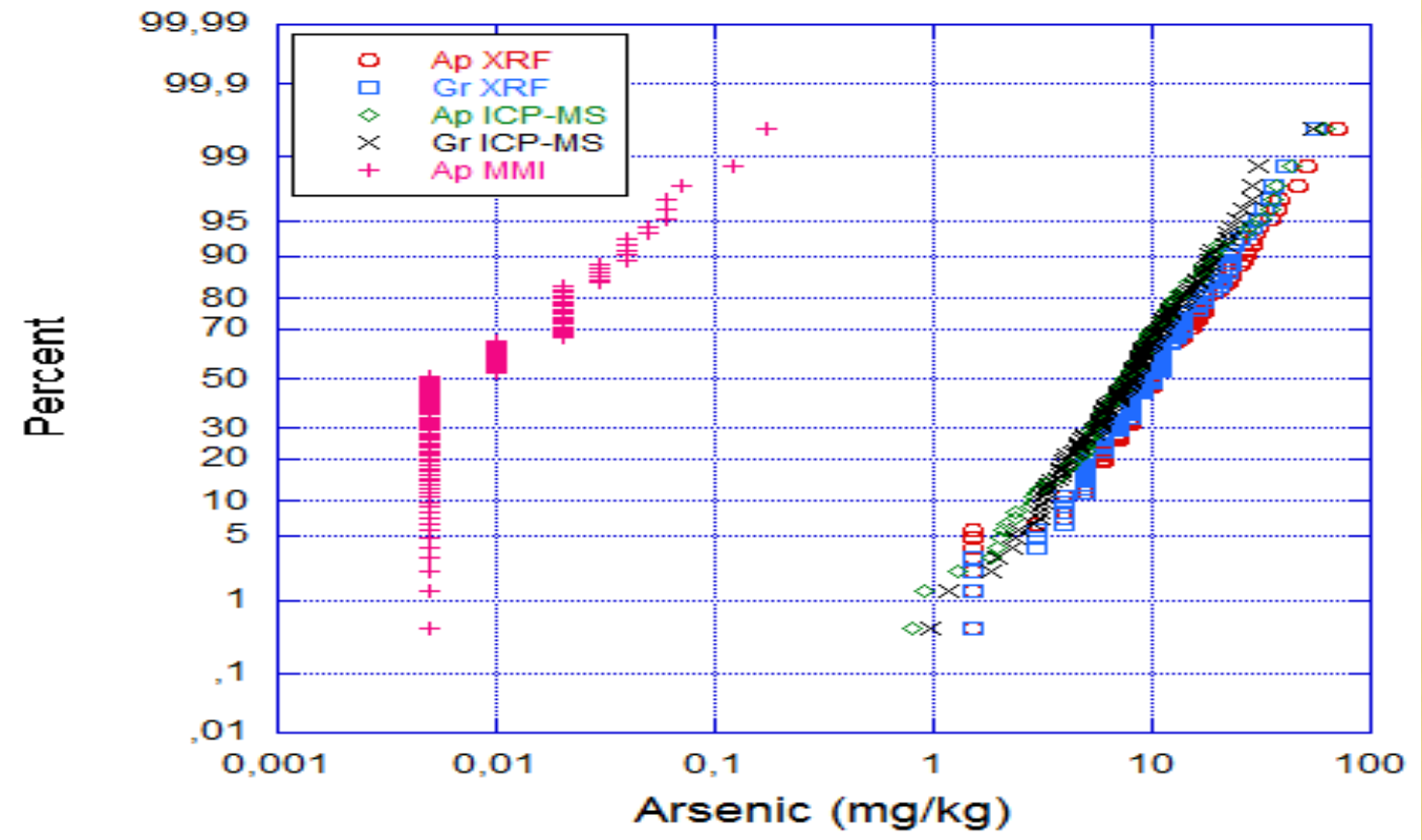


Arsenic distribution

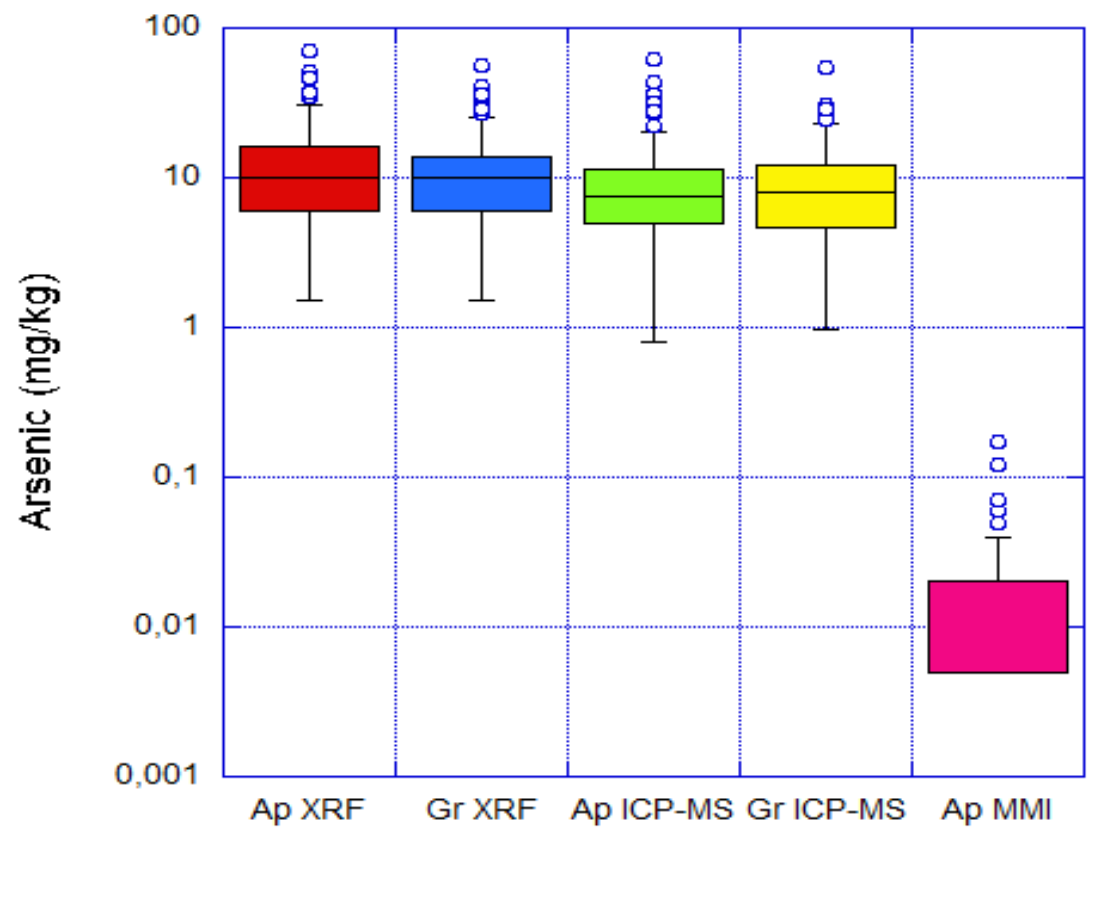
The Italian agricultural (Ap) and grazing (Gr) soils are characterized by quite elevated As concentration with a median values of 7.56 and 8.08 mg/kg respectively well beyond the median values (5.5 and 5.6 mg/kg) of European soils (Reimann et al., 2014; Tarvainen et al., 2013). The mean values is of 10.04 and 9.76 mg/kg for Ap and Gr respectively with a range from a minimum of 0.79 mg/kg up to a maximum of 62.17 mg/kg. The median values in both materials is the same in XRF analysis (10 mg/kg) while As concentrations in the MMI extract are much lower (mean: 0.016 mg/kg), and the maximum value is only 0.17 mg/kg; it is noted that 51.7% of all samples reported values below the detection limit of 0.01 mg/kg.

MATERIAL	METHOD	N	UNIT	DL	%<DL	Min	Q10	Q25	Q50	Mean	Q75	Q90	Max
Ap	MMI	118	mg/kg	0.01	51.7	<0.01	<0.01	<0.01	<0.01	0.016	0.02	0.04	0.17
Ap	ICP-MS	118	mg/kg	0.05	0	0.79	2.83	5	7.56	10.04	11.46	18.84	62.17
Gr	ICP-MS	118	mg/kg	0.05	0	0.97	3.13	4.69	8.08	9.76	12.01	18.68	54.29
Ap	XRF	118	mg/kg	3	5.9	<3	4	6	10	12.94	16.25	27	70
Gr	XRF	118	mg/kg	3	3.4	<3	4	6	10	12.02	14	23	56

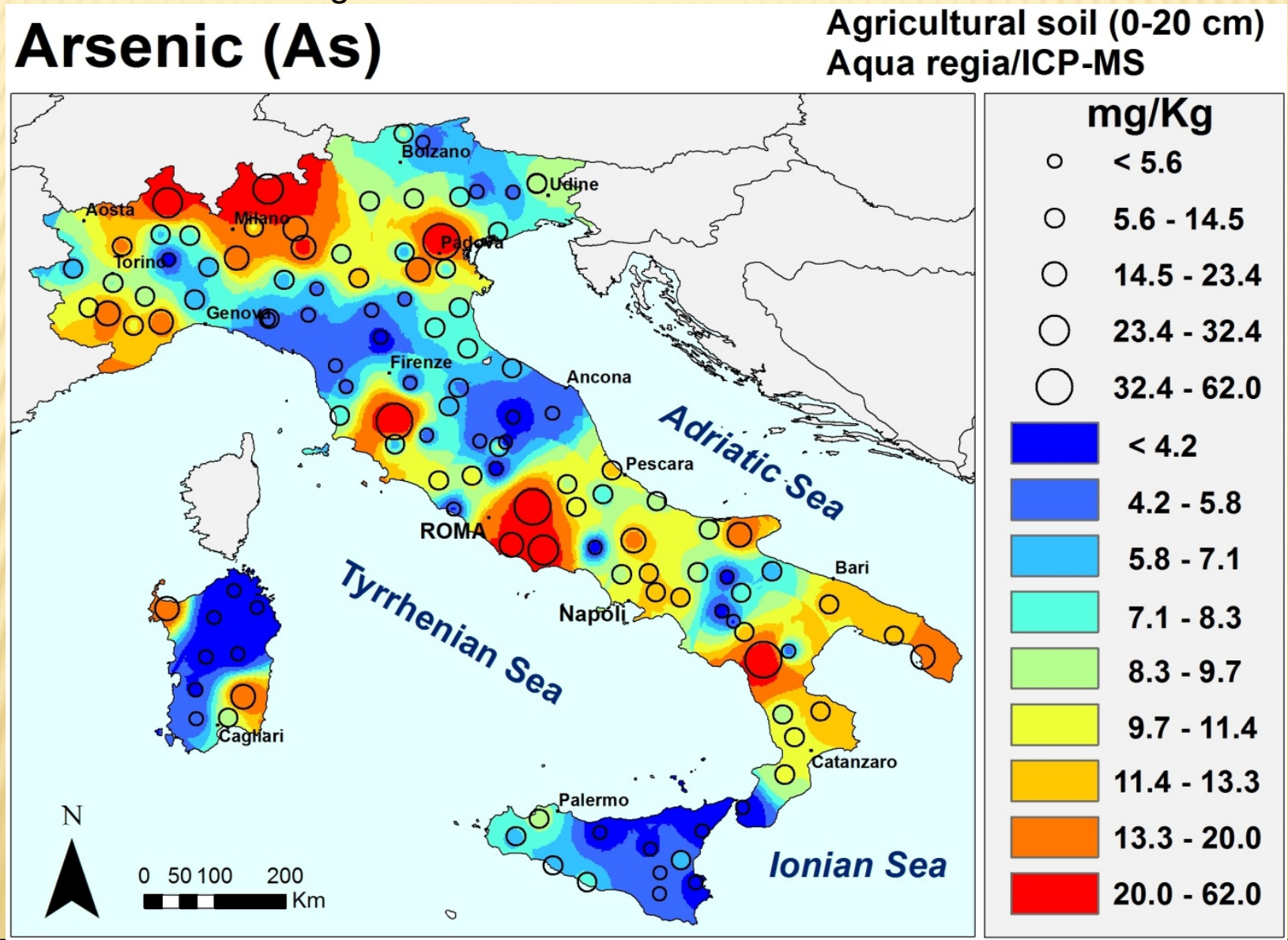
The CP-plot of As shows large differences between the results of the MMI and aqua regia extraction and total concentrations analysed by XRF, while the differences between aqua regia and XRF in Ap and Gr soil samples appear to be minimal. The upper 90% of the distribution curves of the aqua regia and total concentrations almost overlap for the Ap and Gr soil samples. For the MMI analyses the main problem really is the much too high detection limit for this element, more than 50% of all values are below detection for this technique.



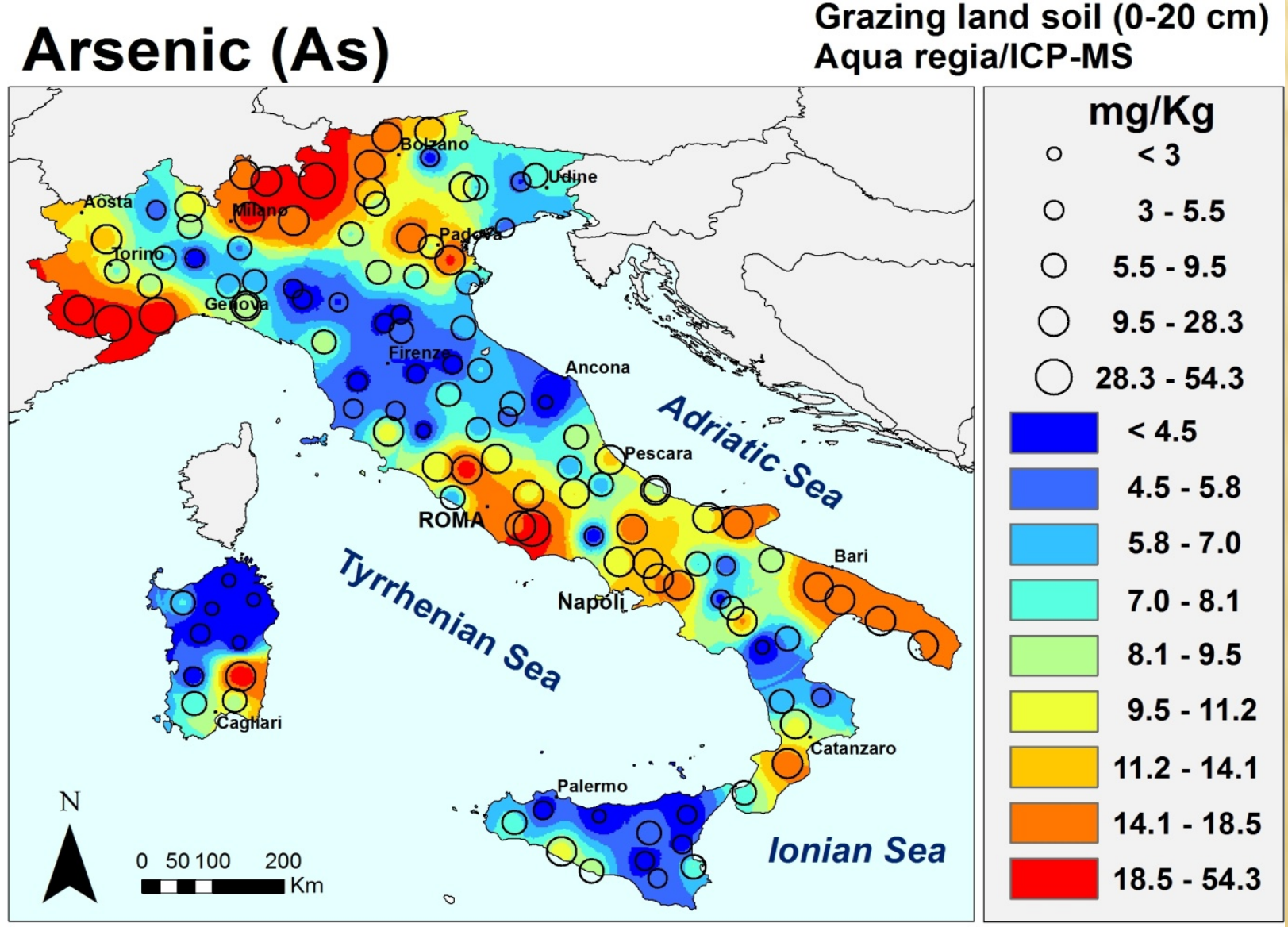
The boxplots comparing the analytical results for As in Ap and Gr soil samples show clearly the differences between the three techniques. The boxplots display a number of upper outliers for the XRF, MMI and for the aqua regia results. Overall, these are not very far away from the main body of data (log-scale). The MMI data are more skewed than the AR and XRF data (see asymmetric box). The absence of the lower whisker in the MMI boxplot and its truncation at the 50th percentile indicates the discontinuity of data due to the detection limit problem.



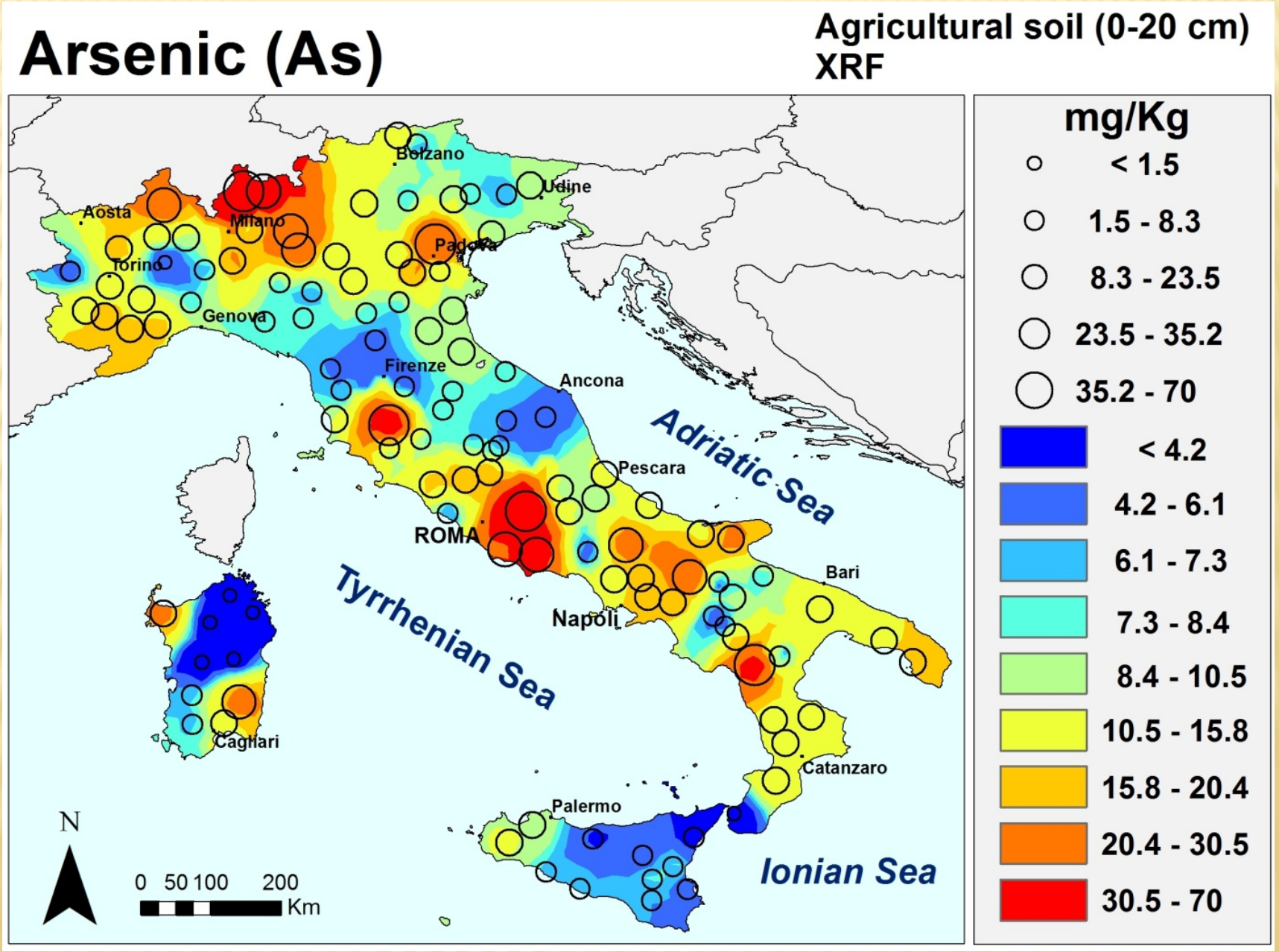
In agricultural soils highest As content (> 20 mg/kg) occur in north Italy between Milano and Aosta, to the west of Padova and in Tuscany south-west of Firenze. Other high values also occur in Roman Neapolitan Volcanic Province, all along Apulia region, in Sardinia near Cagliari and in central Calabria.



The As distribution map of grazing land soils shows a pattern very similar to that of agricultural soils, with particularly high concentrations in Liguria on the border with France. Low values especially occurring in northern Sardinia, eastern Sicily and in north Italy.

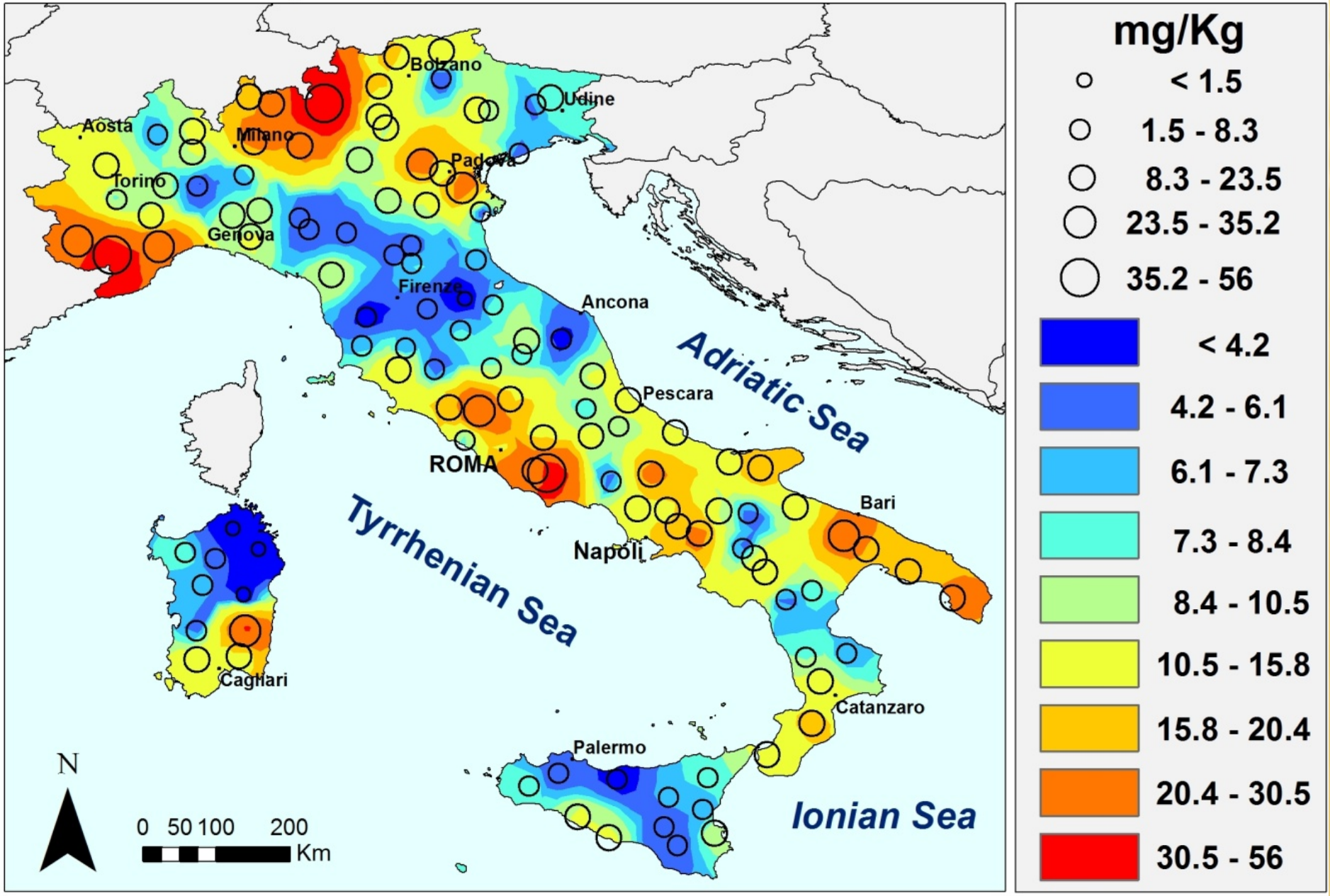


It is observed immediately that there are no particular differences between the maps produced with XRF and ICP-MS analysis.

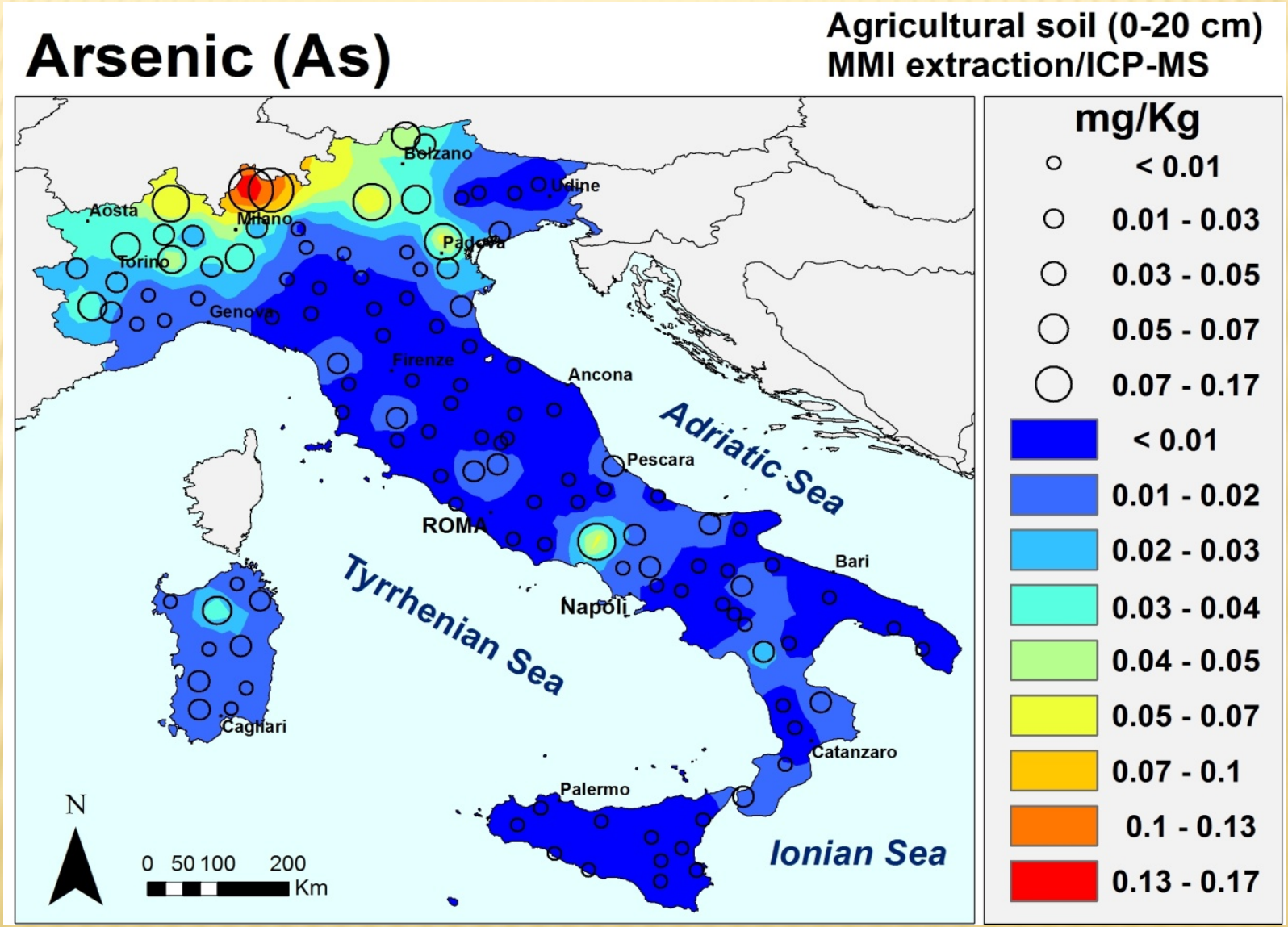


Arsenic (As)

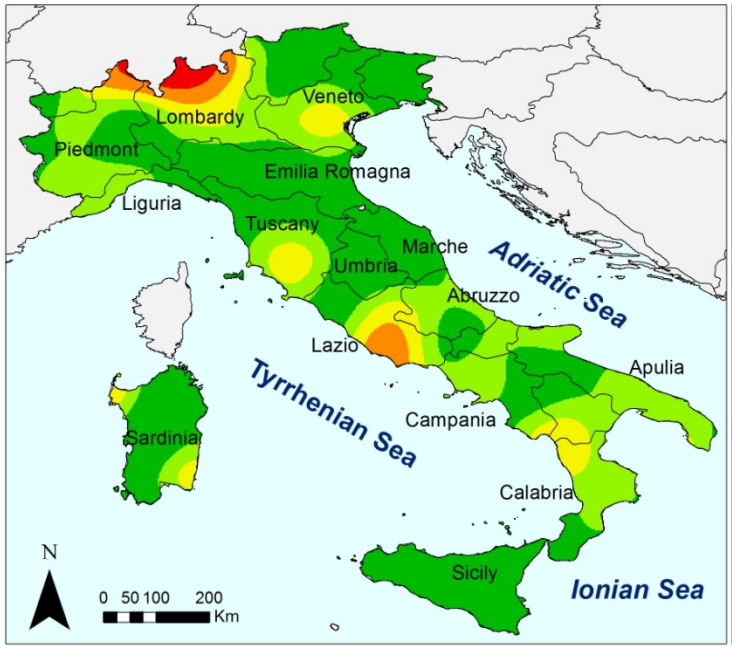
Grazing land soil (0-20 cm)
XRF

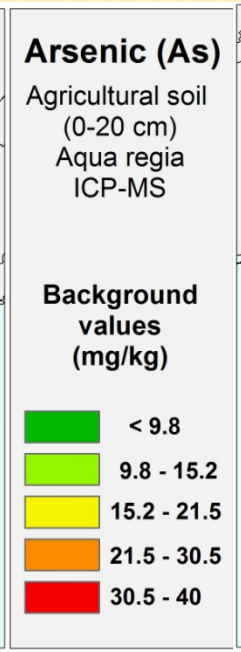


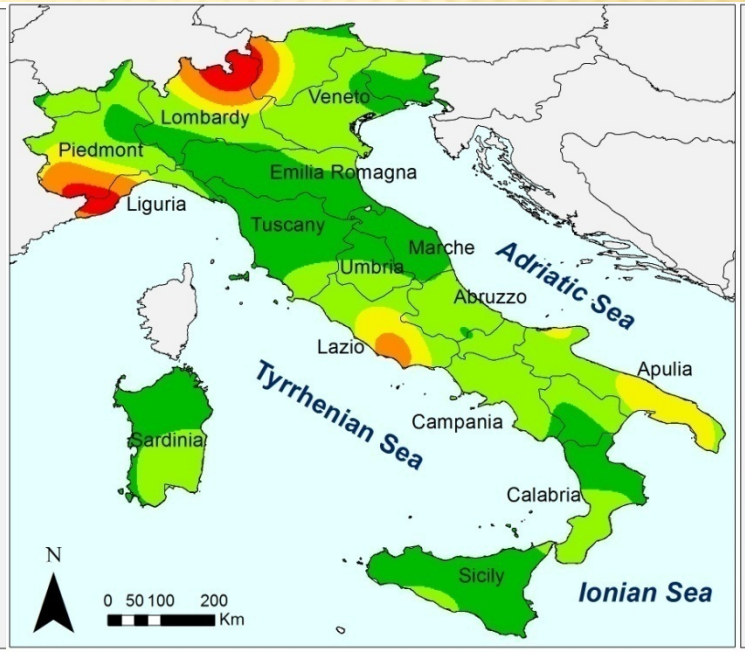
The map of As in an MMI extraction of the Ap samples is very different from those for the aqua regia and total (XRF) As concentrations. it is noted that more than 50% of all samples reported values below the detection limit of 0.01 mg/kg As and the only anomalous values are observed north of Milano.

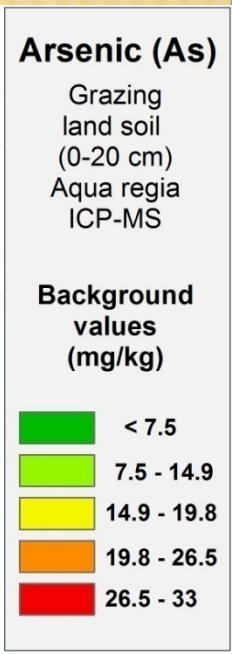


The background values maps show that most of the Italian territory has concentration values lower than 10 mg/kg, only some areas of Lombardia, Lazio, Liguria and Piedmont show background values higher than the residential/recreational intervention limit (20 mg/kg) set by Italian environmental law (D.L. 152/2006).









This study started in the framework of the EuroGeoSurvey Geochemical Expert Group project aimed at the geochemical characterization of groundwater all over Europe.

157 tap waters and 186 bottled mineral waters, covering all the Italian territory, were sampled and analyzed for their inorganic chemical composition.

Chemical analyses were carried out at the German Geological Survey (BGR) in Berlin. Each water sample was analyzed for 69 chemical elements and ions (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, K, La, Li, Lu, Mg,Mn,Mo, Na, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V,W, Y, Yb, Zn, Zr, Br−, HCO3−, Cl−, F−, NH4+, NO2−, NO3−, PO4 3−, SO4 2−, SiO2). Electrical conductivity (Ec) and pH were also measured on each water sample.

Arsenic (As)

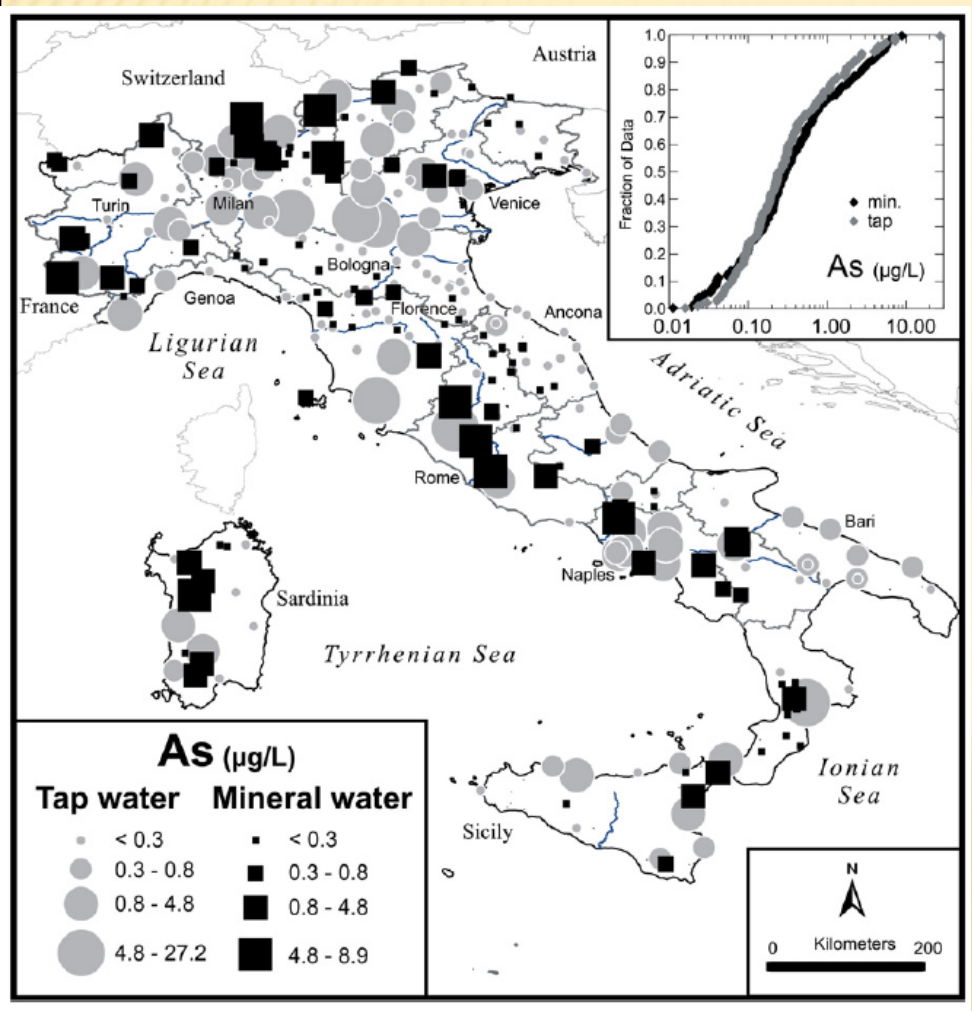
Tap water

Location	Arsenic (µg/L)
Viterbo	27.2
Legal concentration limit	**10**
Grosseto	7.32
Catanzaro	7.31
Villa Poma (MN)	7.29
Mantova	5.51
Cremona	5.18
Lecco	4.46
Albano Laziale (RM)	4.43
Sondrio	4.38
Como	3.95
Trento	2.76
Rionero in Vulture (PZ)	2.73
Napoli, Mezzocannone	2.65
Cardano (BZ)	2.53
Fubine (AL)	2.24
Biella	2.17
Siena	2.11
Trabia (PA)	1.94
Lodi (LO)	1.8
Napoli, Posillipo	1.77
Caserta	1.68
Benevento	1.2
Salerno	1.1
Napoli, Poggioreale	1.08
Avellino	0.906
Napoli, Chiaiano	0.522
Napoli, Bagnoli	0.444
MEDIAN	**0.25**

The combined map of the two data sets identifies common areas with high concentration values, such as the ones near Rome, Naples and in the Mount Vulture area, all being characterized by the presence of Pleistocene alkaline volcanic rocks of the Roman Comagmatic Province and where known anomalies for As in various environmental matrices occur. Few intermediate to high As concentrations occur in bottled mineral water also in the central Alps, partially matched by tap water data, particularly north and north-east of Milan.

Bottled mineral water

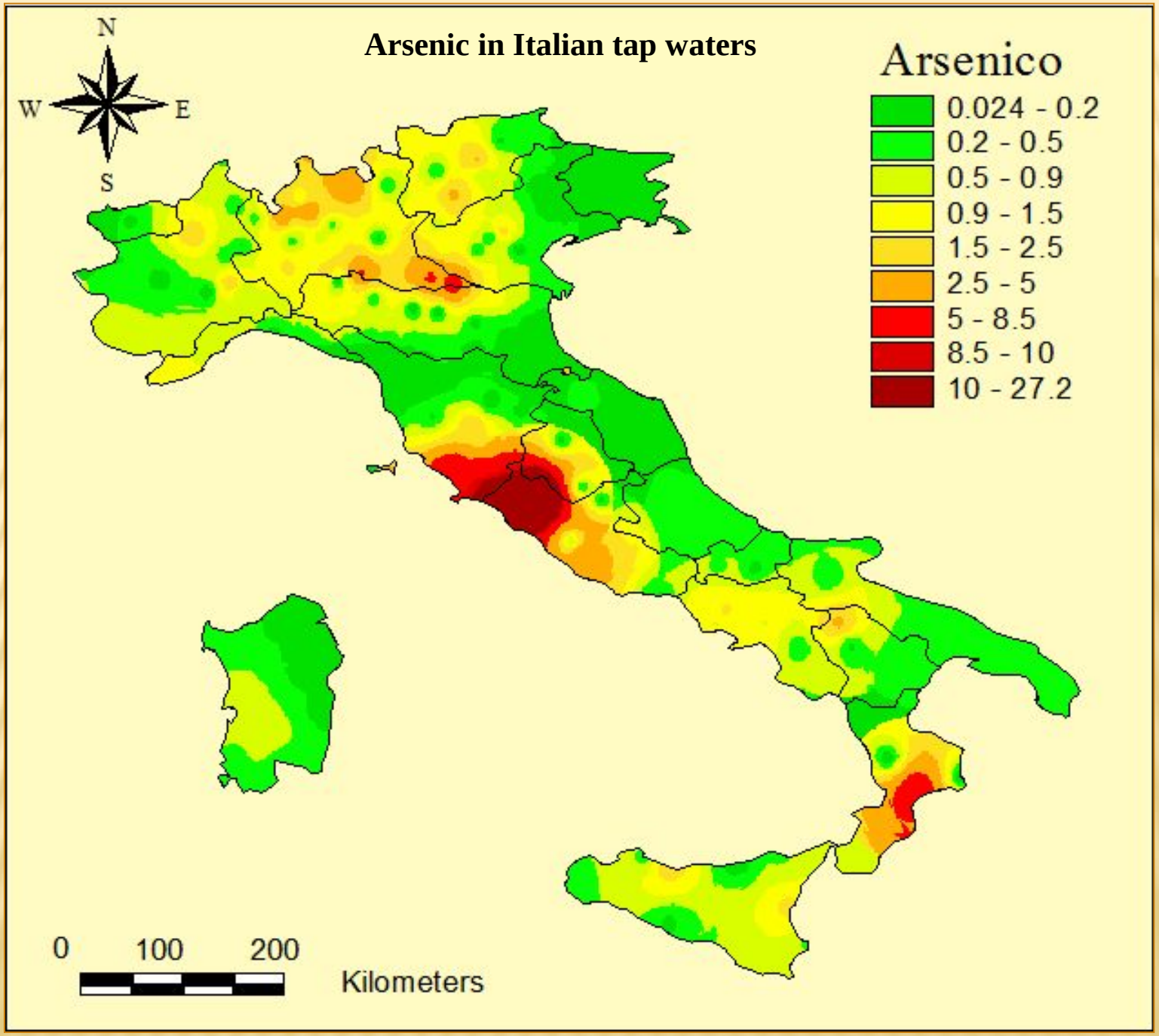
Name	Geology	Region	Arsenic
Legal concentration limit	-	-	**10**
Egeria	VULC	LAZ	8.91
Ferrarelle	SED/VULC	CAM	6.81
Levissima	MET	LOM	6.2
Orvieto	SED	UMB	6.02
Acqua di Nepi	VULC	LAZ	5.71
Funte Fria	VULC	SAR	5.69
Frisia	MET	LOM	5.64
Candida	VULC	SAR	5.41
Vaia	MET	LOM	5.34
Sant'Anna di Vinadio	MET	PIE	5.22
Leggera	VULC	BAS	4.65
Balda	MET	LOM	4.61
Santagata	SED/VULC	CAM	4.22
Federica	SED	SAR	3.44
Futura	MET	CAL	3.29
Valmora	MET	PIE	3.18
Meraner Mineralwasser_avg	MET	TAA	3.04
Leonardo-primaluna alisea	PLU	LOM	2.96
Vivien	VULC	BAS	2.76
Sveva	VULC	BAS	2.74
MEDIAN	-	-	**0.29**



Il D.L. 31/2001 sulle acque destinate al consumo umano e il D.M. 29/12/2003 sulle acque minerali impongono entrambi, relativamente all'As, un limite di 10 µg/l. Tale limite viene superato nelle acque di rubinetto nella sola città di Viterbo, dove la concentrazione riscontrata è di 27,2 µg/l. Il valore mediano delle acque di rubinetto analizzate è di 0,25 µg/l; valori anomali sono stati misurati nelle città di Grosseto (7,3), Catanzaro (7,3), Mantova (5,5), Cremona (5,2), Lecco (4,5), Albano Laziale (4,4), Sondrio (4,4) e Como (4,0).

L'analisi delle acque minerali non ha evidenziato superamenti della soglia di 10 µg/l ma, rispetto al valore mediano di 0,29 µg/l, alcune presentano valori estremamente anomali: Egeria (8,9), Ferrarelle (6,8), Levissima (6,2), Orvieto (6,0), Acqua di Nepi (5,7), Fonte Fria (5,7), Frisia (5,6), Vaia (5,3), Sant'Anna di Vinadio (5,2), Leggera (4,7), Santagata (4,2). Per lo più le sorgenti di queste acque si trovano in regioni come Lazio, Lombardia, Campania e Piemonte, relazionate alle caratteristiche geochimiche delle rocce che ospitano gli acquiferi.

Arsenic in Italian tap waters



The same for Beryllium (Be)

Tap water

Location	Beryllium (µg/L)
Viterbo	0.3220
Rionero in Vulture (PZ)	0.0515
Albano Laziale (RM)	0.0399
Grosseto	0.0260
Carbonia-Iglesias	0.0154
Olbia-Tempio	0.0148
Caronia (ME)	0.0132
Ogliastra	0.0113
Napoli, Mezzocannone	0.0110
Avellino	0.0109
Cavalese (TN)	0.0086
Sassari	0.0080
Messina	0.0074
Roma	0.0052
Patti (ME)	0.0044
Gaeta (LT)	0.0042
Foggia	0.0038
Livorno	0.0035
Cascina	0.0032
Napoli, Chiaiano	0.0032
Napoli, Bagnoli	0.0028
Salerno	0.0026
Napoli, Posillipo	0.0025
Napoli, Poggioreale	0.0024
Benevento	0.0020
Caserta	0.0013
MEDIANA	**< 0.001**

Italian environmental law (D.L. 152/2006) requires intervention for remediation on an aquifer if Be concentration in the groundwater samples exceeds 4 µg/L, even if such waters are not intended for human consumption. Strangely no limits are set by Italian (or European) laws for Be in drinking water. The median Be concentration of all analyzed bottled waters (0.001 µg/L) is far below the guideline value (4 µg/L) set by US-EPA. Only one bottled water from the volcanic area of Lazio exceeds the US-EPA threshold level of 4 µg/L.

Bottled mineral water

Name	Geology	Region	Beryllium
Acqua di Nepi	VULC	LAZ	4.69
D.L. 152/2006	-	-	**4**
Santagata	SED/VULC	CAM	1.86
Egeria	VULC	LAZ	1.64
Gaudianello	VULC	BAS	1.28
Ferrarelle	SED/VULC	CAM	1.04
Claudia	VULC	LAZ	0.838
Sveva	VULC	BAS	0.754
Acqua Light	PLU	SAR	0.576
Leggera	VULC	BAS	0.57
Rocce Sarde	PLU	SAR	0.54
Fonte Napoleone	PLU	TOS	0.178
S'Abba	PLU	SAR	0.168
Sparea	MET	PIE	0.12
Stella del Monviso	MET	PIE	0.0864
Toka	VULC	BAS	0.0773
Quercetta	SED	SAR	0.0762
Lurisia	SED/VULC	PIE	0.0758
Felicia	VULC	BAS	0.0725
Fonte delle Alpi	MET	PIE	0.0651
Alpi Cozie	MET	PIE	0.0615
MEDIAN	-	-	**0.0016**

Grazie
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l'attenzione