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

Benedetto De Vivo (a), Domenico Cicchella (b), Enrico Dinelli (c), Stefano Albanese (a), Lucia Giaccio (a), Paolo Valera (d), Annamaria Lima (a)

(a) Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università Federico II, Napoli
(b) Dipartimento di Scienze e Tecnologie, Università del Sannio, Benevento
(c) Dipartimento di Scienze della Terra e Geologico Ambientali, Università di Bologna
(d) Dipartimento di Geoingegneria e Tecnologie Ambientali, Università di Cagliari
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 km² (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 CaCl₂), 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 publicly available reports.
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 km²
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.
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.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>METHOD</th>
<th>N</th>
<th>UNIT</th>
<th>DL</th>
<th>%&lt;DL</th>
<th>Min</th>
<th>Q10</th>
<th>Q25</th>
<th>Q50</th>
<th>Mean</th>
<th>Q75</th>
<th>Q90</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ap</td>
<td>MMI</td>
<td>118</td>
<td>mg/kg</td>
<td>0.01</td>
<td>51.7</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.016</td>
<td>0.02</td>
<td>0.04</td>
<td>0.17</td>
</tr>
<tr>
<td>Ap</td>
<td>ICP-MS</td>
<td>118</td>
<td>mg/kg</td>
<td>0.05</td>
<td>0</td>
<td>0.79</td>
<td>2.83</td>
<td>5</td>
<td>7.56</td>
<td>10.04</td>
<td>11.46</td>
<td>18.84</td>
<td>62.17</td>
</tr>
<tr>
<td>Gr</td>
<td>ICP-MS</td>
<td>118</td>
<td>mg/kg</td>
<td>0.05</td>
<td>0</td>
<td>0.97</td>
<td>3.13</td>
<td>4.69</td>
<td>8.08</td>
<td>9.76</td>
<td>12.01</td>
<td>18.68</td>
<td>54.29</td>
</tr>
<tr>
<td>Ap</td>
<td>XRF</td>
<td>118</td>
<td>mg/kg</td>
<td>3</td>
<td>5.9</td>
<td>&lt;3</td>
<td>4</td>
<td>6</td>
<td>10</td>
<td>12.94</td>
<td>16.25</td>
<td>27</td>
<td>70</td>
</tr>
<tr>
<td>Gr</td>
<td>XRF</td>
<td>118</td>
<td>mg/kg</td>
<td>3</td>
<td>3.4</td>
<td>&lt;3</td>
<td>4</td>
<td>6</td>
<td>10</td>
<td>12.02</td>
<td>14</td>
<td>23</td>
<td>56</td>
</tr>
</tbody>
</table>
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 50\(^{th}\) 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.
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.
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.
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.
The same for Beryllium (Be)

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.
Grazie X l’attenzione