Arsenic (As) in topsoil

Geo AS Sty (Geochemistry of Athens Soil) is an urban geochemistry project carried out by the Laboratory of Economic Geology & Geochemistry, University of Athens Greece. The geochemical maps of Athens were developed on the basis of a soil survey during 2012. The Greater Athens and Piraeus area was mapped at a sampling density of one site per square km. At each site a topsoil sample was collected from 5-10 cm, comprising a composite of five subsamples from the corners and the center of a 10 x 10 m square. Samples were dried and sieved to <100 μm before analysis to determine the total elemental concentrations by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) after digestion with a mixture of 4 acids. Class intervals on the geochemical maps were defined by natural breaks in the histograms of the original data, and elemental concentrations were plotted as circles with size increasing as a function of concentration. The interpolated surfaces using the Inverse Distance Weighting method (IDW) with a power of 2 were added in the background for better visual inspection of the spatial trends (red being higher and blue being lower). It must be noted that interpolated maps must be used with caution due to the variability between the sampling locations. Concentration ranges are plotted on Box & Whiskers plots comparing the relevant abundance of elements in soil and their enrichment according to urban land use. The maps of population density, historical city expansion and geology are also provided for enabling geochemical data interpretation.

Contact Ariadne Argyraki, email: argyraki@geol.uoa.gr

Legend

As mg/kg
- 6 - 21
- 22 - 32
- 33 - 52
- 53 - 109
- 110 - 204
- AR

Population density map

Historical city boundaries map

Simplified Geology
The summary statistics for As data are presented in Table 1. Arsenic displayed the sixth highest median concentration of all studied elements (24 mg kg⁻¹) and a few outliers on the highest tail of its statistical distribution. In comparison with other cities around the world, Athens’ surface soil is enriched in As (average 29 mg kg⁻¹). This element displays high similarity with the lithogenic elements within the Athens Unit. It is well established that As adsorbs very easily, either as As (III) or As (V), on different soil components such as Fe and Al oxides, and clay minerals. The spatial distribution of As also displays a distinct spatial pattern extending along a NE–SW axis. Arsenic concentrations exceed 100 mg kg⁻¹ in several samples along this axis that coincides with the hilly areas built by alpine rocks of the Athens Unit in the center of the basin. Despite the known geochemical affinity between As and Sb, results of Geographically Weighted Regression indicated that the two metalloids are not spatially correlated in Athens soil. Antimony explained only a small percentage of As spatial variability ($R^2$ adjusted = 24%).

Arsenic concentrations in park and woodland areas are also significantly higher than other land use categories. Although our data provide evidence of correlation between As and the geogenic group of elements we must reserve judgment on the natural origin of this element in Athens soil, as the statistically significantly higher concentrations that were detected in parks and woodland areas might be indicative of anthropogenic airborne sources of As. The use of As based pesticides in the past cannot be excluded. Further research, focused on comparisons of chemistry of the underlying rocks, as well as As speciation in soil, is needed in order to clarify the origin of this element.

### Table 1. Athens soil lead results (mg/kg). Number of samples 238.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mean</th>
<th>SD</th>
<th>Q1</th>
<th>Median</th>
<th>Q3</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>29</td>
<td>21</td>
<td>19</td>
<td>24</td>
<td>31</td>
<td>6</td>
<td>204</td>
</tr>
</tbody>
</table>

Summary of Athens bedrock geology

The bedrock geology of Athens is comprised of 4 different geotectonic units that form and outcrop in the mountains surrounding the city, as well as in hills within the Athens Basin: (a) the lowest basement unit is composed of metamorphic rocks, including marble, dolomite, and mica-schist; (b) this is tectonically overlain by the Alepovouni unit that is also comprised of metamorphic rocks, including crystalline limestone, schist and greenstone; (c) the Athens Unit, which outcrops in the hills of western and central Athens Basin is an Upper Cretaceous mélange that includes pelagic sediments consisting of marly limestone, shale, sandstone, tuff and ophiolithic blocks and neritic limestone; and (d) the Sub-Pelagonian unit, which mainly consists of limestone and dolomite limestone.

Post-orogenic Neogene to Quaternary deposits cover the alpine bedrock. Lithologically, these include Neogene coastal marine, continental and lacustrine carbonate and clastic sediments, and thick Quaternary alluvial fans at the foothills of the surrounding mountains. Natural soil within the city is generally thin. Soil types range from Calcaric-Lithic-Leptosols (renzinas) on the mountainous margins of the basin to Calcaric Fluvisols and Regosols in the western part of the study area and Rhodic Luvisols over the eastern part of the basin.


Contact and further information: Dr. Ariadne Argyraki, University of Athens, email: argyraki@geol.uoa.gr