



## **Accumulation of antimony and other potentially toxic elements in plants around a former antimony mine located in the Ribes Valley (Eastern Pyrenees)**

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Soil contamination by antimony is of increasing environmental concern due to the use of this amphoteric p-block element in many industrial applications such as flame retardant, electronics, alloys, rubber and textile industries. However, little is still known about the response of plants to antimony. Here we report on the accumulation of antimony and other potentially toxic elements (mainly As, Pb and Cu) in plants growing around a former antimony mine in the Ribes Valley located in the Eastern Pyrenees (424078E, 4686100N alt. 1145 m.a.s.l) that was operating approximately between the years 1870 to 1960. The ore mineral veins are included in quartz gangue. The main ores were: Sulphides: Stibnite ( $\text{Sb}_2\text{S}_3$ ), Pyrite ( $\text{FeS}_2$ ), Sphalerite ( $\text{ZnS}$ ), Arsenopyrite ( $\text{FeAs}$ ), Galenite ( $\text{PbS}$ ), Chalcopyrite ( $\text{CuFeS}_2$ ), Tetrahydrite ( $\text{Cu}_5\text{Sb}_2\text{S}_3$ ). Sulphosals: Boulangerite ( $5\text{PbS} \cdot 2\text{Sb}_2\text{S}_3$ ), Jamesonite ( $4\text{PbS} \cdot \text{FeS} \cdot 3\text{Sb}_2\text{S}_3$ ), Zinckenite ( $6\text{PbS} \cdot 7\text{Sb}_2\text{S}_3$ ), Plagionite ( $5\text{PbS} \cdot 4\text{Sb}_2\text{S}_3$ ), Bournonite  $\text{PbCu}(\text{Sb,As})\text{S}_3$ , Pyrargirite ( $\text{Ag}_3\text{SbS}_3$ ). Soil and plant samples were taken at five locations with different levels of Sb, As, and polymetallic contamination. Both pseudototal (aqua regia soluble) and extractable (EDTA) concentrations of metals from sites with low (sites 1 and 2), moderate (site 3 and 4) and high (sites 5 and 6) pollutant burdens were studied. The range of aqua regia and EDTA values in  $\text{mg kg}^{-1}$  is as follows: Sb 8-2904 and 0.88-44; As: 33-16186 and 3.2-167; Pb: 79-4794 and 49-397; Cu: 66-712 and 48-56  $\text{mg kg}^{-1}$ , respectively). While sites 1 to 4 had alkaline soil pH (7.4-8.7), sites 5 and 6 were acidic with values of 6 and 4.6, respectively. Different herbaceous plant species (*Poa annua*, *Echium vulgare*, *Sonchus asper*, *Barbarea verna* among others) at the low and moderately polluted sites were able to efficiently restrict Sb and As transport to shoots showing average concentration ranges between 5.5 and 23  $\text{mg/kg}$  As and 1.21  $\text{mg/kg}$  and 4.9  $\text{mg/kg}$  Sb. However, at the highly polluted acidic sites (5 and 6) only *Agrostis capillaris* was found. This grass was able to withstand up to 240  $\text{mg/kg}$  As and 68  $\text{mg/kg}$  Sb in the shoots. Antimony resistance in this *Agrostis capillaris* ecotype was due to efficient exclusion yet under lab conditions commercial, non-resistant *Agrostis capillaris* plants sown into a 50% mixture of sand with this highly polluted soil showed severe toxicity symptoms and a shoot Sb concentration of 230  $\text{mg/kg}$  Sb. In the original mine spoil soil (100% without sand) from the highly polluted sites the commercial *A. capillaris* was unable to perform. The mechanism of Sb resistance in the mine spoil ecotype of *A. capillaris* deserves further investigation.

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