Antimony in the New Zealand environment

Antimony minerals and Sb environmental mobility

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Principal topics

• Introduction to Sb
• Point sources: geothermal and mines
• Sb minerals and solubility
• Sb mobility in the environment
• Arising Sb environmental issues
Antimony: the new bogey-man?

Metalloids:

<table>
<thead>
<tr>
<th>1 H</th>
<th>2 He</th>
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<tbody>
<tr>
<td>3 Li</td>
<td>4 Be</td>
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<tr>
<td>11 Na</td>
<td>12 Mg</td>
</tr>
<tr>
<td>19 K</td>
<td>20 Ca</td>
</tr>
<tr>
<td>37 Rb</td>
<td>38 Sr</td>
</tr>
<tr>
<td>55 Cs</td>
<td>56 Ba</td>
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<tr>
<td>72 Hf</td>
<td>73 Ta</td>
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<tr>
<td>74 W</td>
<td>75 Re</td>
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<tr>
<td>76 Os</td>
<td>77 Ir</td>
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<td>78 Pt</td>
<td>79 Au</td>
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<tr>
<td>80 Hg</td>
<td>81 Tl</td>
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<td>82 Pb</td>
<td>83 Bi</td>
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<td>84 Po</td>
<td>85 At</td>
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<td>86 Rn</td>
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Chemical behaviour

**Antimony**
- $\text{Sb}^{3+}, \text{Sb}^{5+}$
- Forms oxyanions
- Widely used historically
- No nutritional use in humans
- Highly toxic to humans (mimics P)

**Arsenic**
- $\text{As}^{3+}, \text{As}^{5+}$
- Forms oxyanions
- Widely used historically
- No nutritional use in humans
- Highly toxic to humans (mimics P)
Historic usage

• Water containers in Ancient Egypt
• Cosmetics, especially eye-shadow
  Ancient Egyptians, Queen of Sheba, Jezebel
  Still used in Middle East (=“kohl”, Pb-rich)
• Black pigment for paint
  (cf As in wallpaper pigments)
• Medical, e.g., Tartar emetic (K-Sb tartrate)
  (cf As widely used for skin conditions etc)
• Alchemy
  (As was a more common reagent)
Current usage

- Flame retardants in plastics etc: $\text{Sb}_2\text{O}_3$ (2-3%) with halogens (about 50% of total Sb production)
- Catalysts in plastic production (e.g., Sb-triacetate for PET)
- Alloys, especially with Pb: hardens metals (e.g., batteries; solder)
- Electronics (pure Sb metal)
Sb in global human environment

- Drinking water limit set very low:
  - WHO and NZ: 20 ppb
  - US EPA: 6 ppb  \( (\text{As} = 10 \text{ ppb}) \)
- Mining areas: up to 100 ppb
- Leach Sb, Pb from plumbing: MoH recommends running off first 500 mls
- PET bottles: leach up to 1 ppb Sb
- Stibine \( (\text{SbH}_3) \) from mattresses implicated in cot deaths (controversial)
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Volcanic-hydrothermal zones

- Northland
- Coromandel Peninsula
- Taupo Volcanic Zone

Mines:
- Waihi
- Te Aroha

Metals:
- Gold
- Mercury
- Cu, Pb, Zn
- Sb, As, Cd

pH:
- Hg, As, Sb: 1-7
- Cu, Pb, Zn, Sb, As, Cd: 1-7

Scale: 100 km

Direction: N
Hot spring precipitate with elevated Sb, As, Champagne Pool, Wai-O-Tapu
Quartz-rich spring precipitate with elevated Sb, As, Hg
Puhipuhi, Northland
Hot spring depositing Hg,Sb,As in sediments, Ngawha, Northland
Dissolved Sb through Ngawha geothermal power station

Wilson, Webster-Brown & Brown 2007
New Zealand mesothermal Sb deposits, some mined historically

Sb accompanies Au at most sites

pH = 7
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Stibnite ($\text{Sb}_2\text{S}_3$) in quartz veins
Hillgrove antimony (gold) mine, northern New South Wales:

Modern and historic workings
Rainfall 800 mm/year
Evaporation 1200 mm/year

Natural and historic mine debris is traceable over 300 km downstream
Downstream of Hillgrove mine site: elevated Sb in sediments and waters

Ashley, Craw, Graham & Chappell 2003
Macraes gold mine, Otago, New Zealand

Rainfall c. 600mm/year
Evaporation c. 700 mm/year

Arsenopyrite FeAsS
PIXE image of Macraes arsenopyrite with 2000 ppm Sb

Petrie, Craw & Ryan 2005
Macraes mine: high evaporation in mine pits

- **Boulangerite**: $\text{Pb}_5\text{Sb}_4\text{S}_{11}\text{(rare)}$
- **Arsenopyrite**: FeAsS

- **Mine waters**
- **Mine discharge waters**
- **Ore**

*Source: Craw, Ashley, Wilson & Hunter 2004*
Oxidation of sulphide minerals

Stibnite ($\text{Sb}_2\text{S}_3$): oxidises to various Sb oxides, which are very soluble (up to 50 mg/L)

Oxidised arsenopyrite forms scorodite ($\text{FeAsO}_4.2\text{H}_2\text{O}$),

Stibnite in quartz vein

valentinite on surface
Oxide coating develops on stibnite. Coating dissolves readily to form Sb(V) oxyanion $\text{SbO}_3^-$ or $\text{Sb(OH)}_6^-$

$\text{Sb}_2\text{S}_3 + 18\text{H}_2\text{O} \rightarrow 3\text{SO}_4^{2-} + 2\text{SbO}_3^- + 26\text{e}^- + 36\text{H}^+$

$p\text{H} = 7$

Ashley, Craw, Graham & Chappell 2003
Hillgrove mine tailings, c. 1 month old
Dry, high evaporation conditions
Layering is bedded stibnite and arsenopyrite
Incipient antimony oxide formation and cementation

Ashley, Craw, Graham & Chappell 2003
Antimony oxide: soluble to c. 50 ppm Sb in environment

Experimental solutions

SbO$_3^-$ (aqueous)

Sb$_2$O$_3$ (antimony oxide)

Stibnite, Sb$_2$S$_3$

log$\xi$ S = -3

Theoretical Sb redox phase diagram

Ashley, Craw, Graham & Chappell 2003
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Reefton gold mine, New Zealand: rainfall c. 3000 mm/year
Arsenopyrite, pyrite, stibnite; discharges have HFO precipitates
Reefton adit discharge waters and iron oxyhydroxide precipitates

Craw, Wilson & Ashley 2004
Bulk distribution constants for arsenic and antimony in Reefton iron oxyhydroxide/water

\[ K_d = \frac{\text{Metalloid in solid}}{\text{Metalloid in water}} \]

Craw, Wilson & Ashley 2004
Antimony adsorption/desorption on iron oxyhydroxide

Infrared absorbance of adsorbed Sb

Time, minutes

McComb, Craw & McQuillan 2007
Electron backscatter images: pale zones = As-rich

*Fuchsia excorticata* shoots/leaves
As: 30 mg/kg
Sb: 0.05 mg/kg

Iron oxyhydroxide
As: 10-20 wt%
Sb: 100-1000 mg/kg

\[ K_{2}Fe^{III}_{4}[As^{V}O_{4}]_{3}[OH]_{5}.6H_{2}O \] (pharmacosiderite)

Craw, Rufaut, Haffert & Paterson 2007
Moss, *Pohlia wahlenbergii*

secondary electron images with As X-ray emission

Moss As: 0.8-3 wt%
Moss Sb: 90-200 mg/kg

Substrate As: 3-16 wt%
Sb: 10-1000 mg/kg

Craw, Rufaut, Haffert & Paterson 2007
As/Sb ratio of plants reflects As/Sb ratio of substrates

Craw, Rufaut, Haffert & Paterson 2007
Endeavour Inlet Sb mine (closed 1907)

Queen Charlotte walkway

Sb metal in slag
Endeavour Inlet, Marlborough, historic mine tailings:
Arsenic up to 5 wt% in stibnite
Minor arsenopyrite, pyrite
Antimony adsorbed on to iron oxyhydroxides
from oxidation of iron minerals; more mobile than As

Wilson, Craw & Hunter 2004
Endeavour Inlet, Marlborough, historic antimony mines
No iron oxyhydroxide at adits
c. 1000 mm rainfall/year
Ground and surface water carries Sb for kilometres

[Sb: 3 grams/day
As: 0.5 grams/day]

[Sb: 1200 grams/day
As: 400 grams/day]

Wilson, Craw & Hunter 2004
Flux of Sb from mine sites at neutral pH

Ashley, Craw, Tighe & Wilson 2006
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Metalloids in rocks and soils

**Antimony**
- Background rocks: 0.01-0.1 ppm
- Background soils: <0.1 ppm
- “Contaminated” (ANZECC) 2 ppm trigger value

**Arsenic**
- Background rocks: 2-20 ppm
- Background soils: 0.1-5 ppm
- “Contaminated” (ANZECC) 20 ppm trigger value

Background rock As is near “contaminated” As level;
Background rock Sb is <one tenth of “contaminated”
Arsenic in groundwater: dissolved from background rocks

Affects 30 million people in Bangladesh

A regional problem:

Sb seldom analysed

http://bicn.com/acic/
New Zealand has potential As issues in deeper, slower-flowing groundwater aquifers

- Groundwater with arsenic concentrations > WHO limit (naturally elevated arsenic)
- Rocks have high As background
- As is rarely analysed, so extent of problem is unknown

Sb is less likely to be an issue because of lower background Sb in rocks. No data are available.
Arsenopyrite FeAsS + up to 2000 ppm Sb

Gold is encapsulated in pyrite and arsenopyrite; these are separated by flotation
Pressure-oxidation autoclave

Concentrate slurry is roasted in oxygen atmosphere at 225°C

Results in acid solution (pH =1)
pH raised to 10.5 for cyanidation

Mobilises As and Sb in solution
Macraes mine Sb increase from oxidation and addition of Reefton ore?

- **Ore**: Boulangerite, Pb₅Sb₄S₁₁ (rare)
- **Mine waters**: Arsenopyrite FeAsS
- **Mine discharge waters**: Macraes mine Sb increase from oxidation and addition of Reefton ore?
Waiuta gold mine site, Westland
As condensate was byproduct

Solids: \textbf{As: 11-40 wt\%}  
\textbf{Sb: 50-1000 mg/kg}

\textbf{Condenser}

\textbf{Arsenolite As}_2\textbf{O}_3  
+ Sb impurity
Lead arsenate spray for e.g., codling moth in apples (discontinued in 1970s)

Preparation:

\[ \text{Pb(NO}_3\text{)}_2(aq) + \text{H}_3\text{AsO}_4(aq) = \text{PbHAsO}_4(\text{solid}) + 2\text{HNO}_3(aq) \]

Dissolved As obtained from commercial \text{As}_2\text{O}_3 (soluble)

Much commercial \text{As}_2\text{O}_3 has \text{Sb} impurity (1%)

Sprayed orchards have elevated As in soils
Expect \text{Sb} as well; As/Sb = 100
Conclusions

• Sb is chemically similar to As, but present at lower levels in most rocks
• Natural Sb point sources are found throughout New Zealand
• Sb minerals are soluble and dissolved Sb can be transported for kilometres
• Dissolved Sb is readily attenuated by iron oxyhydroxide, if present
• Levels of Sb in our environment are poorly known because Sb is commonly not on the analysis list