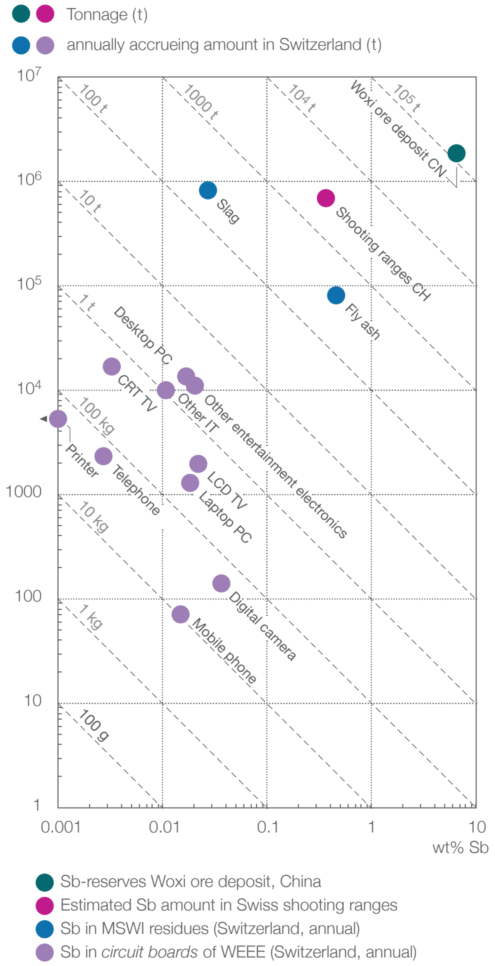
3. Primary/secondary raw materials

Antimony is only found rarely and sparsely throughout Switzerland.[30] The Vorderrhein and Hinterrhein valleys and the St.Gallisch Murg valley are known for their mineralisations of antimony, but the most and best known occurrences are found in the Malcantone in the canton of Ticino.[43] Antimony was once mined there, at Monte Pellegrino in Miglieglia; it is probably the only (former) mining site in Switzerland.[43] But as with all the known antimony deposits in Switzerland, it does not contain enough of the semi-metal to be exploited profitably.

However, there are substantial amounts of secondary (i.e. in products) antimony in Switzerland. In 2001, there was an estimated 1 200 tonnes of antimony in hardened lead projectiles in Swiss bullet berm soils at shooting ranges (Fig. 4) (Fig. 4) and over 1 500 t in residues from waste incineration plants in landfills .[33] If all the antimony from the residues of waste incineration plants in Switzerland had been recovered in 2001 (172 t), about 93 % (116 t) less antimony would have been put into landfills, furthermore, there would not have been the need to export residue (56 t) abroad.[33] These quantities would have been recycled back into production and eased the Swiss net demand for antimony by about 28 % (demand less trade exports); this would have more than doubled the recycling rate of antimony in 2001 (from 19[33] to 47 %). The theoretical complete recovery of antimony from fly ash makes up half of this, about 14 % .

Waste electrical and electronic equipment form another possible source of secondary antimony (Fig. 4). The circuit boards of these devices contain a wealth of critical metals: in addition to iron, aluminium, copper and zinc also antimony.[10] In contrast to the above-mentioned metals, antimony is currently not recovered because as of yet there is no industrial recovery method or it has not been implemented yet.[10] On the other hand, if all the antimony found in all the waste electrical and electronic equipment in Switzerland had been recovered in 2012, only just under 7 t of secondary Sb could have been put back into production;[37,44] this corresponds to 0.45 % of the annual demand of Switzerland in 2001.[33]



◀ **Fig. 4** Levels (weight as a %) and quantities of antimony in primary and secondary raw material sources. The primary source (green) represents the ores of the Woxi deposit in China (39), the remaining data refer to secondary resources in Switzerland (34,37,44). The ordinate has a slightly different meaning depending on the category. Diagonal lines indicate uniform total quantities.

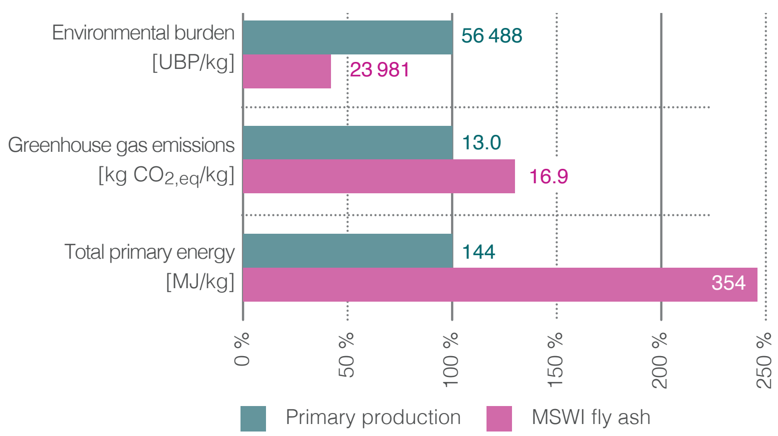
4. Environment

Every year, 34 t of antimony make their way into the Swiss environment, but only 13 t of it leave again (Fig. 3).[33] The amounts are divided almost equally between the stock left behind in berm soils (16.5 t / yr) and emissions into the air (17 t / yr), but the flows into the soil from sewage sludge (0.2 t / yr) and in the hydrosphere from waste water (0.3 t / yr) in 2001 were relatively low.[33] Where the emissions of antimony into the atmosphere exactly originate from is not known; however, a large proportion is likely to come from the wear of brake pads, as the soils next to roads with high volumes of traffic contain considerably more antimony than more remote, rural areas.[26,33] The antimony in the atmosphere returns to the soil sooner or later; estimates suggest that there is a total of 28 t of antimony in the top two centimetres of agricultural soils inSwitzerland. In 2001,[29,33] antimony left the Swiss environment either through the runoff of water to neighbouring countries (10.7 t / yr), or the rehabilitation of contaminated sites (2.7 t / yr); there is no information on how much antimony ends up abroad through the air.[33]

Antimony is considered to be a pollutant;[1,46] yet little is known about its environmental impact and toxicity.[18,36] In chemical terms, antimony behaves in a similar way to arsenic; its toxicity is also often compared to that of arsenic; [22,41] this is also reflected in the high and low tolerance values of the two elements (Tab. 1).

Antimony oxidises relatively quickly in the environment: from Sb (0) to Sb (III) to Sb (V). The oxidation state of antimony plays a major role in the assessment of its toxicity; Sb (III) is therefore more toxic but less soluble and hence less mobile than Sb (V).[28] Thus, Sb (III) dissolved in water should relatively quickly precipitate as Sb (V) which mainly binds to iron (hydr)oxides.[28] This eco-chemical behaviour of antimony has been observed in several studies.[14,19,21] Antimony is not harmless, because absorption and impact of antimony in and on bacteria[12] and plants have been recorded near to sites contaminated with antimony (mine tailings, berm soils).[6,38]

Recovering antimony from the fly ash of a MSWI plant requires more than twice the energy of primary production(Fig. 5).[48] This is due to the production of the chemicals that are required for the process. Nevertheless, the recovery of antimony is more environmentally friendly, since less has to be disposed of into landfills.[48]



◀ **Fig. 5** Rough estimate of the life cycle assessment of primary (green) and secondary antimony from MSWI fly ash (pink)(48). There are uncertainties about the MSWI fly ash because of the scaling of a method described in a laboratory scale to an industrial scale, and the lack of data regarding the recycling of the chemicals required for the secondary production.

5. Technology

Antimony can be extracted from ore by at least six different methods, depending on the nature of the ore (sulphide, oxide, complex ore) and the antimony content (Fig. 6).[11] The majority of these processes work on a pyrometallurgical basis; hydrometallurgical processes are used primarily for complex ores in order to minimise the loss of existing precious metals (primarily gold, silver and copper).[22] Products derived from pyrometallurgical processes generally have to be further refined, in order to obtain the required purity of the antimony to make it fit for further use.[11] Typical impurities in raw antimony are (with decreasing importance) lead, arsenic, sulphur, iron and copper.[11] Antimony may occur as a by-product in the extraction of lead and copper.[22]

Even though in Switzerland almost 100 % of the hardened lead (lead-antimony alloy) is recycled in lead-acid batteries, the overall recycling rate of antimony is surprisingly low.[33] This is because 80 % of antimony is used for non-metallic products (Fig. 1), for which there is still no economically feasible recovery process.[10,16,33] However, there are melting procedures that could be used to recover antimony from, among other things, electrical and electronic waste.[24]

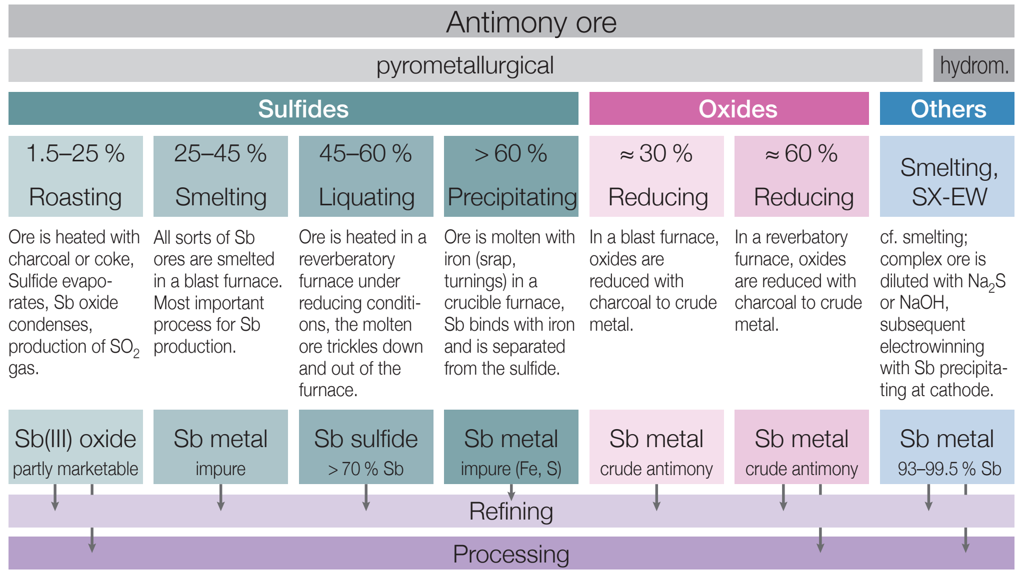


Fig. 6 Procedure for recovering antimony from ore (11). Which pyrometallurgical method is used will depend greatly on the nature of the ore and the concentration of antimony in the ore. Hydrometallurgical methods are mainly used for complex ores. SX-EW: *solvent extraction and electro-winning*: SX-EW is the only hydrometallurgical process in this illustration. "Other" ores consist primarily of mixed ores (from sulphides and oxides) and complex ores. The extraction of antimony as a by-product of the recovery of other metals (Pb, Cu) is not covered here.

The use of antimony as a flame retardant for plastics will be decisive in determining its future demand. For the time being, the demand is likely to increase based on the substitution of antimony is still too expensive. The demand for antimony for hardened lead (lead-acid batteries) is expected to decline in the coming years, while its use in future technologies is likely to increase (semiconductors, liquid crystal displays, photovoltaics).[11,16]

6. Economy

The criticality of antimony stems from a combination of factors: In 2012, 83 % of the primary antimony came from China, the next important producing countries were Canada and Russia, each supplied 4 % .[47] Furthermore, antimony is only extracted in nine countries around the world,[47] as a consequence most nations are completely dependent on the import of antimony, and / or the mining and the commercial readiness of these countries. In addition, the majority of the demand has to be covered by mining of primary antimony, as it so far cannot be recovered from many of its applications (see Chap. 1).[16]

In the early 1970s, the world market prices for antimony were over $ 18 000 / t and then by 2000 they had sunk to around $ 2000 (Fig. 7).[47] After a recent peak of around $ 14 000 / t, the price is currently about $ 9 500 / t.[47]

The mass flow rates of antimony in the Zurich waste incineration plant amount to a total of around 71 t per year (see supplement)[35]. The concentration in the slag is about 0.016 % , which does not make it economically viable to recover. At 0.24 % , the concentration in the fly ash captured by the electrostatic precipitators is higher by more than 10 times. This could be a potential point to start. However, due to the comparatively low concentration (workable ores contain several percent of antimony), a profitable recovery cannot be expected here either.

Efforts to recover secondary antimony are primarily justified by the ecological problem of its accumulation in landfill sites and the one-sided dependence on imports. Since the stock of antimony in the berm soils of Swiss shooting ranges is considered to be relatively high (1 175 t) and as it also has a concentration of up to 3 670 mg / kg, the option of recovery could be examined with the rehabilitation of these facilities.

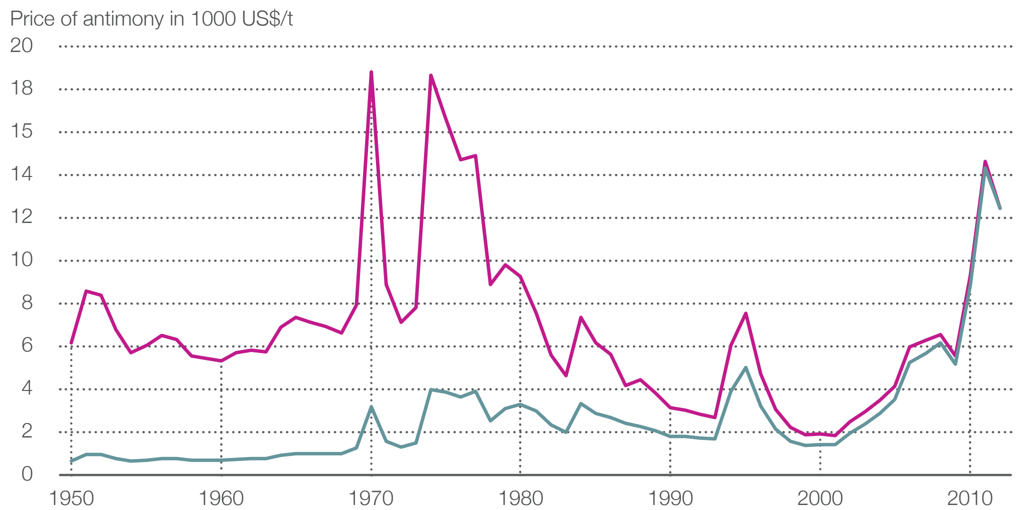


Fig. 7 Price history of antimony from 1950 to 2012 (47). Price in 1000 US$ / t. The pink curve is adjusted to reflect inflation (base year 2012), the grey-green one is not.

Antimony Sb

Substance dossier for the recovery of antimony from selected waste compared to primary production

Baudirektion Kanton Zürich

1. The importance of antimony

Antimony is a very brittle, soft, bluish-white metalloid that has low levels of electrical conductivity.[22,41] It is a rare element (<1 mg Sb / kg in the earth's crust[40]) and is only found very seldomly in its elemental form in nature. The main ore minerals are stibnite (also antimonite, Sb_2S_3) and tetrahedrite (also antimony-tetrahedrite, $(Cu,Fe,Ag,Zn)_{12}Sb_4S_{13}$).[39] Antimony can be leached from the earth's crust by magma, or from fine-grained, clay-rich sediments by thermal waters, then transported closer to the earth's surface and precipitated through the cooling of the water.[39] Exploited deposits have ore grades in excess of 3 % (30 g Sb / kg rock, > 30 000 fold accumulation).[39] China is the main producer of antimony (responsible for 87 % of the annual world production in 2011), other important producing countries are Tajikistan, Bolivia, Russia and South Africa.[8] Antimony is used almost exclusively for industrial applications such as for producing flame-resistant plastics and for the hardening of lead (Fig. 1).[22,33,41] In biological terms, antimony is considered to be non-essential; its toxicity is comparable to that of arsenic.[22,41]

Antimony is considered one of the critical raw materials, because (1) many countries are completely import-dependent, (2) the majority of the production is concentrated in one country (China), (3) very little antimony is recycled (worldwide: 11 % [16]) and (4) it can be difficult to replace with other elements.[7,16] In addition, there appears to be a shortfall in production (Fig. 2).[13]

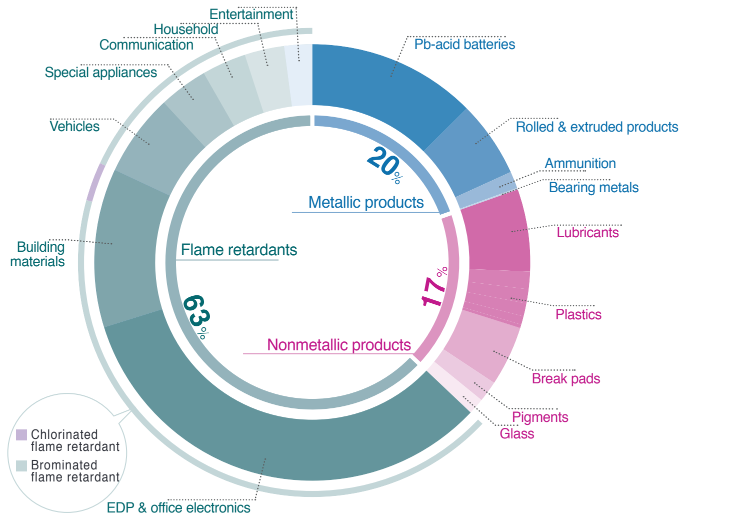


Fig. 1 The use of antimony in Switzerland, 2001 (33).

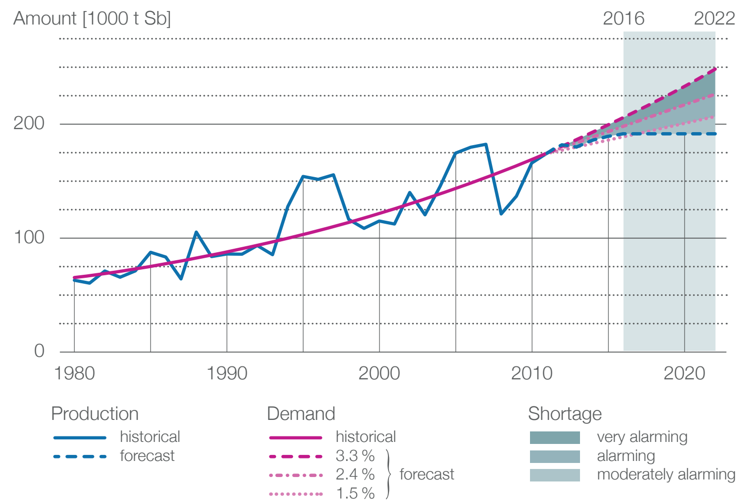


Fig. 2 Annual global production and demand for antimony 1980-2011. The 2011-2022 forecast is based on the increase in demand of 3.3 % from 1980 to 2011(13).

2. Understanding the system

Switzerland's demand for antimony is covered fully by imports,[33] for the most part in the form of antimony trioxide.[17] 1,470 t of antimony were imported in 2001.[33] Statistically, 90 % of this left Switzerland again, either in products or as waste and scrap; the remaining 10 % were delivered to the Swiss antimony storage sites (Fig. 3).[33] In 2001, this included a total 12 705 t of antimony, which can be divided into three major stock types: Industry and products (10 000 t, 79 %), waste management (1 530 t, 12 %) and the environment (1 175 t, 9 %).[33] Around half of the waste antimony produced in Switzerland in 2001 (308 t) was exported, while 35 % was fed back into the production process, and the remaining 16 % went to the waste incineration plants and finally landfill sites.[33]

Landfills are the fastest growing storage sites for antimony in Switzerland.[33] In 2001, approximately 91 % (125 t) of the antimony remaining in Switzerland was sent to landfill sites; an additional 15 % (21 t) remained in the environment (pedo / lithosphere); the excess 6 % (–8 t) were extracted from the consumption stock.[33]

About 464 t of antimony left Switzerland in 2001 through waste management (Fig. 3)[33]. These exports are made up of collected used goods (408 t, 88 %) and fly ash from municipal waste incineration (MSWI) plants (56 t, 12 %).[33] In Switzerland, the resulting MSWI slag is deposited domestically, but antimony is particularly concentrated in fly ash from municipal waste incineration plants (Fig. 4). Fly ash is still partly exported (up to 25 % in 2006[25]).

In Switzerland, only antimony-hardened lead is recycled, the antimony in plastics is simply lost.[33]

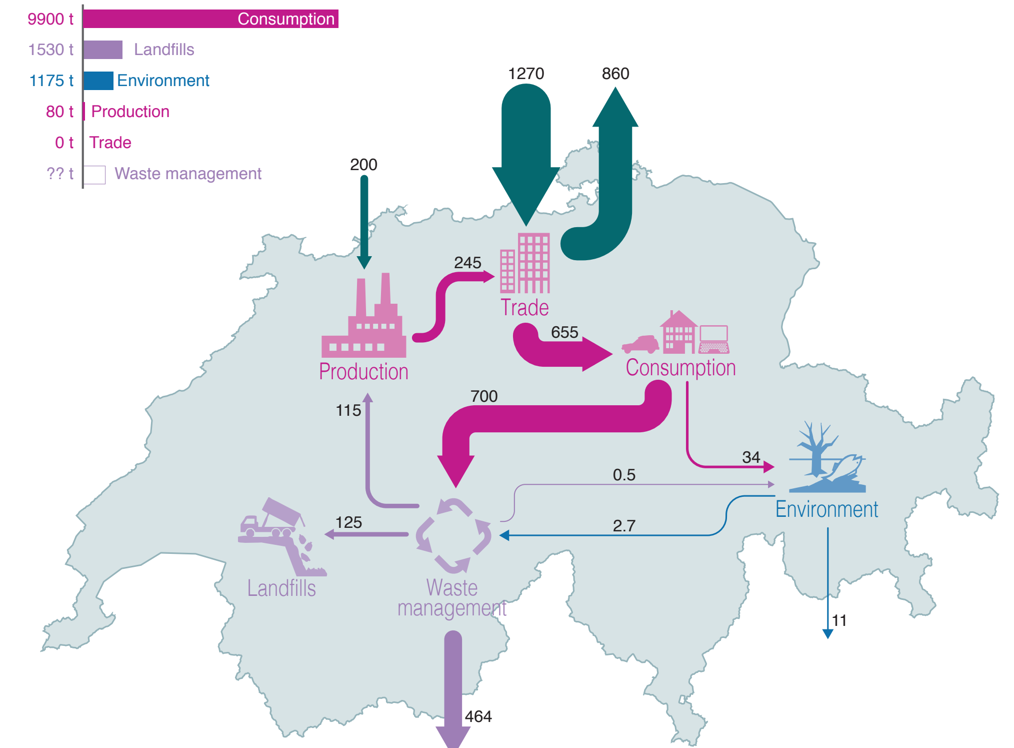


Fig. 3 The flows and stock of antimony in Switzerland in 2001 (33). Flows in t/year, stock in t. To clarify the numbers in the text: The export of antimony by waste management (464 t) in 2001 consisted of waste antimony (308 t), reused antimony (100 t) and MSWI residues (56 t) that had been collected together. 21t (34 t + 0.5 t – 11 t – 2.7 t) remained in the environment.

7. Society

In general, the social impact of antimony is likely to be small. In countries that extract primary antimony, it is only employment that is dependent on antimony or its market. Apart from this, the social relevance of antimony has two backgrounds: On the one hand, its impending supply shortage (criticality) and, on the other hand, its toxicity and its impact on the environment. Both aspects are only linked together to a limited extent. The questions is how to deal with a substance whose exact environmental impact and toxicity are not fully clarified, and the discussion of how reliable human toxicity threshold values are is of interest in terms of its societal impact.

The fact that people living in Switzerland could be affected or even endangered by the antimony in our environment, is rarely addressed. An exception to this are PET bottles, which may contain antimony due to their manufacturing process; over time it could be released into the liquids contained therein.

The measured average concentration of antimony in mineral water in PET bottles is only 0.43 µg / L and is thus one order of magnitude below the limit (Tab. 1).[5]

Antimony poisoning is frequently caused either by exposure at work or through treatment with drugs containing antimony.[45] Symptoms such as irritation of the respiratory tract, lung disease, gastrointestinal symptoms and antimony spots on the skin can be caused by occupational exposure.[45]

For example, in the town of Guiyu in the Chinese province of Guangdong, the concentrations of antimony in the workplace are two to three orders of magnitude higher than the natural background levels;[9] over 100 000 people make a living by unregulated "recycling" of electronic waste.[32]

Over 100 000 tonnes of material are recycled in the Guangdong region annually, most of it coming from legal and illegal imports from the Western world.[32,42]

Antimony is used as a form of therapy for parasitic diseases (leishmaniasis, schistosomiasis) and may have a cardiotoxic effect or lead to inflammation of the pancreas.[45] A carcinogenic effect of the Sb (III) oxide was observed in rats; the data is not conclusive for humans.[27]

Tab. 1 Range of maximum values for antimony (Sb), arsenic (As) and lead (Pb). Sb and As have similar maximum values due to their similar chemical behaviour.

		Sb	As	Pb
Maximum concentration in drinking water[1]	mg / kg	0.005	0.05	0.01
Parameter value, drinking water[2]	µg / L	5	10	10
Minimis threshold value for groundwater[3]	µg / L	5	10	7
Eluate concentration values for the assessment of the impacts of contaminated sites on the waters	mg / L	0.01	0.05	0.05
Concentration values for soils to assess the need for the rehabilitation of soils in domestic and family gardens, children's playgrounds and complexes where children play on a regular basis[4]	mg / kg	50	50	1000
Requirements for the water quality of flowing waters[5]	mg / L	-	-	0.01 (total) 0.001 (released)
Limit in the dry waste for inert substance landfill[6]	mg / kg	30	30	500
Limit in the dry waste for reactor landfill[6]	mg / kg	50	50	2000

[1]20, [2]15, [3]31, [4]1, [5]23, [6]46.

8. Resource management: The overall situation at a glance

Antimony is considered problematic because of its toxicity, but this has not been fully clarified. Antimony is judged as being critical because most of the primary production takes place in China (83 %) and a further 4 % respectively come from Canada and Russia. Efforts to recover secondary antimony are primarily justified by the ecological problem of its accumulation in landfill sites. Measures for the recovery could start with the berm soil in shooting ranges. The antimony levels in the fly ash captured by the electrostatic precipitators at MSWI plants must also be borne in mind. At 0.24 %, the concentration here is significantly higher than that found in the slag.
The public could invest, primarily for ecological reasons, in the recovery of antimony from electrostatic precipitator fly ash and from the contaminated shooting range soils. The corresponding development work should be addressed on a national level.

The quantity that can be recovered will probably not alleviate the import of antimony significantly and if it does, its effects will only be short-term.

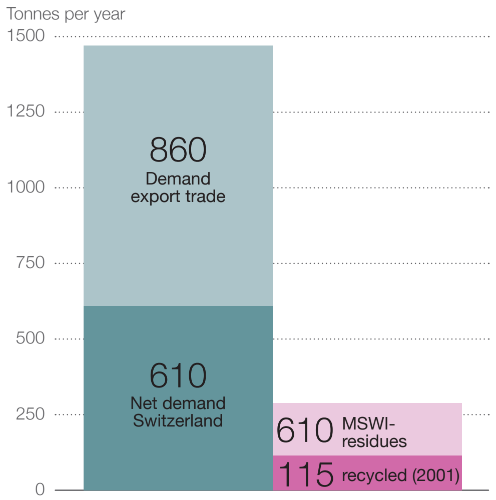


Fig. 8 Comparison of Switzerland's annual demand for antimony (grey-green) and the annual recycling potential (pink) (33). The 1,175 t of antimony in Swiss shooting range soils are not taken into account.

Open issues

1. The toxicity of antimony in various environmental media must be clarified.
2. The process of recovering antimony from fly ash has not been developed.

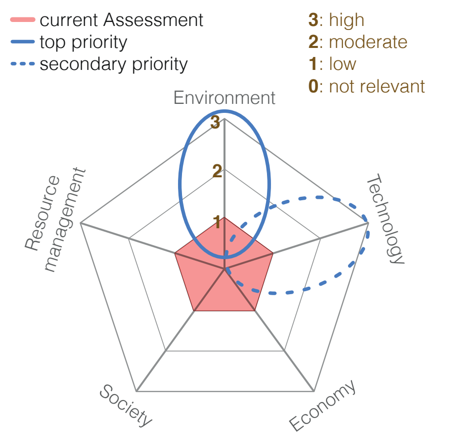


Fig. 9 Evaluation of the recycling potential of antimony based on a qualitative expert assessment.
Criteria: *Environment*: Problematic to reduce emissions, there is no conclusive information; *Technology*: no technology for the recovery of filter dust; *Economy*: no knowledge on the economics of recycling; *Society*: poor working conditions primary production; *Resource management*: Supply criticality, no legal requirements for its recovery

Literature
Due to limited space, the bibliographic references are summarised in a separate document.
http://daten.sgtk.ch/rohstoff-monitoring/AWEL_Antimony_Literature_EN.pdf

This substance dossier was created by Benjamin Jost from the Swiss Geotechnical Commission SGTK in collaboration with the GEO Partner AG for the AWEL.

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