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Magnitudes, spatial scales and processes of environmental antimony mobility from orogenic gold–antimony mineral deposits, Australasia

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Abstract Antimony (Sb) is strongly concentrated into hydrothermal mineral deposits, commonly with gold, in metasedimentary sequences around the Pacific Rim. These deposits represent potential point sources for Sb in the downstream environment, particularly when mines are developed. This study documents the magnitude and scale of Sb mobility near some mineral deposits in Australia and New Zealand. Two examples of New Zealand historic mining areas demonstrate that natural groundwater dissolution of Sb from mineral deposits dominates the Sb load in drainage waters, with Sb concentrations between 3 and 24 µg/L in major streams. Mine-related discharges can exceed 200 µg/L Sb, but volumes are small. Sb flux in principal stream waters is ca 1–14 mg/s, compared to mine tunnel fluxes of ca 0.001 mg/s. Dissolved Sb is strongly attenuated near some mine tunnels by adsorp-

tion on to iron oxyhydroxide precipitates. Similar Sb mobilisation and attenuation processes are occurring downstream of the historic/active Hillgrove antimony–gold mine of New South Wales, Australia, but historic discharges of Sb-bearing debris has resulted in elevated Sb levels in stream sediments (ca 10–100⁺ mg/kg) and riparian plants (up to 100 mg/kg) for ca 300 km downstream. Dissolution of Sb from these sediments ensures that river waters have elevated Sb (ca 10–1,000 µg/L) over that distance. Total Sb flux reaching the Pacific Ocean from the Hillgrove area is ca 8 tonnes/year, of which 7 tonnes/year is particulate and 1 tonne/year is dissolved.

Keywords Antimony · Mine · River · Environmental contamination · New Zealand · Australia

Introduction

Mines are the ultimate source for almost all anthropogenic antimony (Sb) in the environment. Much environmental dispersion of Sb is derived from smelting of sulphide ores, as well as from industrial and urban sites, and transport usage (Adriano 1986; Ainsworth et al. 1990; Filella et al. 2002; Neal and Davies 2003; Wilson et al. 2004a; Shotyky et al. 2005). Nevertheless, major point source discharges of Sb into the environment can occur from mining areas, especially from historic sites

and those with little or no environmental constraints (Mok and Wai 1990; Mori et al. 1999). Antimony occurs in mineralised rocks in a wide range of geological settings, principally as a trace element and closely associated with sulphide minerals. The geological processes associated with the formation of orogenic gold deposits are particularly efficient at concentrating Sb (and As) (Nesbitt et al. 1989). Orogenic gold and Sb deposits are common in deformed metasedimentary terranes around the Pacific Rim (Goldfarb et al. 2001), where the terranes have been accreting on to continental margins for

more than 500 million years. Hence, environmental mobility and fluxes of Sb around the Pacific Rim receive major contributions from this mineral deposit type. The sites described in this study are in metasedimentary terranes of the SW Pacific, in southern New Zealand and eastern Australia (Ashley et al. 2003; Craw et al. 2004). A feature of this mineral deposit type is the abundance of carbonate minerals in mineralised zones and adjacent host rocks. Carbonate minerals have the capacity to neutralise any acid generated during oxidation of sulphide minerals, and all effluent discharges into the environment have near-neutral pH (Ashley et al. 2003; Craw et al. 2004).

Since mineral deposits occur in rocks that may have naturally highly anomalous metal/metalloid concentrations, it can be difficult to distinguish elevated metal/metalloid levels in natural waters in mineralised regions from mining effluents. This distinction is especially difficult to make where there are abandoned historic mines and background water compositions prior to mining are unknown. In this study, we describe two historic mining areas from New Zealand (Globe Hill; Endeavour Inlet; Fig. 1) where natural discharges of Sb predominate over mine-related Sb mobility. We focus on magnitudes and spatial scales of Sb mobility and magnitudes of Sb fluxes from natural sources. We then compare these results to an example from New South Wales (NSW), Australia (Hillgrove; Fig. 2), where historic mining activity has resulted in substantial Sb mobility on a large spatial scale, mainly related to stream sediments affected by wastes from historic mines. Dissolved Sb levels are compared to WHO (1996) recommended drinking water limits, and sediment Sb contents compared to Australasian guidelines (NWQMS 2000).

Methods

This study focuses on concentrations of Sb in water derived from mineralised rocks, the scale of mobility of that Sb, and processes of dispersion. We are principally concerned with metalloid concentrations in waters that exceed drinking water limits. Hence, we focus on Sb concentrations above the 5 µg/L drinking water limit (WHO 1996). In addition, we report on sediment Sb concentrations in the Macleay River catchment, NSW, as these sediments contribute to dissolved Sb load.

Water samples were collected at New Zealand historic mine sites where water discharged from mine tunnels, and in nearby receiving streams, by methods described by Wilson and others (2004a, b). Results of this close-spaced sampling are shown in Fig. 1a, b. All Endeavour Inlet samples were collected on the same day in September 2002, and the Globe Hill samples were collected on the same day in June 2002. Analyses were conducted using graphite furnace AAS with a Perkin

Elmer 4100ZL system controlled with Perkin-Elmer AA Winlab v. 4.1 software. The detection limit for Sb was 5 µg/L.

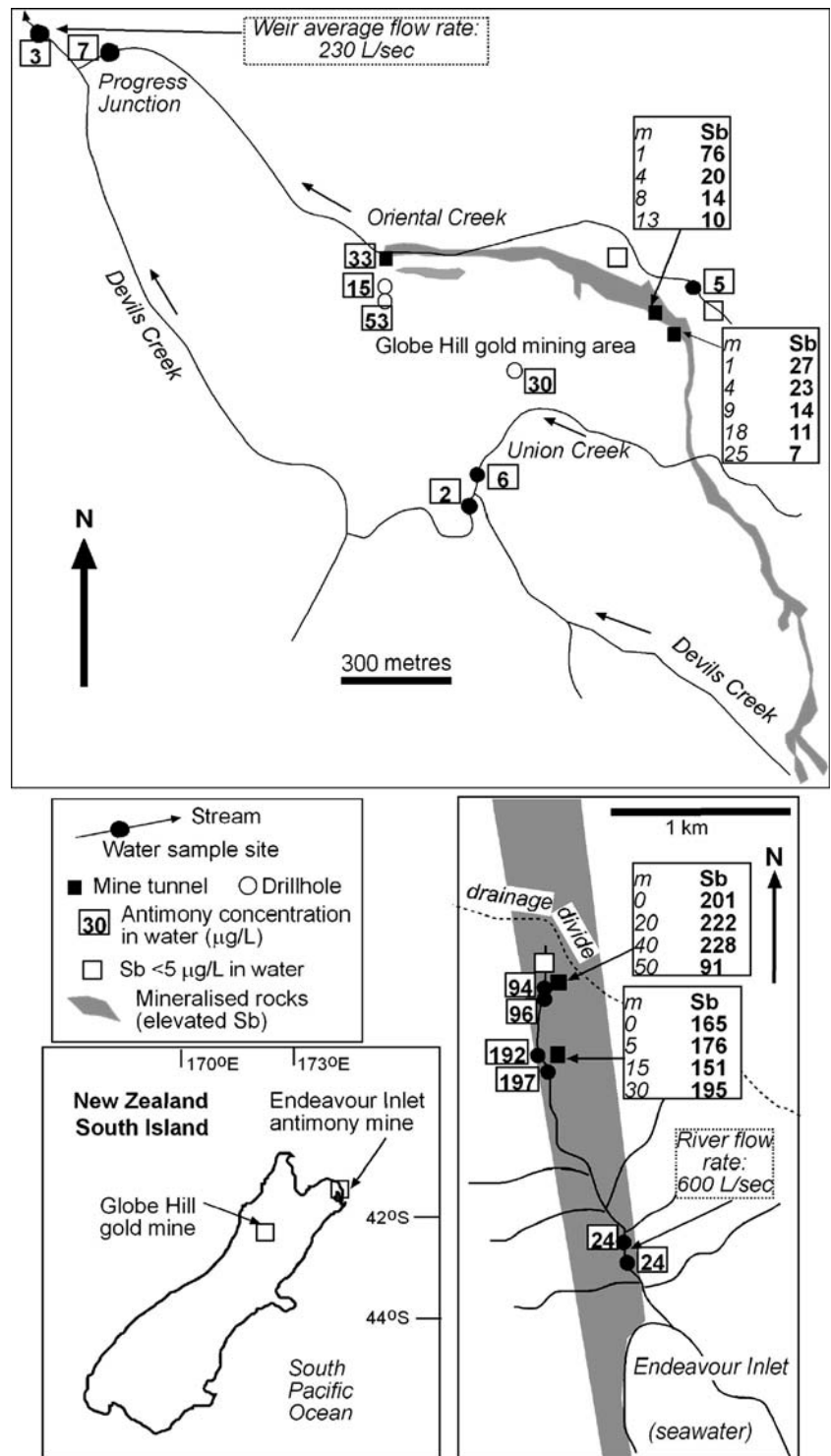
Additional water Sb data for the Globe Hill area were provided by Oceana Gold (NZ) Ltd, from a regional survey of baseline water compositions from streams and drill-holes into basement rocks. The sampling point downstream of Progress Junction (Fig. 1a) was analysed ten times between 1984 and 1993, avoiding high rainfall events. Likewise, other stream waters from Oriental Creek, Union Creek, and Devils Creek near Union Creek (Fig. 1a) were analysed up to 5–10 times over the same period. Results of multiple analyses were consistent, and are depicted in Fig. 1a. All these waters were filtered (<0.45 µm) in the field. Groundwater samples were obtained from purged drill-holes with a Teflon bailer, and these analyses were done by graphite furnace AAS, with an Sb detection limit of 5 µg/L. Stream water analyses were done by ICP-MS at Australian Laboratory Services (ALS), Brisbane, Australia, with an Sb detection limit of 1 µg/L.

Waters from the Hillgrove area were collected at various times between June 1998 and January 2000 in 500 ml acid-washed plastic bottles and subsequently filtered in the laboratory. They were analysed by ICP-MS at ALS, with an Sb detection limit of 1 µg/L. Stream sediment samples were collected between April 1999 and January 2000 and were subsequently digested in aqua regia (US EPA 200.2) and analysed by ICP-MS at ALS. Sequential extractions on Sb-contaminated Macleay catchment sediments were undertaken using the methods of Tessier et al. (1979). The Fe (Mn) oxide specific ammonium oxalate extract was the most effective. Simple leaching experiments were conducted over 32 days with Sb-bearing stream sediments (containing up to 4,640 ppm Sb) and “background” stream water with <1 µg/L Sb. Solutions were held in periodically agitated flasks open to air.

Samples of stream algae and riparian plants were taken from the Macleay River catchment for distances of up to 100 km downstream of Hillgrove at various times between February and June, 2002, to determine the extent of biological uptake of Sb from the sediments. These biological samples were washed in de-ionised water and air-dried at 40°C for 10 h. Weighed samples of vegetation were ashed at 450°C for 6–12 h and the resulting ash weighed and the residual mass proportion calculated (typically 5–10% depending on the species). Ashed vegetation and dried algae were analysed, along with the <180 µm fraction of stream sediments for Sb and As using ICP-MS at ALS following digestion in aqua regia.

Flow-rates for New Zealand mine discharges were estimated by timing the collection of a known volume in a 1 L bottle. Flow rate for larger rivers were estimated using an approximated cross sectional area in a stream

Fig. 1 Antimony distribution in waters at the New Zealand historic mine sites described in the text, as located on the index map (lower left). **a** Globe Hill gold mining area and the Devils Creek catchment which drains the mineralised rocks. **b** Endeavour Inlet antimony mining area (after Pirajno 1979; Wilson et al. 2004b), with Sb data collected in Spring. Closely-spaced sampling outside mine tunnels are shown with distances (m) from tunnel entrances in both **a** and **b**



reach of uniform geometry, and repeated measurements of the time taken for an object to float along a known distance (> 10 m). These methods are crude, but resultant estimates are reproducible to better than order of magnitude. A continuously-monitored V-notch weir on

Devils Creek below Progress Junction (Globe Hill area; Fig. 1a) was used by Oceana Gold (NZ) Ltd. to obtain flow rates every 15 min over 2 years. Estimates of flow rates for Macleay River tributaries were made by similar methods to above, with larger uncertainties in partially

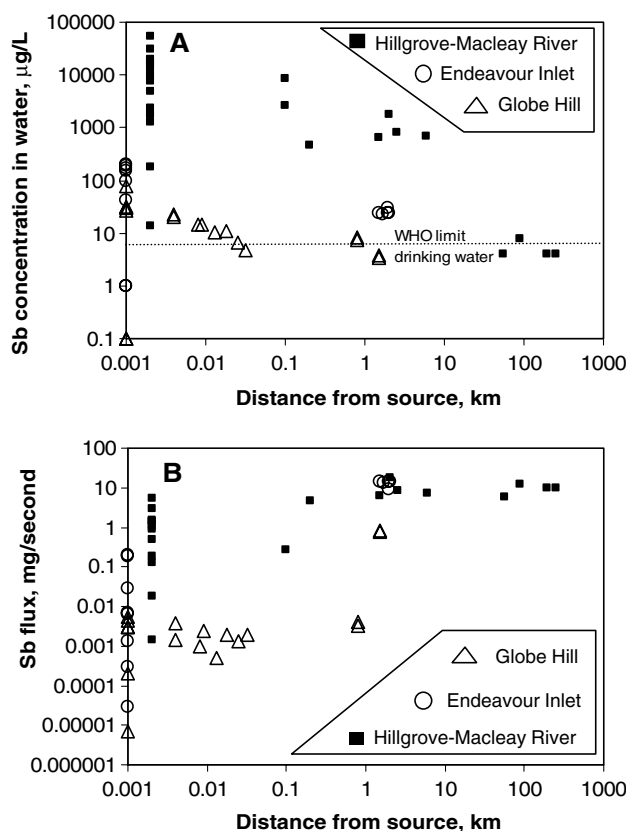


Fig. 2 Variations of Sb with distance from principal mining area sources for the Australasian sites described in the text. Note the logarithmic scales on all axes. **a** Sb concentrations in water. WHO (1996) drinking water limit for Sb is indicated (dotted line) for comparison. **b** Sb flux in water

ephemeral streams. Flow rate for the lower Macleay River, about 240 km downstream of the Hillgrove mine (NSW) was obtained from a long-term monitoring site at Turners Flat, ca 20 km upstream of Kempsey (Fig. 3; NSW Department of Infrastructure, Planning and Natural Resources, unpublished data). Antimony fluxes discussed in this study were determined from the above flow rates, and are believed to be accurate to better than an order of magnitude.

Results

Globe Hill mining area

Historic gold mining in this area occurred along a well-mineralised zone that extends through much of the Devils Creek catchment (Fig. 1a). Most intense mining activity occurred in an extensive network of shafts and tunnels on Globe Hill itself (Fig. 1a) that followed mineralised rocks that extend to a depth of 400 m below surface (Christie and Brathwaite 2003).

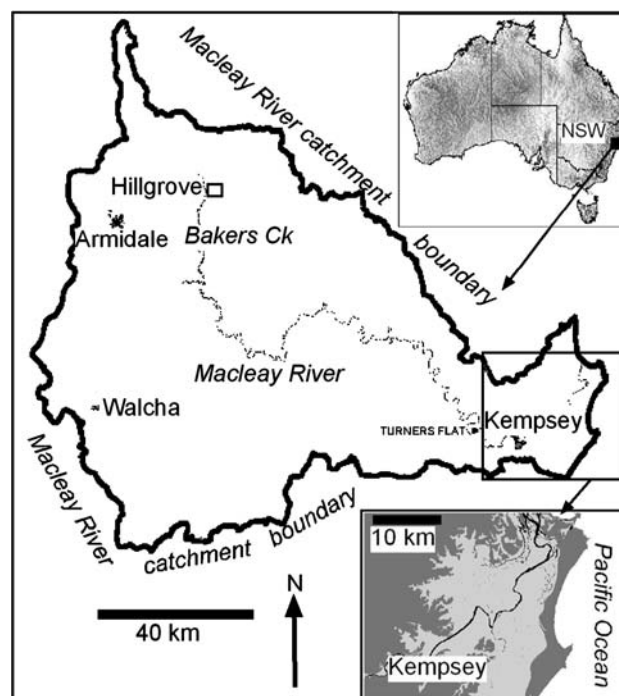


Fig. 3 Map of the Macleay River catchment, NSW, Australia. The Hillgrove mine site is the principal source for Sb in the catchment, and this Sb passes from the Bakers Creek tributary through the Macleay River to the Macleay floodplain (pale shaded area in inset) and the Pacific Ocean, a distance of over 300 km

The mineralised zone contains abundant pyrite (FeS_2), arsenopyrite (FeAsS) and, locally, stibnite (Sb_2S_3). Waters draining from tunnels in this mineralised rock have elevated Sb contents (up to 76 $\mu\text{g/L}$; Fig. 1a). Likewise, exploration drillholes in the region of historic mine workings discharge waters with Sb contents up to 53 $\mu\text{g/L}$ (Fig. 1a). Discharge waters are precipitating amorphous brown iron oxyhydroxide (HFO) deposits for up to 20 m downstream from drillhole and tunnel entrances, and this material readily adsorbs Sb from the waters (Craw et al. 2004). Consequently, the Sb content of waters decreases rapidly downstream, as shown by data from the two tunnels at which closely-spaced samples were taken (Fig. 1a). These mine waters are all discharging at 0.05–0.2 L/s. HFO deposits have Sb concentrations up to 1,200 mg/kg, and distribution coefficient for Sb between HFO and coexisting water ranges between 10^3 and 10^5 (Craw et al. 2004).

Stream waters have low but detectable Sb contents in several places (Figs. 1a, 2a). The highest observed stream Sb (7 $\mu\text{g/L}$) was in the lower reaches of Oriental Creek, downstream of the main mining area (Fig. 1a), which flows at ca 0.5 L/s. Union Creek consistently has 6 $\mu\text{g/L}$ Sb, and this is diluted to 2 $\mu\text{g/L}$ below the confluence with Devils Creek (Fig. 1a). Devils Creek below

Progress Junction is consistently 3 µg/L, and the average flow rate was 230 L/s at this site over the 2 years of flow monitoring (Fig. 1a). Samples of water farther down Devils Creek yield Sb contents at or below the 1 µg/L detection limit.

Endeavour Inlet stibnite mines

Stibnite was mined in this area (Fig. 1b) between 1874 and 1907 (Johnston 1993). Mines were underground tunnels along individual veins that occur in a well-defined zone that trends NNW from the inlet (Fig. 1b). The veins are ca 10 m apart, are ca 1 m thick, and consist mainly of quartz with up to 50% stibnite locally. Waters discharging from two mine tunnels have strongly elevated Sb contents, up to 228 µg/L (Fig. 1b). Unlike the Globe Hill tunnels (above) there is almost no HFO being deposited by discharge waters, and Sb contents of discharge waters are not attenuated by adsorption outside the tunnels (Fig. 1b; Wilson et al. 2004b). Rather, the Sb content of waters rise outside the tunnels because of continuing interaction with stibnite-bearing debris (Wilson et al. 2004b). Flow rates of mine discharge waters were 0.1–0.3 L/s. Water in the principal stream flowing past the mine tunnels shows increasing Sb contents near the mines, up to 197 µg/L (Figs. 1b, 2a). Flow rates increase from 0.3 L/s near the upper tunnel, to 1 L/s at the lower tunnel. Farther downstream, this stream had substantially greater flow rate (600 L/s), and Sb content had lowered to 24 µg/L (Figs. 1b, 2a).

Hillgrove mines–Macleay River catchment

Mining of Sb and Au has occurred intermittently in the Hillgrove region of northern NSW (Fig. 3) since 1877. It has been the largest producer of Sb in Australasia (> 60,000 tonnes stibnite concentrates) as well as being a significant gold producer (Ashley and Craw 2004). There are over 200 known mineralised vein and breccia systems hosted in metasedimentary and granitic host rocks, with about a dozen substantial underground mines extending to depths of hundreds of metres. Stibnite-bearing vein and breccia systems (containing 1–10% Sb) are accompanied by quartz and carbonate, with minor associated arsenopyrite, pyrite and gold. Historic disposal practices (pre-1970) of mine wastes, along with continuing small discharges of mine effluent, has led to severe and extensive environmental contamination by Sb (and As) (Ashley and Graham 2001; Ashley et al. 2003). Although there is natural and anthropogenic Sb contamination of soil and vegetation in the immediate mine vicinity, the main environmental dispersion has been into the Macleay River catchment,

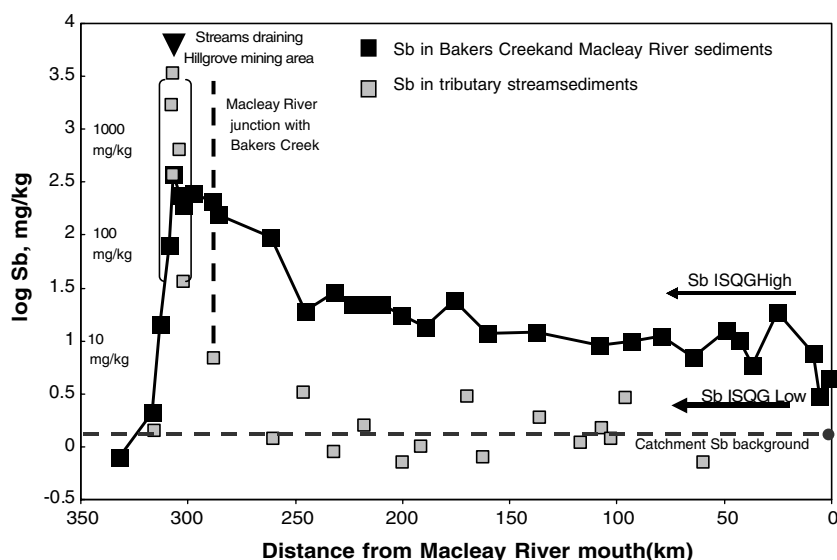
one of the larger (~11,500 km²) coastal river systems in eastern NSW. Several million tonnes of mineralised mine waste were dispersed into Bakers Creek, a major tributary of the Macleay, with subsequent physical and chemical transport of Sb (and As) over 300 km downstream to the Pacific Ocean (Fig. 4) including widespread low-moderate level contamination of the Macleay floodplain and estuary (Tighe et al. 2005). The dispersion constitutes the largest environmental Sb anomaly in Australasia and one of the largest worldwide.

Background stream waters in the Macleay River catchment contain on average 2 µg/L Sb (Ashley and Graham 2001). Mine effluent waters from underground workings and the tailings dam at Hillgrove contain up to 55 mg/L Sb (Fig. 2a). No acid mine drainage occurs due to carbonate buffering of sulphide mineral oxidation reactions and effluent pH values are between 6.2 and 8.5. Some seepages display abundant flocculant precipitates of HFO that contains up to 11.2% Sb and 10.3% As (Ashley et al. 2003). Attenuation of metalloids in the stream system is assisted by dispersal of HFO material. For 20 km downstream of Hillgrove in Bakers Creek, Sb values in stream water range between 0.125 and 1.8 mg/L, with pH values of 7.0–9.1. Downstream of the junction of Bakers Creek with the Macleay River (Fig. 3), there is evidently dilution and/or precipitation of Sb, but river water maintains Sb values (4–30 µg/L) close to or above the drinking water guideline values for most of the distance to the Pacific Ocean (Fig. 2a). The dissolved Sb contents in the Macleay River could be of concern for public health as municipal water supplies are drawn from the lower reaches of the stream. All main tributaries of the Macleay River downstream of Bakers Creek contain “background” Sb values in stream water.

For the initial 50 km downstream of the mines, Bakers Creek and the Macleay River display extremely elevated Sb contents in stream sediments (typically in the range of 200–600 mg/kg Sb, compared to a catchment background of 1.1 mg/kg Sb; Ashley and Graham 2001) (Fig. 4). This material is a sand to boulder bedload and may represent the present extent of coarse grained sediment dispersal since mining began. For at least the first 20 km downstream, the sediments contain relict detrital stibnite and arsenopyrite. Further downstream, and extending to the Pacific Ocean, there is a gradual decay of Sb values in stream sediments from ~30 to ~10 mg/kg (Fig. 4), with an increased proportion of finer silt and mud fractions. The Macleay floodplain (Fig. 3), with an area of 690 km², has an average of 11 mg/kg Sb in topsoil (Tighe et al. 2005).

Recommended environmental sediment quality guideline values for Sb are 2 (low) and 25 mg/kg (high) (NWQMS 2000). Hence, many of the sediments

Fig. 4 Plot of Sb content of stream sediments versus distance along the Bakers Creek–Macleay River system (measured from the Macleay mouth), with Sb data from uncontaminated tributary streams. The regional catchment background value for Sb is 1.1 mg/kg (Ashley and Graham 2001). Australasian sediment quality guideline values (ISQG) for Sb (NWQMS 2000) are indicated by arrows, with the low value at 2 mg/kg and the high value at 25 mg/kg



analysed from the Macleay catchment exceed these guidelines (Fig. 4). Sb-bearing sediment dispersion over the Macleay floodplain has occurred during major flooding events over the past 50–100 years, resulting in 91% of the area containing Sb values above the regional background in soils of 0.3 mg/kg and 7% of the area containing Sb over 20 mg/kg the current Australian ecological investigation level (with values ranging up to 39.4 mg/kg) (Tighe et al. 2005).

Sequential extraction studies of the river sediments indicated that the Fe (Mn) oxide specific ammonium oxalate extract was the most effective, even though only a minor proportion (1.5–2.7%) of total Sb was leached. The results suggested that some Sb is sited in Fe oxyhydroxides, but most remained in residual phases (probably encapsulated in sediment particles). The leaching experiments with river water resulted in up to 6 mg/L Sb being dissolved from the most contaminated sediments at pH values of 6.6–8.2 (Ashley and Graham 2001).

The riparian environment of the Bakers Creek–Macleay River system demonstrates strong uptake of Sb into common plant species (Fig. 5a). Distributions in plants closely mimic those of corresponding stream sediments, although values are typically 1–2 orders of magnitude lower (Fig. 5a). For over 50 km downstream of the Hillgrove mines, Sb values in plants are commonly 3–100× background values for the same species. Similarly, uptake of Sb occurs in aquatic algae with values intermediate between corresponding stream waters and sediments, and up to 2 orders of magnitude above background values (Fig. 5b). Macleay floodplain pasture species, nearly 300 km from Hillgrove, illustrate demonstrable uptake of Sb where growing on Sb-contaminated soil (Tighe et al. 2005).

Discussion

Spatial scale of elevated Sb

Data from our examples show that Sb is readily transported in stream water for long distances from mine sites despite minor attenuation by HFO (Fig. 2a). Both New Zealand examples have Sb concentrations near to drinking water limits about 1 km from source areas (Fig. 2a). Sb concentrations in stream water near the Hillgrove mine site are considerably higher than for the New Zealand sites, and Sb is still near or even above drinking water limits 300 km from the mining area (Fig. 2a). Elevated Sb in Macleay River water arises because of the rapid dissolution of stibnite that occurs in the river sediments (Ashley et al. 2003). Stibnite in contact with oxygenated water typically develops a coating of Sb oxide such as valentinite and/or senarmonite (Sb_2O_3), or stibiconite ($\text{Sb}_3\text{O}_6(\text{OH})$) (Vink 1996; Ashley et al. 2003). Sb_2O_3 dissolution is strongly dependent on redox potential (Fig. 6). The typical observed environmental redox potential range near our Australasian mine sites results in predicted dissolved Sb concentrations up to at least 100 mg/L as SbO_3^- (Fig. 6; Ashley et al. 2003). The relatively low levels of dissolved Sb observed in the Macleay River compared to sites nearer the mine (Fig. 2a) is presumably a result of dilution of SbO_3^- and scavenging by phases such as HFO.

Riparian vegetation in the Macleay catchment (e.g. *Persicaria*; Fig. 5a) and algae (Fig. 5b) create pathways for fluvial cycling of Sb, including into invertebrate and vertebrate fauna. On the Macleay floodplain, potential mobility of Sb can occur due to uptake from sediments

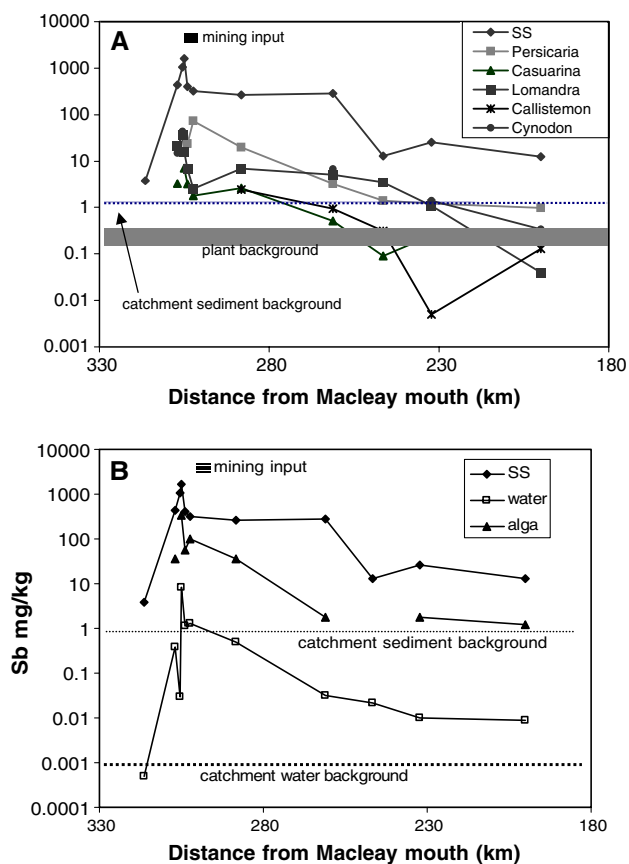


Fig. 5 **a** Plot of Sb contents of ash from five common riparian vegetation species and associated stream sediments (SS) along the Bakers Creek–Macleay River system from the Hillgrove mining area to approximately 100 km downstream. The shaded band labelled “plant background” refers to the typical Sb content of ashed plant material from background (uncontaminated) sites in the Macleay catchment. **b** Plot of Sb contents of dried aquatic algae, and associated stream sediments (SS) and waters along the Bakers Creek–Macleay River system from the Hillgrove mining area to approximately 100 km downstream

into pasture species (Tighe et al. 2005), acid sulphate soil processes and variable flooding regimes, leading to pH and redox changes. The extent of transfer of Sb into grazing animals (cattle), commercial crops, and fish remains unknown in the Macleay catchment.

Sb flux from mineralised areas

Well-defined flow rate and water composition data at the V-notch weir below Progress Junction (Fig. 1a) allows calculation of ca 0.85 mg/s Sb flux from the Globe Hill area. This is at least two orders of magnitude greater flux of Sb than is emerging from any of the tunnels or drillholes on Globe Hill (Fig. 3b). Hence, it is clear that the Sb flux from the area is substantially

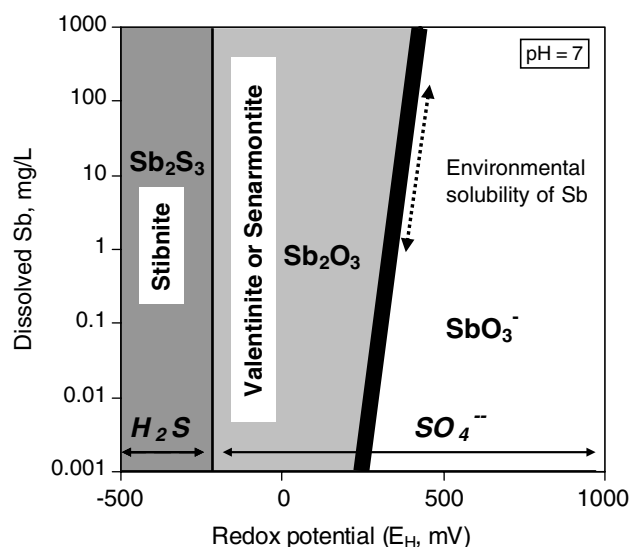


Fig. 6 Solubility of Sb(III) oxides (light shading) to SbO_3^- as a function of redox potential (E_H) at pH=7. This solubility line (heavy black line) was calculated from thermodynamic data in Barin (1989) and Vink (1996), as discussed by Ashley and others (2003). Typical environmental redox potential range, and associated predicted solubilities of Sb, at our Australasian sites is indicated with the dashed arrow, in the sulphate stability field. Stibnite is stable only at very low E_H , in the H_2S stability field (dark shading, left)

greater than that which can be identified from discharging tunnels. A small number of tunnels may have remained undiscovered in the historic mining area, although recent exploration activity has been thorough. We conclude that the relatively high Sb flux in Devils Creek is largely derived from natural dissolution of Sb in the mineralised rocks in the catchment (Fig. 1a). The Sb flux in the main stream entering Endeavour Inlet is ca 14 mg/s (from data in Fig. 1b), about two orders of magnitude higher than the Sb fluxes calculated for mine tunnel discharge waters (Fig. 2b; Wilson et al. 2004b). Hence, Sb discharge flux is predominantly (> 90%) from natural dissolution of Sb in mineralised rocks in these New Zealand examples.

The Sb flux in water down the Macleay River is generally consistent at about 10 mg/s (Fig. 2b). This is similar to some of the higher recorded mine water fluxes (Fig. 2b), and it is possible that the downstream flux represents extremely efficient transport of Sb for 300 km from mine to sea. However, Sb fluxes in Bakers Creek downstream of Hillgrove mine decrease rapidly because of Sb adsorption to HFO (above). Upstream of the junction with Bakers Creek, the Macleay River has Sb flux < 1 mg/s (Fig. 2b). Below the stream junction, the Sb flux rises again because of interaction with stibnite-bearing debris emanating from Bakers Creek (above). Hence, we suggest that the large Sb flux in the Macleay River is mostly an anthropogenic phenomenon.

The dissolved Sb fluxes described in this study are similar in magnitude to those from other mineral deposit-related discharges (Mok and Wai 1990; Mori et al. 1999). Active hot spring systems in northern New Zealand also discharge substantial Sb into the environment, but individual springs such as Champagne Pool (noted for its Sb-rich precipitates) are only discharging Sb at <0.05 mg/s (Giggenbach et al. 1994; Jones et al. 2001). All these mineralization-related fluxes are small compared to industrially-related Sb discharges which can exceed 100 mg/s (e.g., 270 mg/s for Humber River, UK; Neal and Davies 2003). Natural Sb discharges from large rivers also have greater fluxes than those we describe from mineralised rocks, and the Amazon River's 6,000 mg/s Sb flux dominates rock-derived Sb discharges despite abnormally low dissolved Sb concentrations in the river water (Cutter et al. 2001).

In addition to the dissolved Sb flux, the Macleay River has significant particulate Sb flux. The typical annual discharge of the Macleay River is 2–3 million ML (NSW Department of Infrastructure, Planning and Natural Resources, unpublished data). Based on average dissolved Sb contents in water of the lower Macleay River (5 $\mu\text{g/L}$ Sb, above), approximately 1 tonne of Sb is delivered in solution each year to the Pacific Ocean. Average floodplain sediment Sb content is ca 11 mg/kg (Tighe et al. 2005) in a layer at least 10 cm deep across the central floodplain area of 350 km² (Fig. 3). This material has been deposited in flooding events over the past century, yielding a sediment flux of ca 7.2 tonnes Sb/year, considerably higher than the dissolved Sb flux (above). It is estimated that the surface soils of the Macleay floodplain currently contain around 800 tonnes of Sb, and it is predicted that the fluvial, deltaic and estuarine sediments of the lower Macleay will preserve a stratigraphic horizon with anomalous Sb contents into the geologic future.

Conclusions

Dissolution and environmental discharge of Sb from mineralised rocks near Sb–Au mines in New Zealand is dominated by natural groundwater processes, not historic mine-related activity. Sb concentrations are between 3 and 24 $\mu\text{g/L}$ in major streams draining these

historic mine areas, and Sb flux is ca 1–14 mg/s. In comparison, mine-related discharges can exceed 200 $\mu\text{g/L}$ Sb, but volumes are small and mine tunnel discharge water Sb fluxes are only ca 0.001 mg/s. Dissolved Sb is strongly attenuated near some mine tunnels by adsorption on to iron oxyhydroxide precipitates.

Mine water fluxes near the historic/active Hillgrove Sb–Au mine, NSW, Australia, are locally 1–8 mg/s, with dissolved Sb $>10,000$ $\mu\text{g/L}$ Sb, but attenuation by HFO limits environmental mobility of Sb. However, historic discharges of Sb-bearing debris from this mine site has resulted in elevated Sb levels in river sediments (ca 10–100⁺ mg/kg) for ca 300 km downstream. Much of this solid phase Sb is in the form of stibnite, which transforms in river waters to soluble Sb oxides. Dissolution of Sb from stream sediments results in elevated Sb (ca 10–1,800 $\mu\text{g/L}$) in stream waters, and Sb flux to the sea of ca 10 mg/s. Riparian plants and stream algae have absorbed Sb from water and/or sediments, and Sb contents of this biological material is up to ca. 100 mg/kg near the mine site. The Macleay River catchment, draining the Hillgrove mine, is transporting ca 8 tonnes Sb/year, of which $>80\%$ is particulate.

This mineral deposit type is an important local contributor of Sb to the environment, although much of this Sb is mobilised by natural processes or from historic mines, rather than by modern mining activity. Stibnite, the principal Sb phase in these mineral deposits, is readily dissolved by rain and river waters, so solid mine wastes can constitute a long-term source of Sb in the environment after mining has ceased. However, these sources of Sb are small compared to natural Sb discharges from weathering in large rivers such as the Amazon, or those from industrial sources in highly populated areas.

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