CHAPTER 9 - CONCLUSIONS, EXPOSURE ASSESSMENT AND RISK CHARACTERISATION

9.1. SUMMARY OF FINDINGS

This thesis set out to investigate several aspects of the environmental fate and behaviour of Sb, and to a lesser extent As, within the coastal floodplain system of the Macleay catchment in north-eastern NSW, Australia. Several general and specific aims were identified in Chapters 1, 2 and 3. These aims were addressed in subsequent chapters, and can be loosely grouped into the categories of method development, descriptive work, applied investigations into mobility and availability, and soil chemistry.

9.1.1. Method development

In Chapter 4 an appropriate soil digestion method was developed and tested that allowed acceptable analysis of both metalloids by ICP-OES at the University of New England, Armidale. The second aim of this study was to retain as many co-occurring elements in the analysis as possible, with acceptable recoveries and analytical precisions. The microwave aqua regia digestion allowed subsequent analysis of 14 elements, including As and Sb, by ICP-OES at UNE. This made analyses in subsequent chapters possible, and extended the capabilities of routine analysis for the ICP-OES at the University of New England.

Chapter 5 investigated the extension of the ICP-OES analysis into the detection of metalloid concentrations in soil extracts. A sequential extraction scheme that included an oxalate based extract was applied to 2 floodplain soils and critiqued. Acceptable recoveries and precisions were recorded, and some inferences concerning the solid phase fractionation of the metalloids were attempted. It was found that a large proportion of the soil As and Sb was associated with the oxalate extractable phase, which was assumed to quantify the non-crystalline Fe and Al oxide and hydroxide soil phase. The use of an extraction scheme without the oxalate step over-estimated the residual phases of P, As and Sb, which was deemed to be of importance in soils with large amounts of non-crystalline hydroxide phases. The proportion of Sb in the residual phase was also high, which may have implications for predictions of differences in contaminant sourcing between the metalloids. The development and application of this extraction scheme has been one of only a few for Sb to date. The application of both an oxalate based extract and NaOH in the same scheme is the first of its type to be attempted, and shows some potential for fractionation of variable charge surface and organic associations in these soils.

9.1.2. Descriptive work

Chapter 6 extended the analytical development in Chapter 4, and detailed the investigation into metalloid enrichment in the floodplain. The surface and depth distribution of As and Sb within the floodplain was characterised. It was found that approximately 90 % of the floodplain is enriched in As and Sb, and 6 - 8% of the floodplain contains As and Sb levels greater than the current Australian soil environmental investigation guideline values for soil. Variation in surface and depth distributions indicated flood deposition of As and Sb across the major environmental floodplain environments, with the highest accumulation in modern swamp depositional environments. Based on limited data, the highest levels of Sb (in the first 10 cm of swamp soils) were calculated as being deposited over the last 70 - 80 years, which supported the flood deposition - upper catchment dispersion mechanism of Sb enrichment within the floodplain. The higher concentrations of Sb were found to relate to large flood events. The soil enrichment was reflected by pasture uptake (up to 6.4 and 2.2 mg kg^{-1} for As and Sb respectively) and elevated surface water concentrations (up to 10 and 21 times drinking guideline values and 2.9 and 6.9 times freshwater trigger values for protection of 95% of species for As and Sb respectively) of these metalloids. Significant relationships between pasture and total soil levels implied high relative availability in the floodplain compared to grossly contaminated soils.

9.1.3. Applied investigations into mobility and availability

Chapter 7 attempted to elucidate the effects of acid sulfate processes and flooding upon the mobility and availability of As and Sb in 2 soils taken from the modern swamp areas of the floodplain. Following a 20 week glasshouse trial it was found that flooding did increase the uptake of As and Sb into couch and swamp couch (*Cynodon* *dactylon* and *Paspalum distichum*), a relationship that has not been determined for Sb until now. Further increases in As pasture contents in the field implied passive uptake with water availability, while the uptake pattern of Sb under controlled and field conditions was dependent upon the non-crystalline (Fe) hydroxide soil phase and redox conditions (both past and present) ($R = -0.73$). This was the first known attempt to relate Sb availability to probable soil mechanisms controlling mobility.

Changes in the pe and pH of the soil solution could be related to the acid buffering capacity and poise of each soil. Ponded pasture management to reduce ASS discharges in these areas will not produce large changes in redox potential or pH over the short periods practical in the field (i.e. < 20 weeks). While acidic conditions usually increases the binding of metalloids in soils, either of the proposed mechanisms of plant uptake appeared to overcome this limitation, especially in soils with lower proportions of Fe_{ox}. Assuming pH does not decrease too dramatically, an oxidised, active acid sulfate soil appears to reduce the availability of the metalloids to the pasture species examined.

9.1.4. Soil chemistry

Chapter 8 partially addressed the dearth of information on Sb(V) sorption by soils and soil phases. The sorption of Sb(V) by humic acid was found to differ to the only known previous study, showing that > 60 % of added Sb may be sorbed by this phase. The sorption behaviour of Sb(V) by $Fe(OH)_3$ was the first undertaken using this phase. The high (> 95 %) sorption of Sb(V) at most acidic pH values tested indicated this phase is probably controlling the mobility of Sb in soils with significant proportions of such hydroxides. This was supported by the high sorption of Sb(V) across the same pH range by the 2 soils used in Chapter 7, which explained the importance of Fe_{ox} as a controlling variable of Sb availability.

9.1.5. Recommendations

This thesis identified areas requiring further investigations in regards to the environmental behaviour and fate of Sb (and As), and attempted to address some of these in Chapters 5 through 8. The issues not addressed and further work required as a result of this thesis have been detailed within the relevant chapters, and will not be reiterated here. It is of more importance to attempt to address the issue of what the metalloid concentrations in the floodplain mean to the local population and environment. An initial attempt to quantify this using some of the concepts and processes inherent in risk assessment is presented below as an appropriate summation to this project.

9.2. THE FRAMEWORK OF RISK ASSESSMENT

Risk assessment - 'the risk assessment process attempts to estimate the likelihood of an adverse effect occurring in a receiving population due to the presence of contaminants in soil. It is a tool to assist in the decision making process and should not be seen as the only method of determining criteria.' (ANZECC and NHMRC 1992).

Typically risk assessment includes 4 stages.

1. Data collection and evaluation of the chemical condition of the site
2. Toxicity assessment of contaminants
3. Exposure assessment for the population in question
4. Risk characterisation.

These stages are related as shown in Figure 9.1.

Sections of this thesis can be interpreted as addressing and partially addressing points detailed in Figure 9.1. In particular, Chapters 6, 7 and 8 deal with data collection and evaluation. These chapters also examine the release of contaminants from soil, as stated within the exposure assessment section of Figure 9.1. A toxicity assessment is beyond the scope of this thesis, but making some assumptions about exposure and stating the limitations of the assessment can produce a conservative exposure assessment and limited synthesis of this into a risk characterisation.

9.3. EXPOSURE ASSESSMENT

NEPC (1999c) states the minimum number of considerations to be made in an exposure assessment are:

1. Identifying the most significant sources of environmental exposure.

2. Describing the population to be assessed.

3. Describing the basis of the exposure assessment. For example, is exposure measured directly via real time contact of the chemical with the receptor, or is the assessment predictive, using estimates of exposure and availability of the contaminant?

4. Listing the key exposure descriptors to be used.

5. Considering any concerns for multiple or cumulative exposures.

6. Summarising the exposure assessment findings.

A constrained exposure assessment model can be developed, using points 1 through 4 listed above, which is pertinent to the floodplain studies conducted in this thesis. Multiple or cumulative exposures are not considered, and the exposure assessment is summarised in terms of a limited risk characterisation.

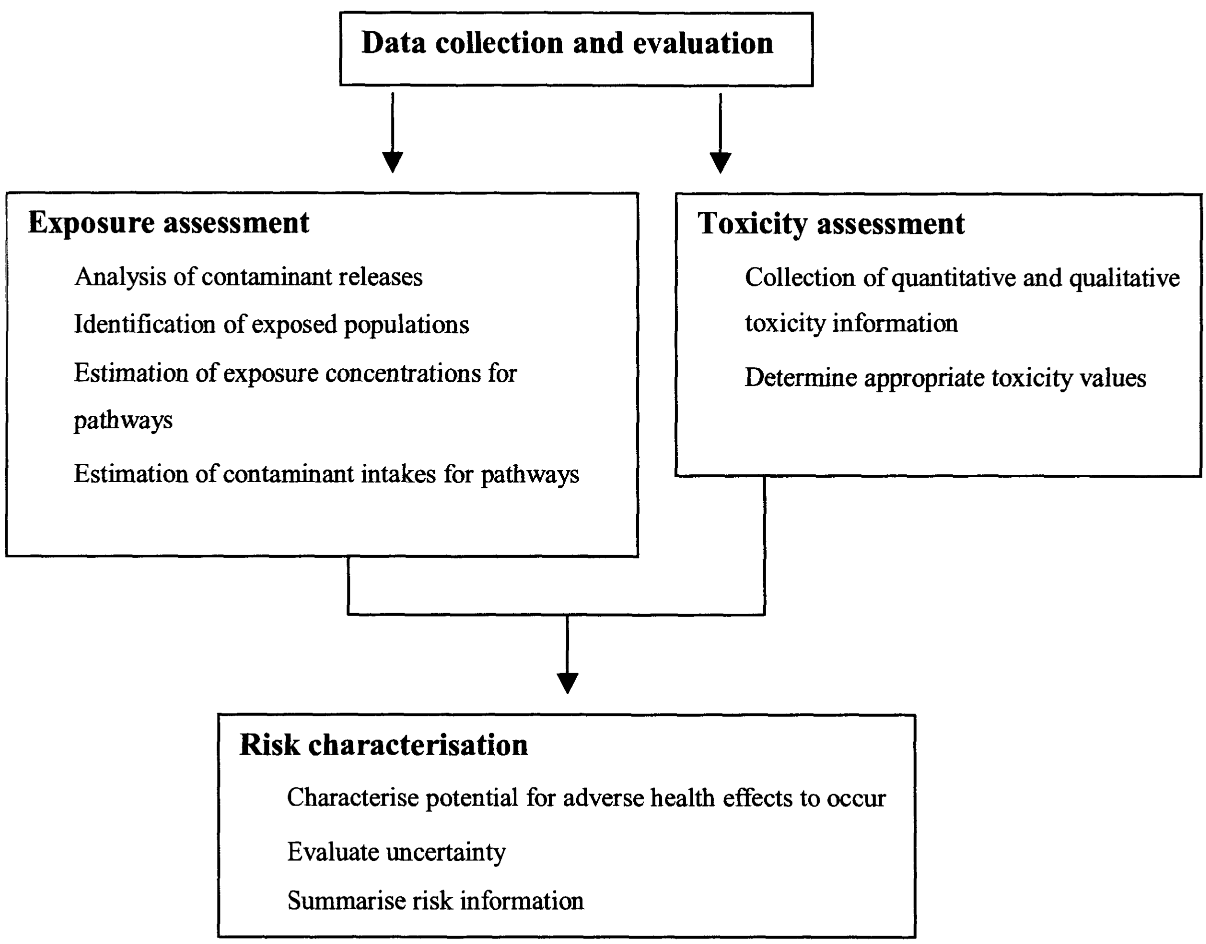

Figure 9.1. The risk assessment model, as adapted from EPA (1989) by ANZECC and NHMRC (1992) and NEPC (1999d).

9.3.1. Sources of environmental exposure

Some pathways, media and receptors of exposure are identified in Figure 9.2.

The limitations that have been imposed on the identification of exposure sources have been based on practical data limitations. These include:

- No consideration of groundwater exposure.
- Limited estimates of exposure via locally grown produce, which may comprise a large proportion of total dietary intake in rural areas.
- No inclusion of aquatic or terrestrial biota as exposure receptors.

These limitations should be addressed in a more comprehensive exposure assessment as part of an overall risk assessment for the area, and may necessitate further data collection and evaluation, for both the concentrations of metalloids in additional exposure pathways, and toxicological data for species to be considered as additional receptors.

9.3.2. The population to be assessed

Two hypothetical populations within the floodplain were chosen for the exposure assessment. These were determined to be the groups within the floodplain with the highest generic exposure, based on land use (Chapter 3), soil metalloid concentrations (Chapter 6), and the potential for surface water consumptive use (Chapter 6). These populations can be represented by:

- Scenario 1: A farmer living in a low-lying, backswamp area. Water for domestic use and consumption is assumed to have the same average metalloid concentrations as the surface water of the Macleay tributaries near these areas, although this is potentially an overestimate, depending on the supply of treated urban water and rainwater to these areas. In the absence of site-specific data, the average availability of As and Sb to pastures under field conditions (Chapter 7) has been used as a surrogate measure of exposure from locally grown fruit and vegetables. Weight is assumed to be 70 kg (ANZECC and NHMRC 1992; EPA 1989; NEPC 1999c).
- Scenario 2: As for scenario 1, but with the exposed individual as a child of 2 - 3 years of age, weighing 13.2 kg (ANZECC and NHMRC 1992; EPA 1989; NEPC 1999c).

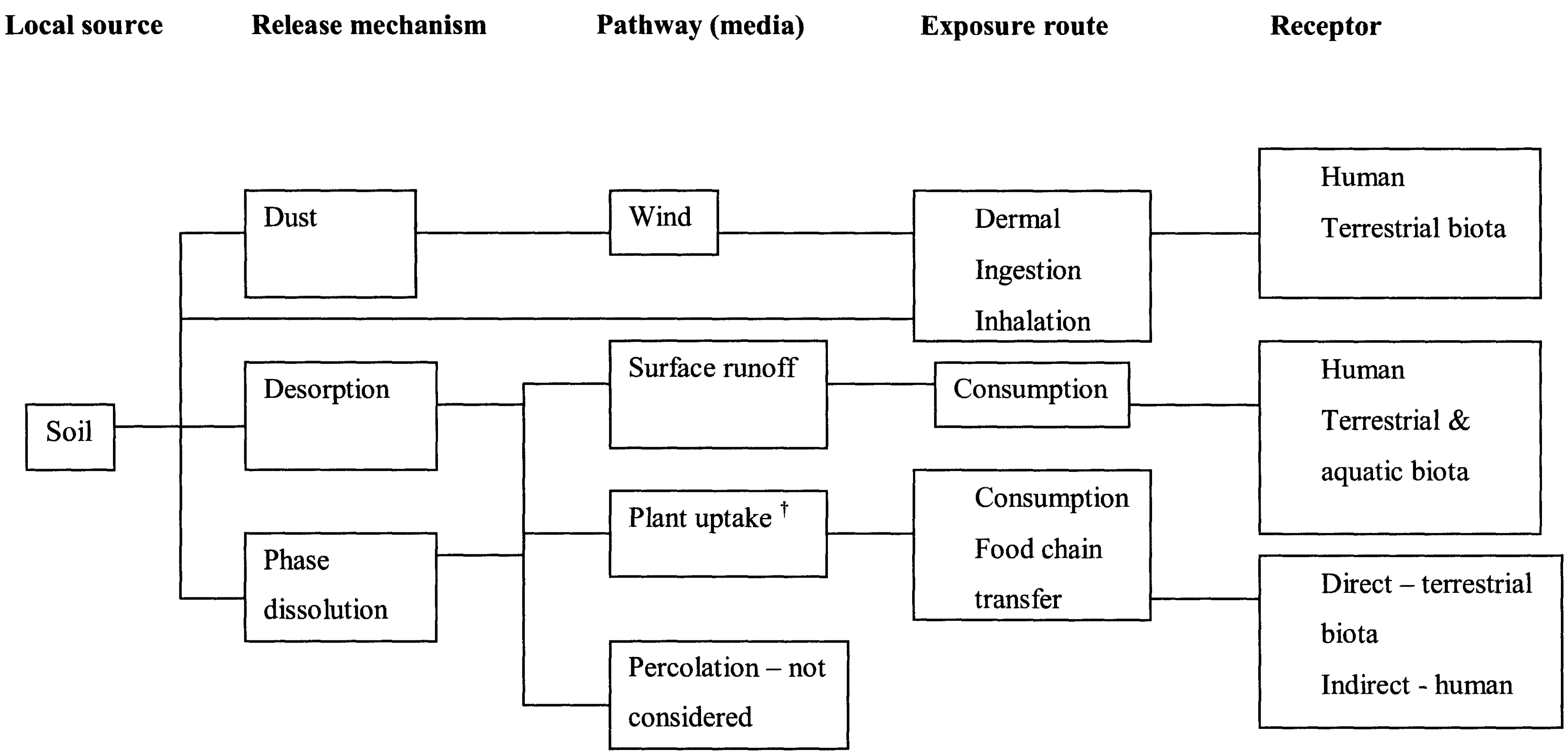

Figure 9.2. A limited model of exposure to soil As or Sb in the floodplain. †Pasture uptake taken as a surrogate for fruit and vegetable exposure.

9.3.3. The basis of the exposure assessment

For this limited assessment, the calculation of the concentrations of As or Sb reaching a receptor has been based on the approach used by ANZECC and NHMRC (1992). Thus, exposure to the metalloids in the floodplain can be expressed as:

Total exposure = BE + Esoil + Ewind + Efoodconsumption + Ewater

Where

BE = background exposure (from all sources)

Esoil = soil exposure

Ewind = wind exposure

Efoodconsumption = exposure from fruit and vegetable ingestion (estimated from pasture uptake).

Ewater = exposure from consumption and contact with water.

Each of these exposure factors may be expressed as:

TEx = Concx × Expx × Biox

Where TEx = total exposure via route x

Concx = Concentration of As or Sb in the exposure media (exposure pathway)

Expx = exposure factor specific for the exposure pathway/amount ingested

Biox = the assumed bioavailability of the metalloid to the receptor

9.3.4. The key exposure descriptors

The key exposure descriptors used in the limited exposure assessment are given in Tables 9.1 through 9.4. The assumptions regarding metalloid concentrations and bioavailability, exposure routes and factors are detailed following each table.

Intake of As and Sb from most food sources has been omitted from the limited exposure assessments. While landholders may grow and harvest a large proportion of their daily intake of fruit, vegetables, poultry products and meat, site specific data on these exposure pathways is not available for the area. A limited estimate of exposure through the consumption of locally grown fruit and vegetables has been included, based in the average pasture uptake values measured under controlled conditions in Chapter 7. This is far from ideal, and the final estimates of exposure given in Table 9.5 are presented with and without the estimates of exposure from this pathway. Some of the assumptions used for exposure of receptors to Sb have been taken from As exposure studies, due to the lack of data.

Table 9.1. Estimates of exposure to As in scenario 1. Assumptions for each exposure pathway are given following the table.

Media	Concentration	Exposure route	Exposure factor	Bioavailability (%)	Total exposure (mg day^{-1})
Soil	16.3 mg kg^{-1} [a]	Ingestion	25 mg day^{-1} [b]	100 (10) [d, e]	4.1×10^{-4} (4.1×10^{-5})
		Inhalation	1 mg day^{-1} [c, d]	100 (10) [d, e]	4×10^{-5} (4×10^{-6})
		Dermal absorption	698 mg day^{-1} [f]	3 [g]	3.4×10^{-4}
Fruits and vegetables	0.21 mg kg^{-1} [j]	Ingestion	201 g day^{-1} [k]	100	0.042
Water	0.011 mg L^{-1} [a]	Ingestion	2.1 L day^{-1} [c]	98 [h]	0.023
		Dermal adsorption	160 L day^{-1} [c]	0.1 [i]	1.8×10^{-3}
				Total exposure	0.068 (0.067)

[a] Given as the average concentrations of As in the modern swamp soils and the Macleay and tributaries surface water.

[b] ANZECC and NHMRC (1992).

[c] 20 m^3 air day^{-1} × 50 μg m^{-3} (Langley *et al.* 2003).

[d] Langley *et al.* (2003).

[e] Based on maximum absorption of As from ingested soil of 100 %, and average absorptions (@ 10 %) from selected animal based studies (ATSDR 2000). Values of exposure using the lower value are shown in the table within brackets.

[f] Mean soil adherence summary data for farmers. Hands: 0.44 mg cm^{-2} × 820 cm^2 = 361 mg. Arms: 0.095 mg cm^{-2} × 2300 cm^2 = 219 mg. Legs: 0.021 mg cm^{-2} × 5500 cm^2 = 118 mg (Langley *et al.* 2003).

[g] Ehlers and Luthy (2003).

[h] Owen (1990).

[i] 0.1 % absorption was taken as an estimate for daily washing activities. This assumes an intake of 160 ml.

[j] Based on an average of 1.28 % of total soil As present in pastures (averaged glasshouse trial results, Chapter 7).

[k] Assuming 127 g of fruit and 275 g of vegetables consumed on average (Langley *et al.* 2003), with an estimate of 50 % of produce being locally grown, and a default value of 100 % bioavailability.

Table 9.2. Estimates of exposure to As in scenario 2. Assumptions for each exposure pathway are given following the table.

Media	Concentration	Exposure route	Exposure factor	Bioavailability (%)	Total exposure (mg day^{-1})
Soil	16.3 mg kg^{-1} [a]	Ingestion	100 mg day^{-1} [b]	100 (10) [d, e]	1.63×10^{-3} (1.63×10^{-4})
		Inhalation	250 µg day^{-1} [c, d]	100 (10) [d, e]	4.1×10^{-6} (4.1×10^{-7})
		Dermal absorption	1074 mg day^{-1} [f]	3 [g]	5.3×10^{-4}
Fruits and vegetables	0.21 mg kg^{-1} [j]	Ingestion	101 g day^{-1} [k]	100	0.021
water	0.011 mg L^{-1} [a]	Ingestion	0.66 L day^{-1} [c]	98 [h]	7.1×10^{-3}
		Dermal adsorption	160 L day^{-1} [c]	0.1 [i]	1.8×10^{-3}
				Total exposure	0.032 (0.031)

[a] Given as the average concentrations of As in the modern swamp soils and the Macleay and tributaries surface water.

[b] ANZECC and NHMRC (1992).

[c] 5 m^3 air day^{-1} × 50 µg m^{-3} (Langley *et al.* 2003).

[d] Langley *et al.* (2003).

[e] Based on maximum absorption of As from ingested soil of 100 %, and average absorptions (@ 10 %) from selected animal based studies (ATSDR 2000). Values of exposure using the lower value are shown in the table within brackets.

[f] NEPC (1999c).

[g] Ehlers and Luthy (2003).

[h] Owen (1990).

[i] 0.1 % absorption was taken as a conservative estimate for daily washing activities. This assumes an intake of 160 ml.

[j] Based on an average of 1.28 % of total soil As present in pastures (averaged glasshouse trial results, Chapter 7).

[k] Assuming 121 g of fruit and 81 g of vegetables consumed on average (Langley *et al.* 2003), with an estimate of 50 % of produce being locally grown, and a default value of 100 % bioavailability.

Table 9.3. Estimates of exposure to Sb in scenario 1. Assumptions for each exposure pathway are given following the table.

Media	Concentration	Exposure route	Exposure factor	Bioavailability (%)	Total exposure (mg day^{-1})
Soil	13.8 mg kg^{-1} [a]	Ingestion	25 mg day^{-1} [b]	100 (10) [d, g]	3.5×10^{-4} (3.5×10^{-5})
		Inhalation	1 mg day^{-1} [c, d]	100 (10) [d, g]	1.4×10^{-5} (1.4×10^{-6})
		Dermal absorption	698 mg day^{-1} [h]	3 [e]	2.9×10^{-4}
Fruits and vegetables	0.12 mg kg^{-1} [j]	Ingestion	201 g day^{-1} [k]	100	0.023
Water	0.005 mg L^{-1} [a]	Ingestion	2.1 L day-1 [c]	98 [f]	0.010
		Dermal adsorption	160 L day-1 [c]	0.1 [I]	8.0×10^{-4}
				Total exposure	0.034 (0.034)

[a] Given as the average concentrations of Sb in the modern swamp soils and the Macleay and tributaries surface water (Chapter 6).

[b] ANZECC and NHMRC (1992).

[c] 5 m^3 air day^{-1} × 50 μg m^{-3} (Langley *et al.* 2003).

[d] Langley *et al.* (2003).

[e] Ehlers and Luthy (2003).

[e] Owen (1990).

[f] Based on maximum absorption of As from ingested soil of 100 %, and average absorptions (@ 10 %) from selected animal studies (ATSDR 2000). Values of exposure using the lower value are shown in the table within brackets.

[g] Mean soil adherence summary data for farmers (Langley *et al.* 2003).

[h] 0.1 % absorption was taken as a conservative estimate for daily washing activities. This assumes an intake of 160 ml.

[i] Based on an average of 0.84 % of total soil Sb present in pastures (averaged glasshouse trial results, Chapter 7).

[j] Assuming 127 g of fruit and 275 g of vegetables consumed on average (Langley *et al.* 2003), with an estimate of 50 % of produce being locally grown, and a default value of 100 % bioavailability.

Table 9.4. Estimates of exposure to Sb in scenario 2. Assumptions for each exposure pathway are given following the table.

Media	Concentration	Exposure route	Exposure factor	Bioavailability (%)	Total exposure ($mg\ day^{-1}$)
Soil	13.8 $mg\ kg^{-1}$ [a]	Ingestion	100 $mg\ day^{-1}$ [b]	100 (10) [d, e]	1.38×10^{-3} (1.38×10^{-4})
		Inhalation	250 $\mu g\ day^{-1}$ [c, d]	100 (10) [d, e]	3.5×10^{-6} (3.5×10^{-7})
		Dermal absorption	1074 $mg\ day^{-1}$ [f]	3 [g]	4.4×10^{-4}
Fruits and vegetables	0.12 $mg\ kg^{-1}$ [j]	Ingestion	101 $g\ day^{-1}$ [k]	100	0.012
Water	0.005 $mg\ L^{-1}$ [a]	Ingestion	0.66 $L\ day^{-1}$ [c]	98 [h]	3.23×10^{-3}
		Dermal adsorption	160 $L\ day^{-1}$ [c]	0.1 [i]	8.0×10^{-4}
				Total exposure	0.018 (0.017)

[a] Given as the average concentrations of As in the modern swamp soils and the Macleay and tributaries surface water.

[b] ANZECC and NHMRC (1992).

[c] 5 m^3 air day^{-1} × 50 $\mu g\ m^{-3}$ (Langley *et al.* 2003).

[d] Langley *et al.* (2003).

[e] Based on maximum absorption of As from ingested soil of 100 %, and average absorptions (@ 10 %) from selected animal studies (ATSDR 2000). Values of exposure using the lower value are shown in the table within brackets.

[f] NEPC (1999c).

[g] Ehlers and Luthy (2003).

[h] Owen (1990).

i 0.1 % absorption was taken as a conservative estimate for daily washing activities. This assumes an intake of 160 ml.

[j] Based on an average of 0.84 % of total soil Sb present in pastures (averaged glasshouse trial results, Chapter 7).

[k] Assuming 121 g of fruit and 81 g of vegetables consumed on average (Langley *et al.* 2003), with an estimate of 50 % of consumed produce being locally grown, and a default value of 100 % bioavailability.

9.3.5. A limited risk characterisation

Without complete exposure and toxicity assessments a complete risk characterisation cannot be undertaken. Within the limitations already specified, however, the calculated exposures for both scenarios can be compared to the Acceptable Daily Intake (ADI) of As and the tolerable Daily Intake (TDI) of Sb (Table 9.5).

Table 9.5. Estimated total exposures (mg kg^{-1} day^{-1}) for scenarios 1 and 2, based on an average body weight of 70 kg (scenario 1) and 13.2 kg (scenario 2) and comparisons with the ADI/TDI values for As and Sb (mg kg^{-1} day^{-1}). Exposures with and without the dominant estimated exposure route of local produce ingestion are given.

		As	Sb
Scenario 1	with local produce intake	9.7×10^{-4}	4.9×10^{-4}
	without local produce intake	3.7×10^{-4}	1.6×10^{-4}
Scenario 2	with local produce intake	2.4×10^{-3}	1.4×10^{-3}
	without local produce intake	8.3×10^{-4}	4.5×10^{-4}
	ADI or TDI [a]	2.0×10^{-3}	6.0×10^{-3}

[a] The ADI of As is as given by WHO (1989). The TDI of Sb is as given by WHO (2003).

Table 9.5 shows that with the assumptions of local produce intake used in the exposure assessment, the total exposures for both As and Sb in scenario 1 are 48 and 8 % of the ADI and TDI for these metalloids, respectively. Exposure is greatest in scenario 2, with the 2 - 3 year old child exposed to 1.2 times the ADI of As, but only 23 % of the TDI of Sb.

When the dominating exposure pathway of consumption of locally grown fruits and vegetables is omitted, the risk (as indicated by total exposures) in both scenarios decreases. For As, the total exposure in scenario 1 decreases to 19 % of the ADI, and to 42 % of the ADI in scenario 2. Exposure to Sb in scenario 1 decreases to 3 % of the TDI, and exposure in scenario 2 decreases to 8 % of the TDI.

While the above exposure assessment and relative risk characterisation is based on very limited data, it indicates both generic and site-specific data shortfalls that need to be addressed. These include:

- The determination of the As and Sb concentrations within locally grown produce, including fruits, vegetables, poultry, dairy, seafood and meat products.
- The proportion of total dietary intakes attributed to the above-mentioned categories.

Actual local sources of water for domestic uses, particularly those households or localities that may source such water from the trunk Macleay or its tributaries.

In addition to the above, the potential use of, and metalloid concentrations in, groundwater.

Determinations of the availability of both As and Sb within the exposure scenarios and pathways presented.

Confirmation of the inhalation, ingestion, and dermal absorption exposure factors used in Tables 9.1 through 9.4.

The estimated exposures listed in Tables 9.1 – 9.5 do not include any estimates of background exposures to As or Sb. In particular, exposures due to the range of dietary components not included in the assessment may have a significant effect upon the final estimates of exposure.

The exposure scenarios used above are very limited. While they are assumed to be generally representative of the highest risk populations within the floodplain, there are several factors that have not been considered. These include:

Individuals receiving high background exposures of either metalloid due to a high proportion of certain foodstuffs in the diet, for example, local seafood or certain vegetables such as tubers.

Individuals displaying pica or soil eating habits.

Individuals with a disproportionate exposure via one pathway, such as quarry or construction workers exposed to high levels of dust.

Scenarios of exposure for aquatic and terrestrial biota, including particularly sensitive organisms, rare or endangered species, and commercial aquaculture and agriculture produce and stock.

Despite these limitations and assumptions, the exposure assessment indicates that the potential risk of exposure in at least one of the scenarios may be high. Particularly, the exposure of a child to As under these circumstances may be unacceptable (providing the exposure assumptions are sound). Some simple management practices that may already be in place in most areas can be used to limit the risk. In order of estimated importance, these are:

1. Limiting the dietary intake of locally grown produce, particularly vegetables such as spinach or root vegetables known to accumulate As.
2. Using reticulated or rainwater for domestic use.
3. Where possible, limiting dermal exposure to soil and water. For example, in the case of a farmer, this may mean wearing long sleeves and pants while working.

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