Wetlands for minewaters

Constructed wetland systems for biological treatment
of mining wastewaters in western Tasmania

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Dedicated to honour the Children

Misha, David & Anunda

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Michael J. Lichon, B.Sc.(Hons).

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy, School of Plant Science, University of Tasmania, Hobart, Australia

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Declaration

This thesis contains no material which has been accepted for a degree or diploma by the University or any other institution, except by way of background and comparative information as duly acknowledged in the Thesis. To the best of the Candidate's knowledge and belief no material included in the thesis is previously published or written by another person except where due acknowledgment is made in the text of the Thesis. All opinions and personal observations are mine except where stated otherwise. Details of public events and widely accepted knowledge are not necessarily referenced. Material is presented in good faith as a true account of this original multidisciplinary research project.

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Michael Lichon
Hobart, Australia, 20 November 2000

Abstract

Mining and lime–treated mineral processing wastewaters from the Hellyer Zn/Pb Mine in western Tasmania, bearing Pb after tailings dam treatment, pass through a series of pilot wetlands. This field–based study focuses on identifying mechanisms behind wetland removal of residual Pb from wastewaters, performance improvement and catchment issues. The background, aims and significance of the industry–sponsored study are outlined. The study site for this applied research project is described and defined. The environmental uncertainties and practical challenges dictated the need for field–based observations supplemented by limited scope experimentation. Problems with sampling are identified and overcome by innovation.

Surprisingly, wastewater Pb sinks in wetlands almost exclusively in the form of PbS in the mud. The 50% suspended fraction of Pb uptake is removed from wastewaters by sedimentation, dependent on quiescent wetland residence time.

Several native emergent wetland plants suitable for treatment of mine wastewaters are identified using several criteria, bulk and experimental plantings. These include *Eleocharis, Juncus, Restio* and *Triglochin*. The wetland plants contribute little to direct removal of Pb from wastewaters; rather, provide structural stability and serve as *in situ* photosynthetic generators of organic matter. Falling into the mud, the organic matter maintains a decomposer–rich, low–Eh anaerobic mire, and fuels a microbial consortium including three genera of sulphate–reducing bacteria (SRB). By dissimilatory respiration, SRB reduce sulphate and thiosalts diffusing into the mud from the wastewaters to H_2S. The "dissolved" (filterable) 50% fraction of wastewater Pb uptake precipitates as PbS by chemical demand of sulphide acting on various complexed and colloidal forms of Pb present in the wastewater stream. This continues to a lesser degree downstream into the catchment with streambed colonisation by SRB consortia.

Wetland operating parameters are measured and evaluated. Key changes to minesite operation and wetland management, including optimising conditions for maximum SRB activity, waste co–treatment and improving wetland hydrology, are implemented or recommended to enhance wetland treatment performance. The river system affected by mine operations is examined applying principles of total catchment management. Catchment areas need a multidisciplinary approach and cooperative, proactive management by stakeholders to minimise disturbance, degradation and water quality problems and apply remedial strategies.

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Acknowledgments

Publications, Lectures and other project outcomes.

From this work has resulted the following:

Lichon MJ (1992) Lecture: "Behaviour of lead in the constructed wetland at the Hellyer Mine site", 24 March 1992, to the Acid Mine Drainage Working Group at Que River site.

Lichon MJ (1992) Lecture: "Environmental management of effluent at the Hellyer Mine site, a case study", 4 August 1992, at *The second forum on mineral development and the environment in western Tasmania; "The effect of mining on the West Coast: pollution, its causes and its cure"*, Geology Department, University of Tasmania, Hobart.

Lichon MJ (1992) Lecture: "What's a Chemist doing in Plant Science?", 1 September 1992, Postgraduate Seminar, Department of Plant Science, University of Tasmania, Hobart.

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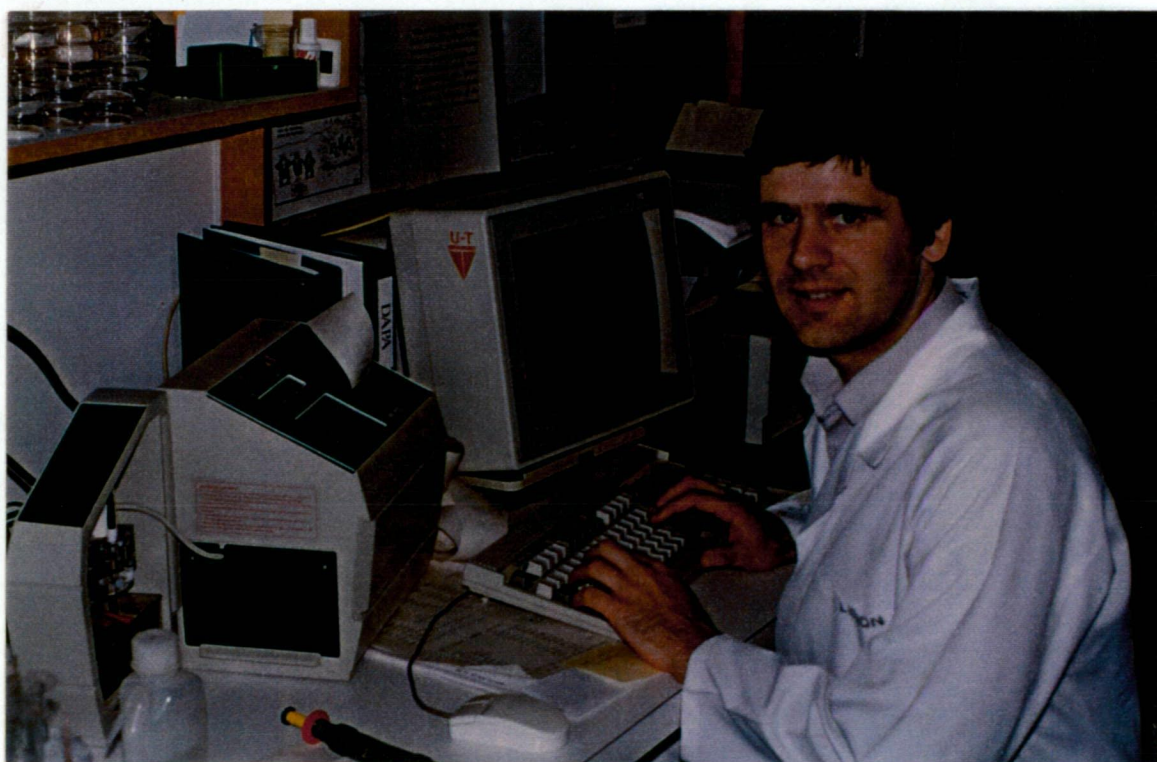
Figure 1: The writer performing ASV determination of Pb in filter cakes.

Figure 2: Aerial photograph of Hellyer wetland & pond treatment system and tailings dam. East to top of page; Scale approx. 1:7000.

Chapter 1: Introduction

1.1 Wetlands for treatment of mining effluent

In recent times, both natural and constructed wetlands have been trialled and used in many parts of the world for treatment of municipal, agricultural and industrial wastewaters (Hammer 1989, Reed *et al.* 1995). Typically these have been operated on the basis of poor understanding other than the outcome of water purification. Primarily used for removal of biological and nutrient pollutants, it was discovered wetlands also reduce metal loading of wastewaters. From the late 1980s the deliberate application of wetland systems has extended to treatment of point source mining wastewaters. Wetlands are emerging as variously effective, low-cost, easily operated, long term alternatives for mining wastewater treatment (Kelly 1988, Ritcey 1989, Sengupta 1993). Reed *et al.* (1995) estimate over 1000 managed wetland treatment systems are in operation worldwide. In Tasmania there are now several mine and mineral processing sites with operating wetland areas for wastewater treatment, at Cleveland Sn since 1988, Que River Zn-Pb since 1988, Hellyer Zn-Pb since 1989, Henty Au since 1992, Beaconsfield Au since 1990, Comalco Al since 1996, and at TEMCO Mn since 1991 ; and others currently on trial (Mt Lyell Cu since 1996) or under consideration (Parish 1996). In view of the history and politics (Section 1.3 and 1.4) of Tasmania in relation to environmental matters, these serve in no small part as public relations foci. The site engineering plans for one of these wetland systems is known to be titled "Ornamental Lagoons", indicating the aesthetic public relations exercise aspect ranks significantly alongside the wastewater treatment outcome in importance. Indeed many of these companies offer site tours to public groups in which the wetland treatment systems feature prominently. There is evidently more than one agenda involved in using wetland treatment. The attractive idea of using nature to remediate man's damage from exploitation, a solution being visible in operation, and mending the rift between sectors of society are not lost on me. However, the pragmatic focus of this work is to gain further understanding into the working mechanisms of wastewater treatment in an operating pilot wetland system, determine means of performance improvement and better site management practice, and examine broader catchment issues.

1.2 The project

In late 1990, Bob Reid from Aberfoyle Resources approached Emeritus Prof. Bill Jackson with questions about how the newly created pilot wetland functions in removing heavy metals from mine effluent at their Hellyer mine, and how its effectiveness may be improved. The idea of using wetlands was based on the latest overseas knowledge and was constructed using information from Ritcey (1989) and current work in NSW by Dunbabin (1989). Speculation was that plants directly take up the metals, and the root zone oxygenation of the mud promoted co-precipitation of metals with hydroxy compounds of Fe and Mn. Together with Dr Ron Crowden, they set up the project as a Ph.D. study under an Australian Postgraduate Research Award (Industry) at the Plant

Science Department of the University of Tasmania, under the initial working title *Chemical nature of metal sequestering processes on plant surfaces.*

The position of the candidate researcher was advertised as vacant in the print media, to which I successfully applied on the basis of demonstrated research and ability to independently undertake the project. The financial input consisted of some $60000 income support over $3\frac{1}{2}$ years from the Commonwealth, Aberfoyle Resources project spending allocation of $21000 in cash over 3 years for equipment, vehicle use etc., and $18000 in kind for accommodation, site works, assays etc. nominally over 3 years (this would have been exceeded in reality), and infrastructure support by the Department and the University. The construction cost of the two wetlands (Figure 2; 0.5 Ha OW "Old Wetland" and the 1 Ha NW "New Wetland") exceeded $300000. Other forms of support came from generosity or cooperation as listed in the Acknowledgments.

1.2.1 Aims of the study

The aim of the project evolved from the initial working title to three principal aims: 1: Investigations to find the mechanisms of metal removal from treatment waters passing through the wetland system, then 2: To research into possibilities for improving treatment performance, and 3: To examine the implications for broader catchment management of the wetland treatment. It became clear a multidisciplinary approach would be required, and learning new skills and knowledge in the fields with which I was less familiar.

Mine management was keen for feedback as to whether to construct a further 9 Ha of wetland systems or use alternative technology to treat the excess discharge. This work is of interest to the wider mining industry, as wetlands have possible future applications at other mines in Tasmania and elsewhere.

1.2.2 Project area location

Tasmania is the southernmost island State of Australia, located in the mid latitude cool temperate westerly winds known as the "Roaring Forties". The Hellyer mine is in the relatively unpopulated western Tasmania (Figure 1.1) some 6 hours drive from Hobart. The basic layout of the mine lease is shown in Figure 1.2, adjacent to the junction of the main arterial road of the west coast, the Murchison Highway, and the newly opened Cradle Mt Link Road connecting to the Cradle Mt-Lake St Clair National Park (World Heritage wilderness) some 25 km to the east. Western Tasmania is an important mining area for Australia, with numerous metal sulphide ore deposits associated with Cambrian Mt Read volcanic belt. The Hellyer mine is sited to the northern end of the complex mineralisation belt (Figure 1.3). The Hellyer deposit is mined and treated to extract Zn, Pb, Cu and Ag concentrates. The tailings contain further metal values including Au. Overflow from the tailings dam containing residual Pb is treated by two pilot scale wetlands (aerial photo, Figure 2) that are the focus of this study. The study area catchment empties into the Que and Huskisson Rivers, then into the Pieman system to the ocean. Further details and descriptions of the study site may be found in Chapter 3.

Figure 1.1: Location of the Hellyer mine
adapted from Koehnken (1992) and Miedecke (1988)

LEGEND

—— Catchment boundary

⚒ Mining site

⌖ Power Station

Monitoring Sites:

★ Lakes

● Tributaries

Produced by TASMAP

Figure 1.2: Basic layout of the mine lease
adapted from Miedecke (1988)

Figure 1.3: A: The complex surface geology around the project area for Legend refer to Figure 1.3 B. adapted from GST (1986)

Figure 1.3: B: Legend to geology Figure 1.3 A.

QUATERNARY — Qu

- Qa — Alluvium, swamp deposits.
- Qg — Glacial deposits, mostly till.

TERTIARY

- Tb — Basalt.

DEVONIAN

- Ddl — Dolerite

EARLY ORDOVICIAN – LATE CAMBRIAN

- €Oo — Siliciclastic conglomerate and minor sandstone of Owen Conglomerate (=Denison Group).

CAMBRIAN

- €p — Quartz-feldspar porphyry
- €ps — Felsic intrusive, commonly spherulitic and flow-banded, feldspar-quartz-phyric.

WEST OF HENTY FAULT ZONE

DUNDAS GROUP

CAMBRIAN

- €p — Quartz-feldspar porphyry.
- €ps — Felsic intrusive, commonly spherulitic and flow-banded, feldspar-quartz-phyric.
- €dg / €dt — Lithicwacke with interbedded siltstone and mudstone and intercalations of felsic tuff (€dt).
- €dt — Felsic tuff, generally quartz-feldspar-phyric, often well bedded, with pumice clasts in some cases.
- €ds / €de — Dominantly shale, siltstone and mudstone, generally black pyritic, with basal lenses of epiclastic agglomerate (€de).
- €dba / €db — Basaltic lavas and breccias, including pillow lavas with inter-pillow chert.
- €da — Andesitic lavas, breccias and tuffs.

€d

- €da / €dba / €de / €dm / €dlf — Epiclastic breccias and grits with clasts of basalt, andesite, felsic lava and massive sulphide (€de). Intercalations of andesitic volcanics (€da), vesicular basaltic-andesitic lava (€dba), flow-banded spherulitic felsic lava (€dlf) and massive sulphide shown.
- €dlf — Felsic lava, generally flow-banded and spherulitic, feldspar-quartz-phyric.
- €dbal / €dal / €dbl / €dtv — Lower sequence of basaltic and andesitic lavas, breccias and tuffs. Some basaltic (€dbl) and andesitic (€dal) units shown. Some intercalations of felsic tuff (€dtv)
- €dt / €dtv — Felsic tuff with intercalations of fine grained vitric tuff and minor felsic lavas (€dtv).
- €dg — Lithicwacke sandstone, commonly micaceous, with interbedded siltstone, felsic tuff and minor basaltic-andesitic volcanics.

WEST AND SOUTH OF MT CHARTER

- €p — Quartz-feldspar porphyry intrusives with possible minor lavas and tuffs

€d

- €ds / €dtv — Dominantly black shale and siltstone with intercalations of felsic vitric tuff (€dtv).
- €dlf / €dlm — Felsic lava, mostly feldspar-phyric, massive to vesicular, with zone of flow breccia and epiclastic rocks indicated (€dlm).
- €dg / €dgm — Dominantly micaceous lithicwacke with interbedded siltstone.
- €dgt — Dominantly tuffaceous lithicwacke with interbedded siltstone.

EAST OF HENTY FAULT ZONE

FARRELL-MURCHISON SEQUENCE

- €f — Slate, sandstone and tuff sequence of Farrell Slates.

TYNDALL GROUP CORRELATES

- €p — Quartz-feldspar porphyry intrusive
- €ps — Felsic intrusive, commonly spherulitic, feldspar-quartz-phyric.

€t

- €tc — Volcaniclastic conglomerate with minor sandstone and siltstone
- €tt / €tl — Felsic tuff and agglomerate generally quartz-feldspar-phyric, with intercalations of felsic lava (€tl).
- €ts — Interbedded lithicwacke and siltstone

OVERPRINTS AND MINERALIZATION

- pyr — Alteration in volcanic rocks, usually with strong schistosity. ser = sericite, pyr = pyrite
- Area of strongly cleaved or disrupted rocks, usually associated with fault zones.
- PQ — Massive sulphide lens with mine designation where applicable.
- Ba — Barite.
- Geological boundary — accurate or approximate.
- Geological boundary — inferred or concealed.
- Fault — accurate or approximate (dip indicated).
- Fault — inferred.
- Fault — concealed.
- Major fold—axial surface trace.
- Early fold.
- Later fold.
- Unconformity.
- Strike and dip of bedding—facing known; overturned; facing unknown; vertical.
- Banding in volcanic or igneous rock; vertical banding.
- Strike and dip of cleavage; vertical cleavage.
- Minor fold with plunge—antiform, synform, unspecified.
- Operating mine, prospect or abandoned mine.
- Fossil locality.

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1.3 Mining history of Tasmania

This section highlights the historical importance of mining to Tasmanian economic life, which continues to dominate the west in particular.

Aboriginal Tasmanians were the first miners, respectful of the land and modest in scale of operation (Plomley 1993, Ryan 1982). They extracted stone, namely chalcedony, hornfels, quartzite and spongolite. Spongolite gave the sharpest edge for tools, and came from areas of the west and northwest parts of the State. Ochre was the other main earth resource, mined in trench excavations from sites at St Valentines Peak, Mt Housetop, Mt Vandyke and the Gog Range. These resources were traded amongst tribes across Tasmania.

In the early 1800s the west coast was visited by whalers, sealers and other mariners often by shipwreck. A penal station was set up on Sarah Island in Macquarie Harbour (1821-1834) as a receptacle for the scum of the convict population (Smith 1985) imprinting white contempt for the area. Piners plundered ancient Huon pines from the banks of the lower reaches of major rivers, the easily worked timber being prized for rot-resistance and boat building. Surveyors westwardly seeking pack trail, and later, railway, routes from the west to population centres discovered the river systems and peaks of the area (Binks 1989, Crawford 2000).

In the later 1800s pioneers began to realise Tasmania's mineral prospectivity. Modern mining began in the west coast with the discovery of the Mt Bischoff tin deposit near Waratah in 1871; and despite increasingly difficult terrain and vegetation, miners moved south. Major mines of the Pieman catchment include Rosebery Zn-Pb (1893-present), Hercules Zn-Pb (1894-1987), North Farrell Pb-Ag (1902-1964), Cleveland Sn (1908-1914, 1968-1986), Renison Sn (1965-present), Savage River Fe (1968-present), Que River Zn-Pb-Ag (1980-1991) and Hellyer Zn-Pb-Cu-Ag (1988-present). Many other short-lived and smaller operations extracted Zn, Pb, Ag, Cu, Au, Os, Ir, Sn, and Fe in the area.

The adjacent Mt Read mineralisation and mining area to the south lies in the King River catchment. Here the legacy of 100 years of unfettered mining and smelting around Queenstown has denuded the Mt Lyell hills and surrounds of once magnificent King Billy pine rainforest vegetation and rendered a major river system dead and choked with tailings (de Blas 1994, Carbon 1995, Crawford 2000, Winterhalder 2000). The length of the lower King has over 100 million tonnes of acid-forming tailings bearing heavy metals, including a 250 Ha delta at its Macquarie Harbour mouth. Of former superlative beauty akin to the Gordon River, where tourist boat cruises annually show 74000 visitors the World Heritage values of the area, the King River is now a toxic wasteland (Carbon 1995, Crawford 2000). Furthermore the aquaculture and fisheries at Macquarie Harbour and beach recreation at Strahan have been adversely affected by the turbidity, acidity and heavy metals.

In contrast to the King, the Pieman River catchment is relatively unpolluted (Koehnken 1992). This is despite a similar length of mining history (for

example, three major mines operated for a similar period to Mt Lyell) and the operation of five major mines during this study, Savage River, Renison, Rosebery, Que River and Hellyer.

The Hellyer deposit was discovered and developed during the life of the Que River mine on the same lease. As the Hellyer ore was very fine grained, it could not be processed by existing facilities at Rosebery as was the case for the Que ore. Therefore a new onsite processing mill was constructed after successful pilot trials using modified equipment at Cleveland. The tailings are pumped as a slurry to a settling and storage dam. Half of the water is recycled for use in the mill, the remainder treated prior to discharge into the Que River, Huskisson and Pieman catchments. In the longer term, no new orebodies have been found for future mining in the lease. However, it is likely the Hellyer tailings will be reprocessed to recover further metal values.

1.4 Political setting, cultural attitudes and the environment

The Hellyer mining activities, and this research project in particular, have not operated in a social vacuum. Political and cultural background and pressures, both real and perceived, are highly pertinent to anyone undertaking this type of study. For one to enter this research field with scant awareness or regard to the scale and pervading influence of these matters could be considered naïve, indeed foolish. Influences of local attitudes operate on and pervade through the viability of commencing such a project, on the ground during fieldwork, in collaborations, at the research base, the mine management responses to recommendations, and in the presentation and publication of results. More fundamentally, the social history has helped shape the very landscape.

The Aboriginal Tasmanians lived with the land and its animals in a culture of sacred respect. Their most environmentally destructive activity was the use of spot fires to encourage new grass growth in woodlands for the benefit of native game species they hunted (Horton 2000). Over thousands of years this practice substantially changed the vegetation of inhabited areas reducing rainforest in favour of fire-tolerant and fire-promoting Eucalypt communities (Williams 1983, Reid et al. 1999). With white invasion, there has been much loss of knowledge, wisdom, ancient "Dreaming" and customs, as Aboriginals became persecuted and genetically and culturally dispersed over generations. In contrast to undiluted Aboriginal culture, the white military invaders with their convicts came with a psyche of fear, ignorance and hostility towards this land, its vegetation, animals and human inhabitants (Horton 2000).

It has been argued that a war of genocide was waged against the Aboriginals whose culture was so foreign to whites as to be unrecognisable, seen as an unacceptable challenge to their own ways that was to be deleted, or at least removed from sight to the smaller islands (Robson 1997). Right from the start, pioneer and convict society was one based on violence (Robson 1997) manifesting in relationships among individuals, classes and genders as well as

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races, and in regard and treatment of the land (Horton 2000). The white pioneers cleared and burnt blanket areas as fast as they were able, radically changing the landscape and vegetation, to "tame" what seemed to them a hostile, and mostly fruitless land. One consideration in granting land parcels to settlers was their ability to clear it for primary production (Robson 1997). Trackcutters, surveyors and prospectors used uncontrolled wildfire to make easier their progress across the alien-vegetated land from which they sought wealth (Binks 1989).

It appears white Tasmanians are still to come to terms with the land. Today, some of these historical matters have changed little, with less than 1% of fires incidence accounted for by natural cause (Bowman & Jackson 1981). Forestry authorities maintain this 10000-fold increase over natural fire influence is sustainable (Lichon 1998). While mining is inherently not a sustainable activity, forestry, fishing and agriculture have the potential to be managed as such. Industries undertake these activities unsustainably, as though they were tree-mining, sea-mining and soil-mining from unlimited resources, locally condoned by what still appear as pioneer attitudes. Consumption and waste in all these sectors, though perhaps recently improving, is still unsustainable by any measure, is typical of contemporary economic rationalist paradigms (Routley & Routley 1973, Pybus & Flanagan 1990, White 1997, Flannery 1998, Suzuki & Dressel 1999, Horton 2000). Native species extinctions and endangerment (e.g. thylacine, emu, several native fish) and land degradation seem with little doubt to be caused by the new land uses and introduction of feral species. Areas set aside as National Parks in Tasmania largely represent "reject" land deemed to be of little use for resource extraction on account of poor topography, prospectivity, and fertility. It has been argued that a lack of aesthetic appreciation, fundamental respect and understanding of the environment has persisted among generations to this day, pervading politics, work and everyday home life (Boyd 1980, Pybus & Flanagan 1990, Robson 1997, Horton 2000). Science, arts, humanity, free-thinking spirituality and respect for the environment are concepts seen to be treated with contempt if not held in deep suspicion by many Tasmanians. Such people have contributed to the election of state governments often seen to favour business interests over environmental concerns, with detrimental environmental consequences.

From early times, with promises of fertile land to free settlers and enticement of Norfolk Islanders with subsidies and compensations which evaporated upon their arrival, there have been examples of Tasmanian governments poorly serving their people. Now, two major political parties, both funded with the aid of large donations from large industrial corporations, are often scarcely distinguishable in their policies and actions, and may be seen as catering to big business and cultivating the lowest common denominators of the Tasmanian electorate (Beder 1997, Robson 1997). Features of local politics include examples of subversion of elections, gerrymanders, bribery, subjugation, parochialism and porkbarrelling, media complicity and marginalised minorities (Pybus & Flanagan 1990, Armstrong 1997). Notable among these minorities is the Greens, who promote environmental sustainability and conservation (Pybus & Flanagan 1990). Examples of political debacles seen as favouring big

business against conservation and at cost to the community include: In the 1970s, the electricity authority interfering with an electoral outcome with public threats of price rises narrowly preventing the election of a United Tasmania Group (Green) member; the suspicious disappearance of a light aeroplane bound for Canberra bearing a petition against the flooding of Lake Pedder, never investigated; In the 1980s, the State referendum offering a choice between two dams on the Gordon excluding the "no dams" option; then with the Gordon scheme stopped by federal order after protests, outcry and global attention, and monetary compensation; then building the west coast power scheme without the demand for what became the nation's most expensive bulk power – plunging the State into ever deeper debt, now some $3.5 billion for the island population of 460000; infrastructure support and headlong construction of logging roads deep into public forests costing another $500 million for the benefit of woodchippers; In the 1990s, attempted bribery of a politician to cross the floor of parliament; constructing a west coast access road through the Tarkine area proposed by the Greens for World Heritage nomination; and collusion to alter the electoral system to eliminate 4 of the 5 Green-held seats (Pybus & Flanagan 1990, Armstrong 1997, Crowley 1999). Conservation activists have been faced with a passive police in the face of violence including assaults and car-bombings, hostile legal system, denial of court standing, fines and jail for up to 30 days for defending public land from corporate exploit. During fieldwork, my physical safety and the university vehicle were threatened by a logging contractor. One might observe that past patterns continue today, with the treatment of people and environment having parallels in third world backwater countries, to benefit corporations condoned by a passive population still with links to a violent convict heritage. Despite this, in the past two decades polling consistently shows that up to 80% of the population quietly identify themselves with environmental ideas (Pybus & Flanagan 1990, Beder 1997). It raises questions as to whether governments are serving interests of corporations better than their democratic constituents, aided by fostering individual voter materialistic satiety ahead of environmental concerns (Crowley 1999).
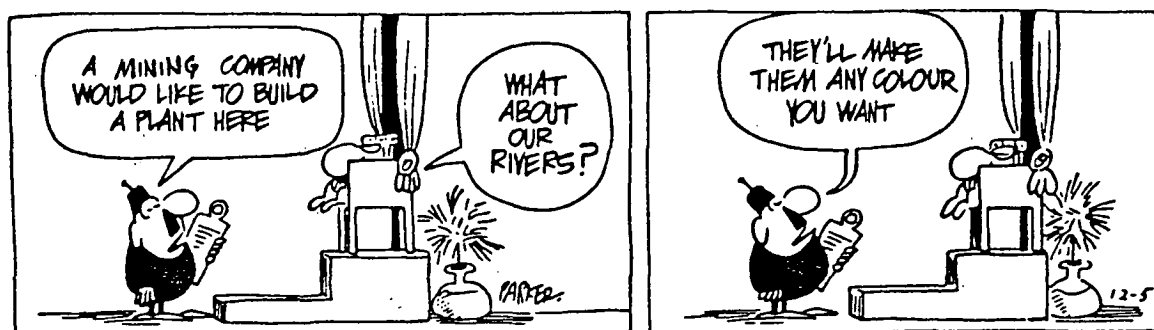
One could conclude Tasmania has had a history and culture of accommodation, perhaps even servitude, towards large corporations, most notably those concerned with extractive heavy industry, mining and woodchips and minimal local downstream processing (Robson 1997). There are examples of Tasmanian state governments supporting corporations with electricity subsidies, pollution

and planning law exemptions, low royalty demands, infrastructure subsidy, research and development support, endorsement of job-shedding, fostering polarisation of public opinion, secrecy, and selective release of information to the media (Pybus & Flanagan 1990, Armstrong 1997, Beder 1997). The results have often been to the long term detriment of the community and environment, lacked public accountability, and limited or closed off future options.

It was refreshing to have the support and full cooperation of Aberfoyle Resources in this research project. This is in contrast to the history of environmental attitudes of mining companies in Tasmania right up to the recent past. In one case during the period of this study, an Honours student and the University of Tasmania received legal threats from Mt Lyell Mining and Railway Co. Ltd. concerning her findings about the impacts of Mt Lyell mine effluent on Macquarie Harbour, should the thesis appear in the University library and/or be publicly available. She was left to publish with a Sydney university (de Blas 1994). Corporate influence and socio-political climate can present risks for environmental researchers (Beder 1997, Martin 1997, 1998).

1.5 Logistical matters and project challenges

The average study has its share of expected and unexpected hurdles to overcome. Outlined in this section, are some of the specific problems encountered and intrinsic to this type of remote, practical field-based study straddling several disciplines, while others arose from factors relating to project location conditions, administration, supervision and support. Added to this were further personal challenges. The sum of these challenges surely exceeded the norm, and extended the duration of the project.

The nature of the project demanded it be a fieldwork-based study. A pre-study experiment required a quantity of mine water to be transported to the University in a 44-gallon drum. The Pb in the water had vanished beyond detection during transport, indicating rapid chemical dynamics were in play. In the interests of accuracy and proper observation, the study demanded that as much as possible it was to be based heavily upon careful observation and measurement in the field supplemented by personally sampling and preserving specimens for laboratory tests. The study location is a day's drive from Hobart; over the 20 extended trips some 40 days was taken up by this driving alone. The study site is a 35 km from field accommodation at Waratah provided by Aberfoyle Resources, and the nearest petrol outlet accepting cards is at Tullah taking extra travel time (Figure 1.1). Apart from commuting to the wetland site and other sites on the mine lease, this study required travel to sites on the Que River and to more remote Huskisson River and Pieman River catchment sites. Field travel exceeded 35000 km. Given the time and distance overhead, field trips were typically planned for 5-14 days, and a complete inventory of equipment and supplies for planned and contingent research activities needed to be assembled for each trip and brought in the vehicle. Fortunately, most of the time, a roomy 8-seater van was available for use, which as a mobile laboratory greatly facilitated fieldwork.

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The vagaries of the west coast climate meant there were often days or part-days where fieldwork was suspended by inclement weather. There was waiting time necessary for plant growth under sub-alpine conditions. It was not until the fourth year that I was able to be on site to make observations under winter conditions. Sometimes cooperation on the study site was slow in coming, due to production related demands having staff priority over my research requests, an example being a 15 month delay in installing a 1.5 km pipeline to direct upwelling nutrient-bearing borewater into the wetland.

There were difficulties with access to laboratory equipment, reagents and consumables. There was a delay of more than two years before I was able to purchase, commission and use two vital field instruments for trace analysis by ASV and spectroscopy. There were problems with financial administration. For three years I had inadequate computer access, after then only to an old machine saved from disposal. This improved when I purchased my own 286 PC for home use. I got access to a shared networked computer in 1996.

Scope for experimentation (in the classic sense) in the field was very limited by the uncontrollable nature of the site, the climate, variability in composition and flowrates of waters, variations associated with plants and animals, and unpredictable activities and disruptions due to mine staff, contractors and others with access to the area. These are further discussed in Chapter 4. The environmental project had to be based more on observation and analysis rather than the type of controlled experiments to which most scientists are accustomed. The nature of this project demanded I take a broad multi-disciplinary approach, in some aspects of which my initial expertise was limited. Inherently the definition, precision and accuracy of results can come under question, and blur the boundary between sciences and other disciplines we use to describe and understand our world.

While I received support from many people as listed in the Acknowledgments, the University could not supply me with the customary direct supervision by an authority in this field of study. This lack of intimate contact with a research mentor had to be compensated for by independent resourcefulness. In a very real sense, I was initially flying blind, and trail-blazing this work into unknown territory. I needed to quickly learn fundamentals and techniques of fields new to me with little guidance, becoming a "Jack of all trades" at risk of being master of none. The lack of a mentor led to more time than is usual being lost pursuing data of ambiguous value and research leading to "dead ends", resulting in large amounts of effort and data not appearing in this volume. Further consequences of not being embraced into an established research group included the need to plan and set up from scratch a specialised working laboratory incorporating field-capable components, and a lack of a secure base in that I was required to relocate my office and laboratory facilities within the Department five times.

During the study period I undertook supervision roles for two Centre for Ore Deposit and Exploration Studies Honours Geology students, and two 3rd year Plant Science students' field projects. I also provided advice on practical and

laboratory procedures and safety within the Plant Science department. I provided professional consultancy for external clients regarding aspects of my work, environmental problems and water assessment. I appeared as an expert witness before the Environment Protection Appeal Board for the Tasmanian Conservation Trust in defence of a natural area near the study site. I also prepared and delivered some 27 publications and lectures.

Beyond the usual level of personal difficulties weathered by Ph.D. candidates, I had to overcome legal difficulties with a former employer, financial challenges after the income support period, ill health, injuries and bereavements.

The sum of this suggests a research experience at the more difficult end of the challenge spectrum. Only resolute commitment and persistence through an extended duration saw this study reach completion.

1.6 Preface to this volume's presentation

This multidisciplinary project necessitated my becoming "Jack of all trades", and this volume reflects the broad approach. Unfortunately in that, I risk for a reader from any single discipline that one may find a lack of rigour in the familiar field along with some bewilderment at other approaches. I endeavour to communicate my research and arguments in a manner inclusive of a broad readership including mine managers. At the same time I attempt to present with as much exactness as possible for this applied environmental study, for all the uncertainty and ambiguity that are hallmarks of the natural systems and human influences I investigated. The multiple approach spans the spectrum from hard science to nature observation and humanity in a complex web, so I present aspects in various styles ranging from more traditional scientific experimental accounts to virtual prose.

Already I have introduced an outline of the project origins, some practical research constraints, and the cultural atmosphere surrounding this study. Chapter 2 provides more background as to lead, the primary metal pollutant of interest in the study, its significance to humans and the environment, and hypotheses as to the working mechanisms of wetlands for lead abatement. Chapter 3 offers a more detailed description of the project area, the environment and mine setting. Chapter 4 appraises challenges for sampling and field experimentation. Chapter 5 examines matters concerning the planting of wetlands. Investigations in Chapter 6 account for the limited degree of Pb uptake by wetland plants, discharging the favoured hypothesis of those in Aberfoyle Resources and the University who initiated and funded the project. The experimental work in Chapters 7-9 put together elements of the dominant working mechanisms of the wetland treatment system, and eliminates the other hypotheses. Chapter 10 deals with matters of wetland design, differentiating the wastewater Pb forms taken up by the wetland, and operational and management strategies for performance improvement. In Chapter 11, I discuss some catchment management issues for the project area. Chapter 12 briefly reviews the achievements and conclusions of the project in executive summary

format. The bibliography is offered as a resource of references, as cited in the body of the text and found to be useful for this research area. A short glossary of abbreviations and terms can be found at the end of the volume.

Chapter 2: Background to lead and lead pollution

In this chapter I outline the importance of lead to man, its occurrence and uses, and its deleterious effects on health and environment. Methods of analysis of environmental concentrations of Pb are discussed. Lead pollution abatement methods are required, and the particular case of the use of wetlands is highlighted and related to the application at the Hellyer Mine. A range of wetland Pb uptake mechanisms are offered as hypotheses for study.

2.1 Lead in nature

The mean concentration of Pb is cited as 12.5 ppm for igneous rocks, 20 ppm for sedimentary rocks, and 10 ppm for soils (Valcović 1975). Pb seems to be largely restricted to crustal association, as ultramafic rocks typically bear <1 ppm Pb (Krauskopf 1979).

Lead is unambiguously a chalcophile element, immobilised under reducing conditions in the earth's crust as galena for the majority of its occurrence. Where subjected to hydrothermal and geothermal activity it can sometimes be concentrated in sufficient richness (measured in %) and quantity to be economically mined. Typical Pb orebody element associations are sulphides of Fe, Zn, Cd, Ag, As & Au. Lead orebodies so formed by concentration of Pb in hydrothermal systems generally precipitate either as vein deposits, notably in limestone host cavities, or as volcanogenic sea floor deposits (as is the Hellyer deposit).

Weathering of galena results commonly in anglesite ($PbSO_4$), cerussite ($PbCO_3$) and minium (Pb_3O_4). These minerals are relatively soluble, and easily leached from catchments into waterways ultimately to the sea.

Another notable occurrence of concentrated Pb is sea-floor manganese nodules with mean concentrations around 0.1% (Valcović 1975).

Ocean water contains 0.03 ppb dissolved Pb as Pb^{2+} $PbOH^+$ and $PbCl^+$ species (Valcović 1975, Mackey & Zirino 1994).

The fate of Pb entering the oceans is largely one of sedimentation. Marine sediments near river outfalls accumulate, in various proportions, inert clay minerals and quartz, biogenic calcite/aragonite, opal, apatite and organic matter, along with precipitated ferromanganese minerals, phosphorite, hydromagnesite, dolomite, barite and pyrite. Lead is ultimately included as galena. The details of the process are complex and still subject to research. Mackey & Zirino (1994) consider river-borne heavy metal complexes sequester to alternate layers of organic matter and clay minerals when river water flocculates out precipitate upon mixing with seawater. Clearly the presence of Pb as galena, associated with pyrite, in sediments and sedimentary rocks indicates reduction as well as precipitation, but the timing may vary depending on the conditions of deposition (Krauskopf 1979, Raiswell 1993).

Animals and plants have no requirement for Pb for biological function. However animals and plants do accumulate Pb from the environment, some to a remarkable degree, such as plankton and brown algae with environmental concentration factors of 41000 and 70000 respectively (Valcovic 1975). Species tolerance to Pb varies considerably, with some plants showing retarded growth with 10 ppm Pb in water (Valcovic 1975). Wetland emergent macrophytes concentrate metals from their environment to varying degrees depending on individual species, metals and conditions. Genera reported as tolerant to metal-contaminated mine sites in Australia include *Typha, Cyperus, Juncus, Phragmites, Eleocharis, Restio, Polygonum* and *Fimbristylis* (Dunbabin 1989).

2.2 Lead and man

Lead has had a chequered history in service of man. As it was easily won from its ore by application of heat, Pb was one of the earlier discovered and used elements – from at least 5000 BC. One of the earliest uses of Pb was galena for eyepaint by the Egyptians. Not being found in the native elemental state, the element was probably discovered accidentally after dropping ore into a fire. Sedimentary and ice core data show elevated levels of Pb since that time, and more particularly for the last century (Berry *et al.* 1993, Emsley 1994). The ancient alchemists of the Nile delta knew lead, along with carbon, sulphur, iron, mercury, copper, tin, silver and gold (Kieffer 1971). Lead is mentioned in tribute lists of Pharaoh Thotmes III from 1500 BC (Berman 1980). Despite all efforts, no treatment or combination with Pb ever yielded gold. There are references to Pb in the scriptures: In Numbers XXXI 22-23, Moses spoke of gold, silver, brass, iron, tin and lead plunder from the Midianites; Jeremiah describes separation of silver from galena.

Being readily malleable, and relatively cheap and corrosion resistant, lead found early application in plumbing (which takes its name from plumbum, latin for Pb and origin of the symbol) by the Egyptians and Romans. Lead pipes, water tanks and weights for fishing nets were used since early Egyptian times, along with uses in amulets, rings, figurines, dishes and trays. The hanging gardens of Babylon were floored in lead. The Roman baths of Bath were lead lined. Phoenicians mined and smelted lead in Cyprus, Sardinia and Spain. Roman consumption of Pb is estimated at 4 kg/y fer capita (Berman 1980), so extensive were its uses. This approaches the 6 kg/y per capita for modern USA (Berman 1980) – remarkable considering their lack of consumption of leaded petrol or batteries. Early Japanese added lead as a bronze flux. Medieval Europeans extended the use of lead to roofing, and many such buildings from the 15th century still stand in original form as testimony.

Today lead ranks after iron, aluminium, manganese, copper and zinc in terms of usage. Lead smelting produced 0.3 Mt/y in 1850; total output (from mining and recycling) has since grown dramatically, and now exceeds 4.6 Mt/y Pb (Edwards-Bert *et al.* 1993). Approximately 60% of Australian consumption is met by recycling, largely due to the effective 85-90% recovery of spent lead-acid batteries (Edwards-Bert *et al.* 1993).

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Australia is the largest primary producer of Pb in the world, mining over 0.5 Mt/y Pb, currently also ranked 1st for reserve volume. Lead was the first metal mined in Australia, in 1841 at Glen Osmond, SA. However it was not until Broken Hill in 1883 that Pb mining became a major industry. Australia's reserves and Pb mines also include Elura, Woodlawn & Cobar NSW; Wilga-Currawong Vic; Mt Isa, Century, Cannington, Thalanga, Dugald River & Hilton Qld; Admiral Bay, Cadjebut & Scuddles WA; McArthur River & Woodcutters NT; and of course Rosebery & Hellyer Tas. Numerous other Pb deposits have been completely mined out in the 150 year history. Some 85% of Australian Pb is exported (Berry *et al.* 1993); as lead bullion to Britain and Korea, ores and concentrates to Japan and Europe, and refined lead to Taiwan, Korea, Indonesia, India and Japan.

2.3 Uses of lead

Most lead (30-40% of world production, 60% of Australian production) is used in lead-acid storage batteries for automotive and other purposes. This use could expand as more people have access to cars, perhaps electric cars, and solar and wind-based energy storage becomes more common. Lead is also used for ammunition, X and γ radiation shielding in medical or nuclear applications, ballast, fishing weights, rolled, extruded and cast alloys, glass manufacture and printing. Australian production figures for manufactured lead product are shown in Table 2.1. Note the consumption would vary from these figures on account of international trading.

Other major, but declining uses of lead include cable sheathing, plumbing & waterproofing (all three uses are in decline as alternatives, particularly plastics, are being used), petrol additive as tetraethyl lead (<10% and declining with the transition to unleaded petrol in response to exposure health concerns), soldering (tin cans, plumbing, electronics), paints (declining for health exposure reasons, now restricted to industrial and marine use) and pigments. Further minor uses include PVC additive, rubber, explosives and other technological stabilisers and lubricants.

Table 2.1: Australian production of Pb products
manufactured in 1990 (after EPA, Anon. 1993)

Products using Pb	kt Pb used
Batteries	45
Rolled or extruded	9.0
Alloys	6.7
Leaded petrol	5.4
Cable sheathing	3.3
Chemicals	3.3
Ammunition and shot	1.6
Total	74

Virtually obsolete (and now illegal in Australia) uses of lead include lead arsenate as insecticide, earthenware & stoneware pottery glazing, and the "lead" in pencils has been graphite since the 19th century. Lead has even been applied as facial makeup in the form of white lead (hydroxyl carbonate) for pallor and red lead (minium) for rouge as fashions went by.

2.4 Lead and human health

Lead is one of the elements that is regarded as non-essential and toxic, having no known positive biological function for humans at any dosage. There is no Recommended Dietary Intake (RDI) for Pb as there are for an increasing number of other trace elements.

Hippocrates (370 BC) described lead cholic in a lead worker. Nicander wrote of symptoms of litharge (lead oxide) intoxication in his book on poisons written in the 1st century BC (Berman 1980). While use of lead pots for cooking and storage gave a sweeter flavour than other wares, illness followed. Tanquerel wrote a definitive treatise on lead poisoning in 1838, with sources, modes of absorption, symptoms, diagnosis, and physiological responses (Berman 1980).

An average modern Pb intake of 45 µg/day typically comprises ⅓ from dietary origin, ⅓ from fluid intake and ⅓ from inhaled sources. Of this 5 µg/day is eliminated in hair, nails and sweat, and the balance mostly in the urine (Valcović 1975). Acute poisoning by lead is rare today; rather the health risk is more that of cumulative poisoning. Lead may be absorbed in either inorganic or organic form, the latter being more toxic (Krenkel 1975, Kelly 1988, Harrison 1990), but fortunately exposure to organolead is much less prevalent. Lead accumulates in bones and in the tissues and blood, more so in the formative years. Symptoms of lead poisoning include constipation, gastrointestinal disturbance, tenderness and gradual paralysis in the muscles and joints especially the arms, raised blood pressure, loss of libido, infertility, irritability, fatigue, headaches, leading to more severe symptoms of anaemia, convulsions, stupor, brain damage and coma (De Zuane 1990, EPA 1998). Further specific symptoms are associated with formative years.

Human Pb exposure may be measured with varying accuracy and intrusiveness by analysis of sweat, hair, nails, urine, blood and bone (Lilley et al. 1988, De Zuane 1990). Such measures are routinely taken to monitor the exposure of people at particular risk, such as mine workers, including those at Hellyer.

Children 0-4 years are particularly susceptible to additional Pb intake from ingestion of house paint dust and flakes, contaminated soil and traffic fallout, sucking painted objects and inhaling traffic fume. They are also particularly vulnerable to the deleterious effects of even low levels of Pb resulting in impaired growth, reduced hearing, learning disabilities and behavioural problems. Similarly Pb is hazardous to pregnant women, exposure implicated in pre-term delivery, low birth weight and increased risk of still birth. Even low levels of maternal Pb can pass through the placenta and damage the foetus.

While the NH&MRC set the blood level for official concern at 25 μg/dL Pb in 1987, levels of blood Pb of 10 μg/dL are known to have harmful effects in susceptible groups (Edwards-Bert *et al.* 1993). In 1993 the NH&MRC set a target that no Australian should have a blood Pb >10 μg/dL (Berry *et al.* 1993), recommending a strategy of reduction of Pb in petrol, price incentives for decreasing use of leaded petrol, dissemination of information on risks from home renovations and safe removal of lead-based paint.

Recent Australian focus on the dangers of lead exposure, particularly for children and workers, is highlighted by the number of comprehensive studies and reports this decade, media reporting, the creation of community support groups like "The Lead Group", distribution of EPA "Lead Alert" booklets about household hazards, and the screening of an episode of the popular ABC medical drama "GP" focusing on lead poisoning in children.

2.5 Environmental Pb pollution and health

Lead plumbing for drinking water supplies has been common from the time of the Roman Empire. Since that time the health hazards of this practice have been known, with numerous poisoning cases reported from this cause. The use of Pb plumbing becomes more dangerous with the extent of the Pb in the system and with the pH of the water departing from the 6-8 range and being more aggressive. While Pb pipes have largely disappeared, only recently have lead-free bronze and brass fittings, taps and solders been in common use as alternatives to their leaded predecessors. Now the use of Pb-bearing plumbing is illegal for drinking water applications in Australia (EPA 1998). Similarly, in the construction industry, it is only recently that the use of sheet Pb for roof flashing, lining and damp course applications has ended (EPA 1998).

Lead emissions from smelters and leaded automobile fumes - exhaust particulates are 20% Pb by mass – have enriched airborne Pb in oceanic lower atmosphere particulates by some 50-fold over expected natural levels ranging as high as 0.3% dry basis (Valcović 1975). Aerosols have measured 20-2000 ng

Pb per m^3 in populated areas, with Pb concentrating in the finer <0.5 μm diameter fraction (Valcović 1975, De Zuane 1990). Olson & Skogerboe (1975) and Hurst *et al.* (1996) show that leaded petrol is a major source of environmental Pb in heavily trafficked areas.

Lead-based paints were widely used from the late 1800s until the recent past, particularly disturbingly for house interiors and toy applications. Lead-based paints containing up to 50% Pb were commonly used until 1970 in Australia (EPA 1998). These paints are now replaced by products using titanium compounds.

Pathways for human Pb exposure identified by Berry *et al.* (1993) are shown in Figure 2.1. Specific sources of lead exposure (Table 2.2) vary for the individual, especially those associated with traffic exposure, contaminated fish and molluscs (Krenkel 1975), home and hobby activities. It is estimated 45% of Australian children 0-4 years, and 60% of those in urban areas have blood Pb levels exceeding 10 μg/dL (Berry *et al.* 1993). Leaded petrol was introduced in 1925, and together with the overall increase in Pb production cycle contributed dramatically to atmospheric fallout, shown by steeply increased icecap Pb recorded from 1940 on (Anon. 1993). However, as the major human exposure source identified as leaded petrol is declining both in use – estimated to reduce to 30% of the 1986 consumption by 1998 – and lead content, these overall figures are expected to improve by 1998 (Berry *et al.* 1993).

Closer to home, there is concern in Hobart at residential exposure to smelter fallout (Guthrie & Chesterman (1991), and to industrial heavy metal pollution of the river resulting in exposure to bathers, and metal accumulation in fish and molluscs caught for food (Bloom 1975, Hore-Lacy 1976). Similarly there has been focus on pollution effects in the King catchment (Locher & Koehnken 1993, de Blas 1994, Carbon 1995). As with other mineral industries, workers at the Hellyer mine are regularly tested for heavy metals (Aberfoyle 1985-96). The Huskisson River, Lake Pieman and lower Pieman River, are visited by recreational anglers, exposed to secondary water contact and fish ingestion.

Table 2.2: Sources of Pb exposure

Type	Sources
Mining	Tailings & spoils, wastewater, dust
Industry	Primary & secondary smelters, electricity generation, burning of sump oil & metals, manufacturing
Transport	Leaded petrol vehicle exhaust, fallout
Point sources	Paints, landfill, shooting ranges, soldering, soil, workplaces, contaminated swimming areas, sinkers, incinerators, chemicals
Ingestion	Food, packaging, containers, utensils, shot game, water supply & reticulation, lead crystal
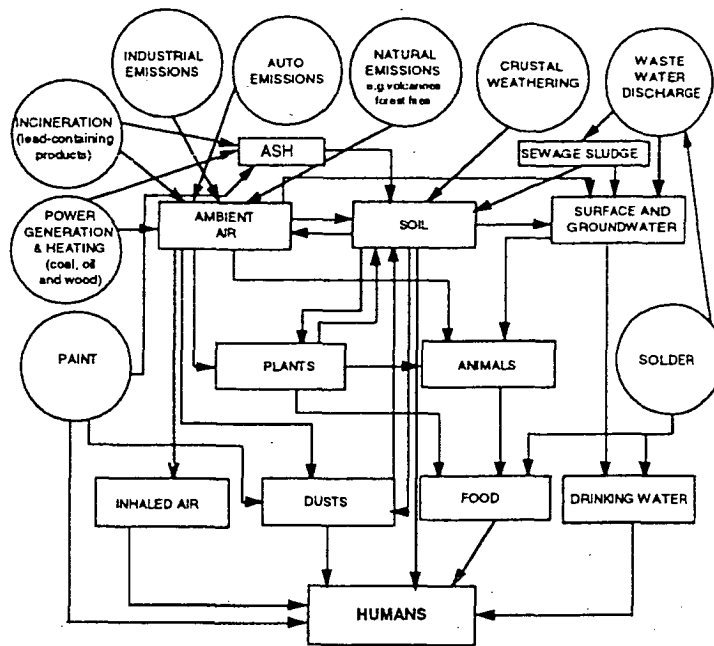
Figure 2.1:   A: Pathways for human exposure to Pb
(after Berry et al 1993)

B: Routes of metal pollutants into the environment
(from Förstner & Wittmann 1981)
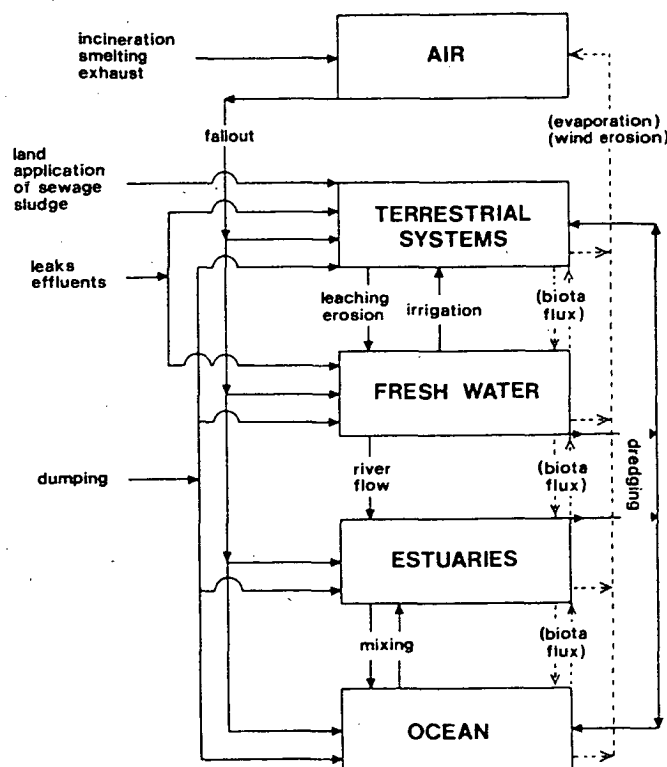
The Australian guidelines for Pb in raw drinking water supply are <50 ppb, and for freshwater environmental protection <1 ppb (ANZEC 1992). The NH&MRC guideline for drinking water was lowered from <50 ppb (NH&MRC/AWRC 1987) to <10 ppb in 1996 (NH&MRC-ARMCANZ 1996). There is currently no regular testing of first flush drinking water at points of consumption, only at sources and supply reservoirs. The Pb in water at the point of consumption in typical Australian homes may be elevated 8-fold over that from the reservoir (Anon. 1993).

2.6 Analysis of Pb in the environment

Vogel (1978), Berman (1980) and APHA/AWWA/WPCF (1989) describe analytical alternatives for measuring environmental Pb as titrimetry, gravimetry, colorimetry (light spectrophotometry), atomic emission spectroscopy including ICPAES, X-ray spectroscopy, X-ray fluorescence, polarography (including ASV - anodic stripping voltammetry), gas chromatography, ion selective electrodes, mass spectrometry (MS) and atomic absorption spectrometry (AAS). More recently, ICP has been coupled with mass spectrometry to increase sensitivity. Vogel (1978) and Schrader (1987) describe the relative accuracy, working range, speed and cost of the methods in general terms. The cost, detection limits and portability of a number of methods of analysis of Pb in practical contention for this work are listed in Table 2.3, along with actual values for methods as used during the project. Note, however, these detection limits may vary with sample dilution or preconcentration. The selection of methods for this study was based on degree of availability, low cost to fit in with the project budget, and field portability for at least one method.

Table 2.3: Lead analysis techniques

Method	cost	DL(µg/L)	P	reference/notes
ICPAES	**	40	N	APHA/AWWA/WPCF (1989)
ICP-MS	***	0.05	N	Schrader (1987)
Ion selective electrode	*	20	Y	Vogel (1978)
AAS (flame ionisation)	**	10-50	N	APHA/AWWA/WPCF (1989)
AAS (graphite furnace)	**	1	N	APHA/AWWA/WPCF (1989)
Colorimetry (dithizone)	*	1	Y	APHA/AWWA/WPCF (1989)
ASV hanging drop electrode	**	0.04	N	Batley (1989) use DC
ASV thin film electrode	*	0.01	Y	Batley (1989) use DC
ASV thin film electrode	**	0.001	N	Batley (1989) use SWDP
As used for this work:				
AAS (flame ionisation)	$6 ea.	50	N	contracted to Analabs
ASV thin film electrode	$15k tot.	1	Y	As Table 2.4, use DC
Colorimetry (dithizone)	$4k tot.	1	Y	Hach (1990) extraction

Cost: * <$20k, ** $20-100k, *** >$100k, ea. per sample, tot. total project cost;
DL: detection limit; P: portability; ICP: inductively coupled plasma analysis;
DC: direct current mode; SWDP; square wave differential pulse mode

Analytical methods may be combined with digestion procedures – like acidification, irradiation, and ashing – and separation techniques such as filtration, precipitation, ion exchange, dialysis, liquid or solid phase extraction chromatography and electrodeposition. These methods were used where appropriate for fractionation studies as part of the research into mechanisms of wetland removal of lead from the mine wastewaters.

2.6.1 Monitoring method – AAS

AAS operates on spectroscopic analysis of an acetylene flame aspirated with analyte solution. The usual method of environmental analysis for total Pb is AAS, being relatively cheap and of adequate sensitivity for routine monitoring. Together with filtration through 0.45 µm membranes and acidified total samples, this was the method of choice for Hellyer monitoring (Blesing 1991). Limitations of sampling and sample preparation observed during monitoring are discussed in Chapter 4. The detection limit for Pb reported by Analabs is 50 ppb. However, for my more detailed studies, with requirements for more advanced preparation, separation and fractionation, I sought analytical techniques with better detection limits and at least some capability for on-site fieldwork analysis.

2.6.2 Experimental methods

2.6.2.1 AAS

The flame ionisation AAS method was used for many analyses in this work, performed by Analabs on samples I took and prepared during fieldwork. Data was also used from the mine environmental monitoring sampling programme using the same laboratory. The details of the assay procedure are as prescribed in Method 316A, of APHA/AWWA/WPCF (1985).

2.6.2.2 Colorimetry

Colorimetric Pb analysis relies on measuring a specified wavelength absorbance of a solution after reaction of analyte Pb with a specific ligand that quantitatively produces a highly coloured complex. A field-portable Hach DR/2000 spectrophotometer was purchased and commissioned for this study, for Pb analysis, but was also used for determination of Fe, P, SO_4, S, and has the capability of measuring a number of other analytes. The colorimetric Pb method, LeadTrak™ Fast Column Extraction (Hach 1990), based on dithizone Pb complexing reaction, was used for field samples in the field and in the laboratory. The method required 100 mL test portions of water samples preserved with 0.15% nitric acid. Other details of analysis procedures, including those for other analytes, and instrument operation may be found in Hach (1990). There was a degree of interference found in some instances, by high concentrations (particularly in summer) of organics, Ca, SO_4, and when base metals Fe, Zn, Cu, Mn reached ppm levels (as found in some Que River mine leachate samples or wetland sediment extracts).

2.6.2.3 ASV

ASV was the third method chosen. This technique involves initially electroplating analyte heavy metals on to a mercury film electrode. The measurement phase involves gradually ramping the cell voltage in reverse to individually strip the amalgamated metals back into solution, recording the current for each metal converted back into ionic solution. The details of principles, limitations and merits of this specialised electrochemical method of analysis are detailed elsewhere (Bond 1980, Batley 1989). A field-portable Chemtronics PDV 2000 ASV unit was purchased and commissioned for this study. The unit was used for both field and laboratory work (Figure 1). Generally, samples were preserved with 1% nitric acid, although in some cases field samples were introduced to the instrument with no preparation, or after subject to some separation procedure. The 5 mL sample were mixed with 5 mL support electrolyte in the ASV cell. Thorough cell rinsing between samples, and control with blanks, standards and spikes ensured the integrity of the results. The ASV analysis for Pb was generally performed according to the parameters in Table 2.4, following the guidance of Chemtronics (1986), my previous professional experience with ASV analysis, and results of trials with wetland waters.

Where possible, the unit was connected to a PC (a laptop was borrowed on some occasions for fieldwork) for control programming and data capture using DisPlot software. Figure 2.2 shows the output from Displot of an example 100 ppb mixed standard and blank scan. The software allowed inspection of peak shapes for interferences, the adjustment of peak measurement parameters, overlay comparison, and zooming in for small peaks. The usual ASV detection limit as used in this project for Pb was 1 μg/L, though this could be enhanced by altering extraction procedure or instrument parameters. More concentrated samples were diluted to assay within the instrument working range. Other details of analysis procedures and instrumental principle and operation of the PDV 2000 may be found in Chemtronics (1986).

Table 2.4: ASV Analyser parameters

```
Instrument: Chemtronics PDV2000
Menu 8: user design Zn, Cd, Pb, Cu
Electrode film: 10 minutes plate; 20 ppm Hg in water
Analytical plating potential: -1300 mV for 60 seconds
Hold time: 15 seconds
Sweep rate: 375 mV/s
Final potential: 0 mV
Strip time: 5 s
Rest potential: -100 mV
Support electrolyte: Ascorbic acid/NaCl, nominal pH 4
Peak integration zones: Zn: -1080 mV to -940 mV
                        Cd: -740 mV to -600 mV
                        Pb: -540 mV to -410 mV
                        Cu: -350 mV to -150 mV
Instrument printout and/or PC capture using DisPlot software.
```

Figure 2.2: Example of ASV output using DisPlot software for blank and 100 µg/L mixed standard solutions.
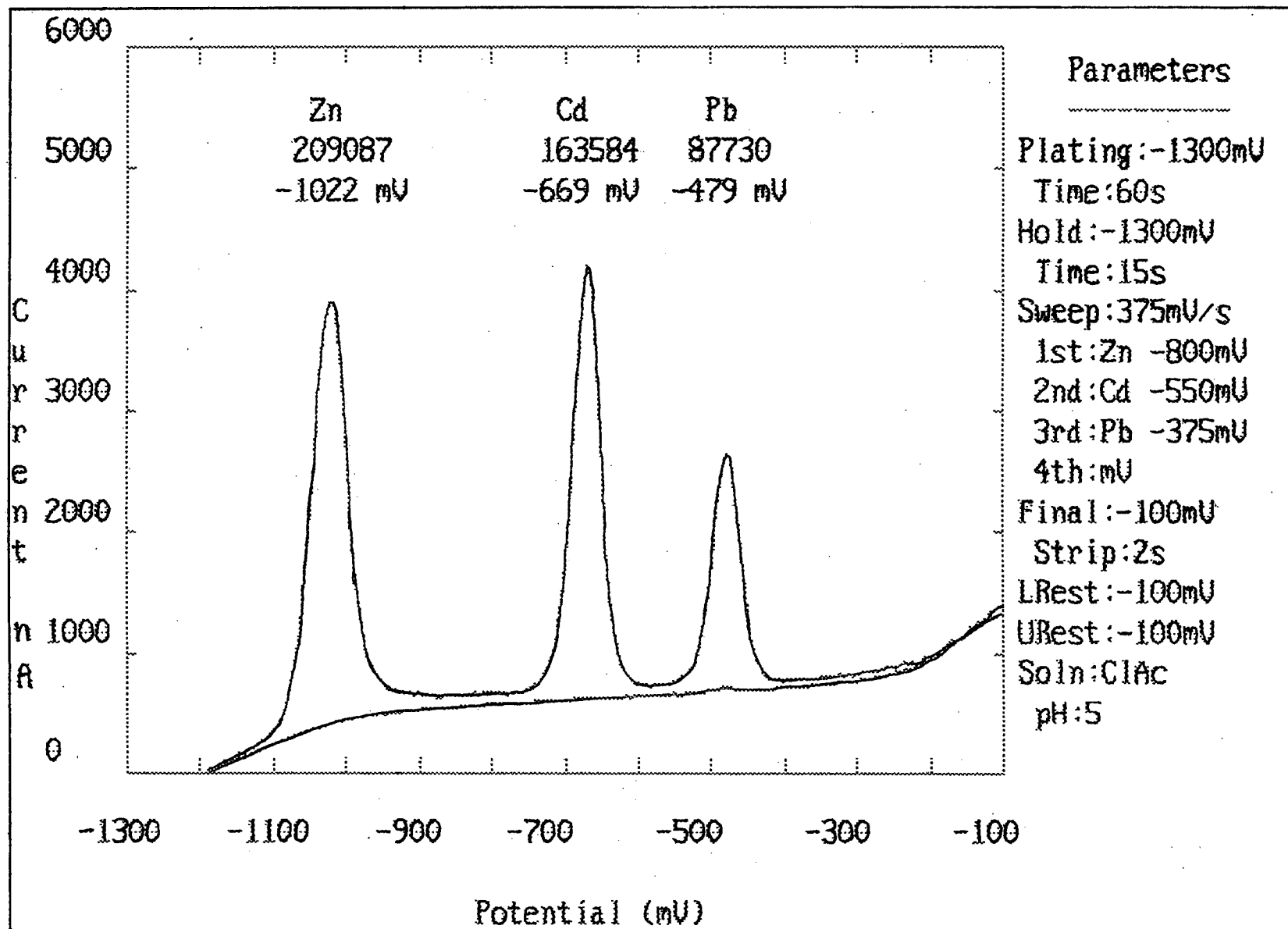
The 4-element scan was enacted to monitor these elements; however Zn, Cd and Cu in the wetlands were below levels of concern, having been successfully removed by lime treatment and tailings settlement, thence essentially sidelined in this study. The integration software was directed to find and measure the largest peak within each target zone, identified by element. The relatively thick working film of the mercury electrode was required for reducing intermetallic and organic interferences, and for durability against film degradation by the somewhat aggressive samples. A thick film would typically be stable for a series of assay runs of 5-20 samples, some 50 determinations in all including blanks and standards. The down side of the thick film, being reduced sensitivity, was not of great concern, as the range of interest for Pb in the context of the project was 1-2000 µg/L in this environment, above the usual expected in a pristine catchment, on account of this part of western Tasmania's natural mineralisation and mining history.

2.7 Lead pollution abatement

With obvious exceptions like petrol and paints, there is ample opportunity for recycling of lead from disused products. Lead is indeed one of man's most recycled resources. Further closure of the lead-use cycle would serve to protect the environment both by reducing the scale of mining and smelting, and the attendant environmental impacts, and by reducing environmental emissions and accumulation from the terminal waste. Continuing research and development will hopefully allow scope for more substitution of Pb uses by less toxic alternatives; a current area in contention is the replacement of Pb shot (which is 100% lost to the environment as a pollutant) by ferrous materials.

Tasmania's response to pollution has come relatively late due to the scattered population in a partly-virgin landscape, and a pioneer attitude and culture fostered by governments and externally owned industries towards resource extraction and waste. The legacy of unfettered mining and smelting pollution are best illustrated by the bare hills, dead rivers and massive tailings delta associated with the 100 years of Mt Lyell mining (de Blas 1994, Crawford 2000, Winterhalder 2000). Concern and action on metal pollution in Tasmania followed the courageous work of Bloom (1975) and others, and public outcry.

There are various artificial treatment systems available for the removal of metals, including Pb, from waters including sand filtration, adsorption trenches, ion exchange, chelation, evaporation, ultrafiltration, reverse osmosis, activated carbon adsorption, solvent extraction, electrolysis, chemical precipitation, flocculation & settling, neutralisation & co-precipitation, and zinc dust cementation (Kelly 1988, Ritcey 1989, Sengupta 1993). These all involve active inputs, performance monitoring and waste disposal during operation, require special designing, commissioning & decommissioning for a specific operating lifetime and tend to be intensive.

Hellyer operates with lime neutralisation of tailings settling; this removes all contaminants to below levels of concern (Blesing 1991) apart from Pb and SO_4.

This is now followed by a sodium silicate precipitation plant (since 1996), working in conjunction with the pilot wetland treatment system.

While lead is not biodegradable *per se*, it should be remembered that Pb is found and cycled in the natural environment (Nriagu 1978, Krauskopf 1979, Trudinger *et al.* 1979, Russell & van Moort 1981, Landner 1987, Vernet 1991), unlike artificial radioisotopes, PCBs and pesticides. There is plenty of scope for harnessing, adapting and enhancing natural processes for treatment of Pb pollution. Recently, even PCBs and pesticides have been found to be slowly broken down by bacterial strains (Field *et al.* 1995, Pieper & Reineke 2000, Wiegel & Wu 2000), fuelling realistic hope for successful use of natural or engineered biological systems for treatment of heavy metal pollution.

2.8 Possibilities for wetland treatment of Pb wastewaters

Wetlands, constructed and natural, have been used for some 30 years for aerobic treatment of municipal wastewaters, primarily to remove N, P and biological oxygen demand. More recently the industrial and mining sectors picked up on the fact that wetlands can act as sinks for metals, and applied wetland treatment to urban runoff, industrial sites and mining operations. Weider & Lang (1982) and Giblin (in Godfrey *et al.* 1985) are among the earliest accounts of macrophyte wetland use for metal wastewater abatement. The behaviour of metals in aquatic systems is reviewed by Förstner & Wittmann (1981) and Batley (1989) amongst others. Wetlands can remove wastewater metals in various ways, including plant uptake, sedimentation, precipitation, substrate ion exchange, adsorption, coprecipitation, or complexation. The advantages of using wetland treatment systems is minimal input, running costs and maintenance required; the provision of long term ultimate solution for waste product; and the inherent satisfaction of using natural processes with minimal overall environmental impact. Such matters are discussed at length elsewhere (Hammer 1989, Sengupta 1993, Eger 1994, Reed *et al.* 1995).

The use of wetland treatment for metal-bearing wastewater is now common, and includes applications in Australia (Robertson 1988, Hammer 1989, Ritcey 1989, Stark 1990, Nairn *et al.* 1991, Knight *et al.* 1992, Leneham 1992, Ryan & Hosking 1992, Wood & Cook 1992, Tarutis & Unz 1994, Bowmer & Jones 1995, Mitchell 1995, Reed *et al.* 1995, van Schilfgaarde 1995, Weeks & Anderson 1995, Woods & Noller 1995, Parish 1996, Tyrrell *et al.* 1997). However more often than not, the metal uptake mechanisms are poorly understood and the systems have been, and still are, applied in "black box" fashion, with vague hopes of reproducing the somewhat mysterious successes of others.

2.8.1 Hypotheses on Pb removal and wetland operation

A key to the possible mechanisms for wetland Pb uptake is to consider the range of conditions and chemical or biological analytes present in various parts of the wetland, and what possible fixed forms Pb may bind into under those

combinations. The phase diagram Figure 2.3 shows forms of Pb found under conditions pertinent to wetland treatment systems. In the absence of artificial chemical additives, the most inert form of Pb is galena, stable in reducing conditions. It would seem Fe could be tied in with the fate of Pb by its abundance in the ore, tailings, wetlands and association in natural occurrence. Figure 2.4 shows a phase diagram for Fe under typical freshwater concentrations.

Figure 2.5 shows the solubility curve for the pH range for a simple water system. This forms the basis of lime treatment of tailings, which precipitates the bulk of the heavy metals. However the minimum Pb solubility in the Hellyer tailings water system under bench conditions is 60 ppb at pH 10.1 (Blesing 1991), indicating some complexed or colloidal forms of Pb sufficiently stable to resist rapid precipitation by simple pH adjustment.

Figure 2.6 shows some postulated reactions of Pb possible under wetland conditions. Figure 2.7 shows possible pathways for removal and fixation of Pb hypothesised for wetland treatment systems, and Figure 2.8 shows how these may apply as fluxes in the wetland. These include adsorption by organic or clay materials, ion exchange, sulphate reduction, coprecipitation, bacterial conversion, plant uptake and sedimentation (Sengupta 1993, DLWC 1998). Precipitation and flocculation may involve such processes in suspension, with subsequent particle aggregation and sedimentation.

Also among questions regarding wetland systems, is that of the role of the plants; Figure 2.9. These may include maintaining the pond structure, involvement in redox processes and oxygen transport, supporting microbial activity in the root zone, production of organic matter for direct metal absorption or supporting anaerobic conditions and bacteria involved in metal uptake, or direct metal uptake into plant tissue (DLWC 1998).

Plant uptake and root-zone fixing were the favoured hypotheses of Pb uptake of the Aberfoyle mine managers and staff at the University, based on the work of Dunbabin (1989) and the appearance of plaques around the *Juncus* stems. To me, this was intuitively under question, given the high wastewater metal loading and the limited 2-dimensional scope for the plaque deposition, and the inherent unsustainability of perpetual direct plant uptake (plants would surely be poisoned by some upper limit of Pb absorption, ending the process).

A more substantial potential Pb sink seemed to lie with the 3-dimensional mud component of the wetlands. However at the outset, there were few immediate strong indicators as to which of the Pb reaction pathways would dominate, or what ultimate form the Pb would take. The components of all the postulated reactions and pathways were known or supposed to be present, so all possibilities were open. No analysis of wastewater within the wetland or wetland mud preceded this project. The challenge was to determine which of these were important, by measuring the presence and/or amounts of the various Pb-bearing components, related reactants, products and conditions in the Hellyer wetland treatment system. Given the common forms of naturally

occurring fixed lead, and the Hellyer sulphide orebody source, it seemed likely that at least some of the wetland Pb would sink in the form of PbS, either directly or by longer chemical pathways.

2.8.2 Conclusion

Artificial technologies exist to remove metals from wastewaters, but have inherent disadvantages. In the context of current (Pb) mining practices continuing, it is desirable that associated mine wastewaters be treated to remove Pb prior to outfall into river systems by means that follow similar lines to Pb fixation in nature. The employment of biological water treatment systems has the potential to effectively and sustainably remove Pb into a stable inert form, with the advantages associated with the use of natural systems. The use of constructed wetlands for such treatment has the propensity to address environmental and human needs. Numerous mechanistic pathways for Pb removal are identified as possible working hypotheses under the Hellyer wetland treatment system.

Pb-H₂O-CO₂-S₈-O₂ stability fields
$$Pb\text{-}H_2O\text{-}CO_2\text{-}S_8\text{-}O_2 \text{ stability fields}$$
(simplified)
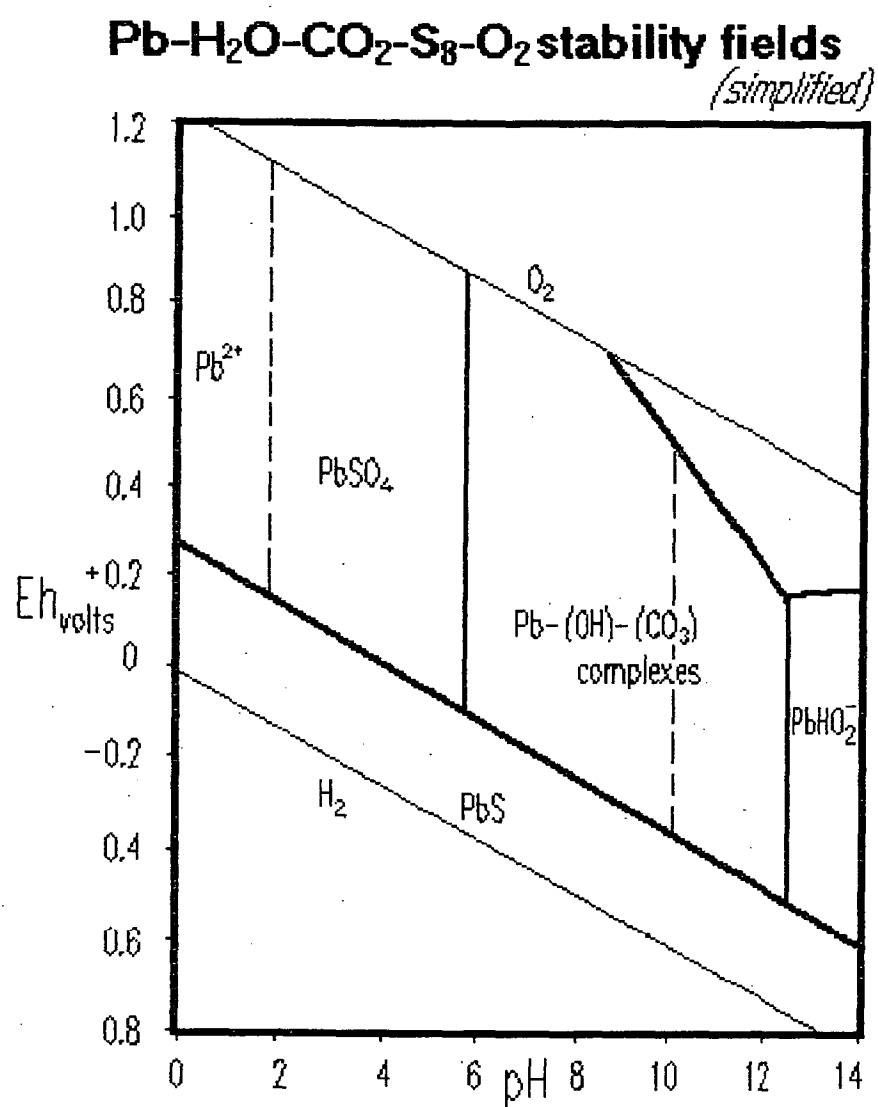
Figure 2.3: Phases for Pb vs Eh and pH
(after Krauskopf 1979)
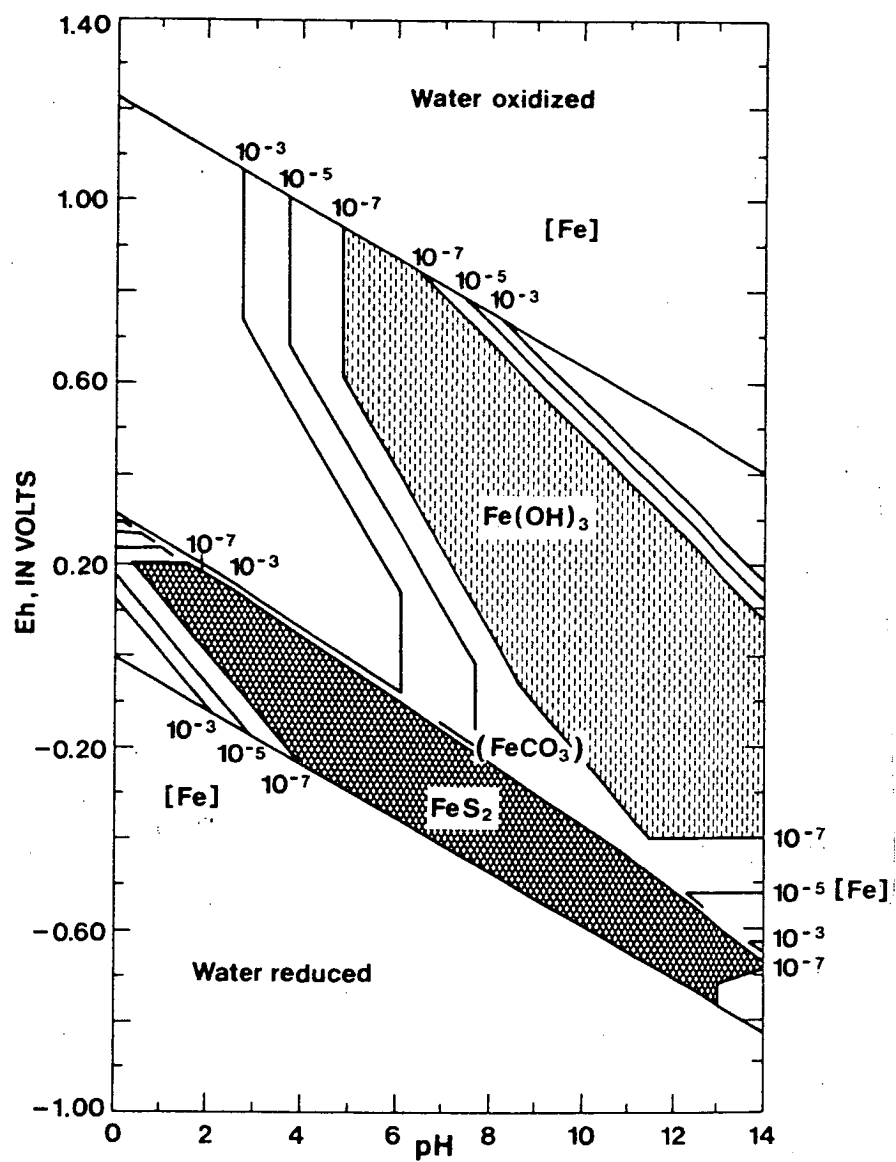
Figure 2.4: Phases for Fe vs Eh and pH
(from Förstner & Wittmann 1981)
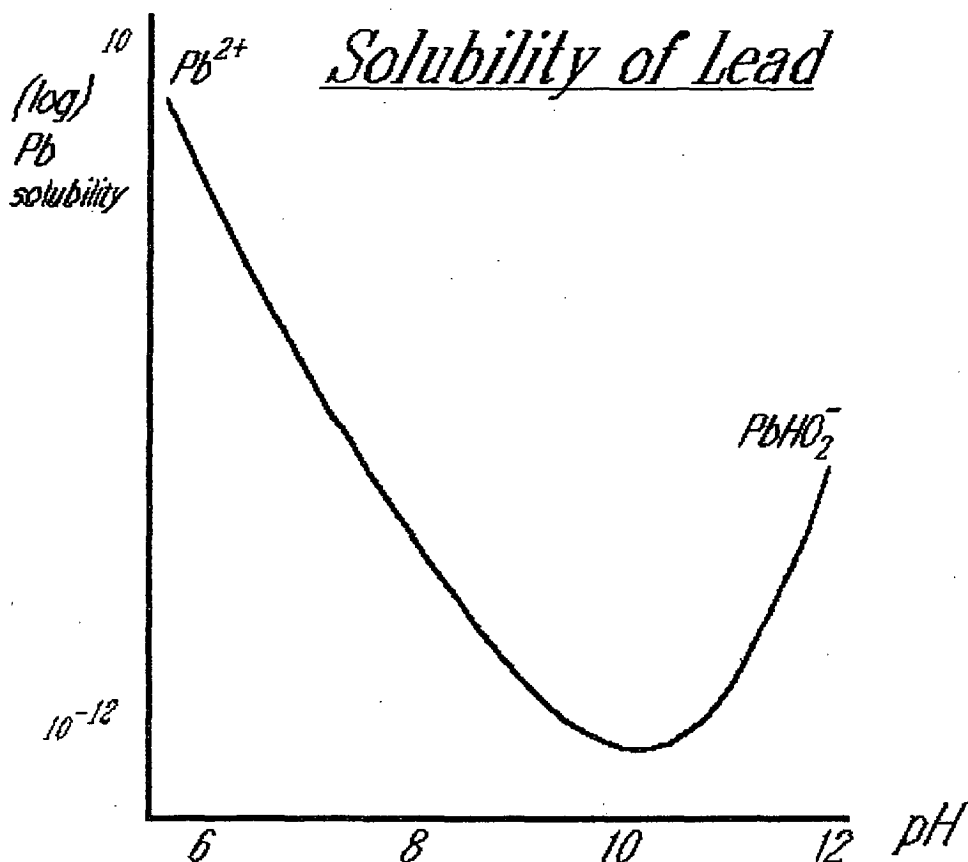
Figure 2.5: Solubility of Pb in a simple water system.

Reactions of lead in wetlands

Pb^{2+} +FeOOH $\longrightarrow$ adsorption complex
Pb^{2+} + free organics $\longrightarrow$ complexes of varying mobility
Pb^{2+} + decaying matter $\longrightarrow$ adsorption complex
Pb^{2+} + clay matter $\longrightarrow$ adsorption/ion exchange
Pb^{2+} + macrophyte $\longrightarrow$ uptake into plant

SO_4^{2-} $\xrightarrow{\text{Desulphovibrio}}$ S^{2-}+Pb^{2+} $\longrightarrow$ PbS

Pb^{2+}+FeS$_2$ $\longrightarrow$ Fe^{2+}+S^0 +PbS

Pb^{2+} $\xrightarrow{\text{bacteria}}$ organolead compounds

Pb^{2+} $\xrightarrow{\text{pH 10.2}}$ Pb(OH)(CO) complexes
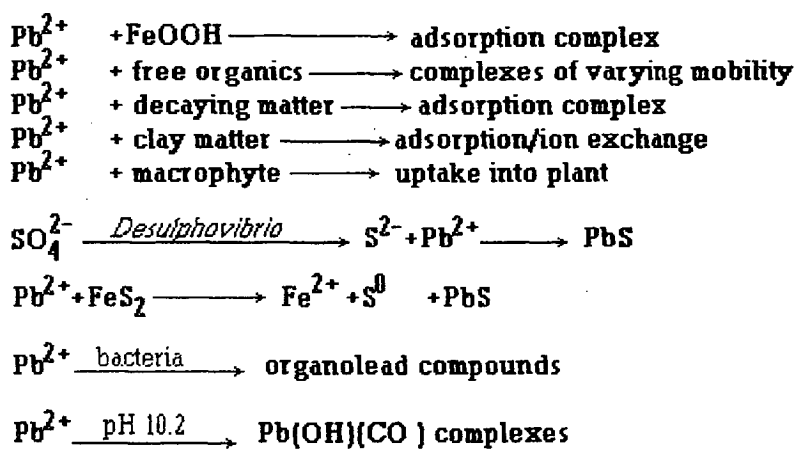
Figure 2.6: Lead reactions

Fixation of Pb.
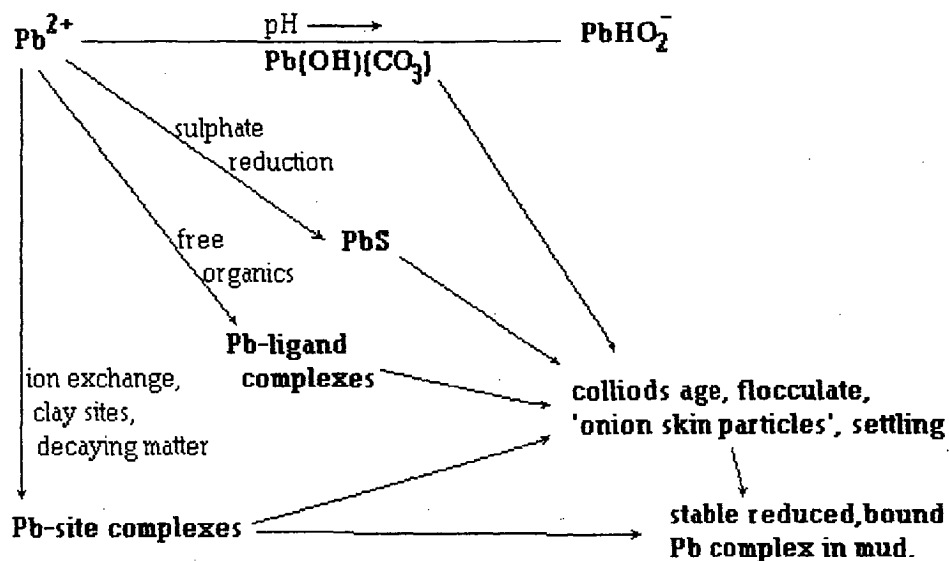
Figure 2.7: Postulated pathways for fixing Pb in wetlands.
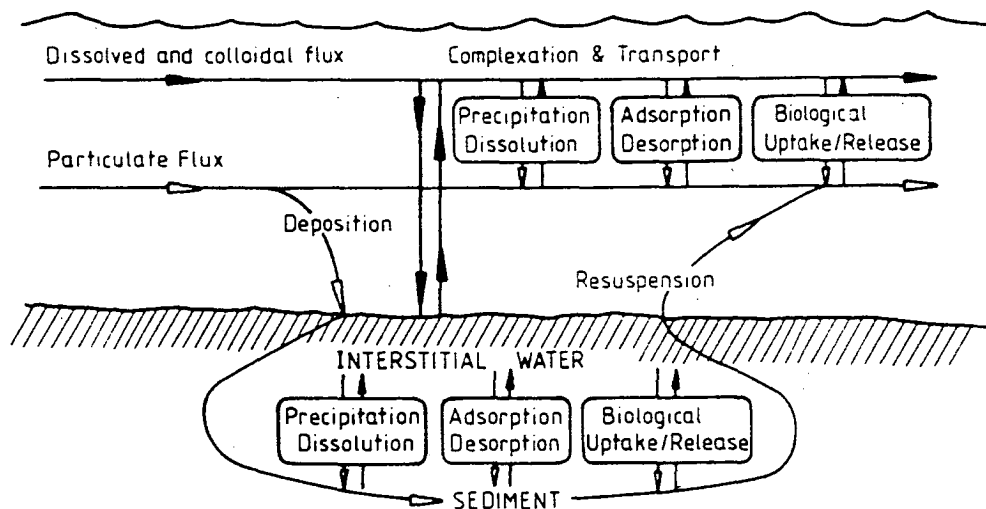
Figure 2.8: Interaction fluxes applicable to wetlands.
(from Bourg & Mouvet, in Kramer & Duinker 1984)

The plants; what do they do?

1. physical stabilisation
2. oxygen pump
3. support rhizosphere ecology
4. production of organic matter
5. direct absorption of Pb.

emergent
macrophyte

rhizosphere

flowing water ←~

mud
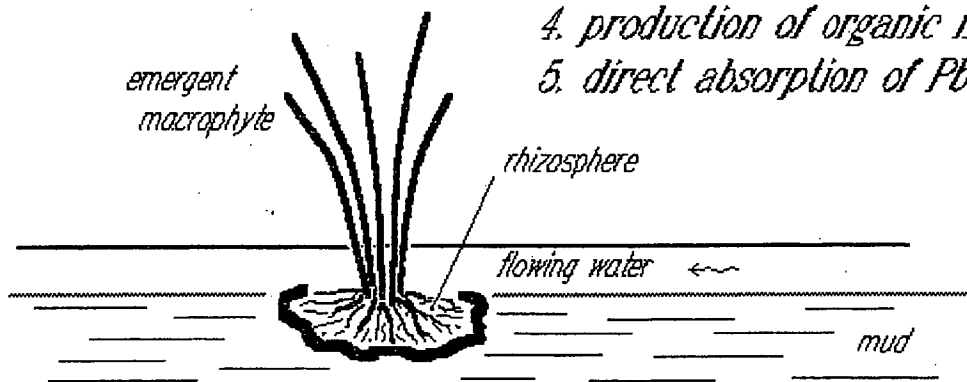
Figure 2.9: Possible roles of the emergent plants

Chapter 3: Project area description

3.1 Western Tasmania and Hellyer overview

The study site is located at the Hellyer mine in Western Tasmania (Figure 1.1, 1.2, Section 1.2.2). Tasmania is the southernmost island State of Australia. The Hellyer Mine is in a highly mineral-prospective region in Western Tasmania (Figure 1.3), an area with a long history of mining (Section 1.3). Currently there are several mining operations and exploration programmes in progress in western Tasmania; and new mines will doubtless replace those that close.

The rugged terrain, thick vegetation, leached soils, inhospitable climate and remoteness from major cities and services make for poor human movement, accommodation and sustenance. There are fewer than 10000 people living in the Pieman catchment, and the nearest settlements to the Hellyer Mine are Waratah, some 33 km by road to the north, and Tullah, about 30 km to the south (Figure 1.1). Hellyer employs some 230 workers, and many others are employed providing support goods and services required by the mine operation and its consequential activity. Some Hellyer workers reside at Waratah. With the new Ridgley section of the highway, many others commute from the more distant north west coastal area towns of Burnie - Wynyard. There are relatively few roads in the Pieman catchment, and most human activity revolves around mining, followed by hydro-electricity generation (the Pieman scheme) and forestry (north of Tullah), and to a lesser extent, apiary, leisure (trout fishing etc) and tourism.

The Hellyer Mine, in full production since 1989, extracts and treats 1.3 million tonnes of Zn-Pb-Ag sulphide ore annually, and stores treated tailings behind a dam. Dam overflow wastewater is passed through a 1.2 Ha experimental constructed wetland system to remove heavy metals, in particular residual Pb. A typical composition of the wetland input is shown in Table 5.1. The Que catchment also includes the Que River Mine (1980-1991) and its effects. These factors added together with remoteness, terrain, climate and relatively intact catchment pose challenges for potential solutions in respect of the modern desire for clean environment. The development and understanding of the wetland treatment system at the Hellyer Mine has direct significance beyond this particular operation in the long term context of Western Tasmania, and relevance to the mining (and other) industries world wide.

3.1.1 Terrain

The area generally has rugged terrain. Western Tasmanian geology features complex faulting and folding of precambrian and paleozoic rocks in an orogenic belt (Figure 1.3). The more recent glaciations have resulted in steep, craggy peaks, deep valleys and scoured plateaux. The present climate has further contributed deep river valley incisions and leached soils. The Hydro Electric Commission (HEC) has built multiple dams in the Pieman catchment to form the impoundments: Lake Pieman (Reece Dam 1986), Lake Rosebery (Bastyn Dam 1983), Lake Mackintosh (1980), Lake Murchison (1982) and Lake Plimsoll

(Anthony) (1993). The study site portion on the Hellyer mining lease including the flotation mill, tailings dam and wetlands is at the south western edge of an undulating 700 m plateau locally drained by the Que river which tumbles steeply into the Huskisson River. This headwater plateau features some patches of Tertiary basalts, and to a lesser extent Cambrian volcanics, which give rise to more fertile soils which support the more climactic forest types in the vegetation mosaic.

Figure 3.1 shows details of topography and drainage of the Hellyer lease area and the location of some key monitoring points. The tailings dam is at 630 m ASL, and the wetlands are at 623 m ASL. The limed tailings are piped to the northwest and northeast corners of the dam, with mill site runoff draining via Mill Creek to the northeast corner. The runoff and creeks to the north and east, and west of the dam are diverted from entering the treatment area to just upstream of H1 by drains E (H9) and W (H11). The drain E crosses Mill Creek by aqueduct. A small catchment area with no creeks along the hillside north of the dam remains undiverted. The water intake for the mill is at the Southwell River (H3), which ultimately transfers 100 L/s (some 14% of mean flow at H3) into the Que catchment. The steeply incised valley of the Southwell is little affected by water quality from the Hellyer or Que operations aside from partial surface runoff and leaching from the Hellyer portal landing and haulage road. Water drainage from the mine is pumped to the mill into the treatment stream.

3.1.2 Soils and water

Weathering of the rocks has left poor, leached soils consisting of resistant minerals which contribute little dissolved material to the groundwater, and very little suspended matter to streams when the soil and vegetation is intact. The rainforests, wet forests, scrub and moorlands have built up peaty soil horizons based on these residual soils, which contribute organic (humic) acids to groundwater to give the characteristic brown colour to western Tasmanian rivers and lakes (Buckney & Tyler 1973, Ling *et al.* 1989). The humic content dominates the water chemistry, with Pieman tributary content ranging 5-15 mg/L measured as dissolved organic carbon (Koehnken 1992). Organic acid molecules in the waters constitute a significant food source for aquatic life (Salonen & Hammar 1986), particularly important as the attenuation from the brown colour limits aquatic photosynthesis. The minor mineral content of these brown waters reflect its dominant origin, with the relative ion composition resembling very dilute seawater. In a few locations in the Pieman catchment (Vale of Belvoir, Mt Cripps, Webbs Creek, Savage River), there are residual carbonate rock deposits which locally add some hardness to the water. The drainage from these karst areas is cryptic (SRCC 1996), with only one known karst resurgence near Hellyer, along the Vale River. The more usual acidic humic-dominated waters are somewhat aggressive in extracting and transporting metals as organic complexes and by adsorption onto particulates, to the extent of being able to mobilise gold (Baker 1977). While some metals may become more soluble by the presence of humic substances in Pieman waters, the complexation renders the metals less available (or toxic) to biota (Koehnken 1992) until release upon mixing with seawater.

PLAIN

Proposed Cradle Mountain Link Road

Proposed Railway Line

Southwell River

Catchment boundary

Flow gauging station

Water quality station

20 Years of Tailings

5 Years of Tailings

MURCHISON HIGHWAY STATE RESERVE

Water Supply

Future Major Tailings Storage

H3

Access Road

Q6

H1

Mill Site

W9 Mine Portal

Q9

H5

Q8

Haul Road

SOUTHWELL RIVER

HIGHWAY RESERVE

0   1 km

WARATAH

CROWN LAND

Ovie River Mine

HELLYER PROJECT

PROJECT AREA DRAINAGE

Figure 3.1: Topography and drainage of the Hellyer lease.
from Miedecke (1988)

Where there is local disturbance without remediation, in the form of clearing, logging, fire or unsealed roading such that the forest, litter and peat cover is lost, the exposed residual mineral soils are readily eroded and contribute high sediment load to streams. Natural revegetation in such cases is very slow, and usually require pro-active rehabilitation. There are many old 4WD tracks entrenched to deepening bedrock gullies in the Pieman catchment, some visible as scars from great distances in open moorland country. The partial soil map in Figure 3.2 shows some of the local complexity around the mill, tailings dam and wetlands area. It follows closely the underlying surface expression of the geology around the lease area, Figure 1.3.

3.1.3 Climate

The climate is best described as wet cool temperate, in a strong westerly stream emanating from the Southern and Indian oceans known as the "Roaring Forties" which colourfully describes both wind speed and latitude. The climate at Hellyer (Figure 3.3) features 2000 mm annual rainfall often falling as drizzle, sleet and snow (Figure 3.4). The wettest period on average, is from April to October, but heavy rain has been recorded in all months. The wetland site is typically cold, with predominantly westerly winds often exceeding 25 knots. However, the local weather is fickle (Figure 3.5), and within a day's fieldwork one can easily experience each of the four seasons thrice or more, or suffer relentless heat, or icy cold, all day that may last several days. The brunt of storms and cold fronts is generally borne by western Tasmania. The instability and unpredictability of the weather presented difficulties with the fieldwork programme for this study.

Within the Pieman catchment, rainfall increases from west to east, ranging from 1120 mm near the coast to over 3000 mm in the more mountainous east which includes the Cradle Mountain National Park (Koehnken 1992). The orographic effect of westerly driven precipitation in this region clearly favours water catchment above 500 m ASL, hence the major contributors to the Pieman are the Murchison (28% of total flow) and Mackintosh (14%) rivers (which now combine in the hydro-electric impoundment, Lake Mackintosh) and, significantly for this study, the Huskisson River (13%). Much of the Huskisson catchment streams fall from the 600–700 m plateau which bears similar rainfall to Hellyer.

3.1.4 Vegetation

The Pieman catchment is clothed in a variety of vegetation types. About half of the area is covered by rainforest (Koehnken 1992). The remainder includes buttongrass and tussock grass moorlands, wet and dry eucalypt forests and wet scrub (Koehnken 1992). The decomposition of vegetation on peat soils and leached bedrock in high rainfall leads to the catchment water being dominated by dissolved organic compounds giving the characteristic clear tea-brown colour. Areas of the Huskisson catchment have been subject to clearfell-burn logging since 1975, after the main access, Huskisson Drive, was pushed through to below the Ramsay River. More recent logging in the Hatfield,

Legend:

- Peat over rhyolite
- Forest peat over rhyolite
- Forest peat over Mt Read volcanics
- Peat over shale
- Forest peat on shale
- Mineral soils on andesites
- Dolerite clays
- Basalt clays
- Alluvial silts, sands and gravels
- Alluvial clay deposits

HELLYER PROJECT

SOIL TYPES

Figure 3.2: Partial soil map of the Hellyer lease.
from Miedecke (1988)
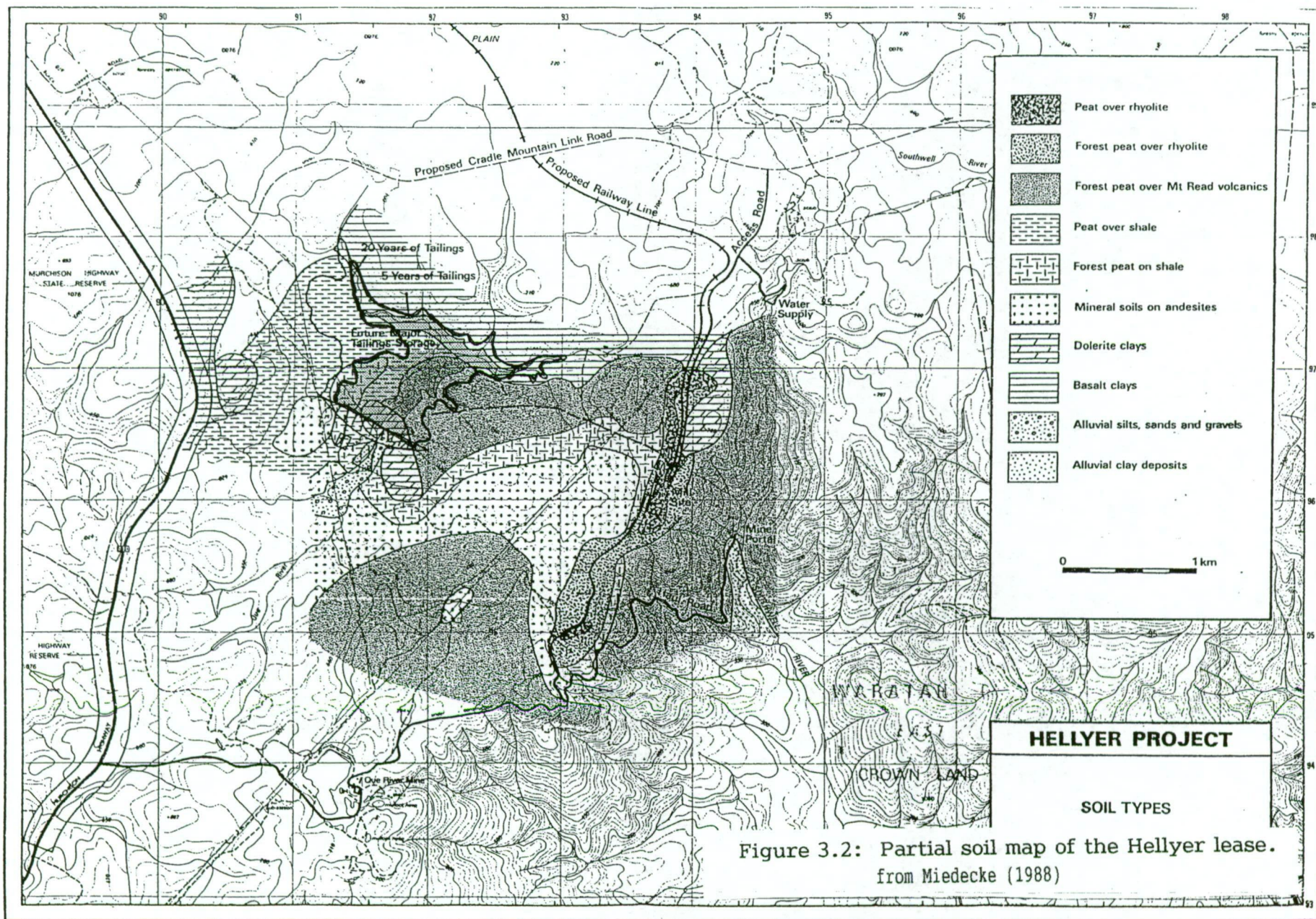
HELLYER MINE, TAS.

1985–1994
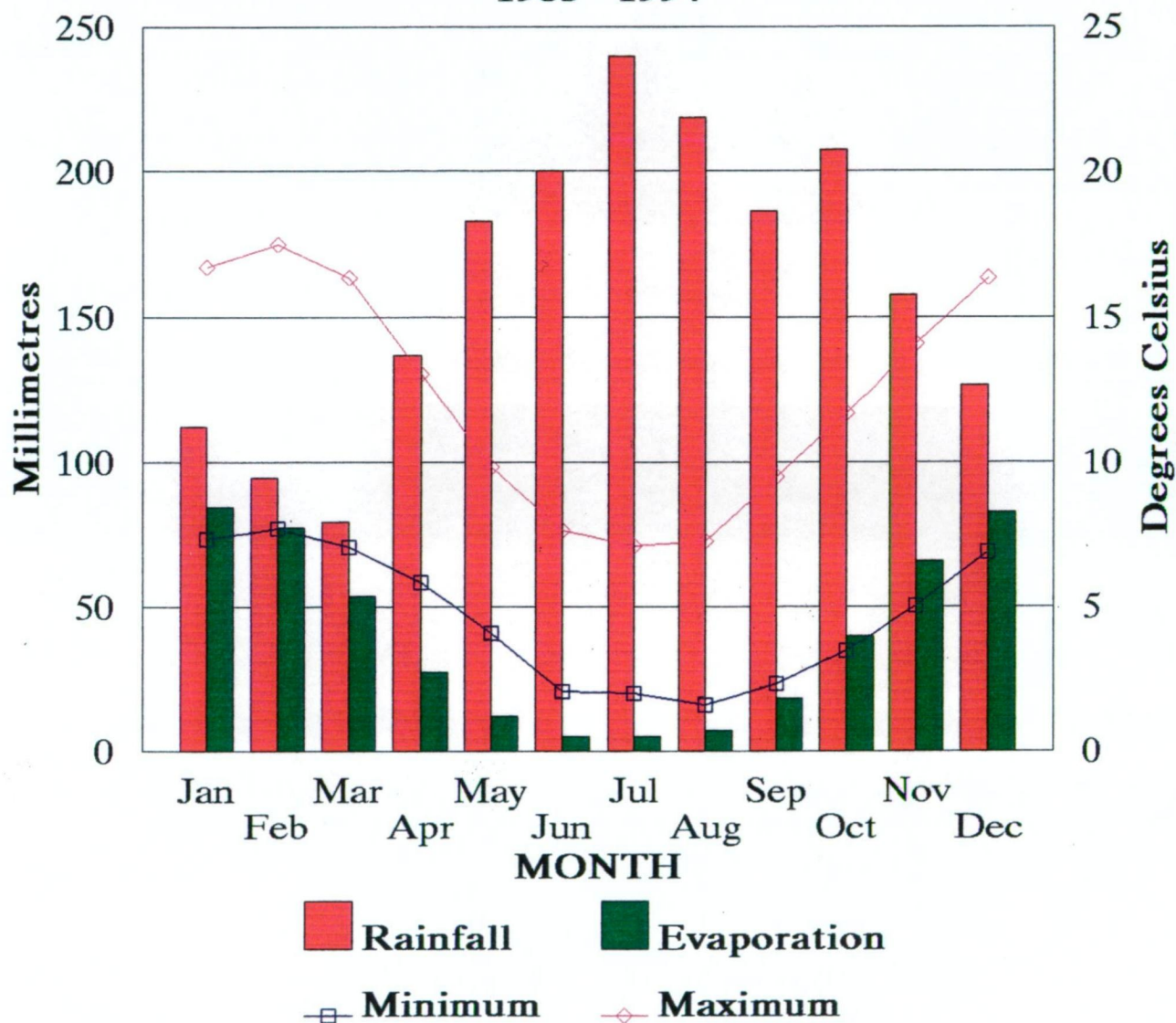
Figure 3.3: Averages for weather recorded at the Hellyer lease
(measured at Que River Mine offices, then at Hellyer Mill)

Figure 3.4: Snow on the wetlands during sampling for this study

Figure 3.5: Tasmanian weather pattern summary.
by Kudelka, *The Mercury* 17/1/97, p18

Que, Bulgobac and John Lynch catchments have contributed to loss of topsoil and forest cover. Many of the logged areas have very poor revegetation, much erosion of denuded soils and significant weed invasion.

Vegetation cover of the upper Que catchment (Figure 3.6) is predominantly natural forest mosaic including rainforest, wet scrub forest, woodlands and moorland. The vegetation locally reflects topography, aspects of complex underlying geology, heavy-rainfall leached soils and patchy fire history (Reid *et al.* 1999). There are cleared areas from human activity with associated erosion, and some areas of regrowth and replanting.

Considering the site in more detail (Technical Services 1976, Miedecke 1988): there are three "grades" of rainforest on the lease. The "first" is 90% dominated by myrtle (*Nothofagus cunninghamii*) typically 30-40 m high with butts 3-4 m in girth, with a few sassafras (*Atherosperma moschatum*) and celerytop pine (*Phyllocladus aspleniifolius*). This callidendrous forest features open understorey of mosses and hepatics with occasional treeferns (*Dicksonia antarctica*). This fully stocked climax community grows on yellow basaltic clays, and is vulnerable to the interests of forestry exploitation. Prime examples of this forest are on the northern hillside overlooking the tailings dam, and to the valley east of the New Wetland. The "second grade" of rainforest on poorer soils is 30 m tall with butt girths 2.5-3.5 m, still dominated by myrtle, but with more sassafras and celerytop, some leatherwood (*Eucryphia lucida*), horizontal (*Andopetalum biglandulosum*) and native plum (*Cenarrhenes nitida*). Leatherwood, native to western Tasmania, is prized for its flower by apiarists, and many sites in the Pieman catchment are seasonally used for hives. The "third grade" rainforest reaches only 10-20 m tall, 2 m butt girth, and occupies localised areas of impeded drainage. The species are the same as for the previous type with the addition of native laurel (*Anopterus glandulosus*). The fringes of "second grade" rainforest grade into Wet Scrub: Smithton Peppermint (*Eucalyptus nitida*), Yellow Gum (*E. subcrenulata*), *Acacia mucronata*, Whitey Wood (*Acradenia frankliniae*), leatherwood, horizontal, native plum, myrtle, sassafras and celerytop. One pure variant of this vegetation type (Gum with celerytop understorey), seen to the west of NW and H1, is poorly reserved (Jackson pers. comm.), and is only known in the headwaters of the Que and Southwell. The better drained slopes west of the wetland treatment area have patchy cover of 30-40 m tall Dry Sclerophyll: of Gum Top (*E. delegatensis*) and Smithton Peppermint with variable understorey of celerytop, native plum, tea tree (*Leptospermum* spp.), native pepper, (*Tasmannia lanceolata*), *Acacia mucronata*, Waratah (*Telopea truncata*), bracken (*Pteridium esculentum*), cutting grass (*Gahnia grandis*) and *Restio* spp. Of this, the Gum Top is of interest to loggers. The areas of poor shallow peat soils with poor drainage are covered by Buttongrass Plains: dominated by buttongrass (*Gymnoschoenus sphaerocephalus*), with other minor sedges, with occasional Swamp Peppermint (*E. rodwayi*). The fringes of Buttongrass Plain grade to Dry Sclerophyll with Smithton Peppermint, Black Peppermint (*E. amygdalina*), *E. brookerana*, *Monotoca* spp., and Mountain berry (*Cyathodes parvifolia*). Fired sites include grasses and native iris (*Diplarrena latifolia*). There are minor localised riparian vegetation communities.

Legend:

- Rainforest
- *Eucalyptus delegatensis* Tall forest
- *Eucalyptus delegatensis* Tall forest, recently cut
- *Eucalyptus nitida (E. brookerana)* Open forest
- *Gymnoschoenus sphaerocephalus* Sedgeland
- Vegetation complex associated with fluvial deposits
- Heavily disturbed ground

HELLYER PROJECT

VEGETATION COMMUNITIES

Figure 3.6: Vegetation map of part of the Hellyer lease.

from Miedecke (1988)

There is a significant total of areas of eroding cleared sites on the lease (Figure 3.6); variously associated with electricity transmission lines, mine workings, water management and mineral exploration, forestry, and road and rail construction. Thus far, in comparison to disturbed areas nearby, there is only minor weed invasion on the Hellyer lease.

There is a patchy fire history of the lease area (Technical Services 1976), though the effects have not been extensive. The Buttongrass Plains and Dry Sclerophyll vegetation shows signs of succession following infrequent natural (lightning) fires. The oldest obvious lease disturbances by humans are 4WD exploration tracks and the gold prospect near the Que dam (ca 1970–73). The lease is cut by active HEC transmission easements, and tracks for selective logging. There are signs of fires associated with these activities, with erosion, and scrub regrowth including cutting grass and tea tree. The sealed Murchison highway, downstream to the west, has been of minor environmental consequence to the Hellyer lease. Less so than the wide cleared breaks either side of the Cradle Link Road, opened in 1991, upstream to the north. Farther to the north beyond the lease, the *Poa* grassy woodlands are partly a result of early pioneer shepherds' (and probably prior Aboriginal) area burning to encourage growth of feed grasses. Doubtless spot-fires from these activities helped shape the current vegetational mosaic at Hellyer.

3.2 The Hellyer Mine

This description draws upon personal site visit observations, personal communications with Bob Reid, Geoff Richmond and Gary McArthur, from Aberfoyle Resources unpublished information, Aberfoyle Limited (1985–96), Miedecke (1988), and Technical Services (1976).

Aberfoyle Limited has a considerable mining history in Tasmania: From the 1930s the company engaged in Sn and W mining including mining at Rossarden, and more recently reworking at Cleveland (1968–1986) and Que (1980–91). Hellyer orebody was discovered on the Que lease in 1983. Drilling to prove reserves and sampling the new ore during 1985-1986, was followed by commencement of trial milling and ore extraction experiments at Luina in 1986–1988. Mill, railway and tailings dam construction and initial underground mine development took place 1987-1988. Full production was reached in a few months of the new mill opening in early 1989. The mine is highly regarded as an efficient and profitable operation, with sufficient margins to insulate against market price fluctuations. Closure of the present operation is expected with orebody exhaustion in 2001. However, further winning of residual base' metals and/or Au from reprocessing of the finely ground tailings is being investigated for the future.

The mine orebody is 300 m below the surface offset some 500 m northwest of the site of the concentrate processing mill. It is accessed by a 1.2 km adit from the Southwell portal by the Southwell River (Figure 3.7). The underground mining is by creation of a (many kilometre) network of 5 m x 5 m incline and drive tunnels surrounding the orebody, drilling and blasting alternating
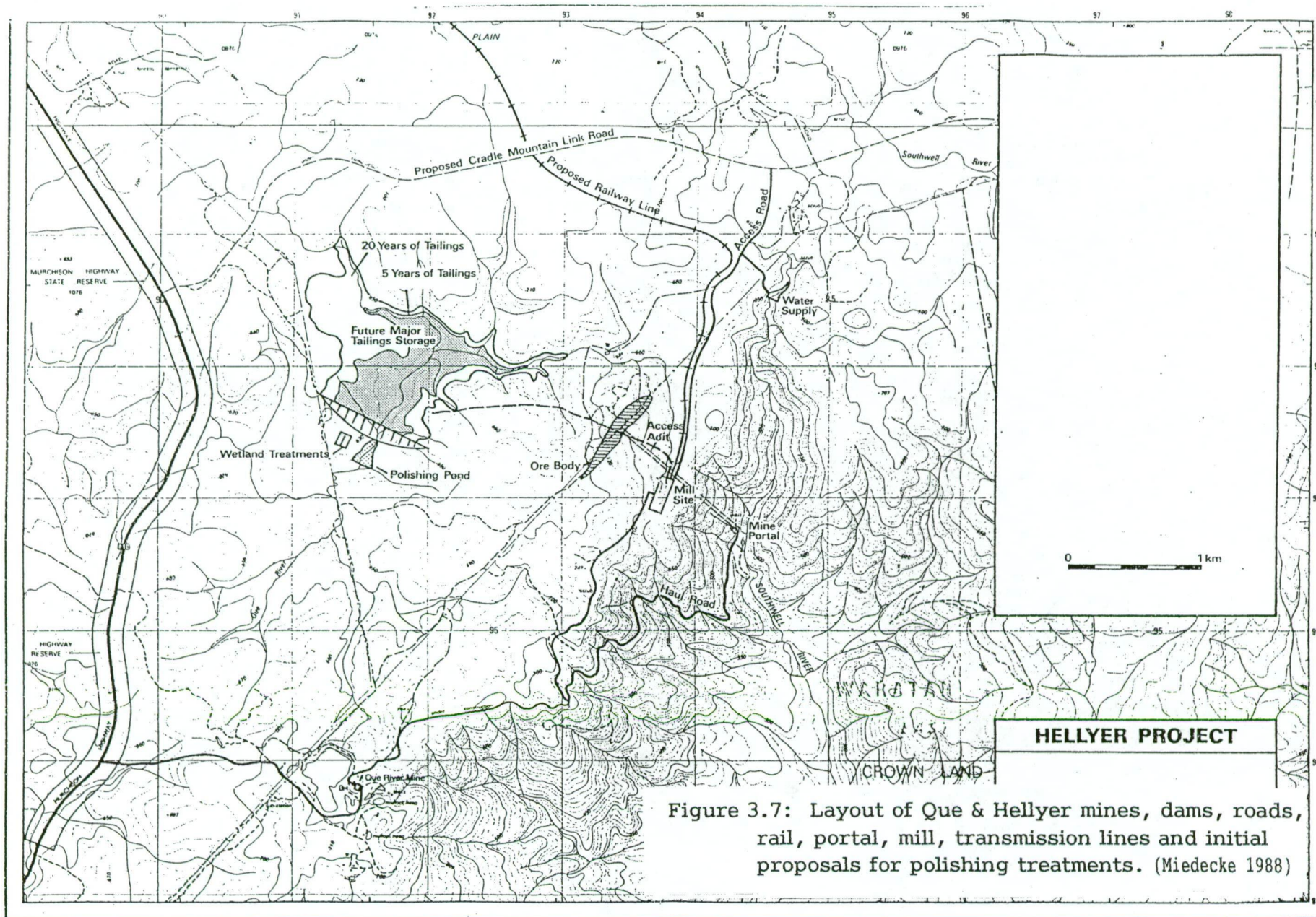
Figure 3.7: Layout of Que & Hellyer mines, dams, roads, rail, portal, mill, transmission lines and initial proposals for polishing treatments. (Miedecke 1988)

20000-100000 t stope sections, loading broken ore rubble from the bottom of the sections onto 35-55 t trucks, cemented waste-rock infilling of voids, then similarly removing the pillar sections. Ore is trucked up the 5 km haulage road from the portal to processing mill stockpiles.

The 16 million t reserve is being mined at 1.3 million t/y over a 12-13 year period of active mine life. The average ore composition is shown in Table 3.1.

3.2.1 Hellyer orebody

In the Cambrian (over 500 million years ago) the mine area was a submarine volcanic zone. Hydrothermal marine waters passed through the volcanic deposits partially dissolving metals from the rocks, then rose to the sea floor to precipitate a single mineralised lenticular mound upon contact with the cold seawater. The geological history that followed included numerous events of further rock deposition, chemical alteration, folding and deformation, raising and lowering, and faulting. The surface geology (Figure 1.3) today is very complex. The present topography hid any expression of the Hellyer orebody prior to its discovery on the Que River Mine lease by a combination of geophysics and test drilling.

The irregular and fault-displaced orebody (Figure 3.8) extends 850 m x 150 m in plan (Figure 3.7), with an average vertical thickness of 35 m (Miedecke 1988). The fine grained polymetallic sulphide ore manifests as four main differentiated compositional "zones" and a barite rich cap (products of deposition, hydrothermal alteration and deformation processes) which are mined and stockpiled separately (Table 3.1). Cap rock usually falls into stope blasts mixed with another ore type.

The mineralogy of the ore is complex, and the composition of individual minerals is also variable (Table 3.2).

Table 3.1: Composition of ore zones, and average ore mined at Hellyer

Zone	%Cu	%Pb	%Zn	ppm Ag	%Ba	%As	%Fe	%S	ppm Au
"yellow" Keel	0.2	5	14	190	0.6	1.1	28		
"blue"	0.7	14	23	150	0.1	1.6	20		
"green"	0.3	11	22	250	1.7	1.4	21		
"red"	0.6	16	24	570	0.2	0.9	19		
"barite" Cap	0.3	5	8.8	95	22	0.4	13		
average ore	0.35	7	13	160		1	26	35	2.3

data courtesy Aberfoyle Resources

Table 3.2: Average mineralogy of the Hellyer ore

Mineral	ore%	formula	details
Pyrite	55	FeS_2	85% crystalline euhedral cubic pyrite, up to 1 mm 15% amorphous primitive "melnikovite", porous and containing Pb, As, Sb & Ag
Sphalerite	20	ZnS	70% coarse annealed masses up to 0.5 m with 2-8% Fe and Pb, Cu & CO_3^{2-} 20% remobilised up to 5 cm with 0-3% Fe and 10% interstitial to cubic pyrite <1 mm with 1-4% Fe
Galena	8	PbS	80% remobilised up to 5 cm grains 10% blebs in annealed sphalerite up to 100 µm 10% very fine grained interstitial <10 µm
Arsenopyrite	1.5	FeAsS	euhedral rhombs/needles up to 500 µm associated with quartz/pyrite
Chalcopyrite	1.5	$CuFeS_2$	80% remobilised <5 cm 15% blebs in annealed sphalerite <100 µm 5% "chalcopyrite disease" in sphalerite, <20 µm
Tetrahedrite	1	$Cu_{12}Sb_4S_{13}$	with partial substitution with ~4%Ag, also Fe, Zn & As 95% remobilised <5 mm 5% blebs in annealed sphalerite <100 µm
"Barren"	13		quartz, chlorite, sericite, calcite, barite

data courtesy Gary McArthur, Aberfoyle Resources

WEST / EAST

Surface

Jack Fault

Adit

STRATIGRAPHIC UNITS

△	Upper Rhyolitic Sequence
—	Que River Shale
▫	Pillow Lava Sequence
o o	Hanging Wall Volcaniclastic Sequence
Ba	Barite
▨	Base Metal Sulphides
	Feldspar Phyric Sequence
▨	Stringer Zone
▨	Stringer Envelope Zone

ALTERATION MINERALOGY

Fu   Fuchsite
Si   Silica
Ab   Albite
Cl   Chlorite
CO   Carbonate
Se   Sericite
Q   Quellite (Sericite-Silica-Pyrite)

0 ————— 100m

Figure 3.8: Diagram of Hellyer orebody structure.
from Miedecke (1988)

HELLYER PROJECT

HELLYER ORE BODY
SCHEMATIC CROSS SECTION

Date: October 1987	Figure: 3.1

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3.2.2 Processing mill

The fine grained and complex ore requires rigorous grinding to 45 μm to break up the minerals prior to separation by flotation on site; much finer than for other Tasmanian west coast mineral extraction operations (Que ore was processed at Rosebery). Combined with the ore reserves, this required development of the new on-site processing mill facility. The design and operation was based on experimental trials at Luina 1986-1988. A simplified schematic of the Hellyer processing mill is shown in Figure 3.9.

The stockpiled ore (four zone segregations which are blended to produce a consistent feed composition) is initially passed through a primary jaw crusher to size <150 mm on to a smaller crushed stockpile. The crushed ore is conveyed to the Mill and enters Semi Autogenous Grinding (SAG) mill with water, screened to 1.5 mm, then to Ball milling to pass hydrocyclones at 45 μm. This raises the temperature of the ore slurry to 40°C (up to 55°C) depending on the ambient conditions. The detail of the flotation process is rather convoluted, but by means of addition of various reagents, manipulating slurry and air flow conditions, long and sequential flotation treatment, regrinding in tower mills to 25 μm, and thickeners; four grades of mineral concentrate are produced (Table 3.3), dried in filter presses and stockpiled for loading onto train and ultimate shipment to refineries in NSW, Japan and Europe. The tailings (Table 3.4) are treated with lime and piped to the tailings storage dam.

Table 3.3: Composition and tonnage of four grades of mineral concentrate produced by the Hellyer mill for sale

Concentrate	t/y	%Cu	%Pb	%Zn	g/t Ag	g/t Au
Copper	10000	13			4500	5
Lead	60000		55		600	
Zinc	250000			50		
Bulk	40000		15	35	200	

data from Aberfoyle Limited (1985-96)

Table 3.4: Composition of Hellyer tailings solids (780000 t/y)

Tails	%FeS$_2$	%Fe	%Cu	%Pb	%Zn	%As	g/t Ag	g/t Au	%S	%NSG
Zn Scavenger	60	30		1	1	1	70	2.5		.30
Bulk Rougher	60	30		6	8	1.2	120	3		2
(combined)		30	0.2	3.7	3.5				32	

NSG=non-sulphide gangue, data courtesy Aberfoyle Resources

HELLYER CONCENTRATOR FLOW SHEET

Figure 3.9: Hellyer processing mill (simplified schematic). courtesy Aberfoyle Resources.

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REAGENTS
Sodium Metabisulphite (SMBS)
Potassium Amyl Xanthate (PAX)
Copper Sulphate (CuSO₄)
Zinc Sulphate (ZnSO₄)
Sodium Cyanide (NaCN)
Interfroth (IF56)
81059 Promoter
Lime

STOCKPILES

BIN

CRUSHER
600 tph

CRUSHED
STOCKPILE
10,000 t <150 mm

160 tph

DSM SCREEN

CYCLONES

SAG MILL

BALL MILL

TOWER MILL

P80 ±45 μm

Cu / Ag
CONDITIONER

Cu / Ag
ROUGHERS

Pb
CONDITIONER

Pb
ROUGHERS

Zn
CONDITIONER

Zn
ROUGHERS

TO
TAILINGS
DAM

BULK
ROUGHERS

BULK
CLEANER

TO TAILINGS
DAM

COLUMN
CELL

COPPER / SILVER
CONCENTRATE
4000 - 5000 g/t Ag
12 -14% Cu

Pb
CLEANER

TOWER MILL

Zn
CONDITIONERS

Zn
CLEANER

TOWER MILL

LEAD CONCENTRATE
55% Pb

ZINC CONCENTRATE
50% Zn

BULK CONCENTRATE
50% COMBINED Zn + Pb

Zn THICKENER

BULK THICKENER

Cu/Ag STOCK TANK

Pb STOCK TANK

Zn STOCK TANK

FLOCCULANT

BULK STOCK TANK

BULK FILTER PRESS

ZINC FILTER PRESS

Cu / Ag

LEAD

BULK

ZINC

LOADER

TRAIN

SHIP

3.2.3 Water and waste management

The basic scheme of water flows at Hellyer is shown in Figure 3.10. Figure 2 shows an aerial view of the water treatment system. See also geographic description in Section 3.1.1 and Figure 3.1. The mill uses approximately 100 L/s Southwell water and 100 L/s recycled water pumped from the tailings dam.

The two tailings streams from the processing mill (Zn scavenger and Bulk rougher, Figure 3.9) including dissolved oxidation products, metals (Table 3.4), thiosalts and SO_4, and residual reagents are combined, and treated with lime (90% $Ca(OH)_2$) to maximise metal precipitation upon entering the tailings storage dam at around pH 12. The carbonate content of the tailings contributes further acid neutralising capacity and the Hellyer residue is reasonably stable to acid mine drainage (AMD) generation in contrast to residues from Que and other mines; however, if left exposed to oxidation, Hellyer tails will generate AMD in 3–5 years (Miedecke 1988). The pH of the reacting limed tailings water falls to 7–9 by the time it reaches the dam discharge point. The tailings water varies in composition, but averages about 50% saturated with $CaSO_4$, the major solute. Buildup of these ions in the mill processing (SO_4 and other thiosalts originating approximately equally from reagent inputs and ore oxidation) is the primary reason why the water cannot be 100% recycled from the tailings dam. A safety margin of 50%-saturation of $CaSO_4$ is reserved for minimal processing interference by gypsum, and in the event the Southwell source stream becomes very low during possible local drought conditions when a period of increased recycling would become necessary.

The volume of tailings discharge (200 L/s water) to the dam is augmented by mine drainage (50 L/s) and mill runoff via Mill Creek. The additional flow from undiverted runoff entering the dam (including mill runoff) varies with rainfall 0–450 L/s (Blesing 1991). This variation is partially dampened by the retention and gradual release by the catchment that remains under organic soil and vegetation cover; however the runoff peaks emanating from other cleared and bared work areas are much more abrupt. The outflow from the dam is therefore 250–700 L/s. With 100 L/s being recycled to the mill, the net discharge from the tailings dam (and wetland treatment system) is 150–600 L/s, as measured at the bypass weir at Pond 1. Pond 1 is now replaced by a chemical sodium silicate flocculation treatment plant (installed in 1996) sited on fill. The chemical treatment removes some 90% of Pb in a floc which is thickener-concentrated and disposed of in the tailings dam (Reid pers. comm.).

The "old" Wetland 1 (OW) (Figure 3.11) treats 10–12 L/s of this discharge, which is recombined in Pond 2. Some 40 L/s of Pond 2 outflow passes through the "new" Wetland 2 (NW) (Figure 3.11), and recombines in Pond 3. Below the water treatment system discharge monitoring station H13, a further small Pond 4 was created in 1995. This pond discharge meets the waters of the diversion drains W and E before monitoring point H1 (the nominal Hellyer discharge).

Figure 3.10: Hellyer water management schematic.

(with adaptions)
by courtesy of
Aberfoyle Resources

HELLYER PROJECT
WATER MANAGEMENT PLAN
AUGUST 1991

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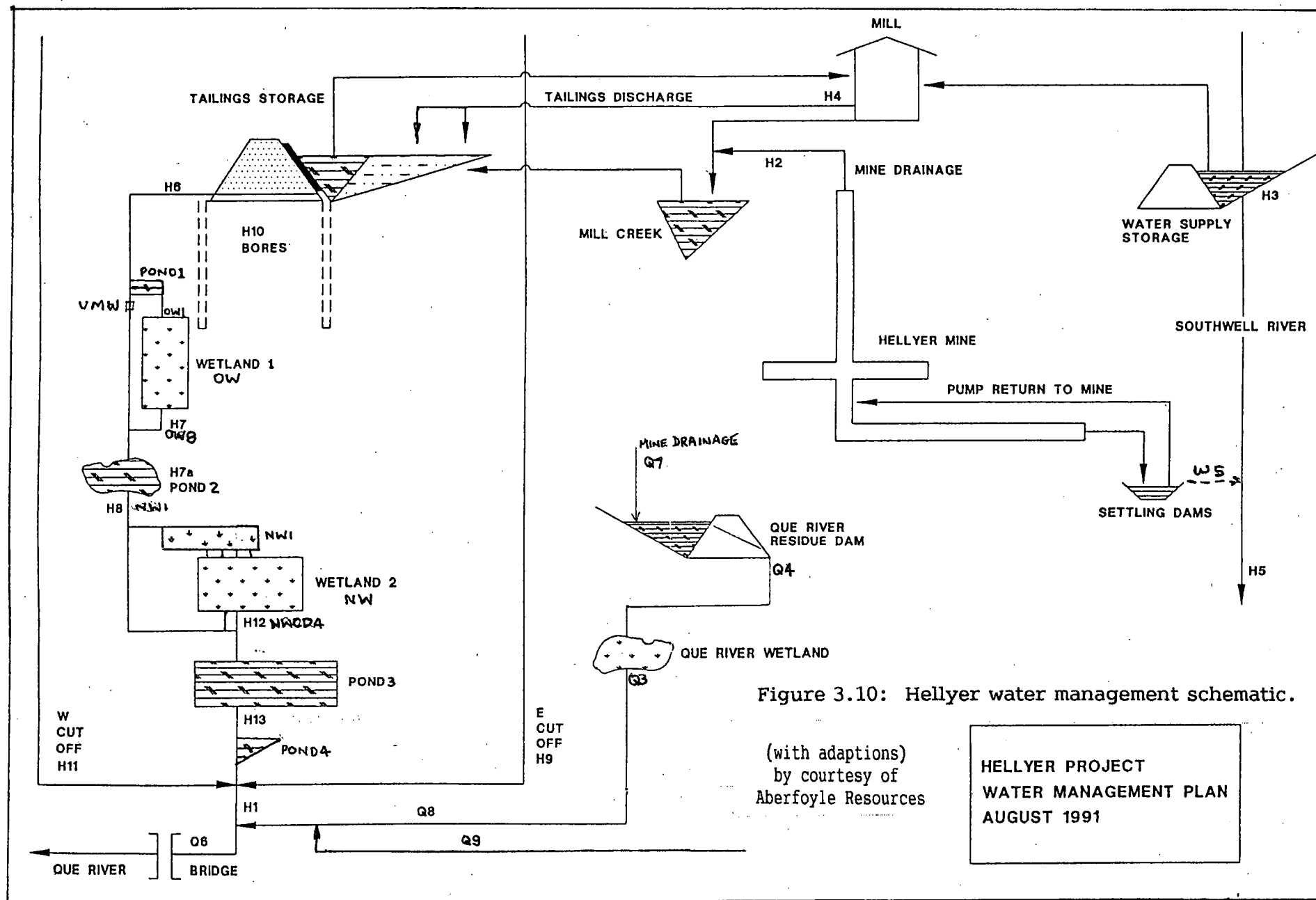
This combined water from Hellyer shortly joins the drainage from the Que River Mine (Q8) and naturally mineralised Amoeba Anomaly tributary (Q9). Before the monitoring point of the Que River at the Murchison highway bridge Q6 (the nominal mining lease boundary discharge) there enter a number of unpolluted tributaries.

Beyond the highway, the Que River is rapidly diluted by tributaries, notably the Bulgobac River with almost half the catchment to the end of the Que River (HQ) at the Huskisson River, where it is joined by the confluence of the Hatfield (HH) and Coldstream (HCS) rivers. The Huskisson gathers more tributaries including the Ramsay River (HR) and Webbs Creek before emptying into the Pieman impoundment (dammed 1986).

Table 3.5 shows the means of data from water quality of the Hellyer wastewater stream monitoring 1990-1995 (before the installation of the chemical treatment plant) from the tailings outflow (H6) to the lower Que River (HQ). The figures for Q6 and HQ are skewed by some high inputs from Que River Mine (Q8) before March 1992. Smaller anomalies and inconsistencies come from data entry errors, sampling and analytical errors (Chapter 4), and missing data from samples not being taken, or partial analyses. Alongside the result summaries are shown drinking water guidelines (which are not regulatory), and Hellyer operating licence targets. Lead is of the most concern, and the prime target of the experimental wetland treatment. Other inputs of concern are Fe, Mn, and SO_4 from both Hellyer and Que; and Zn and acidity from Que River Mine.

Table 3.5: Water quality summary for 1990-1995 monitoring at key sample stations in the Hellyer wastewater stream.

quality	units	licence[1]	drinking[2]	H6[3]	H7	H13	H1	Q6	HQ
pH			6.5-8.5	8.6	6.1	6.2	6.3	4.9	5.0
conductivity	µS			1450	1150	1300	800	700	235
dissolved O_2	ppm	>4.4		7.5	6.5	7.5	8.5	8.5	7.6
hardness-$CaCO_3$	ppm		<500						
SO_4	ppm	<250	<400	520	470	520	310	300	65
Ca	ppm								
Cl^-	ppm	<350	<400	30	29	30	19	16	12
F^-	ppm	<1.5	0.5-1.7	0.8	0.7	0.6	0.4	0.5	0.1
Na	ppm			46	37	41	25	19	9
K	ppm			18	14	16	11	9	2
Mg	ppm			6	8	7	5	5	2
Zn	ppb	<5000	<5000	670	660	800	350	8900	880
Cu	ppb	<1000	<1000	130	80	130	190	100	50
Fe	ppb	{ <1000 }	<300	3200	7000	4600	1600	1900	900
Mn	ppb	{combined}	<100	670	1100	970	500	1000	220
Pb	ppb	<50	<50	640	250	410	220	200	47
As	ppb	<50	<50	22	13	10	5	4	1
Cd	ppb	<10	<3	8	7	9	5	22	5
Hg	ppb	<2	<1	0.5	0.5	0.8	1.4	0.5	0.6

[1]Blesing 1991 [2]NH&MRC/AWRC 1987 [3]station means from unpublished Aberfoyle Resources data

Figure 3.11: Hellyer wetlands: (top) Pond 1 and OW seen from the tailings
dam wall, with white PO_4 pipe entering OW1 and measuring weir,
monitoring hut, and bypass channel on the right; (bottom) NW and
part of Pond 3 seen from a rise to the south, with a portion of the
East cutoff drain passing under the road in the foreground.

Chapter 4: Environmental monitoring - aspects of environmental sampling.

4.1 Introduction

One of the weakest aspects of environmental monitoring is sampling. Samples at the case study site were taken from matrices that can be highly inhomogenous over three dimensional space and time (Pitard 1989). The sampling variation of real-world monitoring can be orders of magnitude greater than the analytical error (Markert in Adriano 1992, Lichon 1992).

Environmental monitoring has its own set of difficulties and variables (ACS 1983, Keith 1991), especially in the context of the Hellyer Mine site, on the West Coast of Tasmania. Hellyer is an underground mine at which Aberfoyle Resources brings ore to the surface for flotation processing into Zn/Pb concentrates for shipping. Study focus is on effluent treatment for the removal of Pb. The site receives over 2000 mm of rainfall per year, some of which falls as sleet, snow and hail, often at near-horizontal angles with the winds of the "Roaring Forties" from the Southern Ocean. Many activities at a mine site have effects on effluent outfall, some less predictable than others in both magnitude, distribution and duration.

This chapter, published in Lichon (1996), discusses aspects of the protocols, sampling technique, field operations and consequences, as applied at the Hellyer Mine site for this study and hopefully also by environmental staff, acting on my advice.

4.2 Nature of the streams

The wastewater and catchment streams of interest were found to be of heterogeneous composition both spatially and temporally.

Some vertical variation in water parameters is to be expected for water bearing suspended material. An unexpected factor that the presence of surfactants, occurring naturally in west coast waters and originating from flotation plants together with light insoluble matter can give rise to surface scums, which tend to attract heavy metals as shown in Table 4.1.

Table 4.1: Pb in samples of scum-laden H6 overflow.

Depth	Concentration Pb mg/L
Surface	3.70
-50 mm	0.65

Grab samples, assayed by AAS (Section 2.6.2.1)

Dissolved matter ought logically to be uniformly distributed, but in reality it interacts with other non-homogenous components including the air and stream

bed surfaces. Colloidal matter is present throughout the depth of the stream, although interaction with the surfaces of insoluble material forms boundary layers. Colloidal organics and suspended organic matter and clays have metal-binding properties, and tend to concentrate metals by their distribution. The lower portion of the streams tend to concentrate heavy suspended material, both fine matter sinking against diffusion and silt held in suspension by turbulent mixing. The degree of depth differentiation of suspended matter depends upon flow rates and local turbulence. The bedload of the stream consists of coarse matter mobilised downstream by saltation and traction, and is particularly significant during high flows. However, sampling the base of streams is fraught with practical difficulties, and is usually ruled out. The most reproducible sampling depth of −50 mm is thus likely to sample the portion of the stream with the lowest total metal content, and hence underestimate the metals in the whole stream.

Horizontal variation in water parameters results from stream braiding over differing substrates, and the lateral entry of tributary streams of differing composition. Figure 4.1 illustrates an example of spatial variation, particularly for Eh, Pb and Zn, across a 5 metre wide stream at one monitoring point. Figure 4.2 illustrates the variation, particularly for conductivity, Eh, D.O., Zn and Pb, across a 200 mm wide drain. The variations in both examples were real and consistent, and well exceeded analytical errors. This demonstrates the common assumption that streams such as these are homogeneous solutions is an erroneous one. Reproducible results can only be obtained from samples taken at the same position, or preferably below a point of thorough turbulent horizontal and vertical mixing.

4.3 Variation over time

Temporal variations in water parameters can vary from annual cycles of rainfall dilution, through diurnal changes, to the short term irregular changes resulting from human activity. Significant changes have been monitored over time scales as short as minutes. Figure 4.3 shows variability of Pb at H6, sampled weekly over 5 years. Figure 4.4 illustrates variations recorded in samples taken at 2-3 day intervals at H6. Figure 4.5 shows the variability of Pb at H6 at a thrice daily sampling regime. It is clear the sampling at weekly and 3-day intervals would miss potentially important variation events detected when sampling each daily work shift. It should be borne in mind H6 samples outflow from the tailings dam to both recycling to the mill and to treatment by the chemical water treatment system and wetlands. The theoretical residence time in the dam being 3 days; however field pH readings at H6 taken each work shift to adjust lime addition to mill discharge show significant variation within the expected residence time (Blesing 1991); indeed, during this study I noted an event of pH change at OW1 of 1 unit over 30 minutes. The temporal variation in Figure 4.5 supports the finding that there is some channelling of flow down the eastern side of the dam (von Gunten *et al.* 1991). The response was to install a second tailings discharge to the northwest corner of the dam. Temporal variation of water quality parameters, and Pb in particular, is due to
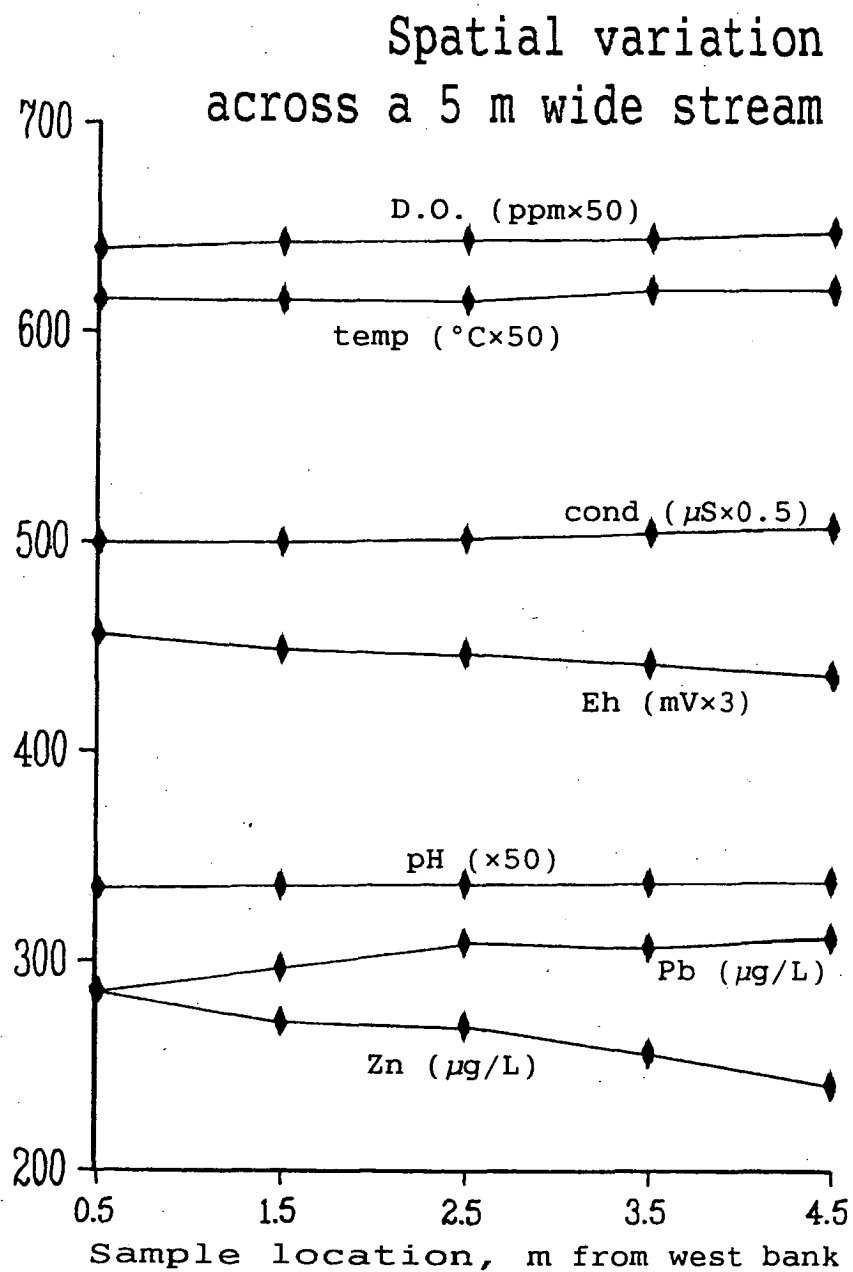
Figure 4.1: Variation of water sampled across the width of H1
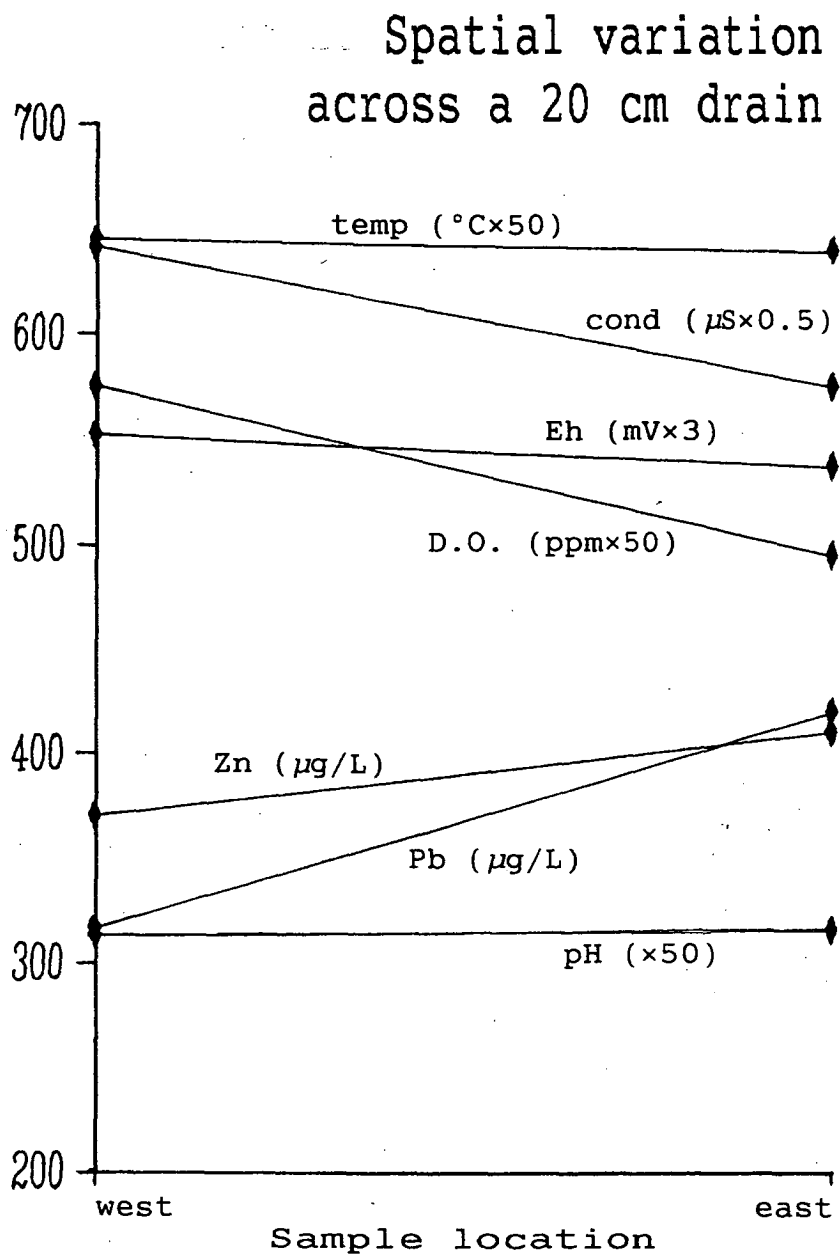
Figure 4.2: Variation of water sampled across NW1

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Figure 4.3: Pb at H6, sampled weekly Oct 1990 – Oct 1995.

sample taken

Temporal variation of Pb
at one site (mg/L)

Date of sampling (approx every 3 days)
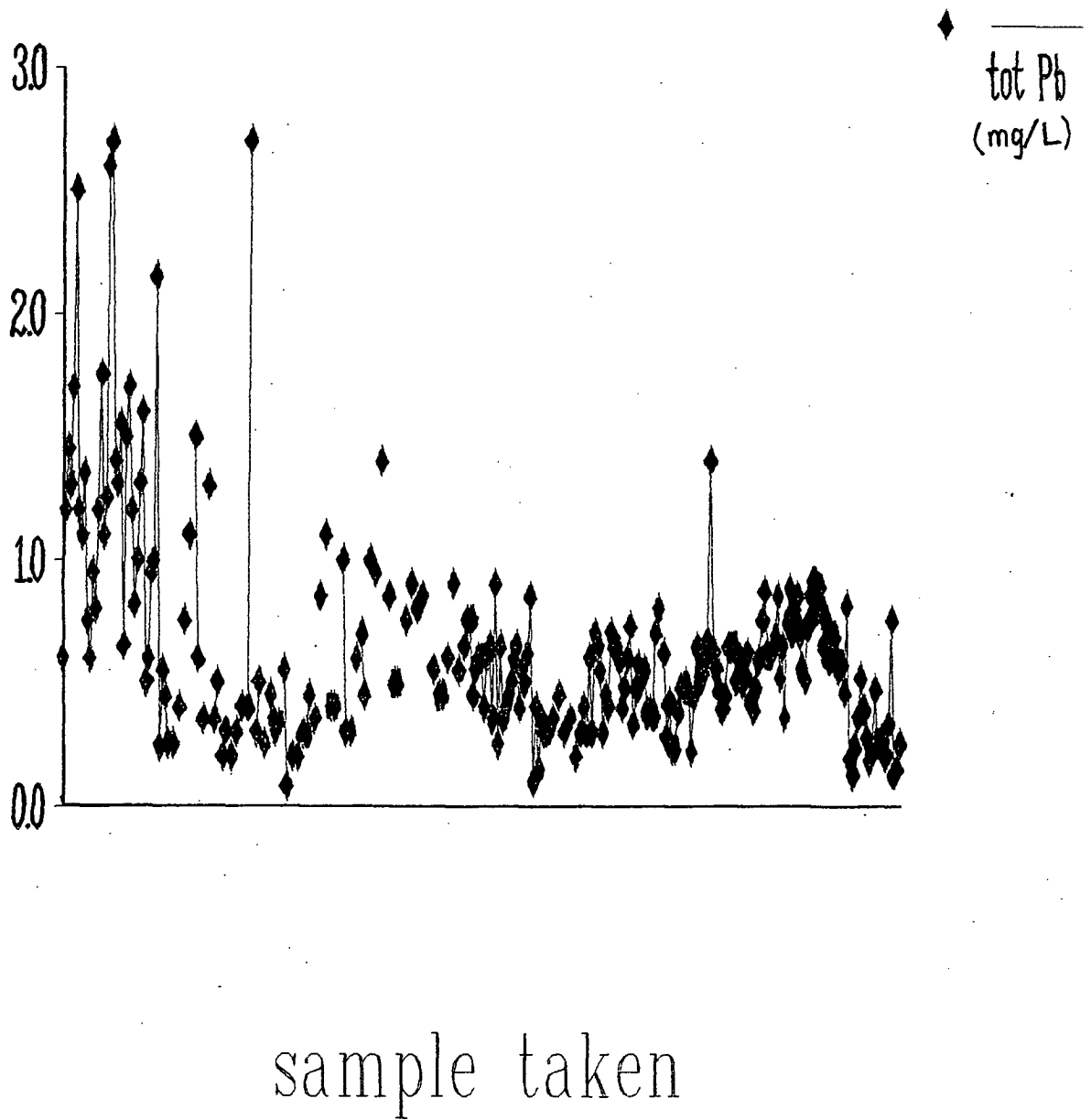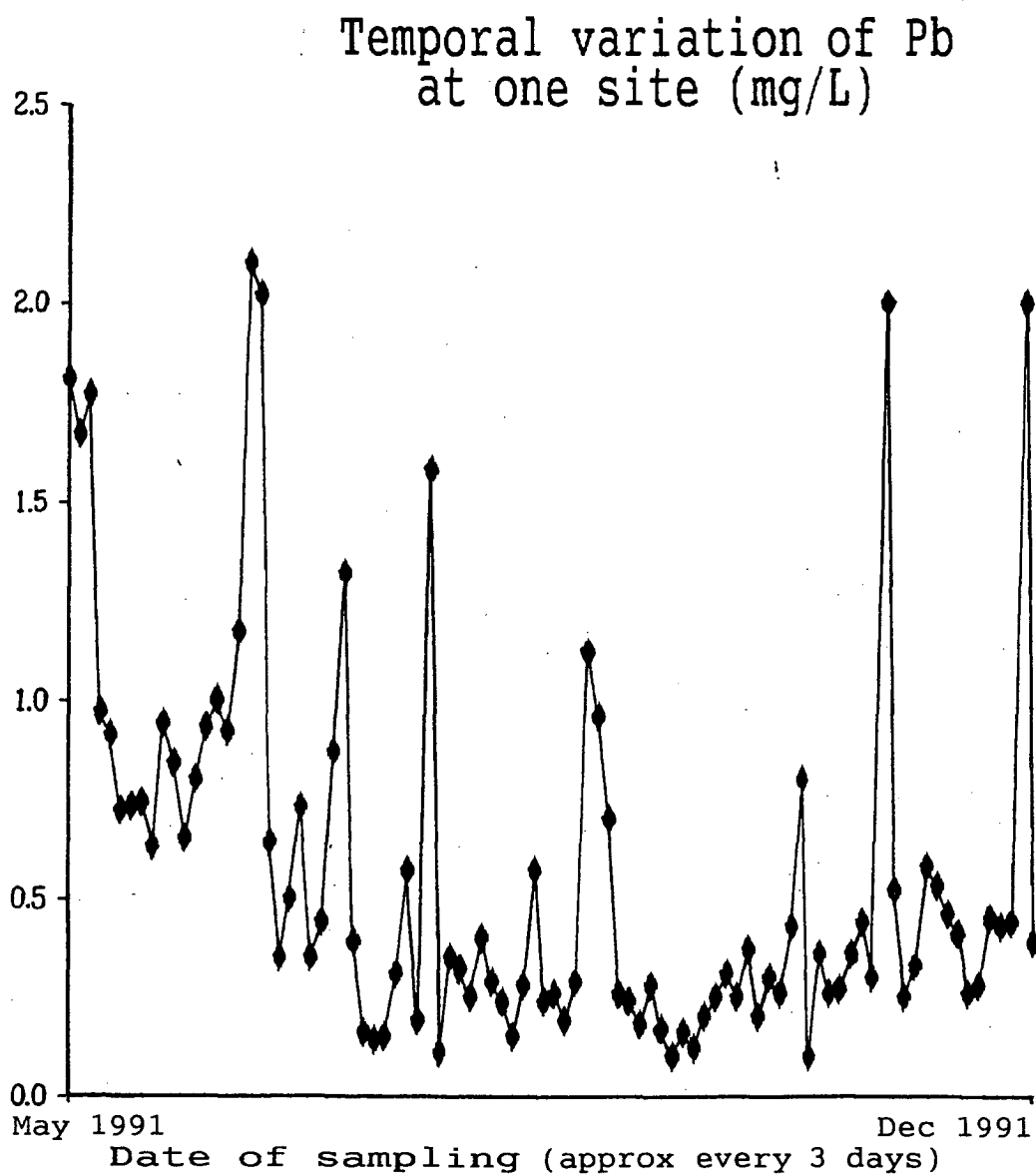
Figure 4.4: Pb at H6, sampled every 2–3 days.

Figure 4.5: Pb at H6, sampled three times per day.

FEED TOTAL Pb

mg/L

SAMPLES TAKEN

61
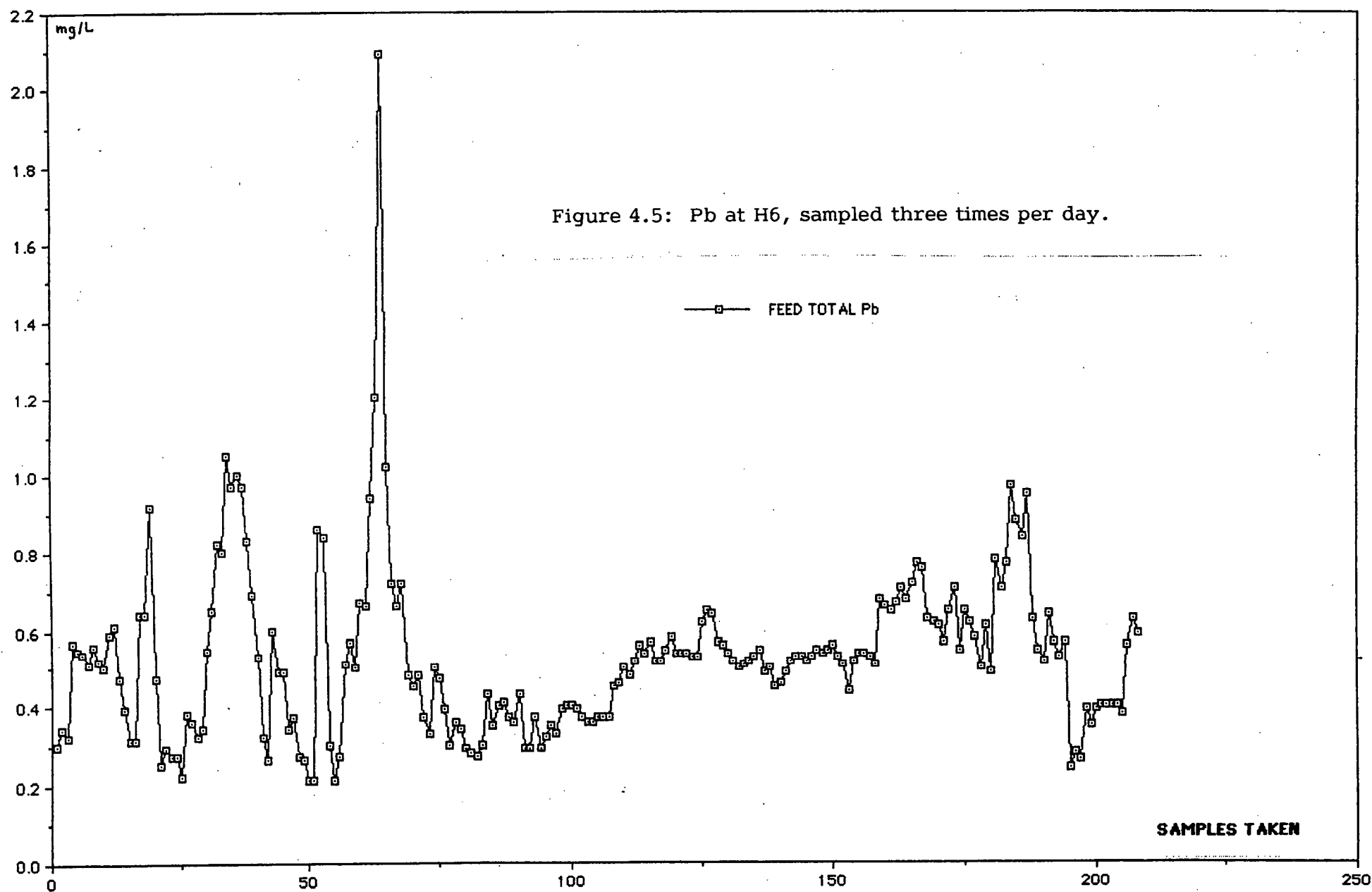
a myriad of factors: temperature, rainfall events, changes in mill effluent, reworking of tailings dam sediment by braiding streams, dam level fluctuations altering tails aerial exposure, machinery disturbance in the catchment area and so the list goes on. Put together these factors make the variation essentially unpredictable to a significant degree.

4.4 Sampling and storage techniques

Sample containers for environmental analysis need to be prewashed with nitric acid and purified water (Batley & Gardner 1977). This is especially so for containers shipped open, with lids supplied separately, and stored in contaminated environments. This being so, it could be the case that even precleaning may not guarantee accuracy. The use of these containers for blank water determinations, while not rigorous, can draw attention to contamination problems. SAA (1986) describes container preparation and sample preservation.

At Hellyer, environmental samples are typically taken just below the stream surface, in three portions: one with no preservatives, filled to the top, for anions and other non-metal assays; one preserved with 1% nitric acid for total metals; and a third filtered through a 0.45 µm porosity membrane then acidified for "dissolved" metals. Colour coded lids backed up the labels on bottles. Onsite readings of pH etc. were made at the time of sampling. Samples were typically assayed within a month. Florence (1977) noted that some unacidified samples can be stable over this time if kept cool. Sometimes precipitation was noted in Hellyer samples in this time interval, which could invalidate some analyses. Errors from these procedures, combined with operator errors (Section 4.5) are likely to have contributed to some of the doubtful results in the 5-year monitoring data sets (e.g. Figures 10.5, 10.9), and most particularly where contamination affected otherwise low-level analyte catchment samples.

For my research, I followed the same broad guidelines as a minimum standard. In addition, all temperature, pH, Eh, Dissolved O_2 and Conductivity was measured on site. With frequent poor weather and wet or muddy hands, I found it helpful to voice-record this type of field data on a dictation recorder kept in a plastic bag, rather than try to keep note paper dry and pens working, and needing two hands. Samples were labelled in two positions with a waterproof marker pen, in case part of one was rubbed off. All the meters, containers and recorder were conveniently carried in a plastic box (that would float if necessary) to the sampling sites, particularly useful for remote ones that required pushing through vegetation for access. All sample containers (usually polypropylene), field and laboratory plastic- and glassware was prepared by soaking in 5% nitric acid for 3 days, rinsing at least 5 times with deionised water, drying and storing sealed with its lid, or covered appropriately. All reagents and filter batches were tested as blanks, and appropriate standards and/or reference materials were used to maintain analytical quality control (Woodget & Cooper 1987). Where practicable,

chemical and SRB analysis was performed on site in the spacious 8-seater van; where not, samples were preserved as appropriate to the analytes (for example, with 1% nitric acid for metal assays) and assayed as soon as possible at accommodation in Waratah, or further afield at laboratory facilities, at University or Analabs.

4.5 Staff problems

Field vehicles are generally filthy, with mineral concentrate coating surfaces inside and out. Sample container preparation, filtering operations and dispatch were conducted in a room within a drill core shed at the Que River mine until 1995. These situations were subject to dirt, mud and mineral dust, and undoubtedly contributed to contamination of samples.

Initially monitoring staff purchased technical grade nitric acid for sample preservation. This point was soon detected and rectified by environmental management. At one later point the monitoring staff unilaterally decided to purchase and use 5.0µm filters in the place of the standard 0.45µm filters, because "it was quicker" to filter the samples. As a significant and variable proportion of suspended matter falls within this filtering range (Section 10.4.3), the assay results for these (non-standard) filtered samples were thus made less meaningful, at a not inconsiderable expense. It was perhaps three months before this practice was adventitiously discovered by the writer in December 1992, and another three months before it was rectified by mine management in March 1993.

Problems continued with these staff, drawn on a part time basis from the pool of geological staff. They were inadequately trained and poorly motivated in respect of their environmental sampling duties. The problems were partly resolved by the end of May 1993 by the employment of off-site laboratory services staff for sampling, who had fuller understanding of the intricacies of environmental sampling, and better motivation to take the necessary care and attention.

4.6 Sampling stations

The monitoring programme at Hellyer required the establishment of sampling points (in space) to define the environmental performance over time. As a result of sampling errors brought to light during this project, it has since been necessary to more rigorously define these sampling points to minimise spatial sampling errors.

The application of spatial sampling to environmental heavy metal sampling is well described by Morrisey *et al.* (1994). Shannon & White (1996) found uneven distributions in wetland processes. The principle of defining consistent sampling stations for repeatedly monitoring changes over time is described by Tattersall (1986), in reference to defining systematic sampling

grids over farm paddocks for monitoring soil fertility. Environmental managers at Hellyer had established a number of monitoring locations; but many of these were found not to be precisely defined sites.

Sampling stations were constructed at many of the Hellyer monitoring locations to allow consistent spatial sampling. This was found to be particularly necessary where a number of different operators take samples. Stations are now clearly labelled by prominent signposts placed as near as possible to the actual sampling point. In this way there can be little ambiguity as to the position of the sample point and the identification of the sample. The sample containers are either labelled on site, or chosen from a pre-labelled collection and checked against the sign before taking the sample.

Construction of stations allows ease of access to the desired sampling point and minimises disturbance and contamination of the sample stream. Approaches to flowing streams are constructed from downstream if possible, so if movement generates turbidity, for example, it does not result in contamination of the sample stream. The construction of a solid landing (Figure 4.6) minimises the disturbance to the wetland site on approach of the operator; bank collapse, vibrational release of silt and gas bubbles are thus minimised. In this case there is also the safety consideration of providing a stable platform to avoid a person slipping into the deep mire (Hunter 1995). At my new wetland sample stations and some of the other monitoring stations, proper support is provided for monitoring probes (pH, conductivity etc.) to better define the sampling point at optimal flow positions and also to encourage the operator to allow sufficiently long time for stable readings (Figure 4.6). In this case the operator can position the probe, retreat to the vehicle in foul weather if necessary, and observe the slow equilibration reading in comfort. Approximate locations of wetland sample stations are mapped in Figure 10.1. Locations of other water sampling sites are shown in Figures 1.1, 3.1 and 3.10, with location details in Table 11.1. The example of Figure 4.7 shows the access to sample point H1, a fast flowing stream which fluctuates in level. The utilisation of a disused mine plant walkway fulfilled the needs of sample point access and safety considerations.

Streamways at several wetland stations were exposed to disturbances. In crossing these by vehicle, there was gross agitation of waters and sediments, and deposition of mineral concentrate from the bottom of the vehicles. Perpetrators included semi-trained samplers (Section 4.5) on the way to downstream sampling stations! As a response to this observation, these sampling points were barred to vehicular access by means of physical log barriers in May 1993.

4.7 Other monitoring

Many factors may have effects on the sampling programme, and are best recorded at regular intervals. Unusual events should especially be noted. In my January 1992 field visit, I discovered the flow to OW was completely cut off,

Figure 4.6: A wetland sampling station constructed for this study

Figure 4.7: Safe access to well defined sampling station H1

and NW running only a trickle. It was during modifications to raise the tailing dam wall. The construction period when there was no flow in the wetlands resulted in oxidation and leaching of wetland sediments, appearing as negative wetland performance in the monitoring data (Figure 10.9), particularly for soluble Pb. Had I not visited the site in this period I would never had known of this, and may have long pondered fruitlessly over the negative data for the period 15 January-25 March 1992. Furthermore, the dam-raise resulted in a new and continuing AMD seep from dam rockfill entering the OW bypass (Section 7.7). This was a more lasting consequence, largely due to use of pyritic shale for dam fill. Along with the raise, the overflow system was changed so as to stop aerating, lowering the DO of wetland feed. Easily overlooked, this type of event information may not be of immediate significance, but later analysis of results may show important trends. Variations in rainfall and evaporation (Figure 3.3), for example, change the dilution of wastewaters (Figure 4.8) dominated by the mill-contributed $CaSO_4$ content. Note, however, that variation of wastewater Pb is more complex, due to multiple factors of which rainfall dilution is only one (Section 4.3, Blesing 1991). Other contaminants follow this theme, and hence toxicity varies. Obviously the gross flow volumes of wastewater vary too, and pose a problem for treatment. Surges and releases, accidental or otherwise should be noted and recorded at the time. Seasonal and daily temperatures affect reaction rates and biological activity. Weather parameters at Hellyer were monitored at 9 am and 3 pm daily.

Flow volumes are monitored at a few sites. This, along with concentration data, is essential to gauge total effluent movements. The gross volumes also indicate likely erosion events and turbidity releases.

Other events of singular, intermittent or periodic nature should be noted. At the Hellyer site there may be localised activity and disruption by wildlife; for example, stirring up silt by traversing a channel. Structure collapses, spills, exploration drilling, road grading, passage of heavy machinery may all have significant short term effects. During the early 1992 tailings dam wall raise, the wetlands flow ceased for a period of weeks, and pyritic shale was included in the dam fill. Both points had lasting effects (Sections 7.7, 10.5). Activities of non-mining interests should also be monitored: the HEC maintains high tension lines across the lease. Runoff & spills from railway, sealed highway and numerous unsealed logging roads outside the mining lease flow into the streams of the lease. Fire and clearing of soil cover releases nutrients and silt, with associated changes in local chemistry (Lichon 1993). The losses of vegetation cover in one part of the Pieman catchment after a fire led to' massive increases in river flood peaks (Livingstone 2000). Delays in revegetation caused soil erosion, turbid streams and pond sedimentation.

One set of monitoring points downstream from the mine compares the catchment waters affected by the mining activities with a converging stream from undisturbed sources. Unknown to the monitoring authority, the mine or the researchers until after the fact, in February 1992 a forest extraction company constructed a road from the confluence up the side of the dividing ridge to the
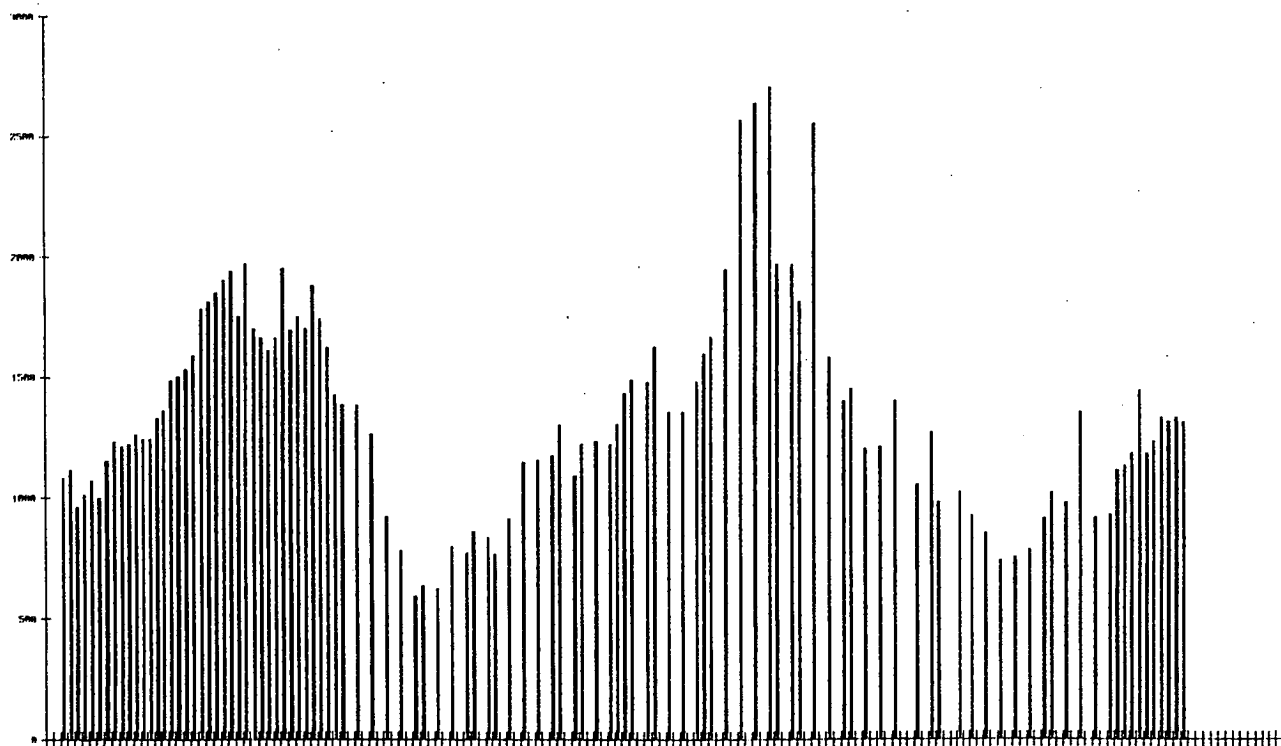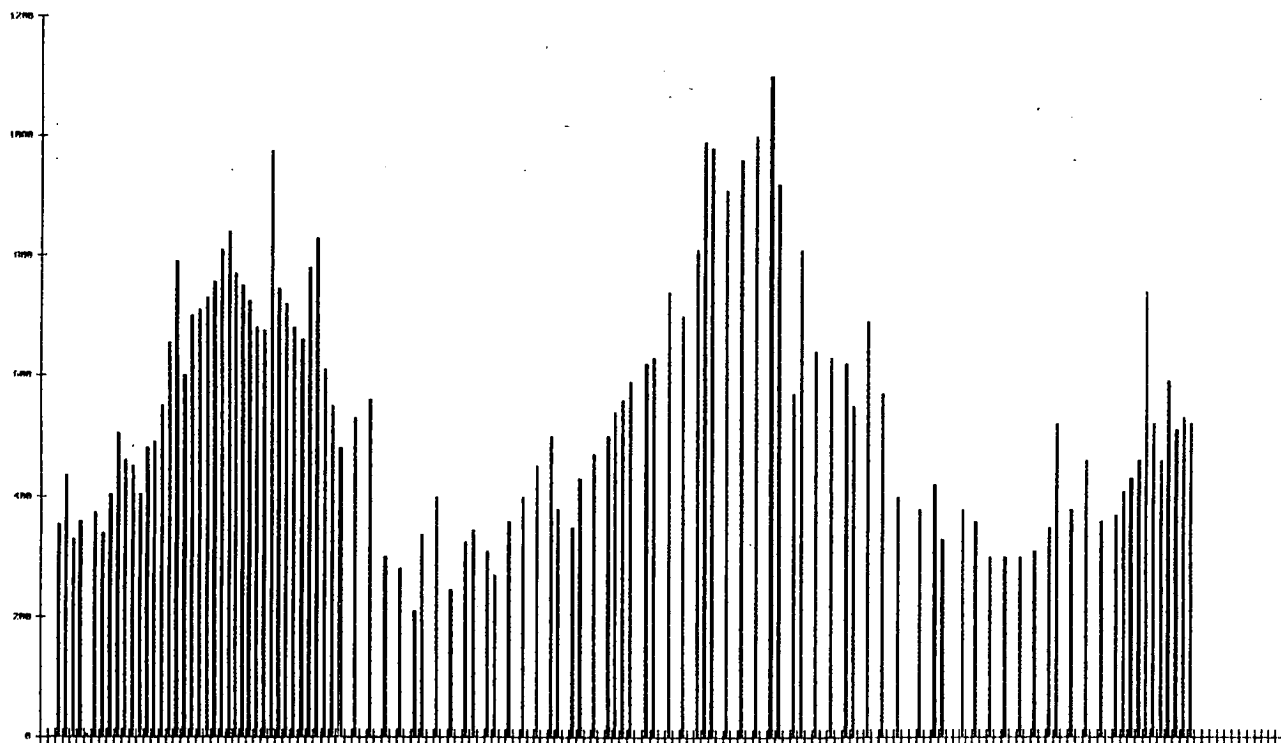
Figure 4.8: Sulphate (top) and conductivity (bottom) for H6 samples broadly varies with seasonal rainfall dilution, taken weekly over 2 years.

top, from which the ridge top and slopes were clearfelled and cable–logged the following year. The road construction and baring of the erodible steep slopes doubtless released turbid waters into both rivers. The exposure of bare ground is likely to result in at least a 200 fold increase of turbidity in water running off this high rainfall area (Lichon 1993), equating to erosion rates of 100–200 t/Ha/year (Haydon *et al*. 1991). Similar erosion rates were found for cleared areas around the tailings dam (Section 11.3). The massive scale of turbidity release was graphically evident during the heavy downpour of 15/2/93 when rivers turned to brown torrents of slurry. Due to the nature of the terrain it is not practicable to venture upstream to monitor either of the rivers above the reaches affected by the logging. The integrity of this part of the monitoring programme has clearly been compromised. It may well be the case that prior consultation could have avoided this situation.

Chemical and biological monitoring can best provide useful information when unaffected control sites are similarly monitored. The use of control sites removes the need for gross assumptions as to what baseline to consider as "normal" or "natural". Such sites may need to be protected from visitation access or other disturbances.

4.8 Conclusion

Care and resources are needed in sampling within an environmental monitoring programme to justify the expense of assays and yield more meaningful results. Spatial variations in 2 or 3 dimensions and temporal variations require study, and a regular sampling programme designed appropriately. Stable and reproducible sampling site establishment removes many errors. Procedures to minimise or eliminate sample contamination need to be followed. Apart from sampling for analyte assays, additional monitoring is required; of flows, water temperature, weather indices, regular and irregular events of natural and artificial origin. Quality assurance audits should confirm adherence to procedures. Pitard (1989) states that the resources put into environmental sampling should be commensurate with the cost of analysis of the samples to maximise the benefit/cost of monitoring of spatially and temporally inhomogenous environments.

In the context of this study, the matrix of erratic, unpredictable and uncontrollable factors together with many others that can be identified, and in some cases even quantified, has resulted in many observations, measurements and experiments often having unmeasurable uncertainties. Sampling was often limited by analytical cost and/or the emerging importance of the mechanism under test. In some cases sampling was deliberately targeted to likely "worst" or "best" cases (as appropriate) to show likely upper or lower limits, while in others I sought "typical" samples to indicate a likely average, based on observations and current understanding. Wherever possible, I undertook measures towards consistency in my sampling, and to some degree also that performed by others, for example by setting up defined sample stations at monitoring sites.

Hence, while mindful of many observed complicating factors, a general multidisciplinary field-applied approach was found to be necessary, at the expense of the more customary rigorous number-crunching associated with exacting pure-discipline controlled laboratory experimentation. It was impossible to meet the assumptions required for valid statistical analysis and other high-order mathematical treatment. My aims were of identifying trends, determining which hypotheses, mechanisms and environmental factors were most important, and looking for the most practical outcomes that may make use of the findings.

Chapter 5: Selection of plants suitable for constructed wetland removal of heavy metals from wastewater at a Western Tasmanian minesite.

5.1 Introduction

The days of releasing untreated tailings into river systems are gone in Australia. Recent enlightened attitudes of the population, governments and corporations demand some treatment of wastewaters released into the environment. In the past decade the use of constructed wetlands for biological treatment of mining effluent has become more popular. They are ill-defined and poorly understood; usually from ad-hoc transfer from application elsewhere.

The Hellyer Mine is in a highly mineral-prospective region in Western Tasmania (Figure 1.3), where there are several mining operations and exploration programmes in progress; and new mines will doubtless replace those that close. The Hellyer site features a cool wet temperate climate (Figure 3.3) with 2000 mm annual rainfall often falling as sleet and snow, cold, and predominantly westerly winds often exceeding 25 knots. The area has rugged terrain with predominantly natural forest mosaic cover, reflecting complex underlying geology, leached soils and patchy fire history. The dam is at 630 m ASL. These factors added together pose challenges for potential solutions. Effluent dam overflow is passed through a 1.2 Ha experimental constructed wetland system to remove heavy metals, in particular Pb. A typical composition of the wetland input is shown in Table 5.1.

Table 5.1: An example composition of H6
wastewater for wetland treatment (mg/L)

Lead	0.6
Dissolved Lead	0.3
Zinc	0.7
Iron	1
Manganese	0.5
Arsenic	0.01
Copper	0.1
Cadmium	0.001
Magnesium	6
Calcium	300
Sodium	40
Potassium	20
Total Suspended Solids	30
Dissolved Organic Carbon	12
Sulphate	550
Total Sulphur	400
Chloride	40
Fluoride	0.6
Cyanide	0.1
Bicarbonate	30
Conductivity	1400 µS
pH	8.5
pH extremes	4.6-11

The development and understanding of this wetland treatment system has direct significance beyond the Hellyer operation in the long term context of Western Tasmania, and relevance to the mining (and other) industries world wide. One of the most basic parameters to define is the ecological design of the wetlands.

Dunbabin (1989) noted the presence of *Typha, Cyperus, Juncus, Phragmites, Eleocharis, Restio, Bulbostylis, Ascolepsis, Kyllinga, Polygonum,* and *Fimbristylis* species from her survey of Australian mine sites. Other workers list additional species of genera *Potamogeton, Equisetum, Scirpus, Baumea, Schoenoplectus, Glyceria, Bolboschoenus, Zizania, Carex, Brassica, Eichhornia, Hydrocotyle, Amblystegium, Lemna, Azolla, Salvinia* and *Sphagnum* as metal tolerant to some degree and/or capable of metal uptake in metal contaminated environments (Kelly 1988, Ritcey 1989, Dushenkov *et al.* 1995, Tanner 1996, Ledin & Pedersen 1996). Guntenspergen *et al.* (in Hammer 1989) further lists *Phalaris, Canna, Iris, Zantedeschia, Colocasia, Egeria, Ceratophyllum, Myriophyllum, Lagorosiphon, Spirodela, Pistia* and *Wolffia* as useful in constructed wetland systems, though these are not cited as being necessarily suitable for mining wastewater applications. Reed *et al.* (1995) cite *Typha, Phragmites, Juncus, Scirpus* and *Carex* as the commonly used emergent plants for wastewater treatment.

This chapter examines the suitability of available macrophyte species for use in the Hellyer Mine wetland site. While some work of this kind has been done elsewhere in the world and mainland Australia (Kelly 1988, Guntenspergen *et al.* in Hammer 1989, Dunbabin 1989, Ritcey 1989, Dushenkov *et al.* 1995, Reed *et al.* 1995, Tanner 1996, Ledin & Pedersen 1996), this is the first study of its kind for Tasmanian conditions. Climate adaption, growth habits, tolerance to transplanting, productivity, local availability, abundance, ecological desirability, tolerance to mine effluent and wetland conditions all contribute to species survival in the wetland treatment system and suitability assessment.

5.2 Methods

Initial bulk plantings at Hellyer (in 1989, 1991) were achieved by opportunistic sourcing within a 10 km radius. Sites used as sources for these plants are listed in Table 5.2. Extraction was achieved with hydraulic excavators, transportation by truck and the whole plant-soil clumps were deposited by hydraulic excavator into the landscaped wetland site. Some supplementation (in 1993-94) by similar means was undertaken to fill spaces in the wetlands where previous planting failed. I undertook sampling and identification of the species, and assessed their survival and suitability for the wetland operation.

After recognising some of the limitations of the dominant bulk plantings, the accessible surrounds within 20 km of Hellyer were examined more closely for more suitable species, with provenance (in particular water depth, altitude and light exposure) not too dissimilar to the wetlands and with reasonable

accessibility, for introduction into the wetlands. These additional plant species were photographed and sampled for identification where necessary. Identification of plants was according to Hughes & Davis (1989), Morris (1991), or with the kind assistance of Alex Buchanan, Dennis Morris and Dr Ron Crowden. Buchanan *et al.* (1989) was the usual nomenclature reference.

Medium-size plants were extracted by hand shovel including some original substrate around the roots, transported in buckets with water. They were hand-planted in the wetlands within 3 hours of extraction. The additional plantings were assessed for survival, growth habit and ability to thrive in the constructed wetland environment.

Apart from visits to potential source sites, several natural and constructed wetland areas of Tasmania were examined for an overview of species habits, ecology and assessment of potentially suitable plants.

Table 5.2: Source sites for wetland plants.

Site	description	AMG Location Aust. Zone 55G	height m ASL	transplanted location
TRAM	Tramway Ck marsh	383300mE 5386200mN	355	OW,NW (BCD)
BOCO1	Boco marsh site 1	383400mE 5387700mN	405	NW (A)
BOCO2	Boco marsh site 2	383400mE 5387600mN	405	NW (A)
BOCO3	Boco marsh site 3	384300mE 5386900mN	405	NW (BCD)
MHA	Animal Ck marsh	384400mE 5389700mN	395	NW (BCD)
MWNE	Murrays W road end marsh 1	394400mE 5397900mN	675	OW
MWSA	Murrays W H3 road marsh 2	394300mE 5397600mN	680	OW
CHAR	Charter powerline marsh	389200mE 5392100mN	710	OW,NW (BCD)
MRRT	Mill rail road junction	394000mE 5397100mN	670	OW
HATQ	Hatfield quarry	387800mE 5301600mN	660	(experimental
FARM	Farm Creek	382700mE 5380900mN	165	plantings
HAT	Hatfield River at highway	388300mE 5409000mN	665	only;
WAD	Waratah Dam	378100mE 5409600mN	608	in
FOS	Fossey River at Highway	384500mE 5410300mN	620	NW)

5.3 Results

5.3.1 Bulk transplants and site vegetation

The rugged process of initial planting was approximately 70% successful, the losses in general being due to death by rough handling, burial, and in many cases by being deposited upside down with no photosynthetic tissue gaining exposure, and other adaption failure reasons like root disturbance, change in altitude, microclimate or water chemistry. The water depth was inconsistent over the wetlands, particularly in NW; the target of 20 cm was poorly met with widespread shallow areas and islands interspersed with braiding water channels. The poorest plant survival rate was noted in the NWA pond series. The possible causes for this particular result include the BOCO1 & 2 sites

being significantly different in some way (although there was nothing unusual about the mud analyses from these sites, Section 7.2), but more probably, that NWA is sited on the northwest side of the wetland, and is subject to more shading from the forest.

The most readily available species was *Juncus bassianus*, sourced from roadside drains and accessible marshes on and nearby the mining lease. The species dominates the wetland at about 80%, Figure 10.15. This may be somewhat surprising, as it was only recently recognised as a specific taxon (Johnson 1991). Other *Juncus* species were included in the transplants, but were much less common at the source sites than *J. bassianus. Juncus* is well known amongst Tasmanian farmers as somewhat of a nuisance plant which colonises wet paddocks, drains and ponds. The other major species used in initial transplants was *Restio tetraphyllus*, which was found in similar sites. In Tasmania, *R. tetraphyllus* is most widely recognised as the primary natural coloniser of the denuded hills around the Mt Lyell copper mine at Queenstown, and also as a hardy domestic garden plant noted for its ornamental foliage. However, neither of these two major species used in the Hellyer constructed wetlands are ideally suited to permanent inundation, preferring wet sites that seasonally (at least) drain to allow aeration of the substrate. Of the surviving plants, only about 20% show any tendency to spread by rhizome extension, suggesting they are not thriving. Many plants in deeper (>10 cm) parts of the wetland died within 2 years. Hughes and Davis (1989) do not regard either genus as being wetland plants, excluding them from their list of aquatic plants of Tasmania. Permanent shallow wetlands would appear to be at the wet extreme of their habitat tolerance.

With the initial plantings came some occurrence of other species such as the monocotyledons *Juncus bulbosus, J. planifolius, J. pallidus, J. procerus, J. articulatus, Leptocarpus tenax, Carex* spp., *Gymnoschoenus sphaerocephalus* (buttongrass); the dicotyledons *Nothofagus cunninghamii* (myrtle), *Leptospermum* sp. (tea tree), *Eucalyptus* spp.; and the fern *Histiopteris incisa* (native bracken). Apart from the *Juncus* species, these survived only on clumps large enough to protrude above the water level, and I regard them as strictly "island" species in this context. Buttongrass, regarded as a marsh dweller of the lowlands of southwest Tasmania, did not survive a nearby effluent irrigation experiment and clearly needs periods of at least partial soil drainage for survival. Of the *Juncus* species, *J. bulbosus* was restricted to shallow edges up to 8 cm depth, and tended to grow into dense mats, diverting water around the periphery of the clumps. In effect they grew into "land" extensions, thus reducing the effective water treatment area. The other *Juncus* species shared the general characteristics of the similar-sized *J. bassianus.*

Surrounding the wetland treatment area is mostly intact mixed forest (Section 3.1.4). Western Tasmanian forest species have been shown to tolerate natural elevations in heavy metals (Russell & van Moort 1981), and are likely to endure any metal exposure levels surrounding the treatment site. It is locally

dominated by *Eucalyptus* spp. and *Nothofagus cunninghamii* growing on paleozoic mafic soils on the east side of NW, and *Eucalyptus* spp. and *Phyllocladus aspleniifolius* (Celerytop Pine) growing on interbedded Cambrian basalt/shale and peats to the west, around Pond 2 and east of OW. West of OW is a patch of buttongrass plain with woodland on the two low spurs. The forest communities provide significant year-round leaf-fall and litter input to the wetlands by means of wind transport. Unfortunately there are some areas around the wetlands that were needlessly cleared, so depriving the wetlands from this additional input; instead there is erosion runoff. The forests also provide some wind protection to the wetlands; conversely they also shade the wetlands from low-angle sun along the east-north-west arc.

5.3.2 Additional experimental transplants and field assessments.

The assessment of species for wetland use is summarised in Table 5.3.

Eleocharis acuta was found in the nearby Hatfield River, in conditions from wet ground to 50 cm deep flowing water. Hughes and Davis (1989) had not noted its distribution in this area. Individual fist-sized clumps were easily transplanted, and survival rate was 100%. The plants thrived in the wetlands, with rhizomes radiating as much as 1 m in the first three months, and spreading vigorously by the second year (Figure 5.1). The source area recovered completely in 1 year, readily taking another harvest. Untrained staff were unable to distinguish most genera in the field. Together with providing some rudimentary field training for staff, I compiled a photo-identikit of useful local wetland species with some key features and notes on growth habit, dimensions etc. for this purpose (Lichon 1994). As an example, the photos in Figure 5.2 show the different reproductive arrangement of *E. acuta* and common *Juncus* sp. in a closeup. More recently, a field guide for wetland plants of temperate Australia (with photographs) became available (Romanowski 1998). A nearby gravel quarry was later found to be a useful nursery of coloniser *E. acuta*. In 1994, technical staff were directed to transplant from the quarry using hand shovels and a utility. Six months later there was no evidence of their plantings surviving in the wetlands; it remains a mystery as to why. Its growth habit is ideal for wetlands, with even distribution and open enough to allow laminar flow through the mass. This is important to minimise channelling of treatment waters. Its productivity is prolific (Figure 5.1). It easily tolerates anaerobic muds. One possible drawback is its deciduous growth cycle, but the nature of this is aesthetic rather than of function. The genus is used in some wetlands elsewhere in Australia (Chambers & McComb 1994, Dawson *et al.* 1995, Dowling & Stephens 1995, Jacobs *et al.* 1995, Noller *et al.* 1994). *E. acuta* was the most suitable and successful species tested in the transplanting programme.

The larger *Eleocharis sphacelata* normally grows in 0.5-2 m water. Its hollow structure was found to be too fragile to withstand handling and transport. However in one northern Tasmanian constructed wetland it has seeded from nearby marshes, demonstrating potential for introduction by that method.
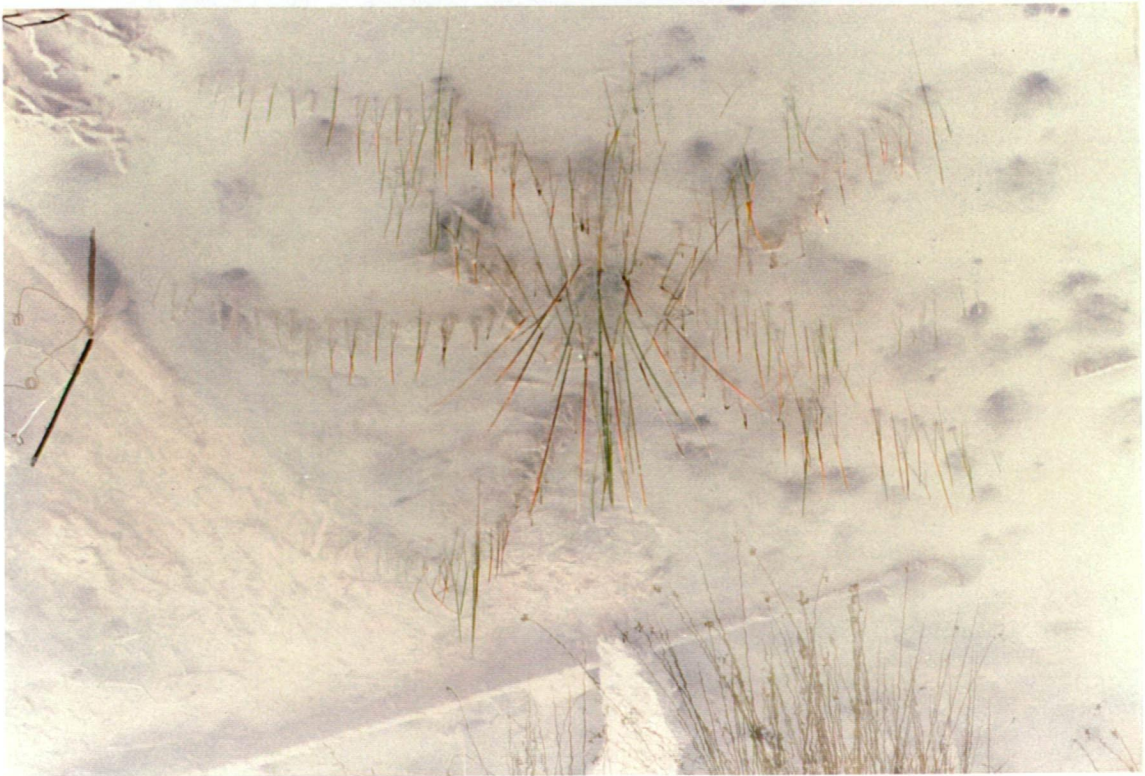
Figure 5.1: A sprig of *Eleocharis acuta* transplanted in February 1993 spread new rhizome growth over 1 m bearing shoots by May 1993 (top); by March 1995 it became a profuse mass spread over 7 x 3 m (bottom).

Figure 5.2: Example from *Field photo identikit* showing the basic difference
between reproductive features of *Juncus bassianus* (left) and
Eleocharis acuta (right) for use by untrained field staff engaged
in restocking the wetlands.

Table 5.3: Assessment of plant species for potential use in constructed wetlands for effluent treatment at Western Tasmanian minesites.

species*	habit	transplanting	result/comment
Juncus bassianus	shallow emergent	70% bulk	adequate
Restio tetraphyllus	shallow emergent	70% bulk	adequate
Juncus pallidus	shallow emergent	70% bulk	adequate
Juncus procerus	shallow emergent	70% bulk	adequate
Juncus articulatus	shallow emergent	13/16 bulk	adequate
Restio australis	shallow emergent	7/9 bulk	adequate
Juncus bulbosus	small emergent	10/10 hand	loss of treatment area
Juncus planifolius	small emergent	5/5 hand	too small
Gunnera cordifolia	carpet former	0/3 hand	unsuitable habit
Azolla filiculoides	free floating	-	warmer climate only
Lemna minor	free floating	-	warmer climate only
Carex appressa	shallow emergent	3/5 hand	marginal
Carex polyantha	shallow emergent	-	marginal
Carex chlorantha	shallow emergent	2/5 hand	marginal
Carex sp	small emergent	-	too small
Leptocarpus tenax	islander	5/12 bulk	islands only
Lepidosperma elatius	shallow emergent	-	marginal
Myriophyllum salsugineum	submerged	0/5 hand	unsuitable
Ranunculus amphitrichus	submerged	0/3 hand	unsuitable
Isolepis fluitans	submerged	0/5 hand	unsuitable
Hydrocotyle hirta	submerged	0/3 hand	unsuitable
Potamogeton tricarinatus	submerged+floating	0/5 hand	unsuitable
Elodea canadensis	submerged	-	unsuitable
Potamogeton ochreatus	submerged	-	unsuitable
Villarsia reniformis	floating+emergent	-	possibly suitable
Triglochin procera	emergent	-	probably suitable
Glyceria maxima	emergent	50% bulk	(Que) not native
Typha orientalis	emergent	-	widely used elsewhere
Phragmites australis	emergent	-	used in warmer areas
Baumea arthrophylla	emergent	-	used on mainland
Cyperus spp	emergent	-	used on mainland
Eleocharis acuta	emergent	24/24 hand	very suitable
Eleocharis sphacelata	deeper emergent	0/3 hand	fragile but possible

* as named in Buchanan *et al.* (1989)   - not attempted (mostly unavailable)

Submerged species (Table 5.3) all died within 1 month of transplanting in the wetland ponds. These deaths were apparently caused essentially by smothering with precipitate settling from the turbid wetland water, attenuating light exposure to green tissues. This occurred both in fast or slow flowing wetland plots. There may have been some water toxicity factoring into the cause of deaths, but this could not be determined.

Potamogeton tricarinatus, with both submerged and floating leaves, also suffered a high death rate. Submerged leaves died off within 1 month, and most plants died completely when floating leaves became wetted and soiled by turbid water during windy periods. The longest survivors were in sheltered backwaters, where wind disturbance was minimal and waters the clearest. However these situations of little or no water throughput contribute little to water treatment, and are best removed by local reconstruction. Members of Menyanthaceae such as *Villarsia reniformis*, with floating and emergent habits, could have more potential. *V. reniformis* was not found near the site, but has a wide natural range, from highland lakes to coastal swamps.

Triglochin procera is one untested native species with good potential. Hughes and Davis (1989) confirm a wide distribution of the species. It ranges from cold highland swamps to warm coastal lagoons. One east coastal location was found with a conductivity of 800 µS, suggesting it may tolerate the wetland waters. It grows prolifically in various water depths and velocity, and can assume a free-floating form in deeper water. It usually roots in anaerobic muds. Some mainland constructed wetlands have been planted with this genus (e.g. Adcock & Ganf 1994) with year-round growth. Winter growth would be an advantage for Hellyer. Unfortunately no sources of *T. procera* were located near the minesite, the closest being known at Corinna, and transplanting could not be evaluated. A further disadvantage of *Triglochin* is that ducks and wallabies are known to browse it.

The small free-floating fern *Azolla filiculoides* is often found covering warmer farm ponds. It is used in some mainland treatment systems, and assists the deoxygenation of waters. Its wetland use is limited to ponds with subsurface outlets, and/or dense emergent growth to prevent losses. It is restricted to lowlands in Tasmania, and unlikely to survive cold. *Lemna* spp. are used in some mainland systems. *Lemna minor* has a similar habit to *Azolla*, and would fulfil similar roles in constructed wetlands. Neither genera were found near Hellyer, and their natural range excludes colder or more elevated regions of Tasmania (Hughes & Davis 1989).

Glyceria maxima was successfully planted (1989) in the nearby Que River Mine wetland. It is an introduced species, hence has inherent ecological problems in a largely undisturbed natural environment. However there is no sign of spread of the species beyond the wetland to date. Being softer than most of its native counterparts, it suffered marsupial browsing where it was accessible, particularly in shallower water.

Typha orientalis is common in farm dams, and often regarded as a weed. It grows in anaerobic muds and tolerates deeper waters. This cosmopolitan species (and other members of the genus) is successfully used in many constructed wetlands throughout the world. It therefore has potential for use in this site. *T. latifolia* has invaded and now dominates a constructed wetland in northern Tasmania, and Jacobs *et al.* (1995) noted *Typha* for its invasiveness and undesirable dominance in New South Wales. It is uncommon in

colder parts of Tasmania, and was not found in the Hellyer area, hence was regarded as ecologically undesirable to introduce.

The native *Phragmites australis* is found in warmer lowland areas of Tasmania, and occupies similar habitats to *Typha*. Several mainland Australian constructed wetlands, and two in a milder part of northern Tasmania (van Oorschot *et al.* 1995, writer's unpublished data 1996) are planted with *Phragmites*. The species was not found in colder Western Tasmania, and probably would not tolerate the climate at Hellyer. Similarly, *Baumea* is commonly used in mainland wetlands; the Tasmanian distribution of *B. arthropylla* and others is restricted to warmer lowlands. *B. juncea* was noted in a contaminated stream in northern Tasmania, and has a habit rather similar to *Eleocharis acuta*. Another genus commonly used for minesite wetlands on the mainland is *Cyperus* (Dunbabin & Bowmer 1992), but is of limited distribution in Tasmania, and not noted near Hellyer.

5.4 Discussion

The potential macrophyte characteristics examined need to be considered in the context of the environmental impact, the practicality of use, and the mechanism of the treatment process.

Reed *et al.* (1995) describe plant functions in wetland treatment systems as nutrient uptake, mud oxygenation, shading against algal growth, stabilising physical structure, and providing substrates for attached microbial growth. To these, Brix (1994) and DLWC (1998) add visual amenity, providing a basis for an ecosystem, promoting even flows, aiding sediment deposition, erosion control by reducing wave energy and root binding of sediment, and direct and indirect facilitation of metal removal.

Unlike most wetlands used for treatment of municipal, industrial and mining wastewaters which function by providing aerobic chemical and biological processes to remove contaminants, the Hellyer wetlands operate mainly by anaerobic processes in the removal of Pb. The details of the various mechanisms of the treatment system are discussed at length elsewhere in this work, but essentially the removal of Pb is largely achieved by precipitation as sulphide (Chapter 7). The sulphide is produced by anaerobic mud-dwelling microbial consortium bearing sulphate-reducing bacteria (SRB) (Chapter 9). The anaerobic consortium is maintained and fed by macrophyte production (and death), litter fall and other minor inputs; the sulphate source being the effluent stream (Table 5.1). Hence the two most vital functions of the plants (Figure 2.9) are firstly, to grow and photosynthesise organic matter to ultimately die and provide organic substrate to feed decomposers and microbes (Chapter 9); and secondly, simultaneously provide the raw material for generating reducing conditions (Section 7.7) to maintain the stable anaerobic environment of the mud suitable for the SRB consortium. Any plant that survives the climate, anaerobic muds and effluent has potential to serve this

dual purpose; but it needs to thrive and be productive enough to be sufficiently useful in meeting biological demand in the treatment process. The third important role of the macrophytes in the Hellyer wetlands is to physically stabilise and hold the wetland structure together, promoting settling and retention of particulates and diffusing the flow of water.
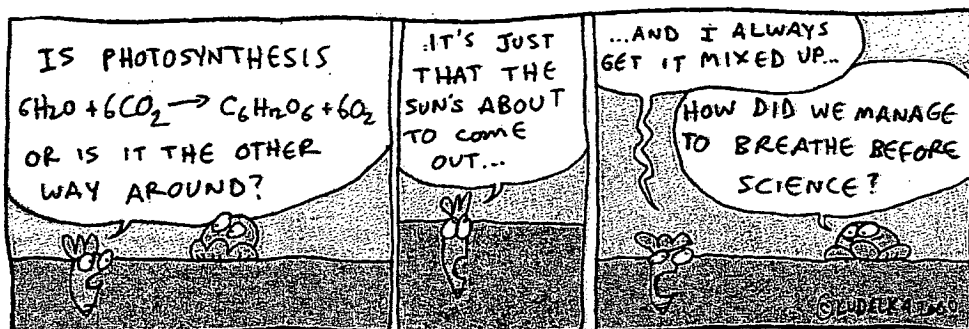
Most mines in Western Tasmania treat sulphide ores, and this is the most common occurrence of heavy metal reserves globally. The nature of the Hellyer effluent and the use of anaerobic process makes this more demanding site (for plant survival) than typical aerobic wetlands. All wetland treatment systems benefit from productive and diverse plant growth; the main conditions of planting, climate and immersion being in common. Hence this plant selection would be sufficiently robust to form a sound basis for wetland construction for any purpose in similar situations, not just for sulphide mining wastewater.

To be practical, plants need to be readily available in close proximity, survive transplanting, have tolerance to turbid waters and anaerobic conditions, and produce sustainable growth so as not to need replacement. The climate, salinity and pH conditions at Hellyer are at the limits of tolerance reported for common wetland species used for water treatment (Reed *et al.* 1995). Indeed, both wetland plants (Reed *et al.* 1995) and SRB (Barnes *et al.* 1992) perform better at temperatures above 15°C. The options for warming the wetlands are limited at Hellyer to reducing forest cover on the shading sides of the wetlands, and retaining forest wind protection on the other flanks.

Propagation by transplanting was the only option considered, as development from seed is risky in a hostile environment and leaves an unacceptably long lead time to full production. In contrast, Chambers and McComb (1994) and Jacobs *et al.* (1995) used both transplanting and germination methods for establishing mainland wetland plants. In warmer northern Tasmania, the TEMCO industrial site runoff treatment wetland initially planted with only *Phragmites* gained a further 12 species in 3 years from seed blown from nearby natural wetlands. At Hellyer it was important to quickly establish plants with emergent foliage habit so as to protrude above the turbid waters and achieve acceptable survival rates.

One important ecological factor is the capability for species source sites to recover from harvesting. All of the harvest sites recovered within two years,

and some were used twice without visible detriment. The provision of plants for constructed wetlands is a major undertaking, the scale of which can easily be underestimated: the initial 1991 charging of the second wetland (0.75 Ha NW) required 525 tip truck loads.

Plants ought to be non-invasive in respect of the general environment, and the downstream catchment in particular. It is preferable that local native plants be used so as to minimise the local ecological disturbance, and influence on natural distribution. Weed species and exotics are undesirable for wetland use (DLWC 1998), particularly in this largely natural environment located high in the catchment area. Weeds present risks of wetland plant losses from preferential browsing (as seen with *Glyceria* in the Que wetland), weed spread and local ecological imbalance.

5.5 Other elements of wetland life

A mix of plant species provides a robust system, such that the various life cycles are staggered over time and space, and the untimely loss of any single species would be both less likely and less significant. The growth and senescence cycle of *Restio* is about 2 months ahead of *Juncus* in the wetland. The species mix would desirably provide habitat and promote a diversity of life in the wetlands apart from the macrophytes themselves (Odum 1971, Williams 1983, Godfrey *et al.* 1985, Jeffries & Mills 1990). Conversely, monitoring the diversity of a wetland community may provide a measure of ecological health in a heavy metal polluted environment (Pankhurst *et al.* 1997).

5.5.1 Non-macrophyte wetland biota

Apart from emergent macrophytes, the wetlands support vigorous algal growth of many varieties during warmer months, and fringe areas of mosses. The wetlands contain localised algae of many colours in areas of poor flow, and more widespread pale yellow-brown filamentous algae in the main channels. The latter type extends its range into the Que River system. There is some green filamentous algae in the west cutoff drain, associated with outfall of HB (the PO_4-bearing upwelling exploration borehole, Section 10.6) into the drain.

By way of animal life, I observed the wetland treatment area supports (either entirely or for regular visitation) brush possums, wombats, pademelons, wallabies, Tasmanian devils, ducks, copperhead snakes, mice, flies, and march flies, and provides active breeding sites for frogs, native hens, mayflies, mosquitos, and three species of predatory diving beetles. Other than the flies, mosquitos, and aquatic beetles, none of the species are particularly abundant in either wetland. For most species the open wetlands form only part of their range in a wider ecosystem.

Particularly for the invertebrate feeders visible to the eye at the lower end of the food chain, as well as the algae, it is apparent there is a rich supporting

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consortium of decomposers and microbiota too small to readily be seen. These reside in the flocculant mud, converting plant matter into food upon which much of the other life exists. Some of this microbiota has potential for roles in the metal uptake. While it became evident there was little direct conversion of Pb into organolead (Section 7.5), the role of sulphate reducing bacteria being supported within the complex microbial consortium of the mud (Chapter 9) is of much more significance in the Pb uptake processes of the wetlands. There is a clear importance in the macrophyte production of organic matter to fall into the water as the primary reduction agent and food for anaerobic microbiota.

5.6 Conclusion

Plants best suited for wetland treatment of mining wastewaters are vigorous emergent macrophytes, native to the area of the treatment site. The single most suitable species assessed was *Eleocharis acuta*, which meets all the criteria. However, rather than to recommend a monoculture, it seems prudent to make use of a mixture of the more suitable species for a more robust wetland system. In addition to proven *Juncus* and *Restio* species, there remains potential for successful use for *Triglochin procera*. While other emergent species also have some potential, these may present problems associated with species introduction, cold tolerance and transplant methods. A species mix is recommended to realise the benefits of diversity.

The importance of plants in wetland treatment include photosynthetic productivity and provision of organic matter for the mire for the dual purpose of maintaining anaerobic redox conditions and feeding the SRB consortium, and the physical structuring of the wetland, distributing flow and promoting sedimentation.

Assessment and selection of suitable plants should be undertaken well in advance of constructing full-scale wetland treatment systems. This study will prove of immediate value to present and future mining operations in Western Tasmania, and be readily adapted to areas of similar climate and vegetation (for example, southern Chile). The principles and methods are applicable worldwide, encompassing treatment systems for industrial as well as mining wastewaters.

Chapter 6: Plant sequestering of Pb

6.1 Introduction

In Figure 2.9, I identified a number of possible roles for plants in the wetland system. There was an assumption held by the mine management that the emergent plants were the direct responsible agents for metal removal from mine waters passed through the wetland treatment system. Indeed the initial title of the project set up by the APRA(I) partnership was "Chemical nature of metal sequestering processes on plant surfaces". Dunbabin (1989) showed *Typha* and *Phagmites* species were able to take up quantities of heavy metals from waters in constructed wetland systems under NSW conditions, suggesting the submerged portion takes up metals in association with oxygenation of the rhizosphere. Preliminary tests suggested there were low levels of Pb accumulation in the aerial parts of plants at Hellyer. The root and rhizomes were more likely sites of Pb uptake. Koeppe (in Lepp 1981) and Alloway (1995) state that plant lead uptake/adsorption tends to be localised around sites of lead exposure, which in treatment wetlands is typically around submerged stems and roots. It was observed, in the Hellyer wetland, around the stems and rhizomes that there were "plaque" deposits, perhaps rich in metals.

Many workers (Godfrey *et al.* 1985, Hammer 1989, Reed *et al.* 1995) note wetland plant uptake of metals from municipal wastewaters; however, metal loading of municipal effluent is orders of magnitude lower than for many industrial or mine wastewaters. One of the management techniques they cite is the harvesting of above-water plant growth to remove accumulated pollutants.

The plant surfaces in contact with water are relatively limited in extent in the wetlands compared with overall volume and area, and would appear of limited capacity in respect of metal uptake from industrial or mine-water loads over any period of time. If wetland plants do indeed directly accumulate Pb, then their finite uptake capacity and longer term survival come into question, as heavy metals stunt roots and new growth (Pankhurst *et al.* 1997). It was clear this avenue of Pb uptake in the Hellyer wetlands required critical investigation, with a view to discharging what seemed an improbable, but prevailing hypothesis as the major mechanism of wetland Pb uptake.

The methods of investigation for this part of the project were wetland mass-balance and investigation of plant anatomy for Pb accumulation.

6.2 Mass balance for Pb accumulation

Metal uptake in wetland system necessarily results in accumulation in the system (Bowmer & Jones 1995). The relationship between input and outflow concentrations, and the physical dimensions of the wetland and its attribute distributions would be expected to shed some light as to the fate of Pb, and the role of the plants. Breen (1990) illustrates the application of the simple concept of mass-balance to wastewater wetland treatment systems.

6.2.1 Experimental

The difference between Pb assays of same-day samples taken of water flowing in and out of OW i.e.: $Pb_{OW1}-Pb_{OW8}$ (H6-H7) were averaged over a 5-year period of weekly records (some weeks missing, and some weeks H6 and H7 were sampled on different days) to yield a figure representing total Pb uptake of the wetland system. This combined with recorded flow rates, wetland area and elapsed time gives total accumulation of Pb.

6.2.2 Results

The mean difference of Pb (total) for concurrent OW1(H6)-OW8(H7) assays was 0.33 ppm. Half of this comes from soluble Pb (Sections 10.4, 10.5). The mean flow rate through OW was 12 L/s (Section 10.3.2). The calculated annual Pb uptake for OW is therefore 125 kg. The gross working area of OW measured 4800 m² (Section 10.2), giving a mean annual Pb accumulation of 26 g/m².

The entire *Juncus* plant mass used in sampling for the electron probe analysis (below) weighed 20 g (dry basis). From the size of the 20 g plant specimens and field observations of plant distribution, I estimated there was some 200 g dry plant mass per m², with this biomass distribution ranging from 20-2000 g depending on localised plant productivity and abundance.

6.2.3 Discussion

It must be borne in mind there are some experimental limitations to these results. While only data pairs from the same day samples were selected, there is no indication these were always taken at around the same time; however H6 and H7 are adjacent to each other, and have been observed to be successively sampled by staff. As with all the monitoring data, there were sampling problems observed to compromise the integrity of the results (Chapter 4), including vehicular disturbance to H7 prior to sampling, before May 1993. The flow rates varied somewhat due to clogging and clearing of inlet conduits and valves, and the rudimentary adjustment and field measurement methods. The uncertainty of plant biomass distribution estimation by visual judgement is obviously significant, however this error could not be great enough to negate the stark results and conclusions.

Over a 2-year period some 50 g Pb would be expected per m² averaged over the wetland. At this point one might expect to find plants with significant accumulated Pb content if direct plant uptake was a major mechanism for Pb uptake in the wetland system. The study of Pb removal from OW water by individual paddy and by size fraction in Section 10.4.3 would suggest pond OW1 would be richer than average in accumulated Pb having reduced depth (Section 10.3.3) from sedimentation. One would be confident plants in OW1 should assay higher Pb content than average, some 25% dry basis, if plant uptake is the sole Pb sink mechanism. This possibility, while rapidly diminishing in likelihood, required finalisation. *Juncus* is the dominant wetland plant species, and was the subject of the following investigation.

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6.3 Electron probe microanalysis

The purpose of this investigation was to examine the Pb distribution within the emergent plant anatomy, and ultimately to confirm the minor role of direct plant uptake in the removal of Pb from wastewaters in the wetland system. Electron probe microanalysis, while most commonly used for rock samples, is a tool well suited for this type of work. The technique is described in Potts (1992). By way of a preliminary investigation, only limited, targeted samples were examined. Various plant sections were prepared to expose and allow microanalysis of distribution of Pb within wetland plants.

6.3.1 Sample Preparation

Samples of whole *Juncus* were extracted from OW1 pond near OW2 after 2 years' wetland operation. These two average sized, growing and rhizome-spreading specimens were taken from a converging flow area, with a greater than average exposure to Pb in the wastewater stream from the pond with the highest Pb concentration. The plants were pulled out, gently shaken of excess mud and loose dead material and placed in a large polycarbonate jar. These were frozen within 3 hours, transported, and freeze dried over 2 weeks.

Small (2-5 mm long) sections of plant as shown schematically in Figure 6.1 were dissected from the dried specimens using tweezers and scalpel. Care was taken using tissue-wipes to avoid cross-contamination; by minimal touching, then only with stainless steel tools, to avoid loss of surface material.

Sections were mounted on sample holders with double-sided adhesive tape, and vacuum sputter-coated with carbon in preparation for analysis. Dried sample material and coated specimen sections were stored in a desiccator over blue indicating silica gel.

6.3.2 Analysis

The samples were examined with the Cameca SX50 electron probe microanalyser at the Central Science Laboratory at the University, operated by Wieslaw Jablonski. Samples were probed with a 15 kV, 5 nA electron beam. Lead was measured using the Mα X-ray emission line, while other elements were measured using their respective Kα lines. The instrument was calibrated against blank and reference materials of known composition (pure metals, metal oxides and natural minerals), at the same instrument settings, scan time and operating conditions used for the samples. Thus the Detection Limits were determined for each element scanned, and appropriate signal factors were used to produce the results. Each specimen sample section was scanned at multiple predetermined target points. The approximate locations and plant origins of these 8 x 10 μm analysis points are shown on Figure 6.1.

6.3.3 Results and discussion

Table 6.1 shows the heavy metal microanalysis results for the freeze-dried
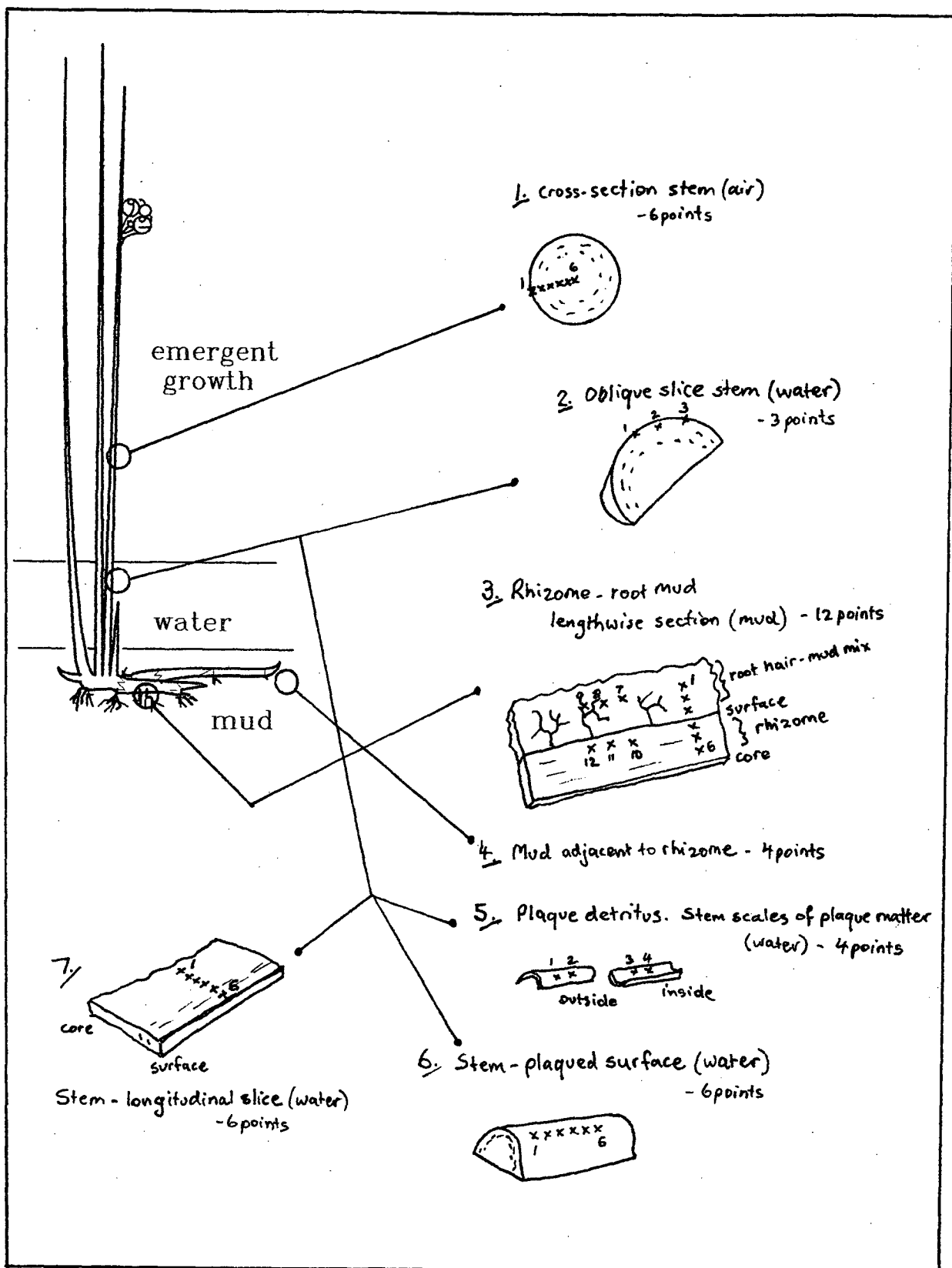
Figure 6.1: Location of sample sections and analysis points used for electron probe microanalysis of various parts of *Juncus* specimens taken from near station OW2.

Table 6.1 Heavy metal Electron Probe Microanalysis of *Juncus* specimen.

Sample (Figure 6.1)	#	(wt%) Mn	Fe	Cu	Zn	Cd	Pb
1: Stem-air;	1	0.05					
	2						
	3						
	4						
	5						
	6						
2: Stem-water;	1		0.67				0.12
	2		0.60				
	3		2.64				0.37
3: Rhizome-mud;	1						
	2		0.17				0.16
	3		1.46				
	4		0.83				
	5		0.28				
	6		0.12				
	7		4.50	0.12	0.17		2.10
	8		3.47	0.15	0.06		0.36
	9		4.98	0.05	0.78		0.61
	10		0.36				
	11		0.27				
	12		1.43				0.11
4: Mud particles;	1		2.78		0.56		0.81
	2		0.07				0.53
	3		2.16	0.05	0.11		0.80
	4		1.37	0.06	0.18		0.21
5: Detritus;	1		10.49	0.29	0.23		1.28
	2		13.20	0.06	0.14		2.09
	3		0.97				
	4		2.20				0.40
6: Stem plaque;	1		3.01				0.72
	2		6.05		0.08		1.34
	3		6.74		0.12		1.56
	4		10.94		0.23		2.12
	5		15.56	0.08	0.32		3.96
	6		20.26	0.05	0.39		1.70
7: Stem-water;	1				0.11		
	2						
	3						
	4						
	5		0.06				
	6		0.44				0.11
		Mn	Fe	Cu	Zn	Cd	Pb
Detection Limit		(wt%) 0.03	0.03	0.03	0.04	0.04	0.06

Blank entries indicate assay below Detection Limit.

dissected *Juncus* samples as shown in Figure 6.1. Sample 1 of the aerial part of the *Juncus* showed little metal accumulation. Indeed even for submerged and mud-immersed portions of the plant, most internal plant tissue sample points showed low levels of metal uptake - Samples 2, 3, and 7. The highest metal concentrations were found on the outside surfaces in contact with water (Sample 6), more specifically the outer surface of the plaque coating of stems (Sample 5). Metals were also found associated with root surfaces and wetland mud. The proportion of the plant volume (including plaque material) bearing significant quantities of metals would seem to be small, and restricted to submerged surfaces and some root areas, less than 5% perhaps closer to 1%.

The low concentration of metals found in the mud associated with plant roots (Table 6.1) contrast with much higher metal concentrations in depositional mud in areas between the plants (Table 7.1), and more closely resemble the profile of muds from plant source locations (Table 7.1).

A small selection from these same samples were further analysed for other elements; Table 6.2. The metal accumulation found in plaqued submerged stem and root zone samples appear to be associated with a variety of other mineral elements. The Fe and Pb are likely in a mixture of forms, of coprecipitated hydroxy Fe compounds as well as sulphides. Little further conclusion could be drawn from these limited assays.

Table 6.2 Further Electron Probe Microanalysis of *Juncus* specimen for some associated elements

Sample (Figure 6.1) (wt%)	Si	P	S	K	Ca	Mn	Fe	Pb
6: stem plaque	0.72	0.15	1.60	0.08	0.51		15.66	2.11
stem plaque	2.88	0.09	3.18	0.81	0.52	0.01	14.42	2.46
clean stem		0.07	0.46	0.05	1.37		0.32	
clean stem		0.05	0.54	0.06	1.21		0.29	
3: root base	7.43	0.14	1.93	0.64	0.25	0.02	4.48	0.30
root base	0.10	0.06	2.74	0.21	0.40		2.80	0.33
Detection Limit	0.03	0.05	0.10	0.06	0.06	0.01	0.10	0.15

Blank entries indicate assay below Detection Limit.

Further sampling and analysis work in this direction was abandoned, as it became more evident that plant sequestering of Pb was overwhelmingly of minor importance (by at least three orders of magnitude). This mechanism could safely be relegated as peripheral to the main wetland uptake mechanism, which after all, was the practical focus of the study.

6.4 Conclusion

The OW accumulation of Pb amounts to 26 g/m²/y. With only 1% of plant mass bearing 1-2% Pb; and only approximately 200 g plant/m²; plant uptake of Pb after 2 years of wetland operation is only 10-20 mg/m². Even that amount would appear to be dominated by a surface plaque phenomenon rather than direct macrophyte uptake. Clearly the plants play only a very minor direct role in wetland Pb uptake, and their importance must lie in other functions suggested in Figure 2.9. Having established the uptake associated with the plants accounted for <0.1% of wetland Pb treatment from this initial study, subsequent research effort was shifted away from further defining plant uptake to studying other Pb pathways.

The low Pb in these wetland plants allays concerns of local wildlife food chain Pb accumulation based on browsing, and puts to rest the potential concern of heavy metal accumulation threatening plant health (Pankhurst *et al.* 1997). Hammer (1989) lists applications where wetland operations include periodic emergent plant-top harvesting to remove pollutant accumulation (in the plant tissues) from the system. Clearly in the Hellyer system, harvesting of emergent portions of wetland growth would capture very little Pb, and be very counterproductive to the other functions performed by the wetland plants (Chapter 5), particularly their provision of organic matter for generation of reducing mud conditions (Chapter 7, 8 and 9) and production of biomass feed for microbial consortium growth (Chapter 9).

The accumulation of Pb from treatment waters and keys to the possible mechanisms must reside with the wetland mud rather than the emergent plants. These aspects are pursued in studies reported in Chapters 7-9, and their detailed application in the treatment wetland appears in Chapter 10.

Chapter 7: Nature of mud in the wetland

7.1 Introduction

The results in Chapter 6 showed the plants by direct uptake were only of minor importance in accumulation of Pb from the wastewater passing through the wetland system. Most of the previously postulated pathways (Figures 2.4 and 2.5) suggest the mud is where the fate of Pb lies. The volume of mud in the wetland also shows greater potential capacity as a Pb sink than the plants. Clearly an investigation of the nature of Pb accumulation and other aspects of the wetland mud was warranted.

7.2 Analysis of mud composition

7.2.1 Experimental

A simple plunger corer was constructed using a 50 cm length of 15 mm I.D. PVC conduit and a leather sealed piston retained by washers and nut to the end of a rod with a T handle. The tip of the corer pipe was honed to a sharp leading edge. The handle was retained to the pipe by a machined screw head. The rod was graduated to measure the core extent.

To serve as control samples, mud was cored from all the known source sites for bulk plantings (shown in Table 5.2). Core samples were taken down from the sediment-water interface. Each location sample comprised five 20 cm x 15 mm cores – each taken from representative areas alongside where plants had evidently been excavated – pooled into a polycarbonate sample jar. Samples were freeze-dried over 2 weeks. The cakes were broken up and mixed thoroughly using stainless steel spatulas.

Wetland muds were sampled after 2 years' operation of OW, and 1 year of NW operation. Mud samples from the wetlands were similarly obtained each with five 20 cm cores, taken near established plants. The OW sites were resampled to examine sediment accumulations in the spaces between the plants. The OW1 site was also sampled at a deeper level (20–40 cm depth). The shallow flocculant mud samples too fluid to core were taken as grab samples (0–10 cm depth) directly into jars. Samples were freeze-dried over 2 weeks.

Dried samples were digested and assayed by Analabs according to established standard methods (APHA *et al.* 1989). Nitric acid digest and AAS was used for Pb and Fe (Section 2.6.2.1). Loss on ignition is the gravimetric loss after heating to 450°C. Total silica was determined by gravimetric HF ignition. Total S was determined by inductively coupled plasma atomic emission spectroscopy.

7.2.2 Results and Discussion

Analysis results for wetland muds show marked elevated levels of Pb when compared with those for muds from source sites (Table 7.1). There can be no

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doubt the elevated Pb found in the wetland mud is the result of accumulation from wastewaters (Section 6.2) treated during wetland operation. The concentration of Pb is highest in the upper horizon layer 0-20 cm depth, associated with the more flocculant black ooze. The other main point that can be drawn from Table 7.1 is the elevated levels of total S in wetland muds.

Table 7.1: Analysis of wetland muds (dry basis).

Sample	Pb ppm	Fe %	SiO_2 %	L.O.I. %	Tot. S ppm
Source site muds					
MHA1	119	0.9	68	16.6	750
MHA2	92	0.6	71	17.2	650
BOCO1	BDL	0.7	83	8.9	250
BOCO2	77	0.9	64	19.7	350
BOCO3	95	1.1	62	19.9	550
MWNE	26	2.0	64	10.6	100
MWSA	BDL	13.5	36	21.2	350
CHAR	47	8.1	47	15.7	150
MRRT	BDL	9.5	39	22.3	400
TRAM	BDL	0.4	81	5.4	150
Muds from wetlands					
OW1	4200	4.9	60	17.5	15700
OW8	440	7.5	54	15.0	3900
NW1	80	6.0	56	14.4	1000
NWA3	240	4.4	62	14.8	2450
NWB3	125	2.9	58	21.3	1850
NWC3	91	2.9	56	22.4	1600
NWD3	100	4.1	51	22.6	1400
OW1S (0-20 cm)	30600	9.0	28	33.8	89800
OW1D (20-40 cm)	6200	5.3	62	12.9	19300
OW1F (0-10 cm)	37700	17.8	24	21.5	145000
OW7F (0-10 cm)	11800	11.8	39	19.6	76000
Detection Limit	25	0.1	0.1	0.05	50

L.O.I.= loss on ignition; BDL= below detection limit;
Source site codes and location details are shown in Table 5.2.
Wetland sample stations locations are shown in Figure 10.1.

7.3 Mineralogy of muds: Analysis of muds by X-ray diffraction

From the results above, the mud is clearly a major sink location for the Pb taken up by the wetland system. A key question to further the understanding of the Pb uptake process was to then examine the chemical nature of the Pb present in the mud solids. X-ray diffraction (XRD) is a useful tool for determining mineralogy, or any crystalline solid components, present in a solid matrix (Hutchison 1974, Press & Siever 1978).

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7.3.1 Procedure

Samples of OW1 and OW7 mud taken as grab samples at 0-15 cm depth below the sediment-water interface after 5 year's wetland operation were freeze-dried over 2 weeks. The cakes were broken up and mixed thoroughly using stainless steel spatulas. Sub-samples were further ground with agate mortar & pestle.

Test portions were mounted and analysed for minerals by XRD at Minerals Resources Tasmania by Ralph Botrill and Roger Woolley. The automated Philips X-ray diffractometer system consisted of PW1729 generator, PW1050 goniometer, PW1710 printing recorder and microprocessor, with nickel-filtered copper radiation at 40 kV - 30 mA, a PW1752 graphite monochromator, sample spinner and a PW1711 sealed gas-filled proportional detector. Data capture and plotting were accomplished with CSIRO software and XPLOT for Windows. The qualitative and semiquantitative mineralogy were determined by manual search-match methods and calibrated mineral standards. The Organic fraction was determined on further test portions by loss on ignition to 450°C

7.3.2 Results and discussion

Limitations of precision dictate that the Table 7.2 results may only be cited in percentage classes listed. Further caution concerns potential peak overlap such that, for example, pyrite may mask the presence of sphalerite. Furthermore minerals in trace amounts, or amorphous minerals, are unlikely to be detected.

The results in Table 7.2 are commensurate with those for chemical analysis in Table 7.1, given they are not from the same samples. As one may expect for the XRD samples taken after 5 years of wetland operation, the observed levels of galena are higher than the Pb found in samples after 2 years' operation (the 0-10 cm samples assayed in Section 7.2); ie. 4.2% for OW1 and 1.4% for OW7 (as PbS). This indicates continuing Pb accumulation in mud throughout the wetland over the period.

Table 7.2: Mineralogy distribution of muds by XRD

Sample	40-60%	25-40%	15-25%	10-15%	5-10%	<5%
OW1 (5-year)	-	quartz	pyrite mica	organic	chlorite galena	kaolinite gibbsite plagioclase
OW7 (5-year)	quartz	-	organic	pyrite	plagioclase	mica chlorite galena gibbsite kaolinite amphibole ?pyroxene

Many of the other abundant minerals come from wetland sedimentation of suspended tailings carryover. Other weathering minerals come from a combination of imported plant source location mud and settlement of suspended sediment in runoff from the immediate surrounds during rains.

7.4 Mud mineralogy: Electron probe microanalysis

7.4.1 Introduction

The Pb would seem from the chemical analysis and XRD mineralogy to be present as galena. The technique of electron probe microanalysis (Press & Siever 1978, Potts 1992) offers a means of examining the micro-distribution of PbS within the mud.

7.4.2 Sample Preparation

Samples of mud were extracted from the first and last paddy of OW after 2 years' wetland operation. These were the same "grab" samples OW1F & OW7F as analysed above. These had been frozen and freeze dried over 2 weeks. All material was stored in desiccators over blue indicating silica gel.

Mud specimens were mounted on microscope slides, embedding into a pool of epoxy glue, then allowed to set. Loose material was lightly brushed away. The slides were vacuum sputter-coated with carbon in preparation for analysis. Acceptable results were obtained after use of thicker epoxy layer to shield the underlying glass, and prolonged carbon coating to improve charge dissipation.

7.4.3 Analysis

Prepared samples were examined with the Cameca SX50 electron probe microanalyser at the Central Science Laboratory of the University, operated by Wieslaw Jablonski. Samples were probed with a 15 kV, 5 nA electron beam. Lead was measured using the $M\alpha$ X-ray emission line, while other elements were measured using their respective $K\alpha$ lines. The instrument was calibrated against blank and reference materials of known composition (pure metals, metal oxides and natural minerals), at the same instrument settings, scan time and operating conditions used for the samples. Thus the Detection Limits were determined for each element scanned, and appropriate signal factors were used to produce the results. Each specimen sample was scanned at multiple predetermined points targeting mounted mud particles. Particles were analysed in groups according to size fractions.

7.4.4 Results and discussion

The results summarised in Table 7.3 show mean Pb and S that agree well with those shown in Table 7.1 for chemical analysis. The high standard deviations, especially for S, reflect the variation in mineralogy content of individual particles. None of the particles assayed as pure PbS. Only one of the particles

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assayed BDL for both elements (one of the 25 small OW7F particles – included in results). A few were very rich in pyrite and sphalerite. Although Pb and S are abundant in both size fractions for both samples, there would appear to be a slight bias of both elements towards larger particles. When sampling such muds at the individual particle level one would expect to see the observed gross heterogeneity in the form of high standard deviations.

Mud samples are especially difficult to examine under the electron probe due to problems of mounting and coating the loose finely divided powder without loss of material during handling and application of vacuum. On many occasions the excess dispersal of sample material and/or buildup of electric charge caused the instrument to abort the runs. Each point in a run accumulates data for each element in turn from the sample and the standard; adding together several points and the high probability of crashing the instrument run made this an expensive and time consuming exercise. The nature of the sampling – of limited selection of particles subjected to losses – limits the interpretation of the results. Finer mud particles, of the size typically trapped upon filtration of wetland feedwater that bear insoluble Pb (0.45–40 μm, Section 10.4.3.2), were not able to be analysed by this technique.

Table 7.3: Electron probe microanalysis of mud samples for Pb and S.

Specimen	N	mean %Pb	s.d.	mean %S	s.d.
OW1F ≥300 μm particles	8	2.12	0.87	8.8	3.1
50-100 μm particles	5	1.61	1.09	6.7	4.9
OW7F 200-300 μm particles	5	1.18	0.75	10.9	11.3
50-100 μm particles	25	1.02	0.88	7.9	12.4
detection limit		0.10		0.02	

N= number of determinations, s.d.= standard deviation

The results for major rock components shown in Table 7.4 omit showing other elements measured (P, Ti, Cr, Mn, Ni, K and Cl) as they were of only minor abundance. Even with the limitations of the measurements, the results for Na and Fe would seem anomalous in light of the XRD mineralogy and the chemical assay results. After the event, and since the software involved was superseded, one could only speculate that these particular results may have been output by a program with transposed headings.

Table 7.4: Electron probe microanalysis of mud: some major rock components.

Specimen	N	%SiO$_2$ mean	s.d.	%CaO mean	s.d.	%Na$_2$O mean	s.d.	%Al$_2$O$_3$ mean	s.d.	%FeO mean	s.d.	%MgO mean	s.d.
OW1F	6	51.4	8.1	4.6	0.6	8.8	1.8	2.5	0.9	1.9	1.2	2.8	0.5
OW7F	3	55.2	2.6	4.0	0.6	8.5	1.4	4.1	1.5	1.9	0.5	2.9	0.3

N= number of determinations, s.d.= standard deviation

In conclusion, the microprobe analysis supports the earlier evidence that the Pb is present in the mud as galena in abundance, and would appear to be the main end product of the wetland functioning as a Pb sink. The galena is not present as large discrete pure particles, rather it would appear to be associated with some of the other substances in the mud in particles >50 µm. PbS is also likely to be present in the mud as 0.5-50 µm precipitate, too fine to examine by this electron probe technique.

7.5 Analysis of mud for organolead species

7.5.1 Introduction

Organometallic compound generation, transport and accumulation in natural systems are better known in association with mercury. However bacteria and microfungi are known to accumulate Pb to significant degrees – up to 50% and 10% dry basis respectively – under experimental conditions (Lepp, in Adriano 1992). The likelihood of bioalkylation of Pb under natural conditions such as found in Hellyer wetland muds is unclear (Tornabene & Edwards 1971, Bernhard et al. 1986, Kelly 1988, Gadd 1990, Harrison 1990), but warrants investigation. These organisms are the most likely agents of organolead chemical pathways. Furthermore, like organomercury, organolead is much more toxic than the inorganic metals, and if present would be some matter of concern. It was therefore sensible to at least initially examine a sample of mud in the wetland for evidence of organolead presence. Freeze-dried mud was extracted with ether. The extract was carefully dried, then digested with nitric acid to fix the Pb in assayable inorganic solution form (Gorsuch 1970, Tornabene & Edwards 1972) and analysed for total Pb by ASV.

7.5.2 Experimental

All glassware was soaked in 5% nitric acid, rinsing with deionised water. Diethyl ether was distilled using Quickfit glassware. Approximately 250 mL A.R. grade ether was placed in a 500 mL long neck round bottom flask. The flask was placed over a hot water bath on a lab jack. To the flask was attached a 400 mm long Vigreux fractionating column to the side arm of a still head. On top of the still head was fitted a coil ether condenser. To the bottom of the still head was attached a 250 mL round bottom collection flask immersed in a cold water bath. Approximately 125 mL of purified ether was collected.

Into a 65 x 20 mm paper Soxhlet thimble was weighed 5.00 g freeze-dried OW1F (2-year) floc-mud sample and a loose plug of cotton wool. The 250 mL flask lifted and to it was attached the loaded Soxhlet extractor and the ether condenser. The flask was immersed in the hot water bath. The extraction was carried out over 3½ hours. At 2-3 extractions per minute the thimble underwent some 500 extractions. The extract was concentrated to dryness in the flask using a rotary evaporator. The extract residue was digested with 0.5 mL A.R. nitric acid over a heating block to dryness.

The residue was taken up in 0.5 mL 10% nitric acid, transferred and made up with deionised water rinsings to 5 mL. The entire (now with 1% nitric acid) solution was transferred into the ASV cell along with 5 mL electrolyte and analysed for Pb by ASV (Section 2.6.2.3). The entire procedure was repeated with a blank sample.

7.5.3 Results and discussion

The blank procedure yielded a final solution with 12 ppb Pb. The OW1F sample yielded a final solution with 62 ppb Pb. Correcting for the procedural blank value and expressed as mud content, the OW1F sample contains 50 ppb organolead dry basis (as Pb); or less than 5 ppb wet basis.

When compared with the 3% total Pb reported in Table 7.1 – at nearly 6 orders of magnitude lower – this trace of organolead is unlikely to represent a major mechanism of Pb uptake in the wetland system, even as a transient species.

The only alternative to bioalkylation of Pb to explain the presence of organolead is possible spillage of leaded petrol or accumulation from incomplete combustion. The mine and contractor vehicles all run on diesel or unleaded petrol, therefore contamination by local spillage is unlikely. However the catchment has been traversed by 4WD exploration vehicles in the 1970s, and Southwell River water passes under and adjacent to the Cradle Mt Link Road (open for 5 years prior to the OW1F sampling) above the mine intake. The Link Road traffic does take a proportion of leaded-petrol vehicles, but the chances of significant unburnt leaded petrol entering the wetlands by this tortuous pathway would seem remote. A further possibility is that the organolead came from the planting source locations, at least MHA1 and MHA2, adjacent to the Murchison Highway, which have more traffic history.

7.6 Wetland gas bubbles

7.6.1 Introduction

Throughout the wetlands, where the flocculant sediment is of greater thickness, there are conical depressions in the sediment–water interface, typically in more open areas between emergent plants. On closer observation, it was found that these depressions are produced after gas bubbles intermittently rise to the surface. The wetland area is characterised by a somewhat unpleasant odour, rather sulphurous. It was uncertain whether the bubbles were its source. As the gas may be of importance to the wetland operation, as a chemical loss pathway, further investigation was warranted.

7.6.2 Sampling, analysis by gas chromatography and mass spectroscopy.

Further physical testing showed these areas occur where the sediment layer exceeds some 20 cm. Attempts to collect gas were made difficult, as the movement made upon approach would cause release of bubbles, before being

able to position collection devices; then typically there would be no further bubbles for a long period. However very careful approach from the embankment, without entering the wetland, reaching far out into a cone pitted area resulted in success. Once in position with collection jar, some gentle movement would usually induce some bubbles to rise. Then it was a matter of luck and patience to have the bubbles rise under and into the wetland water-filled inverted collection jars. Jars were 250 mL, made of glass, and polycarbonate for the respective analysis. They were filled as much as possible and sealed.

Chromatography syringes were filled by piercing the plastic jar lids.

A special semi-quantitative analysis run, with a VG 7035 mass spectrometer not ideally set up for low-mass measurement, was undertaken by Noel Davies at the University of Tasmania Central Science Laboratory for major light gases. A range of masses were subject to multiple ion monitoring after passing the injected gas through a Chrompak column. Gas concentrations exceeding 1% could be roughly measured.

Reduced sulphur gases (H_2S, COS, SO_2, CH_3SH, C_2H_5SH, CS_2, $(CH_3)_2S$ and $(CH_3)_2S_2$) were analysed by gas chromatography after solid adsorbent preconcentration by John van den Hoff at the CSIRO Antarctic Division. Details of the analytical method may be found in Deprez *et al.* (1986). Other workers (Simo *et al.* 1993) have adapted the method to portable equipment. Detection limits for each of these gases was 10 ng/L.

7.6.3 Results and discussion

The major gas found in the first bubble sample was 90% CH_4, along with about 7% N_2 and 3% CO_2. It was somewhat surprising that sulphur gases were not detected in this run; although the odour of H_2S can be detected by smell at very low concentrations (Pomeroy & Cruse 1969). The 28 amu peak was confirmed under high mass resolution to be N_2 and not contain any CO. The elevated CO_2 is expected due to decomposer microbes in the organic-rich mud. The CH_4 is produced from a deeper layer (>20 cm) in the mud by bacteria known as methanogens (Section 9.4), an end product of anaerobic decomposition. Methane production in the wetland could be considered a product of "wasted" organic resource that would otherwise be available for sulphide generation (Section 9.4).

The reduced sulphur gas analysis showed 3 µg/L H_2S and 800 ng/L $(CH_3)_2S$ present in this bubble sample. It must be noted that the gas was stored in the presence of small amounts of wetland water. The water may have partially dissolved, absorbed, or decomposed the sample, as H_2S is moderately soluble, partially dissociating into ions, and reactive. Alternatively, the H_2S may have entered into the gas as the bubbles passed through the sulphidic upper mud horizon (Sections 7.2-7.4) or entered the sample from the water (Table 8.1). The presence of these gases indicate there is some sulphur transformation in the wetland system (Figure 8.1). It is notable that some H_2S escapes the mire

into rising gas bubbles, representing a partial loss of useful Pb-fixing reagent from solution. However the small amount measured is somewhat reassuring, in that much H_2S remains in the mud and water phases for metal binding as sulphide, as shown by the mud analysis in this chapter and the fractionation of S isotopes in the following Chapter 8.

7.7 Examination of the chemical profile of wetland mud

The surface of the flocculant mud is generally brown (FeOOH + organic) in appearance, only millimetres thick before the black sulphidic mire below in most of the wetland area. Since the 1992 dam raise, in Pond 2 in particular, and to a lesser extent Pond 3 and parts of NW, this upper layer became much thicker (up to 0.3 m). This was a result of input of dam wall AMD seepage (≈ 1 L/s flowing to each of UMW and W, pH 2.5-3.2, 30-100 ppm Fe) mixing with OW bypass water precipitating out flocculant FeOOH which settled in the ponds. The new dam fill was sourced from nearby pyritic shales with some alteration zones and stringer veins of low grade mineralisation.

To alleviate the wetland volume being "wasted" by the thick FeOOH floc (reducing the available settling volume and treatment residence time), it would be prudent to install a limestone drain (Sengupta 1993) to intercept and treat the dam seepage before it enters the OW bypass drain and wetland treatment system. I further recommend a similar arrangement at the west end of the dam where seepage flows into the west cutoff drain.

Below the brown layer is a black sulphidic horizon of some 20 cm where the PbS accumulates. The gas bubbling emanates from some greater depth, >30 cm. The pH, Eh (redox potential) and dissolved oxygen could be measured by available portable instruments. It was deemed worthwhile to investigate the depth profile of the mire for these parameters.

Although these are designed for water samples, I found I could use the probes in the more fluid mires, albeit for limited duration before rigorous and careful cleaning. Table 7.5 shows the results of this work.

Table 7.5: Wetland mud profile measurements

Horizon in OW	pH	Eh (mV)	DO (ppm)
water	6.1	100 (-100 to +250)	6.5
mud surface			0.0
-7 cm		-150	0.0
-12 cm		-240	0.0
-20 cm	5.4	-310	0.0

Oxygen is absent from the mire below the surface. The mire pH was stable and consistent, and evidently provides at least some of the buffering observed in

OW, where the wide-ranging pH (4-11.5 over the study period) of the inflow H6 is brought to 6-6.5 by the time it reaches OW8. The dissolved oxygen drops by 1-3 ppm between OW1 and OW8. The water Eh varies seemingly randomly in the range as shown, but generally there is a 90 mV drop between OW1 and OW8. The more interesting feature is the rapid decline of Eh with mud depth to strongly reducing conditions.

The key offered by the data in Table 7.5 is the anaerobic nature of the muds, which offer stability to any sulphides (including PbS) that may be deposited there, or indeed formed there. Sulphides are clearly favoured in the observed mud conditions as stable species for heavy metals (Figure 2.3 and 2.4), and being very insoluble and dense, these muds therefore provide a sink where Pb can remain inert. One major function of the plants is through photosynthesis and providing dead tissue to serve as an in-situ source of organic matter content, sufficient for the muds to enable decomposer microbes to create and maintain anaerobic conditions at low Eh. This in turn, together with the abundance of sulphate and thiosalt offers the potential for sulphate reducing bacteria (SRB) to occupy a niche in the microbial consortium. SRB require a maximum Eh of -100 mV (Barnes *et al.* 1992) and this is well provided by the wetland mud. SRB then generate H_2S, which in turn precipitates out dissolved Pb from the water column. The work in Chapter 9 confirms this proposition.

7.8 Conclusion

The bulk of the wetland uptake of Pb resides in the mud, present (essentially exclusively) as PbS, stable under anaerobic conditions, together with FeS_2. The absence of evidence for presence of other forms of Pb sink species, such as carbonates, suggests alternative deposition pathways (Section 2.8.1) are of little overall significance. During the study period the PbS continued to accumulate in the 0 to -20 cm horizon in a black flocculant mire at a rate of 0.3-1.5% Pb (dry basis) per year of wetland operation with the greater deposition rates at the front end of the wetland. The anaerobic H_2S-producing mud is maintained at low Eh by the decomposing organic content. This provides redox stability for maintaining the mud as a sink for Pb as galena, chemically inert under the conditions. This redox condition needs to be sustainably maintained over the long term, so as to prevent mobilisation and environmental release of the Pb sink (DLWC 1998), reinforcing the important role of the plants in providing organic matter.

Chapter 8: Sulphur cycling in the wetland system

8.1 Introduction

The work from Chapter 7 concluded the wetland's ultimate sink for Pb is as PbS. The wetlands take up soluble as well as suspended Pb in about equal proportion on average (Sections 10.4, 10.5). Clearly the production of galena in sediment from their water column source species involves both chemical transformation (at least for soluble Pb), physical transport through the wetland, and mechanisms for removal from the water column to the mud. The processing mill generates a multitude of sulphur species dominated by SO_4^{2-}, together with various thiosalts (Blesing 1991, 1991a) sourced from reagents ("SMBS"–sodium metabisulphite–NaS_2O_5, $ZnSO_4$, $CuSO_4$, and "SMBT"–sodium mercaptobenzothiazole–$C_7H_4NS_2Na$) and the ore itself reacting while undergoing prolonged grinding and flotation.

The key hypotheses from Section 2.8.1 (those remaining in contention after elimination) can be translated and summarised into mechanisms associated with [S] fluxes in the wetland as shown in Figure 8.1, (Bauld in Bernhard *et al.* 1986, Widdel 1988, Faulkner & Richardson in Hammer 1989, Kriaraponond *et al.* 1992), in particular the dissimilatory reduction of sulphur species by sulphate reducing bacteria (SRB) to generate H_2S which is capable of precipitating out soluble Pb from the wastewater as PbS.

8.2 Sulphur species in the wetlands

Blesing (1991a) found mill waters (50% intake from Southwell, H3, and tailings dam recycling, H6) increased in total [S] from 190 ppm at the ball mill to 460 ppm in the tailings water. Of this 60% of [S] was found as SO_4, the remaining thiosalts comprising 70% $S_2O_3^{2-}$, the remainder as polythionates ($S_3O_6^{2-}$ and $S_4O_6^{2-}$), SO_3^{2-}, and smaller amounts of S^{2-} and SCN^-. The concentration of total [S] dropped in the tailings dam by some 30% mostly by dilution, whereas the thiosalts diminished by some 75% indicating breakdown. It is clear (Chapter 7) the Pb uptake of the wetlands reside essentially as PbS in the mud, implicating [S] chemistry and SRB having a role in uptake of soluble Pb. The purpose of the following investigation was to find what happened to water [S] passing through the wetlands, and its relation the interstitial mud fluid.

8.2.1 Experimental

In contrasting seasons (summer wastewater, vs. diluted winter wastewater) samples of water were membrane-filtered (47 mm ø, 0.45 μm porosity) under gentle positive pressure from above (rather than suction from below which could de-gas the sample). The samples were split into a "preserved" sample with zinc acetate and sodium hydroxide for sulphide assay, and a "natural" sample for chloride, organic carbon, total sulphur, sulphate, sulphite and thiosulphate assays filled to the top of the sample bottle. Samples of flocculant mud at −5 to −15 cm depth were similarly treated, using glass–fibre 45 mm ø (Schleicher & Schull #6) filter pads on top of the membrane to reduce clogging,

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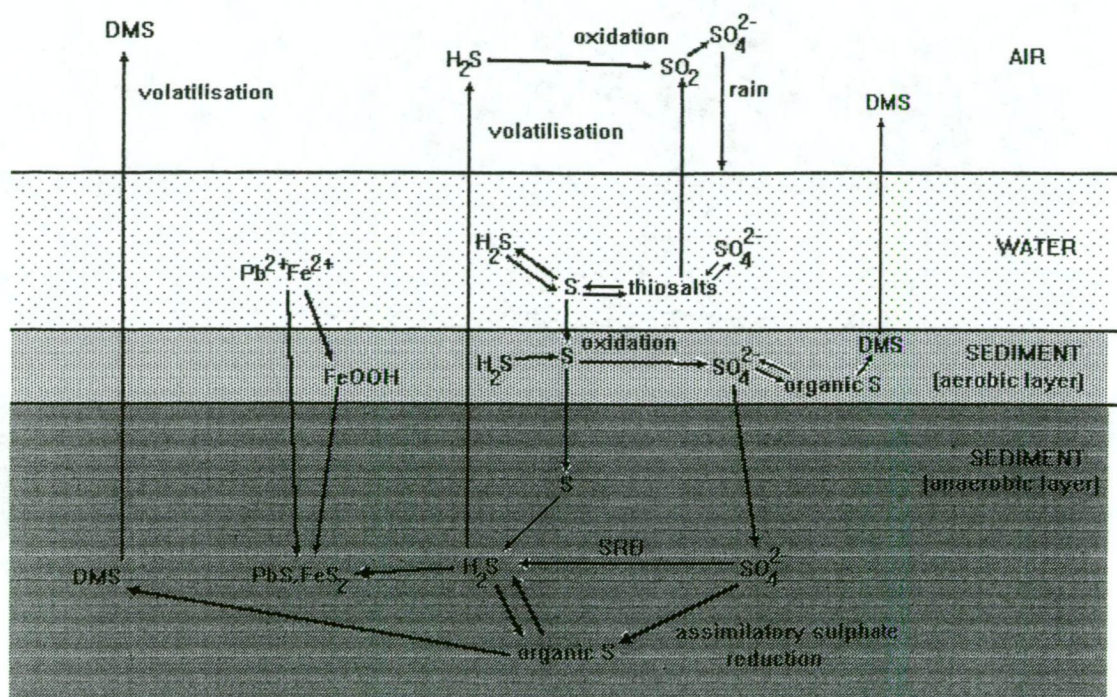
Figure 8.1: Sulphur transformations and transport in wetlands.
SRB: sulphate reducing bacteria; DMS: dimethyl sulphide.

to extract the interstitial fluid from the mud phase. Needless to say, the extraction of large volumes of fluid from mud samples was difficult and required patience. These fluids were similarly preserved.

The assays for total S by inductively coupled plasma atomic emission spectroscopy (ICPAES), for chloride, thiosulphate & sulphate by ion chromatography, for sulphite & sulphide by titrimetry and for dissolved organic carbon (DOC) by persulphate ultraviolet oxidation were performed by Analabs in Burnie (in Melbourne for ICPAES), by standard methods (APHA/AWWA/WPCF 1989).

On an earlier occasion, I sampled the waters and assayed for sulphide using the colorimetric method (Hach 1990), sending samples for other assays as above. The 5-year data (monitoring Oct 1990-Oct 1995) means for chloride and sulphate are included in Table 8.1 for reference, suggesting the limited sampling above could reasonably show values approaching those typical for the wetland system.

8.2.2 Results and discussion

The wastewaters are dominated by Ca^{2+} and SO_4^{2-}. The 2-year plots of SO_4^{2-} and conductivity in Figure 4.8 illustrate this point, and the seasonal dilution of the water chemistry by rainfall (Figure 3.3). There is considerable dynamic change in chemistry over even short periods of time (Chapter 4), and the waters of the wetlands and mud interstitial fluid would be expected to often be in some degree of flux responding more slowly to such changes.

The results for sulphur speciation are summarised in Table 8.1. Regardless of the sampling at different seasonal dilutions, basically the same trends follow for water passing through the wetlands, and less clearly, between the waters and mud fluid, partly masked the flux lag.

It is noteworthy that inert ions (including Cl^- and Na^+) and conductivity diminish through wetland 1 (H6-H7, Table 3.5) indicating some overall dilution source in the wetland. Rainfall exceeds evaporation (Figure 3.3), and is effectively augmented to approximately double for the wetlands by catchment from its aprons (Table 10.1). There were also noted some spring seepages near station OW5, and doubtless some more sources entering more cryptically within the wetland. However these (simple) overall dilutions do not account for the observed (complex) interchanges in sulphur chemistry in Table 8.1.

The work of Blesing (1991a) shows thiosalts rapidly decline in concentration from the mill to the tailings dam. In the wetlands (Table 8.1), the thiosalts diminish downstream and into the mud. This may be a combination of redox dissociation and utilisation (reduction) by SRB (Postgate 1984, Widdel 1988).

Inconsistently between samples, the sulphate diminishes from water to mud, possibly masked by some addition of sulphate from thiosalt redox dissociation.

However total [S] and to a degree SO_4^{2-} diminishes upon wetland passage approximating dilution. The degree of gross conversion of the total [S] passing through the wetland into S^{2-} required to stoichiometrically meet the soluble Pb to convert into PbS is a thousandfold smaller than the total [S]. This $\approx$1‰ increment would be impossible to confirm using gross sulphate mass balance, with the expected difference being lost within the total S or SO_4^{2-} assay error ($\pm$2% of assay). However, the data does confirm the presence of S^{2-} in the wetland system (at levels comparable to Pb levels) and is supported by the confirmation of H_2S presence in the emanating gas (Section 7.6).

The titrimetric H_2S is very high for natural surface water, and far exceeds the taste threshold, and drinking water guideline of <0.05 ppm (NH&MRC 1996) in the operational wetland; even more so if using the ANZEC (1992) river water environmental guideline of <0.002 ppm. The colorimetric results for sulphide are not reliable for these waters, as known interferences include sulphite and thiosulphate (Hach 1990), which are clearly present in significant quantities (Table 8.1, Blesing 1991a).

Table 8.1: Chloride, dissolved organic carbon (DOC) and sulphur speciation in wetlands (mg/L)

species	OW1 water	OW1 mud interstitial	OW7 water	OW7 mud interstitial
May 1993:				
chloride Cl^-	40		33	
total organic carbon	20		13	
sulphide S^{2-}	<0.01		0.36	
sulphate SO_4^{2-}	670		680	
total [S]	420		330	
August 1994:				
chloride Cl^-	26	25	20	22
total organic carbon	13	13	8	9.5
sulphate SO_4^{2-}	370	400	300	350
sulphide S^{2-}	1.8	1.6	2.5	1.0
sulphite SO_3^{2-}	5.2	<0.1	2.5	<0.1
thiosulphate $S_2O_3^{2-}$	42	9.8	24	13
total [S]	220	170	160	150
March 1995:				
chloride Cl^-	41	37	38	31
total organic carbon	24	18	16	25
sulphate SO_4^{2-}	730	1100	880	700
sulphide S^{2-}	1.6	27	2.5	1.4
sulphite SO_3^{2-}	34	7.5	22	<0.2
thiosulphate $S_2O_3^{2-}$	300	98	180	18
total [S]	560	440	490	270
5-year mean:				
chloride Cl^-	41		29	
sulphate SO_4^{2-}	518		468	

The conversion of dissolved Pb in wastewater into precipitated PbS would indeed appear to involve the key step of reduction of sulphate and other thiosalts (whether as intermediaries, straight reduction or redox dissociation) by SRB to produce the required sulphide.

8.3 Sulphur isotope distribution

8.3.1 Introduction

The fractionation leading to stable isotope ratio shifts due to partial melting and magmatic activity is well known to geologists (Krauskopf 1979), however this also occurs in biological sulphur chemistry. Dissimilatory sulphate reduction by sulphate reducing bacteria (SRB) involves a portion of environmental SO_4 diffusing into SRB cells to be reduced to H_2S which then diffuses out quantitatively. The diffusion of sulphate from environmental water across a cell membrane preferentially fractionates the lighter isotope $^{32}SO_4$ into the cell, leaving enriched $^{34}SO_4$ outside (Postgate 1984, Widdel 1988). However sulphur isotopes may also vary in the wetlands by fractionation in diffusion through the sediment column, by the inputs of flotation reagents, rainwater, runoff, by microbial oxidation of ore/tailings components, or by selective reactions in grinding and flotation. This may be complicated by possible mixing due to environmental factors including wind or current movement of plants, large animals and internal bioturbation. A survey of the isotope shift distribution of the water treatment system would be expected to shed further light on which of the hypothesised processes associated with Pb uptake act in the wetland system at Hellyer.

8.3.2 Experimental

Samples of mud (22/2/94), tails and ore feed (5/5/93) were filtered onto 0.45 µm membranes. The cakes were rinsed and freeze-dried, and scraped into vials. The other sulphide samples were freeze-dried, and would include some $CaSO_4$ from interstitial water.

Filtered (0.45 µm) water samples from the wetlands were acidified and precipitated with addition of $BaCl_2$ solution to yield $BaSO_4$. The mixtures were heat-digested (Vogel 1978), cooled and filtered onto 0.45 µm membranes. The $BaSO_4$ filter cakes were rinsed, dried and scraped into vials. Filtered interstitial water from mud samples, tailings discharge and ore feed, and $CuSO_4$ flotation reagent were similarly prepared. The sodium metabisulphite (SMBS) flotation reagent was first oxidised with hydrogen peroxide, boiled, then prepared as described as $BaSO_4$.

The filtered interstitial water in the tails and ore feed were also prepared as evaporites of $CaSO_4.2H_2O$. Other reagents were prepared as dry residues.

These prepared samples were taken to the Central Science Laboratory of the University for isotopic extraction and analysis. The general method is

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described by Robinson & Kusakabe (1975) and Potts (1992), with experimental details as follows. Christine Cook extracted SO_2 from the prepared samples, and Michael Power operated the mass spectrometer.

Sulphide samples (subsample weights varied so as to limit sulphur dioxide yield, equivalent to 8 mg pyrite – 25 mg galena, and were based on previous assays) were each mixed with 150 mg Cu_2O in an agate mortar & pestle. Each ground mixture was placed in a pre-burnt ceramic boat crucible, and inserted into a silica "burn tube" connected to a vacuum line. The line and tube were evacuated to better than 0.001 torr. A furnace at 950°C was then pulled over the crucible, and the mixture was burned for 10 minutes to provide a quantitative preparation of SO_2, trapped in a cryogenic finger. The SO_2 was carefully purified cryogenically to remove traces of H_2O and CO_2.

Sulphate samples (subsample weight 20 mg for barite) were each mixed with 450 mg SiO_2 and 150 mg Cu_2O in an agate mortar & pestle. Each ground mixture was placed into a silica glass tube, the ends of which were plugged with quartz wool, and inserted into a silica glass "burn tube" as above. Once evacuated, it was heated to 1100°C for 30 minutes. The SO_2 produced was passed over copper turnings at 600°C to ensure complete conversion of any SO_3 to SO_2, prior to cryogenic removal of H_2O and CO_2.

The captured SO_2 samples were analysed for isotope composition using a VG SIRA 10 Isoprep stable isotope mass spectrometer. The sulphide results were standardised against BHP galena (+3.4) and Rosebery galena (+12.4) working reference standards; barite results were standardised against Tasul 1 barite (+20.9) and Madame Howard barite (+31.2); all expressed against CDT (Cañon Diabolo meteorite troilite) international standard as $\delta^{34}S_{CDT}$[‰]. Typical sample accuracy achieved with this technique is within ±0.2 of the true value.

8.3.3 Results and discussion

The results from the isotope analysis are shown in Table 8.2. The first column are results expressed as isotope shift against the (somewhat arbitrary) standard Cañon Diabolo meteorite troilite (CDT) with a $^{32}S/^{34}S$ ratio of 22.21, assumed represent the average isotopic composition of terrestrial S (ie. primordial magmatic S).

$$\delta^{34}S_{CDT}[‰] = \left[\frac{(^{34}S/^{32}S)_{sample}}{(^{34}S/^{32}S)_{CDT}} - 1 \right] \times 1000‰$$

The second column of Table 8.2 relates the isotope shifts against the SO_4 in the filtered OW1 water sample, to give more meaningful figures in relation to the dynamics of the wetland system. Raw $CuSO_4.5H_2O$ and SMBS samples were not analysed as the analysis of their corresponding $BaSO_4$ extracts made these technically difficult samples unnecessary to proceed with. SMBT and Na_2S were not analysed for technical reasons. Na_2S was being trialled for sand-filter

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treatment, and SMBT was used intermittently in the mill. SMBT has been implicated in the production of traces of SCN⁻ (Blesing 1991a).

Table 8.2: Sulphur isotope analysis results.

Sample	composition	$\delta^{34}S_{CDT}[\permil]$	$\delta^{34}S_{OW1}[\permil]$
OW1m 11/8/94	by XRD: 20% FeS2 7% PbS	2.10	-4.62
OW7m 11/8/94	by XRD: 12% FeS2 4% PbS	4.29	-2.43
OW1m solid 22/2/94	by assay 2%Pb 5%Fe 4%totS	-0.06	-6.78
OW8m solid 22/2/94	by assay 4%Pb 4%Fe 3%totS	2.23	-4.49
Tails solids 5/5/93	by assay 3%Pb 4%Zn 28%Fe 32%S	7.37	0.65
Ore feed solid 5/5/93	by assay 7%Pb 13%Zn 26%Fe 35%S	9.17	2.45
OW1m sc 12/12/91	by assay 4%Pb 18%Fe	8.23	1.51
OW1m 0-0.2 12/12/91	by assay 3%Pb 9%Fe	0.67	-6.05
OW1m 0.2-0.4 12/12/91	by assay 0.6%Pb 5%Fe	5.06	-1.66
OW7m sc 12/12/91	by assay 1%Pb 12%Fe	6.98	-0.26
OW1 22/2/94 BaSO4	as 95+% BaSO4	6.72	(0.00)
OW2 22/2/94 BaSO4	as 95+% BaSO4	6.93	0.21
OW8 22/2/94 BaSO4	as 95+% BaSO4	7.92	1.20
OW1m is.f. 22/2/94	as 95+% BaSO4	10.02	3.30
OW8m is.f. 22/2/94	as 95+% BaSO4	15.66	8.94
Tails water 5/5/93	as 95+% BaSO4	7.78	1.06
Ore feed water 5/5/93	as 95+% BaSO4	15.48	8.76
SMBS 5/5/93 BaSO4	as 95+% BaSO4	4.26	-2.46
CuSO4 5/5/93 BaSO4	as 95+% BaSO4	6.67	-0.05
Tails water 5/5/93	90-95% CaSO4.2H2O	6.86	0.14
Ore feed water 5/5/93	90-95% CaSO4.2H2O	15.05	8.33
CuSO4 evap 5/5/93	90+% CuSO4.5H2O	ND	ND
SMBS evap 5/5/93	sodium metabisulphite + ?	ND	ND
SMBT 5/5/93	sodium mercaptobenzothiazole	ND	ND
Na2S 5/5/93	90% Na2S	ND	ND

Notes: m=mud sample; solid=filtered cake only; sc=scoop sample;
    0-0.2=core sample mud 0-0.2m depth; 0.2-0.4=core sample 0.2-0.4m depth;
    is.f.=interstitial fluid; SMBS=sodium metabisulphite; SMBT=sodium mercaptobenzothiazole

With these results, one must caution that not all the samples were simultaneous in origin, and preparation details are not uniform. The "duplicate" results for tails and ore water as $BaSO_4$ and $CaSO_4.2H_2O$ illustrate the latter point. This would suggest these δ results may include a sampling/sample preparation error of up to ±0.5‰. The freeze-dried (unfiltered) muds contain interstitial water residue that the other filtered (22/2/94) samples have had removed.

The tails sulphide solids are close in isotope ratio to the water that carries them, and that entering the wetlands at OW1. The significant -δ (against the OW1 wetland feed starting value) for OW mud sulphide solids alone could be either due to the activity of SRB and/or diffusion into the mud column. However this shift coupled with the large +δ for the corresponding interstitial waterborne sulphates make it clear that SRB are responsible. Kaplan &

Rittenberg (1964) and Widdel (1988) cite dissimilatory sulphate reduction of SRB producing isotope shifts ranging from $\delta^{34}S[\permil]$ -5 to -45 relative to experimental reactants, whereas sulphate reduction for assimilation in growth of bacteria falls in the range $\delta^{34}S[\permil]$ -1 to -3. While the observed wetland shifts of $\delta^{34}S_{0W1}[\permil]$ -4.5 to -6.7 would seem at the low end of the dissimilatory [S] reduction range, it must be remembered that some 50% of the wetland PbS mud accumulation is insoluble sulphide material settlement. One would reasonably presume the insoluble PbS settling in the wetlands has the same $\delta^{34}S$ as tails solids. It becomes evident the $\delta^{34}S_{0W1}[\permil]$ for the sulphide in wetland mud originating from H_2S–metal precipitation must be somewhat greater, approaching -9 to -13. Furthermore, with the wetland muds being an open system, there will be some diffusion exchange of interstitial mud sulphate with that in the overlying water, aided by physical mixing processes including bioturbation and rising methane bubble streaming (Section 7.6). This would further depress the observed $\delta^{34}S$ for the wetlands when compared with some of the closed–jar test results reported by Kaplan & Rittenberg (1964) and Widdel (1988).

8.4 Conclusion

There is evidence of sulphide production from the mud. This results from reduction of other [S] species present in water entering the wetland system. The diffusion into the mud and conversion to sulphide results in S isotope fractionation because of dissimilatory [S] reduction by SRB. The proposed mechanism of [S] reduction leading to soluble Pb precipitation appears to be the major mechanism of the uptake of soluble fraction of Pb in the wetlands. The presence of Pb in the wetland mud (exclusively) as PbS was demonstrated in Chapter 7 and the presence of SRB strains in the mud is confirmed in the following Chapter 9.

Chapter 9: Microbiology

9.1 Introduction

The Pb accumulation in the Hellyer wetlands are twofold in origin; from insoluble precipitate sedimentation, and removal from solution. The mud analysis in Chapter 7 indicates the Pb is present only as sulphide. The basic chemistry of the anaerobic mud and sulphur isotope distribution point to the soluble Pb being fixed as galena, the precipitant sulphide ion being microbially generated by sulphate reducing bacteria (SRB). SRB are known to be present in some lake sediments receiving acid drainage (Herlihy & Mills 1985). SRB have the potential to indirectly accumulate and retain PbS as an inert sink, provided the anaerobic conditions are maintained in the muds of the wetland system.

Microbial activity is known to rapidly catalyse environmental redox processes, for example pyrite oxidation proceeds 10^6 times faster than through abiotic processes (Smith *et al.* 1994). Fortin *et al.* (1995) cite SRB activity as a key factor in stabilising tailing dam storages. Furthermore SRB are regarded as useful for treatment of metalliferous wastewaters in wetland and reactor systems (Kleinmann & Hedin 1989, Ledin & Pedersen 1996). Two industrial SRB reactor systems (anaerobic digesters rather like high-tech septic tanks) are in operation treating metal bearing sulphate wastewaters. In the Netherlands (Barnes *et al.* 1992, Scheeren *et al.* 1992), the Budelco reactor is fed by ethanol which is converted to acetate for SRB consumption and reduces waste 250 mg/L Zn, 1.5 mg/L Cd, 0.25 mg/L Co and 0.75 mg/L Cu feed solution to all below 10 µg/L. Wetlands used for AMD treatment are poorly defined, with many believed to remove wastewater metals by FeOOH coprecipitation, direct plant uptake, and ion exchange with limestone, while only a few others are tentatively presumed to operate at least partially by SRB generated sulphide precipitation of metals (Ritcey 1989, Hammer 1989, Sengupta 1993, Witthar, 1993). Very recently the activity of SRB has been more closely examined in wetland treatment of AMD (Webb *et al.* 1998). However, to my knowledge, the design and operation of wetland treatment systems has never been intentionally engineered for promotion of SRB activity for metal removal.

9.2 Analysis of SRB distribution

Whereas I had some basic practical ability and understanding in microbiology, the methods of classical SRB enumeration (McFarlane & Gibson 1991) are demanding of skill, particularly for fieldwork sampling situations. A more practical, rapid field method for SRB enumeration of muds or water samples was found in the use of immunoassay kits (Anon. 1991).

9.2.1 Experimental

I determined the SRB counts on site using Conoco Rapidchek®II Immunoassay Test Kits according to basic instructions (Anon. 1991), at $25 per test. Waters

were tested using up to 1 L sample sizes for extraction to improve the detection limit. Mud samples were generally only 1 mL taken up by disposable pipette. This effectively lowered the test sensitivity for mud samples, but extended the upper limit of the test range. Blank deionised water and the kit standard were used for control tests each test occasion.

9.2.2 Results and discussion

Table 9.1 shows results for SRB testing of water and mud samples associated with the wetland treatment system.

Table 9.1: Distribution of SRB (count/mL)

Waters:		
OW1	16/2/93	<10
	6/5/93	<10
	29/9/93	<10
	10/8/94	<10
OW8	16/2/93	4×10^2
	6/5/93	<5
	29/9/93	10
	10/8/94	10
UMW	18/2/93	4×10
NW1	18/2/93	10
NWA3	18/2/93	4×10
NWB3	18/2/93	4×10
NWC3	18/2/93	4×10
NWD3	18/2/93	4×10
NWCD4	10/5/93	4×10
H13	18/2/93	4×10
Muds:		
Tailings @ mill	22/2/93	$<10^2$
Tailings @ dam	17/2/93	10^5
OW1floc	16/2/93	10^5
OW1mud	10/8/94	10^6
	2/10/93	10^6
OW3mud	2/10/93	4×10^5
OW5mud	2/10/93	10^6
OW7mud	2/10/93	10^6
	11/8/94	4×10^5
OW7floc	10/8/94	10^5
	16/2/93	10^5
NW1floc FeOOH	18/2/93	<10
NWD1mud	21/5/93	10^6
NWA2mud	12/5/93	10^6
H13floc FeOOH	18/2/93	$<10^2$

Water treated by OW and NW picks up a modicum of SRB during passage. It may be surprising to find obligate anaerobes like SRB in aerated water samples, but this result may be explained by any of the following: SRB may survive in the water by attaching to suspended colloidal organic particles in active or spore form, or the kit may be detecting recently dead cells extracted by flow dynamics from wetland muds. The SRB in the UMW sample probably originate from dam wall seepage and agitation of sediments in Pond 1 by the flow of dam discharge.

As may be expected, testing the fresh tailings solids show little evidence of SRB, whereas the dam storage sample showed a significant count. The presence of SRB in the tailings storage would certainly stabilise and assist in abating AMD generation in the storage (Fortin *et al.* 1995). However, without supplementing the tailings with organics, the SRB consortium might not persist through environmental stresses with only meagre organic inputs from humic water (originating from H3), mill reagents, dam apron runoff and scant inblown debris available to feed the consortium.

Little evidence of SRB was detected in the aerobic FeOOH floc samples. This would be expected as SRB are obligate anaerobes.

The black anaerobic mire samples of both wetlands consistently contained appreciable SRB counts, as I had expected from the indications of earlier observations and the literature (Widdel 1988, Zehnder & Stumm 1988, Levett 1990). Together with the abundance of aqueous sulphate, wetland biomass generation, metal sulphide deposition in the mud, and sulphur isotope fractionation data, the determination of abundant SRB in the mire confirms the dominant overall treatment process for removal of soluble Pb (and stabilising captured Pb as sulphide) is precipitation by H_2S as PbS. Webb *et al.* (1998) reach a similar conclusion for the mechanism of three UK wetlands used for treating AMD. The summary in Figure 8.1 shows the anaerobic conversion of sulphate to sulphide by SRB in a wetland system.

The presence of SRB is obviously associated with black organic reducing mires where sulphate is available, typically with high sulphide content and a characteristic foetid odour. SRB require Eh conditions below -100 mV (Barnes *et al.* 1992), which is well provided in the wetland mud (Table 7.5). The availability of organic matter in the wetland mud is required to both maintain anaerobic conditions and provide the SRB consortium with an energy source.

Such mires, apart from in the tailings dam and wetland system, were also found well downstream into the Huskisson River, below the Ramsay confluence, and near Lake Pieman, where the dilution of residual sulphate is appreciable (Chapter 11), in the form of slugs and eddy banks of black, foetid deposits of mixed leaf litter debris, sand and silt. There were also minor deposits with clay interstitial to natural cobble deposits. A feint foetid smell and sulphury taste of Huskisson water persists to its emptying into Lake Pieman. It is highly likely that the sediment fan at the mouth of the Huskisson River contains a SRB consortium.

Postgate (1984), Widdel (1988), and Zehnder & Stumm (1988) note SRB are widespread in the environment and persist under unfavourable transport conditions in spore form. SRB are known to arise "spontaneously" in favourable conditions, often in inconvenient places (Anon. 1994a). The Hellyer wetlands were never deliberately inoculated with SRB, they simply multiplied from existing resident populations when conditions became favourable. I would recommend that for establishing a new wetland for metal removal it may be of advantage, for early operational performance, to inoculate it with some mud from an existing working wetland, or SRB-active environmental source.

9.2.3 Feeding SRB to enhance H₂S generation in wetlands

The SRB are clearly associated with a decomposer consortium (which includes bacteria population at least 10 times the SRB number, Section 9.3.2) which supply the organic raw materials for their respiration in the presence of SO_4. The three SRB genera variously require lactate, pyruvate, hydrogen, formate, acetate or higher fatty acids. Each of these substrates is generated within the wetland mud consortium from decomposition of macrophyte cellulose (Figure 9.1) partially made available in the form of fuel molecules SRB use in dissimilatory reduction of sulphate to sulphide (Widdel 1988). The sulphate is present in oversupply readily diffusing into the mud (Table 8.1), and has no limiting effect on SRB activity, ie. generating H_2S. Therefore the key to optimising H_2S generation and precipitation of soluble Pb as PbS is to maximise food and productivity conditions for SRB. There are two overseas operations where SRB are cultivated in a reactor design for removal of heavy metals from wastewaters; Budelco in the Netherlands (Barnes *et al.* 1992, Scheeren *et al.* 1992), and Biomet in Canada (Koehnken pers. comm.). Further to these, a laboratory study using SRB bioreactors (Drury 1999) charged with cow manure, sawdust and whey demonstrated heavy metal removal from wastewater, and similarly others (Hammack & Edenborn 1991, Dvorak *et al.* 1991, Anon. 1994) using mushroom compost. The Budelco reactor uses industrial ethanol to feed their consortium, and the only limitation other than food to SRB activity is temperature falling below 15°C. Certainly little can be done for the wetlands in respect of temperature other than curbing surrounding shading vegetation and encouraging wind-screening forest. The wetland consortium's food consists of complex organic matter, which is partially decomposed into the simpler molecules required by SRB.

The regular food sources identified for the wetland consortium include turnover of wetland macrophyte growth, so long as it falls into the mud, airborne inputs from the surrounding forest (leaves, bark, litter, limbs), and dissolved organic matter in the water (Section 3.1.2). The initial OW planting was accompanied by input of hay bales (Reid pers. comm.). Kleinmann & Hedin (1989) suggested that wetlands of marginal or seasonal productivity may not provide sufficient organic matter to maintain anaerobic conditions for stable SRB activity, and it would be desirable to add organic material.
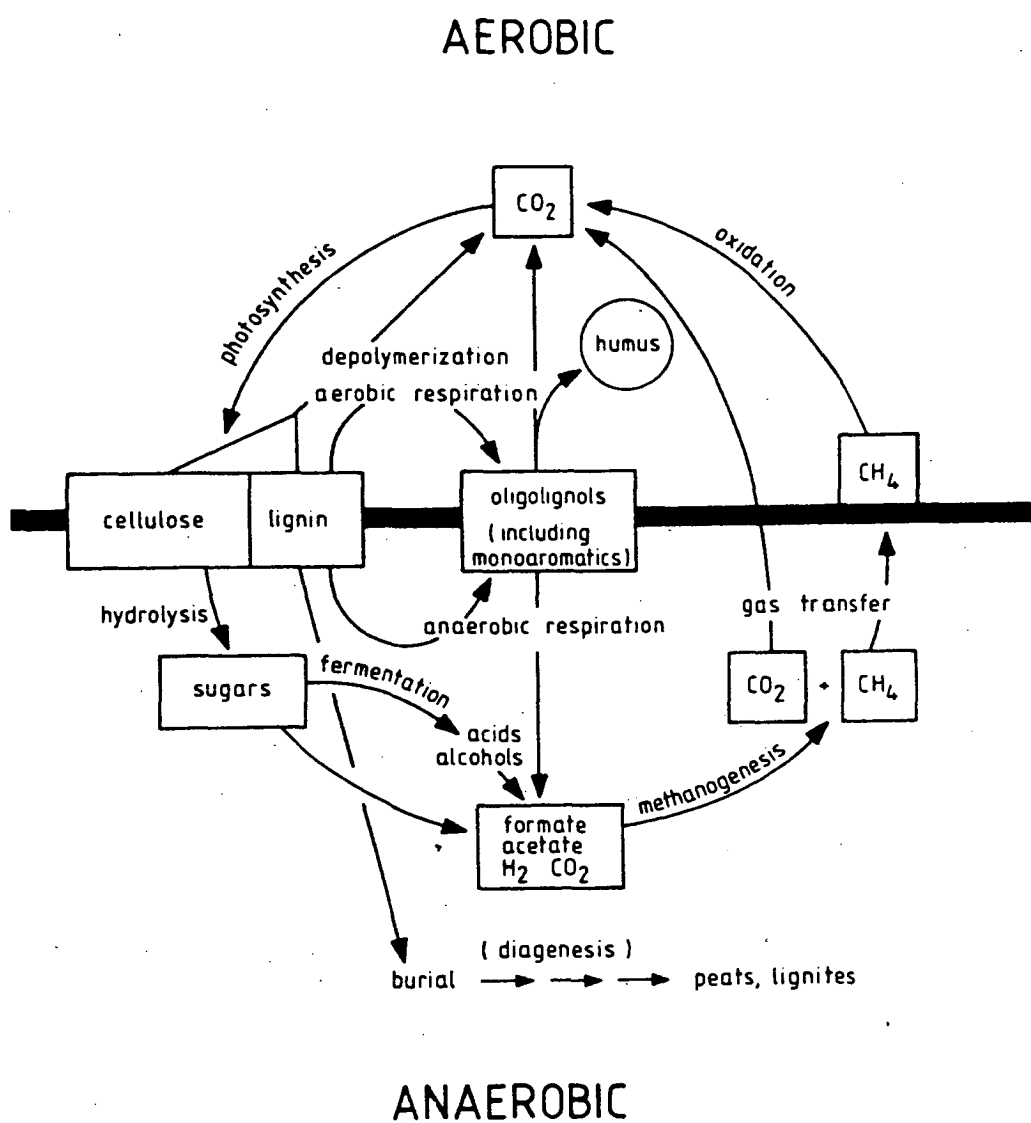
AEROBIC

ANAEROBIC

Figure 9.1: Bio-cycling of lignocellulose carbon, from Colberg 1988

There exists the management opportunity for regular supplementary feeding of the wetland mud consortium. Béchard *et al.* (1994) used alfalfa, hay and straw. I recommend (at least for trial) input of any of a variety of locally and readily available waste materials: minesite sewage, the daily highway patrol roadkill collection, forestry waste – be it bark or sawdust, dairy waste – manure sludge or whey, fish processing waste, potato processing sludge and so on. Alternative to utilising such waste co-treatment measures, non-waste inputs like hay, silage or woodchips could be used to supplement the organic mire of the wetlands. A recent laboratory study (Thompson *et al.* 2000) mixing wetland mud with sawdust showed promise for this type of SRB consortium feeding to be translated to wetland systems.

Another feeding alternative is to indirectly feed the consortium, by promoting macrophyte production of organic mass by the use of rock phosphate, slow-release fertilisers suitable for native species, or piping input of phosphate borewater. While native buttongrass and sedges are known to survive in conditions of poor fertility (as do plants in the Hellyer wetlands) by withdrawing nutrients from foliage before senescence (Jackson 1983), what I was seeking was prolific productivity, not just survival. This option was in fact taken up by the mine at the end of 1993. Table 9.1 shows a tenfold population increase of SRB in OW1 mud between 1993 and 1994, after the installation of the borewater input to improve wetland growth (Section 10.6). While this evidence is weak due to mud SRB sampling uncertainty, it is encouraging to find SRB may have shared in the benefits seen most obviously with the macrophytes (Figure 10.14) so quickly.

9.3 Analysis of phospholipid fatty acid composition of mud

The classical procedures of isolation and identification of SRB genera are a testing challenge for a professional microbiologist, and would represent a complete study programme in itself (McMeekin pers. comm). Recent work has found certain cell membrane molecular fragments – particular individual phospholipid fatty acids (PLFAs) can serve as biomarker indicators for genera of SRB and other sediment biota (Taylor & Parkes 1983, Edlund *et al.* 1985, Dowling *et al.* 1986, Dowling *et al.* 1988, Balkwill *et al.* 1988, Boon *et al.* 1996, Pankhurst *et al.* 1997). Use of modern GC-MS to detect PLFA biomarkers in purified cell extracts formed the SRB identification part of this project work.

9.3.1 Experimental

This analysis was undertaken by Peter Nichols at the CSIRO Marine Laboratory, Hobart. A sample of flocculant OW1 mire was vibrated and settled, decanting 90% as water. The remaining sediment was freeze-dried (88.5% water). A weighed aliquot of this, along with added 19:0 internal standard (for chromatographic quantitation and retention time control), was then chloroform-methanol/saline extracted, then PLFA was separated and purified by column liquid chromatography. The purified PLFA was analysed by capillary GC-MS. Further details of procedures, biomarker PLFAs and origins

of conversion factors may be found in Taylor & Parkes (1983), Edlund *et al.* (1985), Dowling *et al.* (1986), Dowling *et al.* (1988), Balkwill *et al.* (1988) and Boon *et al.* (1996). The data was used to obtain a total cell count (excluding archaebacteria) and proportions of SRB genera in the consortium.

The same sample was also analysed by the immunoassay method, Section 9.2.

9.3.2 Results and discussion

For the total count, CSIRO method assumes the average bacterial PLFA dry content of 27 mg/g, and a density of 5.9×10^{12} cells/g. The total cell count using these assumptions, from the GC–MS peak total measured 364 µgPLFA/g dry concentrate (Table 9.2), is 8×10^{10} cells/g dry basis; or 9×10^8 cells/mL flocculant mire. The two assumptions about cell size and PLFA content are based on findings for marine isolates, and may differ for the average for cells found in the wetland consortium. However for this project the bacterial counts are generally considered only to the precision of 1 order of magnitude, and these assumptions are expected to hold over this range. Hatano *et al.* (1994), using classic colliform counts, found only 7×10^6 cells/g bacteria in mud of a pulp–mill wastewater treatment wetland, of simple ecology. Their low counts could well be due to clumping of consortium bacteria, appearing as single countable colony–forming nuclei. My results are closer to the 10^{10} cells/g total bacteria found in wetland mud in Victoria (Boon *et al.* 1996) using the same PLFA analysis methodology.

The SRB count was found to be 8% of the total, some 7×10^7 cells/mL in the flocculant mire sample. The same sample analysed by the immunoassay method gave a count of 4×10^6 SRB. The discrepancy is significant, but not outside the error limits of the two methods. The immunoassay only claims to have logarithmic precision to an order of magnitude, although I found I could interpolate the colour chart. The immunoassay is calibrated for a *Desulfovibrio desulfuricans* strain; it is not documented how the kit performs quantitatively in relation to other strains of SRB, although the immunoassay detects the enzyme adenosine-5'-phosphosulphate (APS) reductase which is common to all SRB (Anon. 1991). Postgate (1984) and Levett (1990) note that different SRB strains exhibit varying rates of sulphate metabolism, hence presumably may vary in their cellular APS–reductase content. The use of the disposable plastic pipette to take mud and floc samples was noted to somewhat selectively take up a disproportionate amount of interstitial water; this would give somewhat low assays if the SRB tend to associate with solid material as may be expected. Inaccuracy with the chromatographic method may arise from the translation from PLFA calibrations from marine isolates to wetland mud samples.

Table 9.2 shows the individual PLFA chromatography results, including the three SRB biomarkers. The i17:1ω7c peak indicates *Desulfovibrio*, 10:Me16:0 indicates *Desulfobacter*, and cy17/17:1 indicates *Desulfobulbus*. Respectively these comprise 3%, 3% and 2%; SRB totalling 8% of the cell population. The precision of SRB genera proportions may be subject to variation, as the marker PLFA:cell factors are derived from ratios found for experimental data

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using marine SRB isolates.

The presence of three SRB genera is a sign of a robust microbial consortium. *Desulfovibrio* utilises lactate, hydrogen, formate or pyruvate, whereas *Desulfobacter* uses acetate and *Desulfobulbus* uses higher fatty acids or hydrogen (Widdel 1988, Levett 1990). Each of these substrates is generated within the consortium from decomposition of macrophyte cellulose (Figure 9.1) partially into fuel molecules SRB use in dissimilatory reduction of sulphate to sulphide (Widdel 1988).

Table 9.2: Phospholipid fatty acid composition of
OW1 mud sample by gas chromatography
of PLFA methyl esters.

Fatty acid	% composition	
i14:0	0.2	
14:1	0.1	
14:0	3.4	
i15:0	3.9	
a15:0	4.0	
15:1	0.3	
15:0	1.3	
i16:0	0.1	
16:1ω9c	0.6	
16:1ω7c	22.0	
16:1ω7t	2.0	
16:1ω5c	2.8	
16:0	21.1	
i17:1ω7c	0.8	SRB
10:Me16:0	0.6	SRB
i17:0	0.5	
a17:0	1.0	
cy17/17:1	1.0	SRB
17:0	1.1	
18:2ω6	1.9	
18:3ω3	1.1	
18:1ω9c	3.5	
18:1ω7c	23.0	
18:1ω7t	0.9	
18:1ω5c	0.2	
18:0	1.5	
cy19:0	0.8	
(total)	100.0	
PLFA (μg/g dry)	364.1	
PLFA (μg/g wet conc.)	41.9	
PLFA (μg/mL floc)	4.2	

PLFA: phospholipid fatty acid; SRB: sulphate reducing bacteria biomarker
c: cis-; t: trans-; cy: cyclopropyl-; i: iso-; a: anteiso-;
ω: position of unsaturation from the methyl end.

Thiosalts and sulphite are present in the processing mill waters and tailings dam (Blesing 1991a). These are undesirable reactive chemical species for mill chemistry (Blesing 1991), and potential acid-generating pollutants of moderate toxicity. These were confirmed to enter the wetlands and diminish in concentration during passage and diffusion into the mud (Section 8.2). As well as using SO_4, SRB are also capable of reducing thiosalts and sulphite, as they can be utilised as intermediate reactants, to sulphide (Postgate 1984, Widdel 1988). The reduction of these salt concentrations upon entering the mud is likely to be a combination of SRB utilisation and redox dissociation. However, it is of interest that recent research (Escoffier *et al.* 1998) points to a further possibility of substrate-specific thiosulphate reducing bacteria being present.

The sample PLFA profile shows higher than normal trans/cis ratios (Nichols pers. comm.), and the elevated levels of trans- isomers indicates microbiological response to environmental stress (Balkwill *et al.* 1988). The provision of increased organic and nutrient inputs to the wetland muds, may well eliminate this stress and maximise H_2S production and metal sulphide precipitation. Another stressor may be periodic exposure to low temperatures intrinsic to this environment.

9.4 Other bacteria associated with the water treatment system.

The count of bacteria bearing PLFAs exceeds SRB by twelvefold (Section 9.3.2). From a wastewater treatment point of view, the function of these, in ecological partnership with other microscopic decomposers, is to break down the complex molecules of the organic inputs into simpler molecules SRB can use for food (Section 9.2.3). This consortium is diverse, judging by the range of different PLFAs extracted, and would have originated from multiple natural sources including transplanted muds and spore transport.

Methanogens and other archaebacteria do not have PLFA with acetate links as determined by the procedure outlined in Section 9.3.1, but have ether linkages which are not separated or detected by this method. A separate $600 analysis by a different method (Nichols *et al.* 1987) was regarded as unnecessary, methanogens being somewhat peripheral to the project. However, the presence of methanogens in the wetlands is indicated by the gas bubble analysis (Section 7.6). It is evident by the location of bubble cones and emission patterns that methanogens are concentrated in areas of deep (>30 cm) flocculant organic mire, and they reside at this depth. Barnes *et al.* (1992) state methanogens require a maximum Eh of -300 mV. The mud Eh profile in Table 7.5 shows that depths greater than -20 cm can provide sufficiently reducing conditions for methanogen activity. In contrast, wetland sulphide accumulation is concentrated at shallower depth (<20 cm), and SRB appear to favour a horizon mutually exclusive to deeper-lying methanogens, in the Eh range -300 to -100 mV. This pattern of depth segregation of SRB and methanogens is consistent with the findings of Trudinger *et al.* (1979) in lake sediments. From a wetland treatment operational viewpoint, generation of methane is a waste of organic resource that could otherwise fuel the SRB

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Biopolymers

Cellulose
Proteins
Pectins

Biomonomers

Amino Acids
Fatty Acids
Sugars
Alcohols

Methionine
DMTP

Osmoregulatory Amines

Glycine-Betaine
Choline
TMAO

Non-Competitive Substrates

Methanol
Methane Thiol
Dimethylsulfide
Methylated Amines

Methane

Competitive Substrates

$H_2 + CO_2$
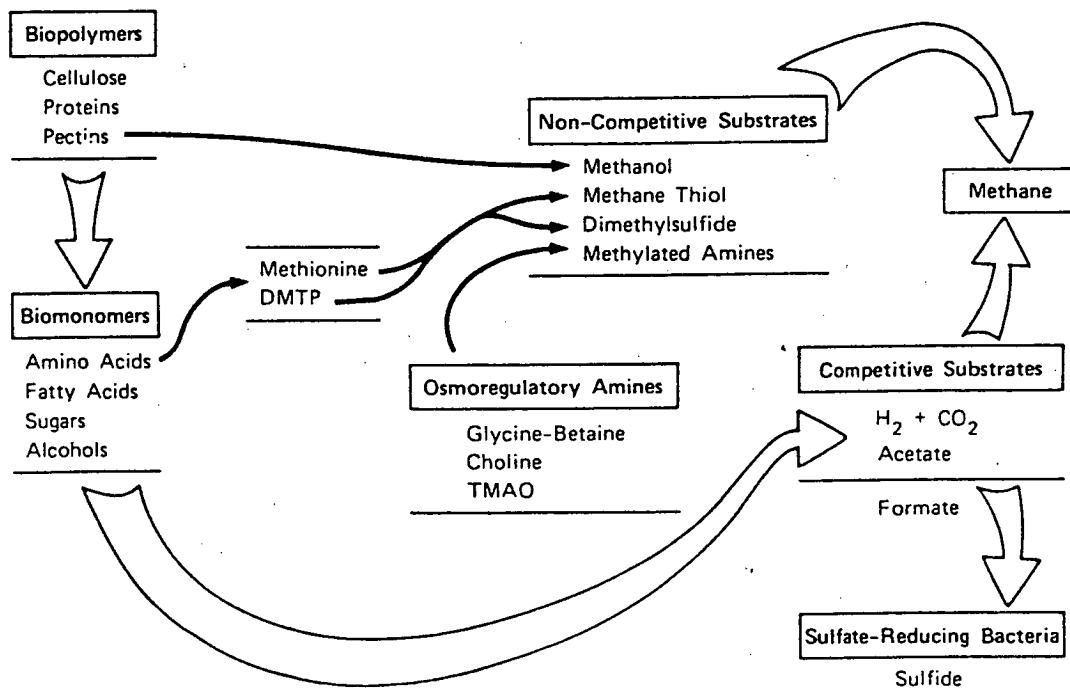Acetate

Formate

Sulfate-Reducing Bacteria

Sulfide

Figure 9.2: Anaerobic food web, from Oremland 1988

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consortium. Not only do methanogens pose as resource competitors for consortium-generated H_2 (Conrad 1996), and acetate (Figure 9.2), but the CH_4 generation is identified as a greenhouse gas (of much greater potency than CO_2). Therefore it would be prudent to engineer such wetlands with a mire depth of no more than 30 cm to reduce such losses. As with SRB (Section 9.2.2), observational evidence of methanogens was found downstream in the Huskisson River in some of the deeper sedimentary slugs.

The low levels of organolead in the wetland mud (Section 7.5) indicates insignificant presence of microbiological strains involved in any direct bio-accumulation of Pb.

The tailings dam is a potential source of acid mine drainage (AMD). AMD is the oxidation of pyrite catalysed by *Thiobacillus* which produces sulphuric acid and mobilises metals into solution (Sengupta 1993) and is a major cause of mining pollution worldwide. The Hellyer ore contains significant carbonate and the tailings are treated with lime to a high pH (Chapter 3). This resident and additional alkalinity has resulted in the dam storage being notably stable towards AMD, despite the very high surface activity from the fine ore milling (Blesing 1991). The presence of SRB in the tailings dam (Table 9.1) helps stabilise the pH against AMD by generating alkalinity (Fortin *et al.* 1995). This stable condition is assisted by maintaining a constant, or managing a very slowly rising, dam water level as far as possible to avoid excessive aerial exposure of the tailings beach. Nevertheless, there is some acid generation activity in the dam, as the pH of the water falls by some 3-5 units from limed tailings discharge to the H6 overflow (von Gunten *et al.* 1991). The 15% of FeS_2 present in Hellyer ore as melnikovite (Section 3.2.1) would be expected to be quite reactive due to its amorphous and porous nature, and be particularly susceptible to oxidation attack and be the main source of AMD from tailings.

The pipelines for mill intake waters from the Southwell River (H3) and from recycling dam water (H6) both suffer from internal wall coating, constricting the flow of waters. The manganese dioxide rich deposits are a result of growth of the budding bacterium *Hyphomicrobium*, which has been identified as commonly coating the inside walls of hydro-electric scheme pipelines (Tyler 1980) carrying Tasmanian waters. This problem is worse with some schemes and others are virtually free of the growth (Tyler 1980). Tasmanian waters are broadly divided into two types divided by an approximately NW/SE boundary: the brown humic waters characteristic of western Tasmania ("brown window"), and the clearer waters of eastern Tasmania ("green window"), (Buckney & Tyler 1973, Ling *et al.* 1989). I associate *Hyphomicrobium* growth prevalence with humic content of waters, and would conclude that humic waters both carry more manganese solubilised by the organic acids (Baker 1977, Aiken *et al.* 1985) and supply organic substrate on which *Hyphomicrobium* feed. This hypothesis is broadly supported by the comparison of water chemistry with severity of pipe deposits across the range of HEC schemes (Tyler 1980). The electricity authority uses mechanical removal to restore the bore of pipelines (Tyler 1980). Hellyer uses a combination of mechanical "pig" scouring and intermittent sodium hypochlorite treatment to clear these pipelines.

9.5 Conclusion

The evidence in the form of presence of reaction products, favourable anaerobic conditions (Chapter 7), sulphur pathways and isotope fractionation (Chapter 8), presence of food source and wetland mud eco-consortium (Chapter 5), and actual wetland removal of Pb and sulphate (Chapter 3, Chapter 10) all strongly suggested SRB working to convert wastewater sulphate into sulphide which in turn fixes wastewater Pb as galena in the mud. The work in this chapter confirmed the presence of abundant and diverse SRB populations in the wetland treatment system. It also confirms the presence of a supporting microbial consortium which provides SRB with suitable substrates from decomposition of plant matter provided by cycling of wetland plants and other inputs.

Put together, the SRB reaction sequence leading to removal of soluble Pb from wastewaters in the wetland is a major mechanism of Pb uptake. The removal of insoluble Pb from wastewaters is clearly one of sedimentation encouraged by the wetland conditions. Other mechanisms of Pb removal have been eliminated or relegated to minor roles by other investigations presented in this volume.

What remains is to further define the wetland system in terms that allow for optimisation of its operation and long term success, and to examine the implications for the larger catchment of mining wastewaters in the context of management and land use. These are considered in Chapter 10 and Chapter 11.

Chapter 10: Wetland performance

10.1 Introduction

Having established an understanding of the major mechanisms of wetland removal of Pb from wastewaters in earlier chapters, it remains to describe the wetlands and their operation in technical and practical detail. The early sections in this chapter focus on defining the physical parameters (wetland area, hydrology, mean retention times, flows, volumes and depths), followed by analysis of suspended and soluble Pb uptake, and performance improvement. Furthermore, I aim to offer ways to raise the wetland wastewater treatment efficiency (particularly for Pb removal) and ultimate effectiveness for the mine life and beyond, and the possibility of transfer of this work to mining and industrial applications elsewhere in the future.

The wetlands are photographed in an aerial view with the tailings dam in Figure 2. Photos of the wetlands from the ground appear in Figure 3.11. Closer details are shown in Figures 3.4, 4.6, 5.1, 10.1, 10.4, 10.14 and 10.15.

10.2 Area of the wetlands

Figure 10.1 shows the original plan for the wetlands. The construction aim was to have OW and NW working with 0.4 and 0.6 Ha respectively. The results on the ground broadly follow the plan, but more precise details were required.

10.2.1 Experimental

Wetland areas were determined by tracing boundaries from a 1:1500 airphoto (or 1:7000 for tailings dam), and weighing the paper cutouts against standard paper areas of 10 x 10 cm. Distances on airphotos were adjusted from the nominal (1:1400) to true 1:1490 by tying to horizontal on-ground measurements visible on the photos in two perpendicular directions (to check for any off-vertical viewing distortion). The area of the NWC pond series was double-checked, as a representative example, with complete ground measurements. Three settling/distribution Pond areas were less accurately estimated from ground observations as these did not appear on the photo: Ponds 1 and 4 were not in existence at the time of the photo being taken, and Pond 2 is obscured by the canopy of drowned forest.

10.2.2 Results

The results from the aerial photograph analysis and ground estimations are shown in Table 10.1. The individual and net results reflect the working area of water/plants. The areas for OW and NW exceed the intended specifications. The effective working area is somewhat less, being reduced by vegetation clumps, islands, bare shallows and isolated pools of still water none of which were measured (poorly defined and variable). The gross areas shown in Table 10.1 constitute the total of working area, dividing bars, associated roadway, and cleared catchment area from which runoff enters the working area.
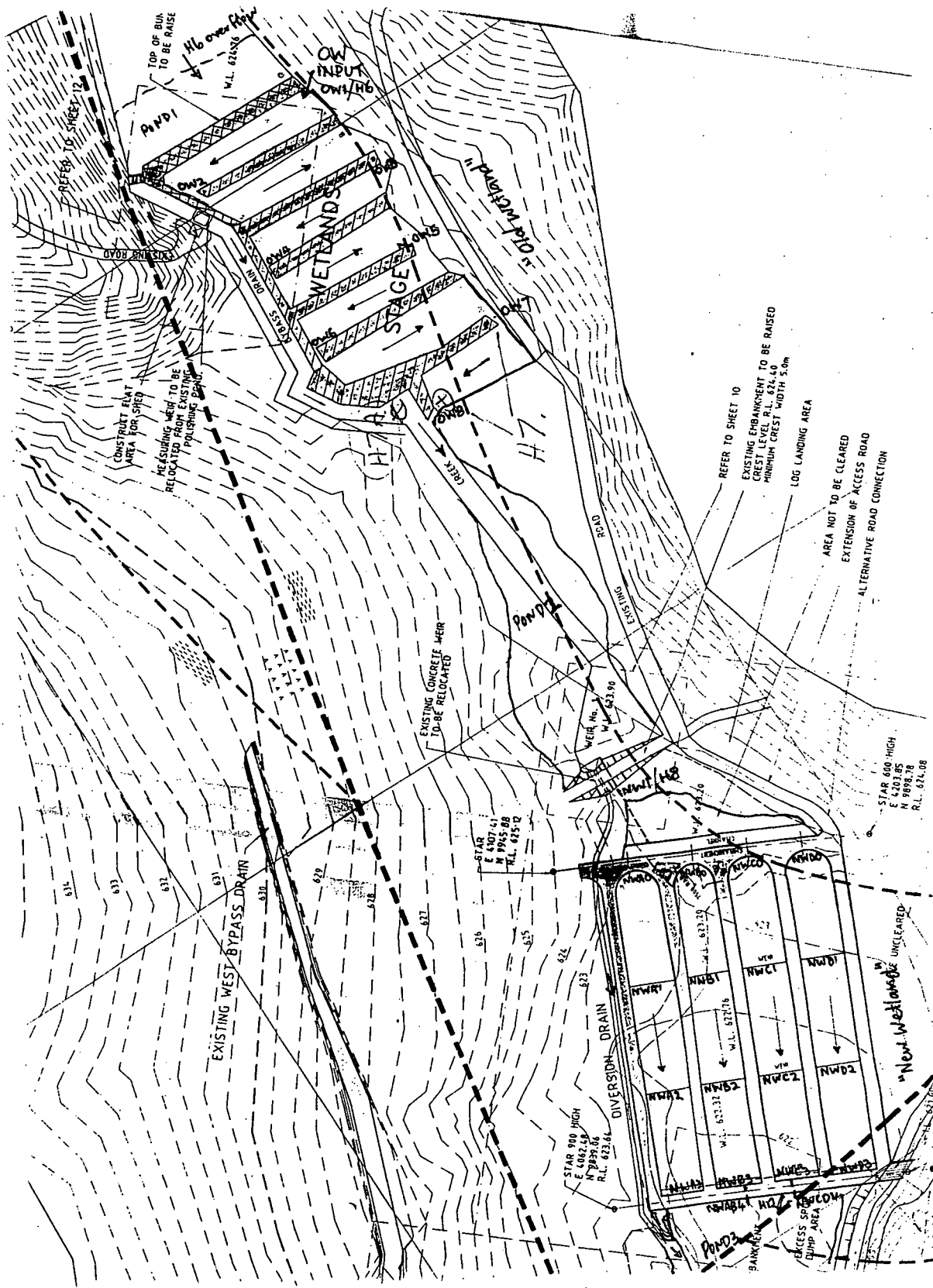
Figure 10.1: Part of the original site plan for the construction
of the wetlands, showing sample station locations.
by courtesy of Aberfoyle Resources

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Table 10.1:   Areas of wetlands and tailings dam

	individual	net	gross
Wetland system (m²)			
Pond 1		1000	10000
OW1	640		
OW2	810		
OW3	670		
OW4	640		
OW5	590		
OW6	860		
OW7	610		
OW total		4800	10700
Pond 2		3000	5000
NW1	1500		
NWA	1500		
NWB	1500		
NWC	1500		
NWD	1500		
NWABCD	6000		
NW total		7500	15000
Pond 3		4900	8300
Pond 4		1000	5900
Total treatment area		22000	55000
Tailings dam (Ha)			
water surface		15	
tailings surface		21	
total		36	74

"individual" and "net" are measures of watered surface areas
"gross" areas also include undiverted runoff catchment aprons

10.3 Hydrology

The wetlands were designed to be 250 m²/L/s (Reid pers. comm.), derived
from recommendations of Ritcey (1989). More recent design criteria may be
found in Crites (1994), Hosokawa & Furukawa (1994), Breen & Spears (1995)
and DLWC (1998). The design flows for OW and NW were 15 L/s and 50 L/s
respectively. The depth was supposed to average 200 mm, though most of the
wetland area was obviously more shallow than this during the study period.

10.3.1 Dye tracing of wetlands

Fundamental to the understanding of the wetland systems is the knowledge of
actual, rather than theoretical gross fluid dynamics. Rather than an evenly
distributed laminar flow, preliminary observation revealed there were chaotic
aspects, including mobile channelled flows, areas of still water, edge effects
around plants, eddies, local variations in pond depth and so on. An even flow
distribution would assist to achieve optimal wetland treatment performance,
and avoid premature release of partially treated wastewaters.

10.3.1.1 Experimental

Ford & Williams (1989) describe the merits and drawbacks of various hydrological tracer methods. The dye of choice was Rhodamine WT, as one of the more non-reactive compounds and stable towards light.

The use of a Turner 112 fluorometer with wavelength cutoff filters #7-60 for excitation and #2A for emission was attempted.

For the analysis, an HPLC spectrofluorescence detector was used to analyse samples. The Hitachi F1000 instrument was set with excitation λ=540 nm, emission λ=576 nm (Monochromator gratings 600 lines/mm, f:3 and f:2.8 respectively, slit width 15 nm, 3 s time, 0.01-100 sensitivity). The HPLC flowcell was replaced with an adapted assembly to manually accept a standard 1 cm pathlength spectroscopy cell. Silica cells were used for this work.

The field protocol was based on Marshall (1994), performed in two separate experiments. At noon, 6/3/95, 25 mL 20% Rhodamine WT was injected at OW1. At 3 pm, 27/11/95, 100 mL 20% dye was injected into NW1. At each of the downstream sample points, 12-19 samples were taken at times with appropriate intervals as necessary to profile the passing of the dye. Sample vials had been soaked in 5% nitric acid, rinsed with deionised water and dried. Samples were stored in the dark until analysis within 24 hours at Waratah, where stable temperature & power supply, dimmed light and adequate bench space allowed for accurate analysis. Dye standards in the range 1-100 ppb were found to give a linear response.

All samples, blanks and standards were filtered using folded 50 mm ø glass fibre filters (Schleicher & Schull #6) mounted directly on vials immediately prior to measurement. Each filtered sample was transferred to a 1 cm cell after rinsing it 3-9 times with deionised water (depending on the strength of the previous sample), and twice with the filtered sample. Where necessary samples with high levels were diluted to within the calibrated range.

Mean residence times (MRT) were determined using practical expression of

$$MRT = \frac{\int C \cdot t \cdot dt}{\int C \cdot dt}$$

where C = concentration of tracer dye, t = time

10.3.1.2 Results and discussion

The filter fluorometer proved unsuitable for this application as the broad background fluorescence of both natural waters bearing humic materials and wetland treatment waters proved far too high to make low level dye tracing

possible. Background levels of wetland waters read equivalent to 30–50 ppb dye in deionised water, and the upper limit of undiluted measurement was 60 ppb dye. Instead, the HPLC detector was acquired and used for the analysis of experimental samples, with a working detection limit of 0.5 ppb.

The dye traces for OW and NW are shown in Figure 10.2 and 10.3 The summary of calculated parameters from the dye traces is shown in Table 10.2.

The MRT for OW is in broad accord with expected after calculations (890 minutes for design parameters, 1330 minutes using measured OW area and flow). The water treatment time through NW is an order of magnitude less than that found for OW, and falls well short of the expected MRT (400 minutes by design, 610 minutes using measured NW area and flow). The immediate conclusion that NW is too shallow is backed up by observation of the initial depth of NW paddies and the poorer Pb uptake performance of NW when compared with OW (crude 5-year monitoring data means show 0.40 mg/L and 0.27 mg/L total uptake from input wastewater for OW and NW respectively, Sections 10.4.2 and 10.5). Furthermore, the NW paddies have accumulated considerable sediment from high flow loading, further reducing water depth.

The fast breakthrough and peak skewing with long tails (Figure 10.2, 10.3) are caused by the observed stream channelling (Figure 10.4) and other non-laminar flow behaviour.

Table 10.2: Dye tracing result summary

| Sample Point | Time from injection (minutes) | | | |
	Breakthrough	Peak	MRT	Ind. MRT
OW1 injection:				
OW2	21	38	51	50
OW3	67	100	150	100
OW4	110	160	250	100
OW5	140	210	320	70
OW6	180	300	480	160
OW7	270	510	800	320
OW8	400	680	1400	600
NW1 injection:				
NWA0	14	31	47	47
NWB0	13	28	35	35
NWC0	28	49	63	63
NWD0	50	77	96	96
NWA3	88	140	180	130
NWB3	65	95	110	75
NWC3	80	120	140	80
NWD3	140	210	270	170

MRT = mean residence time, Ind.MRT = MRT for individual paddy, pond or run.

Figure 10.2: Dye trace result plots for OW, March 1995
relating dye concentration (ppb Rhodamine WT)
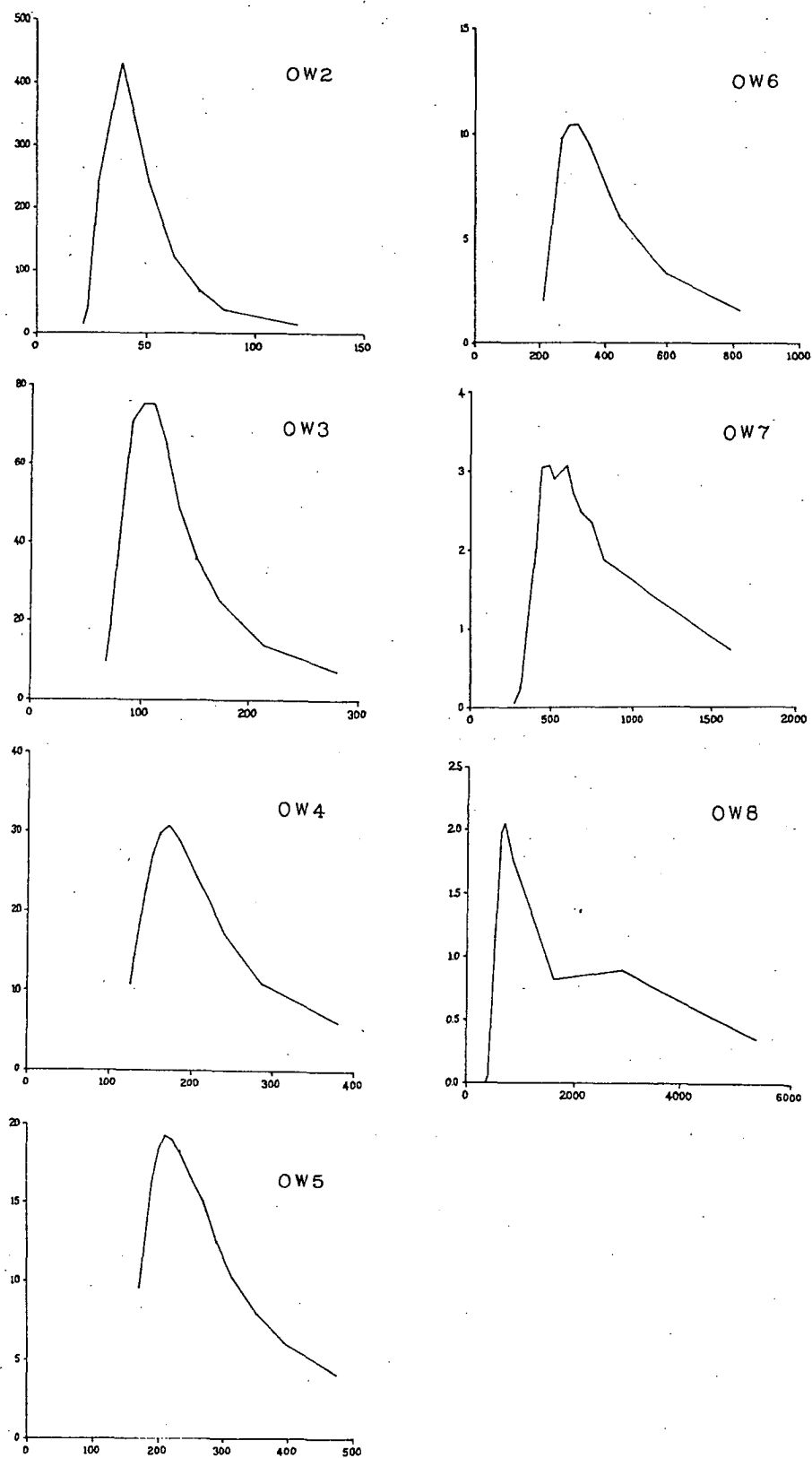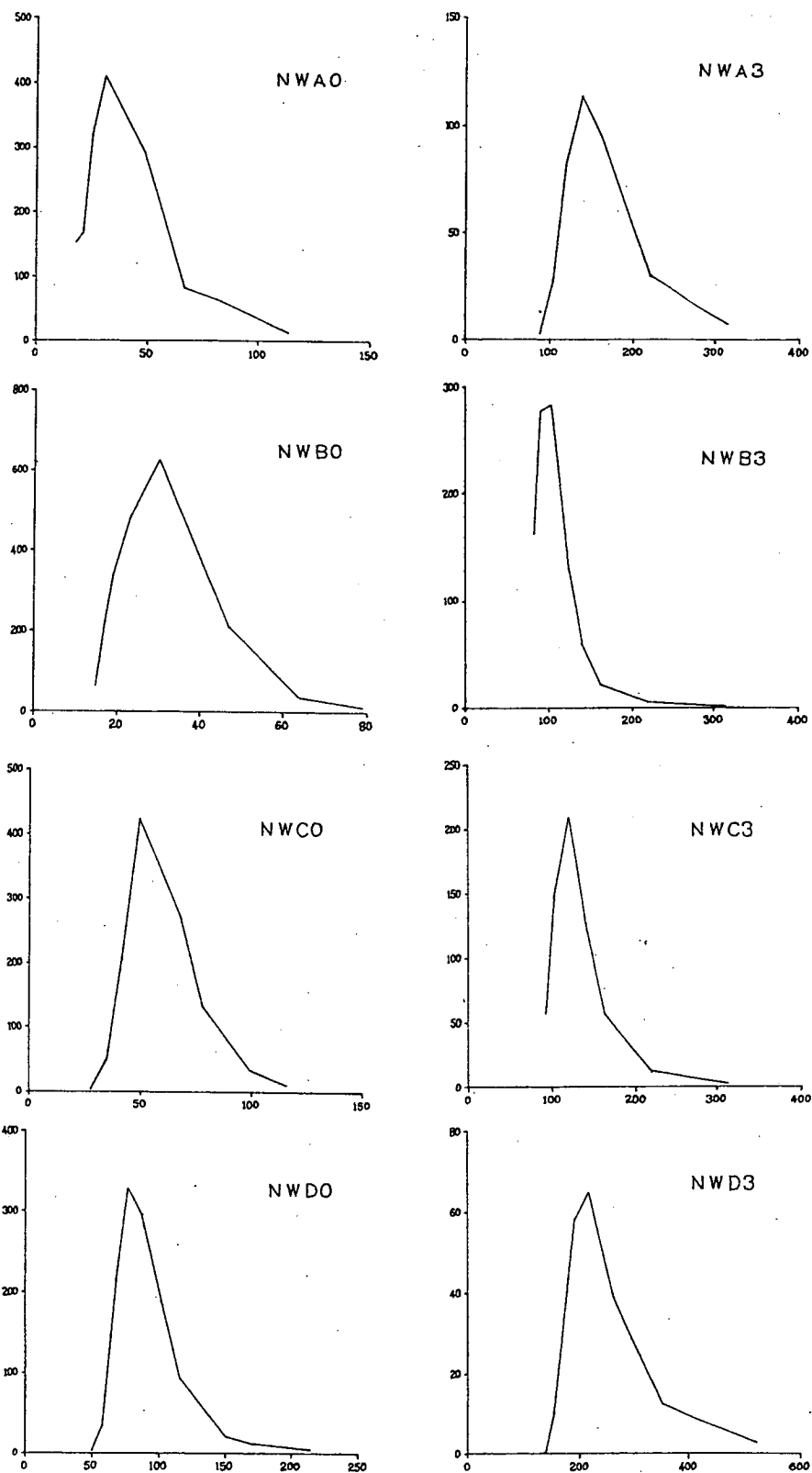against time from injection at OW1 (minutes)

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Figure 10.3: Dye trace result plots for NW, November 1995 relating dye concentration (ppb Rhodamine WT) against time from injection at NW1 (minutes)
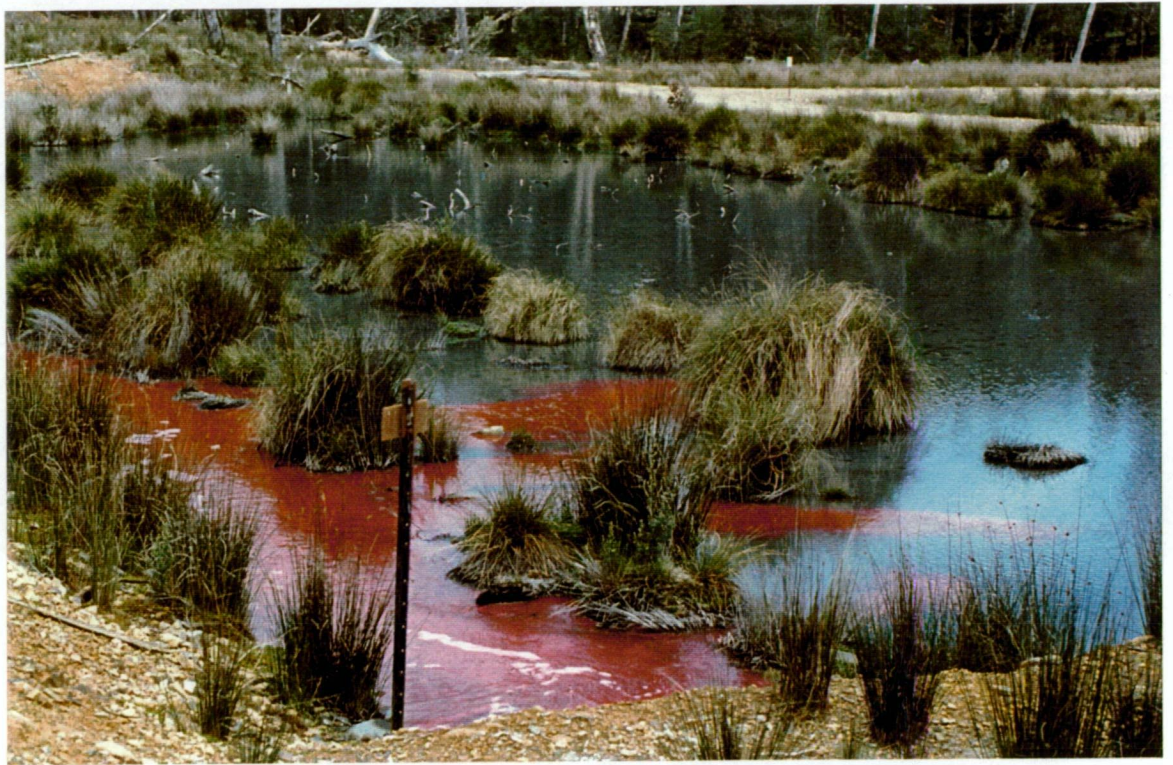
Figure 10.4: Dye trace entering NW1, showing advancing dye fingers
in areas of stream channelling in the shallow pond.

The dye concentrations for OW7, and more particularly OW8, were low, approaching the limits of the technique (Figure 10.2). Consequently, the determination of MRT for OW7 & OW8 required correction for the detection limit (0.5 ppb dye against wetland water background). This reduced the MRT for OW7 & OW8 from raw 1000 & 2800 minutes respectively, to 800 & 1400 minutes corrected, as reported in Table 10.2.

The MRT for OW is some 23 hours, whereas the flow-weighted mean for NW is only 2.6 hours. Witthar (1993) cites the MRT for wetland treatment systems vary from 0.25 to 75 days, averaging 5 days. The wetlands at Ranger U Mine reduce 400 ppm SO_4 by 40% (against concentration by evaporation) over a 12-30 day MRT depending on season (Jones *et al.* 1995, McNally pers. comm.). The Hellyer wetlands are at the very low end of the MRT range, and considering the dilution problems of high rainfall, the lengthening of the MRT by increasing wetland pond depth must be a high priority in improving the efficiency of the wetlands; drastically so for NW. The importance of MRT (Table 10.2) and flow (Table 10.4) is illustrated by the differential Pb measured in the four outflows of the parallel series of NW wetland ponds before recombining at the two NW outlets, NWAB4 and NWCD4/H12 to Pond 3, Figure 10.1, Table 10.3.

Table 10.3: Total Pb (ppm) in water flowing in and out of NW series

date	NW1	NWA3	NWB3	NWC3	NWD3
November 1991	0.60	0.30	0.35	0.35	0.25
March 1992	0.60	0.30	0.35	0.35	0.20
August 1992	0.95	0.70	0.80	0.75	0.55
January 1993	0.50	0.40	0.45	0.35	0.30
November 1995	0.680	0.450	0.525	0.510	0.395

The very short MRT in NW made observations and analysis very difficult, as the wetland treatment effect was often so slight that it entered the quantitative realm of sampling and analytical error. H12 monitoring data was biased, taken only at NWCD4. This is why most of my wetland investigations focused on OW behaviour, where changes were much more easily identified and measured.

10.3.2 Flow measurements

The monitoring and adjustment of the OW1 inlet was required on a regular basis. The valve would gather mineral/*Hyphomicrobium* plaque (Section 9.4) that would restrict flow, or sometimes pressure changes would increase the flow. The plaque was removed by entirely closing the valve and reopening it to the marked, original open set point. The flow was monitored by timing released debris from a quick valve interruption to its appearance at the pipe at OW1. The usual case was for the flow to decline in the weeks between these checks, so the mean flow was probably closer to 10-12 L/s over the study period. The flow of OW was also checked by timing passage of debris over a measured

distance through the two better-defined cross-sections of inter-pond channels at stations OW5 and OW7.

The HB pipe outflow into OW1 (Section 10.6, Figure 3.11) was flexible enough to lift. It consistently filled a 10.8 L bucket in 16 s; that was when there were no leaks or pipe breakages.

The flows in NW were measured by timing the passage of a disturbance at the entry to the 14 x 30 cm submerged connecting culverts (at NWA0, NWB0, NWC0, NWD0, NWAB4, and NWCD4) along their measured length to appearance of debris at the exit end.

The mean results of wetland flow measurements are shown in Table 10.4.

Table 10.4: Flow means for wetlands.

Station	Flow mean L/s	method
OW1	13	interrupt valve
OW5, OW7	12	channel flow
HB pipe	0.7	bucket fill
NWA0	14	culvert
NWB0	16	culvert
NWC0	14	culvert
NWD0	10	culvert
NWAB4	25	culvert
NWCD4	25	culvert
NW tot	50	sum

The NW1 (H8) inflow was regulated by a keyhole orifice in a plate at the Pond 2 weir. The keyhole was regularly cleared of forest debris, and altered in opening size three times during the study period. The total flow through NW averaged 50 L/s over the study period. This varied from 38 L/s to May 1992, adjusted to 58 L/s until December 1992, then 52 L/s until 1994 when it was adjusted to 41 L/s.

The flows at NW(A,B,C,D)0 were regulated in large part by the height of the vegetation/mud base in the first pond rather than the height of the first set of weir boards. These four inputs were even more disparate in December 1992 than previously. I then took action to rectify it somewhat by placing partial baffles over the inlets of the higher-flowing culverts NWA0, NWB0 and NWC0. The flows were still not quite evenly distributed, with NWD0 flow still less than the others. Table 10.3 shows some effect of this action; the Pb removal becomes somewhat less disparate between the series after December 1992.

10.3.3 Determination of effective pond volumes and depths

The measured flows during dye tracing were used with MRT data (Table 10.2) to determine the effective volumes of the wetland ponds. This volume data was

then used with area data from Table 10.1 to calculate the effective mean water depths of the wetland ponds. The term "effective" reflects the base of the evidence in dye-tracing, which to some degree involves and includes a measure of interaction to unknown depths of flocculant mire, but also excludes the volume occupied by plants, and averages out islands against channels etc. However, the results obtained for depths closely resemble ad-hoc spot measurements of depths in accessible parts of the wetlands.

The OW flow during its dye trace was 12 L/s. At the time of the dye trace the NW flow sum of NWA0, NWB0, NWC0 and NWD0 was 41 L/s, (although the mean flow through NW over the study period was 50 L/s) and this figure was used for the volume calculations. The two outflows of NWCD4 (H12) and NWAB4 were nearly equal, and there is some transfer flow from NWB3 to NWC3 which compensates for the unequal inputs to the four parallel inputs from NW1.

In Section 7.7, I identified a problem with AMD seepage from the dam wall entering the OW bypass, where the mixing lead to precipitation of FeOOH floc which occupies (wastes) appreciable volume (up to 30 cm thick) of the wetland system in Pond 2 and beyond. Not only does this deposit reduce the effective volume of the system, this blanket separating the water from the underlying SRB mire would surely slow the diffusion processes necessary for the precipitation and removal of soluble Pb from the wastewater. To curb this problem I recommend installing a limestone drain to intercept and treat the dam seepage before it enters the OW bypass.

The results in Table 10.5 show shallow effective depths of most wetland ponds is contributing to the low wetland MRTs.

DLWC (1998) cite a general recommendation for depth as 0.5-1 m. The Hellyer wetlands are required to perform both functions. More specifically, Witthar (1993) recommends water depths <0.45 m for wetlands involving chemical reactions, and >1 m for ponds involving sedimentation. However a complicating factor at Hellyer is that the wetland plantings are presently dominated by *Juncus* and *Restio*, which generally only tolerate shallow water depths (Section 5.3), although the *Juncus* in OW7 has adapted well to the 0.7 m pond depth. Alternative species *Eleocharis acuta, E. sphacelata, Typha orientalis* and *Triglochin procera* all thrive in deeper waters than that in which *Juncus* is normally found, and these could be phased into the wetlands as their level is raised. Rea & Ganf (1994) found water depth is also an important factor determining constructed wetland plant productivity, but one could be well guided in this regard by the species provenance.

At my recommendation, staff attempted to deepen the NW pond series by raising the boards by 7 cm, in February 1994. This scarcely made any difference beyond a small area above each board, as the sloping plant and mud base in the ponds farther above the boards were previously taking the fall by flow resistance against the shallow water. A much larger raise in water levels is required, and it is consequently likely the service road and embankment system would require additional heightening.

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Table 10.5: Effective volumes and depths of wetlands, with MRTs.

pond	flow L/s	effective volume m³	effective depth m	MRT minutes
OW1	12	36	0.057	50
OW2	12	72	0.089	100
OW3	12	72	0.089	100
OW4	12	50	0.11	70
OW5	12	115	0.20	160
OW6	12	230	0.27	320
OW7	12	430	0.71	600
OW tot/mean	12	1000	0.21	1400
NW1-A0	9	25		47
NW1-B0	14	29		35
NW1-C0	12	45		63
NW1-D0	6	35		96
NW1 tot/mean	41	134	0.090	55
NWA	9	70	0.046	130
NWB	14	63	0.043	75
NWC	12	58	0.037	80
NWD	6	61	0.042	170
NWABCD tot/mean	41	252	0.042	100
NWA3 tot	9	97		180
NWB3 tot	14	92		110
NWC3 tot	12	101		140
NWD3 tot	6	97		270
NW tot/mean	41	387	0.051	160

10.3.4 Conclusion

The conclusion from this series of investigations is that a high priority for improving the performance of Hellyer wetlands would be to increase wetland pond depths, perhaps in stages, with some replanting, to 0.3-0.5 m.

10.4 Sedimentation of insoluble Pb in the wetlands

10.4.1 Nature of insoluble Pb in the wetlands

Lead carryover in suspended matter into the wetlands from the tailings dam averages 270 ppb (as a 5-year mean of the difference of total-filtered Pb assays for samples at H6, Section 10.4.2). The inflowing suspended matter (H6) normally appears as a grey deposit on standard 0.45 µm membrane filters, suggesting mainly black sulphide. The suspended solids of Southwell River water (H3), brown organics, fall mostly in the 0.45-5.0 µm size filter

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fraction, but some also filters in each of the 0.05-0.45 and 5.0-40 μm size fractions. The dam overflow (H6) lacks the brown colour of the source waters, but retains a similar TOC content (12 ppm, seasonally varying 5-20 ppm). The mill process involves addition of small quantities of organic reagents, but these are designed to adhere to the mineral concentrate product. Natural humic acid brown colouration is proportional to the molecular weight (Hall & Lee 1974). It seems the original source TOC largely persists in the water through to the tails stream and into the wetlands, though modified by the milling and process chemistry to lose colour. Upon passage through the wetlands, there is probably some interchange of organics between the mud and water column, with some net loss to the water. The filter fraction of wetland output (H7) is usually much less in quantity than H6, and is light brown in appearance, most likely a mixture of FeOOH and organic matter.

The flotation feed grind is to a nominal 45 μm particle size (Section 3.2.2); but actually includes a size range that encompasses 100 μm down to <3 μm, with 30% <7 μm and 7% <3 μm (Richmond pers. comm.). One would expect the percentage of fines to be increased for tailings, as half the tails stream emerges from the bulk rougher after regrinding to a nominal 25 μm (Figure 3.9). Clearly it is possible that at least some of the insoluble Pb entering the wetlands comes simply as suspended fines after insufficient settling time in the tailings dam.

The lime treatment of tailings is designed to precipitate any dissolved metals. The initial raising of pH to 12-13 gives rise to a degree of solubilisation of Pb as plumbate (von Gunten *et al.* 1991, Blesing 1991, Figure 2.5). This is hoped to precipitate out as the pH drops across the tailings dam past the minimum solubility point (pH 10.2). However, some Pb still carries over as "dissolved" (a mix which may include soluble, colloidal carbonato-hydroxides and organic complex forms of Pb), some possibly coating other particles and some may precipitate out as hydroxy-carbonates or sulphide, partially settling out or carrying over to the wetlands.

10.4.1.1 Composition of suspended matter in wetland waters

The mineralogy of the insoluble portion of wetland water (sampled December 1991) was examined by XRD. Samples at OW1 and OW8 (11/12/91) were filtered (250 mL) onto 47 mm Ø, 0.45 μm porosity membranes, and these were dried. The XRD was performed on the filter cake material by Ralph Bottrill and Roger Woolley at Mineral Resources Tasmania, as described in Section 7.3.1.

Results for this XRD work are shown in Table 10.6. For this set of samples the mineral content of the insoluble fraction of inflow water was entirely deposited in the wetland before emerging as outflow. The total Pb assays by AAS for these water samples were OW1 900 ppb and OW8 150 ppb, whereas insoluble Pb assayed as HNO_3 filter cake digest by ASV were OW1 680 ppb and OW8 30 ppb). The mineral components of suspended material entering OW1 are evidently contributing by sedimentation to the mineralogy of wetland mud (Section 7.3.2); though this is not the only contribution that makes up the mud, as there are further components from the wetland plant source sites and local

erosional runoff. The XRD peaks identified as jarosite and calcite are in analytical question (Bottrill pers. comm.). If actually present in the water and these settled into the wetland mud, jarosite would be reduced in the mire environment, and calcite solubilised into the buffer system as Ca^{2+} and HCO_3^-.

Table 10.6: Mineralogy by XRD on filter cakes.

sample	25-40%	15-25%	10-15%	5-10%	0-5%
OW1	pyrite	mica chlorite	-	quartz	galena jarosite(?) calcite(?)
OW8	-	-	-	-	-

For this pale OW8 filter cake sample, no significant XRD peaks were found. Normally OW8 filter cakes contained some light brown material, but on this day there was only a pale yellow residue – amorphous according to XRD detection. This was one of the occasions the tailings dam and wetland appeared to work well, confirmed by the above assays, with clear water by OW3-OW5. However, a milky haze developed in the last three ponds.

This milkiness at the tail end of OW, though uncommon, was noted on a number of occasions, and warranted some further attention. Further analysis by ICP-MS of the insoluble portion of this (11/12/91) OW8 sample was performed by Ashley Townsend at the Central Science Laboratory of the University of Tasmania. The sample contained Fe 340 ppb, S 330 ppb, Al 100 ppb, Pb 22 ppb, Mg 22 ppb, Zn 10 ppb, Cu 5 ppb, Ba 3 ppb, Mn 2 ppb, Sr 1 ppb, Sn 1 ppb, and Au 0.1 ppb. Na and Ca were present but interferences prevented their measurement. A microscopic examination showed the presence of some algal cells, but too few to make a bloom visible as milkiness (Hallegraeff pers. comm.), and this possibility was contraindicated by the poor nutrient [P] status of the water. Bacterial cause of the haze was unlikely, as this density of bacteria the water would have blocked the filter well before 250 mL passed. Further remaining propositions as to the nature of the haze include precipitation of amorphous sulphur by bacteria and/or as dissociation product of thiosalts, hydroxy-carbonate precipitation by CO_2 generated by the wetland, and flocculation/coprecipitation of colloidal clay-organic complexes. As this contains little Pb, and only manifests occasionally, further investigation of the milkiness was abandoned.

10.4.2 Uptake of insoluble Pb

The 5-year mean for insoluble Pb entering (H6) and leaving (H7) OW is 270 ppb and 70 ppb respectively. For NW, entering at H8 leaving at H12 the soluble Pb means are 160 ppb and 70 ppb. Clearly some effective settling of suspended Pb occurs in Pond 2. The insoluble Pb uptake by OW from the water is consistent throughout the 5-year period (summary of date-paired results for insoluble Pb uptake, Figure 10.5). The occasional negative results in Figure

Pb uptake in OW
insoluble, ppm
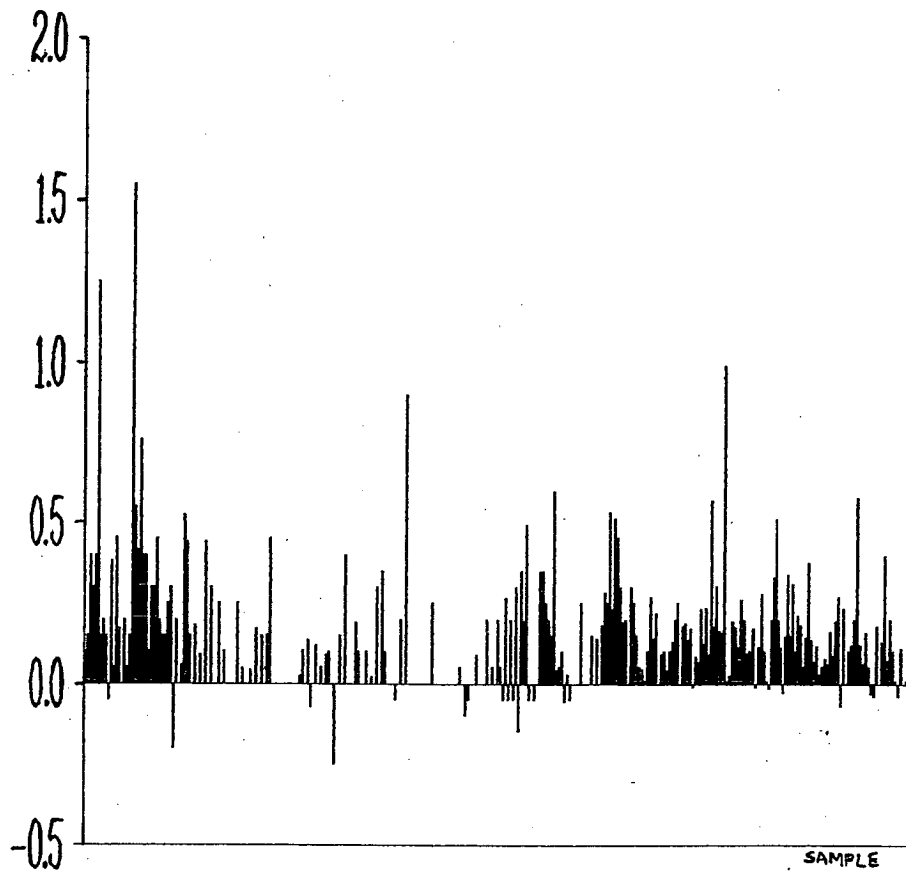
Figure 10.5: Uptake of insoluble Pb in OW.
Insoluble Pb (ppm) vs weekly sample taken.
Plots for differences of date-paired results for H6 and H7,
each expressed as a difference between total and filtered Pb,
from analytical data of samples taken at H6 and H7 for weekly
monitoring over Oct 1990 – Oct 1995. Gaps in the plot are from
missing data, or data not paired by date.

10.5 are either real pulses in wetland sediment erosion, or, much more likely, a manifestation of sampling and contamination problems (Sections 4.4–4.6), and data entry errors. The uptake of insoluble Pb averages 200 µg/L in OW, and 90 µg/L in NW over the whole 5-year data set. Taking only the date-paired results, the mean uptake of insoluble Pb by OW is 180 µg/L.

Sedimentation of suspended matter is a straightforward process, and is optimised by engineering for long MRT, and gentle flows with minimal vertical mixing and turbulence. This would best be achieved by increasing pond depth (Section 10.3.3), and I would recommend from this point of view wetland ponds ought be raised to provide at least 0.5 m water depth, and intervening settling/distribution ponds be raised to at least 1 m depth. The much poorer performance of NW in settling insoluble Pb is clearly due to the short MRT, large proportion of shallow pond depth, faster flows and the observed more turbulent flow that results. Settling may also be promoted by the use of flocculating agents, which at Hellyer would be present only in residual amounts in tailings dam water discharge.

10.4.3 Size fractions of Pb in waters passing through the wetlands

The current knowledge of the wastewater stream had only differentiated Pb and other components as total and filtered (normally >0.45 µm). For a period (Section 4.5) the filters used for environmental monitoring samples were of non-standard porosity (5.0 µm) and the implications of this action in terms of analytical results were unknown. The purpose of this investigation was to further break down this characterisation for wetland waters, and determine the significance of using incorrect filters.

There are complex schemes available for characterisation of insoluble fractions of waters (Tessier *et al.* 1979, Förstner & Wittmann 1981, Stumm & Morgan 1981, Landner 1987, Douglas *et al.* 1992). For this part of the project, a simple four , or two stage filter fractioning yielded sufficient information.

10.4.3.1 Experimental

On 7/5/92 OW1 (500 mL) and OW7 (1000 mL) were sampled and filtered in a 4-tier stack of Sartorius SM#16510 polycarbonate 47 mm Ø filter holders loaded with progressively reduced porosity filters, from the top: 40 µm Nytal #130T nylon mesh, 8 µm Sartorius #11301 cellulose acetate membrane, 0.45 µm Schleicher & Schüll #ME25/21 mixed ester membrane, and finally 0.05 µm Sartorius #11310 mixed ester membrane before collecting filtrate. For OW1, a further 4500 mL was passed through just the 40 µm mesh. On site filtration was assisted by top-pressure and/or bottom-suction applied with a Neward Metyvac hand-operated pump.

On 18/2/93 and 22/2/93 OW1 and OW8 were sampled (all 500 mL) and filtered in 4-tiers, from the top: 40 µm nylon mesh, 5.0 µm Millipore #SM mixed ester membrane, 0.45 µm membrane, and finally 0.05 µm membrane before collecting filtrate.

On 25/2/93, all stations OW1-OW8 were sampled (all 500 mL) and filtered in a dual stack, with top 5.0 μm membrane, and bottom 0.45 μm membrane before collecting filtrate.

The filtrate was acidified to 1% HNO_3 and assayed by ASV (Section 2.6.2.3). Filter cakes were dried and stored in disposable Petri dishes. The cakes/membranes were placed in acid-washed polypropylene bottles and extracted/digested with 2.5 mL HNO_3 for 24 hrs. The volumes were then made up to 250 mL with deionised water and assayed by ASV. Assays were corrected for dilution/concentration to express Pb fractions as ppb in original water samples.

10.4.3.2 Results and discussion

The fractionation results are presented in Figure 10.6 (7/5/92 experiment), Figure 10.7 (18/2/93 and 22/2/93 experiments) and Figure 10.8 A and B (25/2/93 experiment). From the first three experiments it was found very little Pb was collected in the 0.05-0.45 μm range, and thus the use of the (very slow filtering) 0.05 μm membranes was discontinued. The proportion of >40 μm material bearing Pb was also relatively small, and the use of the nylon mesh was discontinued; in its absence this fraction would still be included on cakes of finer filters.

In Figure 10.6 the middle fraction is a sizeable portion; and would mean substitution of 8 μm porosity filters for 0.45 μm filters for monitoring at H6 & H7 would substantially affect the reported total:soluble Pb distribution. The following summer experiments used 5.0 μm instead of 8 μm to better test the significance of the substitution. These results (Figure 10.7) show a much smaller middle fraction; it is unclear how much this reduction was due to simply a shift in size distribution in the different seasons' samples or how much was due to the presence of a significant 5.0-8 μm fraction. Since there were shifts in other fractions (>40 μm in particular), the former explanation would better account for much of the observed shift. This would be reasonable in light of greater tailings dam carryover of larger particles expected in times of higher flows (mid-year seasonal rainfall dilution). In this case I would suggest caution with using monitoring data from samples where 5.0 μm filters were substituted for the standard 0.45 μm membranes. Fortunately the error is not likely to be too disastrous, as it did occur in the summer season for (about) 6 months before March 1993, a relatively short time in the 5-year record used for the study.

The results of the 25/2/93 detailed investigation of wetland fraction behaviour (Figure 10.8) show that at this time the sedimentation of insoluble Pb was concentrated in the latter half of OW. The effective depth estimations (Table 10.5) based on March 1995 dye trace data showed OW1-OW4 to be only 0.06-0.11 m deep. This is probably too shallow to allow much sedimentation. Figure 10.8 confirms that little sedimentation occurs before the fourth pond. Indeed the insoluble content of both size fractions increases initially, as a result of some of the soluble Pb being precipitated by the wetland H_2S diffusing up from

Pb fractions in OW

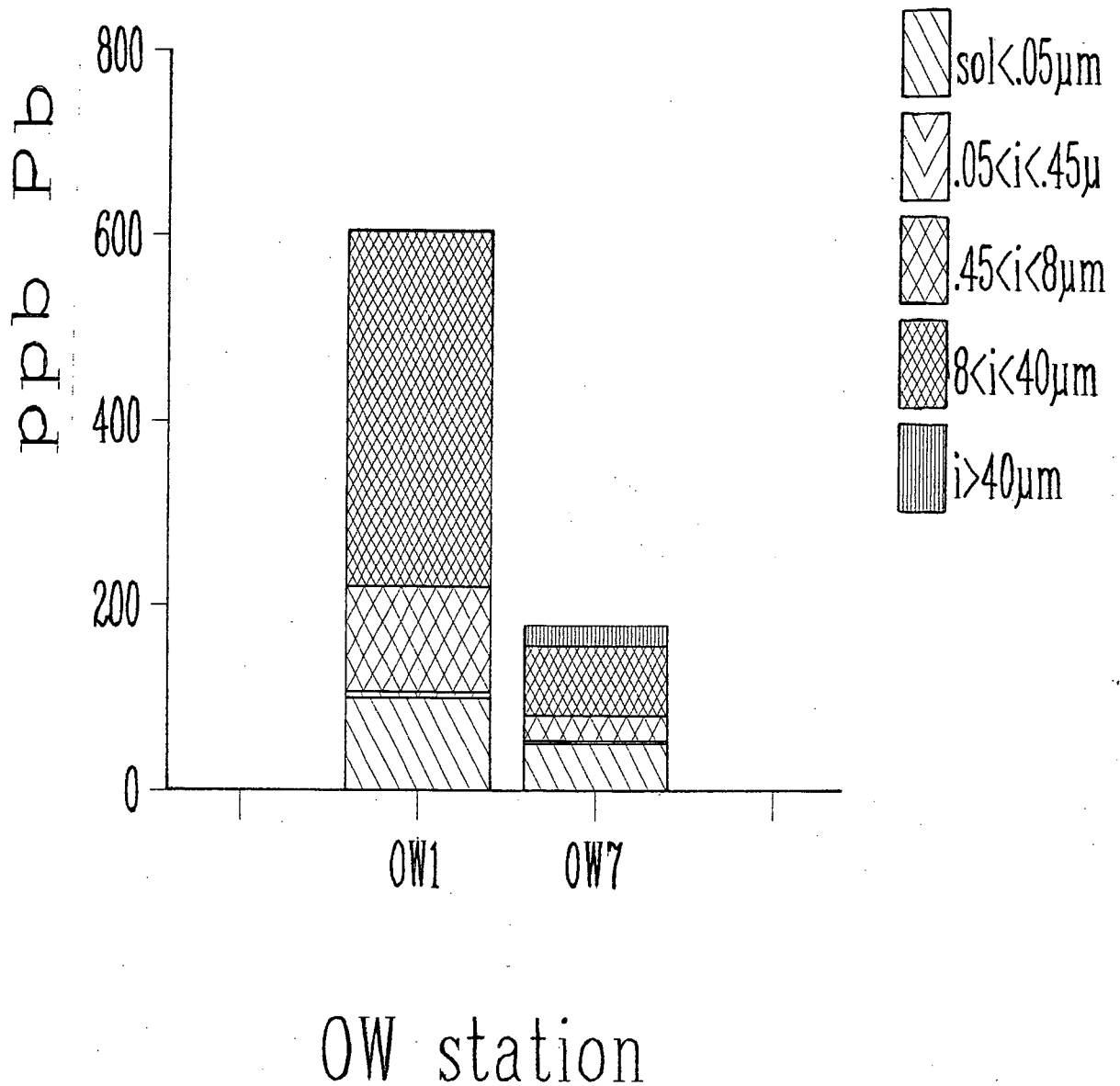Figure 10.6: Pb by filter fraction in OW1 and OW7
from 7/5/92 experiment.
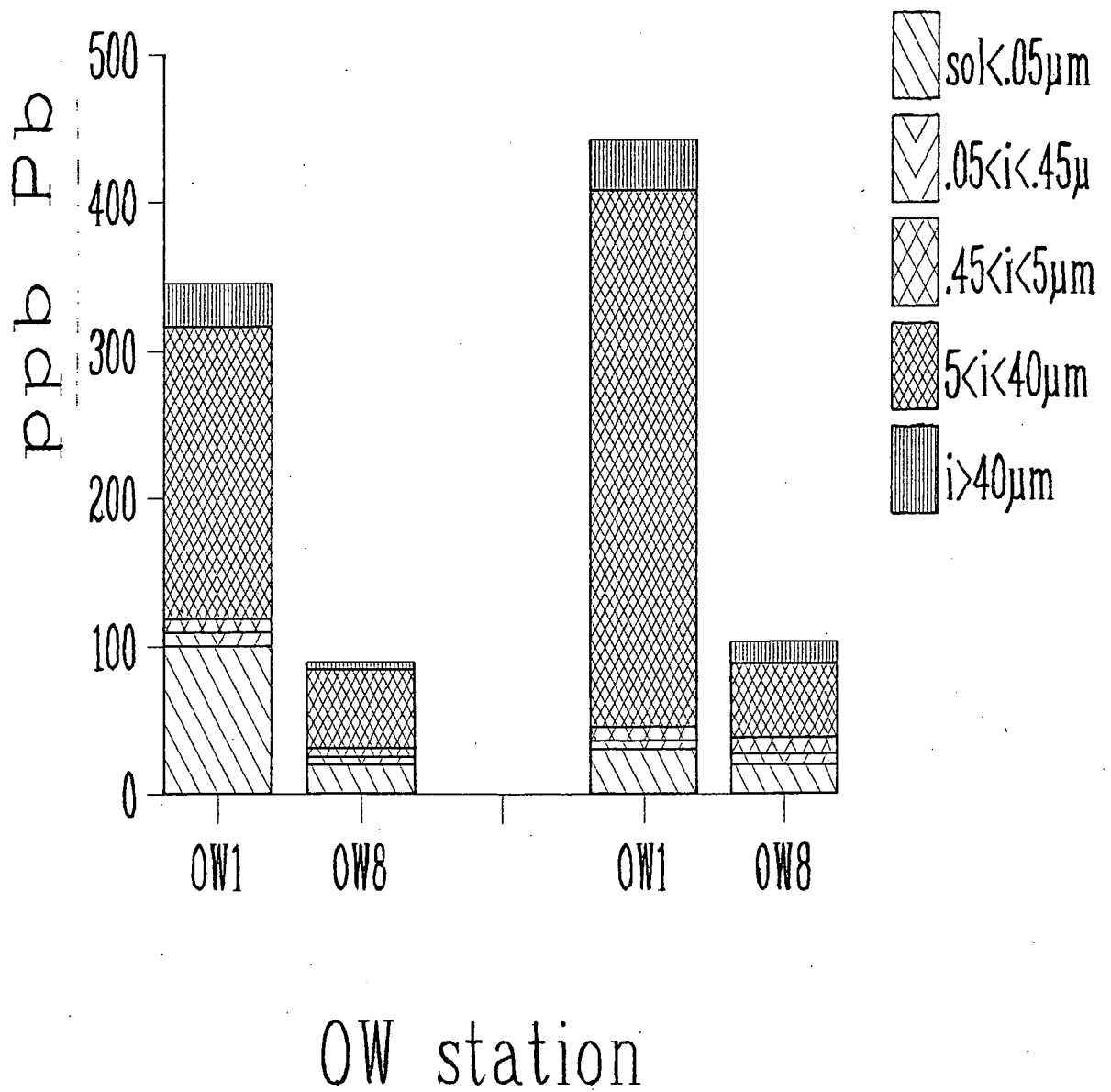
Pb fractions in OW

Figure 10.7: Pb by filter fraction in OW1 and OW8
from 18/2/93 (left) and 22/2/93 (right).
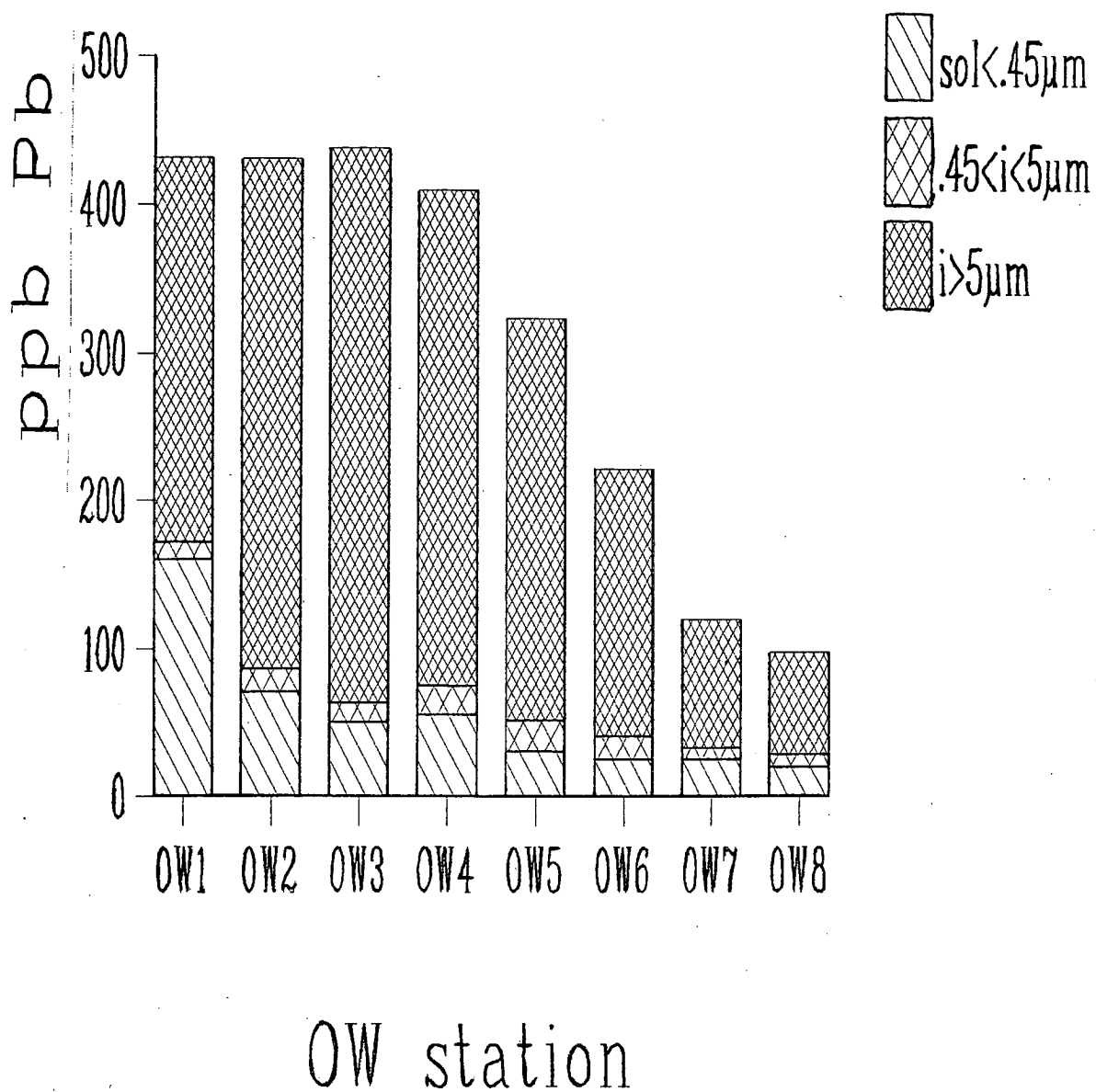
Pb fractions in OW

Figure 10.8 A: Pb by filter fraction through OW
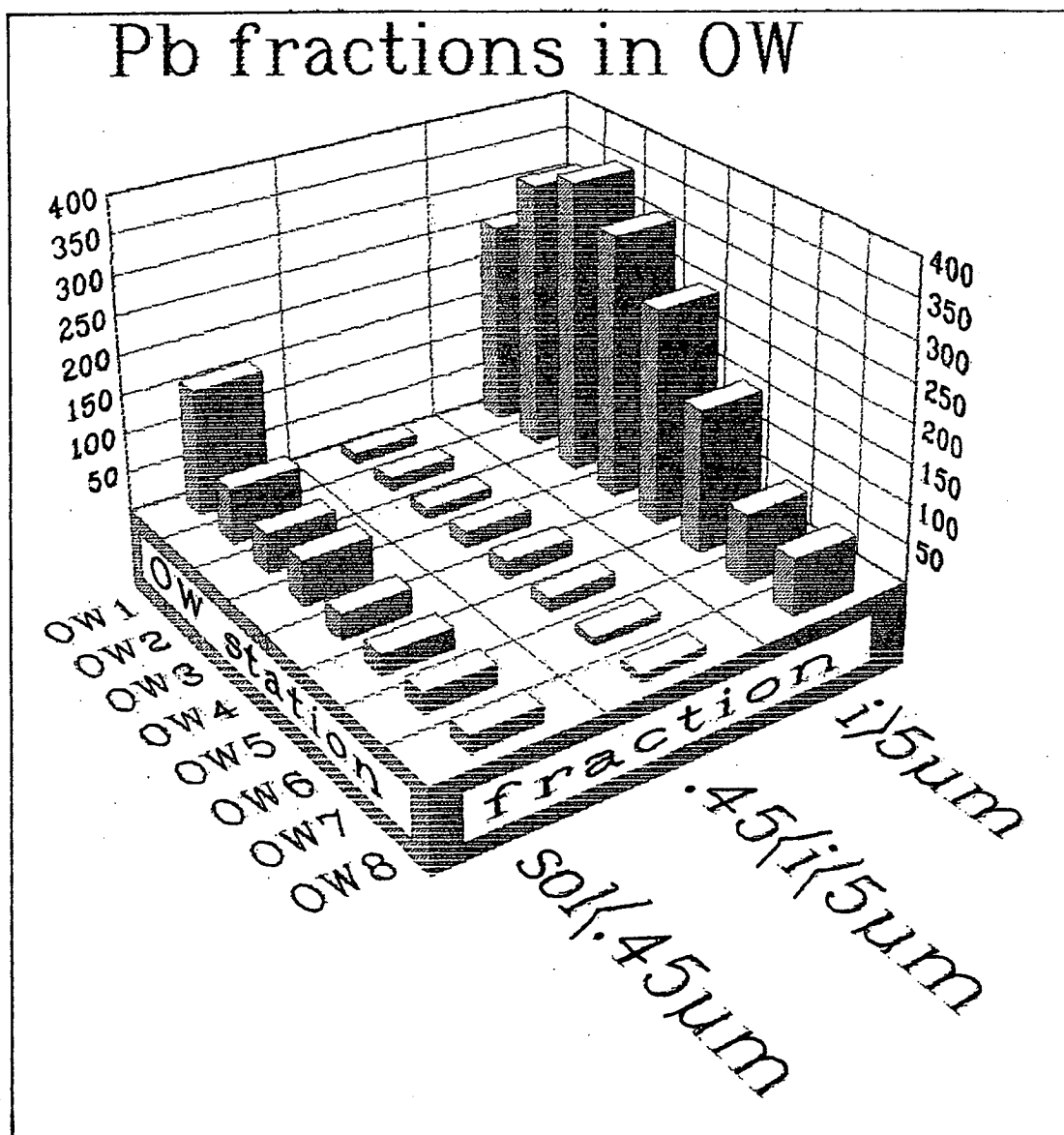   stacked bar graph from 25/2/93 experiment.

Figure 10.8 B: Pb by filter fraction through OW
3D representation from 25/2/93 experiment.

the mud. However the latter part of OW increases in depth 0.2-0.7 m, and this is where the decline in insoluble Pb occurs (Figure 10.8) for both size fractions. By OW5 the larger size fraction has started to settle out, and it is not before OW7 that the finer fraction has started to settle out. Evidently the slower flow in deeper ponds OW6 and OW7 (0.3-0.7 m) and longer pond MRT (5-10 hours) is required for this fraction to deposit. This is further support for my recommendation to increase the wetland water levels.

10.5 Uptake of soluble Pb by the wetlands

The soluble Pb declines throughout the wetlands (Figure 10.8), some of which initially is converted to insoluble form and carried suspended until the flow enters the quiescence of deeper waters (>0.2 m for >5 μm fraction, >0.3 m for 0.45-5 μm fraction). Soluble Pb uptake in the wetland can occur either by H_2S diffusing upwards from the mud leading to precipitation of PbS, or it can occur by Pb diffusing down into the mud and being precipitated *in situ*. For the latter, there is evidence of the soluble Pb being readily capable of diffusion in the dialysis trial in Section 10.5.3.1.

The 5-year mean for soluble Pb entering (H6) and leaving (H7) OW is 380 ppb and 180 ppb respectively. For NW, entering at H8 leaving at H12 the soluble Pb means are 390 ppb and 210 ppb. The soluble Pb uptake by OW from the water is consistent throughout the 5-year period (summary of date-paired results for soluble Pb uptake, Figure 10.9). The occasional negative results in Figure 10.9 are either real pulses in wetland sediment erosion, or much more likely, as with the insoluble Pb uptake records (Figure 10.5), a manifestation of sampling and contamination problems (Sections 4.4-4.6), and data entry errors. There is a disturbing block of data showing soluble Pb release in the period 15 January to 25 March 1992. This is associated with the period of interrupted flow during tailings dam rebuilding (raising), when the wetlands dried out (Section 4.7). There was clearly some oxidation and leaching of wetland sediments during this time (Figure 10.9). It could be considered as unfair to include this block of data in the appraisal of overall wetland performance as it represents a period of mismanagement of the wetlands. However, I have incorporated it in my total 5-year calculations as an aspect of practical reality. The uptake of soluble Pb averages 200 μg/L for OW and 180 μg/L for NW over the whole 5-year data set. Taking only date-paired results for the 5-year OW data, the mean uptake of soluble Pb by OW is 210 μg/L. Removal of the January-March 1992 block from the data set raises the date-paired 5-year mean soluble Pb uptake by OW to 240 μg/L.

10.5.1 Variation of Pb uptake with temperature

While the sedimentation of insoluble Pb would be expected to be independent of temperature, the uptake of soluble Pb could be determined by temperature, depending on the reaction rate-limiting step. If the soluble Pb uptake rate was limited by the SRB biological activity then temperature would be expected to have a significant effect. These living enzyme-mediated processes usually

Pb uptake in OW

ppm, soluble
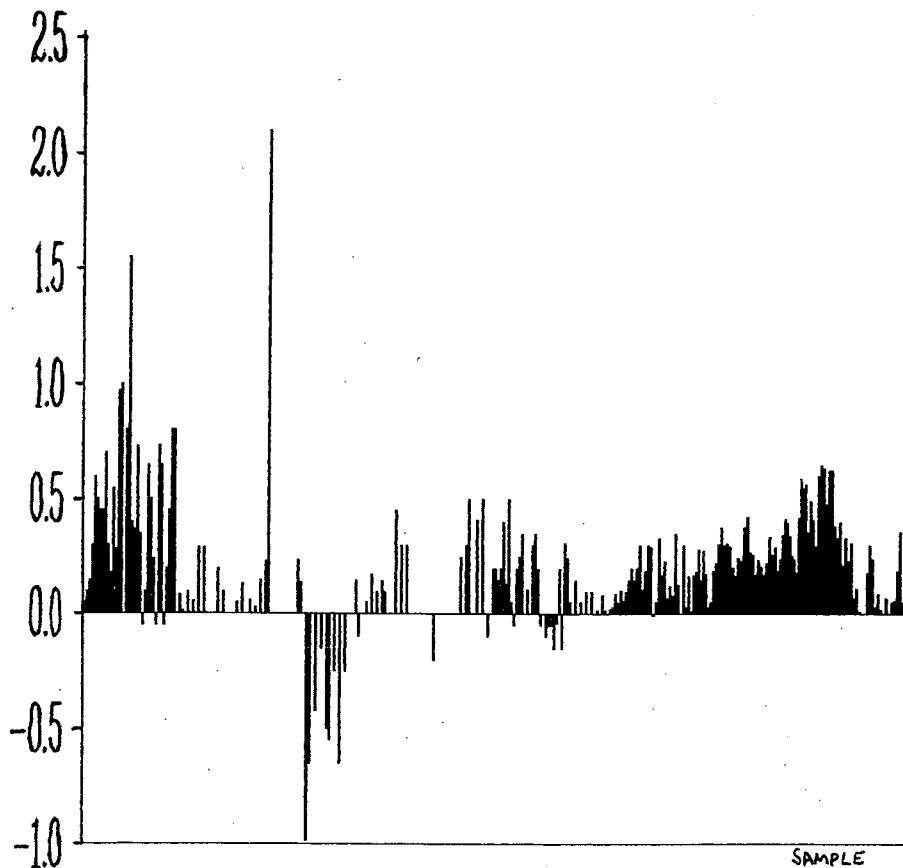
sampled over 5 years

Figure 10.9: Uptake of soluble Pb in OW.
Soluble Pb (ppm) vs weekly sample taken.
Plots for differences of date-paired results for H6 and H7,
from analytical Pb data of filtered samples taken at H6 and H7
for weekly monitoring over Oct 1990 – Oct 1995.

show a marked temperature response over the range experienced in the wetlands. In contrast, if the rate was determined by SO_4 diffusion into or H_2S out of the muds, or precipitate particle growth and settling, then little temperature effect would be expected over the temperature range pertinent to these wetlands. Alternatively the reaction of "soluble" Pb with H_2S may be controlled by dissociation of free Pb from chemical or adsorption complexes, or diffusion from within colloidal particles possibly including "onion skin" type particles of Mackey & Zirino (1994), which would be similarly by little affected by the temperature range experienced in wetlands.

Figure 10.10 shows a plot of wetland Pb uptake between H6 and H7 (date-paired results for $-\Delta Pb_{total}$ and $-\Delta Pb_{soluble}$) against water temperature recorded at H7. The scatterplots clearly show possibilities for detailed analysis are limited, and reflect the variability due to seemingly random combinations of environmental, sampling and analytical factors (Chapter 4). However, the large number of plotted points allowed some trends to emerge. Linear regression lines were produced to describe the plot relationship; any higher-order plot was too complex to rise above the error of the data scatter. The regression lines ($-\Delta Pb_{total}$: solid; $-\Delta Pb_{soluble}$: dotted) show there is a clear positive relation of outlet water temperature with uptake of the soluble Pb against the horizontal zero-temperature effect line; and a much weaker one for insoluble Pb (the difference between the two almost parallel regression lines), most probably zero, within the plot data error. Even for date-paired results, the H7 sample represents water treated from H6 with origins 13-23 hours prior to the corresponding H6 sample (Section 10.3), and some temporal variation of feed wastewater composition occurs within this time frame (Section 4.5).

The regression equations for the components of $-\Delta Pb_{total}$ are:

$$-\Delta Pb_{insoluble} = (0.8 \times T) + 150 \text{ ppb}$$

$$-\Delta Pb_{soluble} = (11.4 \times T) + 50 \text{ ppb}$$

$$\text{where T=temperature } (°C)$$

The uptake of insoluble Pb is, as expected for settling of suspensions, essentially independent of temperature above a base rate of settling. There is a small temperature effect which may be an error artifact, or there may be an element of chemical flocculation, "aging" or cementation of particles (to larger size hence more rapid settling) with weak temperature dependence.

The wetland uptake of "soluble" Pb, in contrast, is markedly more (14-fold) influenced by temperature. This points to a temperature dependent biological activity response of the SRB consortium. Barnes et al. (1992) specifically cite temperature as being a rate-limiting factor in SRB sulphide production for metal precipitation in their anaerobic reactor system, particularly below 15°C. It is likely that most biological activity supporting SRB in the mire consortium is similarly temperature dependent, and may at least in part be responsible for the observed response. Regarding the wetland macrophytes, the influence of

$-\Delta Pb$ tot, sol. vs Temp, OW
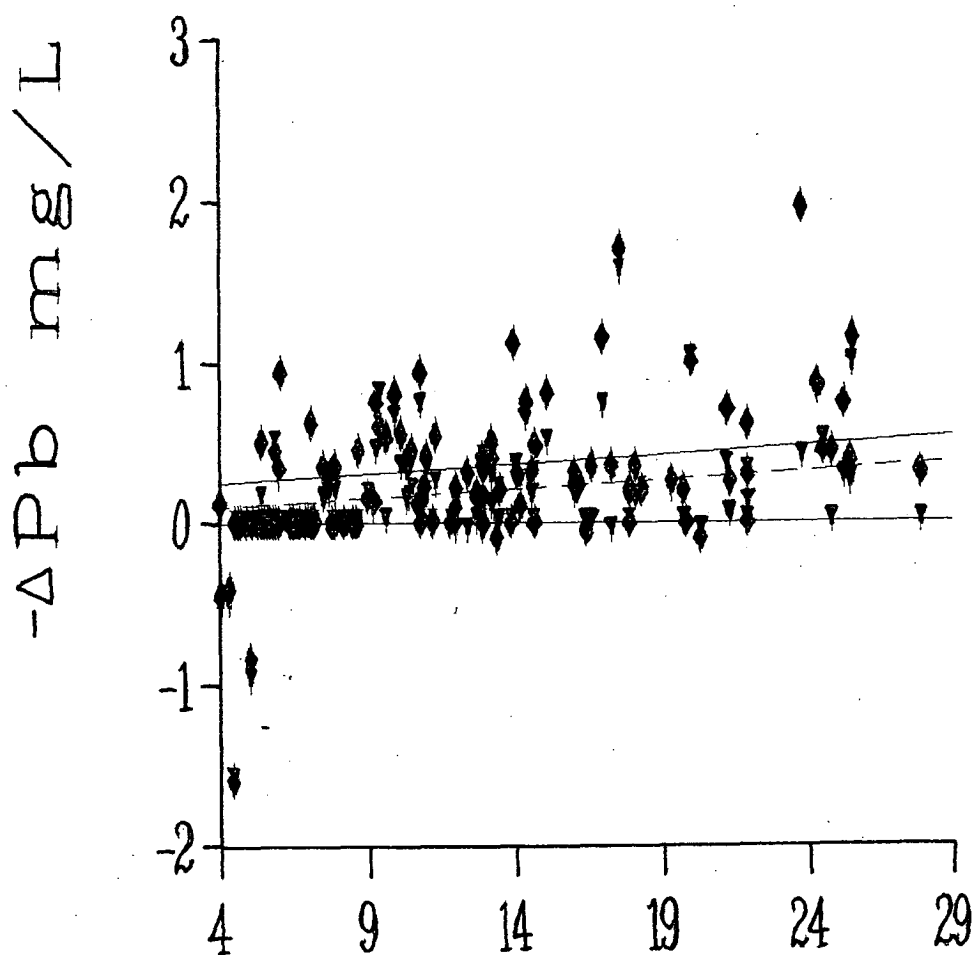
Figure 10.10: Uptake of total and soluble Pb in OW vs water temperature recorded at H7. Linear regression lines are shown in solid (for $-\Delta Pb_{total}$) and dotted (for $-\Delta Pb_{soluble}$)

temperature is well established for the seasonal productivity of plants with annual growth cycles, and hence the long term organic "food" production for the decomposers in the wetland mire.

The temperature values shown for each observation at H7 (OW7) represents somewhat of an extreme for each sample, as the water warms up or cools down from H6 (OW1) during passage through the wetland according to the weather of the day. Not only would the mean wetland water temperature vary less, but the temperature of the insulated underlying mud would respond with even less speed and extremity than the water temperature. Thus the temperature effect shown in Figure 10.10 would likely underestimate the true effect, and indeed temperature factors in the regression equation would be amplified if one used mud temperatures. An alternative would have been to use temperatures at H6 inflow, but these are a much poorer indicator of wetland conditions; more reflecting the tailings dam during its previous MRT, ≈ 3 days. It may have been meaningful to use averaged temperatures for H6 and H7, but the resulting closing up of the temperature scatter may have obscured the trends.

The NW performance for uptake of soluble Pb is somewhat better than expected when compared with OW, considering the short MRT in NW. One possible reason for this is that the mean temperature of NW is higher than OW: the mean temperature record for NW outflow H12 is 12.5°C, compared to OW outflow H7 at 11.5°C. NW is also better "fed" by forest leaf drop, being surrounded more completely by forest, with mature myrtle forest on the east side. Also, the H12 station, at NWCD4, is favourably biased by longer MRTs of C and D series.

10.5.2 Temperature, pH and solubility of Pb

Blesing (1991) relates dissolved Pb in H6 to temperature, although this becomes somewhat unclear when the annual dilution effect is considered. This is also partly related to the oxidation and leaching of tailings beaches (von Gunten *et al.* 1991) during times of low-water exposure.

There was some suggestion that there may be a diurnal effect due to the plant respiration cycle (Dunbabin & Bowmer 1992), or even light or UV having some influence on surface or water organisms or metal speciation. In January 1993, the total Pb at OW1 and OW8 were 0.70 and 0.25 ppm at 7:30 am; and 0.60 and 0.20 ppb at 4 pm. It would seem there is little diurnal effect on Pb uptake.

Figure 10.11 shows a plot of soluble Pb against pH from the 1990–1995 data set. While "dissolved" Pb never reaches the vanishingly small predictions of Figure 2.5, there is a minimum around pH 9–10. Blesing (1991) found a solubility minimum around pH 10.1 of 60 ppb Pb, while Glen (1992) found a minimum solubility at pH 8.8. The origins and scatter of the data made a meaningful curve plot, or further analysis impossible. The data does indicate the speciation of Pb is not a simple one dictated only by pH, and that while the "free" Pb^{2+} ion may be present in accord with Figure 2.5, there must be an overlay of Pb in other chemical forms (probably in dynamic flux, given the general chemistry) which carry the bulk of the total lead.
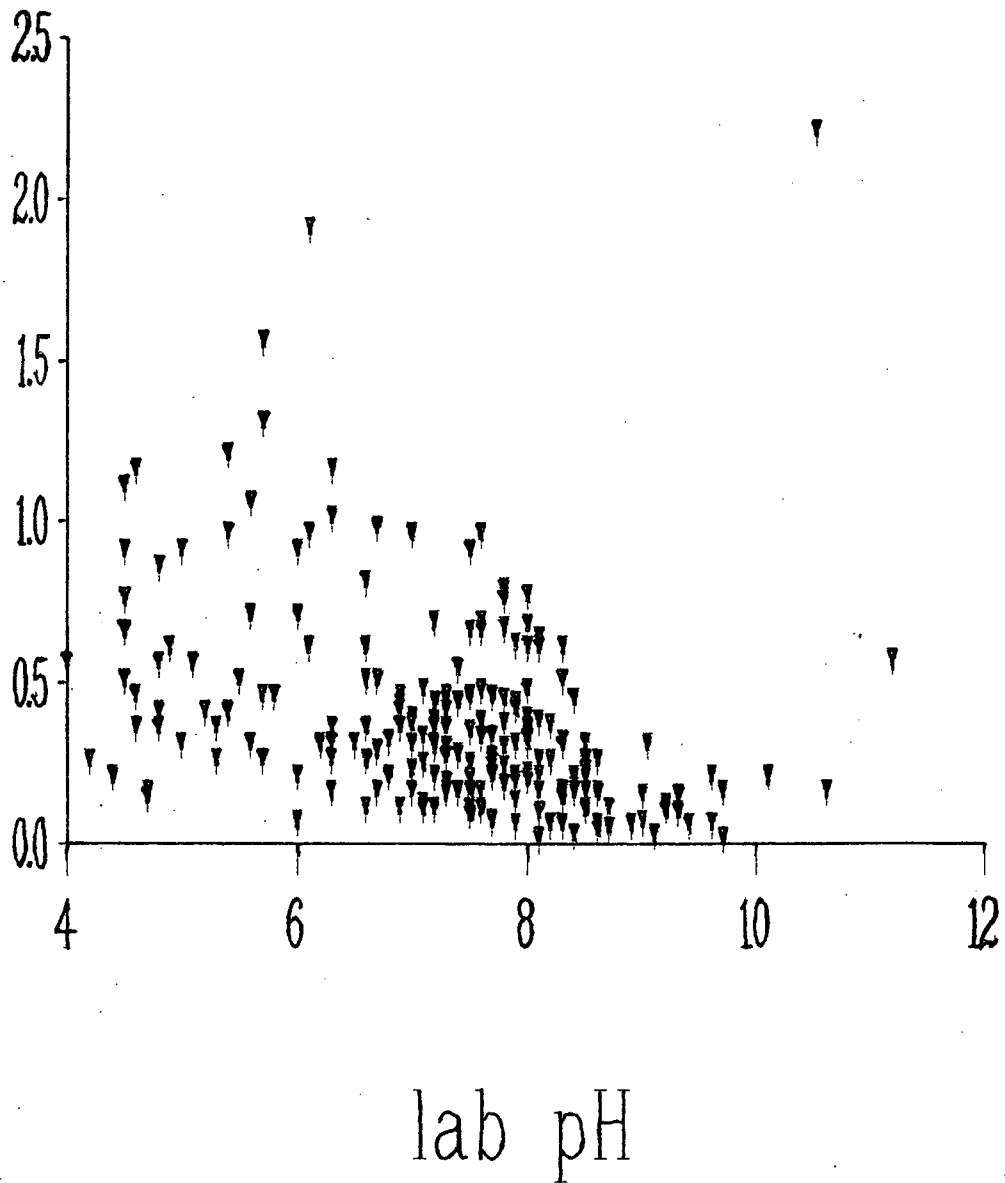
Figure 10.11: Soluble Pb plotted against pH for H6 samples.

10.5.3 Organic and colloidal complexes

The presence of organic and clay in solution or colloidal suspension together with metals can reduce the available free metal by combining as complex-bound species (Hart 1981, Florence 1986, Batley 1989). This is important as it is usually the free metal availability that dictates toxicity (Allen *et al.* 1980, Stumm & Morgan 1981, Hart & McKelvie 1986, Hart & Lake 1987, Koehnken 1992) and hence initial concentrations available for chemical reactions (Stumm & Morgan 1981); in particular for this wetland application, precipitation by SRB-generated sulphide. The presence of complexing organic materials is also significant in dissolving and transport of metals (Baker 1977), as well as metal accumulation in sediments (Phillips & Greenway 1995, Limpitlaw 1996). Organic binding materials are potentially available in the Hellyer wetland muds (Table 7.1), from the ≈ 12 mg/L DOC in the wetland feedwater (Table 5.1), and in natural humic waters of the catchment (Koehnken 1992).

10.5.3.1 Dialysis experiments

Dialysis is one analytical separation tool for unravelling speciation of heavy metal bearing waters (Batley 1989, Koehnken 1992). As part of the chemical characterisation of soluble Pb in the wetlands, I undertook some experimentation using dialysis.

For this work I used laboratory dialysis tubing, 25 mm flat Union Carbide #453105, which was filled (550 mm length - 16 mm Ø took 100 mL) with deionised water. Such tubes were terminated by stationery foldback clips and immersed in the wetland water suspended using the sample station wire installations (Figure 4.6). The contents of the tubes were preserved and analysed by ASV.

For the time trial, a number of tubes were suspended in a 20 L container of OW1 water with magnetic stirring. Pb was assayed by ASV (Section 2.6.2.3), and SO_4 was assayed by turbidimetric method (Hach 1990).

The results of the time trial are shown in Figure 10.12. The initial passage of SO_4 was more rapid than Pb. If these were both present as simple ions, the smaller Pb^{2+} would have passed the membrane at an equal (or even more rapid) rate than the more voluminous SO_4^{2-} (or more correctly HSO_4^-) ion. This is strongly suggestive that Pb is present as species much larger than Pb^{2+}. If the wetland Pb was strongly bound in large organic molecules (molecular weight >1000 amu) it would have been entirely excluded from entering the bag. Koehnken (1992) found by dialysis that about 30% of DOC in the brown humic waters of Lake Pieman had molecular weight <1000 amu. Humic acid molecular weight, proportional to colouration (Hall & Lee 1974), is evidently reduced by the mill process (Section 10.4.1), such that a greater percentage (perhaps most) of organics in water entering the wetland falls into the <1000 amu range. Apart from complexes with large or modified organic molecules, Pb is also known to transport as complexed species such as $PbSO_4$, $PbSiO_3$, $PbCl_2$, $PbCl^+$, $PbCO_3$, $PbOH^+$, $Pb_2(OH)_2CO_3$ (Batley 1989). All of these species may be resistant or slow to release free Pb for precipitation as PbS.
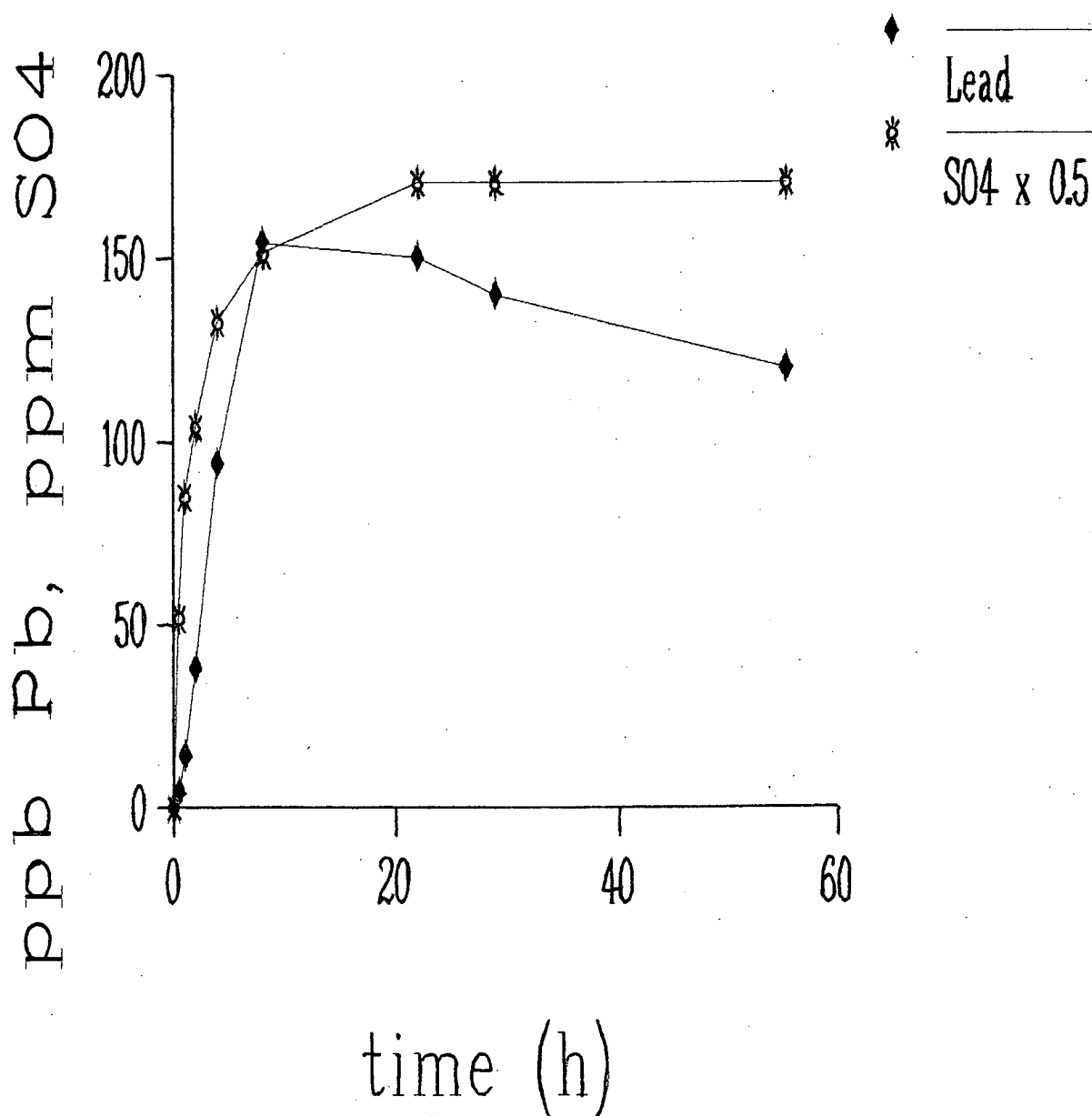
Dialysis time trial

Figure 10.12: Dialysis time trial for Pb, SO$_4$ from wetland water entering a 16 mm Ø dialysis tube of deionised water.

Humic acid complexation is through carboxyl and phenolic functional groups, each some 3-4% of molecular composition (Vernet 1991). Metals like Pb form complexes with increasing stability as pH increases, and lower ionic strength. Among metals, Pb binds relatively strongly with humic acids (Förstner & Wittmann 1981). Humic acids also bind with clay particles, including colloidal forms (Vernet 1991). Metals can be trapped in such forms, including particles with concentric layers of metal/organic/clay (Förstner & Wittmann 1981, Mackey and Zirino 1994). Lead can also bind to colloidal FeOOH and MnO_2 (Florence 1977). The sizes of such fractions vary: simple inorganic complexes are around 1 nm Ø, fulvic complexes 2-4 nm Ø, whereas the colloids with FeOOH, humic acids or both range 10-500 nm Ø (Florence 1986). The mill processing has probably reduced the organic fraction to the lower end of the size range, perhaps in the fulvic range. Certainly, only small amounts of Pb were found in wetland waters in the 0.05-0.45 μm range (Section 10.4.3.1).

The decline of dialysed Pb after 20 hours (Figure 10.12) comes with no explanation, other than to note the temperature of the water in the 20 L vat increased from 8°C to 26°C during the experiment, and to offer the speculation that complexed Pb colloidal particles may have aggregated with aging, making some of the Pb inside the tubing inaccessible to ASV electrodeposition, (Section 10.5.3.2).

Dialysis of other samples proved to differ only marginally with filtering, and the technique was abandoned due to its time-averaging effect. Dialysis lends itself poorly to the study of dynamic waters, a further difficulty being incompatibility with other assays of samples taken at a single point in time.

10.5.3.2 ASV analysis of Pb

For most of this study, I assayed acidified samples for metals, in order to follow the trends for total (or total fraction) Pb. Florence (1986), Batley (1989) and others show that the difference between ASV analysis of acidified ("total" Pb) and unacidified natural ("labile" Pb) accounts for Pb bound in complex form. In September 1993, I undertook such an experiment; the results are presented in Table 10.7.

Table 10.7: Chemical Pb fractions in OW (ppm), 30/9/93.

analyte	OW1	OW3	OW5	OW7
Pb acidified total (AAS)	0.60	0.50	0.40	0.35
Pb natural (ASV)	0.392	0.240	0.172	0.124
Pb (filtered) acidified total (AAS)	0.35	-	-	0.15
Pb (filtered) natural (ASV)	0.276	0.156	0.118	0.102
Pb (cake >0.45μm) acidified total (ASV)	0.310	0.345	0.330	0.254
total [S] (ICPAES)	250	250	230	200
SO_4^{2-} (ion chromatography)	420	420	430	400
Cl^- (ion chromatography)	26	27	26	24
Na (flame emission spectroscopy)	42	41	41	37

From the data it is clear that both "insoluble" and "soluble" fractions of the wetland water include non-ASV-labile Pb; that is, Pb bound to particles and organics strongly enough to resist electrolytic release of Pb, yet will release Pb upon acidification with 1% HNO_3. The ASV assays of natural samples involves repeat electrodeposition/stripping scans until Pb peaks grow from the initial scan to plateau at a maximum. Even so, this falls short of measuring "total" Pb. This is described as "quasilabile" behaviour (Batley 1989), examples of which include Pb-humic, $PbOH^+$ and $PbCO_3$. These will tend to dissociate slowly if there is a chemical demand for Pb (as there is in the wetlands in the form of H_2S). Hence the removal of Pb from wetland water as PbS precipitate is *not* instantaneous (appreciable H_2S and Pb concentrations are observed to temporarily coexist - for example, Table 8.1 August 1994 ≈ 2 ppm sulphide OW samples had from 650 ppb Pb in OW1 to 200 ppb Pb on OW7), but relies on the slow coaxing of free Pb from complex forms. That portion of Pb that is resistant to release by electrodeposition, but measurable after acidification, is best described by the concentric Pb-humic-clay colloid model.

Other more severe methods of extraction of "total" Pb include UV or peroxide treatment in conjunction with acidification prior to ASV. For wetland water samples this was trialled; however, within experimental error, no additional Pb was released above the plain acidification extraction. Furthermore, these treatments added serious risk of contamination during additional manipulation.

10.5.3.2 Mixing experiment

To demonstrate exchange of Pb amongst the complexes, I performed a mixing experiment with Southwell River water and wetland waters, each permutation with only a simple filtering separation stage.

The wetland was sampled at OW1 and OW7, similarly for Southwell River (HS), taking 1 L natural samples of each. On site, of the 1 L samples, were first kept 250 mL for total Pb assay, then another 250 mL filtered (keeping 0.45 μm membrane cake and the filtrate). The remaining 500 mL of the two OW samples were filtered, taking 250 mL of each filtered OW sample for mixing with 250 mL of unfiltered HS. The mixes (500 mL) were allowed to stand at river temperature (4°C) for 2 hours before agitating, and having a 250 mL portion of each filtered (keeping the cake), and keeping both parts 250 mL filtrate and 250 mL unfiltered water samples. The 250 mL aliquots were measured using the graduated Sartorius filtering apparatus. All water samples were acidified (1% HNO_3), and the filters were extracted in a 250 mL polypropylene bottle with 2.5 mL HNO_3 for 8 hours, then made up to 250 mL with deionised water. All of the samples were assayed by ASV (Section 2.6.2.3).

The results in Table 10.8 show that the particulate matter (>0.45 μm) in HS is capable of taking up and binding with Pb from the mixture. One may push this key conclusion to include the likelihood that the smaller uncoloured molecules derived from these organics entering the wetland are capable of similar Pb association or exchange within time frames of the order of 2 hours.

Table 10.8: Results of mixing Southwell water with wetland water, ppb Pb.

fraction	HS	OW1	OW7	50%OW1f+HS (ex)	50%OW1f+HS (as)	50%OW7f+HS (ex)	50%OW7f+HS (as)
total Pb	14	760	226	205	226	40	56
"soluble" Pb	12	396	66	205	192	40	28
Pb >0.45 μm	12	178	133	6	32	6	28

ex: expected for simple mixing; as: actual assay after mixing.

The results also show that HS (Southwell River above the mining operation) contains some Pb. Discrepancies in the data show that there is some sampling, volumetric and contaminant error. There is also room for the possibility of some Pb being unavailable to ASV detection even after acidification.

Wastewater leaving the treatment area is diluted by tributaries carrying more humic matter. Thus downstream, Pb will tend to associate more completely, binding more strongly with optimal complexing sites of the humic matter.

10.6 Diversion of borewater into the wetlands

One of the key aims of the project was to identify ways of optimising metal uptake performance of the wetland system. In Section 9.3.2, I outlined several ways of increasing SRB consortium productivity, and hence sulphide production and precipitation of Pb. This section describes the effect of experimental introduction of a nutrient source to OW.

In November 1991, I came across the borehole HB (location Table 11.1) upwelling water which flowed into the west cutoff drain. What raised my interest was the luxuriant moss and algal growth along the associated dampness (Figure 10.13), and the green filamentous algae growth downstream of where this water entered the drain. The 13°C water has a conductivity of 325 μS, zero Eh and DO, and neutral pH, with a routine assay of 180 ppm HCO_3, 30 ppm Ca, 20 ppm Mg, 8 ppm Cl, 3 ppm DOC, 2 ppm SO_4, 2 ppm Fe, 0.3 ppm Mn, and 50 ppb Zn. At a hunch I assayed for PO_4 by the colorimetric method (Hach 1990). This borewater consistently contained 0.45 ppm PO_4. I sought further information about the borehole core log. Considering the combination of a cost-free source of PO_4 going to waste, the west cutoff algal growth a potential problem, and the struggling Juncus in the wetlands, I requested the bore to be tapped and piped to the wetlands.

The core log of borehole "Mac 15", ended 22/4/88, consisted of: collar-98.2 m: interbedded shale + basalt, 98.2-110.8 m: polymict breccia, and 110.8-EoH at 166.6 m: Animal Creek Greywacke. The source of the phosphate is regarded as the greywacke sequence (McArthur pers. comm.). This micaceous sandstone outcrops in places along road cuttings on the nearby Cradle Link Road, where it is commonly seen to support a rich mossy cover.

Figure 10.13: Site of the "Mac 15" borehole drilled in 1988, upwelling with phosphate-rich water derived from a 50 m section of greywacke 100 m below. Previously the water drained into the west cutoff drain feeding green algae; in 1993 it was piped 1.5 km to the wetlands as a nutrient source.

The 1.5 km pipeline was finally constructed before Christmas 1993. The phosphate was absorbed onto the pipe walls, delivering a reduced 0.29 ppm PO_4 to OW1 (Table 10.9). The absorption of PO_4 into OW is shown by the assay figures in Table 10.9 after 2 and 8 months of pipe delivery of borewater. It is evident the phosphate was initially quickly absorbed at the head of the wetland with no significant PO_4 passing the third pond. Then, as the plants recovered health over time and other mud biota reduced PO_4 demand, less was absorbed at the head of the wetland, and progressively more PO_4 would move downstream to be available to the lower wetland ponds.

It would be hazardous to attempt quantifying the phosphate absorption rate by mass–balance due to uncertainty in the actual quantity of borewater delivered to OW1 over the period. The make–shift pipeline of various bits of various materials and diameters patched together was prone to intermittent failures for unknown periods before flow resumed after failure detection and pipeline repairs. This occurred several times in the observation period.

Table 10.9: Borewater PO_4 absorption in OW

station	phosphate (ppm)	
	Feb 1994	Aug 1994
HB-bore source	0.43	0.39
HB-pipe end	0.29	0.29
OW1 dilution	0.020	0.020
OW2	0.013	0.018
OW3	0.006	0.009
OW7	<0.006	

As well as being a source of phosphate, the analysis of the borewater indicates it would provide the wetlands with buffered alkalinity.

The growth brought on by the injection of borewater into OW1 was dramatic in comparison with the OW6 pond control site after only 2 months of phosphate addition (Figures 10.14, 10.15). The treatment not only reversed the observed decline in OW1 plants, but promoted the OW1 pond from having the poorest to the most profuse macrophyte display in the Old Wetland. The control site at pond OW6, receiving no detectable PO_4 increment at station OW7 (Table 10.8) over the 2 month trial period, remained at the same level. In February 1996 during construction of the chemical treatment plant, the end of the borewater pipe was moved to deliver at OW2.

Native sedgeland plants, of rainwashed western Tasmania with impoverished soils, have developed tenacious nutrient conservation strategies (Reid *et al.* 1999), and thrive on only a modest increment. The progression of PO_4 from OW1 to OW2 in nearly full concentration in (somewhat less than) two months suggests the pond OW1 ecology was effectively satisfied with PO_4 requirement

Figure 10.14: Pond OW1 in May 1991 (top), and in February 1994 (bottom) with prolific growth, only two months after introducing 0.7 L/s piped borewater bearing phosphate into OW1. This is despite having somewhat greater environmental contaminant loading than the control site (shown in Figure 10.15). In September 1993 the plants at OW1 appeared in poorer health and abundance than in 1991, with many plants appearing to be dying off. This was likely due to combined effects of seasonal growth/senescence cycle and stunting by poor nutrient availability and wastewater pollution exposure.
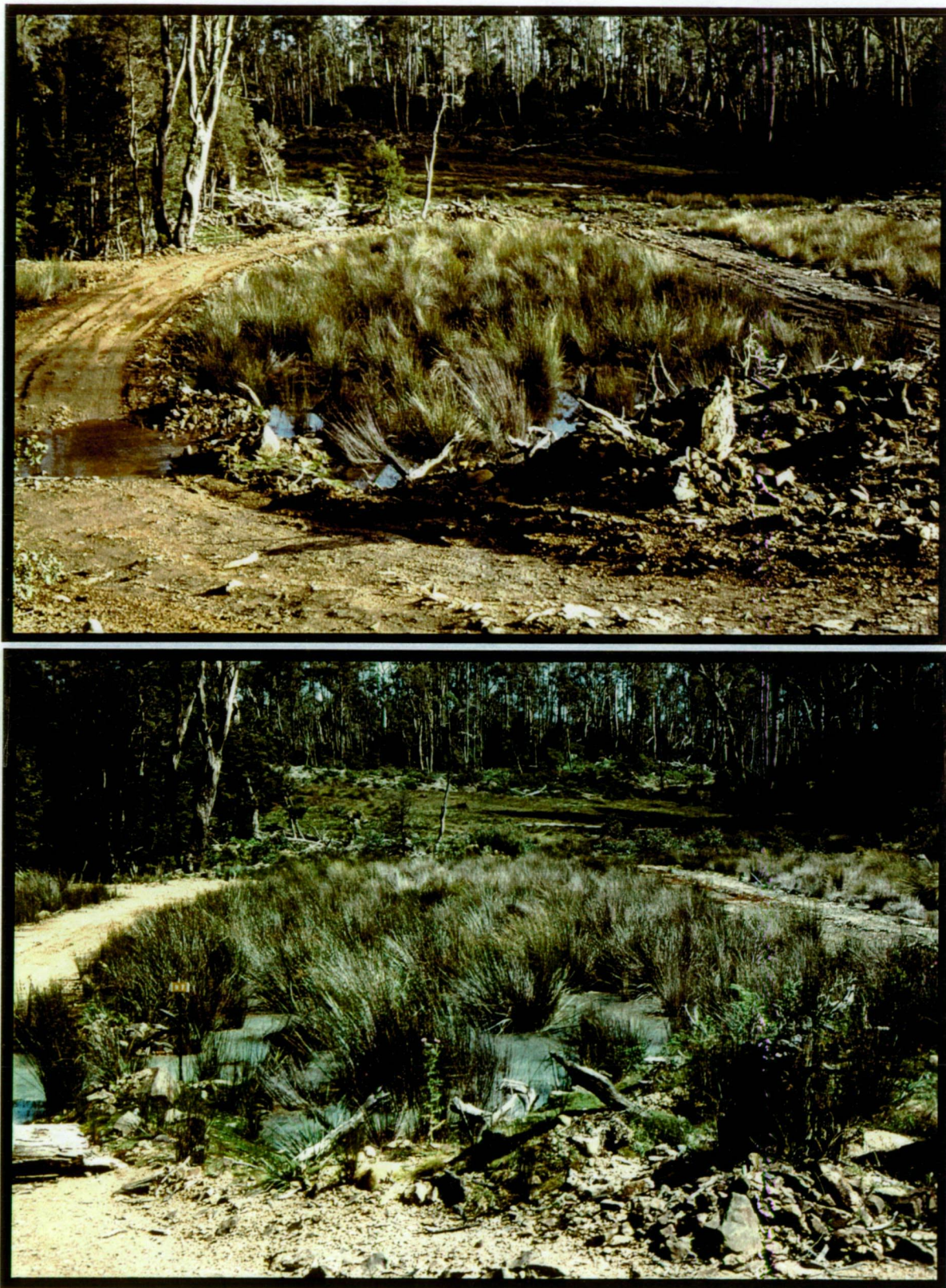
Figure 10.15: Control site for Figure 10.14. Pond OW6 in May 1991 (top), and in February 1994 (bottom), with little increase in growth profusion despite better environmental quality. No residual phosphate was detected in water entering OW6 at the time. The photo colours vary on account of seasonal sunlight change, and growth phase differences of the dominant *Juncus* species; in May the plants are entering the annual foliage senescence period, while February is a period of maximum productivity.

almost to saturation levels, and most PO_4 was passing in turn through to the subsequent ponds. The plants' nutrient tenacity (Reid *et al.* 1999) would place them in good stead for long term health even if the borewater phosphate input was removed at a later time.

10.7 Conclusion

The wetlands remove wastewater-suspended Pb, present as PbS associated with other matter, by settling process into the mud phase. The dissolved Pb, in reality, is mostly present as complexed and colloidal form, which slowly releases free Pb ions to meet chemical demand of SRB-generated sulphide precipitation. This demand is created by H_2S/sulphide generation from wastewater sulphate by SRB in the mire. PbS precipitated from the soluble Pb, along with the insoluble carryover, settles into the mud sink.

The hydrology of the wetlands has room for improvement. The most pressing management issue is the need to increase residence time by raising the water levels to 0.3-0.5 m depth (Section 10.3). The increased residence time is required to facilitate sedimentation of insoluble Pb, and to prolong the exposure of colloidal Pb to H_2S-sulphide (rising from the mud) chemical demand, encouraging a more complete precipitation of the soluble Pb.

Accompanying raising of water levels, I recommend introducing *Eleocharis* and *Triglochin* by hand to the wetlands (Chapter 5), particularly in open areas of flow channelling. This, along with adjustments in NW pond series inlet distribution, would assist the promotion of even flows in the wetlands.

Wetland plant production turnover provides the mire with organic matter to maintain reducing Eh and feed the SRB consortium. The other main plant function is to provide structure, diffuse flow and promote sedimentation.

Plant growth may improve with removal of some of the forest edge on the shading flanks of the wetland, and planting trees on cleared areas on the other flanks. The addition of phosphate-bearing borewater to the wetlands (Section 10.6) promotes plant productivity, and should be continued. This indirect feeding of the SRB consortium could be supplemented by the direct addition of organic waste to the mire in order to maximise H_2S generation (Section 9.2.3).

The optimal mire depth (between water and the clay base) is 20-30 cm; this maximises the SRB habitat zone and reduces losses of organic resource as CH_4 by the activity of deeper-dwelling methanogens (Section 9.4).

The lime pH treatment of tailings should continue so the wetland inputs retain minimal Pb requiring removal. The dam AMD seepage should be intercepted and treated in a limestone drain prior to entering the wetland stream (Section 7.7).

The Hellyer wetlands for wastewater treatment are essentially chemically and biologically sustainable, subject to appropriate management as outlined. In the

long term the accumulation of sulphides may exceed the water level raising capacity and will need dredging (pumping into the tailings dam would be appropriate). At the end of mine life the dam overflow will be reduced to rainfall only, and any AMD generation will be unabated by the current lime treatment. Therefore the Pond 1 area would best serve in modified form as a limestone neutralisation drain to treat tailings dam drainage prior to wetland treatment.

Chapter 11: Catchment management

The purpose of the tailings dam and wetland treatment system is to ameliorate the discharge from the Hellyer operation and to minimise environmental impacts in the catchment. Partly as a measure of success, Aberfoyle Resources undertakes some regular catchment water quality monitoring, and has cooperated in a broader study of the Pieman catchment (Koehnken 1992) which includes other operating mines. This chapter describes my findings in relation to some of the broader issues associated with water management on the Hellyer lease beyond the wetlands, and farther afield within the affected catchment.

11.1 Baseline establishment

A fundamental question of catchment management is "What is the baseline – what are the natural levels in the catchment?". The catchment of the Huskisson has many complicating features.

11.1.1 Elevated levels of stream contaminants by local natural contributions

There are naturally elevated levels of metals in some parts of the catchment. Indeed, the discovery of the Que River deposit followed pursuit of elevated metals in stream samples; up to 24 µg/L Pb, 73 µg/L Cu, 124 µg/L Zn, 11 mg/L Fe (Technical Services 1976), even with springtime (sampled on 27/9/75) rainwater dilution. Mineralised outcrops, subsurface deposits and seeps scattered in the catchment yield leachate and runoff enriched with SO_4 and metals. The leaching is made all the more aggressive by the brown mildly acidic humic content in waters of western Tasmania, even to the extent of dissolving and transporting massive quantities of otherwise inert gold (Baker 1977). These stream metals showings in the 1970s led to the residual "amoeba anomaly" (of no economic value) and then to the discovery of the Que River mineral deposit.

11.1.2 Elevation of stream contaminants by human land use

This part of the West Coast of Tasmania (Figure 1.1), a mining province broadly associated with Mt Read volcanic rocks, has historically been subject to prospecting, exploration and extraction of resources on various scales (Section 1.3). Fuller & Katona (1993) identify this region's catchment waters as subject to heavy metal pollution from mining origins. The Pieman catchment includes inputs from past and present major mines at Rosebery, Renison, Hercules, North Farrell, and many smaller mining and prospecting operations (Figure 1.1, Section 1.3) that contribute heavy metals to Lake Pieman (Koehnken 1992).

In the Huskisson catchment, Que and Hellyer mines dominate as the metal input sources. However, in addition, a number of small operator exploration and mining sites (including Sock Ck, Silver Falls and Mt Charter) dot the areas west of Hellyer, particularly in the catchments of the Que, Coldstream and Ramsay Rivers. The tailing and spoil dumps from these lie exposed to

leaching. Metal contributions in the Huskisson catchment flow into Lake Pieman approximately mid-way its length. For this study Lake Pieman was the practical endpoint of Hellyer-affected drainage.

Further inputs to the Pieman system downstream of the Reece Dam include those from Cleveland (via the Whyte River) and Savage River mines, as well as smaller historic operations, before the river empties into the Indian Ocean.

EARLY INDICATIONS SUGGEST HEAVY METAL CONTAMINATION
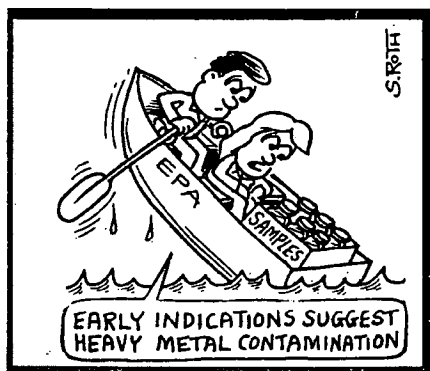
The Emu Bay Railway and Hellyer rail spur carries ore concentrate through the catchment area, and potentially is subject to spillage and dust over time. The Que River Mine operation delivered ore concentrate by truck to a rail siding depot by the Hatfield River, before the new rail spur was constructed to Hellyer. Trucking from Que continued to the Hellyer spur until closure. Trucks continue to haul to the Hellyer mill. As an indication of transport and handling area runoff, a test sample I had taken from the Hatfield siding depot site in 1991 assayed as having 13 mg/L Fe, 68 mg/L Zn and 43 mg/L Pb in undiluted runoff form. After this evidence was offered Aberfoyle undertook a more rigorous cleanup of the siding depot. However this problem will persist in other still-active areas of heavy traffic handling ore and concentrate. Only in some cases will it be ameliorable by diversion, containment, settling and/or treatment of runoff.

During duck season, the marshes of the Hatfield catchment are subject to addition of lead shot, of detriment to water quality (Daly 1989) and soil (Alloway 1995) over the long term. Other wildlife is shot in open woodland areas near roads and tracks. Lead also enters the catchment from the use of leaded petrol vehicles on the Murchison Highway, Cradle Link Road and minor roads as well as 4WD tracks. These Pb inputs are typically diffuse and much diluted by rainfall (Lund et al. 1991). Such diluted Pb manifests in stream water quality as low fluctuating background levels according to random environmental factors including local weather events (Section 4.7).

Rail and logging operations feature heavy use of herbicides. An open dump of chemical containers was found near the Hatfield River during the study.

Logging, land clearing and roading contributes turbid silt loading to streams orders of magnitude above that for undisturbed catchment. These activities have affected much of the Huskisson catchment basin, of most concern is the

clearfell logging baring large expanses of soil, the burning off of all protective vegetation and litter cover, and logging on erodible soils or steep slopes.

11.2 Catchment survey for Hellyer

11.2.1 Experimental

11.2.1.1 Physical

Sites were precisely located on 1:25000 and 1:100000 maps as appropriate. Mine lease sites were subject to accurate survey. Heights above sea level were similarly obtained. Catchment areas were determined by tracing catchment boundaries from 1:100000 scale (plan projection) maps (or 1:250000 scale for HHHSK), and weighing the paper cutouts against standard map areas of 10 x 10 km (or 20 x 20 km). The error of the cutout edges was better than ±1 mm. The onsite recording of temperature, pH and conductivity are reported as means from 5-year monitoring data for 1990–1995, or averaged from my less comprehensive, but more reliable research data.

11.2.1.2 Chemical

The sites were sampled for cation (acidified) and anion (natural) analysis. The lead and sulphate figures or means from my research, monitoring data and Koehnken (1992) are presented. The lower Pb levels are reported from ASV and colorimetric determinations (Section 2.6.2); higher levels are from ion chromatography (anions) and AAS analyses (Pb).

11.2.2 Results and discussion

Table 11.1 shows results for physical aspects of the Hellyer catchment.

Catchment areas give a first, very approximate, indication of relative flow of streams. There are inherent limitations with working with areas from plan projection maps, which inadequately describe the true area exposed to the weather. As Chapter 3 outlines, there are threefold variations in rainfall throughout the Pieman catchment dependent upon proximity to the west coast, local relief, aspect and altitude. The altitude would be second to area in indication of catchment flow. Within any one catchment there is to be expected some considerable local variation. For example, the catchment of the Hatfield (HH) includes parts of Mt Pearse with steep western slopes above 1000 m ASL which would attract far more rainfall than other parts deep in the valley at only 200 m ASL. Therefore, these catchment area estimates should be used with some caution.

It should be noted that the Q6 catchment area is strictly based on the topographic plan; the flow at Q6 is effectively augmented by the mill diversion of a virtually constant (>100 L/s) portion of HS (Southwell River), which becomes proportionally more significant in periods of low rainfall, typically during summer.

Table 11.1: Physical survey of catchment sites pertinent to this project.

Site	AMG Location Aust. Zone 55G	height m ASL	catchment area km²	temp °C[1]	pH ([1])	cond. µS[1]
Tributaries						
HH Hatfield River	375970mE 5393105mN	185	108	9.8	6.6	73
HCS Coldstream River	375745mE 5393145mN	182	58	10.1	6.8	99
HR Ramsay River[2]	373900mE 5391300mN	165	53			
HS Southwell River intake	394695mE 5397660mN	630	14	8.4	6.4	43
HB (Mac 15) borehole[2]	391200mE 5397500mN	650		12.4	7.0	325
W (H11) W cutoff drain	391300mE 5396230mN			11.2	5.8	154
E (H9) E cutoff drain	391395mE 5396165mN			11.0	5.9	64
Q8 Que mine exit stream	391310mE 5395750mN	625		9.6	3.4	754
LR Lake Rosebery[2]	378000mE 5378500mN	~155		8.0	5.6	42
BU Bulgobac River	381400mE 5391900mN	345	66			
Hellyer stream						
OW1 (H6) OW input	391735mE 5396655mN	625		11.8	8.7	1456
OW8 (H7) OW output	391665mE 5396480mN			11.5	6.1	1156
H8 (NW1) pond 2 output	391555mE 5396350mN			11.7	6.4	1283
H12 (NWCD4) NW output	391475mE 5396220mN	622		12.5	6.0	1220
H13 wetland system output	391355mE 5396175mN	622		11.8	6.2	1304
H1 Hellyer mine exit stream	391240mE 5396070mN	618		11.3	6.3	802
Q6 Que River at highway	390070mE 5396190mN	610	18	9.6	4.9	304
HQ Que River at Huskisson	376010mE 5392610mN	180	136	10.4	5.0	234
HHSK Huskisson River[2]	373000mE 5390000mN	150		10.8	6.6	147
HHHSK Lower Huskisson River[2]	370200mE 5378500mN	100	528	10.1	6.3	95
LP Lake Pieman at Reece Dam[2]	345000mE 5378500mN	~95		9.0	5.6	58
TP total Pieman River[3]	326500mN 5385500mN	0	3800	13.0	6.9	178

1: 5-year mean 1990-1995; 2: other research results; 3: results from Koehnken (1992)
Locations of mine lease monitoring sites are shown in Figures 3.1, 3.10 and 10.1,
Wider catchment monitoring sites are plotted in Figure 1.1.

The average flow of the Pieman River at the heads is 190 cumecs, of which 150 cumecs passes at the Reece Dam (Koehnken 1992). The Huskisson is cited as contributing 25 cumecs at HHHSK. Miedecke (1988) cited average gauged flow at Q6 of 900 L/s, (with a 1/100 y peak of 26 m^3/s) and the upper Que yielding a mean 0.05 m^3/km^2.

Table 11.2 shows chemical survey results for the catchment. Other water quality details for key monitoring stations upstream of HQ are shown in Table 3.5. The lower tributaries HH, HCS and HR (Hatfield, Coldstream & Ramsay rivers, Figure 1.1) are substantial streams that dilute the Que River water as they enter the Huskisson River. Even these have been affected to a small degree by past mining practices; the Hatfield includes runoff from the Hatfield ore loading siding and stretches of Emu Bay Railway, whereas the Coldstream and Ramsay both have old mine workings and prospectors dumps dotted throughout their catchments. Lake Rosebery sampled at the damsite (LR) includes inputs from old mining sites such as Chester and North Farrell (Figure 1.1). The Southwell (HS) at H3 also shows metal perturbation from

mineralised ground in its catchment. HS is the water used for Hellyer's processing, which is ultimately diverted to the Que catchment as H6. While the initial streams entering the bypass drains W and E showed <1 ppb Pb upon testing on summer and spring flows, the leaching and runoff from exposures along their excavated routes through the mine lease add modest increments of AMD components. HB is the phosphate bore which ran into W until it was piped into OW1 in February 1994 (Section 10.6). Q8 is the residual stream from the Que tailings dam. H13 combine with W & E into H1 (Figure 3.10). H1 and Q8 combine with other tributaries before Q6. Further tributaries enter the Que River (Figure 1.1) as it tumbles from Q6 at 610 m ASL to down to HQ at 180 m ASL, notably the Bulgobac River (BU) which comprises almost 50% of the HQ catchment area. BU includes AMD from Sock Creek and Mt Charter workings. Near HHSK, a stream including AMD from Silver Falls enters the Huskisson. The Huskisson empties into Lake Pieman, along with upstream Pieman inputs from major mine sites Renison, Rosebery and Hercules along with numerous minor abandoned workings near Tullah, Rosebery, Williamsford and Renison Bell. The Reece damsite is the source location of Lake Pieman (LP) samples.

Table 11.2: Chemical survey of catchment waters pertinent to Hellyer.

Site	Pb[1] ppb	Pb[2] ppb	Pb[3] ppb	Pb[4] ppb	SO$_4$[4] ppm	Pb[5] ppb	SO$_4$[5] ppm	Pb[6] ppb	SO$_4$[6] ppm	Pb[7] ppb	SO$_4$[7] ppm	F[7] ppm
Tributaries												
HH	2		4					20	1.6	2	<2	<0.05
HCS								12	1.7			
HR						1	1.9					
HS		12				0.7		30	1.1			
HB		8			1.5							
W	10							41	43			
E	40							70	10.4			
Q8	140							520	754			
LR				3	2.2					3	<2	<0.05
Hellyer stream												
OW1	410	650	810		380	345		550	518			
OW8	116	160	240		370	50		250	468			
H13	380		650	850	350	320	510	410	524			
H1	80							220	308			
Q6	70	182	332	500	220	128	385	200	304	182	254	0.33
HQ	20		34	26	46	22	68	47	66			
HHSK				18	20	4	23					
HHHSK		10		8	14	1	16			<1	30	0.04
LP				2	5.5					2.5	7	0.05

1 13/5/93; 2 8-10/8/94; 3 28-30/11/95; 4 27/8/92; 5 19/2/93; 6 5-year mean 1990-1995;
7 mean results from Koehnken (1992)

The mean Pb[6] figures for HH, HCS, HS, W, E, and HQ are somewhat high due to two factors: some individual results that were assayed BDL (below detection limit) were entered as the value of the detection limit (instead of zero) into the

database; and there were clearly at least some instances of spuriously high results from contamination (Section 4.5).

The Pb[6] and SO_4[6] cited for OW8 are actually for H7, which was at OW8 until May 1993, when it was moved to OW7 by installing a log barrier (Section 4.6).

The diversion drains E and W are intended to divert runoff and tributary creeks from diluting (and increasing volumes of) tailings water and wetland treatment ponds. Neither are pristine. E cuts through some stringer sulphide veins, and takes some incidental runoff from working areas. Since the tailings dam raising in early 1992, W has taken AMD input (including high acidity and Fe) from sulphidic rocks used in the dam wall, as has UMW (Section 7.7), while OW1 takes piped dam water.

Koehnken (1992) estimated the dilution of the Hellyer-affected stream from Q6 to HHHSK is tenfold. This is supported by the figures for F, which is an inert marker of mining origin, not present in natural tributaries to any significant degree, and also for SO_4. However the catchment area (Table 11.1) and flow data of the previous page suggests it would be more like a 20-fold dilution. It is noteworthy that Pb (and also Cu, Cd, Zn in Koehnken 1992) declines much more than is accounted for by dilution. Under summer flow the lower Huskisson water becomes odorous with sulphide and unpalatable, exceeding the drinking water guideline and taste threshold of 50 ppb (NH&MRC 1996) and hence well exceeding the ANZEC (1992) environmental freshwater guideline limit of 2 ppb. The wetland levels of sulphide are 1-2 ppm (Section 8.2.2). The persistence of sulphide and vigorous decline in Pb, combined with observations of SRB mires present in the streambed of the Huskisson River (Section 9.2.2) indicates some sulphate reduction and metal sulphide precipitation continues far beyond the wetland system downstream to at least the delta where the Huskisson enters Lake Pieman. While in contrast, Koehnken (1992) argues the losses of these metals is due to adsorption onto river bed sediments; this mechanism is not supported by a similar decline in Fe which would be one of the first metals to deposit in this manner under the aerated riverine conditions as hydroxide-carbonate coatings. There may be some association of Pb with the fine black clay-organic deposits interstitial to natural cobble beds in some sections of the river system.

The only significant carbonate rock area in the Huskisson catchment is Webbs Creek, a 2.5 km stretch of the Huskisson River and a small area of John Lynch Creek, all set between HHSK and HHHSK and inaccessible. While SO_4, Zn and Pb decreased (are diluted) from HHSK to HHHSK, Ca remained at the same levels indicating hardness input from the karst. The only known karst spring near Hellyer was visited (on the Vale River, from the Mt Cripps karst), and this water was measured in the field (pH 7.25, cond 274µS). One could expect the bulk of the ion content of this clear water is Ca^{2+} and HCO_3^-, and similar inputs would contribute to the lower Huskisson. Hardness in water reduces the toxicity of some heavy metals including Pb (De Zuane 1990, Koehnken 1992) by complexation, and also provides some pH buffering against AMD.

11.3 Site erosion and sedimentation of wetlands

11.3.1 Experimental

The study of soil pedestal heights was chosen as the simplest robust method of estimation of soil erosion rates around the wetland – tailings dam area. At six years after clearing for construction of the tailings dam, 10 areas dotted around the apron (4 east, 3 north, 3 west) of the storage were examined for gravel-capped soil pedestals. Only the highest ones were measured, assuming these gravel particles sat on the surface after clearing. Lower ones were ignored as they may have been partially buried at the commencement time of exposure immediately after clearing.

11.3.2 Results and discussion

At six years after clearing, 10 sites around the tailings dam consistently showed maximum gravel pedestal height measurements of 6 cm. The estimated mean rate of depth erosion of 1.0 cm/y then approximates to annual soil mass erosion of some 200 t/Ha/y, assuming dry soil density of 2 g/cm^3.

These results are in broad accord with those of Haydon *et al.* (1991), and calculations of Lichon (1993) for other western Tasmanian soils of 100 t/Ha/y where the mean annual rainfall is closer to 1200 mm.

11.3.3 Runoff into wetlands

On 15/2/93 there occurred a downpour of more than 25 mm in an hour. According to probability calculations (Bureau of Meteorology unpublished data) this represented a 1/100 year rain event. My observation of very turbid runoff entering the tailings dam and wetlands, and the turbid floodwaters in the lower Que River brought attention to this particular aspect.

The XRD analysis of flocculant wetland sediment (in Chapter 7) suggests some degree of clay sedimentation from site runoff, which may be diluting the microbial consortium in the treatment precipitate and hastening the total solids level buildup in the wetlands.

From a wetland ecological point of view, the extra sediment may provide stability for root systems struggling in flocculant ooze, dilute toxic treatment precipitates, offer ion exchange sites, add buffering capacity and perhaps provide some nutrients.

From a wetland management point of view this means the premature need for pond wall and outlet heightening, or the difficult option of sediment dredging. In either case there is resultant disturbance to the wetland system.

11.4 Other catchment issues

11.4.1 Logging and clearing erosion

The erosion of logged areas in the catchment varies considerably in the catchment with soil type, slope, exposure, and revegetation success. Opposite the minesite across the Southwell valley, Figure 11.1 shows a steep slope of Mt Cripps, where one logging coupe of some 20 Ha showed severe soil erosion and total forest regeneration failure for 10 years, until some signs of recovery in 1996. Near the Huskisson River HHSK site by the 1975 access road is a logged site of similar age with poor regeneration, inhibited by frost heave and sheet erosion to depths of up to 1 m between residual stump/topsoil pedestals indicating the level of the original forest floor. The current practices of high disturbance clearfell logging followed by residual vegetation and litter burnoff are obviously unsustainable in these situations (Lichon 1993), and lead to the observed forest and catchment degradation, weed invasion and high turbidity and sediment loads in streams, particularly during heavy rain events. There are further consequences of this erosion for stream ecology, water quality and sedimentation of hydro-electric storages (Koehnken 1992, Sengupta 1993, Heap 1999).

11.4.2 Road erosion

The erosion rates for unsealed roaded areas are typically 400% greater than those for exposed soils (McGurk & Fong 1995), largely due to traffic (Haydon et al. 1991), especially under wet conditions. This effect was graphically observed on a new logging road on Olympic Ridge, above the Que – Hatfield confluence (Section 4.7). When the road was constructed the road runoff was highly turbid. On a later occasion after a non-trafficked period of 9 months the road had become protected from further sheet erosion by a shield layer of gravel-pebbles left from prior selective erosion of the topmost dressing. At this time the road runoff was almost clear, and appeared potable. On subsequent occasions of observation when traffic had resumed for logging, the road surface was again muddy and runoff was very turbid.

The rate of gravelling of some minesite roads are necessarily high to compensate for erosion of those bearing heavy (by wheel mass and frequency) traffic in either dusty conditions or wet weather. When not eroding during rain, the haulage road is watered by a truck sprayer to ameliorate dust. Heap (1999) has observed turbidity in the lower Southwell river attributable to runoff from the haulage road and/or spillage from the portal settling dam. Environmental mitigation for road construction is covered in manuals such as Elton (1992).

11.4.3 Hydrology

The clearance of forest, litter and soil cover has been implicated in the destabilisation of ground hydrology and stream flows. The symptoms of altered stream flows include sharper, higher flood peaks, and reduced base flow.

Figure 11.1: Burnt clearfell logging coupe on the slopes of Mt Cripps across the Southwell valley viewed from the Haulage Road switchback. This steep exposed site failed to regenerate for over 10 years; what remains of the soil continues to erode.

These are connected with the loss of moisture absorbance capacity after denudation. A recent study of a part of the upper Whyte River catchment (within the Pieman catchment) which was recently logged (Livingstone 1998) amply demonstrated these symptoms in stark contrast to nearby flow patterns of streams with intact forest cover. To avoid these adverse conditions the management of areas in western Tasmania, it is recommended to minimise area disturbances and clearing, avoid fire, provide regular diffuse drainage for any road or site works, stockpile cleared soil and peat and undertake area rehabilitation as soon as practicable.

The regulation of discharge to maintain tailings dam level means a constant base volume of wastewater (150 L/s) during non-rain periods. These usually coincide with warmer temperatures and increased concentration of metals and sulphate, though this is in part offset by greater metal removal efficiency in the wetland treatment system. It is during these times there is the least dilution by tributary streams on the wastewater journey through the catchment, and the deleterious effects of the discharge reach their maximum extent. There were dry times during the study the quality of water at HHHSK was of the order of HQ at wetter seasons.

11.4.4 Fire

The impacts of fire on the Hellyer lease have been modest and confined (Chapter 3). In contrast, the wider catchment of the Que and Huskisson has suffered significant degradation due to fires lit by humans.

Much of my research findings on this subject is contained within Lichon (1993). While cited application focuses on karst areas (some 5% of Tasmania, much of it in private land and unreserved State forest in western Tasmania) with somewhat unique attendant circumstances, I find evidence that the same soil chemistry, stability of structure, biomass, nutrient and humus retention principles and applications extend to most forested land in (particularly western) Tasmania aside from karst regions.

In summary, the humus and standing forest biomass holds much of the forest vitality in terms of nutrient accumulations maintained by closed cycling and retention (Trudgill 1986, Reid et al. 1999). The naturally leached soils of Tasmania are unable to yield sufficient replenishment after fire events where 60% of above-ground nutrients are in logs, 20% of the rest is lost to sublimation, and 50% of remaining nutrients are lost by runoff and leaching of the ash bed. The loss of organic horizons open the soil, subsoil and bedrock to oxidation and acid drainage derived from pyrite otherwise locked in the rocks and clays of typical paleozoic formations, let alone mineralised rocks. Forestry Tasmania even acknowledges the soil nutrient and structure as vital, and uses humus as an index of fertility (Laffan & Neilsen 1997). Only after many decades of dilute ocean-spray enriched westerly rainfall, and slow undisturbed forest succession may the ecology be fully restored after 500+ years, well beyond rotation periods considered by commercial foresters (Jackson 1983). The present management trend is resulting in natural

ecological losses, and a cultivation of fire-tolerant, fire-requirer & fire-promoter scrub forest which exacerbates the ecological degradation and soil infertility (Bowman & Jackson 1980). Furthermore the post-fire regrowth presents fire hazards and risk to life and property far higher than for previously undisturbed forest (Jackson 1968, Bowman & Jackson 1981a).

It is clear from data in Table 11.3 that Tasmanian forests are being burnt to excess of natural incidence regimes. Most fires are due to unnatural causes, some 99.99% by area, of which 99% is not accidental. Clearly the 10000-fold increase in fire (by area) over what one would assume to be an unchanging (over time) baseline naturally caused fire incidence is worthy of concern. The area increment burnt over this recorded period indicates ecologically unsustainable practices. This is confirmed by the total loss of large swathes of fire sensitive forests (such as King Billy and Pencil Pines) this century. It stands undeniably that a 10000-fold increased fire regime has a dramatic altering effect on natural ecology.

Table 11.3: Tasmanian fire frequency by cause for the 12 year period 1968/69 to 1979/80 from Forestry Commission data, Bowman & Jackson (1981).

Cause	No.	(%)	Area (Ha)	(%)	Mean area (Ha)
Lightning	8	0.6	29	0.01	4
Accident	117	8.1	3010	1.09	26
Silvicultural burn escape	72	5.0	6579	2.39	91
Fuel reduction escape	45	3.1	24170	8.78	537
Other government escape	19	1.3	13316	4.84	701
Rural landowner escape	80	5.5	3522	1.28	44
Rural landowner deliberately lit	320	22.1	155228	56.39	485
Deliberately lit	437	30.2	36228	13.16	83
Unknown	350	24.2	33179	12.05	95
Total	1448		275260		

It is a reasonable first approximation to expect the origins of "unknown" caused fires would follow a similar causal distribution to those of established cause.

In this context present fire use is clearly devastating for cool temperate native forest ecology, and ought to be minimised, aiming towards a natural fire regime. I propose the following recommendations:

1. Fundamental to this aim must be the ending of the official burning ("controlled" burning, "regeneration" burning and such like). This, aside from the direct devastation, serves to foster a pyromanic culture amongst the general community, particularly forest landowners and neighbours and the less environmentally sensitive frequenters of the bush, resulting in additional fires of varying legitimacy under present law.

2. Education of Tasmanians as to the devastation to forest ecology, property

and life by fire ought to begin at compulsory school age, as an integral part of learning about the part of the world in which we live. In my opinion, the government through Forestry Tasmania effectively does the opposite, in enacting and promoting the use of fire and other ecologically unsustainable practices to aid and abet short-term forest exploitation whilst baldly making false public claims of sustainability.

3. The firefighting capacity of Tasmania ought to be increased. The 1997/8 summer's fires was a test of resources and fate, where only favourable weather reduced what could have been a widespread disaster to a very bad event of more localised destruction.

4. The capacity and resources to bring the perpetrators of arson (including that which is presently condoned by authorities) to justice ought to be increased, as should court penalties and other deterrents.

11.4.5 Effects on stream life

Aquatic faunal distribution is typically adversely affected by mine effluent; particularly metal content, siltation, acidity or sulphate. These components, along with SRB-generated H_2S, and other added turbid runoff from forestry operations, persist to through to the emptying of the Huskisson into the Pieman impoundment. Even non-metalliferous mining operations, fire and forestry, with runoff wastewater containing the elements of AMD (acid, metals, sulphate) and turbidity have affected stream fauna in Tasmania (Lichon 1993). This is due to toxicity from pH, metals, ionic strength, sulphide generation, stream gravel habitat infilling and cementation with clay. As observed in Section 5.5.1, the algae in the Que, along with AMD and turbidity, spell bad news for riverine habitat and aquatic conditions for stream fauna in the Que River, and to a lesser extent the Huskisson.
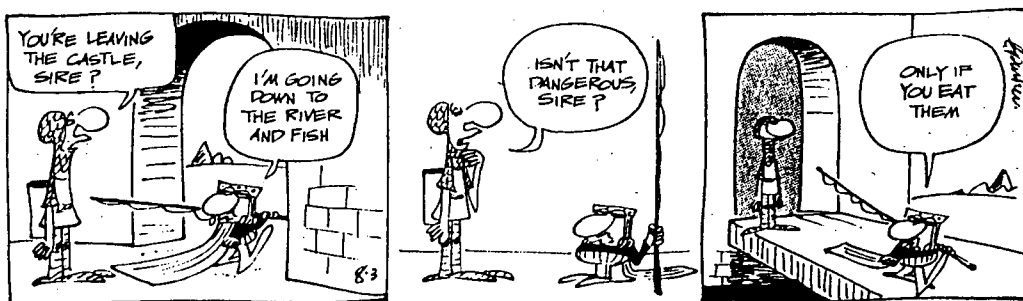
Local fishermen describe the Que River (even at HQ, with the most dilution) as barren of trout, in contrast to the Hatfield and Huskisson (Townsend, Reid, Jackson pers. comm.). Attempts at electrofishing also failed to detect fish in the upper Que (Miedecke 1988). The only evidence of vertebrate aquatic life in the Que River is a report of an eel being caught at HQ (Townsend pers. comm.). Eels are well known for their tolerance to poor quality water. Indeed, I have seen eels in the drains under the Hobart CBD. Faunal surveys of the Que River confirm other (invertebrate) species are in significantly lower abundance relative to adjacent rivers (Chilcott *et al.* 1991), though this was

also the case (though less markedly) before mining commenced (Technical Services 1976) due to weathering, solution and runoff from natural exposure of mineralisation. Sampling at H1 and Q8 both show local diversity and populations are reduced by mine drainage compared to adjacent tributaries (Miedecke 1988).

While metals like Pb are largely complexed with humic acids, inorganics and clays in the riverways, free Pb is low in concentration and hence poses rather less of a toxicity problem (Section 10.5.3, Koehnken 1992). However where some of the Huskisson suspended fraction forms riverine deposits, and a delta upon entry into the still waters of Lake Pieman, there will form a metal-rich substrate on which benthic life may be affected. Remaining colloidal material will precipitate out downstream when it encounters the saline (estuarine) wedge and ocean water. The benthic deposit in the estuary will be another concentrated pool of metals, more toxic in the saline conditions. The high ionic strength promotes dissociation of humic complexes not occluded in coprecipitated "onion" (Mackey & Zirino 1994) particles, liberating more free metal ions, available for accumulation in benthic life. This will be more of a problem in the estuary than in the ocean outfall where dilution will be rapid.

11.5 Conclusion

The Huskisson catchment is suffering somewhat, from the combined impacts of mining at Hellyer and Que River and forestry in particular. The wetland treatment mechanism of sulpide precipitation continues downstream of the mine lease, where SRB have colonised riverbed deposits. Soil erosion, turbid runoff and sedimentation is a major problem in areas of road construction, logging or mine operations. Clearing vegetation, fire and loss of litter and organic topsoil leaves the remaining (mostly highly erodible) soils vulnerable to losses of some 200 t/Ha/y, or up to tenfold more in frost-exposed or steep country. Site management should operate in a regime of absolutely minimal natural vegetation and soil cover disturbance, and where clearing is necessary, rehabilitate at the earliest possible time.

Chapter 12: Summary of findings

12.1 Introduction

Mining and lime-treated mineral processing wastewaters from the Hellyer
Zn/Pb Mine in western Tasmania, bearing Pb after tailings dam treatment, pass
through a series of pilot wetlands. This field-based study focused on
identifying mechanisms behind the "black box" wetland removal of residual Pb
from tailings wastewaters, exploring possibilities for wetland treatment
performance improvement and consideration of wider catchment issues. The
background, aims and significance of the industry-sponsored study were
outlined. The study site for this applied research project was described and
defined.

The environmental uncertainties and practical challenges dictated the need for
field-based observations supplemented by limited scope experimentation. The
wetlands treatment area was found to be subject to spatial and temporal
variations, with complexities and unpredictability reflecting the combined
interacting effects of numerous random and cyclical influences. Problems with
sampling were identified and partly overcome by structural and procedural
innovations. For most studies focus was placed on the better-defined and more
established 0.48 Ha Old Wetland. The 0.75 Ha New Wetland was found to be
more poorly designed, operated and monitored, resulting in less definable
treatment effects at lower levels (closer to error limits), and making its study
less fruitful.

12.2 Wetland ecology

Several native emergent wetland plants suitable for treatment of mine
wastewaters were identified using several criteria, and practical
transplantings both on bulk and experimental scales. The most suitable species
found from nearby accessible sources included those from *Eleocharis, Juncus,
Restio* and *Triglochin* genera. The plants form the basis of a diverse ecology
capable of growing under the site conditions, subject to the wastewater.

The wetland plants contributed little to direct removal of Pb from wastewaters.
Plant and rhizosphere accumulation of Pb, largely by wastewater-exposed
surface adsorption, accounted for less than 0.1% of wetland Pb uptake.
Instead, two important roles of plants are to provide structural stability and
serve as *in situ* photosynthetic generators of organic matter. Falling into the
mud, the organic matter maintains a decomposer-rich, low-Eh anaerobic mire,
and fuels a microbial consortium including sulphate-reducing bacteria (SRB).
By dissimilatory respiration, indicated by the S-isotope fractionation study,
SRB reduce wastewater sulphate and thiosalts diffusing into the mud from the
wastewaters to sulphide/H_2S. In turn, Pb is precipitated from wastewater by
the sulphide as PbS. Only traces of organolead were found in the mire.

The abundance of mire SRB is some 10^7 cells/mL, about 8% in a total bacterial
consortium of some 10^8 cells/mL of the upper 20 cm of mire. Three SRB genera

were found to be present, *Desulfovibrio, Desulfobulbus* and *Desulfobacter*, in approximately equal proportion. At mire depths >20 cm and at lower redox potentials, methanogens were found to "waste" wetland organic matter potentially useful to SRB by generating methane-rich bubbles.

12.3 Wetland uptake of Pb

Wastewater Pb sinks in wetlands almost exclusively in the form of PbS (galena) in the mud, as indicated by chemical analysis, X-ray diffraction and electron probe examination. No evidence of other crystalline forms of Pb (sulphate, carbonate, hydroxy compounds), as possible under the range of hypothesised reaction pathways, was found present in the mud. The overall Pb accumulation was found to be 26 g/m²/y for the Old Wetland, with 0.3-1.5% Pb (dry basis) annual increment in the top 20 cm of mud. The greater deposition rates are found at the head of the wetland.

The ≈50% suspended insoluble Pb fraction taken up by wetlands is removed from wastewaters by sedimentation processes, dependent on wetland residence time, pond depth and non-turbulent flow. Most of insoluble Pb is in the form of PbS, associated with particles in the size range 5-40 μm, with progressively smaller proportions with particles in the size ranges: >40 μm, 0.45-5 μm, and 0.05-0.45 μm. For the Old Wetland, the 5-year overall mean influx of 270 ppb insoluble Pb is reduced to 70 ppb on leaving the wetland. The tighter controlled, paired-date 5-year data set indicates the insoluble Pb wetland uptake increment is 180 ppb.

Water analysis, and dialysis, mixing and ASV experimentation indicate the "soluble" (filterable) Pb in the wetland is present in complexed and colloidal forms, including humic substances up to 1000 amu, with only a small equilibrium presence of free Pb^{2+} ions. In darker catchment waters Pb also associates with larger molecular weight humic substances. In the wetlands, the soluble ≈50% fraction of wastewater Pb uptake precipitates as PbS by chemical demand of SRB-generated sulphide acting on an equilibrium of various complexed and colloidal forms of Pb present in the wastewater stream. Over the 5-year data set, the inflowing 380 ppb soluble Pb is reduced to 180 ppb at the end of the Old Wetland. Date-paired data indicated the uptake is 210 ppb over the whole period, or 240 ppb if a 3-month dry period of wetland leaching is excluded. The uptake of soluble Pb in the wetland shows some temperature dependency reflecting a rate limitation at the sulphide generation step by the biological processes of the SRB consortium.

12.4 Wetland performance improvement

Wetland operating parameters were measured and evaluated against the original design, and examined for influence on Pb uptake. The most pressing improvement would be to increase wetland pond water depths from 0.04-0.2 m to 0.3-0.5 m to increase treatment residence time (from 2.6-23 hours to over 2 days), allow more complete precipitation, facilitate fine-fraction particle sedimentation and distribute flows more evenly. Other hydrology improvements

include increasing planting of *Eleocharis* to infill wetland spaces and areas of channelling, and better regulating the flow distribution to the parallel New Wetland pond series.

The tailings/wastewater should continue (and unchecked AMD sources should begin) to be treated with lime prior to wetland treatment of wastewaters for optimal wetland treatment effect and minimising pond infilling with bulky hydroxides.

The application of phosphate-bearing borewater to the wetlands rapidly increased the productivity of wetland plants. Other recommendations for improving plant productivity include planting additional *Eleocharis* and a variety of other suitable plants including *Triglochin* to promote diversity and broader overall growth season. Addition of organic materials (especially by local waste co-treatment such as roadkill, sewage, dairy waste, forestry waste or food processing waste) would not only fertilise the wetland plant community, but also more directly feed the SRB consortium and assure the maintenance of low mud redox conditions for PbS sink stability.

The depth of the mud/mire (between the free water base and clay lining of the excavated wetland ponds) is optimal at 20-30 cm, simultaneously maximising SRB habitat and minimising organic material losses by methane production.

12.5 Catchment issues

The river system affected by mine operations was examined applying principles of total catchment management. There are measurable low levels of background Pb and other contaminants in the catchment, from both natural and minor human activity sources. The Hellyer and Que River mine operations contribute significant increments of Pb and sulphate over background, which decrease with dilution down the stream catchment, via the Que River and Huskisson River, finally into Lake Pieman and the lower Pieman River. There is evidence for the wetland SRB-sulphide facilitated Pb-fixing mechanism continuing downstream into the catchment with streambed colonisation by SRB consortia, resulting in downstream Pb concentration decrease beyond dilution.

Despite the contaminated water management diversions into the tailings dam treatment area, some mine pollution escapes the lease into the Southwell River, in the form of unintercepted runoff from haulage road and portal landing.

The incidence and area of roading and vegetation clearing disturbance on the minesite and in the wider catchment area needs to be minimised. Bare soil erosion rates on the apron surrounding the tailings dam are 1.0 cm/y (200 t/Ha/y), similar, and up to tenfold higher erosion losses were noted in exposed logging areas in the Huskisson catchment. At the mine, runoff from bare soil results in some sediment infilling of tailings dam and wetland ponds, with the remainder entering the streams. Not only is soil bulk and fertility loss a concern in rain-leached western Tasmania, but erosion from clearing and fire presents ecological problems with long term nutrient loss, vegetation

community alteration, stream turbidity, loss of stream ecology, streambed gravel cementation, and sedimentation in riverine pools and Lake Pieman. The loss of soil, litter and forest cover through clearing and fire also contribute to destabilising ground hydrology and stream flows.

Catchment areas like the Pieman need a multidisciplinary approach and cooperative, proactive management by all stakeholders. The aims being to prevent, minimise and ameliorate clearing and fire disturbance by extent and degree, soil degradation, pollution and water quality problems, and apply timely rehabilitation and remedial strategies.

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Glossary of abbreviations

Note: Symbols and abbreviations for elements and other chemical formulae, Australian States, common imperial and SI units are assumed and not listed.

AAS atomic absorption spectroscopy; for elemental analysis

AMD acid mine drainage

amu atomic mass units

APRA(I) Australian Postgraduate Research Award (Industry), administrative scholarship structure jointly funded by Commonwealth and Industry in partnership with the University, Department and postgraduate candidate.

APS adenosine-5'-phosphosulphate; compound reduced by an enzyme in SRB

ASL altitude (typically in metres) above mean sea level

ASV anodic stripping voltammetry; heavy metal analysis instrument

BDL below detection limit; less analyte than measureable by this method

BOD biological oxygen demand

CBD central business district (of a city)

CDT Cañon Diablo (meteorite) troilite; sulphur isotope ratio standard

cond the electrical conductivity of water (measured in μS) that arises from the presence of total dissolved ionic substances

DO dissolved oxygen (ppm)

DOC dissolved organic carbon

Eh reduction/oxidation potential

EoH end of hole; exploration drilling term, maximum depth of a bore

EPA Environment Protection Authority; in mainland states

GC gas chromatography; separation & analysis of gases

H(nn) designated sampling stations for regular environmental monitoring by Aberfoyle Resources, or stations set up for this research

HEC Tasmanian Hydro Electric Corporation (formerly Commission)

HPLC high performance/pressure liquid chromatography

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ICPAES inductively coupled plasma atomic emission spectroscopy; for
  elemental analysis

MRT mean residence time (typically of water flowing through a pond)

MS mass spectroscopy; analysis by ion particle mass

NH&MRC Australian National Health and Medical Research Council

NW new wetland; second 1990 system of 4 parallel runs A-D of three
  sequential 1-3 paddies headed by distribution pond NW1 and ending in 2
  combined outlets NWAB4 and NWCD4, hence the sample stations NW1,
  NWA0-NWD3 at the start & end of each paddy/pond.

OW old wetland; original 1989 sequential system of 7 paddies OW1-OW7, with
  sample stations OW1-OW8 at start & end of each paddy. Station OW9 site is at
  the wetland bypass prior to the outlet confluence.

PCB polychlorinated biphenyls; a group of persistent organic pollutants

PLFA phospholipid fatty acids; components of cell walls

ppb concentration in parts per billion (μg/L)

ppm concentration in parts per million (mg/L)

PVC polyvinyl chloride (plastic)

Q(nn) designated sampling stations for regular environmental monitoring by
  Aberfoyle Resources related to the Que River mine.

RDI recommended (daily) dietary intake

SMBS sodium metabisulphite; flotation reagent

SMBT sodium mercaptobenzothiazole; flotation reagent

SRB sulphate reducing bacteria

TDS total dissolved solids

TOC total organic carbon

TSS total suspended solids

XRD X-ray diffraction; instrument for analysis of crystal structure

4WD four wheel drive (vehicle)

Site codes & locations: Tables 5.2 & 11.1, and Figures 1.1, 3.1, 3.10 & 10.1.