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The behaviour of residual contaminants at a former station site, Antarctica

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"Capsule": *Minor contamination by metals, phosphorus, and fuel products were found at a former research station site in Antarctica.*

Abstract

In 1994, New Zealand's only mainland Antarctic base, Vanda Station, was removed from the shores of Lake Vanda, in the McMurdo Dry Valleys region of southern Victoria Land, Antarctica. Residual chemical contamination of the station site has been identified, in the form of discrete fuel spills, locally elevated Pb, Zn, Ag and Cd concentrations in soil and elevated Cu, Ni, Co and phosphate concentrations in suprapermafrost fluids in a gully formerly used for domestic washing water disposal. Pathways for contaminant transfer to Lake Vanda, potential environmental impacts and specific remediation/monitoring options are considered. While some contaminants (particularly Zn) could be selectively leached from flooded soil, during a period of rising lake level, the small area of contaminated soils exposed and low level of contamination suggests that this would not adversely affect either shallow lake water quality or the growth of cyanobacteria. Phosphate-enhanced growth of the latter may, however, be a visible consequence of the minor contamination occurring at this site.

Keywords: Trace metals; Fuel; Phosphate; Suprapermafrost; Antarctica; Vanda

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1. Introduction

More than 100 years of human occupation of the Antarctic continent has inevitably led to anthropogenic contamination in the environment, particularly in the ice-free areas. Such contamination is concentrated around occupied and historic bases and stations, as well as field camps, where soils are often visibly contaminated by fuel residues and solid wastes, or stained by domestic waste water. Internationally agreed protocols now prohibit the discharge of any substance onto ice-free areas and soils in Antarctica (e.g. Waterhouse, 1997). However, prior to the implementation of the these protocols, there were less stringent controls on the use, storage and disposal of potential contaminants and less appreciation of the risk posed to the environment by inappropriate use and disposal of these substances. Even now, accidental spills, particularly of fuel, continue to provide a source of potential contamination and are, to some degree, an inevitable consequence of human activity.

Solid waste removal from impacted areas is time-consuming and often expensive, but is achievable. The removal of the organic and inorganic contaminants contained in liquid wastes such as waste waters, fuels, mechanical fluids and chemical reagents, is more difficult as these liquids are physically and chemically redistributed or degraded in the soil profile and meltwaters. While there has been evaluation of the physical mobility of large fuel spills in Antarctic and other frozen soil profiles (e.g. Balks and Campbell, 1995; Braddock and McCarthy, 1996; Aislabie et al., 1999), little is known about the mobility and fate of individual fuel components, trace metals and nutrients in permafrost Antarctic soils.

The inland drainage systems of the McMurdo Dry Valleys in Victoria Land, in the Ross Sea region of

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Antarctica, are particularly vulnerable to the environmental effects of contamination, as contaminants can not be flushed away to the sea. Hence processes facilitating chemical degradation or physical transport of the contaminants become very important in the assessment of potential environmental impacts. Vanda Station, on the shores of Lake Vanda in the Wright Valley, operated as a base to support New Zealand's field activities in the McMurdo Dry Valleys from 1968 to 1993. It was removed in the 1993/1994 austral summer season when rising lake levels threatened to flood the site (Waterhouse, 1997). The level of Lake Vanda, which has no outlet, had been rising consistently since 1980 (Chinn, 1993).

In December 1992, prior to the removal of the station, an assessment was made of past contamination events and waste disposal practices, and of the contaminants which might be readily leached from the soils (Sheppard et al., 1993). Soils in a gully close to the Station, which had been used to routinely dispose of domestic washing water or "greywater" ("Greywater Gully"), and close to the site of the wet chemistry lab and workshop, were identified as being of concern. Soil contamination by fuel residues was not determined, but sites where diesel fuel had leaked during storage or refueling operations, or during routine operation of the helicopter pads, were noted.

Some contaminated soils were removed from the site, but inevitably residual contamination remained. Gradual inundation of the lower lying areas of the Vanda Station site has occurred. By 1995 lake waters were encroaching on soils which had been physically and chemically disturbed by the station and its removal. Lake levels then stabilised (Hawes, 2001), but it is likely that lake waters will rise again in the future with further flooding of contaminated areas. The soil profile has a permafrost layer at ~0.5–1 m depth (on average) below the ground surface. Subsurface contaminant mobility is therefore limited to the zone above the permafrost. Lateral mobility is facilitated by the liquid "suprapermafrost" layer which flows along the surface of the permafrost during the warmest part of the year. The presence of a suprapermafrost layer in the Wright Valley was first identified by Wilson (1979), who noted saline brines at the permafrost surface in gullies leading into the western end of Lake Vanda.

The aim of this study was to:

1. Identify and quantify residual contamination in the surface and subsurface soils at the Vanda Station site
2. Identify potential pathways for contaminant transfer to Lake Vanda, including an assessment of the role of the suprapermafrost fluids in contaminant mobility.
3. Assess the potential for adverse environmental effects in Lake Vanda.

2. Materials and methods

2.1. Sampling

In January 1997, soils, sediments, microbial mats, surface waters and ground waters (suprapermafrost fluids) were collected from the vicinity of the Vanda Station site. Standard trace metal and hydrocarbon sampling techniques were used in the collection of all samples to avoid contamination.

Sampling site localities are shown on Fig. 1a and b. "Control site" samples (Fig. 1a) were collected from around Lake Vanda and the lower Onyx River area, outside the area which had been disturbed by routine activity at Vanda Station. Sites V1 – V5 are profiles in the main body of Lake Vanda and, although data from these sites are used for comparative purposes, they are not specifically reported here (refer Webster and Webster, in preparation). "Station sites" (Fig. 1b) included intensive sampling in Greywater Gully, on former landing helicopter pads and in other selected areas identified in Sheppard et al. (1993) as having elevated contaminant levels. Greywater Gully is 90 m in length, running between the Vanda Station site (GW6) and the edge of Lake Vanda (GW1). The main area of greywater disposal during the operation of the base was in the vicinity of GW4 and 5. A suprapermafrost layer was present at all sites in Greywater Gully except GW6, where the base of the profile was in bedrock.

Additional subsurface soils were collected from vertical profiles at sites HP1, 2, 4, 5, 6, 7 and 10 and at GW3, 4, 5 and 6. Note that sample depths for many soil profiles were irregular due to the presence of boulders in the profile.

To examine the rate of TPH dispersion or loss from the soil profile, a series of in situ experiments were carried out in well-sorted dry soils on the floor of the Wright Valley, approximately 1.5 km NE of the station site. Aliquots of 50 ml of the two types of fuel commonly used in Antarctica were deposited on the soil surface: "JP8" diesel fuel, and "Mogas" which is a lighter fuel commonly used for field generators. Four separate areas of 4 × 6 m were marked out on the soil surface, to be sampled after 1 day, 1 week, 1 month and 1 year respectively. In each area, the two types of fuel were poured onto the soil surface 2 m apart. Consequently there were four replicate sites for each fuel type. The concentrations of TPH at three depths (0–3, 3–6 and 6–10 cm in the profile were measured after the required time intervals, between December 1995 and December 1996. When the experiment concludes, the affected soil will be removed from the valley.

To determine the leaching potential of contaminants bound to the soils, two large (2 kg) soil samples were collected, one from a site visibly contaminated with fuel residues (HP10) and one from a control site of uncontaminated soil (site B).

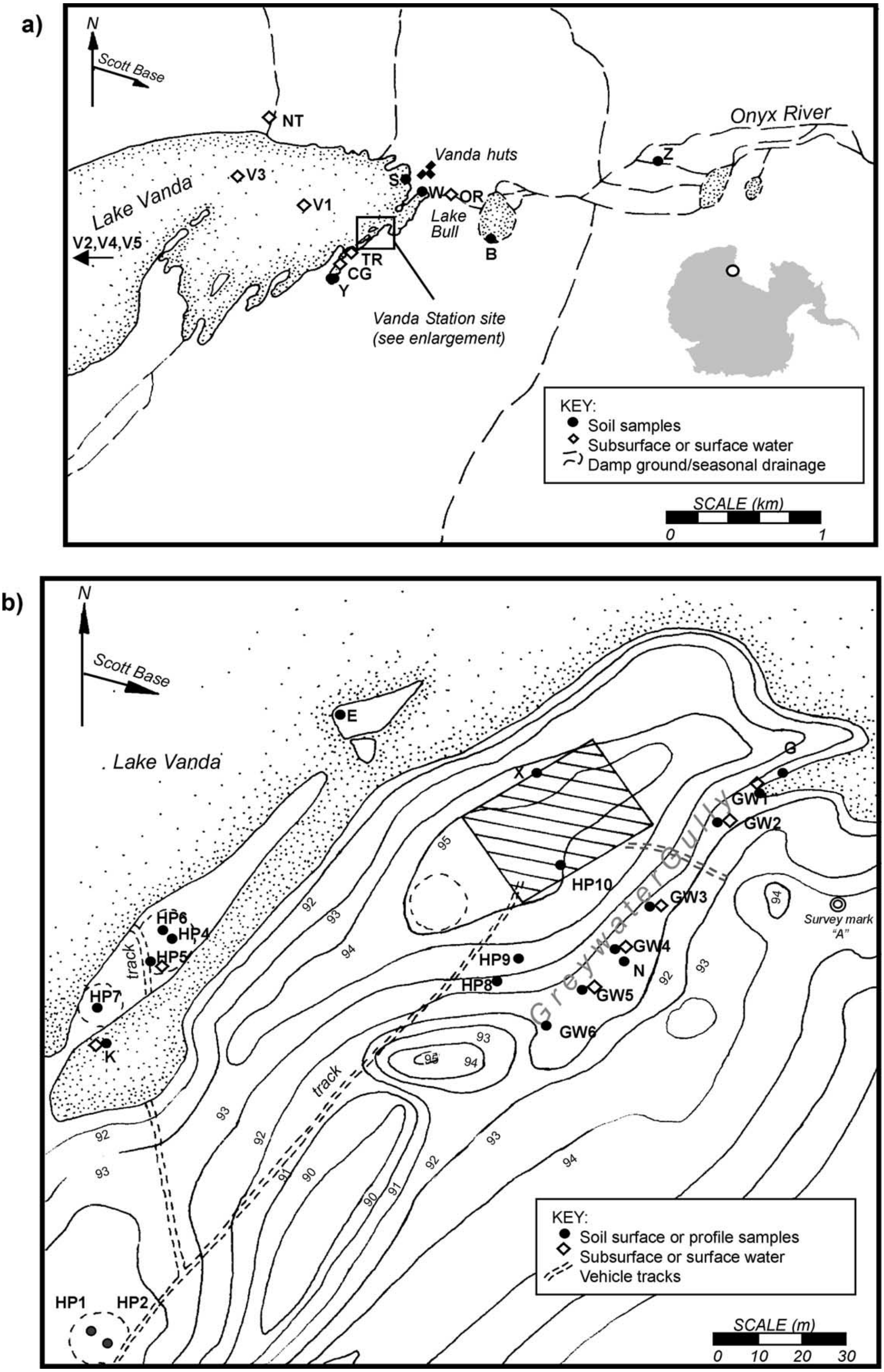

Fig. 1. Sample locality map for (a) the eastern end of Lake Vanda, and (b) an enlargement of the former site of Vanda Station. Contours are shown in meters above sea level, with the lake level shown as surveyed in December 1995 (91.5 m a.s.l.).

2.2. Analytical methods

Soil profile temperatures were measured using a thermocouple inserted into the soil of the sidewall of a small pit. Soil conductivity and pH were measured after soils were mixed with distilled water in ratios of: 20 g soil:100 mls water and left for 30 mins for conductivity measurements, and 10 g soil:30 ml water and left overnight for pH measurements. Representative soil samples were sealed in air-tight bags for soil moisture content determination, and subsequently weighed before and after drying at 40 °C, until no further weight loss occurred (about 72 h). Mineralogy was examined by XRD.

For the determination of trace metals in soils, ca. 100 g of air-dried soil was collected into HDPE containers for transport back to New Zealand. Prior to metal analysis, the samples were dried at 40 °C, sieved through 500 μm nylon mesh, and digested in hot, concentrated HNO_3 (which does not digest the silicate minerals). The digests were analysed by atomic absorption spectrophotometry and ICP–mass spectrometry, with detection limits (recalculated to relate to the sediment) ranging from 0.001 mg kg^{-1} for Ag, to 50 mg kg^{-1} for Al and Fe. For the determination of TPH (total petroleum hydrocarbons) in soils, samples were collected into 500 ml air-tight metal tins, and analysed by infrared spectroscopy (IR) with a detection limit of 2 mg kg^{-1}.

Where suprapermafrost fluids were present, small pits ($\sim$10–20 cm diameter) dug in the soil began to fill with water when the permafrost was reached. This fluid was drawn up with a hand vacuum pump and collected into a glass vessel. Water conductivity, temperature, pH and dissolved oxygen (DO) were measured immediately on site, using standard portable meters. Samples of 50–200 mls of suprapermafrost fluids and lake water were collected and transferred to acid-washed, HDPE bottles. For trace metal determinations, filtered (0.22 μm) samples were collected and acidified to pH <2 with ARISTAR grade conc. HNO_3. Trace metal concentrations were measured by ICP–MS, with detection limits between 0.01 μg kg^{-1} (e.g. Cd, Ag and Co) and 1 μg kg^{-1} (e.g. Fe and Si). The most saline samples (e.g. at site GW5), were analysed by graphite furnace AAS (at CSIRO, NSW, Australia). Water samples were also analysed for total organic carbon (TOC) using a dedicated TOC analyser, and for VOC (volatile organic carbon) by purge and trap—gas chromatography–mass spectrometry (at ESR Laboratories, Wellington, New Zealand). The VOC analyses included aromatics, halogenated aromatics, alkanes, alkenes and trihalo-methane, with detection limits of 0.5 μg kg^{-1} for all except halogenated alkanes and alkenes (detection limit $\sim$1 μg kg^{-1}). Major ion and nitrate concentrations were determined on an unfiltered, non-acidified sample by high pressure ion chromatography (HPIC). HCO_3 was determined by titration against HCl and back titration with NaOH, after purging with N_2 to remove other ions affecting alkalinity. DRP was measured by autoanalyser using the molybdenum-blue method (APHA, 1995).

Experimental leaching of the contaminated (HP10) and uncontaminated (site B) control soil was undertaken using the USEPA TCLP Procedure Method 1311 (USEPA, 1992), with leachates of 1 N acetic acid (650 ml:26 g soil) and distilled water (250 ml:12.5 g soil). Soils were sieved to <5 mm prior to leaching, and tests were carried out at 5 and 25 °C. Note that the TCLP test does not quantify the rate at which contaminants can be leached from the soil, and is not independent of the type of soil used (e.g. Romeu et al., 1990), but is the most widely accepted leaching test used. The leachates were analysed by ICP–MS for trace metals, and by high resolution gas chromatography—mass spectrometry (GC–MS) for polycyclic aromatic hydrocarbons (PAHs). The 16 USEPA priority pollutant PAHs were determined: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a) pyrene, indeno(123cd) pyrene, dibenz(ah)anthracene and benzo(ghi)perylene. Detection limits for each component varied between samples, but ranged from 0.5 μg kg^{-1} to 100 μg kg^{-1}.

3. Results

3.1. Characterising the soil profile

A comprehensive description of McMurdo Dry Valley soil profile characteristics and salt content is given in Campbell et al. (1994, 1998). A brief survey of typical "dry" soil profiles (i.e. without suprapermafrost fluids) at the Vanda Station site was made in this study to confirm consistency with previous results. Profiles were examined in detail at HP1, 2 and 4 on the former helicopter pads, with a reduced set of soil parameters measured in pits at other HP- and GW-sites. The depth to the permafrost at the HP-sites typically ranged from 25 to 65 cm, and there was no evidence of liquid at the permafrost surface. The moisture content was low (typically between 0.56 and 3.9%) and increased with depth. Dry soil temperatures ranged from 14 °C at the surface to −1.8 °C at the permafrost. Soil conductivities were high, particularly in the salt-rich soils at the surface, where they ranged from 190 to 435 μS cm^{-1} (measured at 12–14 °C), and pH was constant at 6.9–7.5, showing no recognisable trend with depth.

Soil mineralogy, as determined by XRD, was consistent with derivation from the predominantly granitoid bedrocks, with abundant quartz and plagioclase feldspars, and minor Na-feldspars and clay minerals (illite, smectite and chlorite) as well as ferro-magnesium silicates; magnetite and hornblende. Traces of calcite and gypsum were also present.

3.2. Soil contaminants

Surface soil samples from the sites shown in Fig. 1a and b, and subsurface soils collected from vertical profiles at sites HP1, 2, 4, 5, 6, 7 & 10 and at GW3, 4, 5 & 6, were analysed for a suite of trace metals (Fe, Mn, Cu, Pb, Zn, Ni, Co, Cd and Ag) or, if fuel residues were evident or suspected to be present, for total petroleum hydrocarbons (TPH). All soil analyses are given in Appendix A.

Of the profiles examined, significantly elevated TPH concentrations were evident in only two; HP 1 on the main helicopter pad (570–2040 mg kg^{-1} TPH), and HP 10 beside the former site of the main bunkroom of Vanda Station (450–3140 mg kg^{-1} TPH), where diesel fuel had been stored for vehicle use. Profiles at HP 2, HP 4, HP 6, HP 7 contained <2 mg kg^{-1} TPH in the soil at all depths. Surface soils take from HP 8 and HP 9, where visible fuel contamination was evident on the soil, registered 2240 and 4190 mg kg^{-1} TPH respectively (Appendix A).

An indication of background trace metal concentrations was provided by control site soil samples (Z, Y, B, W and S), as distinct from the station soil samples (K, N, G, E and X) and the visibly contaminated soils of Greywater Gully and two helo pad sites (refer to Fig. 2 and Appendix A). Station soils K, G and E contained background levels of all trace metals, but soils at site X had elevated Pb and Ag concentrations, as did soils in Greywater Gully at GW 4 (and the nearby site N). Zn was also elevated in soil at GW 4. Cd showed a minor degree of enrichment in surface soils at site X and in GW 4, 5 and 6. There was little evidence of Cu, Co, Ni or Mn enrichment in soils at the sites sampled.

3.3. Contaminant mobility

3.3.1. Fuel residues

TPH concentrations as a function of depth in HP1 and HP10 vertical soil profiles are shown in Fig. 3a. TPH had clearly permeated as far as the permafrost at 40 cm depth in HP10, which had a maximum TPH concentration at ~15 cm depth. The presence of boulders in HP1 resulted in a less complete profile, but evidence of TPH migration to at least 20 cm was observed.

TPH dispersion or loss in a vertical soil profile was further examined in a series of in situ experiments, which involved pouring 50 ml aliquots of JP-8 and Mogas onto well-sorted dry soils on the floor of the Wright Valley. TPH concentrations for four replicate sites for each fuel type sampled are shown in Fig. 3b. In terms of TPH loss from the total 10 cm profile, for the JP 8 spills 15–65% had been lost within a week, 45–90% within a month and consistently ~90% within one year. This was similar to the results for the Mogas spills where 10–85% had been lost within a week, 30–100% after a month and 60–100% after 1 year. The variability between replicates may be due heterogeneity in the soil structure and particle size, which will affect both fuel movement and sampling procedures.

3.3.2. Trace metals

Trace metals were measured at three depths in soils profiles in Greywater Gully, which showed trace metal enrichment (Fig. 2), and at site HP5, which did not. Samples were collected from the surface, from the permafrost (or bed rock in the case of GW6) and from a point midway in-between. The analytical results are given in Appendix A, and plotted for Cd, Pb, Ag and Zn in Fig. 4. The remaining trace metals; Cu, Co, Mn and Ni, were not elevated at any depth in the soil profile (Appendix A), consistent with the general absence of Cu, Co, Mn, and Ni contamination in station site soils (Fig. 2).

For Pb, elevated levels occur in the soil at GW4, where the highest levels occur in the surface soil and decrease with depth. For Cd, Ag and Zn, site GW4 again shows the greatest degree of enrichment in these metals, but GW5 and GW6 are also affected. For these metals there is no consistent trend observed with depth. Somewhat unexpectedly, the soils in the base of GW6 (a "dry" profile) are relatively enriched in Ag and Cd.

3.3.3. Contaminant leaching potential

The results of the TCLP test on contaminated (HP10) and control site (site B) soils are shown in Fig. 5. Distilled water proved to be incapable of leaching metals from the soil at control site B, but did leach measurable Cu, Zn, Ni and Cd concentrations from the contaminated soils from site HP 10. However, Co, Pb and Ag were not readily removed from the soil. Using the acetic acid leachate increased the degree of leaching of all metals except Ag, but Cu, Zn, Ni and Cd remained the most readily removed metals. Measurable PAH concentrations were present only in acetic acid leachates of the contaminated soil at HP10 (Fig. 5). The leachates contained 34–47 μg l^{-1} naphthalene, 0.54–0.78 μg l^{-1} acenaphthene, 0.89–1.38 μg l^{-1} fluorene and 0.14–0.23 μg l^{-1} phenanthrene. The remaining of the 16 USEPA Priority Pollutant PAH compounds were below detectable levels in the leachate.

The effect of temperature change (5–25 °C) on the leaching process was not considered significant. The differences were not consistent, and generally within or close to the estimated analytical error of this experiment (±10%).

3.4. Suprapermafrost layer characterization

Suprapermafrost liquids are an agency of transport for contaminants in the soil profile. Unlike the soils,

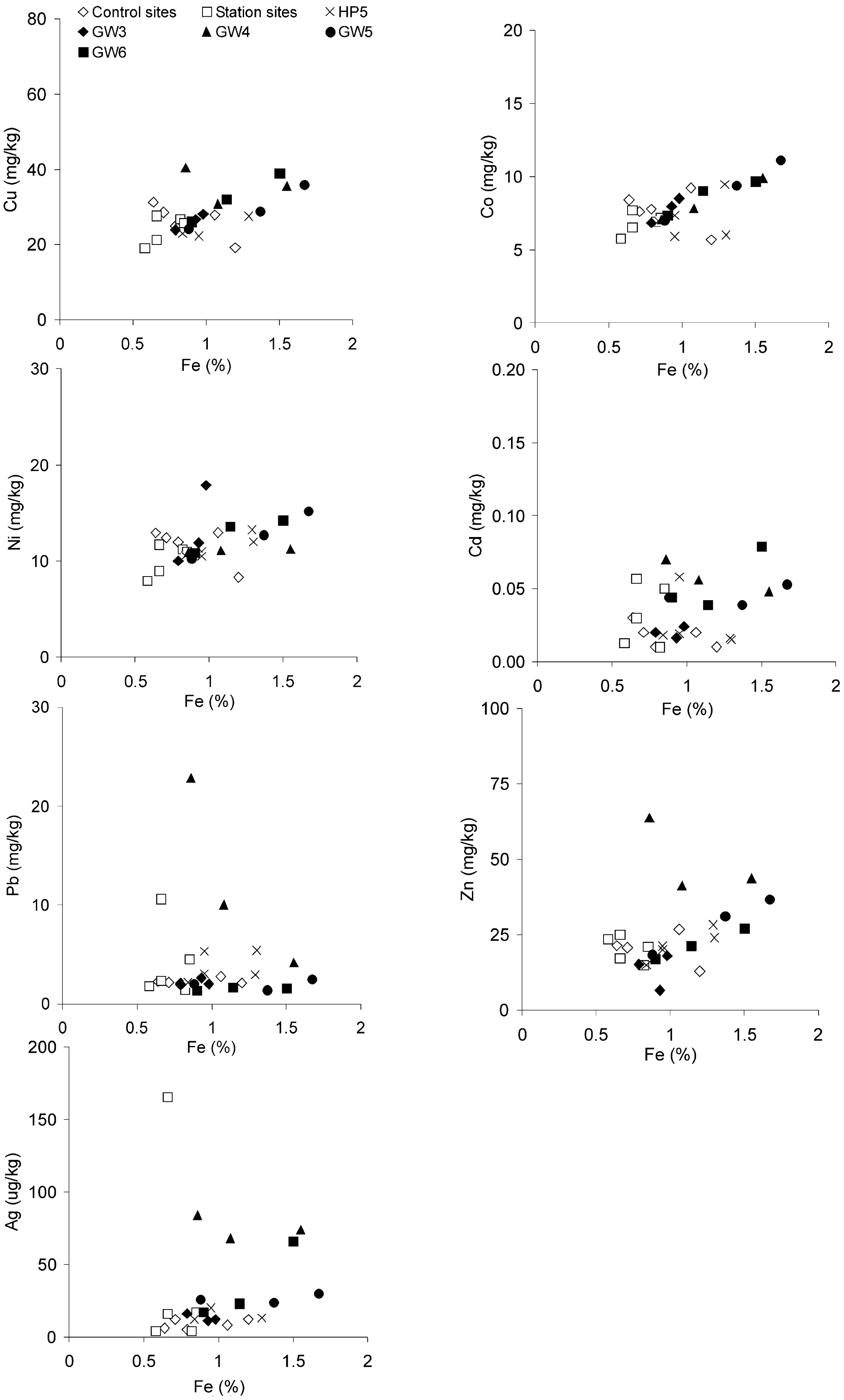

Fig. 2. Trace metal concentrations (mg kg^{-1}) in the soils samples at the sites indicated in Fig. 1. The vertical scales have been arbitrarily adjusted to ensure clustering of data for the uncontaminated control site soils, so that samples with elevated metal concentration are clearly evident.

their characteristics have not previously been studied beyond the initial identification of Ca–Cl brines on the surface of permafrost at the western end of Lake Vanda (Wilson, 1979). In order to be able to recognize the signature of suprapermafrost fluids in freshwaters, and identify pathways for contaminant transfer to freshwaters via this route, the chemistry of the suprapermafrost fluids needs to be characterised.

3.4.1. *Suprapermafrost chemistry*

Suprapermafrost fluids were collected from Greywater Gully, as well as a gully draining into the north side of Lake Vanda (NT), control sites to the west of Vanda Station site (CG and TR) and at HP5. The major ion chemistry of the fluids is given in Appendix B. In Fig. 6, major ion ternary plots show the comparison between suprapermafrost fluids and local surface waters in Lake Vanda (GW1, K), as well as waters immediately beneath the ice cover in the eastern end of Vanda (V1 and V3). Data for the Onyx River (OR) and saline brines at 50, 60 and 70 m depth in the western lobe of Lake Vanda are also shown for comparison, as well as for Don Juan Pond, a very saline Ca-Cl brine pond to the west of Lake Vanda (Webster, 1994),

The suprapermafrost fluids are chloride-rich brines, with the Greywater Gully, HP5, CG and TR site fluids showing similar anionic ratios to both the shallow (V1 and V3) and deep (V2) lake waters in Lake Vanda, but with a slightly higher proportion of SO_4. The dilute suprapermafrost fluids at site NT, a steep gully on the north side of Lake Vanda, were the exception. All suprapermafrost fluids sampled were Na- or Ca-dominated brines. In Lake Vanda, the proportion of Ca increases with increasing salinity (Fig. 6). This trend was not evident in the suprapermafrost fluids where the most saline suprapermafrost fluid sampled (GW 5) was a Na-dominated brine. Although fluids at TR and GW3 were marginally Ca-dominated, none of the suprapermafrost fluids sampled showed the high Ca (18,100 mg kg^{-1}) and Cl (61,400 mg kg^{-1}) concentrations reported in suprapermafrost fluids at the western end of Lake Vanda by Wilson (1979), or in nearby Don Juan Pond (Webster, 1994).

In surface waters, at GW1 the anionic composition clearly reflected that of the Onyx River (OR), while at site K in the inlet the anionic composition was more Cl-rich than the Onyx River. The distinctions between GW1 and site K are not as evident in the cation chemistry, but site K is enriched in Na relative to either lake water at GW1 or the OR waters.

3.5. *Contaminants in the suprapermafrost fluids*

The suprapermafrost fluids of upper Greywater Gully (GW 5 and GW4) were visibly foaming and had low DO and high total organic carbon (TOC) concentrations when sampled (Appendix B). XRD identified in pyrite (FeS_2) in the wet, blackened soils at surface of the permafrost, testifying to anoxic conditions. Nutrient concentrations were also anomalous in these fluids. Dissolved reactive phosphorous (DRP) levels were high, as might be expected given the use of phosphate-bearing surfactants in the detergents and soaps present in the domestic wastewater discharged into this gully. Nitrate concentrations, on the other hand, were less than those measured elsewhere around the station site, including Control Gully (CG) and lower Greywater Gully. This would be consistent with enhanced bacterial activity at GW4 and GW5, brought about by greater availability of organic carbon and perhaps DRP. In lower Greywater gully (GW2 and GW3) fluids were saturated with

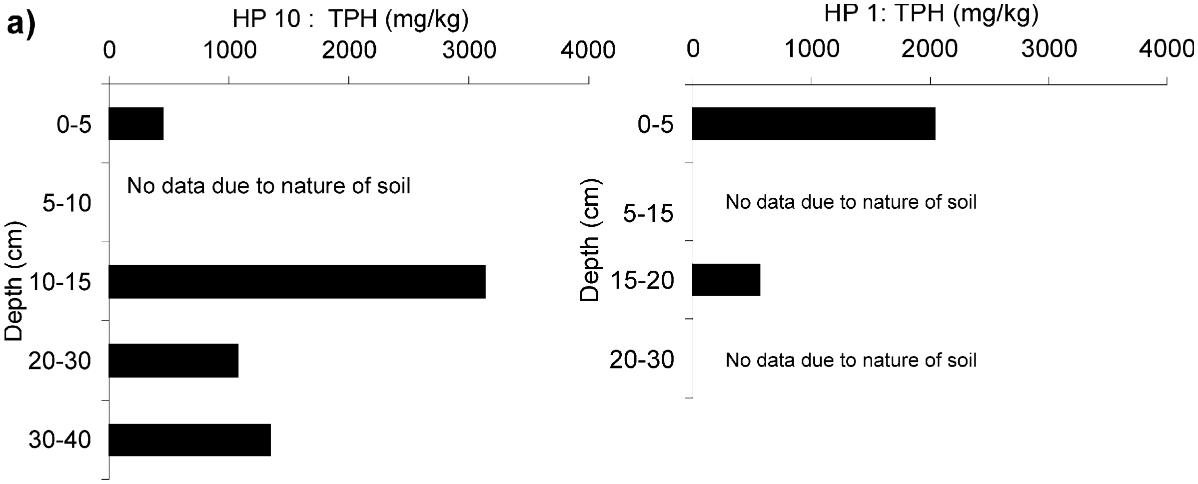

Fig. 3. Fuel contamination measured in field soil profiles at (a) HP 10 and HP1, and (b) experimental fuel (JP8 and Mogas) spillage test sites in Bull Pass, 5 km east of the Vanda Station site. Where no value is indicated, TPH was below detectable levels (2 mg kg^{-1}, for all except 365 day samples, where detection limit = 20 mg kg^{-1}).

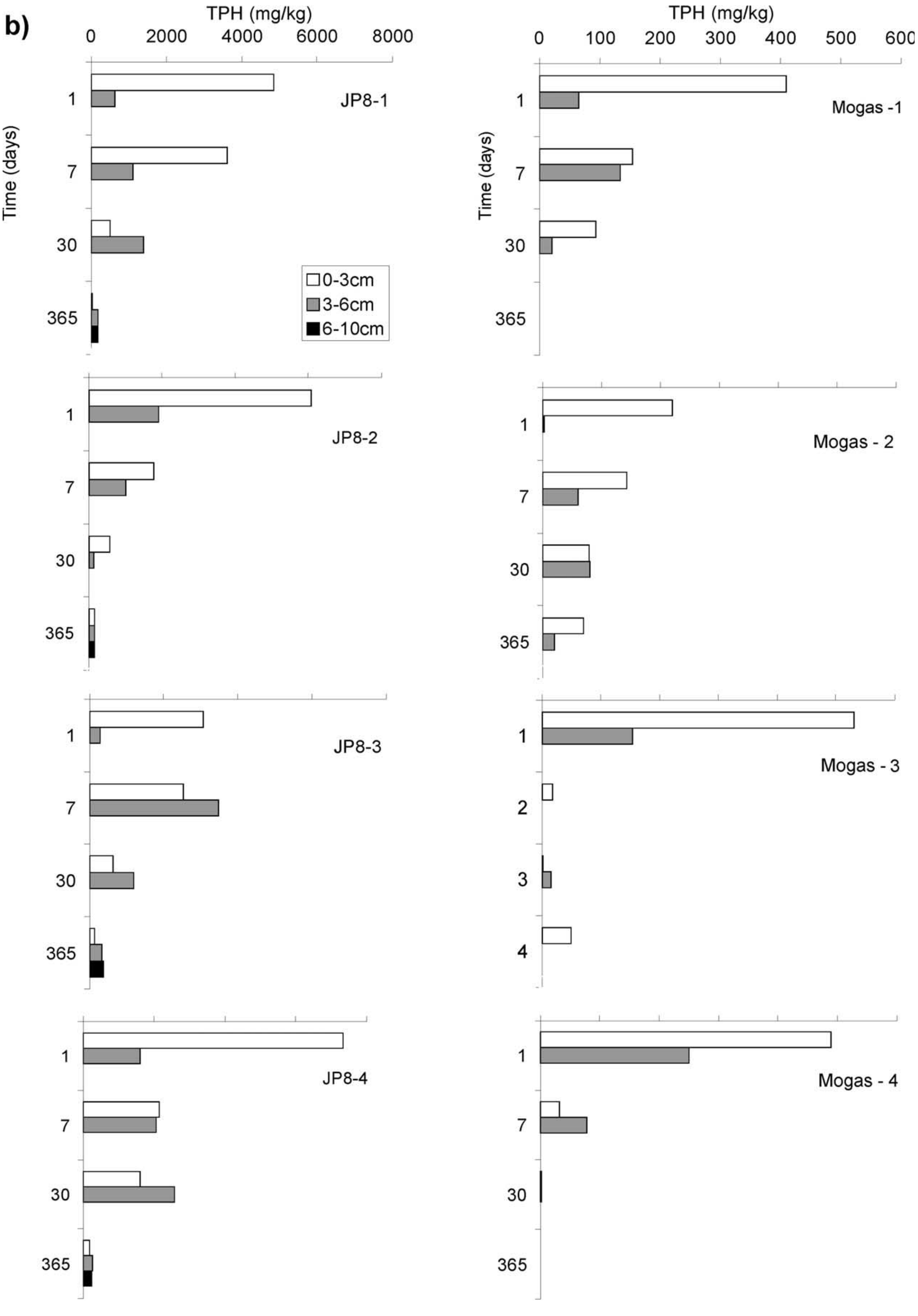

Fig. 3 (*continued*).

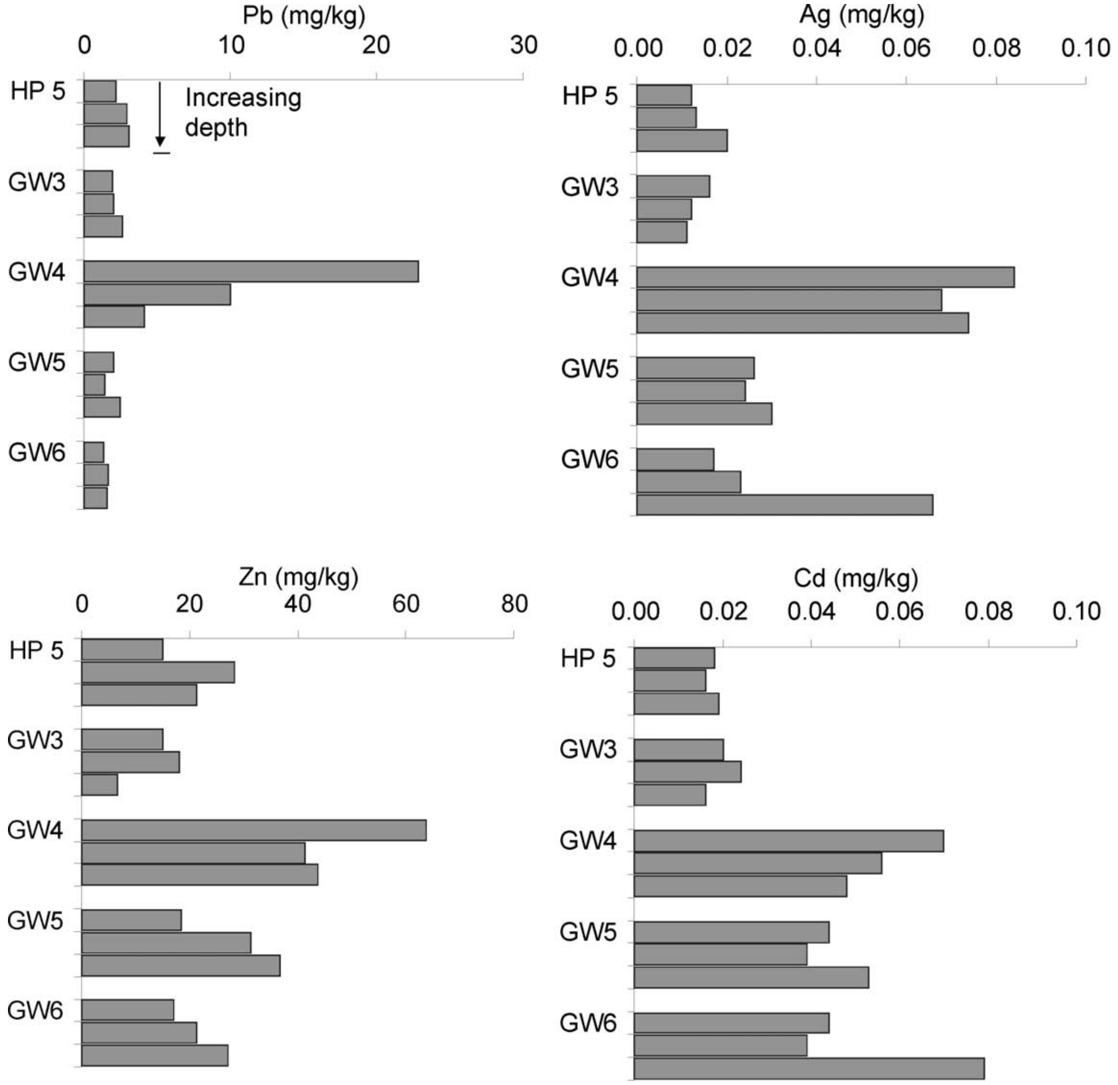

Fig. 4. Metal concentrations in soils of Greywater Gully and HP5 profiles. Analyses are shown for surface soils, soils at the permafrost, and for a soil midway between. No enrichment was observed at any depth for Cu, Ni or Co.

dissolved oxygen. At GW3, however, TOC and DRP levels were slightly elevated, reflecting those at GW4 and 5, and NO_3 concentrations at GW3 were higher than observed in any other suprapermafrost fluids.

3.5.1. Fuel contaminants

No suprapermafrost layer was present at the principal sites of fuel contamination identified and sampled in this study. Fuel contamination, measured as the presence of VOCs, was below detectable levels in all of the suprapermafrost fluids sampled (Appendix B). VOCs were also undetectable in the surface water at the entrance to Greywater Gully, at GW1, in the inlet at site K.

3.5.2. Trace metals

Trace metal concentrations in the suprapermafrost fluids and local surface lake waters are shown as a function of Cl concentration in Fig. 7 (refer to Appendix B for raw data). Concentrations were compared with those of metals in other Wright Valley brines to help identify contamination as distinct from naturally elevated metal concentrations, caused by dissolution of salts and minerals and by evaporation. (e.g. Jones and Faure, 1967; Webster et al., 1994). As the Cl ion remains conservative during most evaporative processes, this was used as the common parameter for Fig. 7.

The concentrations of Cu, Ni and Co in suprapermafrost fluids at GW3, 4 and 5 and HP 5 are elevated considerably above those of oxic brines of similar salinity in Lake Vanda, anoxic brines of higher salinity ($>10{,}000$ mg kg^{-1} Cl) in Lake Vanda, and oxic brines of (much) higher salinity in Don Juan Pond. However, the elevated Pb and Zn concentrations in fluids at HP 5 and GW3, 4 and 5, are not necessarily greater than those which might be expected in a natural brine. Don

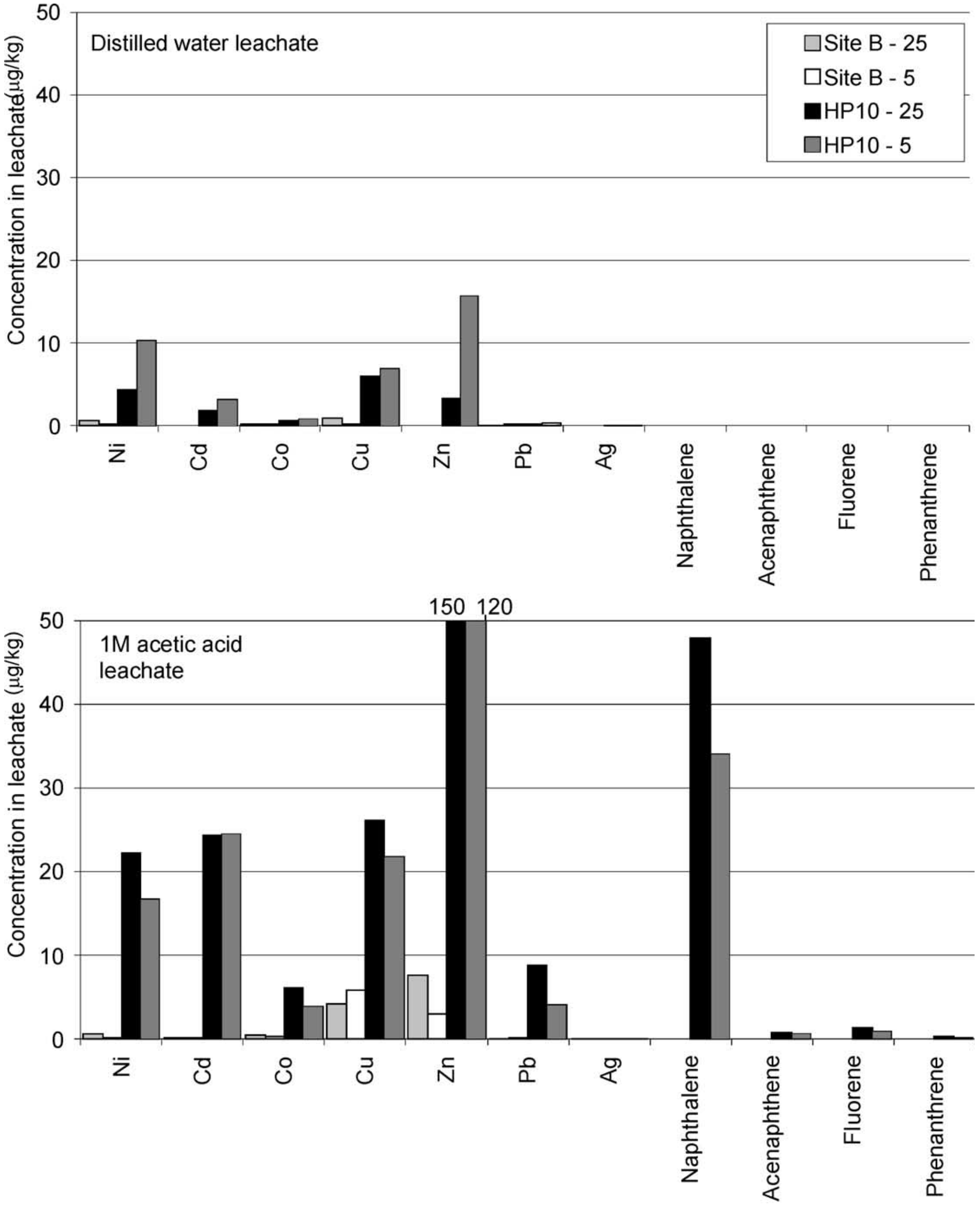

Fig. 5. The results of leaching tests using a TCLP procedure (USEPA, 1992) at 5 °C and 25 °C, with 1 M acetic acid and distilled water leachates. The contaminated soils are taken from site HP10, and the control site soil from Site B.

Juan Pond contains very high levels of Pb and Zn (Fig. 7). Other suprapermafrost fluids analysed (TR, CG and NT) did not show elevated metal concentrations. The surface lake waters at sites K and GW 1 also did not show evidence of metal contamination. Although Zn concentrations at site K (3.0 µg kg^{-1}) were higher than those at the Onyx River and GW1 (0.4 and 0.9 µg kg^{-1}, respectively), the surface waters of the lake typically do have relatively high Zn concentrations (Webster, 1994; also site V1 Zn = 6.8 µg kg^{-1}).

4. Discussion

4.1. Fuel contamination and mobility in the soil profile.

The speed of TPH loss from the experimental fuel spill soil profiles (up to 97% after 1 week) suggests that rapid volatilisation of the lighter hydrocarbons is an important process. Adsorption onto mineral surfaces is the major mechanism limiting hydrocarbon mobility and vaporisation in low moisture soils (Batterman et al., 1995). Only in "wet" soils (>4% moisture) will

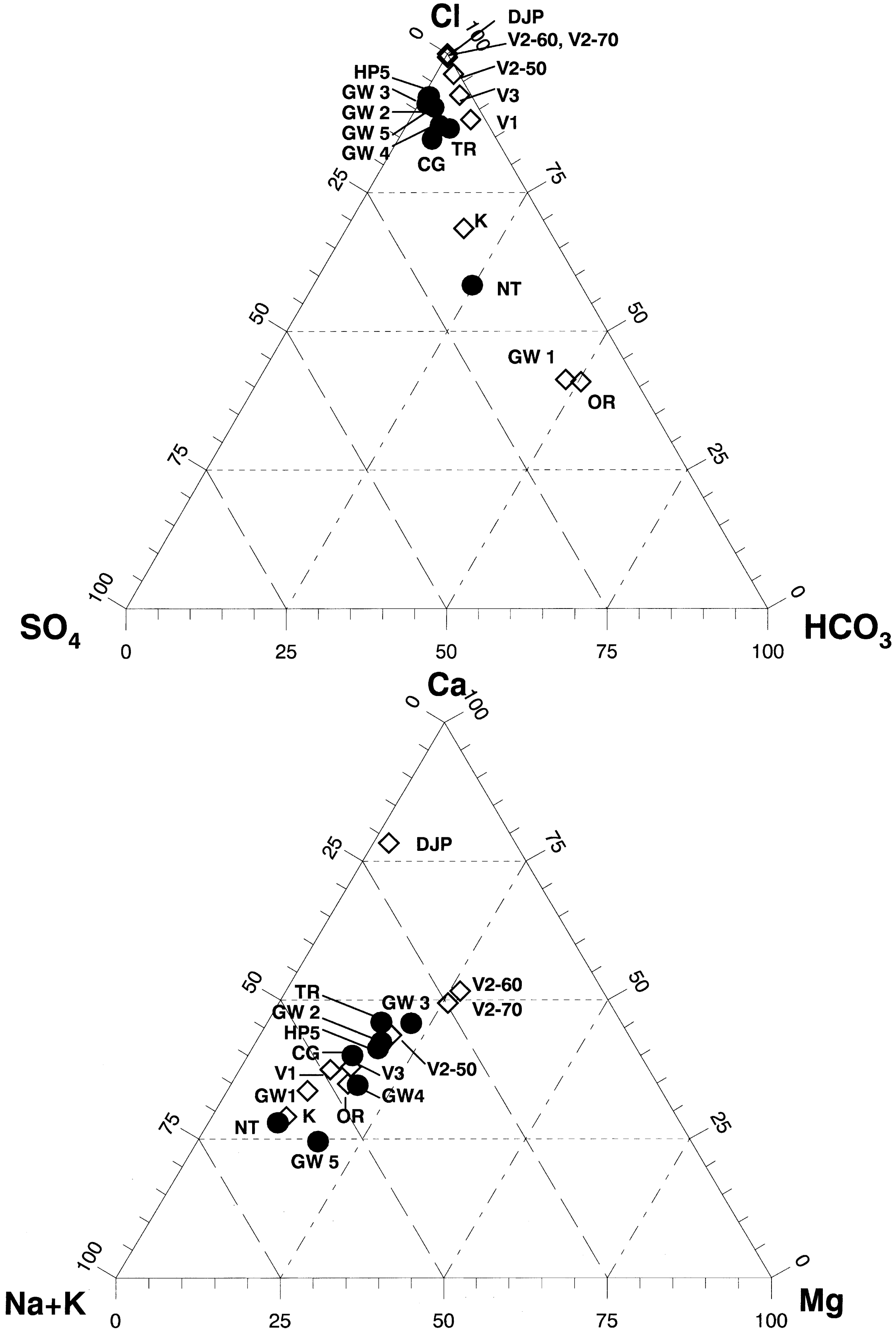

Fig. 6. Ternary diagrams portraying the major ion chemistry of suprapermafrost fluids (•) relative to other catchment waters (o): the Onyx River (OR), Lake Vanda surface waters (V1, V3, K, GW1), Lake Vanda saline brines (V2-50, −60 and −70 m depth) and Don Juan Pond (DJP). Data for OR, V1-V3 and DJP from Webster and Webster (in preparation), and Webster (1994).

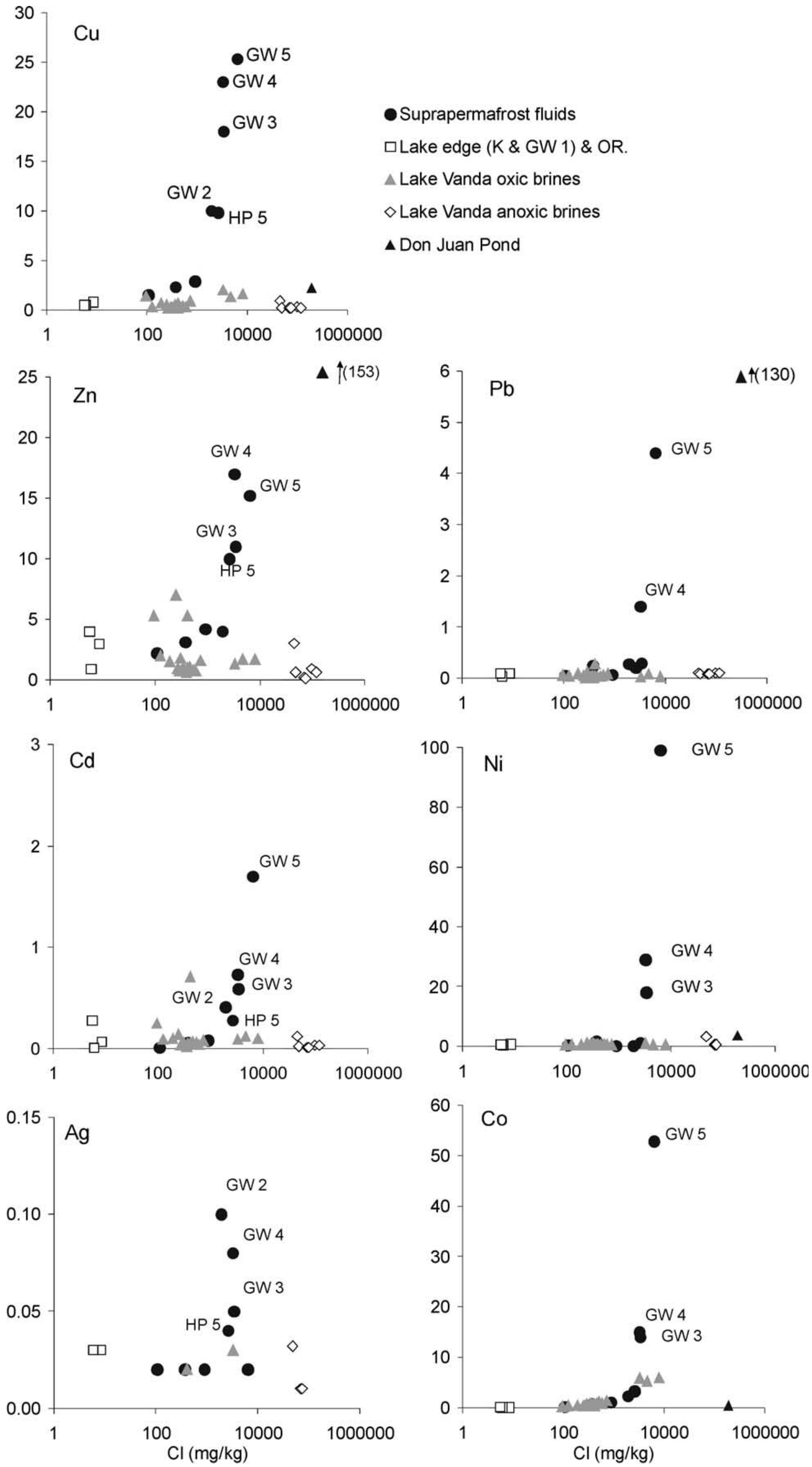

Fig. 7. Trace metal concentrations ($\mu g\ kg^{-1}$) in filtered suprapermafrost fluids (●) plotted as a function of chloride concentration, relative to other catchment waters (as described in Fig. 6).

adsorption onto to organic surfaces become important. Consequently, in the low moisture, low organic soils of the Wright Valley, adsorption onto mineral surfaces is the only retention mechanism. This is clearly not very effective in the period immediately following the spill when mineral adsorption sites are likely to become quickly oversaturated.

The rate of vertical migration was slow. Only 2–11% of the original JP 8 TPH had migrated 10 cm after 1 year (Fig. 3b). No Mogas TPH was evident at 10 cm depth after 1 year, and very little was present in the profile at all after this time period. The inference here is that discrete small fuels spills, such as spills made while filling generators or stoves, or minor leaks from storage vessels, are unlikely to disperse rapidly or to reach the permafrost. Consequently, small spill remediation by soil removal may be the most practical option for JP8 and heavier fuel types. For lighter fuels such as Mogas, it could be argued that disturbance of the soil profile may outweigh any benefit to be gained by removing the small amount of contaminated soil remaining after one year. However, further study would be required to confirm this.

These observations pertain only to small scale fuel spillages, and not to larger fuel releases such as a continuous leak from a storage drum, or where the presence of large rocks or cracks in the profile facilitates downward movement of fuel. There is little evidence of any major fuel contamination of the surface and subsurface soils remaining at the Vanda Station site. Of the visibly affected areas, fuel had reached the level of permafrost surface only at HP 10. Here, fuel may have moved laterally along the surface if sufficient volume was released. Permafrost topography usually reflects that of the ground surface, which suggests that this fuel would ultimately have reported to Greywater Gully. In 1997, there was no evidence of fuel contamination of the suprapermafrost fluids in Greywater Gully (or elsewhere).

Biodegradation of hydrocarbons may also aid in the remediation of fuel contaminated areas. Alkane and aromatic-hydrocarbon degrading bacteria have been isolated from Antarctic soils (Aislabie et al., 1998, 2000), and there is evidence to suggest that the addition of a required nutrient such as nitrogen could enhance bioremediative processes (Aislabie et al., 1998). Hydrocarbon oxidising organisms, also stimulated by nutrient addition, have also been reported in contaminated permafrost soil from Alaska, USA (Braddock and McCarthy, 1996); further evidence that cold, dry conditions will not prevent microbial mineralization of petroleum compounds. Hydrocarbon degraders have not been reported from Wright Valley meltwaters or from the saline suprapermafrost layer as yet. However, their presence is expected (e.g. Margesin and Schinner, 2001), given the natural production of hydrocarbons in Antarctica by cyanobacteria, and may eliminate any evidence of hydrocarbon contamination in these fluids.

4.2. Trace metals and their mobility in suprapermafrost fluids

The only soils on the Vanda Station site with metal concentrations elevated above background levels were in Greywater Gully (Pb, Zn, Ag and Cd), and at site X near the site of the former wet chemistry lab (Ag and Pb). To assess the possibility that fine solid waste residues included in the soil sample might be influencing these results, a survey of exotic material in these soils was undertaken. Fine fragments of wood and other building materials, often painted green, and splashes of green and orange paint on rock surfaces were present. The latter had been used to mark out helicopter pads on the site. Representative paint flakes were analysed by SEM-EDAX, proving that the red paint contained traces of Pb. The paints were otherwise predominantly Si and Ti, with minor Fe (green) or predominantly Si and Fe (red). Therefore, while a component of the Pb contamination may be due to the inclusion of paint flakes in the sample, the Ag, Zn and Cd present is more likely to be entirely adsorbed to soil minerals.

The soils in upper Greywater Gully have elevated concentrations of Pb, Zn, Ag and Cd at all depths between the ground surface and permafrost, but these are not the only metals present. The suprapermafrost fluids have elevated concentrations of Cu, Ni and Co, despite the fact that these metals are not elevated in the soil. There is clearly little retention of Cu, Ni and Co on the soil when the leachate is a saline suprapermafrost fluid. The suprapermafrost fluid in Greywater Gully also has elevated Pb and Zn, but only very minor enrichment of Ag and Cd.

The major ion chemistry of the suprapermafrost layer was variable, but showed a similar range in composition (Na- and Ca-rich Cl brines) and salinity to other surface and lake water brines in the Wright Valley, and is evidently an integral part of the hydrological cycle of this catchment. A comparison of trace metal concentrations in the suprapermafrost fluids in Greywater Gully with those of other saline brines in the McMurdo Dry Valleys was made, particularly the oxic Ca–Cl brine in Don Juan Pond and the brines in the depths of Lake Vanda. The latter are also very saline, but anoxic, and precipitation of metal sulphides limits metal concentrations (Green et al., 1989; Webster, 1994). The presence of Cu, Ni and Co at higher concentrations in Greywater Gully fluids was clear evidence of contamination. However, the elevated Pb and Zn concentrations in fluids at HP5 and GW3, 4 and 5, were not necessarily greater than those which might be expected in a natural brine such as Don Juan Pond (Fig. 7). Cadmium and Ag concentrations are also elevated (albeit less significantly) in the suprapermafrost fluids, but concentrations for Don Juan Pond have not yet been reported so a comparison can not be made.

4.3. Other contaminants in the suprapermafrost fluids

Chemical perturbation of the suprapermafrost fluids of Greywater Gully is not limited to trace metal concentrations. In the upper gully there are anomalously high levels of DRP (mainly as phosphate) and TOC, and low DO. Sheppard et al. (1993) noted that an experimental water leach of soil collected from upper Greywater Gully showed high levels of leachable phosphate. The consequences of the addition of high concentrations of phosphate to Lake Vanda could be serious as cyanobacteria growth in the lake is phosphate-limited (Vincent and Vincent, 1982). However, this assumes that the phosphate-rich, metal-rich suprapermafrost fluids will ultimately reach the lake.

4.4. Pathways for contaminant transfer to Lake Vanda

4.4.1. Suprapermafrost fluid movement

Emergence of saline suprapermafrost fluids into the side or base of the main body of the lake may not be evident in the surface water chemistry, as the saline fluids will remain at the level dictated by the density gradient already present in the water column. However, emergence into the shallow, ice-free embayments and inlets in the moat in the vicinity of Vanda Station (Fig. 1a) should be detectable. This water is well mixed by wind action, but unlikely to be rapidly mixed and diluted with main lake water.

There was no evidence to suggest that the suprapermafrost fluids in Greywater Gully are actively moving ‘‘down gully’’ towards Lake Vanda. Major ion chemistry (Fig. 6) suggests that lake water composition at the mouth of this gully (GW1) is very similar to that of the Onyx River. The Onyx River enters the lake in the same embayment in the shore line, and only 40m away from GW1 (Fig. 1a). There was no evidence of trace metal or phosphate contamination of the lake waters at GW 1. Another (ongoing) monitoring study at GW 1, carried out routinely since December 1994, has similarly failed to detect elevated phosphate concentrations in these lake waters (Hawes, 2001). Salinity increases towards the station site, which suggest that there could be mixing and dilution with incursive lake water near the lake edge, and possibly even a general subsurface flow of lake water ‘‘up’’ the Gully. Metal concentrations in the suprapermafrost fluids were consistently higher in GW5, than in GW4, whereas concentrations in the soil (where present) were generally higher in GW4. It is reasonable to speculate that these fluids should not move out of this area in the foreseeable future.

Suprapermafrost fluids at sites CG, TR and HP5 did not show evidence of contamination. These fluids are close to the shore and have a greater potential to mix with lake water; particularly, at HP 5, with water lying between the station site and the recently-formed islands (Fig. 1b). The higher proportion of Cl and Na in surface water at site K (Fig. 6), compared to that of the Onyx River and at GW1, could be reflecting either the influence of suprapermafrost fluids or dissolution of soil salts.

4.4.2. Flooding

Another way in which contaminants could be transferred into Lake Vanda is through inundation of the station site soils by lake water. In the event that Greywater Gully, or other low-lying metal-contaminated soils (e.g. site X) become flooded during a period of rising lake level, a degree of contamination of lake water will inevitably occur. It seems unlikely that the suprapermafrost fluids in Greywater Gully would mix readily with overlying flood water, even in a saturated profile, given the high density of the more saline fluids. Therefore contaminant leaching from soils is the main mechanism to be considered.

The TCLP results suggest fuel residues are unlikely to dissolve readily in neutral pH lake waters. Although the acetic acid leaching experiments indicate that the more soluble hydrocarbons such as naphthalene, acenaphthene, fluorene and phenanthrene may be leached from the soil by a more acidic, organic-rich leachate, this scenario is of dubious relevance. Although Aislabie et al. (1999) identified naphthalene and phenanthrene as dominant components of the fuel residues in the surface soil at HP 10, waters in contact with these soils tend to become alkaline, rather than acidic, through their reaction with soils salts (Sheppard et al., 1993). The activity of hydrocarbon-degrading bacteria in the lake water may also effectively remove any evidence of such low level contamination.

Trace metals are also unlikely to be significantly mobilised by neutral pH lake waters. Zinc seems the most likely metal to become locally elevated in the overlying water, as it is both elevated in contaminated soils and relatively readily leached. It would be an obvious choice as an indicator for water quality monitoring purposes. Again, an acidic, organic-rich leachate would be a more effective leachate for all metals, but this is unlikely to occur. Sheppard et al. (2000) undertook a leaching study of contaminated Antarctic soils from Scott Base on Ross Island, showing that Ag, As, Cd, Cu, Pb, and Zn concentrations became elevated in (an alkaline) water leachate. Unfortunately metal concentrations in the soil were not reported so comparison with the results of this study is difficult. Metal leaching from the soil is unlikely to give rise to more than a temporary, local effect in the overlying water column, given the small area of contaminated soils exposed at the Vanda Station site, the relatively low levels of contamination present and, ultimately, the large dilution available in the main body of the lake.

4.5. Potential environmental impacts

The use of water and sediment quality criteria, developed for more temperate environments, to assess potential contaminant impacts in this environment is inappropriate. Cyanobacterial mats are the predominant life-form, and they are considered to be very tolerant of chemical and physical changes to their environment. During this study, cyanobacteria was observed by the authors to be growing directly on the red (Pb-bearing) paint, testifying to tolerance for Pb at least. In experimental growth trials, cyanobacterial mat growth was not inhibited, but was instead enhanced on contaminated Vanda Station soils (Hawes et al., 1999), due to the higher levels of required nutrients such as phosphate. The effect on biodiversity in the mat was not reported in this study. There is little evidence to suggest that trace metals constitute ''required nutrients'' as the cyanobacteria do not take up or accumulate trace metals from the soil or water column (Webster and Webster, in preparation). The growth of cyanobacterial mats over the sediment/surface interface, was reported to inhibit contaminant release from the sediment, at least during periods of active growth (Hawes et al., 1999). Consequently the growth of cyanobacteria on flooded soils is unlikely to be inhibited by the degree of contamination present. The visual impact of enhanced growth is of greater concern, particularly in areas of phosphate contamination such as Greywater Gully.

In terms of the fate of trace metals in this catchment, trace metals entering Lake Vanda will be removed as sulphide precipitates in the anoxic base of the lake (Webster, 1994; Webster et al., 1997; Green et al., 1989). Phosphate is also ultimately removed in the base of Lake Vanda as hydroxyapatite (Canfield and Green, 1985). However, as the residence time for metals in Dry Valley Lakes has been estimated to be comparable to those in the oceans (Green et al., 1986), this mechanism would provide little comfort in a major contamination event.

5. Conclusions

1. After the removal of Vanda Station, residual chemical contamination of the soil profile exists in the form of minor discrete fuel spills, and trace metal and phosphate contamination of soil and suprapermafrost fluids in a gully used for greywater disposal.
2. Investigation of two small fuel spills, as well as in situ experimental studies of fuel dispersion rates in the dry, frozen soil profiles, suggested that vertical movement of the fuel is limited in spills of this size, and that loss by volatilisation is rapid. Remediation by soil removal should be an effective option for small diesel spills. For lighter fuels, the residues will be less significant and the benefits of soil removal may be equivocal.
3. Suprapermafrost fluids in upper Greywater Gully had elevated phosphate, Cu, Ni, and Co concentrations as a result of contamination. Elevated Pb and Zn concentrations were present, but also occur naturally in brines elsewhere in the catchment. There was no evidence of fuel contamination of these suprapermafrost fluids. The soils in upper Greywater Gully had elevated levels of Pb, Zn, Ag and Cd.
4. The contaminated suprapermafrost fluids in Greywater Gully did not appear to be moving towards the lake, and there was no evidence of lake water contamination in the vicinity of the Vanda Station site.
5. Flooding of the Vanda Station site may result in a slight increase in contaminant concentrations (particularly Zn) in the water column. This is unlikely to be a widespread or long term effect, given the small area of contaminated soils exposed at the Vanda Station site, the relatively low levels of contamination present, and ultimately the large dilution available in the lake.
6. Flooding would also facilitate the growth of cyanobacteria and perhaps other aquatic organisms on contaminated soils. Cyanobacteria has proven to be tolerant of the contaminant levels present in these soils, and enhanced mat growth could occur on the phosphate-enriched soils in Greywater Gully.

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Appendix A

TPH and trace metal contaminant concentrations (mg kg^{-1}) in soils (<500 μm fraction) of the Lake Vanda region

Control sites	Depth (cm)	TPH	Fe (%)	Mn	Cu	Zn	Cd	Pb	Co	Ni	Ag
Z			1.1	150	28	27	0.020	2.8	9.2	13	0.008
Y			0.79	97	25	15	0.010	2.1	7.8	12	0.005
B		<2	0.64	110	31	21	0.030	2.3	8.4	13	0.006
W			0.71	120	29	21	0.020	2.2	7.6	12	0.012
S			1.2	74	19	13	0.010	2.1	5.7	8.3	0.012
Station sites											
K			0.82	82	27	15	0.010	1.4	7.0	11	0.004
N			0.85	73	26	21	0.050	4.5	7.2	11	0.017
G			0.66	79	28	17	0.030	2.3	7.7	12	0.016
E			0.58	59	19	23	0.013	1.8	5.8	8.0	0.004
X			0.66	80	21	25	0.057	11	6.5	9.3	0.12
HP 8		2240									
HP 9		4190									
Profiles											
HP1a	0	2040	0.95	120	30	20	0.058	5.3	5.9	11	<0.4
HP1b	12	<2									
HP1c	14	570	1.3	140	30	24	0.015	5.4	6.0	12	<0.4
HP1d	25	<2									
HP2a-c	0–22	<2									
HP 4a	0	<2									
HP4b	12	<2									
HP4c	22	28									
HP4d	36	<2									
HP5a	0		0.84	80	23	15	0.018	2.2	7.0	11	0.012
HP5b	35		1.3	170	28	28	0.016	2.9	9.5	13	0.013
HP5c	70		1.0	110	22	21	0.019	3.0	7.4	11	0.020
GW3/0	0		0.79	68	24	15	0.020	1.9	6.8	10	0.016
GW3/1	30		1.0	79	28	18	0.024	2.0	8.5	18	0.012
GW3/2	60		0.93	75	27	6.6	0.016	2.6	8.0	12	0.011
GW4/0	0		0.86	70	40	64	0.070	23	7.1	11	0.084
GW4/1	25		1.1	96	31	41	0.056	10	7.8	11	0.068
GW4/2	50		1.6	180	36	44	0.048	4.2	9.9	11	0.074
GW5/0	0		0.88	100	24	18	0.044	2.1	7.0	10	0.026
GW5/1	25		1.4	100	29	31	0.039	1.4	9.4	13	0.024
GW5/2	50		1.7	160	36	37	0.053	2.5	11	15	0.030
GW6/0	0		0.90	89	26	17	0.044	1.4	7.4	11	0.017
GW6/1	30		1.1	110	32	21	0.039	1.6	9.0	14	0.023
GW6/2	60		1.5	130	39	27	0.079	1.6	9.7	14	0.066
HP6a-d	0–65	<2									
HP7a-d	0–50	<2									
HP10	0	830									
HP10	0	650									
HP10a	0	450									
HP10b	15	3140									
HP10c	35	1070									
HP10d	38	1340									

Appendix B

Suprapermafrost fluid and surface water major ion, dissolved trace metal (μg kg^{-1}) and nutrient chemistry (mg kg^{-1}), and other physiochemical parameters: depth (cm), DO (mg l^{-1}), and conductivity (μS cm^{-1}).

"na" = not analysed, and "<dl" = less than detectable levels. Site "FB" is the field blank for trace metal analysis (values shown have not been corrected for field blank metal concentrations).

Site	Depth	pH	Temp	Cond	DO	TOC	DRP	NO_3
HP5	70	7.47	0.9	4700	nd	7.4	0.003	76
CG	10	7.20	7.1	2000	4.5	1.7	0.01	201
TR	45	6.96	3.1	850	14.9	1.1	0.003	28.5
NT	23	6.96	−0.1	390	nd	nd	nd	18.9
GW2	30	6.80	3.5	3800	12.7	6.8	0.001	133
GW3	60	6.88	1.5	6100	13.2	15	0.032	313
GW4	50	7.35	5.2	5900	5.1	65	0.29	19.9
GW5	50	7.03	4.4	10500	4.1	180	0.021	24.9
GW1	0	7.56	6.3	31.9	13.0	0.60	0.001	0.40
K	0	7.21	7.1	36.0	13.9	0.60	0.002	0.74
OR	0	6.77	1.5	89.5	13.3	na	na	0.52
V1	0	8.48	3.4	536	15.5	na	na	1.4

	Cl	Na	K	Mg	Ca	HCO_3	SO_4	VOC
HP5	2600	445	68.6	251	889	47.7	529	<dl
CG	892	183	50.9	82.0	339	99.4	286	na
TR	371	58.3	19.1	35.0	153	53.3	73.0	<dl
NT	106	58.0	4.41	11.1	48.1	78.2	83.4	na
GW2	1905	319	56.2	186	679	52.1	436	<dl
GW3	3359	456	79.4	366	1256	69.4	657	<dl
GW4	3230	644	129	323	951	345	772	<dl
GW5	6302	1707	253	639	1396	354	1295	<dl
GW1	5.9	3.7	1.3	1.1	4.9	11.8	4.2	<dl
K	8.3	4.3	2.8	1.2	5.0	3.8	4.3	<dl
OR	5.5	2.8	1.5	1.5	4.8	14.8	3.3	na
V1	246	49.5	12.5	17	76	43.2	19.4	na

	Fe	Mn	Cu	Pb	Zn	Cd	Ag	Ni	Co
GW2	<dl	73	10	0.28	4.0	0.41	0.10	<dl	2.3
GW3	<dl	1800	18	0.29	11	0.59	0.05	18	14
GW4	34	2200	23	1.4	17	0.73	0.08	29	15
GW5	250	2490	25	4.4	15	1.7	0.02	99	53
TR	77	15	2.3	0.24	3.1	0.06	0.02	1.5	0.7
HP5	<dl	26	9.8	0.20	10	0.28	0.04	1.1	3.3
NT	17	1.2	1.5	0.05	2.2	0.01	0.02	0.3	0.2
CG	21	0.6	2.9	0.07	4.2	0.08	0.02	<dl	1.1
GW1	38	0.7	0.47	0.04	0.87	0.01	0.03	0.4	0.06
K	48	1.1	0.78	0.10	3.0	0.07	0.03	0.7	0.06
OR	3	0.4	0.2	0.03	0.4	0.02	na	<dl	0.03
V1	9	1.3	0.5	0.06	6.8	0.13	na	<dl	0.32
FB	18	<dl	0.06	<dl	0.93	0.02	<dl	<dl	0.02

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