

Evaluation of cleanup following loss of cyanide in flight to Tolukuma (Papua New Guinea) gold mine

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ABSTRACT

On 5 April 2000 the site of impact of a crate of sodium cyanide in mountainous terrain between Port Moresby and Tolukuma Gold Mine, Papua New Guinea, was visited to determine the extent of the impact of the incident and effectiveness of cleanup. Samples of soil, sediment and water were collected variously at the Impact Site Area, along Impact Creek (the creek below the point of impact); and downstream Inai and Yaloge Rivers to the first inhabited village (Inaina Village). The water samples were collected and processed at the mine assay laboratory to minimise losses of cyanide and its complexes before dispatch by air for analysis at an accredited laboratory in Australia. Apart from cyanide as weak acid dissociable (WAD) and as total and its species, water samples were also analysed for cyanide degradation products (thiocyanate, cyanate, total nitrogen, nitrite, nitrate and ammonia), other nutrients (phosphorus) and trace elements. Soil and sediment samples were analysed for WAD and total cyanide concentrations and (%)moisture.

The study showed the following:

- That the impact site has been decontaminated. Although small cyanide residues were still present in soil and fire ash on 5 April 2000, continued removal of soil from the impact site had reduced soil cyanide to background levels,
- The species of cyanide remaining in soil at the impact site included a significant proportion of soluble cyanide forms measured as WAD cyanide. Most of the total cyanide was present as WAD cyanide. Burning of vegetation concentrated cyanide in the fire ash giving levels which were similar to those in soil,
- Levels of cyanide in Impact Creek sediment were present at much lower concentrations than those in soil at the impact. Transfer of the sediment in Impact Creek to at least the next major tributary removed the localised concentration of cyanide in sediment adjacent to the impact site, and
- Although cyanide was present in the creek sediment, the results for cyanide in water showed that the WAD cyanide concentration in Impact Creek did not exceed drinking water criteria (0.08mg/l) and that there was no detectable WAD cyanide (which includes free cyanide) in river water at the first downstream village. There is no risk from cyanide to these people through drinking the river water, based on comparison with drinking water criteria. Evidence from trace element data for cobalt (Co) which forms a very strong cyanide complex shows that rapid dilution occurs for both surface runoff and seepage through soil to Impact Creek waters. There appears to be some cyanide present from natural sources, probably vegetation. Levels of cyanide species, thiocyanate and cyanate were at respective detection limits. The results for WAD and total cyanide concentrations in water were most useful. There was no ongoing impact observed to aquatic biota in the creek.

It was concluded that there was no long term impact from the loss of cyanide and that the site, where the lost cyanide had impacted, was effectively cleaned up. © 2004 SDU. All rights reserved.

Keywords: Cyanide; Cleanup; Degradation; Environmental impact; Health effect

1. INTRODUCTION

The Tolukuma Gold Mine is a medium-scale, high-grade mining and processing operation in Papua New Guinea. It is located in mountainous terrain 100km north of Port Moresby (Figure 1).

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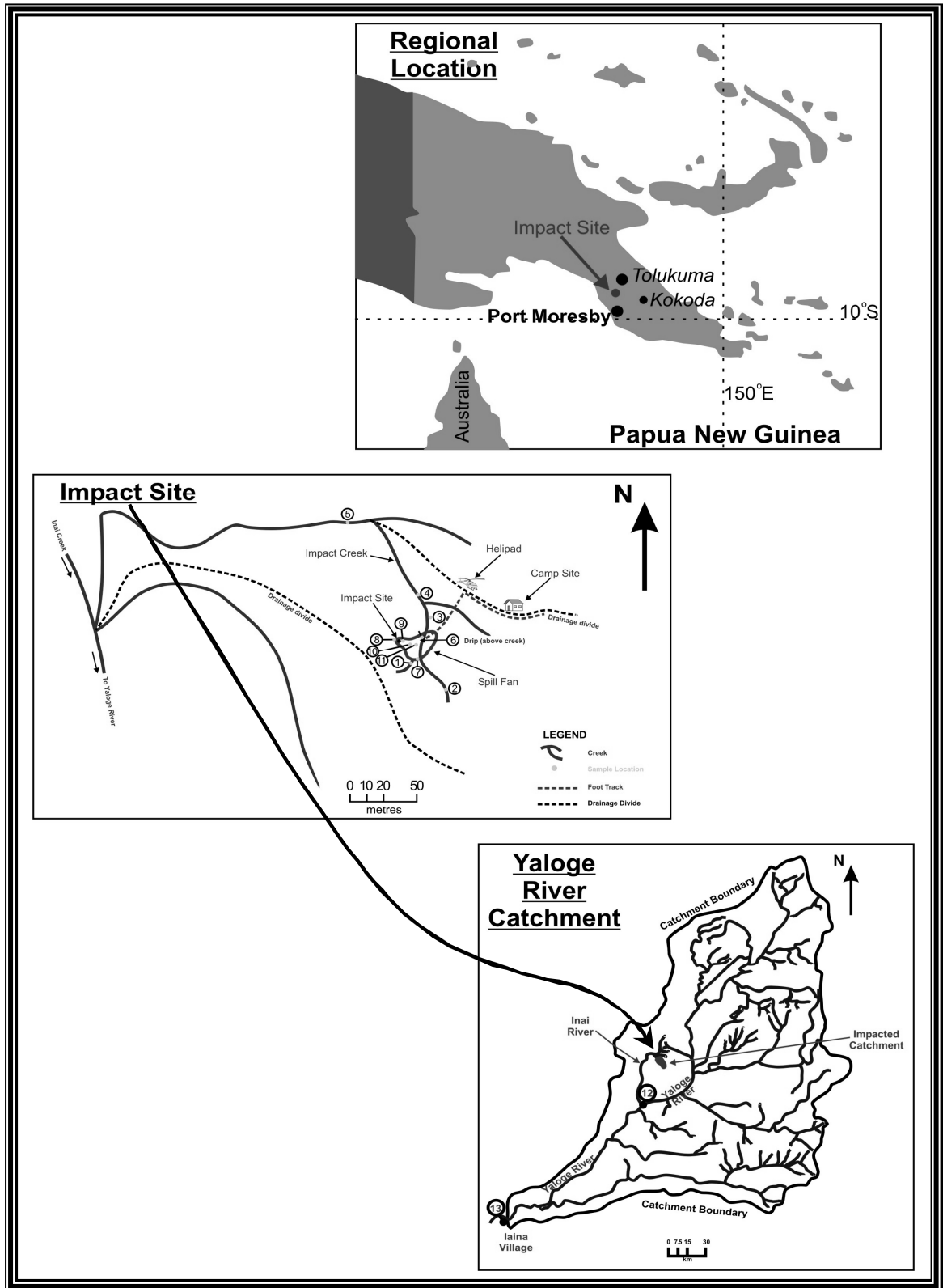


Figure 1. Maps showing regional location, Yaloge River catchment and impact site

Since the commencement of activities on site in 1995 all materials and personnel have been transported entirely by helicopters. Gold extraction is via dissolution in sodium cyanide (NaCN) solution following mining of ore and grinding. Following extraction, cyanide in tailings is destroyed prior to discharge.

On 21 March 2000, a crate of 1 tonne of sodium cyanide was lost by the mine's transport contractor from a helicopter flying to the Tolukuma Gold Mine. The site of impact was in mountainous terrain 85km north of Port Moresby, in uninhabited jungle. Access to the impact site was by helicopter, landing at a temporary clearing. Most (about 98%) of the sodium cyanide was recovered as the crate did not shatter completely. About 20kg of sodium cyanide pellets ejected from the crate and covered a diamond shaped area 50m long. This area was treated with ferrous sulphate which converts the free cyanide to ferrocyanide. The toxicity of ferrocyanide is more than 1000 times less than that of free cyanide (Dreisbach, 1983). The ferrocyanide reacts with further iron to give the precipitate of Prussian blue, a characteristic reaction indicating deactivation of cyanide. Thus any visible pellets could be treated to deactivate their toxicity. However, it was possible that pellets could have landed in the surrounding jungle and were solubilised by rainwater. The solution could then enter the creeks and flow downstream. In addition, insoluble iron cyanide, including Prussian blue, may break down slowly under UV light and release cyanide.

Another source of cyanide, which cannot be ruled out, is the natural production of cyanide containing compounds by plants (Dreisbach, 1983). It is therefore possible to have a natural background of cyanide. Following neutralisation of cyanide at the impact site trees were removed and burnt, leaving some piles of ash. Soil was manually removed, placed in bags and then taken to the mill at Tolukuma Gold Mine for processing. This was the simplest method for safe disposal of cyanide.

Creek flow at the impact site is quite heavy and is continuous; even the smallest tributaries are flowing. At the time of sampling the impact site on the morning of Wednesday 5 April 2000 a large amount of soil had already been removed from the impact site. The following examination of the site and collection of water, sediment and soil sample was undertaken entirely on 5 April 2000. Samples were stored overnight then transported to Port Moresby and Brisbane on 6 April 2000, then dispatched to respective laboratories where they arrived on 7 April 2000.

The purpose of the study was as follows:

1. Evaluate the impact site and the surrounding scatter zone to determine:
 - If the impact site has been effectively decontaminated;
 - The species of cyanide remaining at the impact site and in what form they are in and if they represent any long-term danger to the environment and the Riverine System;
 - The effectiveness of the mine recovery and residual decontamination process and any other action that should be taken to remove any further potential source of contamination.
2. Sample the downstream Riverine System to determine if the water system was contaminated or not; ie determine if there was any risk to human health.

2. MATERIALS AND METHODS

2.1. Outline of sampling program

It was proposed that the water and soil samples be examined using a comprehensive analytical scheme as follows:

1. Water samples for total cyanide and weak acid dissociable (WAD) cyanide concentrations to be processed and preserved on site following collection, according to the procedure of Schulz and Noller (1998).
2. Water samples for cyanide speciation (copper, gold, nickel, chromium and iron cyanide species) and nitrogen species (total nitrogen, nitrite, nitrate and ammonium) total phosphorus and other cyanide degradation species (thiocyanate and cyanate).
3. Water samples for scans of trace elements in samples, by ICP-MS (inductively-coupled plasma mass spectrometry) scan. Trace element patterns may indicate specific relationships to source.
4. Soil and sediment samples for total and WAD cyanide concentrations.

Water and soil / sediment samples for cyanide and nutrient-related determinations would be dispatched to the Chemistry Centre of WA, Perth. This laboratory is recognised as the Australian reference laboratory for cyanide and related determinations and is NATA (the National Association of Testing Authorities) accredited (ISO 17025). This is the only accredited laboratory in Australia for comprehensive cyanide analysis, ie including cyanide species. Water samples for ICP-MS scan of trace elements were dispatched to CHEMNORTH Pty. Ltd. Darwin. Several prepared sample bottles obtained from Queensland Health Scientific Services, Brisbane, were brought to site. A number of 1L dark plastic bottles, 250ml plain polyethylene bottles and unused polyethylene bags for soil / sediment samples were supplied by the Assay Laboratory at Tolukuma Gold Mine. The facilities of the Tolukuma Mine Assay Laboratory were also used for sample

preparation. The availability of such a facility was extremely important for undertaking the sample preparation in reasonable time to prevent loss of cyanide from water samples before dispatch for analysis.

2.2. Site visit

After an initial evaluation of the impact site, samples of water, sediment and soil were taken noting the scoping requirements and specific aspects of the terrain:

- Include samples above the point of impact,
- Assess residues remaining on the impact site,
- Assess the pathway for removal of cyanide from the impact site, particularly to Impact Creek, taking note of the ongoing site clean up,
- Assess downstream evidence of dispersion,
- Assess the ecological and environmental health impacts, to the most at risk groups downstream of the impact.

Sample collection was made in a sequential fashion taking into account all factors identified. The sample sites are shown in Figure 1. The maps showing all sample sites were prepared after returning to Tolukuma Gold Mine from the impact site on 5 April 2000.

Table 1
Sample collection details (5 April 2000)

Sample Number	Time (hr)	Sample Type	Description of Sample Collected
1	9.19	Water	Very small creek 25m adjacent to the impact site. First point of seepage as close to above the point of impact as could be sampled. Invertebrates were present.
2	9.39	Water	Impact Creek, 50m upstream of impact site (creek flowing past impact site).
3	10.14	Sediment	Impact Creek, 60m downstream of impact site.
4	10.36	Water	Invertebrates were present.
4	10.36	Sediment	Impact Creek downstream of impact site below small tributary crossing path to helicopter pad. This is a regular sampling point.
5	11.10	Water	Downstream of Impact Creek junction and longer creek (flowing to Inai Creek) below helicopter pad. This is a regular sampling point.
5	11.10	Sediment	
6	11.40	Water	Seepage drips under impact site from hanging slope, dripping (flowing to) into Impact Creek.
7	11.50	Water	Ponded surface flow adjacent impact site, flowing into Impact Creek (below 1).
7	11.50	Sediment	
8	12.00	Soil	Above impact crater, approximate 2m above in the virgin rain forest.
9	12.10	Soil	2m below impact crater.
10	12.20	Soil	9m below impact crater.
11	12.30	Soil / Ash	Fire ash at bottom of impact zone, near edge of drop to Impact Creek.
12	13.02	Water	Inai River before junction with Yaloge River (about 100m from the junction). (Very clear water)
13	13.45	Water	First downstream village (Inaina Village), downstream Yaloge River.
13	13.45	Sediment	

2.3. Sample collection, preparation, preservation and dispatch

Water samples taken at each site comprised:

- a) A 1L sample for WAD and total cyanide (500ml) processing and nutrients (no processing of remaining 500ml subsequently used for nutrient determinations);
- b) 250ml sample for cyanide speciation measurement; and
- c) 250ml sample (acid-washed bottle) for ICP-MS scan of trace elements (no processing).

Each sample bottle was rinsed three times before taking the water sample. PVC gloves, without powder, were worn most of the time during sample collection. Soil and sediment samples were taken with a garden spatula which was "wiped" in the sample a number of times before the sample was taken and placed in the plastic bag with seal.

All samples were placed in eskies containing ice as soon as possible following collection and were transported to the Tolukuma Gold Mine assay laboratory by helicopter for processing and labelling. Arrival back at Tolukuma was at 1500hr. Samples were transferred to refrigerator (4 °C) from the eskies as quickly as possible and held until processing could commence. It was necessary to set up sample handling equipment (filtration gear and pump, pH metre, wash bottles, various measuring cylinders, volumetric flasks, beakers etc). Laboratory distilled water was used for all washing and make up of solutions. It was also necessary to locate and make up various reagents:

- a) Lead carbonate for removal of sulfide. Mixing solutions of lead nitrate and sodium carbonate giving a precipitate of lead carbonate made this. As the precipitate was colloidal and difficult to filter, the lead carbonate was added to each sample during treatment as slurry (2ml using a dropping pipette). The excess reagent in the slurry was sodium carbonate, which has no effect on cyanide. Sulfide displaced carbonate from lead carbonate to form lead sulfide, as the latter (PbS) is more insoluble.
- b) Sodium arsenite solution using sodium arsenate dissolved in a minimum of water and making up with concentrated hydrochloric acid. This solution was used to treat samples for oxidants. There was no sodium arsenite available on site. Although sodium arsenate does not convert quantitatively to sodium arsenite, the preparation relied on the presence of sodium arsenite in catalytic amounts. 1 ml portions of the prepared solution were added to each sample for oxidant treatment.
- c) Sodium hydroxide pellets for final pH adjustment to >12. It was found that 6 pellets achieved this pH following dissolution in the sample. The pH of each sample was checked by measuring with the laboratory pH meter (calibrated using 2 buffer solutions).

The summarised procedure for processing of water samples for total and WAD cyanide measurements is given in Table 2, based on the procedure described by Schulz and Noller (1998). The treated samples were stored in dark bottles in the refrigerator. Three treatment blanks were prepared at the start, middle and end of processing but were stored in translucent plastic bottles due to the availability of a limited number of dark bottles. All bottles used to store treated cyanide samples were rinsed vigorously with laboratory distilled water before use. This is because the history of some of these bottles was not known and blank levels could not be checked on site. Labelling was undertaken as each sample set was processed.

Table 2

Summary of procedure used for preservation of water samples for WAD and total cyanide determination (according to Schulz and Noller, 1998)

Step	Procedure
1	Five hundreds ml of water sample were filtered through a Whatman No. 1 filter paper. The filter paper with any cyanide particulates was returned (see step 5).
2	The filtrate was transferred to a 1L bottle, 2ml lead carbonate slurry added; the contents were shaken, allowed to stand and filtered. The filter was discarded.
3	The filtrate was transferred to the dark bottle for subsequent storage. 1ml "sodium arsenate solution" was added and mixed.
4	Six sodium hydroxide pellets were added to the filtrate in the dark bottle and the pH measured by immersing the pH electrode into the filtrate bottle. If the pH did not exceed 12 an additional pellet was added.
5	The filter with cyanide particulates was transferred to the treated sample in the dark bottle and shaken.
6	The treated sample was labelled and stored in the refrigerator at 4°C.

Processing commenced at 20.30hrs and continued until 00.30hrs (6 April). Packaging of samples in eskies for transport was undertaken before leaving Tolukuma Gold Mine on the morning of 6 April. Copies of AQIS (Australian Quarantine Inspection Service) permits to import water and soil samples into Australia were obtained by fax from the various laboratories used for analytical work. Each laboratory was sent a list of samples and details of analyses required by fax from Brisbane. Both laboratories confirmed arrival of respective samples on Friday 7 April 2000.

3. RESULTS AND DISCUSSION

The results are summarised in the following tables:

- Table 3 gives results for WAD and total, cyanide, ammonia, nitrite, nitrate, total nitrogen, total phosphorus and cyanate concentrations. Both thiocyanate (detection limit 0.1mg/l) and all cyanide species (Cu, Co, Fe 0.05mg/l, Ni 0.2mg/l and Au and Cr 0.5mg/l respectively) were at their respective detection limits which are in fact higher than the detection limits for WAD and total cyanide (<0.002mg/l). Metal cyanide species may therefore be present at concentrations below the detection limits.

- Table 4 gives results for WAD and total cyanide in soil and sediment samples. Percentage moisture in each sample is also given. Sample 13 sediment was not received by the laboratory and may have been left at Tolukuma Gold Mine. A significant amount of water is retained in soil compared with sediment.
- Table 5 gives ICP-MS scan of trace elements in water samples. These samples were acidified with ultra pure quartz distilled nitric acid following arrival at CHEMNORTH Pty. Ltd. in Darwin. No sample is removed before acidification. The results correspond to acid-leachable "total" concentrations of trace elements.
- The results in Tables 3-5 have been grouped as follows:
 - Impact Site Area,
 - Along Impact Creek, and
 - Downstream Inai and Yaloge Rivers.

This formatting enables results to be interpreted in terms of impacted area and transfer to creek and beyond.

Table 3
 Results for WAD and total cyanide, ammonia, nitrite, nitrate, total nitrogen, total phosphorus and cyanate concentrations in water samples

Sample Number and destination	WAD Cyanide (mg/l)	Total Cyanide (mg/l)	Ammonia NH ₃ -N (mg/l)	Nitrite NO ₂ -N (mg/l)	Nitrate NO ₃ -N (mg/l)	Total Nitrogen TN (mg/l)	Total Phosphorus TP (mg/l)	Cyanate CNO (mg/l)
<u>Adjacent Impact Site</u>								
1. Seepage from above site flowing adjacent	<0.002	0.03	0.03	<0.02	0.04	2.9	0.17	<0.1
7. Surface flow below Site 1	0.019	0.032	0.7	<0.02	0.09	3.4	0.31	<0.1
6. Seepage drips under impact site, above creek	0.006	0.017	0.02	<0.02	<0.02	0.02	0.13	<0.1
<u>Impact Creek</u>								
2. 50m upstream	0.003	0.016	<0.02	<0.02	0.03	0.05	0.07	<0.1
3. 60m downstream	<0.002	0.007	0.02	<0.02	0.03	0.08	0.07	<0.1
4. below tributary crossing to helicopter pad	<0.002	0.003	<0.02	<0.02	0.03	0.06	0.06	<0.1
5. Downstream of Impact creek junction with tributary of Inai River	<0.002	0.008	<0.02	<0.02	<0.04	0.06	0.05	<0.1

continued (Table 3)

Sample Number and destination	WAD Cyanide (mg/l)	Total Cyanide (mg/l)	Ammonia NH ₃ -N (mg/l)	Nitrite NO ₂ -N (mg/l)	Nitrate NO ₃ -N (mg/l)	Total Nitrogen TN (mg/l)	Total Phosphorus TP (mg/l)	Cyanate CNO (mg/l)
<u>Inai River</u>								
12. Inai River above Yaloge River	<0.002	0.008	<0.02	<0.02	0.04	0.08	0.08	<0.1
13. First Village downstream (Inaina Village)	<0.002	0.011	<0.02	<0.02	0.08	0.13	0.08	<0.1
<u>Blanks</u>								
Blank 1	0.002	0.002	N/A	N/A	N/A	N/A	N/A	<0.1
Blank 2	0.002	0.002	<0.02	<0.02	<0.02	<0.02	<0.01	<0.1
Blank 3	<0.002	0.002	<0.02	<0.02	<0.02	<0.02	<0.01	<0.1

Table 4
 Results for WAD and total cyanide concentrations in soil and sediments (dry weight basis mg/kg) and % moisture in each sample

Sample number and destination	WAD Cyanide (mg/kg)	Total Cyanide (mg/kg)	Moisture (%)
<u>Impact Site</u>			
7. Soil associated with surface flow adjacent site	25	49	40
8. Soil 2m above impact crater in virgin forest	<0.5	<0.5	40
9. Soil 2m below impact crater	130	140	35
10. Soil 9m below impact crater	140	200	44
11. Soil / Ash at bottom of impact zone	60	140	41
<u>Impact Creek</u>			
2. Sediment 50m upstream	<0.5	0.6	13
3. Sediment 60m downstream	2.4	4.3	19
4. Sediment below tributary crossing to helicopter pad	<0.5	0.5	17
5. Sediment downstream of Impact Creek junction with tributary of Inai River	<0.5	<0.5	23

3.1. Cyanide degradation products and nutrients in water

Both free cyanide and its degradation product are all nutrients when present at concentrations that biota can take up and assimilate. Reference has already been made to the likelihood that cyanide is present in creek water from natural sources, probably plants (Dreisbach, 1983). This is based on the observation of measurable total cyanide upstream and at downstream Yaloge River (Table 3). Although the total concentration is low, it is nevertheless above the detection limit. The higher level of ammonia observed at Site 7 is clearly a degradation product of cyanide but not present in seepage, ie it is absorbed in soil (Table 3). This is the expected behaviour of ammonia in soil. Both nitrite and nitrate concentrations are low although nitrate at Site 7 is probably derived from cyanide degradation. There is no detectable nitrite or nitrate from seepage through soil. The presence of high total nitrogen concentrations at Sites 1 and 7 (Table 3) shows a soil/plant association rather than indicating the degradation products of cyanide. The sum of cyanide and ammonia concentrations show a large difference from total nitrogen indicating that most of the nitrogen is present in organic forms of nitrogen, ie derived from plant decay. A similar situation exists for total phosphorus, which is derived from plant / soil interactions (Table 3).

Table 5
 Results for trace elements in water samples (ppb)

Element	Ag	Al	Al	As	Au	B	Ba	Be	Bi	Br	Ca	Ca	Cd	Ce
Adjacent Impact site														
1. Seepage from above site flowing adjacent	0.04	>LWR	8590	1.21	<0.01	1.9	41.22	0.3	0.09	3	461	-	0.09	5.90
7. Surface flow below Site 1	0.01	>LWR	8411	1.81	<0.01	7.5	87.53	0.1	0.07	4	>LWR	4993	0.04	7.45
6. Seepage drips under impact site, above creek	<0.01	681.72	-	0.48	<0.01	1.8	19.41	<0.1	<0.01	1	818	-	<0.02	1.53
Impact Creek	0.01	68.14	-	0.26	<0.01	4.1	15.85	0.1	<0.01	1	>LWR	5955	<0.02	0.06
2. 50m upstream	0.01	97.90	-	0.51	<0.01	3.0	16.68	<0.1	<0.01	1	>LWR	5975	0.03	0.10
3. 60m downstream	<0.01	131.68	-	0.30	<0.01	2.6	15.90	<0.1	<0.01	1	>LWR	5585	<0.02	0.12
4. Below tributary crossing to helicopter pad	<0.01	58.29	-	0.41	<0.01	5.4	8.58	<0.1	<0.01	1	>LWR	4233	<0.02	0.08
5. Downstream of Impact Creek junction with tributary of Inai River	0.03	92.92	-	0.47	<0.01	5.4	6.64	0.1	<0.01	2	>LWR	5209	0.03	0.07
Inai River	0.10	262.32	-	0.63	<0.01	5.6	6.19	<0.1	<0.01	2	>LWR	6861	0.04	0.19
12. Inai River above Yaloge River	0.10	262.32	-	0.63	<0.01	5.6	6.19	<0.1	<0.01	2	>LWR	6861	0.04	0.19
13. First Village downstream (Inaina Village)	0.10	262.32	-	0.63	<0.01	5.6	6.19	<0.1	<0.01	2	>LWR	6861	0.04	0.19
Adjacent Impact site														
1. Seepage from above site flowing adjacent	0.04	>LWR	8590	1.21	<0.01	1.9	41.22	0.3	0.09	3	461	-	0.09	5.90
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Impact Creek	0.01	68.14	-	0.26	<0.01	4.1	15.85	0.1	<0.01	1	>LWR	5955	<0.02	0.06
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3. 60m downstream	<0.01	131.68	-	0.30	<0.01	2.6	15.90	<0.1	<0.01	1	>LWR	5585	<0.02	0.12
4. Below tributary crossing to helicopter pad	<0.01	58.29	-	0.41	<0.01	5.4	8.58	<0.1	<0.01	1	>LWR	4233	<0.02	0.08
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Inai River	0.10	262.32	-	0.63	<0.01	5.6	6.19	<0.1	<0.01	2	>LWR	6861	0.04	0.19
12. Inai River above Yaloge River	0.10	262.32	-	0.63	<0.01	5.6	6.19	<0.1	<0.01	2	>LWR	6861	0.04	0.19
Yaloge River	0.10	262.32	-	0.63	<0.01	5.6	6.19	<0.1	<0.01	2	>LWR	6861	0.04	0.19
13. First Village downstream (Inaina Village)	0.10	262.32	-	0.63	<0.01	5.6	6.19	<0.1	<0.01	2	>LWR	6861	0.04	0.19

continued (Table 5)

Element	Ho	I	In	K	La	Li	Lu	Mg	Mg	Mn	Mn	Mo	Na	Nb
Adjacent Impact site														
1. Seepage from above site flowing adjacent	0.07	<5	<0.01	393	2.50	5.0	0.02	421	-	43.09	-	0.31	842	0.26
7. Surface flow below Site 1	0.09	<5	<0.01	2266	2.99	7.3	0.02	>LWR	1325	>LWR	1170	0.26	5615	0.58
6. Seepage drips under impact site, above creek	0.07	<5	<0.01	277	0.96	3.9	0.01	594	-	>LWR	207	0.02	1193	0.03
Impact Creek	<0.01	<5	<0.01	985	0.03	1.2	<0.01	>LWR	1336	1.16	-	0.09	3688	<0.02
2. 50m upstream	<0.01	<5	<0.01	1062	0.05	1.5	<0.01	>LWR	1358	11.12	-	0.08	3818	<0.02
3. 60m downstream	<0.01	<5	<0.01	990	0.06	1.1	<0.01	>LWR	1274	11.54	-	0.08	3423	<0.02
4. Below tributary crossing to helicopter pad	<0.01	<5	<0.01	653	0.04	1.3	<0.01	738	-	3.72	-	0.07	3082	<0.02
5. Downstream of Impact Creek junction with tributary of Inai River	<0.01	<5	<0.01	863	0.03	1.1	<0.01	>LWR	1988	2.42	-	0.10	2544	<0.02
Inai River	<0.01	<5	<0.01	1025	0.09	0.9	<0.01	>LWR	2764	8.76	-	0.11	2504	<0.02
12. Inai River above Yaloge River	<0.01	<5	<0.01	1025	0.09	0.9	<0.01	>LWR	2764	8.76	-	0.11	2504	<0.02
Yaloge River	<0.01	<5	<0.01	1025	0.09	0.9	<0.01	>LWR	2764	8.76	-	0.11	2504	<0.02
13. First Village downstream (Inaina Village)	<0.01	<5	<0.01	1025	0.09	0.9	<0.01	>LWR	2764	8.76	-	0.11	2504	<0.02

continued (Table 5)

Element	Nd	Ni	Os	Pb	Pd	Pr	Pt	Rb	Re	Ru	Sb	Sc	Se	Sm	S-SO ₄
Adjacent Impact site															
1. Seepage from above site flowing adjacent	2.95	3.44	<0.1	5.21	<0.01	0.63	<0.01	3.55	<0.05	<0.01	0.05	2.8	<0.2	0.62	1108
7. Surface flow below Site 1	3.56	5.66	<0.1	3.83	<0.01	0.77	<0.01	5.00	<0.05	<0.01	0.03	3.3	0.2	0.73	38840
6. Seepage drips under impact site, above creek	1.41	1.06	<0.1	0.75	<0.01	0.29	<0.01	0.65	<0.05	<0.01	<0.01	0.7	<0.2	0.37	7142
Impact Creek	0.03	0.04	<0.1	0.15	<0.01	<0.01	<0.01	1.98	<0.05	<0.01	<0.01	1.5	<0.2	<0.01	2418
2. 50m upstream	0.05	0.58	<0.1	0.43	<0.01	0.01	<0.01	2.01	<0.05	<0.01	<0.01	1.5	<0.2	0.01	2974
3. 60m downstream	0.07	0.04	<0.1	0.12	<0.01	0.01	<0.01	1.93	<0.05	<0.01	<0.01	1.4	<0.2	0.01	2824
4. Below tributary crossing to helicopter pad	0.05	0.37	<0.1	0.02	<0.01	<0.01	<0.01	1.01	<0.05	<0.01	<0.01	1.1	<0.2	0.01	3983
5. Downstream of Impact Creek junction with tributary of Inai River	0.04	0.42	<0.1	0.41	<0.01	<0.01	<0.01	2.56	<0.05	<0.01	<0.01	1.3	<0.2	<0.01	3051
12. Inai River above Yaloge River	0.11	0.44	<0.1	0.97	<0.01	0.02	<0.01	3.57	<0.05	<0.01	0.02	1.5	<0.2	0.02	3155
Yaloge River															
13. First Village downstream (Inaina Village)															
Element	Sr	Ta	Tb	Te	Th	Ti	Tl	Tm	U	V	W	Y	Yb	Zn	Zr
Adjacent Impact site															
1. Seepage from above site flowing adjacent	9.25	<0.01	0.07	<0.1	1.01	335	0.06	0.03	0.177	17.68	0.05	1.58	0.12	12.4	5.74
7. Surface flow below Site 1	53.39	<0.01	0.09	<0.1	1.08	448	0.06	0.03	0.180	20.97	0.05	2.65	0.18	22.5	5.71
6. Seepage drips under impact site, above creek	9.36	<0.01	0.07	<0.1	0.07	9	<0.01	0.02	0.006	0.67	<0.01	2.07	0.09	8.3	0.18
Impact Creek	86.25	<0.01	<0.01	<0.1	<0.01	2	<0.01	<0.01	<0.001	1.36	<0.01	0.03	<0.01	1.5	<0.05
2. 50m upstream	86.59	<0.01	<0.01	<0.1	<0.01	3	<0.01	<0.01	0.002	1.36	<0.01	0.05	0.03	6.4	<0.05
3. 60m downstream	81.97	<0.01	<0.01	<0.1	<0.01	6	<0.01	<0.01	0.001	1.39	<0.01	0.06	<0.01	1.1	<0.05
4. Below tributary crossing to helicopter pad	50.41	<0.01	<0.01	<0.1	<0.01	2	<0.01	<0.01	0.002	0.60	<0.01	0.04	0.02	4.7	<0.05
5. Downstream of Impact Creek junction with tributary of Inai River	53.03	<0.01	<0.01	<0.1	<0.01	4	<0.01	<0.01	0.006	1.86	<0.01	0.04	0.02	11.3	0.05
Inai River															
12. Inai River above Yaloge River	61.79	<0.01	<0.01	<0.1	<0.01	10	<0.01	<0.01	0.009	3.68	0.01	0.11	0.03	10.6	0.13
Yaloge River															
13. First Village downstream (Inaina Village)															

3.2. Indicative trace elements in water

An examination of the sets of trace element given in Table 5 shows various associations:

(a) Trace elements derived from soil.

Comparison of Sites 1, 7 and to some extent 6 with other data shows a relationship with runoff including contact with soil: Fe, Al, Ti, Ga, V, W, Zr, Th, rare earth elements and to a lesser extent Cr, Cu, Mn and Ni. Visual examination of the water sample indicated the presence of suspended particles derived directly from soil.

(b) Trace elements derived from treatment of soil, not present above impact area and not in background creek or river waters.

The presence of Fe and SO₄ in surface runoff (Site 7) and the seepage through soil (Site 6) but not at Site 1 show an indication of the presence of ferrous sulfate from cyanide treatment. Of all the elements Co and to a lesser extent Y are uniquely present at levels only at Sites 7 and 6 and in excess of that derived from Site 1.

The presence of cobalt at levels 10 times those coming from soil alone is hypothesised to be elevated because:

- Cobalt is probably an impurity in the ferrous sulfate, due to the chemical similarity between iron and cobalt
- Cobalt forms one of the strongest complexes with cyanide and probably exists as the anionic cobalt cyanide complex which is quite stable and not easily broken down. Because cobalt levels in the creek water are very low, the dramatic decrease in cobalt concentration is demonstrating that its dispersion and that of cyanide, by dilution in creek water is quite effective. If present as the cobalt cyanide complex, such cyanide species are also being rapidly dispersed. Whilst most trace elements are attenuated during passage of water through soil (Category (a)), cobalt is not. This supports its presence in the seepage at Site 6 as an anionic complex as they are not absorbed by soil.

(c) Trace elements in downstream waters at levels, which are lower than or similar to water in contact with, soil at the impact site.

These elements tend to be the soluble ones: B, Ca, Mg, Na, Sulfate (S-SO₄), and Sr. Their respective concentrations show relatively uniform levels at the various points in the catchment.

3.3. Cyanide in soil and sediment

The total cyanide in soil at Site 8 is relatively low and probably reflects a natural background (Table 4). The total cyanide levels at Sites 8, 9, 10 and 11 are indicative of cyanide contamination as they are accompanied by measurable WAD cyanide levels. Also the levels of both WAD and total cyanide at Site 11 compared with Sites 9 and 10 indicate that burning of vegetation at the impact site did not give volatilisation of cyanide. In fact the degradation product of ferrocyanide is cyanide (Vogel, 1965). Sediment levels of both WAD and total cyanide at Sites 2, 4 and 5 show background levels both upstream and well downstream of the impact site. However, at Site 3 there are appreciable levels of both WAD and total cyanide in the creek sediment indicating that creek sediment may be contaminated from the point of impact to at least 100m downstream (Site 4).

3.4. General findings

A summary of relevant health and environment criteria is given in Table 6. It is clear that the drinking water criteria for both NH&MRC/ARMCANZ (1996), (0.08mg/l) and WHO (1993), (0.07mg/l) are not exceeded in the downstream waters from the impact site for samples taken on 5 April 2000. River water at the first village downstream, Inaina Village shows the WAD cyanide to be at the detection limit but that there is some detectable total cyanide, believed to be associated with natural vegetation sources. Even the waters in Impact Creek did not exceed drinking water criteria. Further evidence for the lack of any likely impact from cyanide in downstream water is made by simple comparison of catchment areas indicating the predicted dilution.

Figure 1 shows the whole of catchment of the Yalogue River above Inaina village, which corresponds to an area of 449km². This compares with 0.27km² for the catchment of Impact Creek or a ratio of 1: 1663. A more accurate "impacted" catchment area corresponds to the area of the impact site alone. Allowing for some scatter of cyanide pellets an area 200m x 200m is not unreasonable, corresponding to an area of 0.04km² and giving a dilution of 1: 11225. To exceed drinking water criteria of 0.08mg/l cyanide at Inaina Village would require a measured concentration of 898mg/l cyanide at the entry to the creek leaving the impact site continuously. The best comparison is with the measured WAD cyanide concentration at Site 7, which was 0.019mg/l (Table 3). The dilution process is supported by the observations of Co concentration (Table 5) leaving the impacted site. Even if some cyanide is present in surface runoff and seepage through soil, dilution is rapid. Any cyanide in solution which is able to percolate through soil is reduced in

concentration by a factor of 2 (Table 3). For ammonia the reduction in concentration is to background levels. Therefore it is beneficial to have runoff from the impacted area to seep through soil before it reaches the creek below.

The levels of WAD cyanide in soils at Sites 9, 10 and 11 were measurable within the impact site but these values were not considered to be of significance as they would not have exceeded a lethal dose if ingested. The lethal dose of cyanide salts is 2mg/kg body weight (Table 6). It was very unlikely that the residual cyanide would present a hazardous site because removal of contaminated soil was continued until it was all removed from the impact site. Reduction of any residual hazard from creek sediment was undertaken by flushing sediment in the tributary creek below the site of impact into the first main creek a few hundred metres downstream. This ensured further dispersal to reduce the localised sediment concentration near the impact site. Thiocyanate and cyanate concentrations were not present at levels which could be toxic to aquatic biota (Table 6). A similar general finding can be made for environmental levels in the creek waters. These also do not exceed the ANZECC (1992) Criteria of 0.005mg/l for free cyanide in fresh waters when compared with the concentrations for WAD cyanide. In fact the presence of invertebrates, observed in Impact Creek confirms that the criteria are real.

Table 6
 Summary of health and environmental criteria

Human Health	
NH&MRC/ARMCANZ (1996) criteria for cyanide in drinking water	0.08mg/l (based on 2L/day average consumption for a 70kg adult).
WHO (1993) guideline for cyanide	0.07mg/l (based on 2L/day average consumption for a 60kg adult).
Lethal dose LD 50 (mg/kg) (Dreisbach, 1983)	Cyanide salts 2 Ferricyanide 1600 Ferrocyanide 1600
Ecological	
Free cyanide in fresh and marine waters (ANZECC, 1992)	0.005mg/l
Toxicity to fish LC50 (Environment Australia, 1998)	Thiocyanate 50-200mg/l Cyanate 34-54mg/l
Toxic level of cyanide to birds (Smith and Mudder, 1991)	50mg/l

3.5. Significance of cyanide and related species

The analytical procedures used to measure both WAD and total cyanide are able to detect down to 0.002mg/l. This is well below the drinking water criteria and sufficiently lower than ecological criteria for freshwaters given in Table 6. The analytical technique employed for cyanide speciation is not as sensitive (0.05 up to 0.5mg/l depending on cyanide species) and therefore prevented the measurement of cyanide species concentrations in samples as listed (Table 3). The measured concentrations of Cu, Co, Fe, Ni, Au, and Cr (Table 5) in creek waters compared with WAD and total cyanide concentrations show that the concentrations of respective cyanide species must also be low. In the case of Fe, most is present in non-cyanide forms.

The partially degraded forms of cyanide, thiocyanate and cyanate both have a detection limit of 0.1mg/l. All samples were at the detection limit for both thiocyanate and cyanate. Both are less toxic than free cyanide and forms present as WAD cyanide. The concentrations of both ions in the samples listed in Table 3 are considered to be of little significance. The degradation of cyanide also gives rise to the formation of nitrite, nitrate and ammonia. Of these three forms only ammonia is present at any concentrations of consequence (Table 3). Ammonia may be toxic to aquatic biota. It is, however, only measurable at Site 7 (Table 3) and is quickly diluted in Impact Creek. Seeping through soil removes ammonia (see above).

3.6. Stability of cyanide compounds in the tropics

Whilst the impact of the spill described in this study is almost trivial, it is appropriate to elaborate on the fate of cyanide and its compounds under tropical conditions. It is known that cyanide breaks down via biological oxidation to bicarbonate and ammonia (Environment Australia, 1998). Hydrogen cyanide gas in air is oxidised to ammonia and carbon dioxide. Cyanide complexes with metals such as nickel, copper and zinc undergo oxidation and are destroyed releasing free metal ions for subsequently complexing, eg with organic matter. The complexes of iron with cyanide pose the greatest threat because complexes including ferrocyanide and ferricyanide are broken down under UV light to release cyanide. Under tropical conditions and where cyanide may be treated with ferrous sulfate to give ferrocyanide and ferricyanide, exposure of soil to light can pose a threat if allowed to remain even though the toxicity of both complexes is much less

than free cyanide (Table 6). It is therefore appropriate to remove contaminated soil from site and process it through the mill at the mine site where there is a final degradation step to destroy the residual cyanide. Ultimately it is important to have monitoring data for both soil and water which shows the boundaries of the impact. These have been demonstrated in the current study.

4. CONCLUSIONS

The study has shown the following :

- That most of the impact site has been decontaminated . Although cyanide residues were still present in soil and fire ash on 5 April 2000, continued removal of soil from the impact site should now reduce soil cyanide to acceptable levels;
- The species of cyanide remaining in soil at the impact site included a significant proportion of soluble cyanide forms measured as WAD cyanide. Most of the total cyanide was present as WAD cyanide. Burning of vegetation concentrated cyanide in the fire ash giving levels which were similar to those in soil;
- Levels of cyanide in Impact Creek sediment were present at much lower concentrations than those in soil at the impact site. Transfer of the sediment in Impact Creek to at least the next major tributary was used to remove the localised concentration of cyanide in sediment adjacent to the impact site; and
- Although cyanide was present in the creek sediment, the results for cyanide in water showed that the WAD cyanide concentration in Impact Creek did not exceed drinking water criteria (0.08mg/l) and that there was no detectable WAD cyanide (which includes free cyanide) in river water at the first downstream village. There is no risk from cyanide to these people through drinking the river water. Evidence from trace element data for cobalt (Co) which forms a very strong cyanide complex shows that rapid dilution occurs for both surface runoff and seepage through soil to Impact Creek waters. There appears to be some cyanide present from natural sources, probably vegetation.

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