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WATER QUALITY OF THE SURFACE WATERS AT AVOCA MINES AND THE AVOCA RIVER: Interim Report May to October, 1994.

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EXECUTIVE SUMMARY

During this interim period of six months, 42 separate surface water sites were monitored. Surface waters were classified into nine discrete source categories. These are 1. Springs and seepage from spoil; 2. Surface runoff; 3. Leachate streams; 4. River mixing zone; 5. Contaminated river; 6 .Uncontaminated surface runoff; 7. Contaminated streams containing leachate; 8. Uncontaminated river; and 9. The lake in Cronebane Pit. Each source category has a distinctive water chemistry, although there is some overlap between categories for some parameters. The mine derived waters were all significantly affected by acid mine generation on the site. While the river was severely impacted by the discharge of diluted AMD via leachate streams (adits), contaminated streams, interflow and groundwater. The results show that the Avoca mine is an active acid mine producing site causing severe surface water pollution.

While categories 1 and 2 waters can be classed as raw AMD (mean AMDI 10.0 and 24.2 respectively), the water in the leachate streams (category 3) are significantly diluted and buffered by groundwater infiltration. This category comprises of three separate leachate streams and each one is significantly different. The Shallow Adit is least diluted and so has the highest metal concentrations. While of the two that discharge into the river, the Deep Adit is the more polluting. The mean AMDI for these adits are 10.6 for the Shallow Adit, 26.6 for the Deep Adit, and 32.6 for the Ballymurtagh Adit. Compared to other similar mine sites, the leachate emanating from the Avoca mining area is highly polluting.

The river is severely impacted by the AMD (category 5) downstream of the mines, although in terms of water chemistry the river recovers fairly quickly. Two factors are influential in this recovery. First the effect of the Aughrim River which has a similar flow to the Avoca River and which is more buffered due to a small area of limestone within its sub-catchment. Secondly, the effect of the fertilizer factory (IFI) downstream of the confluence of the two rivers which discharges a large volume of strong ammonia wastewater.

The upstream uncontaminated river site shows a largely clean river with trace amounts of Zn, Fe and Cu (mean AMDI 97.0). However from the data this site may be subject to occasional AMD contamination. The absence of any surface water input would suggest that groundwater discharge is affecting the river at this site, even though this is not reflected by the biological investigations. A site further upstream should be selected for future work.

In terms of identifying and quantifying AMD, and AMD impacted surface waters, both pH and AMDI are powerful at discriminating between source categories. However, the AMDI is also able to quantify AMD contamination in terms of the strength of the AMD and the actual impact and recovery within the river.

INTRODUCTION

Due to a variety of factors, mainly prolonged illness of staff, routine monitoring of the surface waters of the mine site and the Avoca River was interrupted for a number of months. Discharge of settled sewage into the upper mine workings at Conary by the County Council also made water sampling difficult during the period of December 1993 to May 1994. In May, 1994, it was decided that routine monitoring should recommence. This was achieved by Prof. Gray carrying out the actual filed work, while Ms C. O'Neill was employed on a part-time basis to carry out the analysis. The situation was made more urgent by restrictions on access by both Wicklow County Council and the Department of Energy, constructional work carried out by the former, and finally the problem of field neutralization trials carried out under the EU LIFE programme on the site by the County Council. Attempts were made to co-ordinate the neutralization experiments, which would have altered the chemical status of the river water and sediments, as well as one of the major leachate streams, with the current project. However, these were vigorously rejected by the Council who felt as they were the Regulatory Authority in regard to the river that they should have complete priority and independence of any work done at the site. In order to attempt to complete as much of the background chemical and physical characterisation of the mine and river waters as possible, a number of temporary staff were employed to complete the work on metal fluxes in the river and the in-situ toxicity work before the neutralization trials by the Council got underway. In this Report the results of the intensive sampling of the mine and river waters from May to October, 1994 is presented.

OBJECTIVES

- To identify surface waters on the East Avoca mine site
- To characterize surface waters chemically and physically
- To assess the chemical and physical impact of AMD from both East and West Avoca mine sites on the Avoca River
- To provide a data base for modelling mine and surface water hydrology

SAMPLING SITES FOR WATER ANALYSIS

All surface waters on the East Avoca mine site were sampled. These included springs, leachate streams, surface runoff, temporary and permanent ponds and the lake at the base of the Cronebane Pit. Access to the Tigroney pit was only made available on the 13th October 1994, where there is a permanent pond fed by a stream emanating from a number of springs, therefore information on these waters is limited and is not included in the present report. The impact on the river was assessed by a sites upstream of the mines and downstream of the mines. Down stream samples were taken outside the mixing zone, and took into account the impact of dilution from the Aughrim river, leaching from Shelton Abbey, neutralization from the IFI fertilizer factory, and finally the effects of the estuary. The mixing zone was examined separately as were the various minor contaminated streams that also enter the river below the mine zone.

In all 42 separate sites were monitored, although not all were sampled regularly. For example a number of the sites dried up during the summer, or were only present during or after periods of heavy rainfall. Therefore there is a considerable variation in the number of replicate samples for each site. The sites were categorized into a number of similar groups based on source classification. These are:

1. Springs and seepage from spoil
2. Surface runoff
3. Leachate streams
4. River mixing zone
5. Contaminated river
6. Uncontaminated surface runoff
7. Contaminated streams containing leachate
8. Uncontaminated river
9. Lake in Cronebane Pit

Detailed description of sampling sites

1. Springs and seepage from spoil

1.1 Spring at the base of Mount Platt

Samples are taken from a spring which wells up from the ground and which flows into a number of pools. The site is at the north-eastern end of Mt. Platt, on the left hand side of the entrance to Cronebane Pit, and on the right hand side of the road which goes up the mountain. The flow is constant and high.

1.2 Spring feed into pond at the base of Mount Platt

These are the ponds into which 1.1 flows. They are situated approximately 4m away across the road running up the mountain. The ponds are medium sized and permanent.

1.3 Spring coming out of Mount Platt going into small ponds

This is a small spring discharging about 2m above road level on the side of Mt. Platt. The spring is situated almost at the south-western end of the heap and runs across the road into a number of small permanent ponds. The flow is usually quite low, although never quite dries up.

1.4 Small ponds fed by the spring coming out of Mount Platt

These are the ponds fed by 1.3 on the far side of the road to Mt. Platt. They eventually discharge into the forestry.

1.5 Seepage from bank downstream Miners Park

This is seepage from the exposed bank just downstream of the Miners Park, the temporary tailings pond, which is opposite the landfill site. The embankment weeps water constantly.

1.6 Seepage from river bank at Ballymurtagh leachate inlet (interflow)

Along the bank, just upstream of the weir at the outfall of the Ballymurtagh leachate stream, there is interflow discharging. This does in fact dry up in summer, but is quite heavy at other times. The interflow causes areas of red sediment often overgrown by a thick grey microbial growth.

2. Surface runoff

2.1 Surface ponds at the base of Mount Platt

These are temporary ponds located in the area to the right of the entrance to Cronebane pit. They receive surface runoff from the flat area of spoil which is very heavily compacted. Exact site located close to abandoned mine processing equipment.

2.2 Surface ponds at the edge of Mount Platt

As 2.1 but these ponds are located in the wide road that runs alongside Mt. Platt.

2.3 Surface runoff from Mount Platt

This is the main surface runoff from Mt. Platt at the south-west end close to site 1.3. The flow can be extremely heavy during persistent or heavy rain. The majority of the water falls into Tigroney Open Pit while a proportion flows down the road.

2.31 Surface runoff from midway along Mount Platt

Surface runoff from Mt. Platt about halfway along its length.

2.32 Surface runoff from North East end of Mount Platt

Surface runoff down into Cronebane Open Pit. Can be very heavy after prolonged rainfall.

2.4 Small lake (surface runoff) adjacent to Castle Howard boundary

Surface pool at the base of the spoil close to old crusher and positioned close to the Castle Howard boundary wall.

2.5 Surface runoff going into Deep Adit

This is the surface runoff channel which is connected at the exit of the Deep Adit.

2.6 Road runoff

The surface water flowing along the road and under the Railway bridge close to the Deep Adit.

2.7 Deep adit and surface runoff

The leachate and surface runoff mixed at the Deep Adit weir.

2.8 Surface runoff

Surface runoff along road between the Shallow adit and the old crusher. This does not include leachate from 3.3 which mixes with 2.8 further down the road.

3. Leachate streams

3.1 Deep Adit

The leachate only, without any surface runoff, as measured at the weir.

3.2 Ballymurtagh Adit

The Ballymurtagh leachate stream has been split into two by the council. The major flow enters the river via a weir at 3.22. The overflow passes through the council yard over a weir to the river. Therefore, while the flows from both sites are required, water samples are only taken from 3.22

3.21 Ballymurtagh Adit via council yard

See 3.2. The site is situated in the council yard along the main road from the White Bridge to Avoca.

3.22 Ballymurtagh Adit via main weir

See 3.2. The site is situated passed the council yard along the main road from the White Bridge to Avoca, downstream of site 3.21.

3.3 Shallow Adit

This is a named adit which drains the Cronebane area of the site. It has a low but reasonably constant flow.

4. River mixing zone

4.1 Deep Adit into river

These comprise a mixture of sites around the entry of the leachate from the Deep Adit into the river.

4.2 River at Miners Park

The river taken from the bank at the edge of the Miners Park

4.3 River below Ballymurtagh

These comprise a mixture of sites around the entry of the leachate from the Ballymurtagh Adit into the river.

5. Contaminated River

5.1 Avoca Bridge

Water taken at the river at Avoca Bridge from the deep central area.

5.11 Monica's site

This site is also at Avoca, but downstream of the Bridge below the septic tank outfall for the village. These samples are taken in association with the biological sampling.

5.2 Golf Club

Samples taken 50m downstream of the bridge at golf club.

5.3 Upstream IFI

Access from car park outside actual factory close to railway marshalling yard. Approximately 100m upstream of factory bridge over river.

5.4 Downstream IFI

Small lane on the left past Iropharm on the way into Arklow. Samples taken by bucket upstream of water intake station. Can be tidal, so time of sampling important.

5.5 Arklow Bridge

Water samples taken just upstream of Arklow Bridge, away from major sewage outfalls. There will be some influence from sewage, also tidal, so time of sampling important.

5.9 East side of river upstream of Deep Adit contaminated by interflow

Turbid zone immediately downstream of White Bridge but ,upstream of the entry of Deep

Adit. Samples taken from the bank from the Deep Adit side of the river, at the old site of entry of the Deep Adit to river.

6 Uncontaminated surface runoff

7. Contaminated streams containing leachate.

7.4 Shroughmore

This is a leachate stream that runs along the road some 200m down the hill from Conary Cross-roads. It dries up in the summer, and possibly receives drainage from the adjacent fields.

7.4.1 Second stream running parallel to Shroughmore

This is a parallel stream to 7.4 which runs across the fields to join 7.4 as it runs along Porters Lane.

7.5 Old leachate stream (Virgin Mary)

This was a small stream that had a small discharge that ran along the boundary wall of the council yard where 3.21 is located and the adjacent house. There was a weir installed on this stream, but the flow was too low to be recorded accurately. It also took road drainage. It has been filled in by the council and now discharges behind the house and generally has a steady but low flow.

7.6 Madam Butler's

This is a named adit which discharges from the mines through the forestry and under the Conary Tigroney West road to emerge within the yard of Murphy Farm.

7.7 Other leachate stream

This is a very small stream receiving septic tank waste. It is overgrown with sewage fungus and contains raw faecal material. The stream is heavily contaminated by AMD and discharges through Sharps Coal yard into the river.

7.8 Morans Garage

This is a large stream, contaminated with AMD as seen by the red deposition. It flows along the Red Road, under the main road where their is a weir located under the tunnel. However, this has been subject to considerable silting and maintenance problems.

7.9 Drainage from Miners' Park into river

This is the main outlet pipe draining the Miners Park. The flow is normally low.

8. Uncontaminated River

8.1 River upstream of mines

This site is approximately 300m upstream of the White Bridge opposite Moores Pub. It is uncontaminated by the mines. Access is by the steps opposite Moores Pub on the main Meetings to Avoca road.

8.2 Aughrim River

Samples are taken just upstream of the confluence of the Goldmine River at Woodenbridge.

9. Lake at base of Cronebane pit

This is the large lake at the base of Cronebane Open Pit. Samples are taken form the bank, and the flow out of the lake is noted. Variation in height can be estimated from the tide marks on the far wall. It receives surface runoff from site 2.32.

METHODS

Samples were filtered in the field through a 0.45μm pore sized cellulose nitrate filter. Routinely three separate samples were taken, each of 50 ml. One each for metal analysis, for sulphate, conductivity and pH measurement, and a separate sample for aluminium analysis. Filter papers were retained for each site and used to calculate the metal composition of the particulate fraction.

Analysis of water samples were by Standard Methods, and have been described in detail in an earlier report (Gray and Doyle, 1994). The use of the acid mine drainage index (AMDI) has also been described elsewhere (Gray, 1994).

RESULTS

The raw data is presented in appendix I, as a sorted version (by site).

Source categories

Considering sets of data from different sites under broad classifications allows some comparison between different sources of AMD and impact areas. Summary data (mean, median, range, standard deviation) for all source categories identified is given in Table 1.

The data is clustered for each source category, although there is a wide variation due to the very different nature of each site making up each category.

Category 1 included all springs and seepages associated with the spoil and mine workings. These were all very acidic in nature with a medium pH of 2.7 (range 2.4-3.3), and a high sulphate concentration of over 10,500 mg/l although there was a wide range 1,280-24,668 mg/l. Waters in this category were very rich in metals with mean values of Zn 362, Fe 1,031, Cu 243 mg/l and Cd 1,198 μg/l. Maximum values are often double this at 1,426, 2,384, 590 mg/l and 2,480 μg/l respectively. The resultant mean AMDI was 10.0, ranging from 0.8 to 28.4 (Table 1).

Table 1. Mean and median concentrations, number of samples (no.), standard deviation (sd), minimum and maximum concentrations for all the main source categories

1 Springs and seepage from spoil

Parameter	Mean	Median	No.	sd	Min	Max
pH	2.70	2.7	22	0.29	2.4	3.3
Zn mg/l	362	306	22	343	33	1526
Fe mg/l	1031	1106	22	896	33	2384
Cu mg/l	243	206	22	207	4.5	590
Cd μg/l	1198	1360	22	839	30	2480
SO4 mg/l	10579	8720	22	7599	1280	24668
Conductivity μS	8010	8510	21	4378	1750	15700
AMDI	9.99	4.70	22	10.06	0.79	28.44

2. Surface runoff

Parameter	Mean	Median	No.	sd	Min	Max
pH	2.6	2.7	16	0.51	2.1	3.6
Zn mg/l	93	26	16	141	1.2	509
Fe mg/l	1050	159	16	1767	0.75	5447
Cu mg/l	48	18	16	62	1	197
Cd μg/l	156	85	16	180	0	560
SO4 mg/l	5290	1501	16	8201	159	26050
Conductivity μS	4019	1965	16	4549	360	13900
AMDI	24.22	23.37	16	17.99	1.49	57.09

3. Leachate streams

Parameter	Mean	Median	No.	sd	Min	Max
pH	3.6	3.7	52	0.37	2.6	4
Zn mg/l	66	69	51	50	1.5	215
Fe mg/l	177	128	52	140	91	731
Cu mg/l	9.2	2.3	52	16	1.0	70
Cd μg/l	242	220	52	255	0	910
SO4 mg/l	2015	1618	52	1126	1094	6330
Conductivity μS	2490	2135	52	977	1760	5220
AMDI	26.86	28.44	52	7.28	9	36

4. Mixing zone in river

Parameter	Mean	Median	No.	sd	Min	Max
pH	4.7	4.9	8	1.0	3.4	6.1
Zn mg/l	18	2.4	8	30	0.14	70
Fe mg/l	39	9.3	8	55	0.06	127
Cu mg/l	2.2	0.41	8	3.5	0.04	8.1
Cd µg/l	73	0	8	134	0	290
SO4 mg/l	375	153	8	453	24	1104
Conductivity µS	635	240	8	750	70	1800
AMDI	59.42	66.77	8	23.89	25	87.11

5. Contaminated river

Parameter	Mean	Median	No.	sd	Min	Max
pH	6.7	6.3	87	1.3	4.3	10
Zn mg/l	0.52	0.43	87	0.40	0.01	2.7
Fe mg/l	0.80	0.38	87	1.30	0	7.2
Cu mg/l	0.04	0	87	0.06	0	0.33
Cd µg/l	0.11	0	87	1.07	0	10
SO4 mg/l	27	26	79	11	8.0	80
Conductivity µS	206	120	85	419	59	3750
AMDI	85.61	87.11	79	6.37	67.6	95.6

7. Contaminated streams containing leachate

Parameter	Mean	Median	No.	sd	Min	Max
pH	4.9	4.4	12	1.4	3.5	6.7
Zn mg/l	5.5	3.4	12	8.0	0.10	29
Fe mg/l	13.9	0.56	12	42	0	146
Cu mg/l	2.1	0.50	12	3.1	0.01	9.4
Cd µg/l	5.8	0	12	17	0	60
SO4 mg/l	507	240	11	697	26	2000
Conductivity µS	735	350	12	846	130	2620
AMDI	63.07	58.78	11	19.53	28.44	91.31

8. Uncontaminated river

Parameter	Mean	Median	No.	sd	Min	Max
pH	6.8	6.8	32	0.43	5.5	7.4
Zn mg/l	0.05	0.04	32	0.04	0	0.18
Fe mg/l	0.11	0.08	32	0.17	0	0.86
Cu mg/l	0.01	0	32	0.05	0	0.30
Cd µg/l	0	0	32	0	0	0
SO4 mg/l	6.4	6	32	28	3	19
Conductivity µS	78	74	31	29	42	220
AMDI	96.99	97.79	32	3.15	87.11	100

9. Lake at Cronebane pit

Parameter	Mean	Median	No.	sd	Min	Max
pH	2.9	2.9	5	0.04	2.9	3
Zn mg/l	13	14	5	5.1	7.4	18
Fe mg/l	37	20	5	34	8.1	88
Cu mg/l	10	9.4	5	4.7	5.4	17
Cd µg/l	40	40	5	25	10	70
SO4 mg/l	410	400	5	121	239	540
Conductivity µS	1024	1040	5	283	700	1450
AMDI	36.89	36	5	3.89	32.11	41.53

Category 2 included all surface runoff from the mine site (east side only). It was expected that the nature of the surface runoff would be highly variable and this was indeed the case for all parameters except pH. Surface runoff was all very acidic with a mean pH of 2.7 and a small range similar to category 1 from pH 2.1 to 3.6. Mean metal concentrations were less than category 1 (Table 2) at Zn 93, Fe 1,050, Cu 48 mg/l and Cd 156 µg/l. However the low pH values resulted in high maximum metal values of 509, 5,447, 197 mg/l and 560 µg/l respectively, showing that surface runoff could be as polluting as category 1 waters and more polluting than leachate (category 3). Iron concentrations were elevated in relation to the other metals. The mean sulphate concentration was 5,290 mg/l although maximum values as high as 26,050 mg/l were recorded. The AMDI reflected the variability of the other parameters and varied from a 1.5 to 57.1, with a mean value of 24.2.

Category 3 included the three main leachate streams, and in particular the two main inputs of acid mine drainage to the river. Here the AMD, as characterized in categories 1 and 2, has been diluted and buffered by ground water infiltration. The water table in the mine is lower than the surrounding water table with a net influx of ground water into the workings and adits (Flynn, 1994). This has increased the pH to an average of 3.6 with a reasonably narrow range of 2.6 to 4.0. While still rich in metals they have been diluted down to an average concentration of Zn 66 (215), Fe 177 (731), Cu 9.2 (70) mg/l and Cd 242 (910) μg/l, with maximum concentrations given in parentheses. Mean sulphate concentration was 2015 mg/l with a maximum recorded concentration of 6,330 mg/l. The leachate streams had an overall mean AMDI value of 26.9 (sd 2.8). The leachate appears similar in character and strength to the weaker surface runoff.

Category 4 includes various sites within the mixing zone of the river, and so is extremely variable. The river is clearly severely impacted in the mixing zone, with the pH in particular severely reduced compared to upstream values, ranging form 3.4 to 6.1 and with an average value of 4.7. Metal concentrations are also very elevated compared to normal river water with mean (and maximum) values of Zn 18 (70) , Fe 39 (127), Cu 2.2 (8.1) mg/l, and Cd 73 (290) μg/l. The sulphate concentration is particularly high at times ranging from 24 to 1,104 mg/l, with a mean of 375 mg/l. The AMDI has a mean of 59.4 although this ranges from 25 to 87.

Category 5 includes all the river sites downstream of the mines, excluding the mixing zone. The pH varies from 4.3 to 10.0 due to the influence of the mine and fertilizer factory (IFI) which discharges AMD and waste ammonia into the river respectively. The mean pH is 6.7. Metal concentrations are elevated compared to the uncontaminated river (site 8.1) with mean (and maximum) concentrations of Zn 0.52 (2.7) , Fe 0.80 (7.2), Cu 0.04 (0.33) mg/l, and Cd 0.11 (10) μg/l. However, over this 12 km stretch of river, there is considerable variation in all the parameters measured including sulphate (Table 1). This is reflected by the AMDI ranging from 68 to 96, with a mean value of 85.6.

Category 7 includes all the streams entering the river which are contaminated by AMD. As expected the quality of these waters vary between the quality of category 3 and 5 waters, and are similar in nature to the mixing zone (category 4). The pH is variable between 3.5 and 6.7, with a mean of 4.9. Metal concentrations are on average high, although there is a wide variability as seen in Table 1. Mean values are Zn 5.5 , Fe 13.9, Cu 2.1 mg/l, and Cd 5.8 μg/l. Sulphate ranges from 26 to 2,000 mg/l (mean 63.1 mg/l).

Category 8 includes the uncontaminated river sites within the catchment. This shows the natural variability of the rivers. For example the pH has a mean of 6.8, although it varied over the short sampling period from 5.5 to 7.4. Mean sulphate concentration was low (mean 6.4 mg/l) and the AMDI reflected the high but variable natural quality of the river which ranged from 87.1 to 100, with a mean of 97.0.

Category 9 represented a single site, the lake at the base of the Cronebane Pit. The pH was very stable at 2.9, although the metal concentrations varied due to the effects of precipitation, surface runoff and evaporation. During this period there was no other sources of discharge of water into the lake. Mean (and maximum) metal concentrations were Zn 13 (18) , Fe

57 (88), Cu 10 (17) mg/l, and Cd 40 (70) μg/l. Sulphate was low, although the SO_4:Fe ratio was very similar to that for category 1, as was the Fe:Zn and Zn:Cu ratios (Table 2).

Table 2. Summary of the mean concentrations and ratios for the main categories of surface waters at Avoca. Units as for Table 1.

	Source categories							
Parameter	1	2	3	4	5	7	8	9
pH	2.7	2.6	3.6	4.7	6.7	4.9	6.8	2.9
Zinc	362	93	66	18	0.52	5.5	0.05	13
Iron	1031	1050	177	39	0.80	13.9	0.11	37
Copper	243	48	9.2	2.2	0.04	2.1	0.01	10
Cadmium	1193	156	242	73	0.11	5.8	0.00	40
Sulphate	10579	5290	2015	375	27	507	96	410
AMDI	10	24	27	59	86	63	97	37
SO_4:Fe	1.32	1.32	0.81	0.59	0.13	0.69	0.08	0.40
Fe:Zn	1.49	1.94	7.17	8.18	13.0	2.62	5.00	1.30
Zn:Cu	2.85	11.29	2.68	2.17	1.54	2.53	2.20	2.85

Table 3 compares the means of key parameters for the source categories. In most cases source categories were significantly different. However, similarities were found: *Category 1* sources were similar to category 2 in terms of pH, Fe and sulphate. *Category 2* sources were similar to categories 3 and 4 for most parameters although not for pH which was significantly different in both cases ($p<0.001$). *Category 3* was significantly different to all other categories except categories 2 and 9 for Cu only. *Category 4* was not significantly different from category 7. It was similar to category 2 in terms of Zn and Cd. Categories 5 and 8 were also similar to category 4 for all parameters except pH and AMDI, and to category 9 except for pH, AMDI and Cu which were significantly different. *Category 5* was significantly different to the other categories except those involving the river. Similarities were identified for Zn, Fe, Cd, conductivity with category 7 sites, pH, Cu. Cd at category 8 sites, and all parameters at category 4 sites with the exception of pH and AMDI. Category 5 was not significantly different to category 9 for Fe only. *Category 7*, as already mentioned, was not significantly different to category 4 for all parameters. Similar values for Fe and Cd were found with category 8, and Fe, sulphate and conductivity with category 9. *Category 8* was significantly different to mine waters, but similarities existed with category 4 for Zn, Fe, Cu, Cd, sulphate and conductivity; category 5 for pH, Cu, Cd; category 7 for Fe and Cd; and category 9 for Fe.

pH was very powerful at discriminating between source categories, failing only to discriminate between categories 1-3, 4-7, and 5-8. AMDI also proved powerful distinguishing significant differences between all categories except

2-3 and 4-7.

Correlations between parameters for all the site data and the site data broken down into source categories is given in Table 4. When all the data is considered (n=234) then very highly significant correlations are found between all the parameters examined ($p<0.001$). The AMDI and pH are negatively correlated with all the parameters, but positively correlated with each other ($p<0.001$; $r=0.919$). Strongest correlations are seen between sulphate and conductivity ($r=0.973$), Cd and Cu ($r=939$), and between sulphate and Cu ($r=0.906$).

Category 1: Only zinc showed limited correlation with no association with Fe, Cu, Cd or sulphate ($p>0.05$), but with all the other parameters significantly correlated with each other. AMDI and pH are negatively correlated with the other parameters but positively correlated with each other ($p<0.001$). Sulphate and conductivity are very strongly correlated ($p<0.001$; $r=0.983$), and both were strongly correlated with Cd, Cu and Fe, as was AMDI.

Category 2: As before with only Zn showing poor correlations with no association with Fe, Cd or sulphate ($p>0.05$). All other parameters are significantly correlated with AMDI and pH negatively correlated with the other parameters, but positively correlated with each other ($p<0.001$). Some very strong correlations are reported in Table 4, for example between sulphate and conductivity ($r=0.985$); between Fe and both sulphate and conductivity ($r=0.999$, 0.985).

Category 3: All parameters are very highly correlated ($p<0.001$) with many r values in excess of 0.950. Interestingly, although still highly significant ($p<0.001$), the weakest correlation is between sulphate and conductivity ($r=0.490$).

Category 4: All parameters are significantly correlated with each other with extremely high levels of significance for all parameter associations due in part to the wide variation of each parameter.

Category 5: The conditions in the river downstream of the mines fluctuates widely. Unlike the previous mine-based sites a different pattern of correlations are seen. Cd is not correlated to any other parameter due to its extremely low concentrations in the river where it is normally undetectable. Zinc, Cu and Fe are found in measurable concentrations at most sites and this is reflected by significant correlations between them. Sulphate is only correlated with conductivity ($p<0.01$), while AMDI is very highly correlated to all the parameters except Cd and conductivity which are not included in the calculation of the index.

Category 7: The pH is independent of the other parameters except AMDI ($p<0.001$). All the other parameters are correlated except Cu with Zn and Fe, and Cd with Cu. The strongest correlation is between conductivity and sulphate ($P<0.001$; $r=0.998$).

Category 8: No correlations are recorded between Cd, Cu, sulphate and conductivity and the other parameters, except AMDI with Cu ($p<0.05$). The lack of correlation between parameters is partially due to the problem of measuring very low concentrations of ions in what is an extremely clean river. Correlations are recorded between pH with Zn and Fe, Zn with Fe, Conductivity with sulphate, and AMDI with pH, Zn, Fe and Cu.

Category 9: pH is positively correlated with Fe ($p<0.05$), Zn with Fe and Cu ($p<0.05$) and Cd ($p<0.001$). Cadmium is negatively correlated with sulphate ($p<0.05$) but positively with Cu ($p<0.05$). Conductivity and sulphate are correlated($p<0.05$) while AMDI is negatively correlated with Zn, Cu and Cd only.

Specific sites

Summary data for those sites where sufficient data is available (i.e. 1.1, 1.3, 1.6; 2.1, 2.32; 3.1, 3.22, 3.3; 4.1; 5.1, 5.2, 5.3, 5.4, 5.5, 5.9; 7.8; 8.1; and 9) is given in Table 5.

Table 3. Significant difference between source categories for major parameters analysed. Levels of significance are given as $p<0.05$*, $p<0.01$**, $p<0.001$***, and NS is no significant difference.

site		pH	sig	Zn	sig	Fe	sig	Cu	sig	Cd	sig	SO4	sig	Cond	sig	AMDI	sig
1	2	0.6877	NS	0.0025	**	0.9697	NS	0.0003	***	≤0.0001	***	0.0519	NS	0.0115	*	p.0095	**
1	3	≤0.0001	***	0.0006	***	0.0002	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***
1	4	0.0010	**	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	0.0008	***
1	5	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***
1	7	0.0002	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***
1	8	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***
1	9	0.0023	**	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***
2	3	≤0.0001	***	0.4667	NS	0.0672	NS	0.0268	*	0.1383	NS	0.1587	NS	0.2019	NS	0.5956	NS
2	4	0.0007	***	0.0576	NS	0.0371	*	0.0106	*	0.2195	NS	0.0304	*	0.0105	*	0.0036	**
2	5	≤0.0001	***	0.0190	*	0.0313	*	0.0078	**	0.0035	**	0.0215	*	0.0044	**	≤0.0001	***
2	7	≤0.0001	***	0.0255	*	0.0332	*	0.0103	*	0.0047	**	0.0348	*	0.0123	*	≤0.0001	***
2	8	≤0.0001	***	0.0185	*	0.0312	*	0.0078	**	0.0035	**	0.0211	*	0.0035	**	≤0.0001	***
2	9	0.0452	*	0.0387	*	0.0368	*	0.0295	*	0.0239	*	0.0311	*	0.0194	*	0.0171	*
3	4	0.0166	*	0.0020	**	≤0.0001	***	0.0089	**	0.0111	*	≤0.0001	***	≤0.0001	***	0.0063	**
3	5	≤0.0001	***	≤0.0001	***	≤0.0001	***	0.0002	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***
3	7	0.0068	**	≤0.0001	***	≤0.0001	***	0.0045	**	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***
3	8	≤0.0001	***	≤0.0001	***	≤0.0001	***	0.0002	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***
3	9	≤0.0001	***	≤0.0001	***	≤0.0001	***	0.7975	NS	≤0.0001	***	≤0.0001	***	≤0.0001	***	0.0015	**
4	5	0.0008	***	0.1394	NS	0.0925	NS	0.1268	NS	0.1711	NS	0.0667	NS	0.1553	NS	0.0175	*
4	7	0.7614	NS	0.2805	NS	0.3004	NS	0.9339	NS	0.2051	NS	0.6243	NS	0.7844	NS	0.7286	NS
4	8	0.0009	***	0.1306	NS	0.0878	NS	0.1234	NS	0.1705	NS	0.0566	NS	0.0739	NS	0.0031	**
4	9	0.0017	**	0.6523	NS	0.9494	NS	0.0188	*	0.5269	NS	0.8407	NS	0.2182	NS	0.0347	*
5	7	0.0011	**	0.0550	NS	0.2993	NS	0.0419	*	0.2766	NS	0.0455	*	0.0565	NS	0.0035	**
5	8	0.3382	NS	≤0.0001	***	≤0.0001	***	0.0503	NS	0.3201	NS	≤0.0001	***	0.0061	**	≤0.0001	***
5	9	≤0.0001	***	0.0053	**	0.0785	NS	0.0089	**	0.0249	*	0.0021	**	0.0017	**	≤0.0001	***
7	8	0.0006	***	0.0385	*	0.2757	NS	0.0400	*	0.2674	NS	0.0393	*	0.0209	*	0.0002	***
7	9	0.0004	***	0.0398	*	0.2673	NS	0.0176	*	0.0406	*	0.6640	NS	0.3113	NS	0.0013	**
8	9	≤0.0001	***	0.0046	**	0.0748	NS	0.0089	**	0.0247	*	0.0018	**	0.0017	**	≤0.0001	***

Table 4 Pearson product-moment correlation for all the data and source categories.

All data (n=210)

	pH	**Zn mg/l**	**Fe mg/l**	**Cu mg/l**	**Cdμg/l**	**SO4mg/l**	**Cond μS**	**AMDI**
pH	1.000							
Zn mg/l	-0.457	1.000						
Fe mg/l	-0.430	0.515	1.000					
Cu mg/l	-0.394	0.655	0.678	1.000				
Cdμg/l	-0.495	0.702	0.627	0.939	1.000			
SO4mg/l	-0.516	0.611	0.867	0.894	0.859	1.000		
Cond μS	-0.603	0.801	0.837	0.882	0.888	0.963	1.000	
AMDI	0.919	-0.549	-0.512	-0.491	-0.615	-0.622	-0.741	1.000

Group 1 Springs and seepage from spoil (n=21)

	pH	**Zn mg/l**	**Fe mg/l**	**Cu mg/l**	**Cdμg/l**	**SO4mg/l**	**Cond μS**	**AMDI**
pH	1.000							
Zn mg/l	-0.609	1.000						
Fe mg/l	-0.561	0.360	1.000					
Cu mg/l	-0.491	0.300	0.791	1.000				
Cdμg/l	-0.615	0.337	0.815	0.963	1.000			
SO4mg/l	-0.474	0.249	0.752	0.986	0.957	1.000		
Cond μS	-0.628	0.581	0.784	0.976	0.976	0.983	1.000	
AMDI	0.854	-0.568	-0.791	-0.814	-0.899	-0.790	-0.868	1.000

Group 2 Surface runoff (n=16)

	pH	**Zn mg/l**	**Fe mg/l**	**Cu mg/l**	**Cdμg/l**	**SO4mg/l**	**Cond μS**	**AMDI**
pH	1.000							
Zn mg/l	-0.581	1.000						
Fe mg/l	-0.613	0.416	1.000					
Cu mg/l	-0.688	0.532	0.928	1.000				
Cdμg/l	-0.507	0.444	0.920	0.855	1.000			
SO4mg/l	-0.618	0.430	0.999	0.918	0.924	1.000		
Cond μS	-0.703	0.518	0.985	0.956	0.926	0.985	1.000	
AMDI	0.820	-0.637	-0.705	-0.770	-0.793	-0.713	-0.794	1.000

Group 3 Leachate streams (n=51)

	pH	**Zn mg/l**	**Fe mg/l**	**Cu mg/l**	**Cdμg/l**	**SO4mg/l**	**Cond μS**	**AMDI**
pH	1.000							
Zn mg/l	-0.878	1.000						
Fe mg/l	-0.818	0.821	1.000					
Cu mg/l	-0.877	0.870	0.977	1.000				
Cdμg/l	-0.944	0.949	0.847	0.910	1.000			
SO4mg/l	-0.796	0.701	0.881	0.883	0.823	1.000		
Cond μS	-0.768	0.732	0.900	0.891	0.799	0.862	1.000	
AMDI	0.960	-0.917	-0.839	-0.901	-0.979	-0.803	-0.773	1.000

Group 4 River mixing zone (n=8)

	pH	**Zn mg/l**	**Fe mg/l**	**Cu mg/l**	**Cdμg/l**	**SO4mg/l**	**Cond μS**	**AMDI**
pH	1.000							
Zn mg/l	-0.824	1.000						
Fe mg/l	-0.897	0.981	1.000					
Cu mg/l	-0.813	0.995	0.977	1.000				
Cdμg/l	-0.787	0.996	0.970	0.998	1.000			
SO4mg/l	-0.904	0.970	0.995	0.960	0.953	1.000		
Cond μS	-0.924	0.963	0.996	0.956	0.946	0.996	1.000	
AMDI	0.980	-0.916	-0.964	-0.907	-0.889	-0.968	-0.978	1.000

Group 5 Contaminated river (n=79)

	pH	**Zn mg/l**	**Fe mg/l**	**Cu mg/l**	**Cdμg/l**	**SO4mg/l**	**Cond μS**	**AMDI**
pH	1.000							
Zn mg/l	-0.541	1.000						
Fe mg/l	-0.409	0.837	1.000					
Cu mg/l	-0.366	0.710	0.730	1.000				
Cdμg/l	-0.112	0.094	-0.004	0.059	1.000			
SO4mg/l	-0.111	0.059	0.157	0.205	0.161	1.000		
Cond μS	0.385	-0.196	-0.132	-0.113	-0.018	0.294	1.000	
AMDI	0.659	-0.634	-0.661	-0.584	-0.188	-0.497	0.151	1.000

Group 7 Contaminated streams containing leachate (n=11)

	pH	Zn mg/l	Fe mg/l	Cu mg/l	Cdμg/l	SO4mg/l	Cond μS	AMDI
pH	1.000							
Zn mg/l	-0.512	1.000						
Fe mg/l	-0.320	0.920	1.000					
Cu mg/l	-0.533	0.277	0.081	1.000				
Cdμg/l	-0.323	0.952	0.982	0.050	1.000			
SO4mg/l	-0.532	0.808	0.708	0.693	0.697	1.000		
Cond μS	-0.567	0.813	0.701	0.702	0.694	0.998	1.000	
AMDI	0.857	-0.774	-0.594	-0.623	-0.602	-0.822	-0.828	1.000

Group 8 Uncontaminated river (n=31)

	pH	Zn mg/l	Fe mg/l	Cu mg/l	Cdμg/l	SO4mg/l	Cond μS	AMDI
pH	1.000							
Zn mg/l	-0.503	1.000						
Fe mg/l	-0.578	0.830	1.000					
Cu mg/l	-0.199	0.078	0.124	1.000				
Cdμg/l	•	•	•	•	•			
SO4mg/l	-0.202	0.171	0.029	-0.056	•	1.000		
Cond μS	0.218	-0.343	-0.210	0.018	•	0.430	1.000	
AMDI	0.562	-0.800	-0.815	-0.379	•	-0.0871	0.165	1.000

Group 9 Lake at base of Cronebane Pit (n=5)

	pH	Zn mg/l	Fe mg/l	Cu mg/l	Cdμg/l	SO4mg/l	Cond μS	AMDI
pH	1.000							
Zn mg/l	0.540	1.000						
Fe mg/l	0.827	0.824	1.000					
Cu mg/l	0.236	0.916	0.700	1.000				
Cdμg/l	0.658	0.985	0.893	0.860	1.000			
SO4mg/l	-0.788	-0.537	-0.858	-0.389	-0.666	1.000		
Cond μS	-0.640	-0.128	-0.654	-0.076	-0.263	0.830	1.000	
AMDI	-0.317	-0.952	-0.668	-0.950	-0.886	0.278	-0.083	1.000

Table 5. Mean and median concentration, number of samples (no.), standard deviation (sd), minimum and maximum concentration for samples from each main site examined.

Site 1.1 Spring at base of Mount Platt (NE end) .

Parameter	Mean	Median	No.	sd	Min	Max
pH	2.4	2.4	6	0.05	2.4	2.5
Zn mg/l	633	350	6	511	294	1526
Fe mg/l	1050	1239	6	609	96	1626
Cu mg/l	188	206	6	58	98	252
Cd μg/l	1215	1360	6	409	550	1670
SO4 mg/l	8242	8720	6	2861	4230	11400
Conductivity μS	7812	8510	5	1990	4320	9340
AMDI	5.41	4.7	6	1.90	3.57	8.35

Site 1.3 Spring from Mount Platt (SW end)

Parameter	Mean	Median	No.	sd	Min	Max
pH	2.6	2.5	6	0.13	2.5	2.8
Zn mg/l	404	433	6	123	162	516
Fe mg/l	1484	2038	6	1078	45	2384
Cu mg/l	464	496	6	139	191	590
Cd μg/l	1915	2025	6	573	810	2480
SO4 mg/l	18339	19400	6	5895	7594	24668
Conductivity μS	12002	12390	6	3290	5850	15700
AMDI	3.71	1.93	6	4.44	0.79	12.64

Site 1.6 Seepage on western river bank (interflow)

Parameter	Mean	Median	No.	sd	Min	Max
pH	2.9	2.9	3	0.06	2.9	3.0
Zn mg/l	48	47	3	13	36	61
Fe mg/l	38	36	3	6.8	33	46
Cu mg/l	14	13	3	4.5	9.8	19
Cd μg/l	63	60	3	35	30	100
SO4 mg/l	3349	3183	3	752	2694	4170
Conductivity μS	3750	3470	3	913	3010	4770
AMDI	24.30	25	3	2.25	21.78	26.12

Site 3.22 Ballymurtagh adit leachate stream

Parameter	Mean	Median	No.	sd	Min	Max
pH	3.9	3.9	20	0.13	3.5	4.0
Zn mg/l	27	27	20	6.8	1.5	35
Fe mg/l	133	133	20	26	91	182
Cu mg/l	1.8	1.7	20	0.35	1.3	2.4
Cd µg/l	40	50	20	26	0	80
SO4 mg/l	1668	1655	20	134	1439	2050
Conductivity µS	2346	2270	20	269	2100	3310
AMDI	32.64	32.11	20	1.97	30.86	36

Site 3.3 Shallow adit leachate stream

Parameter	Mean	Median	No.	sd	Min	Max
pH	2.7	2.8	7	0.08	2.6	2.8
Zn mg/l	172	186	7	45	90	215
Fe mg/l	511	524	7	111	404	731
Cu mg/l	48	47	7	12	36	70
Cd µg/l	823	850	7	94	640	910
SO4 mg/l	4570	4800	7	1347	2780	6330
Conductivity µS	4829	4880	7	421	3970	5220
AMDI	10.61	11.11	7	0.99	9	11.86

Site 4.1 Mixing zone in river from deep adit

Parameter	Mean	Median	No.	sd	Min	Max
pH	4.7	4.6	4	1.5	3.4	6.1
Zn mg/l	33	32	4	38	0.14	70
Fe mg/l	63	62	4	72	0.06	127
Cu mg/l	4.0	3.9	4	4.6	0.04	8.1
Cd µg/l	145	145	4	167	0	290
SO4 mg/l	572	581	4	582	24	1104
Conductivity µS	928	920	4	990	70	1800
AMDI	54.03	52.01	4	33.68	25	87.11

Site 5.1 Contaminated river at Avoca Bridge

Parameter	Mean	Median	No.	sd	Min	Max
pH	5.9	5.8	31	0.6	4.6	7.2
Zn mg/l	0.73	0.68	31	0.40	0.20	2.3
Fe mg/l	1.5	1	31	1.7	0	7.2
Cu mg/l	0.06	0.05	31	0.06	0	0.28
Cd μg/l	0	0	31	0	0	0
SO4 mg/l	26	25	30	8.3	10	50
Conductivity μS	110	114	30	20	59	140
AMDI	81.01	81	30	5.22	69.44	91.31

Site 5.2 Contaminated river at Golf Club

Parameter	Mean	Median	No.	sd	Min	Max
pH	6.1	6.0	11	0.66	5.3	7.7
Zn mg/l	0.58	0.60	11	0.18	0.24	0.87
Fe mg/l	0.61	0.54	11	0.29	0.22	1.0
Cu mg/l	0.03	0.02	11	0.03	0	0.07
Cd μg/l	0.91	0	11	3.0	0	10
SO4 mg/l	28	28	11	10	10	44
Conductivity μS	113	120	11	23	62	140
AMDI	84.58	85.05	11	5.66	75.11	91.31

Site 5.3 Contaminated river upstream of IFI

Parameter	Mean	Median	No.	sd	Min	Max
pH	6.4	6.5	20	0.21	6	7
Zn mg/l	0.39	0.40	20	0.07	0.19	0.55
Fe mg/l	0.24	0.27	20	0.13	0.05	0.43
Cu mg/l	0.0	0	20	0.01	0	0.02
Cd μg/l	0	0	20	0	0	0
SO4 mg/l	25	25	20	5.2	10	31
Conductivity μS	117	117	19	17	67	149
AMDI	89.84	91.31	20	2.05	85.05	91.31

Site 5.4 Contaminated river downstream of IFI

Parameter	Mean	Median	No.	sd	Min	Max
pH	8.7	9.3	11	1.4	6.7	10.1
Zn mg/l	0.21	0.19	11	0.09	0.07	0.38
Fe mg/l	0.17	0.16	11	0.13	0	0.37
Cu mg/l	0.0	0	11	0.01	0	0.04
Cd μg/l	0	0	11	0	0	0
SO4 mg/l	24	23	11	13	11	59
Conductivity μS	188	200	11	71	75	311
AMDI	91.70	91.31	11	1.85	87.11	93.44

Site 5.5 Contaminated river at Arklow bridge

Parameter	Mean	Median	No.	sd	Min	Max
pH	8.2	8.3	11	1.2	6.2	9.5
Zn mg/l	0.20	0.19	11	0.11	0.01	0.34
Fe mg/l	0.14	0.05	11	0.16	0	0.38
Cu mg/l	0	0	11	0.02	0	0.05
Cd μg/l	0	0	11	0	0	0
SO4 mg/l	33	34	4	7.7	25	40
Conductivity μS	763	353	11	1034	145	3750
AMDI	91.33	90.25	4	3.02	89.20	95.60

Site 5.9 East side of river upstream of Deep Adit contaminated by interflow

Parameter	Mean	Median	No.	sd	Min	Max
pH	5.3	5.3	3	1	4.3	6.3
Zn mg/l	1.3	0.75	3	1.19	0.54	2.7
Fe mg/l	3.0	4.2	3	2.6	0.01	4.9
Cu mg/l	0.26	0.27	3	0.08	0.17	0.33
Cd μg/l	0	0	3	0	0	0
SO4 mg/l	40	33	3	37	8.0	80
Conductivity μS	103	120	3	38	60	130
AMDI	77.22	79.01	3	8.86	67.6	85.05

Site 7.8 Stream at Morans Garage contaminated by leachate

Parameter	Mean	Median	No.	sd	Min	Max
pH	6.7	6.7	4	0.06	6.6	6.7
Zn mg/l	0.58	0.16	4	0.88	0.10	1.9
Fe mg/l	2.15	0.44	4	3.5	0.31	7.4
Cu mg/l	0.05	0.02	4	0.06	0.01	0.14
Cd μg/l	0	0	4	0	0	0
SO4 mg/l	41	26	3	25	26	70
Conductivity μS	197	190	4	28	170	237
AMDI	86.56	91.31	3	8.23	77.05	91.31

Site 8.1 River upstream of mines

Parameter	Mean	Median	No.	sd	Min	Max
pH	6.8	6.8	32	0.43	5.5	7.4
Zn mg/l	0.05	0.04	32	0.04	0	0.18
Fe mg/l	0.11	0.08	32	0.17	0	0.86
Cu mg/l	0.01	0	32	0.05	0	0.30
Cd μg/l	0	0	32	0	0	0
SO4 mg/l	6.4	6	32	2.78	3	19
Conductivity μS	78	74	31	29	42	220
AMDI	96.99	97.79	32	3.15	87.11	100

Site 9 Lake at base of Cronebane Pit

Parameter	Mean	Median	No.	sd	Min	Max
pH	2.9	2.9	5	0.04	2.9	3.0
Zn mg/l	13	14	5	5.1	7.4	18
Fe mg/l	37	20	5	34	8.1	88
Cu mg/l	10	9.4	5	4.7	5.4	17
Cd μg/l	40	40	5	25	10	70
SO4 mg/l	410	400	5	121	239	540
Conductivity μS	1024	1040	5	283	700	1450
AMDI	36.89	36	5	3.89	32.11	41.53

Site 1.1
This was very clear, transparent, water coming from a spring at the base of Mount Platt. It is raw AMD and represents the most acidic and polluted water on the site. The pH remained constant over the sampling period although the other parameters varied. Mean (and maximum) concentrations recorded are Zn 633 (1526), Fe 1,050 (1,626), Cu 188 (252) mg/l and Cd 1,215 (1,670) μg/l. Mean (and maximum) sulphate concentration is 8,242 (11,400) mg/l and conductivity 7,812 (9,340) μS/cm. The AMDI ranged from 3.6 to 8.4 with a mean value of 5.4.

Due to the small variation in parameter concentrations few correlations were identified (Table 6). Copper is positively correlated with Cd, sulphate and conductivity ($p<0.001$), while Cd is also correlated with sulphate and conductivity ($p<0.001$). Sulphate and conductivity are significantly correlated ($P<0.01$) while zinc is negatively correlated with conductivity, AMDI and Fe ($p<0.01$). The ratio of sulphate:conductivity is 1.1, Zn:Cu 3.4 and Fe:Zn 1.7 (Table 7).

Site 1.3
The water from the spring emanating from the side of Mount Platt at the southern end is also raw AMD. Although similar to site 1.1, it has significantly more Cu and Cd with double the sulphate concentration. Mean (and maximum) concentrations recorded for key parameters are Zn 404 (516), Fe 1,484 (2,384), Cu 464 (590) mg/l, Cd 1,915 (2,480) μg/l, sulphate 18,339 (24,668) mg/l, and conductivity 12,002 (15,700) μS/cm. The mean pH is 2.6 and the AMDI 3.7 although this varies from a very low 0.8 to 12.6. The AMD became stronger during the summer as the flow diminished.

There are significant correlations between all the metals ($p<0.001$) excluding Fe, although pH is negatively correlated with Zn and Fe ($p<0.05$). AMDI is also negatively correlated with all parameters except pH. Sulphate and conductivity is very highly significantly correlated ($p<0.001$) (Table 6). The ratio of sulphate:conductivity is 1.5, Zn:Cu 0.9, and Fe:Zn 3.7 (Table 7).

Site 1.6
This site is different to the other sites in category 1 as it is interflow entering the river. It has a very different nature compared to either sites 1.1 or 1.3, being significantly less acidic (mean pH 2.9) and less contaminated. This is reflected by the higher mean AMDI of 24.3 (range 21.9-26.1). Mean (and maximum) parameter concentrations are Zn 48 (61), Fe 38 (46), Cu 14 (19) mg/l, Cd 63 (100) μg/l, sulphate 3,349 (4,170) mg/l, and conductivity 3,750 (4,770) μS/cm. It is much similar in nature to the leachate indicating that this AMD has been diluted by groundwater (Table 5).

Correlations are similar to those for site 1.3 with all the metals, excluding Fe, sulphate, conductivity and AMDI, significantly correlated. pH is only significantly (and negatively) correlated with Fe ($p<0.05$), while sulphate and conductivity were very highly correlated ($P<0.001$; $r=0.997$). The ratio of sulphate:conductivity is 0.9, Zn:Cu 3.4 and Fe:Zn 0.8.

Table 6 Pearson product-moment correlation for all major indivdual sites.

Site 1.1 Spring at base of Mount Platt (NE end) (n=5)

	pH	**Zn mg/l**	**Fe mg/l**	**Cu mg/l**	**Cdμg/l**	**SO4mg/l**	**Cond μS**	**AMDI**
pH	1.000							
Zn mg/l	-0.429	1.000						
Fe mg/l	0.679	-0.164	1.000					
Cu mg/l	0.587	-0.777	0.511	1.000				
Cdμg/l	0.569	-0.751	0.458	0.995	1.000			
SO4mg/l	0.457	-0.793	0.438	0.979	0.969	1.000		
Cond μS	0.469	-0.951	0.426	0.980	0.992	0.947	1.000	
AMDI	-0.567	0.086	-0.970	-0.524	-0.478	-0.482	-0.478	1.000

Site 1.3 Spring from Mount Platt (SW end) (n=6)

	pH	**Zn mg/l**	**Fe mg/l**	**Cu mg/l**	**Cdμg/l**	**SO4mg/l**	**Cond μS**	**AMDI**
pH	1.000							
Zn mg/l	-0.773	1.000						
Fe mg/l	-0.826	0.732	1.000					
Cu mg/l	-0.698	0.992	0.715	1.000				
Cdμg/l	-0.644	0.978	0.618	0.989	1.000			
SO4mg/l	-0.578	0.933	0.527	0.950	0.982	1.000		
Cond μS	-0.680	0.975	0.608	0.976	0.993	0.979	1.000	
AMDI	0.740	-0.985	-0.759	-0.985	-0.956	-0.903	-0.934	1.000

Site 1.6 Seepage on western river bank (interflow) (n=3)

	pH	**Zn mg/l**	**Fe mg/l**	**Cu mg/l**	**Cdμg/l**	**SO4mg/l**	**Cond μS**	**AMDI**
pH	1.000							
Zn mg/l	-0.069	1.000						
Fe mg/l	0.975	-0.287	1.000					
Cu mg/l	-0.109	0.999	-0.325	1.000				
Cdμg/l	-0.082	1.000	-0.300	1.000	1.000			
SO4mg/l	-0.192	0.992	-0.403	0.996	0.994	1.000		
Cond μS	-0.266	0.980	-0.472	0.987	0.983	0.997	1.000	
AMDI	0.269	-0.979	0.475	-0.987	-0.982	-0.997	-1.000	1.000

Site 2.1 Surface runoff in ponds at base of Mount Platt (n=3)

	pH	Zn mg/l	Fe mg/l	Cu mg/l	Cdμg/l	SO4mg/l	Cond μS	AMDI
pH	1.000							
Zn mg/l	-0.979	1.000						
Fe mg/l	-0.971	0.999	1.000					
Cu mg/l	-1.000	0.974	0.966	1.000				
Cdμg/l	-0.972	0.999	1.000	0.966	1.000			
SO4mg/l	-0.973	1.000	1.000	0.968	1.000	1.000		
Cond μS	-0.994	0.996	0.992	0.991	0.992	0.993	1.000	
AMDI	0.999	-0.989	-0.983	-0.997	-0.983	-0.984	-0.998	1.000

Site 2.32 Surface runoff from NE end of Mount Platt (n=4)

	pH	Zn mg/l	Fe mg/l	Cu mg/l	Cdμg/l	SO4mg/l	Cond μS	AMDI
pH	1.000							
Zn mg/l	-0.690	1.000						
Fe mg/l	-0.534	-0.044	1.000					
Cu mg/l	-0.583	0.048	0.995	1.000				
Cdμg/l	-0.420	-0.196	0.988	0.970	1.000			
SO4mg/l	-0.594	0.012	0.997	0.996	0.977	1.000		
Cond μS	-0.647	0.082	0.990	0.995	0.960	0.997	1.000	
AMDI	0.894	-0.513	-0.824	-0.867	-0.731	-0.859	-0.893	1.000

Site 3.1 Deep Adit leachate stream (n=23)

	pH	Zn mg/l	Fe mg/l	Cu mg/l	Cdμg/l	SO4mg/l	Cond μS	AMDI
pH	1.000							
Zn mg/l	0.316	1.000						
Fe mg/l	-0.092	0.015	1.000					
Cu mg/l	-0.349	0.138	0.569	1.000				
Cdμg/l	-0.227	0.340	0.702	0.795	1.000			
SO4mg/l	-0.177	-0.431	-0.105	-0.119	0.001	1.000		
Cond μS	0.075	-0.077	-0.595	-0.488	-0.611	-0.359	1.000	
AMDI	0.694	-0.193	-0.332	-0.727	-0.715	0.000	0.270	1.000

Site 3.22 Ballymurtagh Adit leachate stream (n=20)

	pH	**Zn mg/l**	**Fe mg/l**	**Cu mg/l**	**Cdμg/l**	**SO4mg/l**	**Cond μS**	**AMDI**
pH	1.000							
Zn mg/l	0.673	1.000						
Fe mg/l	0.044	0.104	1.000					
Cu mg/l	0.349	0.553	0.264	1.000				
Cdμg/l	-0.258	-0.220	0.132	-0.733	1.000			
SO4mg/l	-0.289	-0.294	0.717	0.107	-0.004	1.000		
Cond μS	-0.179	-0.136	-0.018	-0.144	0.120	0.193	1.000	
AMDI	0.373	0.247	-0.391	0.509	-0.886	-0.243	-0.156	1.000

Site 3.3 Shallow Adit leachate stream (n=7)

	pH	**Zn mg/l**	**Fe mg/l**	**Cu mg/l**	**Cdμg/l**	**SO4mg/l**	**Cond μS**	**AMDI**
pH	1.000							
Zn mg/l	-0.522	1.000						
Fe mg/l	-0.358	0.448	1.000					
Cu mg/l	-0.317	0.327	0.955	1.000				
Cdμg/l	-0.607	0.588	0.166	0.188	1.000			
SO4mg/l	-0.334	-0.404	0.168	0.165	0.194	1.000		
Cond μS	0.016	0.068	-0.364	-0.190	0.629	-0.094	1.000	
AMDI	0.782	-0.364	-0.668	-0.748	-0.385	-0.239	0.039	1.000

Site 4.1 Mixing zone in river below Deep Adit (n=4)

	pH	**Zn mg/l**	**Fe mg/l**	**Cu mg/l**	**Cdμg/l**	**SO4mg/l**	**Cond μS**	**AMDI**
pH	1.000							
Zn mg/l	-0.994	1.000						
Fe mg/l	-0.996	0.995	1.000					
Cu mg/l	-0.996	0.995	1.000	1.000				
Cdμg/l	-0.997	0.997	1.000	1.000	1.000			
SO4mg/l	-0.999	0.997	0.996	0.996	0.997	1.000		
Cond μS	-0.996	0.996	1.000	1.000	1.000	0.996	1.000	
AMDI	1.000	-0.993	-0.995	-0.995	-0.995	-0.999	-0.995	1.000

Site 5.1 Contaminated river at Avoca bridge (n=30)

	pH	Zn mg/l	Fe mg/l	Cu mg/l	Cdµg/l	SO4mg/l	Cond µS	AMDI
pH	1.000							
Zn mg/l	-0.612	1.000						
Fe mg/l	-0.481	0.919	1.000					
Cu mg/l	-0.106	0.522	0.603	1.000				
Cdµg/l	●	●	●	●	●			
SO4mg/l	-0.243	0.356	0.136	0.055	●	1.000		
Cond µS	-0.137	0.272	-0.058	-0.011	●	0.643	1.000	
AMDI	0.827	-0.773	-0.661	-0.362	●	-0.517	-0.348	1.000

Site 5.2 Contaminated river at Golf Club (n=11)

	pH	Zn mg/l	Fe mg/l	Cu mg/l	Cdµg/l	SO4mg/l	Cond µS	AMDI
pH	1.000							
Zn mg/l	-0.271	1.000						
Fe mg/l	-0.023	0.746	1.000					
Cu mg/l	-0.253	0.878	0.897	1.000				
Cdµg/l	-0.422	0.539	0.170	0.516	1.000			
SO4mg/l	-0.384	0.843	0.617	0.661	0.432	1.000		
Cond µS	-0.085	0.850	0.699	0.790	0.337	0.743	1.000	
AMDI	0.678	-0.827	-0.586	-0.740	-0.555	-0.869	-0.636	1.000

Site 5.3 Contaminated river upstream of IFI (n=11)

	pH	Zn mg/l	Fe mg/l	Cu mg/l	Cdµg/l	SO4mg/l	Cond µS	AMDI
pH	1.000							
Zn mg/l	-0.175	1.000						
Fe mg/l	-0.081	-0.048	1.000					
Cu mg/l	0.069	0.335	-0.253	1.000				
Cdµg/l	●	●	●	●	●			
SO4mg/l	-0.191	0.799	0.066	0.176	●	1.000		
Cond µS	0.005	0.831	-0.473	0.564	●	0.715	1.000	
AMDI	0.685	-0.588	-0.162	-0.147	●	-0.529	-0.325	1.000

Site 5.4 Contaminated river downstream of IFI (n=11)

	pH	Zn mg/l	Fe mg/l	Cu mg/l	Cdμg/l	SO4mg/l	Cond μS	AMDI
pH	1.000							
Zn mg/l	-0.757	1.000						
Fe mg/l	-0.100	0.134	1.000					
Cu mg/l	0.256	-0.093	0.031	1.000				
Cdμg/l	•	•	•	•	•			
SO4mg/l	0.389	-0.140	-0.417	-0.009	•	1.000		
Cond μS	0.875	-0.570	-0.417	0.247	•	0.653	1.000	
AMDI	-0.305	0.011	0.010	-0.071	•	-0.823	-0.517	1.000

Site 5.5 Contaminated river at Arklow Bridge (n=4)

	pH	Zn mg/l	Fe mg/l	Cu mg/l	Cdμg/l	SO4mg/l	Cond μS	AMDI
pH	1.000							
Zn mg/l	-0.825	1.000						
Fe mg/l	0.146	0.155	1.000					
Cu mg/l	-0.289	0.356	-0.289	1.000				
Cdμg/l	•	•	•	•	•			
SO4mg/l	0.310	0.369	0.776	•	•	1.000		
Cond μS	0.384	-0.212	-0.262	0.012	•	0.783	1.000	
AMDI	0.053	-0.651	-0.645	•	•	-0.912	-0.618	1.000

Site 5.9East side of river upstream of Deep Adit contaminated by interflow (n=3)

	pH	Zn mg/l	Fe mg/l	Cu mg/l	Cdμg/l	SO4mg/l	Cond μS	AMDI
pH	1.000							
Zn mg/l	0.907	1.000						
Fe mg/l	0.132	0.538	1.000					
Cu mg/l	0.371	0.728	0.970	1.000				
Cdμg/l	•	•	•	•	•			
SO4mg/l	-0.985	-0.821	0.039	-0.207	•	1.000		
Cond μS	-0.924	-0.999	-0.500	-0.697	•	0.846	1.000	
AMDI	0.985	0.819	-0.043	0.203	•	-1.000	-0.844	1.000

Site 7.8 Stream at Moran's garage contaminated by leachate (n=3)

	pH	Zn mg/l	Fe mg/l	Cu mg/l	Cdμg/l	SO4mg/l	Cond μS	AMDI
pH	1.000							
Zn mg/l	0.551	1.000						
Fe mg/l	0.563	1.000	1.000					
Cu mg/l	0.636	0.994	0.996	1.000				
Cdμg/l	●	●	●	●	●			
SO4mg/l	1.000	1.000	1.000	1.000	●	1.000		
Cond μS	0.274	0.954	0.949	0.916	●	1.000	1.000	
AMDI	-1.000	-1.000	-1.000	-1.000	●	-1.000	-1.000	1.000

Site 8.1 Unpolluted river upstream of the mines (n=31)

	pH	Zn mg/l	Fe mg/l	Cu mg/l	Cdμg/l	SO4mg/l	Cond μS	AMDI
pH	1.000							
Zn mg/l	-0.503	1.000						
Fe mg/l	-0.578	0.830	1.000					
Cu mg/l	-0.199	0.078	0.124	1.000				
Cdμg/l	●	●	●	●	●			
SO4mg/l	0.202	-0.171	-0.029	0.056	●	1.000		
Cond μS	0.218	-0.343	-0.210	0.018	●	0.430	1.000	
AMDI	0.562	-0.806	-0.815	-0.379	●	-0.087	0.165	1.000

Site 9 Lake at base of Cronebane Pit (n=5)

	pH	Zn mg/l	Fe mg/l	Cu mg/l	Cdμg/l	SO4mg/l	Cond μS	AMDI
pH	1.000							
Zn mg/l	0.540	1.000						
Fe mg/l	0.827	0.824	1.000					
Cu mg/l	0.236	0.916	0.700	1.000				
Cdμg/l	0.658	0.985	0.893	0.860	1.000			
SO4mg/l	-0.788	-0.537	-0.858	-0.389	-0.666	1.000		
Cond μS	-0.640	-0.128	-0.654	-0.076	-0.263	0.830	1.000	
AMDI	-0.317	-0.952	-0.668	-0.950	-0.886	0.278	-0.083	1.000

Site 2.1

This includes surface runoff collected in ponds around the base of Mount Platt. The water is extremely acidic and can be classified as raw AMD, although they vary significantly in overall quality. For example the mean pH is 2.3 but the AMDI varies from 1.5 to 16.9 (mean 6.9). Iron concentration is extremely high as is the sulphate concentration, indicating high pyrite in the surrounding spoil., while the other metals although elevated are lower than recorded at sites 1.1 and 1.3. Mean (and maximum) parameter concentration are Zn 120 (179), Fe 3,343 (5,447), Cu 107 (146) mg/l, Cd 373 (560) μg/l, sulphate 15,950 (26,050) mg/l and conductivity 9,600 (13,900) μS/cm (Table 5).

Significant correlations are found between all parameters, although only three replicates were available. The ratio of sulphate:conductivity is 1.7, Zn:Cu 1.1 and Fe:Zn 27.9.

Site 2.32

Surface runoff from the north-eastern end of Mount Platt discharges into the lake at the base of Cronebane Pit (site 9). It is very similar in nature to the AMD retained in the surface pools (site 2.1), although Zn levels are elevated. With a mean pH of 2.2, this is largely raw AMD and with a mean AMDI of 8.8 (3.2-16.9). Mean (and maximum) parameter concentrations are Zn 247 (509), Fe 1,559 (3,763), Cu 91 (197) mg/l, Cd 225 (400) μg/l, sulphate 7,522 (16,840) mg/l and conductivity 6,218 (11,360) μS/cm (table 5).

Only Fe, Cu, Cd, sulphate and Cd show significant correlations with each other (Table 6), while the ratio of sulphate:conductivity is 1.2, Zn:Cu 2.7, and Fe:Zn 6.3 (Table 7).

Site 3.1

This is the Deep Adit which is the main leachate stream discharging into the Avoca River. Variability of the leachate is low for all parameters (Table 5). The mean pH is 3.6 while the mean (and maximum) parameter values are Zn 70 (75), Fe 117 (140), Cu 4.3 (8.2) mg/l, Cd 250 (320) μg/l, sulphate 1,596 (1,810) mg/l and conductivity 1,938 (2,090) μS/cm. This shows that the AMD is significantly diluted with groundwater, which is reflected by the relatively high AMDI of 26.6 (23.9-29.0).

There are few correlations due to the low variability of the data. However, Zn is negatively correlated with sulphate ($p<0.05$); Fe is negatively correlated with conductivity ($p<0.01$) and positively with Cu ($p<0.01$) and Cd ($p<0.001$); Cu is negatively correlated with AMDI ($p<0.001$) and conductivity ($p<0.05$) and positively with Cd ($p<0.001$). Finally Cd is also negatively correlated with conductivity ($p<0.01$) and AMDI ($p<0.001$) (Table 6). The ratio of sulphate:conductivity is 0.8, Zn:Cu 16.3 and Fe:Zn 1.7.

Site 3.22

This is the Ballymurtagh Adit leachate stream and the other major input of AMD to the River Avoca. It drains the western mining area. It is very different in quality to the Deep Adit being less acidic (mean pH 3.9), has less Zn (mean 27 mg/l and maximum 35 mg/l), similar Fe concentration (mean 133 mg/l and maximum 182 mg/l), less Cu (mean 1.8 mg/l and

Table 7. Summary of mean concentrations of (a) key parameters and (b) derived parameters from selected sites.

(a) Selected parameters

Site	pH	Zn mg/l	Fe mg/l	Cu mg/l	Cd μg/l	SO_4 mg/l	Cond. μS/cm
1.1	2.4	633	1050	188	1215	8242	7812
1.3	2.6	404	1484	464	1915	18339	12002
1.6	2.9	48	38	14	63	3349	3750
2.1	2.3	120	3343	107	373	15950	9600
2.32	2.2	247	1559	91	225	7522	6218
3.1	3.6	70	117	4.3	250	1596	1938
3.22	3.9	27	133	1.8	40	1668	2346
3.3	2.7	172	511	48	823	4570	4829
4.1	4.7	33	63	4	145	572	928
5.1	5.9	0.73	1.5	0.06	0.00	26	110
5.2	6.1	0.58	0.61	0.03	0.91	28	113
5.3	6.4	0.39	0.24	0.00	0.00	25	117
5.4	8.7	0.21	0.17	0.00	0.00	24	188
5.5	8.2	0.20	0.14	0.00	0.00	33	763
5.9	5.3	1.3	3.0	0.26	0.00	40	103
7.8	6.7	0.58	2.2	0.05	0.00	41 1	97
8.1	6.8	0.05	0.11	0.01	0.00	6.4	78
9	2.9	13	37	10	40	410	1024

(b) Derived parameters

Site	AMDI	SO_4:Cond.	Zn:Cu	Fe:Zn
1.1	5.4	1.1	3.4	1.7
1.3	3.7	1.5	0.9	3.7
1.6	24.3	0.9	3.4	0.8
2.1	6.9	1.7	1.1	27.9
2.32	8.8	1.2	2.7	6.3
3.1	26.6	0.8	16.3	1.7
3.22	32.6	0.7	15.0	4.9
3.3	10.6	1.0	3.6	3.0
4.1	54.0	0.6	8.3	1.9
5.1	81.0	0.2	12.2	2.1
5.2	84.6	0.3	19.3	1.1
5.3	89.8	0.2	-	0.6
5.4	91.7	0.1	-	0.8
5.5	91.3	0.04	-	0.7
5.9	77.2	0.4	5.0	2.3
7.8	86.6	0.2	11.6	3.7
8.1	97.0	0.08	5.0	2.2
9	36.9	0.4	1.3	2.9

maximum 2.4 mg/l), much less Cd (mean 40 μg/l and maximum 80 μg/l), similar sulphate (mean 1,668 mg/l and maximum 2,050 mg/l), although the conductivity is higher (mean 2,346 μS/cm and maximum 3,310 μS/cm). This results in a much higher AMDI compared to site 3.1 of 32.6 (range 30.9-36.0).

T-tests between sites 3.1 and 3.22 show pH, Zn. Cu, Cd, Conductivity and AMDI all to be highly significantly different ($p<0.001$), with Fe just significantly different at ($p<0.05$), while sulphate is not significantly different (Table 8). So the two main adits are clearly significantly different chemically with the Deep Adit more polluting than the Ballymurtagh Adit as measured by the AMDI. As with site 3.1 the low variability makes correlations difficult to establish. Zinc is correlated with pH ($p<0.001$), Zn with Cu ($p<0.001$), Fe with sulphate ($p<0.001$). Negative correlations are found between Cu and Cd ($p<0.001$) and AMDI ($p<0.01$), and also between AMDI and Cd ($p<0.001$). The ratio of sulphate:conductivity was 0.7, Zn:Cu 15.0, and Fe:Zn 4.9.

Site 3.3
The Shallow Adit drains the upper workings of the Cronebane mine area. It is more acidic than the other leachates (mean pH 2.7) and with elevated metal concentrations, although not as high as category 1 or 2 AMD. Mean (and maximum) parameter values are Zn 172 (215), Fe 511 (731), Cu 48 (70) mg/l, Cd 823 (910) μg/l, sulphate 4,570 (6,330) mg/l, and conductivity 4,829 (5,220) μS/cm. This results in a low AMDI of 10.6 with a low standard deviation of 1.0, making it considerably stronger than either the other leachate streams, and similar in strength to surface runoff. T tests shows this adit to be highly significantly different for all parameters measured than either the Deep or Ballymurtagh Adits (Table 8). As with the other leachate streams there is a poor correlation between individual parameters. Only Fe and Cu ($p<0.001$) are positively correlated while Cu and pH are both negatively correlated with AMDI ($p<0.05$). The ratio of sulphate:conductivity is 0.8, Zn:Cu 16.3, and Fe:Zn 1.7.

Site 4.1
As expected the conditions in the mixing zone are very variable, with maximum values almost identical to the Deep Adit, while minimum values are similar to upstream uncontaminated water quality. The mean pH is 4.7 with mean concentrations for key parameters of Zn 33, Fe 63, Cu 4.0 mg/l, and Cd 145 μg/l. Mean sulphate concentration was 572 mg/l although this ranged from 24 to 1,104 mg/l. The resultant mean AMDI is 45.0 with an equally wide range of 25.0 to 87.1. Due to the wide variability of the data all parameters are significantly correlated ($p<0.001$) with each other. pH is negatively correlated with all parameters, as is AMDI, although they are positively correlated with each other. All the other parameters are positively correlated (Table 6). The ratio of sulphate:conductivity is 0.6, Zn:Cu 8.3, and Fe:Zn 1.9 (Table 7).

Sites 5.1 to 5.5
These are the impacted river sites downstream of the mine site. The data is given in Table 5 and the means compared in Table 7.

Between site 5.1 (Avoca bridge) and site 5.2 (Golf Club) the mean pH increases from 5.9 to 6.1, although this is not significantly different

($p>0.05$). Zinc concentration is not significantly reduced being 0.78 and 0.58 mg/l at the two sites respectively ($p>0.05$). Only Fe and Cu are significantly reduced from 1.5 to 0.61 mg/l ($p<0.01$), and 0.06 to 0.03 mg/l ($p<0.05$) respectively. Cd is largely undetectable at both sites while sulphate, conductivity and AMDI show no significant difference between the sites. The mean AMDI increases from 81.0 at site 5.1 to 84.6 at site 2. Correlations between key parameters are shown in Table 6. At site 5.1 pH was negatively correlated with Zn ($p<0.001$) and Fe ($p<0.01$), AMDI also negatively correlated with all parameters in particular Fe and Zn and positively correlated with pH ($p<0.001$). Conductivity and sulphate are positively correlated ($p<0.001$) as is Zn and Fe ($p<0.001$). At site 5.2 pH and conductivity were not correlated with the other parameters except for pH with AMDI. The strongest correlations are with Zn.

At site 5.3 the Avoca river is significantly diluted (by approximately 100%) by the Aughrim River which is has a high water quality. The mean pH increases to 6.4 although this is not significantly different to the previous site (Table 8). The dilution significantly reduces the concentration of the metals present. The mean (and maximum) metal concentrations recorded at site 5.3 are Zn 0.39 (0.55) ($p<0.001$), Fe 0.24 (0.43) ($p<0.01$) and Cu 0.00 (0.02) mg/l ($p<0.05$), while mean sulphate and conductivity concentrations remained similar to the previous site at 25 mg/l and 117 μg/l respectively ($p>0.05$). The mean AMDI at 89.8 (range 85.0-91.3) showed a significant improvement in water quality compared to the previous site ($p<0.05$). Table 6 shows few correlations between parameters at this site. Conductivity and sulphate are both correlated with Zn and with each other ($p<0.001$), conductivity with Fe ($p<0.05$) and Cu ($p<0.01$), while AMDI is correlated with pH ($p<0.001$), Zn ($p<0.01$) and sulphate ($p<0.05$).

Site 5.4 is downstream of the fertilizer factory (IFI). This site is subjected to a considerable discharge of ammonia wastewater from the plant. Here the pH is significantly increased to a mean of 8.7 ($p<0.001$), although the median and maximum are higher at 9.3 and 10.1 respectively. The reduced mean is due in part to the variability of the discharge in relation to the river flow. Mean (and maximum) metal concentrations are Zn 0.21 (0.38) ($p<0.001$), Fe 0.17 (0.37) ($p>0.05$), Cu 0.0 (0.04) mg/l ($p>0.05$), although minimum values for Zn and Fe are 0.07 and 0.00 respectively. Mean sulphate concentration remained similar to the previous site ($p>0.05$) although mean conductivity significantly increases to 188 μS/cm ($p<0.01$). The AMDI increased to 91.7 (range 87.1-93.4) which showed a significant improvement in water quality from the previous station. ($p<0.05$), although in water toxicity terms the high pH and high ammonia concentration makes this section of the river potentially lethal to many freshwater organisms, and to fish in particular. Only conductivity is correlated with pH ($p<0.001$) and sulphate ($p<0.05$), while AMDI is negatively correlated with sulphate ($p<0.001$) (Table 6).

The final river site (5.5) is in the estuary at Arklow Bridge. Here the pH is stabilized to a mean of 8.2. The water quality shows no significant difference to the previous site ($p>0.05$), although sulphate and conductivity shows wider variations due to the influx of sea water. The mean AMDI remains similar to the previous site at 91.3 although the range indicates a marginal improvement in water quality (range 89.2 - 95.6) (Tables 5 and 8). Apart from sulphate with Fe ($p<0.01$), and AMDI with Fe and sulphate ($p<0.001$) there were no other correlations (Table 6).

The ratio of sulphate:conductivity remains constant for sites 51. to 5.3 at 0.2, but falls to 0.1 at site 5.4, and to 0.04 by site 5.5. The Zn:Cu ratio increases as the Cu is removed from the water from 12.2 to 19.3 at sites 5.1 and 5.2 respectively, although it can not be calculated due to zero Cu at the remaining sites. Fe:Zn showed a similar effect as the iron is rapidly removed from solution by the increase in pH downstream. The ratio falls from 2.1 at site 5.1 to 0.6 at site 5.3 where it remains until it reaches the sea.

Site 5.9
This is another river sampling site located on the east side of the river above the first main leachate input which is affected by interflow. It has a mean pH of 5.3 with elevated metal concentrations of Zn 1.3, Fe 3.0, Cu 0.26 mg/l. Sulphate concentration is 40 mg/l although quite variable (8-80 mg/l). The mean AMDI is 77.2 although this ranges from 67.6 to 85.1 (Table 5). pH and AMDI are both negatively correlated with sulphate ($p<0.01$ and $p<0.001$ respectively), while positive correlations are recorded for pH with AMDI ($p<0.05$) and conductivity and Zn ($p<0.001$). Table 8 shows this site to only be significantly contaminated compared to the upstream water quality (site 8.1) in terms of copper concentration ($p<0.05$). Surprisingly the AMDI is not significantly different, even though the ranges do not overlap, with the maximum AMDI for site 5.9 at 85.1 and the minimum value for site 8.1 at 87.1. The ratio of sulphate:conductivity is 0.4, Zn:Cu 5.0 and Fe:Zn 2.3.

Site 7.8
This is an example of a surface stream contaminated by AMD. The mean pH is very stable at 6.7 (sd 0.06). Metal concentrations are not high with mean (and maximum) values of Zn 0.58 (1.9), Fe 2.2 (7.4), Cu 0.05 (0.14) mg/l. Cd is non-detectable while the sulphate concentration is elevated at 41 mg/l (range 26-70 mg/l). The AMDI is good at 86.6 (range 77.1-91.3). In terms of water quality this site is similar to the downstream river sites in particular sites 5.2 and 5.3. The small data base shows significant correlations between most parameters (Table 6). The ratio of sulphate:conductivity is 0.2, Zn:Cu 11.6 and Fe:Zn 3.7.

Site 8.1
This is the upstream river site which was assumed to be uncontaminated by the mines and AMD. It shows much less variability in pH compared to the first impacted river site downstream of the mines outside of the mixing zone (site 5.1) , with a mean pH of 6.8 (range of 5.5 to 7.4). The water does in fact have some natural background contamination with mean (and maximum) metal concentrations of Zn 0.05 (0.18), Fe 0.11 (0.86), Cu 0.01 (0.30) mg/l but with no Cd detectable. Sulphate is low with a mean concentration of 6.4 and a range of 3-19 mg/l. AMDI is quite variable from 87.1 to 100, with a mean of 97.0. The results suggest that at certain times the site may be subject to AMD contamination. The levels of difference between the upstream site and the impacted downstream sites (Table 8) are summarized below in Table 9.

The pH is clearly significantly impacted at site 5.1 by the AMD and slowly recovers downstream. It remains significantly different to the upstream

Table 8. Significant difference between major individual sites for key parameters analysed. Levels of significance are given as $p<0.05$*, $p<0.01$**, $p<0.001$***, and NS is no significant difference.

site		pH	sig	Zn	sig	Fe	sig	Cu	sig	Cd	sig	SO4	sig	Cond	sig	AMDI	sig
3.1	3.22	≤0.0001	***	≤0.0001	***	0.0172	*	≤0.0001	***	≤0.0001	***	0.3928	NS	≤0.0001	***	≤0.0001	***
3.1	3.3	≤0.0001	***	0.0010	**	≤0.0001	***	≤0.0001	***	≤0.0001	***	0.0018	**	≤0.0001	***	≤0.0001	***
3.22	3.3	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	0.0013	**	≤0.0001	***	≤0.0001	***
5.1	5.2	0.2715	NS	0.1178	NS	0.0093	**	0.0160	*	0.3409	NS	0.5581	NS	0.6972	NS	0.0869	NS
5.1	5.3	≤0.0001	***	≤0.0001	***	0.0003	***	≤0.0001	***	-		0.4091	NS	0.2223	NS	≤0.0001	***
5.1	5.4	≤0.0001	***	≤0.0001	***	0.0002	***	≤0.0001	***	-		0.6555	NS	0.0052	**	≤0.0001	***
5.1	5.5	≤0.0001	***	≤0.0001	***	≤0.0001	***	≤0.0001	***	-		0.1840	NS	0.0627	NS	0.0022	**
5.1	5.9	0.4266	NS	0.4743	NS	0.4217	NS	0.0553	NS	-		0.5737	NS	0.7932	NS	0.5417	NS
5.1	8.1	≤0.0001	***	≤0.0001	***	≤0.0001	***	0.0013	**	-		≤0.0001	***	≤0.0001	***	≤0.0001	***
5.2	5.3	0.2061	NS	0.0051	**	0.0017	**	0.0190	*	0.3409	NS	0.2939	NS	0.6545	NS	0.0125	*
5.2	5.4	≤0.0001	***	≤0.0001	***	0.0004	***	0.0281	*	0.3409	NS	0.4343	NS	0.0070	**	0.0019	**
5.2	5.5	0.0002	***	≤0.0001	***	0.0002	***	0.0381	*	0.3409	NS	0.3458	NS	0.0637	NS	0.0142	*
5.2	5.9	0.3042	NS	0.3919	NS	0.2537	NS	0.0399	*	0.3409	NS	0.6304	NS	0.7129	NS	0.3056	NS
5.2	8.1	0.0076	**	≤0.0001	***	≤0.0001	***	0.2800	NS	0.3409	NS	≤0.0001	***	0.0004	***	≤0.0001	***
5.3	5.4	0.0003	***	≤0.0001	***	0.1303	NS	0.7723	NS	-		0.9371	NS	0.0087	**	0.0170	*
5.3	5.5	0.0008	***	0.0002	***	0.0658	NS	0.6724	NS	-		0.1193	NS	0.0649	NS	0.4153	NS
5.3	5.9	0.1954	NS	0.3049	NS	0.2089	NS	0.0321	*	-		0.5352	NS	0.6105	NS	0.1333	NS
5.3	8.1	≤0.0001	***	≤0.0001	***	0.0022	**	0.2982	NS	-		≤0.0001	***	≤0.0001	***	≤0.0001	***
5.4	5.5	0.3727	NS	0.9174	NS	0.5951	NS	0.8775	NS	-		0.1342	NS	0.0955	NS	0.8305	NS
5.4	5.9	0.0090	**	0.2439	NS	0.2011	NS	0.0326	*	-		0.5332	NS	0.0333	*	0.1065	NS
5.4	8.1	0.0012	**	0.0002	***	0.2413	NS	0.3836	NS	-		0.0042	**	0.0004	***	≤0.0001	***
5.5	5.9	0.0250	*	0.2427	NS	0.1979	NS	0.0329	*	-		0.7765	NS	0.0610	NS	0.1182	NS
5.5	8.1	0.0047	**	0.0009	***	0.6493	NS	0.4497	NS	-		0.0020	**	0.0526	NS	0.0300	*
5.9	8.1	0.1226	NS	0.2031	NS	0.1953	NS	0.0360	*	-		0.2777	NS	0.3720	NS	0.0633	NS

pH due to the excessive alkalinity of the IFI discharge and subsequently the estuary, even though the pH has almost fully recovered by site 5.3. Zinc remains significantly enhanced at all downstream sites ($p<0.001$), while Fe is only reduced to background concentrations by the IFI influent causes a massive shift in pH. Copper concentration recovers very quickly, being reduced to normal background levels by site 5.2. Sulphate remains elevated at all sites below the mines, as does conductivity. The AMDI shows a wide variation at site 8.1, although all the downstream sites indicate a reduced water quality, even though recovery from the initial impact of AMD is clearly reflected (Table 7; Fig.1).

Table 9 Level of difference between the uncontaminated upstream site (8.1) and the various downstream sites below the mines. (sites 5.1 to 5.5). Levels of significance are $p<0.001$***, $p<0.01$**, $p<0.05$*, NSD (no significant difference), and - (no estimation made).

Site	pH	Zn	Fe	Cu	Cd	SO_4	cond[1]	AMDI
5.1	***	***	***	**	-	***	***	***
5.2	**	***	***	NSD	NSD	***	***	***
5.3	***	***	**	NSD	-	***	***	***
5.4	**	***	NSD	NSD	-	**	***	***
5.5	**	***	NSD	NSD	-	**	NSD	*

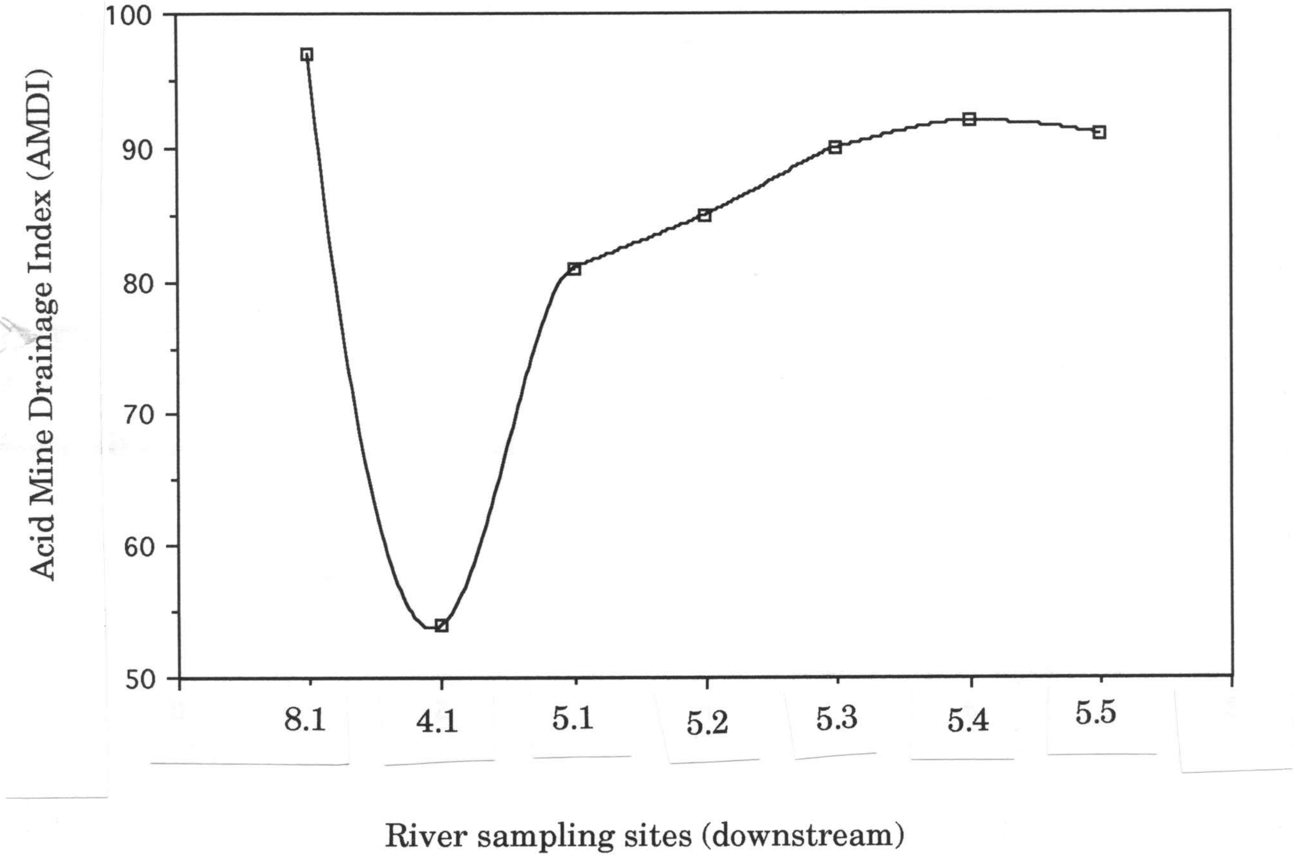
[1] Cond is conductivity

The ratio of sulphate:conductivity is 0.1, Zn:Cu 5.0 and Fe:Zn 2.2. It is interesting that the Zn:Cu and Fe:Zn ratios are almost identical to those for site 5.9 which supports the idea of some contamination of the upstream site by interflow or groundwater discharge, as no surface inputs of AMD have been identified.

Site 9

This last site is the lake at the bottom of Cronebane Open Pit. This has been discussed fully in the previous section, where it was found that while the water was very acidic at pH 2.9, metal concentrations although elevated were not as high as other mine waters. Few correlations between parameters are seen (Table 6). These include Sulphate and conductivity ($p<0.05$), Zn with Fe and Cu ($p<0.05$), and Cd ($p<0.001$). Cadmium is correlated with Cu and Fe ($p<0.05$), Fe negatively with sulphate ($p<0.05$), and AMDI negatively with Zn, Cu ($p<0.01$) and Cd ($p<0.05$).

Fig. 1. The variation of AMDI in the Avoca River from site 8.1, through the mixing zone (site 4.1) and downstream to the estuary (sites 5.1 to 5.5).



DISCUSSION

During this interim period, 42 separate sites were monitored. Surface waters were classified into nine discrete source categories. These are 1. Springs and seepage from spoil; 2. Surface runoff; 3. Leachate streams; 4. River mixing zone; 5. Contaminated river; 6 .Uncontaminated surface runoff; 7. Contaminated streams containing leachate; 8. Uncontaminated river; and 9. The lake in Cronebane Pit. Each source category has a distinctive water chemistry, although there is some overlap between categories for some parameters. The mine derived waters were all significantly affected by acid mine generation on the site. While the river was severely impacted by the discharge of diluted AMD via leachate streams (adits), contaminated streams, interflow and groundwater. The results show that the Avoca mine is an active acid mine producing site causing severe surface water pollution.

Springs and seepages from the spoil (category 1) all proved to be highly acidic, rich in sulphate and iron, and very heavily contaminated with other metals. This is reflected by the very low mean AMDI of 10.0 (sd 10.1). This is the strongest AMD found so far on the site, although some of the surface runoff is also exceptionally strong.

Surface runoff (category 2) is a phenomenon of high rainfall only, and are identical to category 1 waters in terms of pH, Fe and sulphate. Highly acidic in nature (mean pH 2.6) but very variable in terms of Fe and sulphate concentrations. Other metals, although elevated are significantly lower than in category 1 waters. The mean AMDI is 24.2 (sd 18.0).

While categories 1 and 2 waters can be classed as raw AMD, the water in the leachate streams (category 3) is significantly diluted and buffered by groundwater infiltration. The mean AMDI is similar to category 2 at 26.9 (sd 7.3). This category comprises of three separate leachate streams and each one is significantly different. The Shallow Adit is least diluted and so has the highest metal concentrations. While of the two that discharge into the river, the Deep Adit is the more polluting. The mean AMDI for these adits are 10.6 (sd 1.0) for the Shallow Adit, 26.6 (sd 1.83) for the Deep Adit, and 32.6 (sd 2.0) for the Ballymurtagh Adit. The leachate emanating from the Avoca site is highly polluting. In Table 10 the Avoca leachate is compared with three leachate streams from the Wheal Jane and Twelveheads mining complex which drain into the Carnon River in Cornwall. From this table it is apparent that while the pH of the leachates discharging into both rivers are similar, metal concentrations are higher in the Avoca leachate streams. The Shallow Adit is significantly more acidic and metal rich than those reported from the Cornish site.

The mixing zone in the river (category 4) is severely impacted with a wide variation in parameter concentrations. This ranges from clean unpolluted river water to raw leachate in quality. The mean AMDI is 594 (sd 23.9).

Downstream the river is severely impacted by the AMD (category 5), although the river is recovering in terms of water chemistry fairly quickly (Fig. 1). Two factors are influential in this recovery. First the effect of the Aughrim River which has a similar flow to the Avoca River and which is more buffered due to a small area of limestone within its sub-catchment. Secondly, the effect of the fertilizer factory (IFI) downstream of the confluence of the two rivers. This factory discharges a large volume of ammonia wastewater causing very alkaline pH concentrations in the river. The mean AMDI for category 5 waters is 85.6 (sd 6.37).

A number of minor streams enter the Avoca river which are also contaminated by AMD. As expected the water quality of these waters are similar to category 3 and 4, being very variable. The mean AMDI is 63.1 (sd 19.5) which is similar to the mixing zone.

The uncontaminated river (category 8) is a site upstream of the mines. It shows a largely clean river with trace amounts of Zn, Fe and Cu. It is clear that this site is subject to occasional AMD contamination. The absence of any surface water input would suggest that groundwater discharge is affecting the river at this site, even though this is not reflected by the biological investigations. A site further upstream should be selected for future work. Mean AMDI is 97.0 (sd 3.2), showing the site to be exceptionally clean.

Table 10. Leachate water quality of the three main adits from the Wheal Jane and Twelveheads mining complex in Cornwall (Johnson and Thornton, 1987) compared to the main Avoca Adits.

Adit	pH	Fe	Cu mg/l	Zn
Cornwall				
Country Adit	4.0	0.5	0.9	3.1
Wellington Adit	3.4	50	1.2	12
Wheal Jane Adit	3.9	74	0.4	2.4
Avoca				
Deep Adit	3.6	117	4.3	70
Ballymurtagh Adit	3.9	133	1.8	27
Shallow Adit	2.7	511	48	172

Category 9 represented a single site, the lake at the base of the Cronebane Pit. This is a permanent lake although the water level fluctuates greatly. During this sampling period it was established that there was no flow through the lake, as seen during the winter, and that water was only entering the lake as precipitation or surface runoff. The surface runoff (site 2.32) is very acidic and results in the contaminated water found in the lake. The mean AMDI is 36.9 (sd 3.9), which is similar to the weaker leachate.

The source categories of AMD and impacted waters are very different, ranging from raw AMD to the uncontaminated river water. In terms of identifying and quantifying AMD and AMD impact then pH is very powerful at discriminating between source categories failing only to discriminate between categories 1-3, 4-7, and 5-8. The AMDI is even more sensitive in that is was able to quantify AMD contamination in terms of the strength of the AMD and the actual impact and recovery within the river. In terms of discriminating between source categories only categories 2-8 and 4-7 proved not to be significantly different in terms of the AMDI. pH is only one indicator of AMD whereas the AMDI takes into consideration pH, Zn, Fe, Cu, Cd sulphate and Al as well.

Further interpretation of this data will be given in subsequent reports as seasonal trends are measured, particulate metal concentrations are evaluated, and flow rates are taken in consideration.

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APPENDIX

Appendix I: Raw data ordered by site number

No.	site	grp	subsit	coll.	date	pH	Zn mg/l	Fe mg/l	Cu mg/l	Cd mg/l	Cdμg/l	Al mg/l	SO4mg/l	Cond μS	WQI	AMDI
61	1.1	1	1	NG	94.06.08	2.4	299	96	200	1.4	1360		8980	8560	26	8.35
88	1.1	1	1	NG	94.06.22	2.4	294	1404	226	1.4	1440	409.6	10860	8510	18	4.00
91	1.1	1	1	NG	94.07.13	2.4	1526	1074	139	0.91	910	5100	5520		20	4.94
100	1.1	1	1	NG	94.08.03	2.4	977	556	98	0.55	550	0.304	4230	4320	24	7.11
117	1.1	1	1	NG	94.09.07	2.5	386	1541	252	1.7	1670	851.1	11400	9340	17	3.57
138	1.1	1	1	NG	94.10.13	2.5	313.5	1626	211	1.36	1360		8460	8330	19	4.46
86	1.2	1	2	NG	94.06.22	2.4	282	1540	215	1.45	1450	74	10660	8510	18	4.00
139	1.2	1	2	NG	94.10.13	2.6	229.5	1137	151	1.02	1020		7500	5640	21	5.44
9	1.3	1	3	NG	94.05.16	2.8	162	45	191	0.81	810		7594	5850	32	12.64
60	1.3	1	3	NG	94.06.08	2.7	427	164	495	2.2	2180		22070	13500	16	3.16
84	1.3	1	3	NG	94.06.22	2.5	516	2384	590	2.48	2480	218	24668	15700	8	0.79
90	1.3	1	3	NG	94.07.13	2.5	453	2069	497	2.0	1970	1990	16900	12480	13	2.09
105	1.3	1	3	NG	94.08.03	2.5	438	2237	491	1.97	1970	0.129	19400	12180	12	1.78
136	1.3	1	3	NG	94.10.12	2.7	428	2007	521	2.08	2080		19400	12300	12	1.78
116	1.4	1	4	NG	94.09.07	2.7	488	2099.5	512	2.3	2280	1987	21840	13300	11	1.49
137	1.4	1	4	NG	94.10.12	2.7	458	2147	492	2.14	2140		18600	12400	12	1.78
27	1.5	1	5	NG	94.05.17	3.3	33	89	6.5	0.04	40		2030	2480	48	28.44
30	1.6	1	6	NG	94.05.17	3.0	47	46	13.39	0.06	60		3183	3470	45	25.00
31	1.6	1	6	NG	94.05.17	2.9	36	36	9.8	0.03	30		2694	3010	46	26.12
54	1.6	1	6	NG	94.06.08	2.9	61	33	18.66	0.1	100		4170	4770	42	21.78
145	1.7	1	7	NG	94.10.13	3.3	60.5	183	4.5	0.24	240		1310	1750	46	26.12
144	1.8	1	8	NG	94.10.13	3.2	58	175	4.5	0.22	220		1280	1800	45	25.00
119	2.1	2	1	NG	94.09.07	2.1	148	4194	146	0.45	450	1106.7	20190	12500	14	2.42
120	2.1	2	1	NG	94.09.07	2.1	179	5447	143	0.56	560	1371.7	26050	13900	11	1.49
142	2.1	2	1	NG	94.10.13	2.6	33.4	387	33	0.11	110		1610	2400	37	16.90
107	2.2	2	2	NG	94.08.03	2.3	13	98	13	0.04	40	0.013	1220	2190	45	25.00
143	2.2	2	2	NG	94.10.13	2.7	10.7	14	12	0.02	20		810	1670	51	32.11
10	2.3	2	3	NG	94.05.16	2.7	22	163	24	0.06	60		1501	1420	43	22.83
11	2.31	2	31	NG	94.05.16	2.9	5.4	40.45	6.08	0.00	0		402	880	57	40.11
12	2.32	2	32	NG	94.05.16	2.4	29	312	22	0.15	150		1566	2530	37	16.90
102	2.32	2	32	NG	94.08.03	2.1	314	633	43	0.15	150	0.154	4080	4440	28	9.68
103	2.32	2	32	NG	94.08.03	2.1	509	1529	100	0.2	200	0.027	7600	6540	21	5.44
141	2.32	2	32	NG	94.10.13	2.1	135.5	3762.5	197	0.4	400		16840	11360	16	3.16
7	2.4	2	4	NG	94.05.16	3.6	1.2	0.75	4.8	0.00	0		206	360	68	57.09
2	2.5	2	5	NG	94.05.16	2.8	17	38	9.4	0.05	50		634	1230	50	30.86
3	2.7	2	7	NG	94.05.16	3.6	67	154	8.1	0.30	300		1501	1740	44	23.90
5	2.8	2	8	NG	94.05.16	3.0	2.2	18	1.0	0.00	0		159	530	63	49.00
8	2.8	2	8	NG	94.05.16	3.1	4.5	6.6	4.0	0.00	0		268	610	64	50.57
1	3.1	3	1	NG	94.05.16	3.6	70	136	8.2	0.32	320		1519	1800	45	25.00
22	3.1	3	1	NG	94.05.17	3.4	68	127	8.1	0.30	300		1616	1800	44	23.90
23	3.1	3	1	NG	94.05.17	3.4	69	130	8.2	0.29	290		1585	1810	44	23.90
24	3.1	3	1	NG	94.05.17	3.5	71	131	8.2	0.3	300		1712	1780	45	25.00
25	3.1	3	1	NG	94.05.17	3.5	70	140	8.2	0.29	290		1738	1760	45	25.00
44	3.1	3	1	NG	94.06.02	3.6	74	110	6.3	0.26	260		1560	2080	45	25.00
45	3.1	3	1	NG	94.06.02	3.5	72	135	6.2	0.25	250		1220	2090	46	26.12
55	3.1	3	1	NG	94.06.08	3.6	72	104	5.5	0.25	250		1590	2020	45	25.00
56	3.1	3	1	NG	94.06.08	3.5	73	108	5.5	0.25	250		1620	2010	45	25.00
72	3.1	3	1	NG	94.06.16	3.5	68	99	4.7	0.22	220		1582	1990	48	28.44
81	3.1	3	1	NG	94.06.22	3.4	67	101	4.2	0.22	220	570.78	1553	1980	46	26.12
93	3.1	3	1	NG	94.07.13	3.4	75	110	3.4	0.27	270	256	1630	1980	44	23.90
108	3.1	3	1	NG	94.08.03	3.3	74	114	2.3	0.26	260	0.035	1690	1970	45	25.00
113	3.1	3	1	NG	94.09.07	3.6	75	114	1.4	0.24	240	75.65	1600	1960	47	27.27
123	3.1	3	1	NG	94.10.12	3.4	24	114	1.03	0.19	190		1810	2010	48	28.44
41	3.1	3	1	CH	94.07.06	3.7	72	106	3.3	0.21	210		1589	1910	48	28.44
44	3.1	3	1	CH	94.07.14	3.8		119	3.1	0.26	260		1636	1971	42	28.99
56	3.1	3	1	CH	94.07.20	3.7	74	129	2.8	0.25	250		1598	1936	48	28.44
64	3.1	3	1	CH	94.07.27	3.7	74	117	2.4	0.24	240		1570	1925	48	28.44
71	3.1	3	1	CH	94.08.04	3.5	75.25	114	2.16	0.23	230		1560	1950	46	26.12
77	3.1	3	1	CH	94.08.10	3.7	74	109	2	0.24	240		1590	1958	48	28.44
82	3.1	3	1	CH	94.08.17	3.7	72	109	1.8	0.23	230		1610	1948	48	28.44
94	3.1	3	1	CH	94.08.24	3.7	74	113	1.6	0.22	220		1560	1930	48	28.44

101	3.1	3	1	CH	94.08.31	3.7	70	112	1.5	0.22	220		1570	1933	48	28.44
35	3.21	3	21	NG	94.05.17	3.7	33	187	2.3	0.03	30		1094	2250	51	32.11
28	3.22	3	22	NG	94.05.17	3.9	33	182	2.4	0.03	30		1822	2250	51	32.11
29	3.22	3	22	NG	94.05.17	3.8	33	182	2.4	0.03	30		1804	2180	50	30.86
42	3.22	3	22	NG	94.06.02	4.0	34	149	2.2	0.00	0		1720	2480	54	36.00
43	3.22	3	22	NG	94.06.02	4.0	35	145	2.2	0.02	20		1790	2560	53	34.68
52	3.22	3	22	NG	94.06.08	3.9	30	125	2.2	0.01	10		1730	2420	53	34.68
53	3.22	3	22	NG	94.06.08	3.8	30	133	2.1	0.02	20		1720	2420	52	33.38
73	3.22	3	22	NG	94.06.16	3.8	25	92	2.2	0.01	10		1512	2150	53	34.68
80	3.22	3	22	NG	94.06.22	3.8	25	91	2.0	0.01	10	118.9	1439	2140	54	36.00
109	3.22	3	22	NG	94.08.03	3.7	27	116	1.6	0.07	70	0.042	1670	2230	50	30.86
112	3.22	3	22	NG	94.09.07	3.7	29	139	1.4	0.08	80	41.57	1610	2330	50	30.86
124	3.22	3	22	NG	94.10.12	3.5	1.47	160	1.33	0.05	50		2050	2620	50	30.86
42	3.22	3	22	CH	94.07.06	3.9	25	101	1.7	0.00	0		1550	2100	54	36.00
45	3.22	3	22	CH	94.07.14	4.0	26	159	1.8	0.06	60		1591	2130	50	30.86
55	3.22	3	22	CH	94.07.20	4.0	26	123	1.7	0.06	60		1630	2190	51	32.11
63	3.22	3	22	CH	94.07.27	3.8	26	108	1.6	0.06	60		1540	3310	50	30.86
72	3.22	3	22	CH	94.08.04	3.8	26.9	138	1.56	0.06	60		1590	2220	50	30.86
78	3.22	3	22	CH	94.08.10	3.9	26	136	1.6	0.06	60		1610	2260	51	32.11
83	3.22	3	22	CH	94.08.17	3.8	26	111	1.5	0.06	60		1650	2280	50	30.86
93	3.22	3	22	CH	94.08.24	4.0	29	130	1.5	0.05	50		1660	2310	51	32.11
97	3.22	3	22	CH	94.08.31	3.9	29	133	1.5	0.06	60		1680	2340	51	32.11
6	3.3	3	3	NG	94.05.16	2.8	133	524	47	0.64	640		4470	3970	30	11.11
59	3.3	3	3	NG	94.06.08	2.8	176	531	54	0.77	770		2780	5090	29	10.38
85	3.3	3	3	NG	94.06.22	2.7	215	731	70	0.91	910	64	5554	4706	28	9.68
89	3.3	3	3	NG	94.07.13	2.7	186	450	37	0.85	850	1890	5250	4820	30	11.11
106	3.3	3	3	NG	94.08.03	2.6	198	525	52	0.9	900	0.385	4800	4880	27	9.00
115	3.3	3	3	NG	94.09.07	2.8	204	404	36	0.87	870	539	2810	5120	31	11.86
135	3.3	3	3	NG	94.10.12	2.8	90	410	42.4	0.82	820		6330	5220	30	11.11
18	4.1	4	1	NG	94.05.17	3.4	63	127	8.1	0.29	290		1046	1800	45	25.00
19	4.1	4	1	NG	94.05.17	5.8	0.23	0.10	0.04	0.00	0		116	70	80	79.01
20	4.1	4	1	NG	94.05.17	6.1	0.14	0.06	0.04	0.00	0		24	70	84	87.11
21	4.1	4	1	NG	94.05.17	3.4	70	123	7.8	0.29	290		1104	1770	45	25.00
16	4.2	4	2	NG	94.05.17	5.1	1.1	1.52	0.28	0.00	0		33	110	76	71.31
126	4.2	4	2	NG	94.10.12	5.3	0.95	1.4	0.54	0.00	0		40	99	78	75.11
32	4.3	4	3	NG	94.05.17	4.0	6.3	39	0.60	0.00	0		445	790	64	50.57
34	4.3	4	3	NG	94.05.17	4.7	3.7	17	0.28	0.00	0		189	370	71	62.23
33	5.1	5	1	NG	94.05.17	5.9	1.1	4.6	0.10	0.00	0		16	70	80	79.01
36	5.1	5	1	NG	94.05.17	6.1	0.20	0.52	0.05	0.00	0		20	70	83	85.05
40	5.1	5	1	NG	94.06.02	6.8	0.56	1.3	0.07	0.00	0		28	120	83	85.05
41	5.1	5	1	NG	94.06.02	6.7	0.56	1.3	0.07	0.00	0		27	120	83	85.05
48	5.1	5	1	NG	94.06.08	6.8	0.52	1.16	0.28	0.00	0		24	110	83	85.05
49	5.1	5	1	NG	94.06.08	6.9	0.52	1.09	0.05	0.00	0		26	110	83	85.05
64	5.1	5	1	NG	94.06.12	5.8	0.70	1.1	0.07	0.00	0		28	120	80	79.01
74	5.1	5	1	NG	94.06.16	4.9	2.3	7.2	0.21	0.00	0		47	140	75	69.44
79	5.1	5	1	NG	94.06.22	7.2	0.42	0.48	0.00	0.00	0	0.11	18	90	86	91.31
110	5.1	5	1	NG	94.08.03	4.6	1.8	7.1	0.17	0	0	0.346	17	80	75	69.44
111	5.1	5	1	NG	94.09.07	5.2	0.59	0.97	0.02	0	0	0.293	24	107	81	81.00
130	5.1	5	1	NG	94.10.12	5.8	0.54	0.72	0.00	0.00	0		50	99	80	79.01
4	5.1	5	1	CH	94.06.16	5.5	0.78	0.00	0.05	0.00	0			131.9	58	
5	5.1	5	1	CH	94.06.16	5.5	0.78	1.2	0.06	0.00	0		34	130.9	78	75.11
6	5.1	5	1	CH	94.06.16	5.5	0.78	1.3	0.07	0.00	0		33		78	75.11
10	5.1	5	1	CH	94.06.23	5.6	0.68	1.0	0.05	0.00	0		27	113.8	80	79.01
11	5.1	5	1	CH	94.06.23	6.6	0.67	1.0	0.06	0.00	0		27	114.3	83	85.05
12	5.1	5	1	CH	94.06.23	5.6	0.68	1.0	0.05	0.00	0		23	113.4	80	79.01
18	5.1	5	1	CH	94.06.29	5.7	0.73	1.4	0.05	0.00	0		30	129.8	79	77.05
19	5.1	5	1	CH	94.06.29	5.7	0.73	1.3	0.05	0.00	0		31	128.7	79	77.05
35	5.1	5	1	CH	94.07.06	6.0	0.68	0.98	0.02	0.00	0		22	121	83	85.05
36	5.1	5	1	CH	94.07.06	6.0	0.68	0.96	0.02	0.00	0		22	121	83	85.05
37	5.1	5	1	CH	94.07.06	6.0	0.66	0.95	0.02	0.00	0		22	120	83	85.05
46	5.1	5	1	CH	94.07.14	5.6	0.57	0.77	0.01	0.00	0		23	94	82	83.01
52	5.1	5	1	CH	94.07.20	5.6	0.80	1.2	0.05	0.00	0		32	128	79	77.05

58	5.1	5	1	CH	94.07.27	6.1	0.48	0.65	0.00	0.00	0		21	100	84	87.11
66	5.1	5	1	CH	94.08.04	6.0	0.50	0.71	0.01	0.00	0		22	96	83	85.05
74	5.1	5	1	CH	94.08.10	5.5	0.91	1.3	0.06	0.00	0		36	136	78	75.11
81	5.1	5	1	CH	94.08.17	5.6	0.70	1	0.04	0.00	0		29	115	81	81.00
88	5.1	5	1	CH	94.08.24	6.0	0.24	0.51	0.11	0.00	0		10	59	84	87.11
96	5.1	5	1	CH	94.08.31	5.5	0.64	1	0.03	0.00	0		20	110	80	79.01
66	5.2	5	2	NG	94.06.12	6.5	0.68	0.9	0.05	0.00	0		28	125	84	87.11
75	5.2	5	2	NG	94.06.16	5.4	0.74	1.0	0.06	0.00	0		44	140	78	75.11
83	5.2	5	2	NG	94.06.22	6.6	0.39	0.29	0.00	0.00	0	0.07	19	120	86	91.31
131	5.2	5	2	NG	94.10.12	6.0	0.56	0.50	0.00	0.00	0		40	104	82	83.01
23	5.2	5	2	CH	94.06.29	5.7	0.68	0.90	0.05	0.00	0		29	127.7	81	81.00
24	5.2	5	2	CH	94.06.29	7.7	0.68	0.90	0.04	0.00	0		30	127.7	84	87.11
47	5.2	5	2	CH	94.07.14	5.9	0.52	0.22	0.00	0.00	0		21	95	83	85.05
59	5.2	5	2	CH	94.07.27	6.0	0.60	0.54	0.02	0.00	0		26	106	83	85.05
67	5.2	5	2	CH	94.08.04	6.2	0.45	0.29	0.00	0.00	0		23	100	85	89.20
79	5.2	5	2	CH	94.08.10	5.3	0.87	0.76	0.07	0.01	10		42	136	78	75.11
89	5.2	5	2	CH	94.08.24	6.2	0.24	0.43	0.00	0.00	0		10	62	86	91.31
67	5.3	5	3	NG	94.06.12	7.0	0.40	0.16	0.01	0.00	0		23	132	86	91.31
76	5.3	5	3	NG	94.06.16	6.2	0.40	0.05	0.00	0.00	0		31	130	84	87.11
132	5.3	5	3	NG	94.10.12	6.5	0.37	0.34	0.00	0.00	0		30	108	85	89.20
13	5.3	5	3	CH	94.06.23	6.6	0.38	0.10	0.00	0.00	0		23	117.9	86	91.31
14	5.3	5	3	CH	94.06.23	6.5	0.38	0.11	0.01	0.00	0		21	117.7	86	91.31
15	5.3	5	3	CH	94.06.23	6.5	0.38	0.12	0.00	0.00	0		21	117.5	86	91.31
20	5.3	5	3	CH	94.06.29	6.2	0.43	0.09	0.02	0.00	0		29	148.8	85	89.20
21	5.3	5	3	CH	94.06.29	6.3	0.42	0.11	0.00	0.00	0		24	127.7	85	89.20
22	5.3	5	3	CH	94.06.29	6.2	0.42	0.08	0.00	0.00	0		24		85	89.20
38	5.3	5	3	CH	94.07.06	6.5	0.41	0.35	0.00	0.00	0		28	117	86	91.31
39	5.3	5	3	CH	94.07.06	6.5	0.41	0.37	0.00	0.00	0		28	116	86	91.31
40	5.3	5	3	CH	94.07.06	6.5	0.40	0.37	0.00	0.00	0		28	116	86	91.31
48	5.3	5	3	CH	94.07.14	6.3	0.34	0.30	0.00	0.00	0		19	102	85	89.20
53	5.3	5	3	CH	94.07.20	6.3	0.46	0.26	0.00	0.00	0		26	130	85	89.20
60	5.3	5	3	CH	94.07.27	6.5	0.33	0.26	0.00	0.00	0		20	102	86	91.31
68	5.3	5	3	CH	94.08.04	6.5	0.31	0.29	0.00	0.00	0		21	104	86	91.31
75	5.3	5	3	CH	94.08.10	6.3	0.55	0.43	0.01	0.00	0		31	132	83	85.05
84	5.3	5	3	CH	94.08.17	6.5	0.37	0.28	0.00	0.00	0		27	116	86	91.31
90	5.3	5	3	CH	94.08.24	6.3	0.19	0.39	0.00	0.00	0		10	67	86	91.31
98	5.3	5	3	CH	94.08.31	6.0	0.44	0.41	0.00	0.00	0		30	114	83	85.05
68	5.4	5	4	NG	94.06.12	7.1	0.38	0.00	0.00	0.00	0		23	144	87	93.44
77	5.4	5	4	NG	94.06.16	9.3	0.07	0.00	0.00	0.00	0		29	210	87	93.44
133	5.4	5	4	NG	94.10.12	9.0	0.24	0.32	0.00	0.00	0		25	183	86	91.31
49	5.4	5	4	CH	94.07.14	6.7	0.31	0.24	0.00	0.00	0		19	109	86	91.31
54	5.4	5	4	CH	94.07.20	9.5	0.10	0.05	0.00	0.00	0		28	236	86	91.31
61	5.4	5	4	CH	94.07.27	6.8	0.27	0.15	0.00	0.00	0		19	111	86	91.31
69	5.4	5	4	CH	94.08.04	10.1	0.17	0.29	0.00	0.00	0		21	200	86	91.31
76	5.4	5	4	CH	94.08.10	9.9	0.19	0.09	0.00	0.00	0		59	311	84	87.11
86	5.4	5	4	CH	94.08.17	9.7	0.18	0.18	0.04	0.00	0		24	241	86	91.31
91	5.4	5	4	CH	94.08.24	7.4	0.21	0.37	0.00	0.00	0		11	75	87	93.44
99	5.4	5	4	CH	94.08.31	9.7	0.14	0.16	0.00	0.00	0		10	245	87	93.44
65	5.5	5	5	NG	94.06.12	8.8	0.01	0.00	0.00	0.00	0		25	235	88	95.60
78	5.5	5	5	NG	94.06.16	6.2	0.34	0.00	0.00	0.00	0		29	160	86	91.31
134	5.5	5	5	NG	94.10.12	7.8	0.34	0.34	0.00	0.00	0		40	475	85	89.20
25	5.5	5	5	CH	94.06.29	6.9	0.25	0.00	0.00	0.00	0			831	64	
26	5.5	5	5	CH	94.06.29	7.1	0.32	0.00	0.05	0.00	0			801	63	
50	5.5	5	5	CH	94.07.14	7.0	0.27	0.26	0.00	0.00	0			145	63	
62	5.5	5	5	CH	94.07.27	9.4	0.09	0.04	0.00	0.00	0			353	64	
70	5.5	5	5	CH	94.08.04	8.3	0.19	0.32	0.00	0.00	0			352	63	
85	5.5	5	5	CH	94.08.17	9.5	0.12	0.05	0.00	0.00	0			3750	63	
92	5.5	5	5	CH	94.08.24	9.2	0.15	0.38	0.00	0.00	0			262	63	
100	5.5	5	5	CH	94.08.31	9.5	0.13	0.10	0.00	0.00	0		40	1030	85	89.20
4	5.9	5	9	NG	94.05.16	6.3	2.7	4.9	0.33	0.00	0		8	60	83	85.05
71	5.9	5	9	NG	94.06.16	5.3	0.75	0.01	0.17	0.00	0		33	120	80	79.01
122	5.9	5	9	NG	94.10.12	4.3	0.54	4.2	0.27	0.00	0		80	130	74	67.60

14	7.4	7	4	NG	94.05.16	3.7	3.4	0.33	0.35	0.00	0		140	270	71	62.23
62	7.4	7	4	NG	94.06.08	3.5	3.4	3.0	0.64	0.00	0		240	610	68	57.09
15	7.41	7	41	NG	94.05.16	4.9	0.87	0.00	0.18	0.00	0		35	130	79	77.05
127	7.5	7	5	NG	94.10.12	3.5	29	146	2.8	0.06	60		2000	2620	48	28.44
13	7.6	7	6	NG	94.05.16	4.0	5.7	4.02	4.5	0.00	0		255	430	68	57.09
129	7.7	7	7	NG	94.10.12	4.8	10.0	0.20	0.71	0.01	10		310	585	69	58.78
37	7.8	7	8	NG	94.05.17	6.7	0.10	0.31	0.02	0.00	0			170	63	
50	7.8	7	8	NG	94.06.08	6.6	0.16	0.42	0.01	0.00	0		26	190	86	91.31
51	7.8	7	8	NG	94.06.08	6.6	0.16	0.46	0.01	0.00	0		26	190	86	91.31
128	7.8	7	8	NG	94.10.12	6.7	1.9	7.4	0.14	0.00	0		70	237	79	77.05
26	7.9	7	9	NG	94.05.17	3.7	3.6	4.07	6.2	0.00	0		802	1150	62	47.46
125	7.9	7	9	NG	94.10.12	4.0	7.7	0.66	9.4	0.00	0		1670	2240	61	45.94
17	8.1	8	1	NG	94.05.17	6.8	0.02	0.03	0.02	0.00	0		9	100	90	100.00
38	8.1	8	1	NG	94.05.17	6.7	0.00	0.00	0.00	0.00	0		7	60	90	100.00
39	8.1	8	1	NG	94.05.17	6.6	0.00	0.00	0.00	0.00	0		6	60	90	100.00
46	8.1	8	1	NG	94.06.02	7.2	0.08	0.42	0.02	0.00	0		7	90	88	95.60
47	8.1	8	1	NG	94.06.02	7.2	0.05	0.16	0.00	0.00	0		8	90	88	95.60
57	8.1	8	1	NG	94.06.08	6.4	0.05	0.14	0.30	0.00	0		7	80	86	91.31
58	8.1	8	1	NG	94.06.08	6.4	0.02	0.12	0.00	0.00	0		6	80	88	95.60
63	8.1	8	1	NG	94.06.12	7.4	0.07	0.00	0.02	0.00	0		7	85	89	97.79
70	8.1	8	1	NG	94.06.16	6.8	0.00	0.00	0.00	0.00	0		11	220	89	97.79
82	8.1	8	1	NG	94.06.22	6.8	0.04	0.00	0.00	0.00	0	0.07	5	60	90	100.00
104	8.1	8	1	NG	94.08.03	5.5	0.18	0.86	0.03	0	0	0.196	8	60	84	87.11
114	8.1	8	1	NG	94.09.07	5.9	0.12	0.26	0.00	0	0	0.19	5	62	86	91.31
121	8.1	8	1	NG	94.10.12	6.5	0.12	0.24	0.00	0.00	0		9	69	88	95.60
1	8.1	8	1	CH	94.06.16	7.4	0.02	0.00	0.00	0.00	0		6	85.6	90	100.00
2	8.1	8	1	CH	94.06.16	7.4	0.01	0.00	0.00	0.00	0		19	85.3	88	95.60
3	8.1	8	1	CH	94.06.16	7.4	0.00	0.00	0.00	0.00	0		6		90	100.00
7	8.1	8	1	CH	94.06.23	6.5	0.01	0.00	0.00	0.00	0		5	74.2	90	100.00
8	8.1	8	1	CH	94.06.23	6.5	0.00	0.00	0.00	0.00	0		5	73.7	90	100.00
9	8.1	8	1	CH	94.06.23	6.5	0.01	0.00	0.00	0.00	0		5	75	90	100.00
16	8.1	8	1	CH	94.06.29	7.2	0.00	0.00	0.00	0.00	0		6	79.2	90	100.00
17	8.1	8	1	CH	94.06.29	7.1	0.02	0.00	0.00	0.00	0		5	77.5	90	100.00
32	8.1	8	1	CH	94.07.06	7.1	0.04	0.10	0.00	0.00	0		5	75	89	97.79
33	8.1	8	1	CH	94.07.06	7.1	0.05	0.09	0.00	0.00	0		5	74	88	95.60
34	8.1	8	1	CH	94.07.06	7.1	0.04	0.08	0.00	0.00	0		5	71	89	97.79
43	8.1	8	1	CH	94.07.14	6.9	0.06	0.16	0.01	0.00	0		5	62	88	95.60
51	8.1	8	1	CH	94.07.20	6.9	0.04	0.08	0.00	0.00	0		6	75	89	97.79
57	8.1	8	1	CH	94.07.27	6.8	0.06	0.11	0.00	0.00	0		5	69	88	95.60
65	8.1	8	1	CH	94.08.04	6.7	0.05	0.14	0.00	0.00	0		6	60	88	95.60
73	8.1	8	1	CH	94.08.10	6.9	0.04	0.04	0.00	0.00	0		6	79	90	100.00
80	8.1	8	1	CH	94.08.17	6.9	0.07	0.08	0.00	0.00	0		5	70	88	95.60
87	8.1	8	1	CH	94.08.24	6.4	0.12	0.23	0.00	0.00	0		3	42	87	93.44
95	8.1	8	1	CH	94.08.31	6.8	0.11	0.17	0.00	0.00	0		4	65	88	95.60
87	9	9	0	NG	94.06.22	3.0	18	88	12	0.07	70	64.28	239	700	53	34.68
92	9	9	0	NG	94.07.13	2.9	8.3	20	6.3	0.02	20	17.7	360	850	58	41.53
101	9	9	0	NG	94.08.03	2.9	7.4	8.1	5.4	0.01	10	0.144	540	1080	57	40.11
118	9	9	0	NG	94.09.07	2.9	18	57	17	0.06	60	16.95	400	1040	51	32.11
140	9	9	0	NG	94.10.13	2.9	13.7	12	9.4	0.04	40		510	1450	54	36.00