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## BUREAU OF MINERAL RESOURCES, GEOLOGY AND GEOPHYSICS

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ZINC POLLUTION IN THE MOLONGLO RIVER SYSTEM

by

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Fig. 2 Location of tailings dumps, Lake George Mine.

## SUMMARY

Following the outcome of testing of geochemical prospecting techniques applied to stream sediments and waters, the distribution of zinc in the Molonglo River, N.S.W., has been investigated over a period of twelve years. Zinc was found to enter the river from the Lake George Mine at Captains Flat (abandoned in 1962). Individual sources of zinc and other pollutants are identified. The collapse of tailings ponds in 1939 and 1942 spread soluble and suspended material over the river flood plain, and this is considered to contribute to the zinc load in the river.

The behaviour of zinc and copper is discussed. Copper is removed rapidly from solution, and zinc much later. A mechanism of precipitation of copper as a basic sulphate at pH 5 to 5.5, and zinc as a basic carbonate at higher pH is proposed.

Sediment formed by precipitation was found to contain anomalously high amounts of trace metals derived from the mine effluents - notably copper, lead, and zinc. Sediments carried downstream for 70 to 80 km still showed high values for lead and zinc.

## INTRODUCTION

Water pollution is defined as the introduction of substances which alter the natural quality of the water so as to impair its usefulness or render it offensive to sight, taste, and smell. It is in this sense that 'pollution' is used in this report. On the other hand, contamination of water is the introduction of pathogenic organisms or toxic substances that render the water unfit for domestic consumption.

The first systematic sampling of the Molonglo River by the Bureau of Mineral Resources arose from an investigation of geochemical prospecting methods for stream sediments and waters during 1959. The only earlier records of water analyses of the Molonglo River upstream of Burbong (site 9, Fig. 1) are one sample taken in July 1943, and another in December 1958. The anomalous amounts of zinc found in the waters and sediments of the river led to its selection for a study of the behaviour of metal ions in a natural stream. Elucidation of the pattern of the pollution in the river follows from this investigation.

The Molonglo River rises in New South Wales about 52 km south-south-east of Canberra at an elevation of about 1200 m. The course of the river as far as Lake Burley Griffin and the location of sampling points are shown in Figure 1. About 11 km downstream, the river flows through the town of Captains Flat where the abandoned Lake George Mine is located.

Sulphide mineralization at Captains Flat was discovered in 1878 and mining began in 1880. Activity was spasmodic until 1937 when Lake George Mines Pty Ltd reopened the mine. Production was continuous from January 1939 until March 1962; the mine was finally abandoned in July 1962. It was during this latter period of operation that pollution of the river first came under close examination, although the first report of pollution of the Molonglo River by mining at Captains Flat is recorded in the Annual Report of the N.S.W. Department of Mines for 1911.

During August 1939, a slimes pond (A, Fig. 2) used for the settlement of tailings from the floatation plant burst its retaining wall and discharged tailings and mill water directly into the Molonglo River near the high-level road bridge immediately downstream of Captains Flat township. There is no record available of any investigation of the effects of this collapse.

In July 1942 - there was another collapse, this time in the dumps immediately adjacent to and uphill of the town reservoir (B, Fig. 2). An estimated 30 000 m<sup>3</sup> of tailings consisting mainly of siliceous gangue, pyrite, and weathering products slipped into the reservoir displacing an equivalent volume of water which carried tailings and soluble material into the Molonglo

River. Suspended material was subsequently deposited as far downstream as Sutton Road Bridge (Site 10, Fig. 1). Vegetation was destroyed along the Molonglo valley, particularly between Sites 5 and 6 (Fig. 1). This is considered to be due mainly to soluble sulphates and associated acidity. Some of the affected areas have not yet recovered fully.

During the period of mining from 1939 to 1962, water pumped from the lower levels in the mine together with waste water from the floatation plant and other mine drainage flowed into the Molonglo River via Copper Creek. When the mine closed, pumping ceased and the workings quickly flooded to overflow through the ventilation shaft at the northern end opposite the high-level road bridge. The overflow was investigated by the N.S.W. Department of Mines and was effectively sealed in December 1966. No further leakage has occurred from the ventilation shaft.

#### SOURCES OF POLLUTION

Pollution in the Molonglo River now is from the addition of zinc which is highly toxic to fish. During the operation of the mine other pollutants e.g. floatation reagents containing thiocyanate, cyanide and phenolic compounds were present, also the river had a characteristic odour which occasionally is still noticeable as far downstream as the Hoskinstown Road Bridge (Site 5).

Semiquantitative field testing in July 1959 showed no zinc or copper in the Molonglo waters above Captains Flat. At the same time zinc and copper were found in water draining from the mine via Copper Creek and zinc was detected in river water as far downstream as Site 10. Zinc was also detected in alluvium along the river course between Sites 5 and 6. Subsequent investigation confirmed the presence of zinc in the flanking alluvium from 3 km downstream of Lake George Mine to Site 10 at Sutton Road Bridge.

Detailed sampling around Captains Flat has indicated pollutants entering the river at the following points:-

- (1) from the southern dumps at a point immediately below the town reservoir at the pump house (Forsters Creek)
- (2) immediately upstream of the high-level road bridge opposite the northern dumps
- (3) from Copper Creek.

**Fig. 1 MOLONGLO RIVER AREA**  
**(SAMPLING STATIONS & GEOLOGY)**

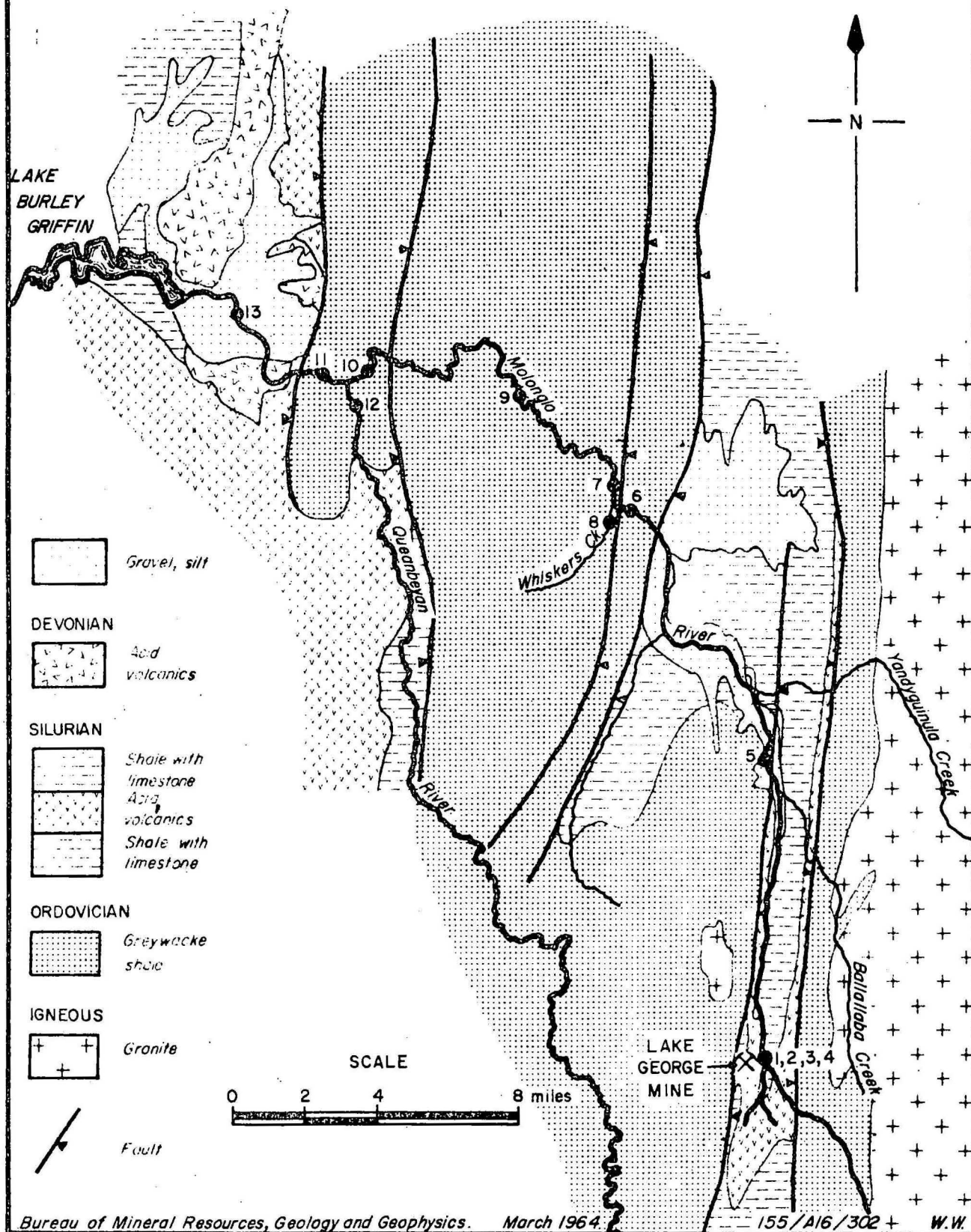
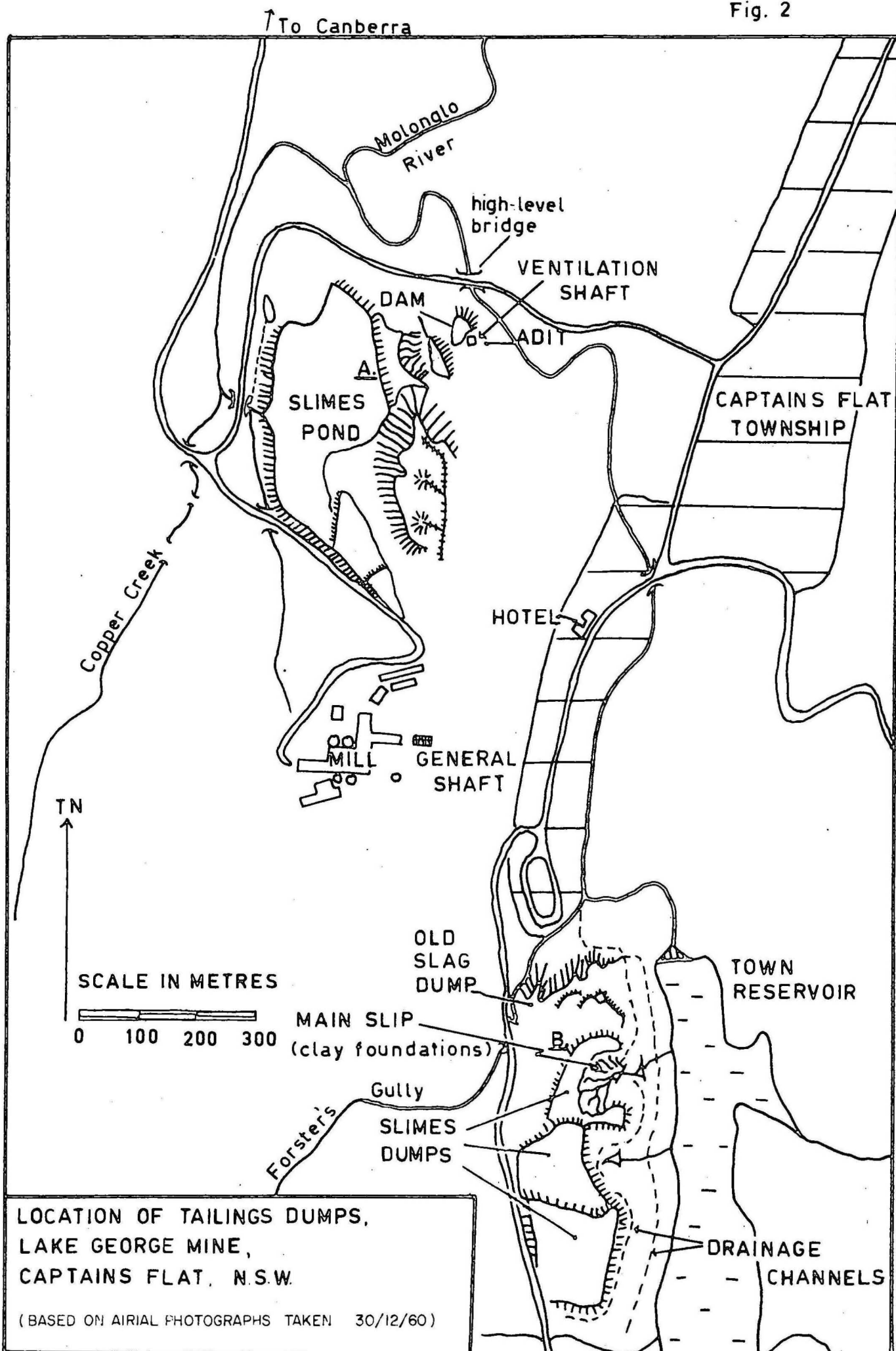




Fig. 2





Water entering the river at Forsters Creek below the dam is drainage from the southern dumps and may contain high levels of iron, aluminium, magnesium, and sulphate in addition to zinc and other metals. Partial analysis of water samples from various ponds and drains is shown in Table 1.

TABLE 1. Water samples from southern dumps, Captains Flat, N.S.W.

| Date    | pH  | Conductivity<br>( $\text{mho} \times 10^{-6}/\text{cm}$ ) | Cu<br>ppm | Pb<br>ppm | Zn<br>ppm | Cd<br>ppm |
|---------|-----|---|-----------|-----------|-----------|-----------|
| 24-8-65 | 2.8 | 6500  | -         | -         | 180       | -         |
| 20-4-70 | 2.3 | 13300   | 63.8      | $<0.2$    | 2400      | 4.5       |
| 7-7-71  | 2.5 | 25900   | 63.2      | $<0.2$    | 6200      | 4.9       |

In addition, water is draining directly into the reservoir from the upper levels of the southern dumps. The quantity of pollutants entering the river from the dumps depends on rainfall, being greatest in concentration and amount following substantial rain after a dry spell.

Several inspection pits dug in the two most southerly dumps suggest that active oxidation of the sulphides contained in the dumps is restricted to a zone 15 to 30 cm below the surface. The main residual pyrite weathering products are jarosite/plumbojarosite, gypsum, and goethite; soluble products are removed in drainage water.

Water draining from the northern dumps flows into the river via Copper Creek and a concrete drainpipe set in the lower of the two settling dams adjacent to the ventilation shaft. Partial analyses of these waters are given in Tables 2 and 3.

TABLE 2. Water samples from northern dumps, Captains Flat, N.S.W.

| Source               | Date     | pH  | Conductivity<br>( $\text{mho} \times 10^{-6}/\text{cm}$ ) | Cu<br>ppm | Pb<br>ppm | Zn<br>ppm |
|----------------------|----------|-----|---|-----------|-----------|-----------|
| Drainpipe            | 14-9-64  | 3.2 | 11900   | -         | -         | 3760      |
| "                    | 23-8-65  | 2.9 | 10700   | 0.2       | -         | 2840      |
| "                    | 20-4-70  | 2.5 | 6000  | 0.6       | $<0.2$    | 200       |
| "                    | 7-7-71   | 2.9 | 11600   | 0.8       | $<0.2$    | 600       |
| Ventilation<br>Shaft | 3-11-64  | 3.6 |   | 0.1       | 2.0       | 3000      |
| "                    | 28-8-65  | 3.4 | 10600   | 0.2       | -         | 3840      |
| "                    | 18-10-67 | 3.6 | 8100  | -         | -         | 920       |

Other metals detected in dump drainage and mine water are cadmium, cobalt, nickel, and chromium. Mercury was not detected.

Analyses of mine water flowing into the river from the ventilation shaft are also included in Table 2. Pollution from this source ceased in December 1966 and no further activity is anticipated. However, water from the mine continues to seep into the river from bedrock fissures and from a disused adit immediately upstream of the ventilation shaft. These must be considered as a potential source of pollution, particularly if any purging of the leakage path occurs.

Copper Creek forms the natural drainage line for the mine area and at present carries surface water draining away from the mill site and northern slimes ponds. During operation of the mine it also carried water pumped from the mine workings and other mine effluent. Table 3 gives partial analysis for mine water, a number of samples from Copper Creek, and water ponded at the mill site.

TABLE 3. Mine water and Copper Creek, Captains Flat, N.S.W.

| Source       | Date     | pH  | Cu<br>ppm | Zn<br>ppm | CNS<br>ppm | SO <sub>4</sub><br>ppm |
|--------------|----------|-----|-----------|-----------|------------|------------------------|
| Mine water   | 1948     | 3.1 | 8         | 850       | nil        | 2720                   |
| " "          | 25-9-61  | 5.6 | 11        | 530       | nil        | 3410                   |
| Copper Creek | 16-3-60  | 3.6 |           | 310       | 40         | 1600                   |
| " "          | 30-3-60  | 3.2 | 5         | 640       | nil        | 2300                   |
| " "          | 13-4-60  | 3.7 | 5         | 540       | 30         | 2630                   |
| " "          | 25-10-61 | 3.7 | 3         | 480       | 26         | 2930                   |
| Mill pond*   | 20-4-70  | 2.4 | 37        | 700       | nil        |                        |

\* also contains 1.5 ppm Pb and 1.4 ppm Cd.

Thiocyanate (CNS) is derived from the floatation process where it is used as a depressant and clearly indicates pollution by water from the floatation plant. This water would also contain other floatation reagents e.g. cyanide, xanthates, cresols, sulphides, and phenols. It cannot be assumed that these pollutants would entirely disappear after the closure of the mill as the slimes dumps would initially be saturated with mill water and the floatation agents would only be removed as the natural leaching of the dumps proceeded. There is no information at present to indicate whether all the floatation reagents have been leached from the slimes dumps.

A further source of pollution exists outside the mine area as a result of the 1939 and 1942 slimes dumps collapses which spread tailings material over the Molonglo flood plain.

No quantitative data are available on the amount of tailings material dispersed over the flood plain or on the rate of release and leaching of pollutants into the river. The gradual re-establishment of vegetation in the denuded area over a period of 30 years can be taken as indirect evidence of the leaching of toxic substances from the soils of the flood plain. Qualitative testing of spring water seeping from the river banks has established that zinc enters the river; however, further quantitative investigation is needed to establish the extent to which this source contributes to pollution of the river.

It is evident that during its active life the Lake George Mine caused substantial pollution of the Molonglo River. Closure of the mine has eliminated one source of pollution, namely mine effluent, but seepage as well as the drainage from the dumps and flood-plain deposits still remains. This is illustrated in Table 4 which shows the average zinc concentration for a number of sites along the river both before and after sealing of the ventilation shaft in December 1966.

**TABLE 4.** Average monthly zinc content of Molonglo River

| Source              | Mar. 1965 to Dec. 1966 | Jan. 1967 to Jan. 1969 |
|---------------------|------------------------|------------------------|
|                     | ppm                    | ppm                    |
| Site 1 Fig. 1       | 100                    | 18                     |
| 5                   | 63                     | 23                     |
| 6                   | 30                     | 7.4                    |
| 10                  | 11                     | 2.3                    |
| 13                  | 0.9                    | 0.3                    |
| Lake Burley Griffin | 0.1                    | 0.1                    |

Although there has been a substantial reduction in the zinc level, sealing of the mine leakage has not resulted in the elimination of zinc from the river. As zinc is less than 0.02 ppm in the Molonglo River above Captains Flat the zinc concentration at Site 1 after December 1966 is a measure of the pollution resulting from drainage from the dumps. Also the higher zinc value at Site 5 relative to Site 1 for the period January 1967 to January 1969 suggests that the level of zinc is being maintained by leaching from the flanking river alluvium. The marked drop in zinc level between Sites 10 and 13 is due mainly to dilution by the Queanbeyan River.

## BEHAVIOUR OF METALLIC POLLUTANTS

The two metals for which there are sufficient data to determine their gross behaviour along the length of the river are copper and zinc. Proceeding downstream the copper concentration falls with rising pH of the water at a comparatively rapid rate (as shown in Table 5) so that in a distance of less than 30 km the river is cleared of all abnormal dissolved copper.

The behaviour of zinc is similar, but precipitation occurs much later and zinc persists at a high level for a distance of at least 61 km. At this point dilution by the Queanbeyan River causes a substantial reduction in the zinc concentration.

**TABLE 5.** Partial analysis of Molonglo River water 13-4-60

| Source         | Distance from<br>Captains Flat<br>(km) | pH  | Cu<br>ppm | Zn<br>ppm | SO <sub>4</sub><br>ppm | HCO <sub>3</sub><br>ppm |
|----------------|--|-----|-----------|-----------|------------------------|-------------------------|
| Copper Ck      |  | 3.7 | 5.0       | 540       | 2630                   | nil                     |
| Site 2, Fig. 1 | 4                                      | 3.8 | 1.5       | 210       | 1450                   | nil                     |
| 5              | 13                                     | 4.8 | 0.5       | 90        | 540                    | nil                     |
| 6              | 31                                     | 6.4 | 0.05      | 54        | 375                    | 7                       |
| 9              | 46                                     | 7.3 | <0.05     | 39        | 310                    | 42                      |
| 10             | 61                                     | 7.3 | <0.05     | 38        | 410                    | 26                      |
| 13             | 71                                     | 7.6 | <0.05     | 3         | 60                     | 75                      |
| Corkhills      | 84                                     | 8.0 | <0.05     | 0.5       | 46                     | 99                      |

The fall in copper and zinc levels between Copper Creek and the first Molonglo River sample at Site 2 is due partly to dilution and partly to the precipitation of basic salts. Below a pH of about 3.5, both copper and zinc exist solely in the dissolved (ionic) state; as the pH of the water rises hydrolysis increases, resulting in the formation of basic salts at a progressively faster rate as the pH approaches that required for complete precipitation. In the case of copper this process occurs over the range of about pH 4 to pH 5-5.5.

Copper forms a basic sulphate and two basic carbonates, all of which are insoluble. The abundance of sulphate ions and the absence of bicarbonate ions at Sites 2 and 5 would lead to the formation of a basic copper sulphate as the precipitating species.

Zinc is not so readily precipitated as is copper and differs in not forming a basic sulphate but only insoluble carbonates. Co-precipitation/adsorption phenomena are considered to be mainly responsible for the removal of dissolved zinc in the more acid regions of the river. The precipitation of zinc must wait until the bicarbonate level, and consequently the pH, has risen sufficiently for the formation of a basic zinc carbonate. The latter is the main mechanism for the removal of zinc from solution in the lower reaches of the Molonglo and in Lake Burley Griffin. For example, at Site 13 downstream of the confluence of the Molonglo and Queanbeyan Rivers the reduction in zinc level cannot be accounted for by simple dilution, the additional bicarbonate supplied by the Queanbeyan River also contributing to the removal of dissolved zinc as insoluble carbonate.

#### RIVER SEDIMENTS

With the removal of dissolved zinc and copper as insoluble 'basic salts' any sediment forming from colloids carried by the river would be expected to contain both zinc and copper. These 'colloid' sediments are to be distinguished from clastic material derived by erosion of the river banks which are known to contain zinc and copper from the slimes dump collapses. Table 6 gives the partial analysis of flocculated colloid sediments taken from the bed of the river at Sites 2 and 5 in September 1965. Great care was exercised when collecting these samples to completely eliminate any clastic material derived from the river bed. Also included are the corresponding values for four sediment samples taken from silt pans located in Lake Burley Griffin. These samples were collected during November 1969 by the Dept of Works.

TABLE 6. Partial analysis of river and lake sediments

| Source                     | Cu<br>ppm | Pb<br>ppm | Zn<br>ppm | Mn<br>ppm | Fe<br>% |
|----------------------------|-----------|-----------|-----------|-----------|---------|
| <u>Molonglo River</u>      |           |           |           |           |         |
| Site 2                     | 340       | 8950      | 1350      | 440       | 7.8     |
| Site 5                     | 1020      | 3040      | 2170      | 110       | 9.1     |
| <u>Lake Burley Griffin</u> |           |           |           |           |         |
| East Basin                 | *         | 220       | 2100      | 1280      | 4.0     |
| West Lake                  | *         | 220       | 1720      | 1280      | 3.5     |
| Yarralumla Bay             | *         | 180       | 1820      | 1080      | 3.7     |
| Nursery Bay                | 40        | 400       | 1040      | 960       | 2.4     |

\* Cu values are not given for East Basin, West Lake, and Yarralumla Bay as samples were collected in copper pans.

The lead values in the sediments at Sites 2 and 5 are remarkable in that lead has been detected in the mine water and dump drainage only, never in the Molonglo River. Its behaviour is controlled by the formation of lead sulphates. These are insoluble even in acid mine water so that very little lead is ever brought into solution. The separation of a sediment containing 0.9% Pb from water in which lead could not be detected is recorded at present and is left as an interesting problem in geochemistry for future study.

The results for sediment samples from silt pans in Lake Burley Griffin require analysis in terms of sediment load. They are included here for comparison with the sediments formed in the upper reaches of the river when mine water was still entering the river and pollution was much higher. They support the observation made in 1965 that metal-rich sediments can separate from water carrying only trace amounts of the metal.

The lead and zinc values are anomalously high and could not be found in any sediment derived from normal soils. Their source can only be from Lake George Mine and whether they enter Lake Burley Griffin as dissolved salts or as suspended material does not affect the potential source of pollution formed by the buildup over the greater portion of the lake of a bottom sediment containing 0.1 to 0.2% zinc. The lake sediments have also been found to contain abnormal concentrations of cadmium.

The effect of high levels of zinc and cadmium on the lake flora and its indirect effect on lake fauna are not known at present. No investigation has been made as it is considered to be outside the scope of the present work.