CHAPTER ONE

INTRODUCTION

1.1. GENERAL DESCRIPTION OF THE STUDY AREA

Kinghorn Loch is a small lake situated 1.5 km W.N.W. of the Burgh of Kinghorn within the Fife Region of Scotland and 13.3 km due north of the City of Edinburgh. It has a surface area of 11.3 ha and a maximum depth of 12.8 m. Since 1947 the loch has been the recipient of a highly alkaline discharge issuing from nearby Whinnyhall Tip, a landfill site operated by BA Chemicals Ltd., part of British Alcan Aluminium Company Limited, for the disposal of red mud.

Red mud is a waste product of bauxite dressing by the Bayer process during the production of alumina. It consists of iron and clay solids, being that part of the bauxite insoluble in concentrated sodium hydroxide at high temperature and pressure. However it also contains an aqueous phase (approximately 45% wet weight) comprising alkali not removed by the mud washing process. This phase contains alkali at a concentration of approximately 0.4 M and pH 13.4. The aqueous phase, in contrast to the solids, contains a proportion of all those ions which were dissolved from the bauxite including aluminium, arsenic, vanadium, sulphur, selenium, phosphorus, fluorine, and silicon. In addition commercial quality sodium hydroxide can contain mercury as a contaminant but none has been found during the study.

1.1.1. HISTORY OF POLLUTION.

Tipping of the material at Whinnyhall began in 1944-45 when the original coastal tip, operated since 1917, became filled. Drainage from this elevated site had been arranged by re-routing at least one spring to Kinghorn Loch. However by 1951 percolate was beginning to appear through the south wall of the tip and this seeped down the hillside to the Kirkton Burn and thence flowed west to the Firth of

Forth. This discharge quickly destroyed vegetation, including trees and was finally channelled to the burn in a system of drains.

By 1983 these two discharges, illustrated in Figure 1.1, had destroyed aquatic life in the Kirkton Burn and severely limited life in Kinghorn Loch. The leachate to the Kirkton Burn appeared to be "pure" leachate containing a little rain water percolate, and is the more alkaline of the two, averaging pH 12.8. Leachate to Kinghorn Loch averaged pH 12.1 due to its prior mixing with native spring water and was considerably lower in dissolved organic matter. By 1983 the pH of the loch had reached a level in excess of pH 10.

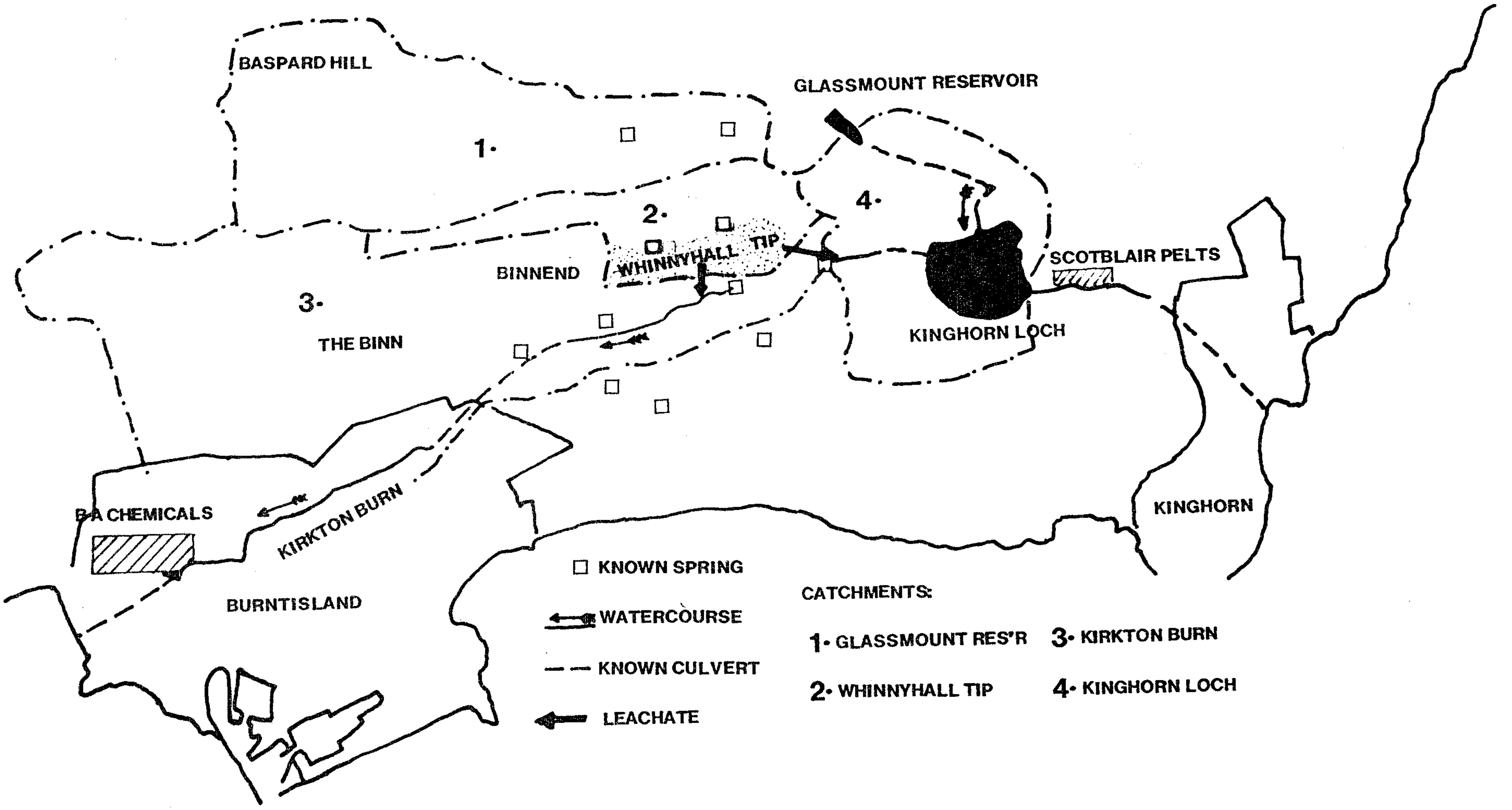
1.1.2. RECOVERY FROM POLLUTED STATE.

On the 25th May 1983, three years into the present study, this discharge was removed from the loch as part of a scheme designed to present the leachate for suitable treatment and disposal elsewhere. At the time of writing it is being pumped to the Kirkton Burn catchment to join its sister leachate. Proper disposal of the discharges is envisaged within an agreed timetable.

1.2. PREVIOUS WORK

Previous study of the loch had consisted almost entirely of the routine, and essentially passive, chemical analysis of the state of the water and of the incoming leachates performed by the F.R.P.B. Such analyses were carried out four times a year at best, and prior to 1978 were even less frequent. In 1978 the F.R.P.B. determined to improve the state of Kinghorn Loch and Kirkton Burn by the removal and proper treatment of the leachates. Chemical analytical effort was concentrated on the higher pH leachate to the Kirkton Burn and

FIGURE 1.1. Map showing the study area indicating locations named in the text



work, carried out in conjunction with BA Chemicals Ltd. was co-ordinated by the present author as an employee of the Board. It was intended to devise a treatment process more suited to the situation of the burn, than had been proposed by consultants to the company. This led to a conserted analytical effort with regard to the Kirkton Burn and confirmed that conceptually suitable treatment processes were available and considered economically viable.

The Biology Section of the F.R.P.B. had carried out faunal and floral surveys of the loch at intervals of 2-3 years. Weed sweep, benthic grab and plankton netting had been employed. The results had been used to detail the decline in biological activity and diversity in the loch.

1.3. AIMS OF THE STUDY

The primary aims have been to collate historical information and to provide analytical data, particularly chemical and geochemical but also ecological, in order to describe the situation found in the loch and its sediments prior to rehabilitation, and to follow, as far as the short duration of the study would allow, its recovery. To this end the development of a chemical speciation model was undertaken in order to endeavour to conclude what mineralization might occur and to quantify the chemical deposition of sediments.

The situation of the loch as an enclosed freshwater body of long residence time, and the way in which it received the discharge appears to be unique. Red mud is often disposed of by discharge to marine lagoons and the effect on the marine environment has been studied by several workers including Baseden[1] in Australia and

Hamada[2] in Japan. Burrows[3], in reviewing the marine ecological effects of red mud found that the presence of such a large quantity of extremely fine red mud caused ingestion problems for organisms that swamped any other effects. Effects due to ionic aluminium were also limited by the buffering capacity of the sea water.

In Kinghorn Loch only limited quantities of red mud reached the loch and the sediment load was derived from reaction with spring waters prior to reaching the loch and within the loch water itself. The buffering within the loch was in favour of the soluble ions present in the leachate as the natural waters have little buffering capacity. Thus the system has provided an opportunity to study chemical processes such as carbonate mineral formation and aluminosilicate formation and diagenesis under chemically favourable environmental conditions.

CHAPTER THREE

ORIGIN AND CHEMICAL COMPOSITION OF NATIVE WATERS

FIGURE 3.1. Solid geology of the catchments

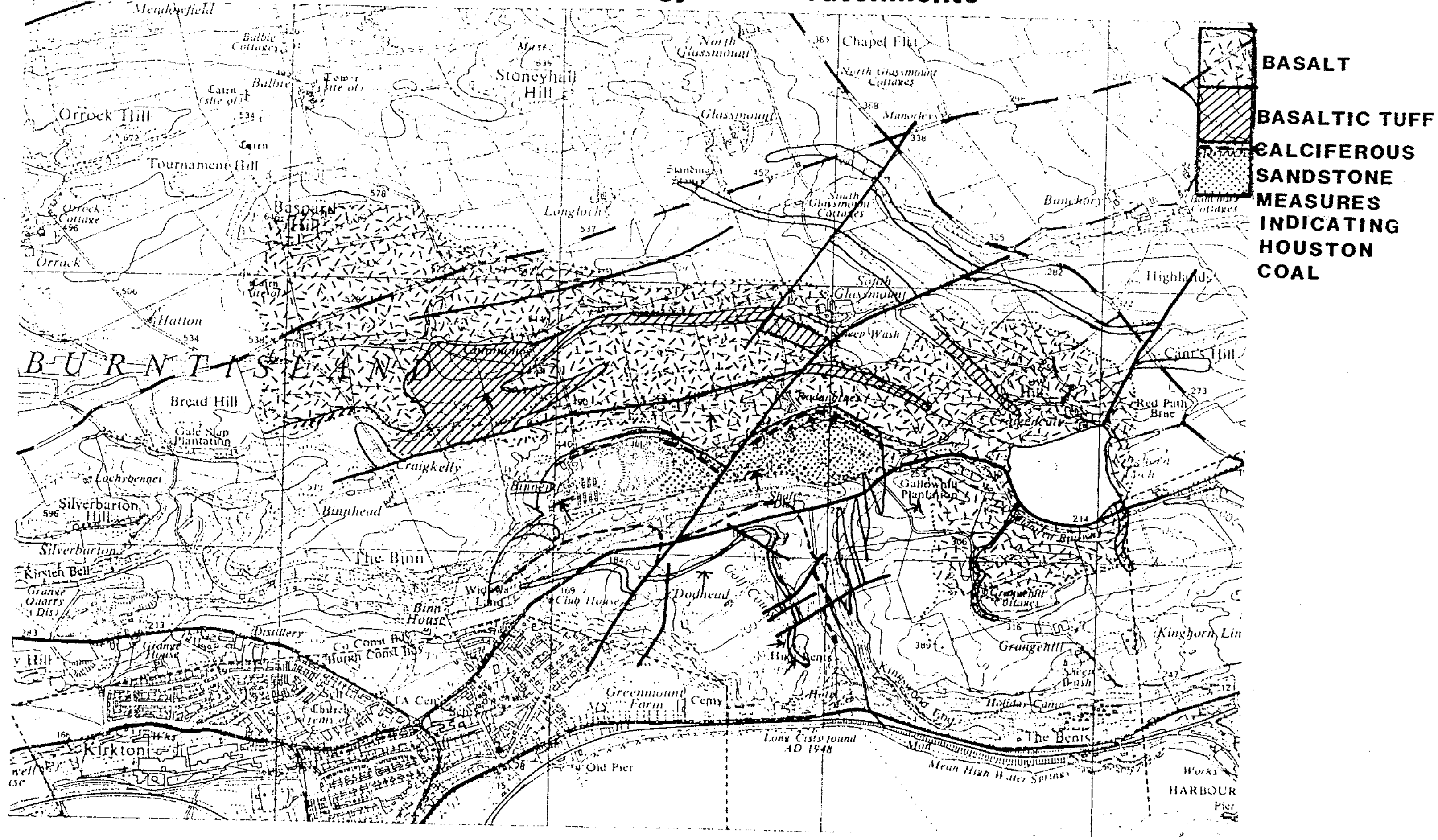
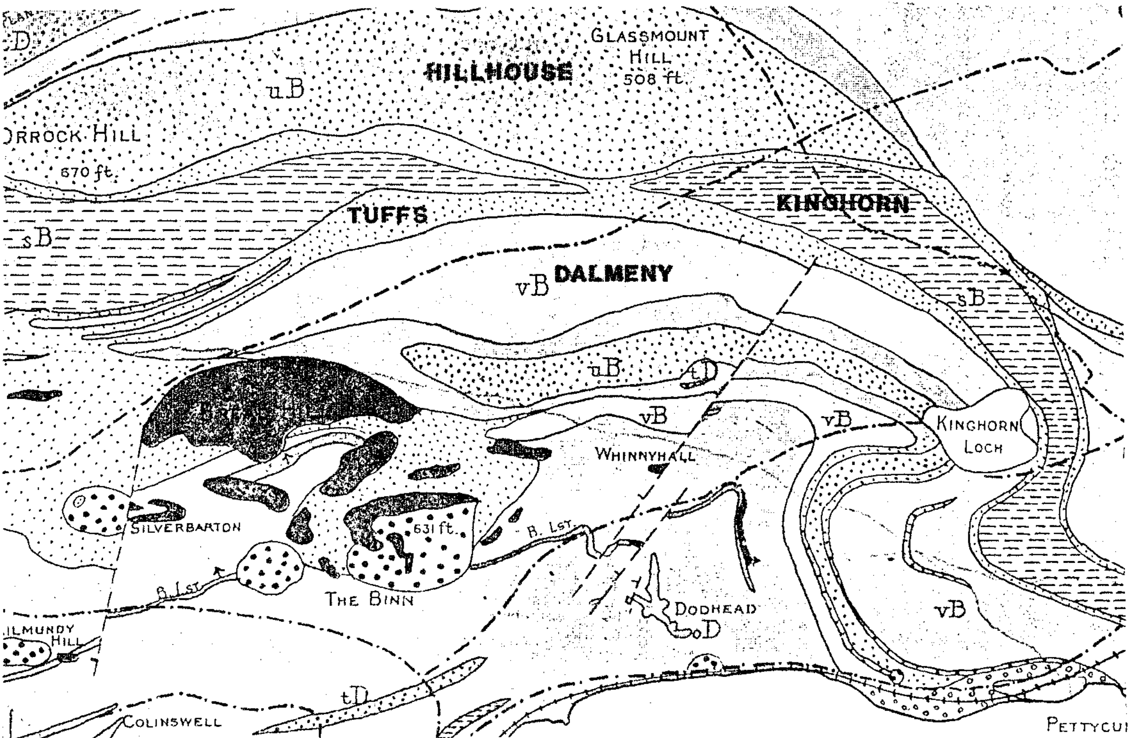


FIGURE 3.2. Basalt rock types : after Allan[16]



3.Kinghorn Type. A rock carrying many phenocrysts of olivine and augite in nearly equal proportions. The pyroxene, which is in slightly smaller crystals than the olivine, is somewhat purplish, and has a strong tendency to glomeroporphyritic aggregation. The groundmass is dark and fine-grained, consisting of laths of felspar, granules of augite, sometimes a little olivine, and specks of black iron oxide, together with a considerable quantity of uncrystallised base.

Elemental analysis of the types is also given, and reproduced here as Table 3.1. It will be noted that all are very similar in chemical composition.

	Dalmeny	Hillhouse	Kinghorn
SiO_2	46.28	42.49	43.56
Al_2O_3	14.18	13.85	13.77
Fe_2O_3	11.13	11.91	12.01
MgO	10.82	11.21	10.81
CaO	9.88	9.76	10.00
Na_2O	2.58	2.39	2.72
K_2O	1.01	0.87	0.46
TiO_2	2.06	2.51	2.85
P_2O_5	0.44	0.61	0.27
MnO	0.09	0.29	0.24

TABLE 3.1. Elemental Analysis of Basalt Rock Types. (analysis of Dalmeny type actually labelled Craiglockhart type - a similar rock.) Analysis is in % of gross weight.

Allan found that the tuffs contained not only volcanic material but dark shale, sandstones, thin limestone and coal, similar in diversity to those occuring below the lavas.

Whinnyhall Tip and the Kirkton Burn lie below the base of the lava. The scarp, forming the north edge of the tip, is topped by lavas lying over 4 m of sandstone with a coal seam, the Houston Coal, at its base. This coal seam was less than 0.5m thick and consisted of inferior coal containing much pyrite. The sandstone has a thickness of some 40 m above the Fells limestone and underlies Whinnyhall

Tip[15]. It is said to be of inferior quality, being soft and friable and containing silt and mudstones. It was used as an aquifer for public supply prior to becoming polluted and was believed to be artesian. Some 90 m below the lava base are the Dunnet Shale beds from which oil was extracted.

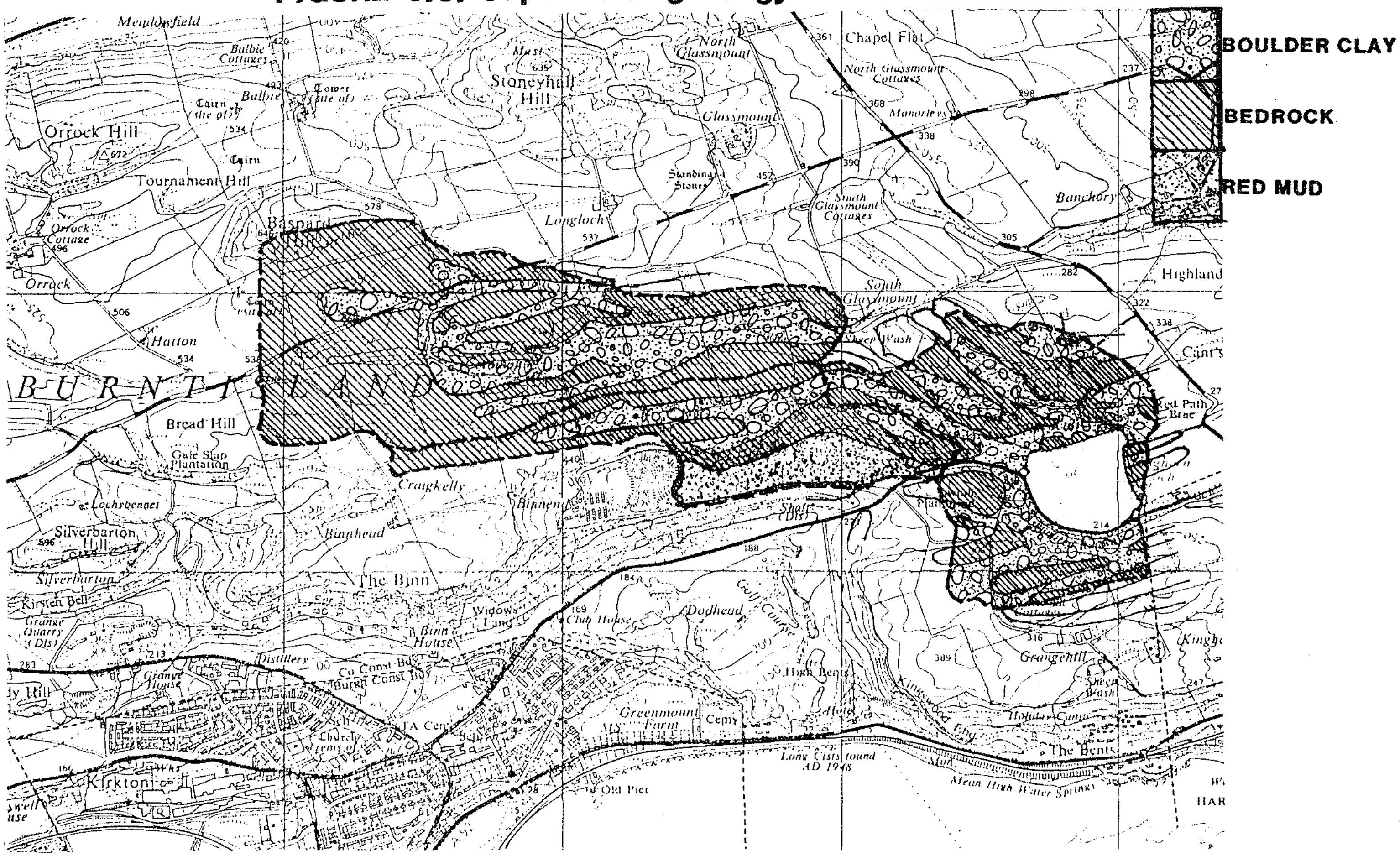
Figure 3.3. shows the superficial geology of the area. The boulder clay situated on the volcanic rocks are stiff clays containing many boulders and are rusty brown in colour[15]. Several of the hollows contained kettle holes and these are filled with peat. Boulder clay also overlay the sandstones of Whinnyhall Tip. This hollow held a lake and its section, as seen in 1887 during the railway construction, consisted of 0.3m peat, 0.3m marl, 1m greenish clay with shells, and 0.3m clay without shells over boulder clay[15]. It is probable that the construction of this cutting diverted drainage of the natural waters of Whinnyhall Tip from Kirkton Burn to Kinghorn Loch.

3.1.2. DRAINAGE PATTERN

In Figure 1.1. drainage to the loch had been divided into three "catchments" - Whinnyhall Tip, Glassmount Reservoir, and Kinghorn Loch. This is because of the special considerations required in considering flows from Whinnyhall Tip and because the water obtained via Glassmount Reservoir has been intercepted from its natural course.

If we assume that the area of Whinnyhall Tip that drains to Kinghorn Loch is 0.05 km^2 then:

FIGURE 3.3. Superficial geology of the catchments



For average annual rainfall(ex.Meteorological Office) = 750 mm

For mean evapotranspiration(ex MAFF Bulletin No.16) = 470 mm

For loss to groundwater through boulder clay; say = 50 mm

Then volume of run off =0.36 $l\ s^{-1}$

In fact the flow was 2.73 $l\ s^{-1}$ for 1981 to 1983.

Thus this simple treatment is inadequate. It is probable that the drainage from the whole of the valley goes to Kinghorn Loch and that the leachate to the Kirkton Burn acts as an overflow carrying drainage from above the consolidated red mud. Thus the loch would receive drainage from as far as Binnend at the head of the valley but not necessarily its fair share from the tipped red mud. Seepage to groundwater is likely to be much greater at Binnend where there is little boulder clay. Further although there may be losses by evaporation there is unlikely to be any through transpiration over much of the tip area. It is not considered that the red mud itself will in a net way contribute significantly to any flows. The situation is further complicated by the fact that much of the water draining this valley is spring water issuing from a line of springs at the base of the basalt. By consideration of the relative level of sodium (as a conservative parameter) in the red mud interstitial water, native water [taken from Craigencalt Farm (North) inlet analysis] and rainwater compared to that in the leachate, it is possible to estimate that the red mud interstitial water is diluted approximately 5:1 by native water and rainwater in forming the leachate.

When the loch was surveyed in 1905 as part of the Royal Geographical Survey[17] the catchment area was stated as being less than 60 ha, a ratio of only 5:1 compared to the surface area of the loch. Apart from some channelling of the marshy ground at the north west end of the loch and a wet area to the west of the main Craigencalt Farm (North) inlet there are no obvious flows into the loch within its own natural catchment.

Glassmount Reservoir collects water from an extensive series of underground culverts draining the area due west of the reservoir as far as Baspard Hill. The full extent of this collector system is not known but from the number of known springs in the area it is reasonable to assume that a significant proportion of the water going to the reservoir is derived from the basaltic tuff aquifers extensively outcropping in the area. In fact if a similar calculation to that given above is applied to a calculation of likely flow passing the mill at Craigencalt Farm then, for a catchment area of 1.4 km^2, the mean flow would be 9.9 $l\ s^{-1}$. This compares with an actual flow of 15±2.7 $l\ s^{-1}$ for 1981-1983. The precision available for the calculated value is not known. The evapotranspiration in the area is unlikely to be typically average and indeed is likely to be below average due to the lack of tree cover. The estimated contribution from groundwater loss is based on a layer of average boulder clay which presents a considerable resistance to hydraulic transfer. Much of the catchment valley floor is on permeable tuff which contains several springs. If springs can rise in this area then it is likely that discrete pathways exist for water to sink as well. If it is assumed that evapotranspiration could be 20% lower and that the variance in groundwater losses could be ±100% then the precision of the estimate becomes 10.8±3.1 $l\ s^{-1}$ (95% c.l.). Thus it is probable that at least 25% of the flow past the farm will have originated as groundwater.

Agricultural development of this catchment is greater than in the other catchment areas involved. Even so the majority of the area is given over to enclosed pasture and rough grazing with a smaller contribution from arable and animal feedstock production. It is unusual that this reservoir has consistently produced water with a high nitrate level (up to 10 mg l^{-1} as N) and this problem finally led to its use being discontinued in 1975. It was brought back into use in 1980 for a short time but at all other times full flow has been entering the loch (mean flow for 1981 to 1983 was 15 l s^{-1}). Problems with high nitrate levels are known, by the Water Supply Services of Fife Regional Council, to arise in areas of high aquifer production. The reason for this is not known.

The water flowing from this small reservoir is culverted to a filter house and thence to a mill pond serving the disused mill at Craigencalt Farm. It passes down the mill race into the loch.

3.2. CHEMICAL COMPOSITION.

Samples of the native water inputs to the loch have been collected and analysed on a weekly basis from January 1st 1981 until 1984. The data have been conveniently divided into pre- and post-May 1983; the time when the leachate flow was removed from the loch. Prior to this time the only discrete unpolluted native water input was the north inlet past Craigencalt Farm and the analysis is collated in Table A.2. of Appendix A.3. By reference to the statistical appraisal given in Appendix A it will be seen that for all important parameters (other than phosphate which is very low anyway) the requirement for the long-term mean to be within 10% of the true figure is met for concentration measurement but only at 20% for loadings (at 95% c.l.).

After May 1983 the flow at the settlement pond dam decreased but did not cease due to the flow from a natural spring at the head of the cutting. The water flowing from the settlement pond was redesignated as the west inlet. Post-May 1983 samples of the north inlet are collated in Table A.3. and of the west inlet in Table A.4. of Appendix A.3.

The north inlet possesses an unusually high pH for an oligotrophic water, averaging 8.1. pH's in excess of 8 would normally only be met, in the United Kingdom, by productive waters. The water is also moderately high in dissolved silicon (that which passes a 0.1um membrane) averaging 4.3 mg l^{-1} as Si. It is this input in particular which allows an interest in clay or aluminosilicate synthesis in the loch as the leachate, which is high in aluminium, is deficient in silicon. Due to the mode of collection of the north inlet water and its retention by Glassmount Reservoir, the inlet makes only a minor contribution to the suspended load to and within the loch. This is estimated (from Table A.2) at 5000 kg detrital solids each year.

No reliable information appears to be available concerning the composition of the water from the springs lying beneath the red mud. Those analyses that are available are, in the main, incomplete and apparently inconsistent and, excepting one from 1958, have not been considered here. However data are available from the author's study of the Kirkton Burn catchment between 1977 and 1979, carried out in pursuance of his normal duties with the F.R.P.B. These data are illustrated in Table 3.2. and include analyses of the source of the Kirkton Burn and several native springs draining to the Kirkton Burn within 0.5 km of its source.

location	I	II	III	IV	V
pH	7.5	8.3	8.5	7.2	.....
calcium	212	213	177	224	189*
magnesium	66	62	47	50	19*
sodium	184	144	85	96	108
potassium	9.6	20	13	12	.....
iron	.17*	.63*	.08*	11.8*	2.8*
manganese	.004	.205	.024	.237	.....
zinc	<.001	.003	.005	.004	.....
nickel	.002	.011	.004	.009	.....
copper	<.001	<.001	<.001	<.001	.....
chromium	.009	.005	.008	.012	.....
lead	.013	.015	.010	.004	.....
cadmium	.002	.002	.003	.005	.....
vanadium	.3	<.1	<.1	<.1	.....
aluminium	<.1	.1	.2	.2	2.6*
arsenic	.06	<.005	<.005	<.005	.....
alkalinity (as$CaCO_3$)	390	210	290	270	6.5@
hardness (as$CaCO_3$)	.....	.....	.....	.....	645*
chloride	55	36	26	27	33
sulphate (as S)	126	.....	.....	.....	130
nitrate (as N)	.15	.....	.....	.....	.....
ammonia (as N)	.8	.....	.....	.....	.....
phosphate (as P)	<.002	.....	.....	.....	.....
silica (as Si)	.....	.....	.....	.....	3.3*

TABLE 3.2. Analysis of Springs Rising Within the Calciferous Sandstone Series.
I rising of the Kirkton Burn
II water collected by pipe 100m downstream of I
III spring water entering burn 150m downstream of I
IV ferruginous spring water entering burn 300m downstream of I
V analysis of spring water from Whinnyhall Tip ex.oilshale workings (BA Chemicals - 1958).
All results in mg/l dissolved determinand other than marked * for total determinand. @ is considered an erroneous result.

All of these risings probably exit from mine workings within the Dunnet Shale beds but should be reasonably typical of the water contained within the Calciferous Sandstone Series proper. The west inlet to the loch originates from a similar source but may be affected to some extent by leachate seeping through the wall of

Whinnyhall Tip and also by the sediments still in the settlement pond. Vanadium and arsenic levels found in the Kirkton Burn rising indicate that it too was polluted by seepage from Whinnyhall Tip. It will be noted that the analysis of a spring, now buried by the tip, performed by BA Chemicals Ltd in 1958, is of a high sulphate, high calcium and moderate sodium and chloride type water similar to the other sources shown. However the alkalinity of this sample appears erroneous and no pH is provided. These waters are considerably more mineral-rich than the north inlet to Kinghorn Loch, though of a similar type. Thus the ratio of native water:leachate leaving Whinnyhall Tip of 5:1, as previously postulated on the basis of north inlet water analysis, may be an underestimate of the dilution available. The Kirkton Burn rising shows a much lower nitrogen status than the north inlet. Apart from the west inlet spring however, seepage to the loch from non-discrete sources would come off the basalt bedrock or its derived boulder clay and would therefore be expected to have a composition similar to that of the north inlet.