

Volcanic waters of
North Sulawesi,
Indonesia:
geochemistry and
environmental pollution.

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1. Introduction

North Sulawesi is a volcanically active area, with volcanoes, hot springs, hot mud pools and fumaroles. Waters descending from active areas are enriched with cations and anions. These waters are sometimes used to irrigate, as washing water or drinking water. Too high concentrations of (toxic) elements may lead to human hazards or growth retardation of vegetation. Early research on human hazards or safe use of the waters and mud in North Sulawesi was done by Heringa in 1895. The geochemistry of these waters has not been studied yet. This study investigates the geochemistry of the volcanic waters of North-Sulawesi and the dangers with the use of these waters as irrigation and drinking water.

Because not much is known about the active areas the first aim of this study is to make an inventory of active hydrothermal areas and their waters. For that reason the following locations and their surroundings were visited: Danau Linow, Lahendong, the Kawah Masem, the Mahawu, the lake of Tondano, the Ambang mountains and its descending river, Kali Putih. At many locations water and sediments were sampled. The sample locations are described in chapter 2.

Further, the best method to analyse these volcanic waters is sought for, because high concentrations may cause problems with the standard method of analysis. This study focussed mainly on the determination of anion concentrations, like chloride and fluoride. The sampling method and results of the analyses are described in chapter 3. In chapter 4 a model to classify the samples in neutral or acid and sulphate or chloride rich waters is constructed. The visited locations are discussed in this chapter, with respect of the homogeneity of lakes, origin of rivers, mixing of rivers, precipitation in rivers and chemical composition of waters and mud. The composition of the waters is also compared with that of other volcanic waters, sampled in Indonesia or in other parts of the world.

To get a better insight in the water chemistry the behaviour and existence of aqueous species in the water phase and the saturation of minerals is investigated. The aqueous species and mineral saturations are determined with SOLVEQ. The change in aqueous species in a profile from the acid, hot waters of the Ambang to the neutral cool river Kali Putih is investigated. In addition, the influence of temperature, redox potential and pH on the saturation of minerals is investigated. Further, a model for the sudden precipitation of hematite in sample KM4-1 is made.

Finally, the environmental pollution of the waters and their hazards for human (and animal) health and vegetation are investigated. Several aspects are discussed a) the guidelines, which are used to determine whether the volcanic water are polluted; b) the problems using these guidelines; c) the hazards of the element concentrations, which are found in this study; d) waters that might give problems to human health or growth of vegetation.

2. Setting and previous work

2.1. Introduction to the island of North Sulawesi

2.1.1. Setting of North Sulawesi

Sulawesi is a K-shaped island east of the island Kalimantan, Indonesia (see Map 1, Appendix I). Sulawesi is about 600 km from west to east and 1000 km from north to south. North Sulawesi forms in the east of the northern arm of Sulawesi. The northern arm is constructed by volcanic deposits, which are andesitic. Outcrops of corals or lime rich sediments were found in the north (Kemmerling, 1923). The fertile land and the climate cause a luxuriant natural vegetation and create a good soil for agriculture. The development of North Sulawesi is advanced by the fertile soil and by the infrastructure of this area.

North Sulawesi can be divided in three regions, the north, middle and south region. The north contains the volcanoes Klabat, D. Soedoera, the Tongkoko (or the G. Batoe Angoes) and the Manado Tua, which is situated west of Manado in the sea (see Map 1). The volcanoes are quiet, while the Klabat still lightly degasses. The middle region of North Sulawesi, Minahassa, begins south of Manado and contains the most active hydrothermal region (see Map 1 and 3, Appendix I). Active volcanoes are the Tompaluan, within the Lokon-Empung complex, the Mahawu and the Soputan. The middle region contains also several active fumarolic areas. These areas are the Kawah Masem, an old crater lake east of the Soputan, the Danau Linow, the Lahendong and the area, south of the Tondano lake. The southern region is situated in the bow of the north arm of Sulawesi (see Map 1 and 4 in Appendix I). In this region is situated the lightly active hydrothermal area the Ambang with the important outlet Kali Putih. Between the active mountain complex the Ambang and the Minahassa is situated a probably non-volcanic-active area. The maps and literature do not give indications for any volcanic activity.

2.1.2. Geological history and structure of North Sulawesi

The origin of the island Sulawesi is controlled by four plates, the Indian-Australian, the North New Guinea, the Philippine Sea and the Eurasian. Fifty million years ago, the Indian-Australian plate moved north, converged in the centre with the North New Guinea plate, which moved south, and both subducted underneath the Eurasian plate. Five million years later (Middle Eocene), the North New Guinea plate was being subducted beneath the eastern Philippine Sea plate, which caused a forearc magmatism. In this time, the north arm of Sulawesi was formed just north of the Indian-Australian plate subduction zone, in the western part of the Philippine Sea plate. The north arm was situated, at that moment east of Kalimantan, while the south-eastern part of Sulawesi was situated at the Indian-Australian plate, south of Kalimantan and the west part of Sulawesi was situated at the Eurasian plate, south of Kalimantan. The south-eastern part moved to the north-east by subduction of the Indian-Australian plate under the Eurasian and Philippine Sea plate. Around 25 Ma, the northern, western and south-eastern part of Sulawesi came close together and this process generated ophiolite collision complexes in the southern part of Sulawesi (Hall, 1996).

Around 10 million years ago, the present north arm of Sulawesi was connected to the rest of the island. Hall (1996) mentioned that the north arm of Sulawesi is formed in its present orientation, while other authors mentioned a rotation of the, foregoing north-south trending

north arm, to a clockwise rotation of 60° (Shibuya *et al.*, 1991) to 90° (Silver, 1979), caused by a push northwards. Five million years ago (End Miocene), subduction at the north Sulawesi trench occurred and the Sula platform collided with the eastern side of Sulawesi (Hall, 1996).

Today, a Molucca Sea collision zone between the north arm of Sulawesi and Halmahera is present (figure 2.1). The north arm of Sulawesi is surrounded by subduction zones, north in the western part of the arm and east in the east side of the arm. The two subduction zones are probably connected by a transform fault system (Katili, 1975) crossing the north arm of Sulawesi (figure 2.1). Today, no volcanic activity is observed in this subduction zone, but only late Miocene volcanism (Rangin and Silver, 1990).

According to Simandjuntak and Barber (1996), the Minahassa Thrust is situated north of the north arm of Sulawesi. The Sangihe Thrust is situated east of North Sulawesi. Simandjuntak and Barber did not support the probable connection of these two subduction zones, by a transform fault system through the north arm.

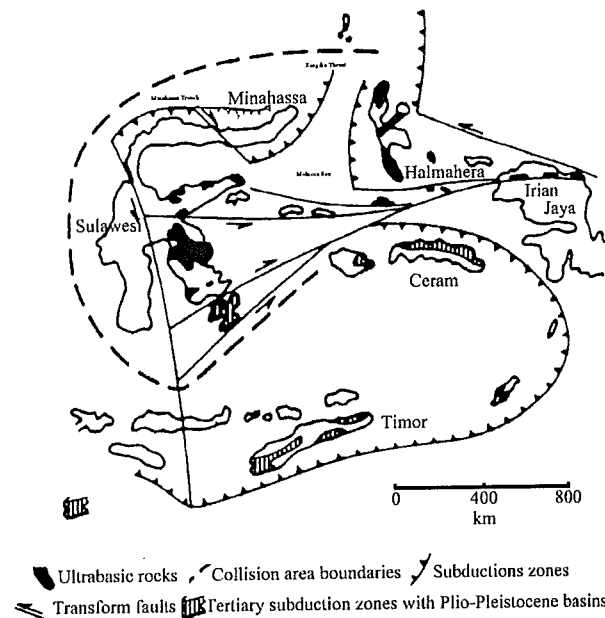


Figure 2.1. Tectonic map of the Sulawesi area, showing subduction zones north and east of the Minahassa peninsula (modified from Katili 1975).

The north arm of Sulawesi consists of Neogene volcanic rocks. Only the northernmost tip is covered by Quaternary volcanic rocks (Simandjuntak and Barber, 1996), which is related to westward subduction of the Molucca Sea Plate (Rangin and Silver,

1990). The active subduction system is responsible for the volcanism of the Minahassa peninsula and the Sangihe island arc (Jezek *et al.*, 1981). In the vicinity of the Tondano river the predominant rocks are Pliocene andesites and pyroclastics, which are covered by one to several metres of overburden. Andesitic rocks form the underlying layer (Müller *et al.*, 1984).

Tertiary volcanic rocks of the southwestern arm of Sulawesi comprise trachytic, andesitic, dacitic pyroclastic rocks, lavas and lahar deposits. Intermediate volcanic and basic volcanic rocks consisting of volcanic breccia, lava, pillow lava and tuff are present in the southwestern arm western of Central Sulawesi and in the northwestern side of Sulawesi (Müller *et al.*, 1984). The most eastern parts of the island are constructed on continental crust. In the central part of Sulawesi metamorphic and ophiolitic rocks are present (Simandjuntak and Barber, 1996).

2.1.3. The climate of North Sulawesi

North Sulawesi has a wet tropical climate. The average year temperature is 25° C and the annual rainfall is 2000 to 3000 mm. Usually, the rain falls the whole year, but a relatively dry season is from November to July. The amount of rainfall and the temperature are indicated on Map 2 (Appendix I). Müller *et al.* (1984) mentioned an annual rainfall of 1935 mm as the average over a long period. The rainfall of the Ambang area is 1000 mm more than in the middle region of North Sulawesi. Nearly no rain fell in the sampling period and during the month before the field trip.

2.1.4. Previous work on North Sulawesi and the use of its water

Several researchers visited the island Sulawesi, described its volcanoes, hot springs, mud pools and mud volcanoes, and investigated its structure and build up in the beginning of this century. Heringa (1895) focussed his research on the waters and mud used for medical purpose, and on the use of rivers for irrigation. Other important researchers were: Kemmerling (1923), Padang (1951), P. & F. Sarasin's, Koperberg (1928), Verbeek and R.W. van Bemmel.

2.1.5. Selected areas in this study

In this study several areas were selected to investigate volcanic waters and their hazard for human health and the growth of vegetation. Areas were selected, which show volcanic activity, like fumaroles, mud pools, hot springs and (acid) crater lakes. Further, the rivers were investigated, which derive their water from active hydrothermal areas. Waters which are used for irrigation and which are probably polluted were also selected and sampled. This selection was made by using maps, literature, field observations and by asking the local people.

To be more precise, in this research were selected a) the Danau Linow and its near surroundings, because the Danau Linow is an acid lake and its surroundings are influenced by fumaroles; b) the Lahendong area, because this area is build up by mud pools and acid water pools. In the near surroundings rice fields are polluted by fumaroles; c) the Kawah Masem crater lake and the river R. Maasem, because this river has an acid origin and streams through rice fields; d) the Mahawu volcano, because it contains a large (acid) crater lake, which probably has outlets; e) the south area of Tondano, because it is slightly active and contains much hot pools and mud pools; f) the Ambang mountain complex, because it is a very active area, with much hot springs and sulphur deposits; g) the river Kali Putih, because it drains the hot and acid waters of the Ambang and because this river is used as irrigation water.

2.2. The Danau Linow and the near surrounding

2.2.1. The Danau Linow, its input and output river and near surrounding

The Danau Linow (Danow Linow) is a lake west of the Tondano lake and 6 km south of Tomohon (see Map 3 and 5, Appendix I). The coordinates are N 01° 16 3, E 124° 49 5. The lake is situated south of the Kentur Toulangkow, north-west of the Kentur Kasuratan and east of the settlement Lahendong. North-west of the Danau Linow is situated the Lahendong area with much fumarolic activity, mud pools and mud volcanoes. South of the settlement Lahendong is a small road from which it is possible to reach the lake. At this side the old volcano G. Tampusu can be seen (Photo 2, Appendix III).

The lake has a size of 550 * 850 m. It has a rim around it, with much vegetation. In the rim fumaroles are present. The colour of the lake is blue-green at the coast and deep blue in the middle, but clear. The depth was difficult to determine, but may be 5 to 10 m.

The Danau Linow has several inlets, but only one is clear. The clear one (DL9-1, Photo 17, Appendix III) enters the lake in the north from the east side. The river is not indicated on Map 5 (Appendix I) at this location. On the other hand, a river which is not found in the field is indicated more south. The stream area of the inlet begins west of the G. Tampusu and probably comprises an outlet of the old crater lake Danau Tampusu, the Sosoan Loar. The inlet drains also the south side of the Kentur Toulangkow and its short surrounding (see Map 5). This inlet river streams, before it enters the lake, through a fumarolic active area, which is situated north-east of the lake. Small, ill-defined rivers stream at the east marshy side of the

Danau Linow. One of these rivers streams in south direction and has an extra input of hot water from a small hot pool (DL3-1, Photo 4, Appendix III). This river (DL4-1) streams through the rice fields and is used for irrigation.

The outlet of the Danau Linow is situated to the south-west and was called R. Randang by Kemmerling (1923). It streams through a fumarolic active area with mud pools and under the bridge above Leilem. Further, it streams south of the Lahendong area and forms the Royongan Ranoraindang (see Map 5). Finally, the river enters the Royongan Nimanga, which streams towards the Bay of Amurang.

Fumarolic active areas are found a) near the road to the lake; b) at the north-east and west sides of the lake and c) around the beginning of the outlet. Small fumaroles are found south of the lake, which were also mentioned by Kemmerling (1923). The fumarolic active area at the west side of the lake degasses in the ringwall, beach and water. Kemmerling mentioned a highly fumarolic active area at this location, while it is just quiet today. He also mentioned a white beach, composed of kaolinite. Today, the beach has a white precipitate, mud and sand.

At the south-east side of the lake fish is observed and at the west side larvae. Both organisms can live in the water, even though the pH is 2.5. Heringa (1895) described the Danau Linow as a fish-rich water. Therefore, the fish was used for food in these days. It is not clear whether the fish is used for food today.

The large variety in names of the Danau Linow, used today and in the past, may create confusion. Heringa (1895) called the lake 'Linow', which means lake. Further, he mentioned that the local people called it Sasajokan, which is never found again in the literature. According to his descriptions of the location of the lake, it must be the Danau Linow. Kemmerling (1923) called the Danau Linow, Linow Lahendong, but according to his descriptions of the location and the comparison of his photo (Photo 1, Appendix III with the G. Tampusu at the background) and a recent photo (Photo 2, Appendix III) must be concluded that the Linow Lahendong is the Danau Linow. Padang (1951) described the lake Linow Lahendong at other coordinates than the Danau Linow. On the other hand, the large scale of his map and his descriptions of the lake are in accordance with the Danau Linow. His descriptions were: depth 10-12 m, 700 m wide and a surrounded rim of 50-75 m altitude. Further, the positions of the fumaroles, which he described are the same as the positions of fumaroles around the Danau Linow today. Therefore, it can be concluded that the Linow Lahendong is the same lake as the Danau Linow.

Heringa (1895) investigated the composition of waters around the Danau Linow. He also mentioned the composition of the Lino water, analysed by Ludwig. The Lino probably is the same water as the Danau Linow. The composition of the Lino is given in Table 2.1. The supposed accuracy is questionable.

Table 2.1.
Chemical composition of the Lino (1878).
Analysed by Ludwig (Heringa, 1895).

Component	amount (g)
Sulphuric acid	0.0055
Chloride	0.01381
Carbonic acid	0.11308
Silicic acid	0.158
Iron oxide and alumina	0.0153
Lime	0.0557
Magnesia	0.02376
Potassium and sodium	0.0771
Total	0.46226

The chemical compositions of five samples analysed by Heringa (1895) are listed in Table 2.2. The samples were taken in the near surroundings of the Danau Linow. The samples 57-59 were taken from mud pools at the north side of the lake. The samples 60 and 61 were taken near the outlet of the lake, probably near the sample DL6-1. The Danau Linow sample was not analysed, since the sample bottle was broken.

Table 2.2.
Chemical composition of five samples, sampled near the Danau Linow, analysed by Heringa (1895).

Sample	57	58	59	60	61
Smell	H ₂ S	no	no	no	no
Colour	no	no	no	lightly yellow	no
Clearness	quite clear	not much precipitate	not much precipitate	much lightly grey mud	much lightly grey mud
Temp. (Celsius)	87.5	62.5	77.5	94	96
pH	acid	acid	acid	acid	acid
K ₂ O (g)	0.214	+	+	-	0.169
Na ₂ O (g)	-	-	less	0.179	-
CaO (g)	+	+	+	0.3	+
MgO (g)	+	+	+	0.221	+
Al ₂ O ₃ (g)	+	-	+	0.498	+
Fe (g)	+	+	-	0.399	+
Cl (g)	0.024	0.071	0.123	0.04	0.041
Tot. SO ₃ (g)	1.796	1.493	much	3.58	0.928
SiO ₂ (g)	0.19	+	+	0.2	0.194
P ₂ O ₅	-	+	+	+	+
H ₂ S	+				
Organic matter	+				

(+) present

(-) not present

2.2.2. Description of sample locations near the Danau Linow

A small road leads from the road between Leilem and Lahendong to the Danau Linow (see Map 5, Appendix I). Half the road, at the right side of the road, gases escaped from a large fumarole (Photo 2 and 15, Appendix III). It made a lot of noise and a rotten eggs smell was observed. About 15 m around the fumarole, the area is weathered and shows green surface deposits, from bacterial or algae activity, and boiling mud and water pools. A rock with green surface deposits is sampled near the outlet (DLFUM1).

The first sample of the lake (DL1-1) was taken just before the outlet of the lake (Photo 14). No fumarolic activity was observed at this location. Sample location DL1-1A is situated in the active area west of the lake (Map 5, Appendix I). At this location, gases escaped from the walls, the beach and the water. The water temperatures was 80 °C in some small pools at the beach. No sulphur floated on the lake surface. At this location, water, mud and surface deposits of the fumaroles were sampled.

North of DL1-1A the area is still active. Though, there are no fumaroles, a peculiar 'bubbling' effect was observed in the water. Since, the water was not boiling, a water or gas inlet might cause the bubbling effect. At this location (DL1-1B) foam floated on the water. Here, sediments and water samples were taken. At the opposite side of the lake, sample DL8-1 was taken, two metres from the side. The soil was very marshy and burnt.

The inlet river of the Danau Linow (DL9-1, Photo 17) is situated in the north of the lake and it streams from the east side. It streams through a fumarolic active area, where the pH is lowered and the ionic strength is increased. Before it enters the Danau Linow, the river flows through a mud rich area, with a large (ø 3 m.) mud volcano (Photo 17). The soil here is very soft, slippery and has a very weathered surface. The colour of the mud was grey-blue or red

and the colour of the river, which streams along the mud volcano, was turbid blue-white. The red colour indicates the oxidized state of the mud. The discharge of the inlet is 3 l/s, and it may contain water of river DL4-1 and rice field water.

DL5-1 is a small, quite neutral (pH 6.5) river. It is situated in the midst of the forest and is hard to reach. Frogs live here in the water. The water can be a component for the inlet DL9-1 or a component for the river DL4-1. The water is used for irrigation.

East of the Danau Linow, a small river (DL4-1) streams in south direction. The river is entered by an outlet of hot pool DL3-1 (Photo 4, Appendix III). The hot pool had a blue-grey colour and a temperature of 86 °C. The surrounding rocks were weathered, but above the pool vegetation grew. No H₂S odour was observed. Sample DL4-1 was taken after the point where out flow of the pool (DL3-1) and the parallel streaming river are joined (Photo 4). The water temperature was 45 °C at the sample location. The parallel river shows two colours of precipitate. The first is blue-grey and is formed when the water level is low. The other precipitate has a red colour and is formed at a high water level.

The mud/straw wall (DL2-1) in the rice field opposite to hot pool DL3-1, is a strange phenomenon. This O-shaped wall contains yellow white water (Photo 3), with a pH of 2. The location degasses continuously, which can be seen by the enormous amount of bubbles in the water. The surrounded rice field water is not acid.

One of the fumarolic active areas is situated downstream of the outlet of the Danau Linow on the west side, named DL6-1 (Map 5, Appendix I). The fumarolic field is oblong and fumaroles degas in this area. Near the water surface, the walls and rocks were covered with green ropes, composed of algae or bacteria. The surrounding rocks were very weathered, and therefore were very brittle. The holes of fumaroles were covered with yellow sulphur precipitate, while the rocks are coloured white and grey. The water had a blue green colour.

Sample location DL7-1 is situated further downstream, where most degassing in the river has stopped. The colour of the water was turbid white-blue. At this location a hot spring, from the Kentur Kasuratan, enters the river. A small mud pool released mud in the river (Photo 16). Much degassing occurs between DL6-1 and DL7-1. East of DL7-1 small houses are built, where water and mud were used for healing.

2.2.3. Samples location in the surroundings of the Danau Linow

The small lake Danau Panolombian (PL1-1) is situated south east of the Danau Linow, north east of the Kentur Kasuratan and west of the Kuntung Tampusu (Map 5, Appendix I). The coordinates are: N 01° 15 9, E 124° 50 5. The Danau Panolombian possibly is an old crater lake.

A small old crater lake Danau Tampusu is situated at the summit of the Kuntung Tampusu. An outlet river of the crater lake was visited, because it was not possible to reach the lake. The outlet river Sosoan Loar was not found. On the other hand, a dry bed of a small river 1 km north of the Tampusu is found (Map 5).

2.3. The Lahendong region

2.3.1. The Lahendong area and its output river

The Lahendong is a weathered area, with mud pools, mud lakes and mud volcanoes. The Lahendong is situated north of the settlement Lahendong and between the districts Tomohon en Sonder (Maps 3 and 5, Appendix I, and Photo 19 and 20, Appendix III). The coordinates are N 01° 17 5, E 124° 49. The surface of this flat area is 1000 * 500 m. Around the weathered

area grows a luxuriant vegetation. The soil was dry at the moment of this study, but at the west side a oblong lake covered the surface. The depth of the degassing lake is probable 5 to 20 cm. Mud pools and small water pools (Photo 18, 19 and 20) were brown grey to black and had temperatures from 30 to 99 degrees, which are the same temperatures as measured by Kemmerling (1923). The soil near the lake was weathered and covered by kaolinite and yellow precipitate. A small river flows through the field in north direction. It had a white green colour. In the north, two mud volcanoes are found, with an altitude of 1.5 m (Photo 21). They were not active.

The only inlet found (LA1-1) in the Lahendong area is used for irrigation, before it enters the weathered area. The water comes from the south and has a discharge of 2 l/s. A probable outlet (LH2-1) is situated in the north, parallel to the road Tomohon-Sonder. The outlet is small and difficult to follow through the Lahendong. The water of the outlet is used for washing, by people who live near the river. Map 3 shows that the Lahendong area has probably many outlets, which are indicated as striped lines. They are probably filled in the wet seasons. The outlet rivers enter (if they contain water) the Sosoan Ranourang, and after a few hundred metres the river Sosoan Ranoesem (esem, asem = acid). The S. Ranoesem (RNE1-1) flows first between the two settlements Sawangan and Pinaras and contains water of the Danau Linow. The river flows together with the Royongan Nimanga (NMG2-1), which streams out in the Bay of Amurang (Map 5). The drained area of the Sosoan Ranoesem and the Royongan Ranoraindang (RND1-1) is situated between the south side of the road Pinaras to Kampungjawa, west of the Kentur Toulangkow, west of the Kentur Kasuratan and north of Sonder. The drainage of the R. Nimanga (before the sample point NMG3-1) is much bigger. This drainage occupies the regions of the R. Ranoraindang and the S. Ranoesem, and the area between the Kentur Timbukar, Kuntung Lenkoan, Kuntung Semelenduk, Tompaso, G. Sempoe, and then from the Soputan straight to the Kentur Timbukar.

The Lahendong region has been investigated in the past. Padang (1951) estimated the size of the Lahendong 1000 * 500 m. Kemmerling (1923) mentioned the presence of two fields, divided by a rim. During the field trip the most northern field was visited. The soil contained

Table 2.3.
Chemical composition of seven water samples of the Lahendong, analysed by Heringa (1895).

Sample	62	63	64	65	66	67	68
Smell	no	no	no	no	no	no	no
Colour	no	no	no	no	no	no	lightly yellow
Clearness	much large precipitate	less precipitate	almost no precipitate	almost no precipitate	large particles precipitate	large particles precipitate	many large particles
Temp. (Celsius)	96	70	65	37.5	44	32	69
pH	acid	acid	neutral	neutral	neutral	acid	acid
K ₂ O (g)	+	+	+	+	much	less	+
Na ₂ O (g)	less	much	much	much	much	less	less
CaO (g)	+	+	+	+	+	+	0.03
MgO (g)	+	+	+	+	+	+	0.018
Al ₂ O ₃ (g)	-					-	0.289
Fe (g)	+	+	+	+	+	+	0.1015
Cl (g)	0.044	0.353	0.175	0.08	0.09	0.011	less
Tot. SO ₃ (g)	2.089	0.515	0.198	0.104	0.134	0.3769	2.898
SiO ₂ (g)	0.276					0.0865	0.2897
CO ₂			+	+	+		
P ₂ O ₅	+	+	+	+	+	+	+
Mn							-
Organic matter		+					+

(+) present

(-) not present

kaolinite and it coloured orange, white and yellow (Kemmerling, 1923). Kemmerling mentioned that the largest region of the area was covered with water in rainy seasons. He called the outlet, found at the north east side of the Lahendong, Rano Koelo.

Heringa analysed seven waters in this area. He sampled two springs in the Lahendong, nr. 62 and 63, the R. Koelo (67) and a small river near the R. Koelo (68). The last sample contained much iron, which gave it a lightly yellow colour (Heringa, 1895). Further, he took samples of springs around the outlet river Sosoan Ranoesem (65 and 66) and the Royongan Ranoraindang (nr. 64). The chemical compositions of the water samples analysed by Heringa are given in Table 2.3.

2.3.2. The sample locations in the surroundings of Lahendong

Three samples were taken in the rice fields south of the Lahendong area. The first sample was taken at an inlet in this area (LA1-1). It seemed to be only rainwater, which comes from the hill and flows through a bamboo in the rice-fields. The water is used for irrigation. Further, sample LA2-1 was taken from a small rice field (5 * 5 m), which is contaminated by small degassing fumaroles. The fumaroles excrete white sediments in the water and lower the pH from 6 to 3.6. To determine the amount of contamination sample LA3-1 was taken from a not infected rice field 70 cm above sample point LA2-1. In surrounding fields also fumaroles are active, which, however, are mostly separated from the rice fields.

The mud pools and lakes of the Lahendong were investigated. They were described and measured (pH, conductivity and temperature), to make a general classification.

The possible outlet of the Lahendong (LH2-1) was sampled at a location where cows might drink this water. The sediments were brown and might be contaminated with cows faeces. At the surface of the river was a oil like layer, possibly floating iron. This river possibly is the Rano Koelo.

Sample RNE1-1 was taken from the Sosoan Ranoesem, south of the settlement Pinaras (Map 3, Appendix I). A hot spring (43 °C) entered the river at this location. The river water was blue with a small trace white. The surroundings were richly over grown.

Sample RND1-1 was taken from the Royongan Ranoraindang, between the paddy fields, 800 m east of Rambunan (Map 3, Appendix I). The river contains water of the Danau Linow and possibly some polluted water of the fumaroles at the south side of the Lahendong (Heringa, 1895). Upstream and downstream of sample RND1-1, water from the paddy fields entered the R. Ranoraindang. The water had a blue grey green colour and was neutral (pH 7). The local people do not use the water to irrigate, because the river contains a lot of sulphur. Red surface deposits is formed on the bed of the river in wet seasons. The discharge of the river is about 500 l/s.

The Sosoan Ranoesem joins with the Royongan Ranoraindang further downstream (see Map 3). Sample NMG1-1 was taken just before the joined river enters the Royongan Nimanga. The discharge is about 4000 l/s. The colour of the river was brown-grey-blue and the water was fairly turbid. The environment was over grown and aquatic organisms lived on the water surface.

The Royongan Nimanga (NMG2-1) contains water of the R. Maasem (a river from the Kawah Masem, see paragraph 2.4.), which streams via the Royongan Ranowangko in the Royongan Nimanga. The R. Nimanga has the same amount of discharge as the joined R. Ranoraindang. The colour of the water was brown and it was very trouble. Sample NMG3-1 was taken after the join of NMG1-1 and NMG2-1 (Map 3). The colour of the water after the join was brown blue and trouble. Sample NMG3-1 was taken south of Timbukar, with a boat in the middle of the river.

2.4. The Kawah Masem crater lake and the river R. Maasem

2.4.1. The Kawah Masem crater lake and the river R. Maasem

The Kawah Masem crater lake is situated north east of the active volcano Soputan and west of the G. Sempu, east of the Ketengak and two kilometres west of the Kuntung Soputan Tua (Map 3, Appendix I). The Kawah Masem crater lake coordinates are N 01° 08 15, E 124° 45 14. The crater lake is named Walelang by Kemmerling (1923), but this name is not used today. Padang (1951) mentioned that the crater is part of the Sempu complex. The G. Sempu is a caldera with a central volcano and the maar Kawah Masem.

The crater rim is 450 * 350 m, according to Kemmerling (1923). The bottom is much smaller: 220 * 180 m. The size of the lake was 200 * 100 m in 1923, but is 20 * 20 m today (Photo 5 and 22, Appendix III). The altitude of the bottom of the maar in 1951, was the same as today, 1345 m above sea level. The water levels of the crater lake observed in 1921 and 1997 are indicated on Map 7 (Appendix I).

The rim of the crater consists of weathered rocks and contains fumaroles. The locations of the fumaroles are indicated on Map 7. The most active fumaroles are situated at the north side of the rim (Photo 5). Kemmerling (1923) mentioned the white colour of the rim, but in this study the colours grey and yellow (sulfur) were observed. Kemmerling (1923) had observed yellow condensed sulfur pillars of a few metres. In this study, fumaroles were only found on the bottom or in the walls of the crater. Gases escaped from holes and the edges of these holes were covered by yellow, condensed sulfur. The holes had sizes ranging from 10 cm to more than 1 m.

The colour of the lake was grey and turbid (Photo 22), instead of yellow, as described by Kemmerling (1923). Further, much gases escaped from the lake, so it seemed to be boiling. The depth of the lake could not be determined, because the lake was very turbid. The pH of the lake was low, near 2. Likely, the water input of the lake is mainly caused by rain fall. No clear observation may base an input of water from beneath. Kemmerling (1923) mentioned a large stream of water to the maar, descending from the large sandy plain, which is situated in the south (Map 7).

The edge of the lake existed of grey, layered mud. The surroundings of the lake contained mud and degassing holes. The mud was lightly grey and seemed to be stable by the drying out cleavages. When walking over it, it can be very slippery at once. The mud probably is sulphur mud. In 1923, it contained 52.8% S (Kemmerling). In this study, half the bottom of the crater was found to be covered with mud. Sulphur mud can only precipitate in the water phase. Therefore, the crater lake must have been larger in earlier times (Padang, 1951). The rims and bottom of the Kawah Masem were slightly covered by bushes and low vegetation, like grass. On the rim more vegetation grew (Photo 5).

In the next table, the situations of the Kawah Masem in the last century are given.

Table 2.4
Situations of the Kawah Masem crater lake.

Year	Lake size	Colour lake	Activity of the crater	Mud	Reference *
1821	large	yellow	much degassing of area and lake	white rims, yellow, grey mud	1
1921	15 March 200*100 m. 4 April: 60*100 m.		fumarolic degassing	mud 52.8 %	1
1951	200*100 m.		fumarolic degassing		2
1997	30 June: 20*20 m.	grey, turbid	fumarolic degassing	weathered rims, grey slippery mud	this study

* References: (1) Kemmerling (1923); (2) Padang (1951).

A lightly fumarolic active area is situated just north of the crater lake and is 200 m wide. The bed rocks of the small rivers in this area indicate that water flows in north direction. The soil and rocks were weathered. More north, a luxuriant vegetation covered the soil. Between this vegetation a small, white coloured bed rock started. These bed rocks possibly are of the river Maasem (Map 7).

Further, a not highly active, but very weathered fumarolic area is situated about 600 m north of the crater lake. This location (Photo 23, Appendix III), called Kawah Sui (Padang, 1951), possibly contains an outlet of the Kawah Masem. This hypothesis is supported by Kemmerling (1923). The water is colourless and clear, though the water of the Kawah Masem is grey and turbid. The bed rock is coloured white yellow.

The water of the spring flows in east direction, through the lightly active fumarolic area and joins together with a five times larger neutral river. This river comes from the Kuntung Rindengen (Map 3, Appendix I). The new river follows the feet of the Kuntung Soputan Tua (G. Sempu) at the north side and streams south of the feet of the G. Tonderoekan. This river (Royongan Maasem) turns left and streams near Pinabetengan, near Kawangkoan. There it joins with a lot of other rivers, descending from the Kuntung Rindengan and the Tompasso area, thereby forming the Royongan Ranowangko (Map 3, Appendix I). This river flows into the Royongan Nimanga, which ended in the sea (Lesuk Amurang). The R. Maasem collects rain water of the south side of the Rindengan and the G. Tonderoekan and of the north side of the G. Sempu. A river, which collects water of the north side of the G. Tonderoekan, enters the Royongan Maasem, near Kawangkoan.

2.4.2. Description of sample locations of the Kawah Masem and the river R. Maasem

The Kawah Masem crater lake was sampled on two days. On the first day with a drinking bottle (KM1-1) and on the second day with the usual equipment (KM1-2). A detailed description of the Kawah Masem crater lake is given in section 2.4.1. A detailed situation of the area around the Kawah Masem and its possible outlet, Kawah Sui, are drawn on Map 8 (Appendix I).

The possible outlet point of the Kawah Masem is situated 600 m north of the crater. The water (KM2-1) comes out of the rock wall with a discharge of about 1 l/s. Throughout the years, it has eroded a deep gab of 1.5 m deep (Photo 23). The bed rocks contain large amounts of white yellow precipitate. Today, the area is lightly fumarolic active, and spreads a H_2S smell.

Sample KM3-1 was taken from a small river (5 l/s), which comes from a gab in the rocks. This sample location is situated 100 m east of KM2-1 (Map 8, Appendix I). Upstream from KM2-1, the small river streams through a camping area. It is not clear whether this water is contaminated by camping waste or not. The water is used for cooking and washing by the people on the camping. At the point where this water joins the acid water (KM2-1), it was contaminated with soap. Downstream, the river pad had a red colour of precipitated iron. This red colour persisted for at least a 50 m (Photo 12, Appendix III). In this section, sample KM4-1 is taken. From the north side a small stream (1 l/s) enters the river (KM5-1).

Sample KM6-1 was taken downstream near the settlement Pinabetengan, before a bridge. The discharge of this river was 250 l/s. Unless the remarkably low pH of 3 in this river, the water is used to wash cows and horses. The water comes from the rice fields and streams further under the bridge to Kawangkoan. Just before and aside Kawangkoan the samples KM7-1 and SP8-1 were taken. At sample location KM7-1 people use the water to wash themselves and their clothes. The local people do not use this brown, turbid water for drinking or cooking, because they think the water has a high content of sulphur.

Ten kilometre south west of the Soputan (Map 4) and west of the Tomatu, is situated a very strange shaped lake, Danau Bulilin, with the coordinates N 01° 02' 48" and E 124° 40' 41". The Danau Bulilin (or Luah Bulilin) is supported by two other small lakes Luah Kawelaan and Luah Sosong. The people of the small settlement, which is situated near the lake, swim in and catch fish from the water. There are no clear inlets or outlets of this blue coloured and neutral (pH 6.7) lake.

2.5. The Mahawu volcano

2.5.1. The Mahawu volcano and the springs on the flanks

The Mahawu crater is situated in a cone of the SSW-NNE trending volcanic row with the Soputan and Kawah Masem (Padang, 1951). The Mahawu is situated east of the Lokon-Empung complex (Map 3, Appendix I) and its coordinates are N 01° 21' 3" E 124° 51' 8". The Mahawu is enclosed by three probably old volcanoes, the Kentur Tingtingon, Kuntung Temboan and south Kentur Masarang (Koperberg, 1928).

The shape of the volcano is like a plateau with a small summit, instead of the classical model like the Lokon (see front page). The crater rim has dimensions of 460 * 420 m at the altitude of ~1370 m. The rim inside the volcano is very steep (Photo 6 and 24, Appendix III). The blue-green crater lake is situated more than 75 m below the summit (Photo 24). About 80% of the bottom is covered by the lake (Photo 6). The surface of the lake is about 125,000 m². The lake may be acid, because it contained active fumaroles and it is had a typical blue green colour.

Fumarolic activity was observed in the north region, where the fumaroles formed yellow surface deposits. The fumaroles and the shape of the lake (1921 and 1997) are indicated on Map 9 (Appendix I). The lake was found to be larger than in 1921. In the past, the bottom has been covered with sulphur mud with a sulphur percentage of 74% (Padang, 1951). In this study, the bottom of the crater is covered by the lake. Grey mud, with drying-out cracks was situated around the crater lake. Stones and weathered rocks, covered with sulphur surface deposits, was situated near the rim.

The history of the Mahawu volcano is interesting. The Mahawu had a very heavy eruption in 1789. In 1821, Reinwardt mentioned only fumarolic activity at the bottom of the crater, and the existence of a small white lake (Kemmerling, 1923). The fumarolic activity decreased in the years after 1821, and increased from 1900. The crater lake was boiling and degassing in 1913, which killed the vegetation in the near surroundings of the crater top. The crater lake was nearly dry in 1920 (Photo 7, Appendix III) and totally dry in 1922. A small activity of fumaroles was observed in 1922 (Photo 8, Appendix III, Kemmerling, 1923).

Today, the walls of the crater are very steep and high (75 to 150 m.). A path to the bottom of the lake is indicated on Map 8. Photo 9 (Appendix III) shows the wall of the Mahawu with an altitude of 10 m. The altitude of the crater a.s.l. has been changed, from 1300 m in 1923 to 1370 m today. It can be concluded that the shape, bottom and the walls have been significantly changed during time. The changes took place due to the last three eruptions of the Mahawu in 1952, 1958 and 1977 (Simkin and Siebert, 1994). The situations of the Mahawu crater during the last two hundred years are summarized in Table 2.5.

Table 2.5.
The situations of the Mahawu crater during the last two hundred years.

Year	Lake	Colour of the lake	Activity/eruption	Mud	Reference *
1789			heavy eruption		1
1821	small	white	little S-degassing	S-sediment	1
1846			flank vent, phreatic		2
1894			very small amount of degassing		1
1904			much smoke, probably S-mud flow		1,2
1913	boiling		high fumarolic activity		1
1922	mostly dry		high fumarolic activity	S-sediments 74%	1
1958			central explosive, with fatal damage by mud flow		2
1977			crater lake, phreatic		2
1997	125,000 m ²	blue-green	light fumarolic activity	grey brown	this study

* References: (1) Kemmerling (1923); (2) Simkin and Siebert (1994).

The crater lake has no direct outlet river. However, in the north, the river Sosoan Rayow (MHW3-1) appears, which might be an outlet of the crater lake (Map 3, Appendix I). This river is acid. The parallel river (Sosoan Saluesem, MHW2-1) was expected to be acid, because it contains 'esem' in its name (esem = acid). Further, the river originates a few hundred metres from the crater lake. However, the Sosoan Saluesem appeared to be neutral. Though the Sosoan Rayow originates at a lower altitude, further from the crater lake, it had a pH of 3.5.

A lot of small rivers start at the north west side of the crater. They possibly are composed of rain water. They join together in the Kuala Malalayang, Kuala Sario, Sosoan Tambelang and Sosoan Kendis. The rivers contain also rain water from the Lokon complex. They flow downstream to Manado, where they end in the sea.

2.5.2. Description of sample locations of the springs and rivers

The first sample (MHW1-1) was taken from a spring south east of the foot of the Mahawu, near Kakaskasen 2 (Map 3, Appendix I). The small spring (discharge 1 l/s) comes out of the Mahawu mountain, through a bamboo tube (3 m long) and enters a small basin. The tube contained a white precipitate and small lines of green algae. The spring did not spread a clear H₂S smell. The basin is situated in the paddy fields and the water might be used to irrigate. The vegetation around the basin seemed not to be affected by this water, which had a pH of 6 and a temperature of 37 °C.

The next sample (MHW2-1) was taken of the Sosoan Saluesem, six km north of the Mahawu, before the join with the Sosoan Rayow (Map 3). It is not clear whether this neutral water (pH 6.5) is used for irrigation or not. The Sosoan Rayow (MHW3-1) is an acid river, pH 4, and was sampled 300 m west of MHW2-1. The local people say that the water originates in an acid basin. In spite of the pH, animals and plants were observed in the water. Children have no problem to wash themselves in this river.

Finally, two rivers, which are situated around the Mahawu volcano, were checked for their pH. First, the Kuala Keketan (KK1-1), with an inlet river from the south, which has a pH of 6.7. The water comes from the Kuntung Temboan, a mountain east of the Mahawu. Further, the Kuala Ranowailan (MA7-1), near the road Tondano - Kembes, a small river (6 l/s) with a pH of 6.5.

2.6. The Tondano lake and the southern active hydrothermal area

2.6.1. The Tondano lake and the southern active hydrothermal area

The Tondano lake is a large lake (10*3.5-5 km) situated in the centre of the Minahassa, with the coordinates N 01° 11 to N 01° 17 and E124° 53 5 to 124° 56. The south side of the lake is wider than the north side (Map 3, Appendix I). The outlet river is situated in the north of the lake, near de city Tondano. A large rim is situated at the east side of the lake and might be an indication for the old caldera of Tondano (Map 1, Appendix I). The Tondano crater must at that moment have had a radius of 13.5 km. (Kemmerling, 1923). After the collapse of the crater rim at several places, new volcanoes developed, under which the Soputan. However, the origin and development of the Tondano lake are still speculation.

The lake is situated in the high area of the Minahassa, at 680 m. a.s.l. (Kemmerling, 1923). The lake drains the surrounded area, included by the Kuntung Makalonsouw, K. Kaluta, K. Pulutan, K. Rintis, K. Kamington, K. Lembean, K. Kaweng, K. Tombangan, north-west area of the Soputan, K. Semelenduk, K. Tampusu, Kentur Paketengan and the Kentur Masarang, (Map 3, Appendix I). The outlet river of the lake streams through the city of Tondano, before it drops in the waterfalls 4 km north of Tondano. The river flows north to Airmadidi Bawah, turns left and finally ends in the sea near Manado.

Kemmerling (1923) mentioned the decrease of the size of the lake in the years before 1923. The flat alluvial area supports his statement. The original lake size was about 20 m higher than in 1923. The water was found neutral (pH 6.5) and may be used as drink water. There was no volcanic activity (like bubbles or fumaroles) found. However, some people mentioned a small volcanic activity at the south west side of the lake.

Slightly active areas are situated south west of the lake. At these locations fumaroles, hot pools, mud pools and acid hot lakes are found (see section 2.6.2.). Heringa investigated waters and mud in this area. Around Remboken (west of the Tondano lake) are much hot springs, which are used as washing or drinking water (Heringa, 1895). Around and between Passo and

Table 2.6
Chemical composition of five water samples, taken south west of the lake Tondano, analysed by Heringa (1895).

Sample	10	14	15	17	18
Area	south of the K. Tempang/Wowok	south of the K. Tempang/Wowok	south of the K. Tempang/Wowok	Tanakulo, possibly TDS1	small lake Talitep possibly TDS 1 / 2
Smell	no	musty	no	no	no
Colour	yellow-brown	light brown	no	brown	light yellow brown
Clearness	much large particles sediments	many flocks troubling	much precipitate	many flocks	flocks
Temp. (Celsius)	87.5	81		100	44
pH	alkaline	alkaline	not very acid	alkaline	neutral
K ₂ O	+	+	+	+	+
Na ₂ O	+	+	-	+	+
CaO	+	+	+	+	+
MgO	+	+	+	+	+
Al ₂ O ₃			+		
Fe	less	+	+	trace	-
Cl (g)	0.49	0.76	0.013	1.06	0.48
Tot. SO ₃ (g)	+	+	+	+	0.166
SiO ₂	+	+	+	+	+
CO ₂	+	-	-	+	
P ₂ O ₅	+	+	trace	trace	trace
Organic matter	+	+	+	+	+

(+) present

(-) not present

Table 2.7.
Chemical composition of five mud samples, taken south west of the lake Tondano, analysed by Heringa (1895).

Sample	11	12	13	16	19
Location	south of the K. Tempang/ Wowok	south of the K. Tempang/ Wowok	south of the K. Tempang/ Wowok	Tanakulo, eleven mud pools	mud pool, near Wontoöran
Smell	no	no	acid milk	no	no
Colour	no	brown	no	no	no
Clearness	contaminated with 1/3 grey mud	much troubling and precipitate	mostly mud	½ grey mud	much light grey mud
Temp. (Celsius)	94	56	75	76	44
pH	less acid	less acid	acid	acid	less acid
K ₂ O	+	+	+	+	+
Na ₂ O	less	+	?	less	+
CaO	+	+	+	+	+
MgO	+	+	+	+	+
Al ₂ O ₃	+	-	-	-	-
Fe	+	-	much	+	trace
Cl (g)	0.15	0.16	+	0.46	0.5
Tot. SO ₃	+	+	+	+	+
SiO ₂	+	+	-	+	+
CO ₂	-	-	-	-	-
P ₂ O ₅	trace	trace	trace	-	trace
Organic matter	+	+	+	+	+

(+) present

(-) not present

Kakas (Map 3) hot springs are present and some of them are used to irrigate the rice fields (Heringa, 1895). In Table 2.6 the chemical composition of five water samples are given, which are analysed by Heringa. The samples of Heringa were taken around locations, which were visited in this field trip. In Table 2.7 the chemical compositions of mud samples analysed by Heringa are given. These samples were also taken near locations visited in this field trip. These locations are situated south of K. Wowok, near Tempang, Toraget and Tompasso and more north near Panasen and Totolan.

2.6.2. Description of sample locations of Tondano and its southern area

The outlet of the Tondano lake (TDO1) was sampled south of the city Tondano. The sample was taken as far as possible near the beginning of the outlet, in order to prevent contamination of the water by waste. Since the outlet streams through a 15 m wide canal, it has not the characteristic delta like it had in earlier years (Map 1, Appendix I). The water was turbid, had a dark green blue colour and didn't flow fast.

In the south west area of Tondano, the river Royongan Panasen was visited. The river is situated above Panasen, west of the Tondano lake (Map 3, Appendix I). This possibly acid river was not measured or sampled. According to the use of this water, it not expected to be (very) acid or dangerous.

The next observation was done south west of the settlement Totolan and 1.5 km west of Tolok. This location was covered with dry mud and with wet mud pools (Photo 25, Appendix III). One hot hole in the soil is used for warming up the corncobs. The holes are more then 1 m deep and contain boiling mud or black grey mud with drying out cracks. A few fumaroles were observed. From a small degassing lake (Ø 6 m) comes hot steam. The temperature of this water may be hotter then 70°C.

In addition, an area rich in hot waters and mud volcanoes is situated south east of Tompasso, north of Toraget and west of the Kuntung Wowok. At this location (TDS1), a house and wash places were built. Near the house is situated a very hot lake (40 * 40 m), from where steam escaped. The colour of the lake was white blue green and it smelled nasty. A clear water spring supplied the lake of water. The water of the lake has been used for washing and

for healing. Before the people use the water, it is filtered and cleaned, by a device. A lot of mud volcanoes and fumaroles are situated before the washing rooms. Some of the volcanoes are active, and produce grey hot mud.

South of TDS1 and north of Toraget, is situated an area with small, hot lakes. One of these lakes, has a size of 4 * 7 m and a temperature of 80 °C. This lake is situated above the soil level in a basin. Another, is a large and strange shaped lake. This lake is used as a washing place by the local people and horses. The water was quite warm (35 °C) and had a green clear colour. The outlet of this lake streams slowly through a fumarolic and mud volcanoes active area (not very active, only altered), and flows to the paddy fields.

The lake, situated in between these two lakes, had a round shape (Ø 50 m) and a temperature of 52 °C (Photo 26, Appendix III). The walls of the lake were very steep, and it was not possible to estimate the depth of the lake, but it must be at least 3 m. The water had a green, blue colour and was very clear, but white stuff was whirling through the water, which indicates the turbulence of this water. Sample TDS2 was taken at the side of the small hot lake. At the opposite of the lake, brown stuff floats on the surface, which is probably mud or waist, but no sulphur.

2.7. The Ambang mountains

2.7.1. The Ambang mountains

The Ambang is a strato volcano (Padang, 1951), which is situated in the bow of the northern arm of Sulawesi (Map 1, Appendix I). The coordinates of these mountains are N 00° 44 5, E 124°24 5. The Ambang is an old volcano, with its last eruption around 1840 (Padang, 1951). Today, a highly fumarolic active field produces gases and hot water with temperatures up to 80 °C. It is difficult to define the exact area of the Ambang, because the Ambang mountains have several summits. The most important mountains of the Ambang are the Bulud Moyayat (east), Bulud Tudutalong (north), Bulud Pinupulan (north-west) and the Bulud Mooat (south). The complex ends at the (lake) Danow Mooat on the east side, see Map 4 (Appendix I).

In the mountains of the Ambang two lakes are present. The first is 200 * 350 m large and is situated 1.5 km south of the B. Tudutalong. The other, Danow Tabang, has a size of 250 * 500 m and a shape comparable with the Danow Mooat. It is situated 1 km west of the B. Moyayat. The lakes were not visited.

South of the Bulud Moyayat and north west of the Bulud Mooat, is situated a very active fumarolic area, in a kind of a valley (Photo 7, Appendix III), with a drainage at the south west side. No inlet river was observed in this area, but hot water appeared from holes in the mountains. The whole area was weathered and was covered with yellow (sulphur) and white precipitate. The area contained also large degassing fumaroles with large yellow pipes or much surface deposits. Water splashed and boiled in holes. The odour in the area smelled like rotten eggs. The waters escaping from holes and springs joined together and flowed downstream and formed the Kali Putih, which will be discussed in section 2.8.

The Danow Mooat (Photo 27) is a large (4.5 * 1.4 km) lake, and is situated east of the Ambang. Its coordinates are N 00° 45, E 124° 27 5. Koperberg (1928) called the lake Danaoe. The lake might be an old crater lake, though this was not revealed by Koperberg. The origin might be comparable with the probable caldera Tondano lake. The shape of the Danow Mooat also resembles the Tondano lake, though the Danow Mooat is smaller in the south than in the north. A small island, at the west side in the middle, is named Pulau Mintu. North of the small island the lake is 500 m wider. The lake drains a large area, enclosed by the east side of the

Bulud Moyayat, north and west of the Bulud Tungkeng, the Bulud Siyungon and the Bulud Kuladolan (Map 4, Appendix I). The outlet river of the Danow Mooat streams north of the lake at the west side in the wide river Ongkag Poigair. The Onkag Poigar becomes smaller downstream, flows around the Bulud Molibut, and enters the Lour Holoi, a lake in the northern mountains (Map 4). The outlet of this lake begins at the north west side of the lake and flows in that direction to the sea.

2.7.2. Description of sample locations of the Ambang mountains and surroundings

Sample AMB1-1 was taken 20 m west of AMB2-1 (see the detailed Map 10, Appendix I). The surroundings of the river were covered with yellow, green surface deposits. The water came from a fumarole upstream. The water was quite acid (pH 1.5), which caused the death of a snake. Sample AMB2-1 is situated 10 m east of AMB1-1 (Photo 13, Appendix III). At this location, a lot of sulphur was deposited. The water came from a fumarole and the temperature was 82 °C. The weathered rocks were coloured white and grey and were covered with yellow and white surface deposits with some red colours.

Probably, the two rivers AMB1-1 and AMB2-1 join (see Map 10) and form a small river, with a discharge of about 10 l/s. Downstream of this river, sample AMB4-1 was taken. The water had a green blue (yellow) white colour. The sediment had a lightly green colour, and the surrounded surface deposits had a dark green colour, probably of algae. In the weathered, surrounded walls and the water small fumaroles were observed.

Downstream of this sample location, a small river enters the river. The discharge of this small river is 5 l/s. Sample AMB3-1 was taken up stream of this river. The water had a lightly white green blue colour and seemed to be turbid, but after filtering there was almost no precipitate. The last sample taken in this fumarolic active area of the Ambang mountains was AMB5-1. This sample was taken from the river, which may be the outlet river of the Ambang mountains. The discharge of this green blue water was about 15 l/s.

Sample AMB6-1 was taken in the mountains, about 100 m higher then the fumarolic area (Map 10). The water is a spring with a temperature of about 30 °C and is used as drinking and washing water. The water comes from the northern mountain Bulud Moyayat. The Volcanological Survey of Indonesia (VSI) has also sampled the spring (DTA1-1).

The Danow Mooat (D.Moat) was sampled in the south of the lake (Map 4). The water was rich in fish and surrounded by vegetation. The water was neutral (pH 6.4) and no volcanic activity is observed, today. One inlet stream of the lake was measured (M2). It enters the lake at the west side, and comes from the Bulud Mooat, at the east side. At the opposite side of the mountain is situated the active area, where samples AMB1-1 to AMB5-1 were taken. The water M2 was warm and used in a washing place. The broad outlet of the Danow Mooat (20 m wide) is used for fishing and washing. The outlet (M3) streams very slow. With a boat, a sample was taken in the middle of the grey blue river.

Danow Tandok is a small lake (700 * 400 m) two kilometre south west of Danow Mooat (Map 4, Appendix I). The water had a pH of 6. Since its appearance suggested that the water was polluted, the water was not sampled. The lake was surrounded by a green rim and contained much fish.

A small lake (500 * 200 m) is situated near Tuduaog and is surrounded by one road, which goes to Bilalang. The VSI had sampled this lake (DTD1-1). From the map it is not clear whether there are inlets and outlets or not. The colour of the water sample was lightly yellow

and it was turbid. Further, sample BW1-1 was taken by the VSI from the lake Bangunan Wuwuk HS. These samples probably come from one of two lakes at the Ambang mountains B. Tudutalong or Danow Tabang.

2.8. The discharge river of the Ambang, the Kali Putih

2.8.1. The discharge river of the Ambang, the Kali Putih

The Kali Putih (means white river) is, in this study, the name used to indicate an acid river coming from the Ambang. In literature, a lot of different names are used for the discharge river of the Ambang. Padang (1951) mentioned that the drainage of the Ambang mountains occurred through by the 'rivulet Putih'. A river named Tapa Putih, which starts 2 km west of the fumarolic area of the Ambang and streams through Moyongkota, is indicated on Map 4 (Appendix I). This river was not found in the field. The local people know a Kali Putih, which is situated east of Modayag and streams under a bridge, indicated as KP1-1 on Map 4. It had indeed a white coloured bed rock and its pH was 2.5. However, according to Map 4, the river is named Tapa Matadingin. In addition, the Tapa Matadingin has its origin west of the fumarolic field of the Ambang mountains. On the contrary, the Tapa Maayat started in the fumarolic area, but is only a small neutral river, which streams through the rice fields and is used for irrigation. In conclusion, the field observations and pH and conductivity measurements indicate that the Tapa Matadingin is the outlet river of the Ambang.

From sample location AMB5-1 to KP1-1 the discharge of the Kali Putih increases from 15 to 600 l/s, but there are no inlets observed along the river. Maybe, the total amount of water is increased near sample location AMB5-1. The first (small) dilution of the Kali Putih occurs at the Tapa Maayat near the bridge of Modayag (Photo 28).

The Kali Putih becomes very diluted (3.5 times) south of Modayag, near sample location TBG1-1. At this location, two large rivers flow in the Kali Putih and the pH increases from 2.5 to 4.3. The neutralizing rivers, Tubig Tobongon and Tubig Lombiyawan, come from the east and drain the south of the Bulud Mooat and the mountains Bulud Toyot and Bulud Mologuyon. The Tapa Tombat, coming from the west of the Ambang, enters the Kali Putih from the north. Further, the river drains the north of the mountains Bulud Tuui and Bulud Nanasi. The river streams under a bridge, which is situated in the middle of the road Kotamobagu and Bakan (M4). At this location, the river is 20 m wide and joins after the bridge with a very wide river Ongkag Mongondow, which flows north to the Celebes Sea.

2.8.2. Description of sample locations of the river Kali Putih

Sample KP1-1 was taken of the acid (pH 2.5) river Kali Putih under the bridge, 500 m east of the Pos Observasi in Modayag (see the detailed Map 11, Appendix I). The water was clear and had a discharge of 600 l/s at this location. The sediments existed of small and large grey white rocks and sand. There was no life or vegetation in the river. Further, upstream in the Kali Putih, sample MD1-1 was taken (Photo 28, Appendix III). This location looked the same as KP1-1.

A small inlet TM1-1 enters the Kali Putih via a waterfall from the east side, two hundred metres upstream of KP1-1 (Map 11). This water (Tapa Maayat) comes from the rice field. The neutral inlet was followed in the paddy fields and a basin with neutral water was found 1 km east of TM1-1, which is used to irrigate the paddy fields. A dry bed rock and two small rivers are situated 2 km north east of TM1-1, but not indicated on Map 4. The small neutral (pH 7) rivers (TM2-1 and TM3-1) come from a basin upstream, which is used for irrigation.

The two combined rivers Tubig Tobongon and Tubig Lombiyawan are sampled and named TBG1-1. The rivers stream very fast and come from the paddy fields. The pH was 7 and the total discharge was about 1500 l/s. The Tubig Lombiyawan (500 l/s) was quite clear and had a blue-green colour. The Tubig Tobongon was very turbid and brown coloured. The rocks in the bed rock were covered by fresh green algae. The local people told that the Tubig Tobongon contains gold. In the river a machine was built to get gold, probably by using silver nitrate.

KP2-1 was sampled downstream of KP1-1 after the input of the two combined rivers. The discharge of the river was now about 2500 l/s. The river was 4 m wide and it had a brown turbid colour. No clear surface deposits was observed.

The river, which enters the Kali Putih from the north, was sampled in the settlement Modayag. The river Tapa Tombat (TB1-1) contained a lot of rubbish. The colour was green-blue, with a white flair.

Sample KP3-1 was taken three kilometre south Kobo Kecil and five kilometre north east of M4 (Map 4). At this location, 1000 l/s is taken from the Kali Putih for irrigation of the rice fields (Photo 8, Appendix III). The colour of the river was brown and the river was very turbid, but not acid (pH 5.5).

Before the Kali Putih enters the Ongkag Mongondow, sample M4 is taken (Map 4). The river is 20 m wide and not deep and therefore used to wash cars and cows. The discharge is difficult to estimate, but is about 6000 l/s.

3. Sampling strategy, analytical techniques and results

3.1. Sampling schedule

The fieldwork was done in June and July of 1997. In the Minahassa the following places were visited: the Danau Linow and its surroundings, the Lahendong area and its surrounded rice fields, the Kawah Masem crater lake and the river R. Maasem and the Tondano lake with its southern active hydrothermal area. The Ambang mountains and its discharge river, the Kali Putih, were visited too. Further, single lakes, rivers and possible old crater lakes were visited in North Sulawesi. The locations were investigated, described, measured and sampled. The complete sampling schedule of the field activities is given in Appendix IV. The sample locations are discussed in chapter 2, the sample locations are indicated on Map 3 and 4 (Appendix I).

3.2. Field measurements

The areas described in section 3.1. were visited and investigated. The pH, temperature and conductivity of the waters were measured. Furthermore, the discharge of the river or the surface of a lake were estimated. Finally, the position of the sample location was determined and a short description of the location was made. In this field trip 80 locations were visited. The pH of 66 waters was determined, while the conductivity and temperature of 57 samples were measured. The results of the measurements are given in a final data set, which is given in Table 3.1. The analytical procedure of pH and conductivity measurements are described in section 3.5. and 3.6., respectively.

The temperature was measured with the temperature sensor of the conductivity-meter. The results must be taken indicative, because temperature of air and water can vary with the amount of sunlight and rain. The MVO had also measured some temperatures. To determine the final temperature, the measurements of the Utrecht team were taken, because these measurements were all done in the same way. If no temperatures data of the Utrecht team were available the temperatures measured by the MVO were taken.

The discharge of rivers and surface of lakes were estimated visually. The results were not very accurate. However, when two rivers flow together, the discharge will indicate the proportion of both rivers. The position of the visited locations were determined with a GPS, the Garmin 12 XL. The accuracy depends on the amount of free air, which may be influenced by mountains and trees and was about 15 to 50 m. The coordinates of sample location, where GPS measurements were impossible, were determined with GPS coordinates of surrounding locations and with the use of the map.

3.3. The way of sampling

The samples were taken with two acid rinsed polyethylene bottles (for acid waters: one of 200 ml and one of 500 ml, and for the neutral waters two of 500 ml). Furthermore, one small bottle for isotope determination was taken. A bottle for polythionates analysis was filled, when the pH of a water was lower than 3. To these last bottles 0.5 g hydroxylamine hydrochloride was added in 50 ml sample, to conserve the polythionates. Before sampling, the acid cleaned bottles were rinsed with the water, that had to be sampled. The samples were taken a few centimetres below the surface of the water and as far as possible in the middle of the river or lake. In this field trip 54 water samples and ten samples for polythionates analysis were

taken. At fifteen locations sediments, rocks with red precipitate and condensed sulphur were sampled.

The water samples were filtered through 0.45 μm filters, in the observation posts of the Volcanological Survey of Indonesia (VSI) or in the field. The samples were filtered within three days after sampling. The filtered samples were separated in two 'acidified' bottles and two 'diluted' bottles. The 'acidified' bottles were prepared by adding a few drops concentrated HNO_3 to the samples. The 'diluted' bottles were prepared by diluting the filtered waters 2 to 10 times, depending on the pH and conductivity. One of the two identical bottles was sent to the MVO for analysis, to compare the chemical composition of the waters with the analysis done in Utrecht. The water samples for polythionates analysis were not filtered, except when they were very dirty.

3.4. Transport and storage

The acidified water samples, isotope-bottles, sediment and rock samples were transported under normal condition of pressure and temperature to the Netherlands. The diluted and plain water samples were sent to the Netherlands in a wooden box by aeroplane and boat under cool and low pressure conditions. The samples were stored at room temperature and pressure.

The box was unpacked at the beginning of October 1997. Two samples (MHW1-1, plain and MHW2-1, D2x) had lost a few ml water. Three samples had some mould on the bottles, but this was removed carefully and the mould had not affected the sample. All the samples arrived in the Netherlands without observable changes, except the samples DL2-1 and LH2-1. The colour of DL2-1 was lightly white yellow in Indonesia, but it had changed to deep red, by red deposits in the flask. The diluted DL2-1 sample had a red orange precipitate, while the acidified version was less red than the plain sample. Sample LH2-1 was a colourless sample, but the colour of the plain version was turned to yellow.

The sediments and rocks arrived in the Netherlands in a good state and though one third of the sachets were wet no contamination was observed. The sediments were dried on glasses at a temperature of 110 $^{\circ}\text{C}$, except the sulphur mud, which was dried at 30 $^{\circ}\text{C}$. The samples were stored in plastic cups under normal conditions of temperature and pressure.

3.5. The pH measurement

The pH of rivers, lakes and pools were measured with pH-paper, because the pH-meter failed. To increase the accuracy of the pH measurement, several types of pH-paper were used, but the papers in the low pH-range (<4) are not accurate. Therefore, pH measurements with a pH meter were done in the Netherlands, two month after the sampling period. For this analysis a METROHM 654 pH meter and the diluted and plain bottles were used. The meter was gauged with buffers of pH 2 and 4 for samples with a pH of 0 - 4, and with buffers pH 4 and 7 for samples with a higher pH. The accuracy of the pH-gauge solution was 0.02 pH. The total accuracy of the measurement was about 0.05 pH.

The final pH was determined for samples with a pH lower than 5, by taking the laboratory results of the measured diluted samples and to compare this pH with the measured pH of the plain samples, pH measurements done by the MVO and field measurements with pH-paper. For the other samples the pH paper measurements were mainly taken and not the laboratory measured pH's, because the pH of neutral samples may change easily, by new chemical equilibrium, caused through bacterial activity, CO_2 input and temperature. The finally inaccuracy of the pH was about 0.5. The pH of all samples is given in Table 3.1.

3.6. The conductivity measurement

The conductivity of rivers, lakes and pools was measured with a conductivity meter. The Kawah Masem samples and PL1-1, DTD1-1, BW1-1 and AMB6-1 were not measured in the field, but in the laboratory, because the meter failed in the field. The final conductivity was determined by taking the field measurements done by the Utrecht team and, if these were not available, by taking the measurements of the Indonesian team. The conductivity of the samples, which were only measured in the laboratory, must be taken with care if the conductivity was more than 500 $\mu\text{S}/\text{cm}$, because the conductivity of samples measured in the field and in the laboratory show an increase of conductivity up to 20% after sampling till the measurement in the laboratory. The final conductivity of the water samples is given in Table 3.1. The inaccuracy of the conductivity measurements was about 10%.

3.7. Determination of polythionates

A sample for the analysis of polythionates was taken when there was a possibility for volcanic activity and the pH of the water was lower than 3. Ten samples were taken, but only three samples (DL1-1B, KM1-2 and AMB5-1) were sent to the university of Tokyo, because these three samples had high magnesium and sulphate concentrations and are representative for the samples in North Sulawesi.

The samples were prepared and measured with Ion Chromatography and/or microbore High-Performance Liquid Chromatography, with the techniques developed by Takano and Watanuki (1990), see also Rowe *et al.* (1992b). The detection limit is 10 ppm for the tri-, tetra- and pentathionates measured with Ion Chromatography. The detection limit is 10 ppm for trithionates, and 0.2 ppm for tetra-, penta- and hexathionates measured with microbore High-Performance Liquid Chromatography.

In none of the three samples any polythionates had been found. This can be due to lack of polythionates, but also to the (too) low concentration of these components and their decomposition. If present, polythionates are stable when the concentration is higher than 100 ppm or when the pH is between 1.2 and 1.8 (Rowe *et al.*, 1992b). The stability decreases at low concentrations (<100 ppm), which could be prevented by hydroxylamine hydrochloride (Takano and Watanuki, 1990). Despite the use of anticipant, the stability of polythionates is just 21 days (Takano and Watanuki, 1990). A decrease of polythionates may be caused by the long time between the sampling and the analysis of the polythionates. From this the conclusion can be drawn that the polythionate concentrations were too low to determine, if present.

3.8. The determination of cations, sulphur and phosphorus with ICP-AES

The cations, sulphur and phosphorus concentrations of the acidified water samples were analysed with the inductively coupled plasma atomic emission spectroscopy (ICP-AES). The analysis were done in two series. In both series the ion concentrations, accuracy and drift were determined and the influences of added acid or dilution were investigated. For the water samples the 'Watertaak' was used.

In order to bring the pH at zero, 0.4 ml HNO_3 was added in 8 ml sample before measuring, because the pH of the samples was 1.5 to 2. In the field a few drops were only added concentrated HNO_3 at 200 ml sample. To determine the influences of additional acid, no extra acid was added to three samples. The influence of additional acid is remarkable (see sample KM1-1 in Table 1, Appendix II). The ion concentrations were higher in samples where no extra acid was added, however, it will be expected that the concentrations were lower, because in general better results are obtained at low pH with ICP. No clear explanation had been found for this phenomenon. The influence of adding HCl in stead of HNO_3 was investigated and no

clear difference can be seen at the ion concentrations in sample KP1-1 and AMB6-1 (Table 1). Thus, adding HCl or HNO₃ does not affect the results.

In the first series, a blank was added after four or five water samples, or if the conductivity of a sample was higher than 3 mS. From these blanks it can be concluded that there is no memory effect, because they did not show an ion concentration. Furthermore, some samples were measured in duplicate to control the accuracy and the drift. The samples, which were measured in duplicate, showed a variation of less than 1% (see sample DL1-1, KP1-1 and KM1-1 in Table 1). The accuracy and drift were good.

In the second series samples were diluted, if they had ion concentrations higher than the calibration curve. In order to measure very high ion concentrations, the samples were diluted in such a way that the ion concentration fell just a little below the highest value of the calibration curve. The dilution varied from 2 to 30 times. The accuracy of measurements of diluted samples was lower compared to that of not diluted samples (see sample DL4-1, DL7-1 and AMB5-1, in Table 1). The accuracy of elements with concentrations above the calibration curve were increased after dilution.

In the water samples of Sulawesi the following elements had been found: Al, B, Ba, Ca, Fe, K, Mn, Na, P, S, Si, Sr, V, Y and Zn (Table 3.1.a.). The following elements were analysed, but were not detected in the North Sulawesi samples: Ag, Bi, Cd, Co, Cr, Cu, Li, Ni, Pb, Sn, Ti, Zr, Be, Sc, Mo, As, Se and Sb. The detection limit of the elements was between 0.05 and 0.30 ppm. The elements Ba, P, V, Y and Zn were found in only a few samples (Table 3.1.b.). Because in many samples the S and Si and, in a few cases, the Al, Ca and Fe concentrations exceed the calibration curve, the determination of the concentrations of the other elements can be influenced by these highly concentrated elements; e.g. high concentrations of Fe influence the determination of B.

The results of both series were averaged and given in Table 3.1. The sulphate concentration will be discussed in section 3.13. The results of elements, with concentrations above the calibration curve are excluded from the calculation of the average value. In these cases, the diluted version was recalculated to the right concentrations. Element concentrations, which become too small upon dilution, were not used for the average.

The given inaccuracy of the ICP is about 10% if the concentration is up to 5 times higher than the detection limit. For concentrations, which are 50 to 100 times higher than the detection limit, the inaccuracy is 2%. However, the Sulawesi samples can have a higher inaccuracy, caused by their strong matrix. Cations like B, Ba, Mn, P, V, Y, Sr and Zn are mainly present in such a low concentration, that in, respect of the detection limit, it must be concluded that these results were not very accurate.

It can be concluded that the results are quite good, also with respect to the matrix of these samples. The inaccuracy was mainly caused by the matrix and by dilution. For the determination of trace elements ICP-MS is the preferred technique (Sriwana *et al.*, 1998).

3.9. Determination of anion concentrations with Ion Chromatography

The anion concentration of the water samples was analysed with Ion Chromatography. The anions fluoride, chloride, nitrate, bromide, phosphate (HPO₄²⁻) and sulphate were determined in the diluted water samples. For the analysis the QIC-Dionex with an Ionpac AS4A column and the AG4A as a pre-column was used. As suppressor an Anion Micro Membrane Suppressor was used. The detector was a suppressed conductivity detector, with a detection range of 30 µS/cm for a 5 ppm concentration of the mixed standard. A Shimadzu C-R4A is used as integrator. The used eluent (2.0 ml/min) was a 1.8 mM Na₂CO₃ / 1.7 mM NaHCO₃ solution.

The regenerant (2.5 ml/min) was a 12.5 mM H_2SO_4 solution.

The Ion Chromatograph was gauged with a mixed standard of 5 ppm F, Br, Cl and NO_3 and 10 ppm sulphate and a standard with the double concentrations. Further, the drift and the accuracy of Ion Chromatography were determined with the standard solutions. Samples with a chloride and/or sulphate concentration above the upper detection limit (~ 35 ppm) were diluted and measured again. Acid samples were neutralized by adding 50 μl concentrated NaOH to 5 ml sample, because the column will be destructed by a low pH and the best measurements are obtained at a pH of 7.

The anion concentrations of the water samples are given in Table 2 (Appendix II), except the phosphate concentrations, because no samples contained phosphate. Fluoride was found in five samples (see Table 2), with a maximum concentration of 0.6 ppm. The bad detection of fluoride may be caused by the forming of Al-complexes or by the low fluoride concentrations. The fluoride concentrations, determined with the use of the Ion Chromatograph, were not used further in this study.

The anions chloride and sulphate were well detected, because they were present in high concentrations. The analysis of the samples MHW1-1 and AMB1-1 may be inaccurate, because probably they were not diluted enough. DL2-1 and the Ambang samples may be less accurate, because they were diluted up to 200 times. The chloride and sulphate concentrations are compared with other analysis in section 3.13.

The bromide and nitrate concentration were low (<0.2 and <1.5 ppm, respectively), and therefore not very accurate. The anion nitrate is not stable at room temperature, so it can be expected that the nitrate concentrations in the Sulawesi samples had decreased during the time between sampling and measuring. The bromide and nitrate concentration of the samples are listed in Table 3.1.a.

From the analysis of standards it can be concluded that the measurements were quite stable and accurate. The duplicate measurements support this conclusion. The standard deviation, determined with the standards, were for F, Cl, Br and NO_3 0.1 to 0.3 ppm, at a concentration of 5 ppm. The standard deviation of sulphate (10 ppm) was 0.4 ppm. The in duplicate measured samples had a maximum variation of 5%, but at diluted samples the variation increased up to 10%.

It can be concluded that the results are quite good for chloride and sulphate, while fluoride and phosphate are in most cases not found. The bromide and nitrate concentrations are low and can be used as indicative only.

3.10. Fluoride with the ISE

Next to the fluoride determination with Ion Chromatography, fluoride was measured with an ion selective electrode (ISE). The ORION EA 940 Expandable IonAnalyser and an ORION Fluoride electrode 94-09, with a LaF_3 crystal were used for the fluoride determination. The reference electrode used, was a double junction electrode model 90-02, filled with an (inner) AgCl and an outer KNO_3 solution.

To eliminate differences of ionic strength and to decomplex the bound fluoride a TISAB III buffer was used. The buffer is also used to keep the pH on 5.5, because otherwise F^- is competing with OH^- at high pH or with HF and HF_2 at low pH (Potts, 1987). The TISAB III buffer was made by dissolving 58 g NaCl, 57 ml glacial acetic acid, 4 g CDTA IV and 243 g tri-ammonium citrate in one litre of distilled water. With a few ml concentrated NaOH the pH was set on 5.5. The ORION manual advised to use a TISAB I buffer solution composed of 58 g NaCl, 294 g Na-citrate, 18,2 g CDTA IV and 2 g NaOH in one litre with a pH of 5.9 to 6.0, but Potts (1987) mentioned a rapidly decreases of the precision below 100 ppm and an effec-

tive detection limit of 30 ppm. Nicolson (1981) investigated the best way to measure the fluoride concentration and the usefulness of several buffers. His conclusion was that the best buffer was a TISAB III (with tri-ammonium citrate), which is confirmed by Crompton (1996).

The measurements were done by direct measurement, with the use of a calibration curve. The calibration curve was made by standards of 0, 1, 2 and 5 (10) ppm fluoride and should give a slope of -59 mV/10 ppm. A good way to measure the fluoride concentration with ISE is made from own experience and from advise of Nicolson (1981, 1982) and an unpublished paper (Loffeld *et al.*, 1997) and is described beneath. The fluoride electrode and the IonAnalyser were used as described in the ORION manual. The samples were prepared by adding 15 ml buffer at 5 ml sample in a Teflon flask. In order to decomplex the fluoride, the mix was stored for 24 hours before measuring. The electrode was placed in the sample for five minutes, before measurement, in order to stabilize the electrode.

The fluoride concentrations, standard deviations and number of measurements are summarized in Table 3 (Appendix II). The fluoride concentrations were quite low (<1 ppm). The high standard deviation of samples with a high (>1 ppm) fluoride concentration is caused by dilution of these samples in Indonesia.

The main problem with the fluoride measurement was the inaccuracy of the calibration curve and the drift of the ISE. To prevent inaccurate measurements, many calibration curves had been made and all samples were measured at least twice. Very good results, however, were not obtained with the low fluoride concentrations of the Sulawesi samples, which can have strong matrices. Better results can be obtained with higher fluoride concentration (> 10 ppm). It can be concluded that the measurements can give good indications of the fluoride concentrations. They are relatively good with respect to the low concentrations, and therefore given in Table 3.1.

3.11. Chloride with the ISE

Next to the chloride determination with the Ion Chromatograph, the chloride concentration was analysed with the ion selective electrode (ISE). The ORION EA 940 Expandable IonAnalyser and the chloride electrode of ORION were used for this analysis. The reference electrode was a double junction electrode model 90-02, filled with an inner AgCl and an outer KNO₃ solution.

To diminish the differences in ionic strength of the samples an ISAB buffer was added to the samples, with the next composition: 60 g NH₄NO₃, 21 g NaNO₃ and 20 g Na-acetate in one litre distilled water and set on pH 3 with concentrated HNO₃. The samples were prepared by adding 12.5 ml buffer to 5 ml sample in a Teflon flask. The mix was stored for 4 hours before measuring. The electrode was placed in the flask one or two minutes before the measurement was done, in order to stabilize the electrode.

The measurements were done by direct measurement with the use of a calibration curve. The calibration curve was made with standard solutions and should had a slope of -59 mV/10 ppm. For samples with a low content of chloride a calibration curve from 0 to 10 ppm was used and for samples with higher chloride concentrations standards up to 100 ppm were used.

The chloride concentrations, standard deviations and number of measurements are given in Table 4 (Appendix II). The standard deviations of the samples DL 1-1A/B, LH2-1 and KM1-1 were very high with respect to the total concentration, which was caused by the strong dilution of the samples. The analysis of chloride was not very good. Single measurements did not give problems, but calibration curves stayed inaccurate. Therefore, point calibration was used to anticipate the calibration curve problems. This way was accurate, but not precise. To get a more precise chloride concentration, the samples were measured 3 to 10 times, with different

point calibrations. Samples with a minimal concentration of 10 ppm, give more accurate values. The determination of the final chloride concentration for the samples of North Sulawesi is described in section 3.13. It can be concluded that the analysis of chloride with the ISE was relative good, in respect to the low concentrations.

3.12. Potentiometric titration of chloride

The last way in this study to analyse the chloride concentration, was the potentiometric titration of chloride with silver nitrate. The procedure followed is described in the 'Handleiding voor het Geochemisch Prakticum' (1996). First, the concentration of the titration solution was determined after which the samples were measured. The used silver nitrate solution had a molarity of 0.1. The available amount of sample, used for the potentiometric analysis, is 0.1 ml. However, the chloride concentrations of the North Sulawesi samples were too low to get accurate analysis with the amount of 0.1 ml sample. Therefore, 1 to 5 ml sample for the determination of the chloride concentration was taken. The potential shifts were used to determine the chloride concentration of the sample.

The turnover point was difficult to determine because the samples had low chloride concentrations (<50 ppm), which caused the absence of a steep slope. Nearly all the Sulawesi samples had measurable concentrations of 10 ppm or less. So the potentiometric titration was only used for four samples MHW1-1, MHW3-1, RND1-1 and AMB1-1. The chloride concentrations of these samples are given in Table 3.2 and discussed in section 3.13. From the in duplicate measured samples, can be concluded that the measurements were accurate. It can be concluded that this method is very accurate for concentrations of 100 ppm and up. However, the Sulawesi samples had (much) lower concentrations and therefore, this method was not useful.

3.13. The final data set of cations and anions of the North Sulawesi waters samples

In Table 3.1 the final chemical compositions and the field measurements of the waters of North Sulawesi are given. The cation and P concentrations, measured with ICP-AES were used as the final cation and P concentration. The final fluoride concentrations were based on the ISE analysis. The nitrate and bromide concentrations, measured with Ion Chromatography, were used as the final nitrate and bromide concentrations, however they must be taken indicative. Further, the cation concentrations, which were measured just above the detection limit, must be taken indicative. This is the case for Ba, V, Y, Zn, Sr and Mn.

The chloride values were based on a comparison of the analysis of ISE, Ion Chromatography and potentiometric titration of four samples. In Table 3.2 the chloride concentrations of these four samples of the three determination methods are given.

Table 3.2
Chloride concentrations of four samples (in ppm).

Sample	ISE	Ion Chromatography	Potentiometric titration	Average ISE and Ion Chromatograph
RND 1-1	874	723	801	798
MHW 1-1	155	165	159	160
MHW 3-1	309	232	271	270
AMB 1-1	109	79	953	939

From this table it can be concluded that averaging of ISE and Ion Chromatograph leads to acceptable values, because the average chloride concentration agrees with the determined chloride concentration by potentiometric titration, which is an accurate method. The averaging of the chloride concentrations had given problems for the samples: DL9-1, LA2-1, LH2-1,

Table 3.1 a.
Final data set. Field measurements and chemical compositions of the North Sulawesi water samples.

Sample	pH	Ec microS	T water Celcius	T air Celsius	GPS N	GPS E	discharge/ surface	Al ppm	B ppm	Ca ppm	Fe ppm	K ppm	Mg ppm	Mn ppm	Na ppm	Si ppm	Sr ppm	F ppm	Cl ppm	SO4 ppm	Br ppm	NO3 ppm
DL 1-1	2.6	1330	27.2	25.8	01 16 145	124 49 416		3.83	0.17	13.4	9.15	3.62	5.85	< b.g.	13.7	28.3	< b.g.	0.49	4.92	261	n.a.	0.26
DL 1-1A	2.3	1370	28.9	30.7	01 16 262	124 49 454		2.57	< b.g.	7.77	5.10	2.10	3.15	< b.g.	7.80	17.0	< b.g.	1.71	5.48	309	0.13	0.85
DL 1-1B	2.4	1380	27.1	30.7	01 16 317	124 49 422		4.02	0.17	13.8	9.37	3.69	5.66	< b.g.	13.4	30.1	0.06	1.42	5.05	281	0.08	1.60
DL 2-1	2.0	6520	27.0	29.0	01 16 357	124 49 919		1494	5.12	419	2394	27.4	218	22.6	67.1	246	1.60	3.83	13.1	14762	0.9	1.20
DL 4-1	3.5	700	45.0	29.0	01 16 357	124 49 919		0.56	1.90	37.3	3.34	29.1	14.2	0.17	76.0	78.6	< b.g.	0.61	39.3	322	0.09	0.18
DL 5-1	6.5	150	22.4	24.3	01 16 477	124 49 979		< b.g.	< b.g.	13.5	< b.g.	2.81	6.16	< b.g.	8.22	25.0	< b.g.	0.78	2.55	20.4	0.06	0.05
DL 6-1	2.2	2170	30.4	27.4	01 16 008	124 49 139		27.4	0.53	32.5	19.8	5.17	13.3	0.24	24.6	43.8	0.10	1.99	39.6	587	0.1	0.23
DL 7-1	2.2	2310	34.8	27.4	01 15 972	124 49 042		32.5	0.68	39.1	22.9	5.96	16.0	0.53	25.9	51.6	0.12	1.55	37.3	662	0.08	0.75
DL 8-1	2.5	1410	25.3	25.1	01 16 106	124 49 761		4.37	0.17	14.0	9.44	3.92	6.06	< b.g.	14.3	29.3	0.05	0.70	5.04	293	0.05	0.16
DL 9-1	2.4	1480	35.8	26.8	01 16 423	124 49 651	3 l/s	27.2	0.19	21.5	37.0	3.99	12.9	0.14	16.7	62.6	0.07	0.77	4.64	503	n.a.	0.30
LA 1-1	6.5	120	25.5	28.4	01 16 977	124 49 375		< b.g.	< b.g.	10.3	< b.g.	0.97	5.57	< b.g.	6.38	13.0	< b.g.	0.37	1.12	7.6	n.a.	n.a.
LA 2-1	3.6	240	29.6	25.6	01 16 973	124 49 367		0.25	< b.g.	7.12	2.83	0.36	4.35	< b.g.	6.93	12.1	< b.g.	0.28	0.97	59.1	0.01	0.14
LA 3-1	6.0	100	27.2	25.6	01 16 973	124 49 367		< b.g.	< b.g.	7.40	< b.g.	< b.g.	5.40	< b.g.	6.58	9.90	< b.g.	0.27	0.98	20.6	n.a.	n.a.
LH 2-1	2.5	1150	26.7	26.4	01 17 326	124 49 456		13.6	0.39	23.6	42.9	5.40	7.86	< b.g.	12.0	73.9	0.10	1.41	7.53	363	0.17	1.25
RND 1-1	7.0	800	30.9	25.1	01 16 567	124 47 111	500 l/s	< b.g.	2.58	59.5	< b.g.	14.3	23.8	0.19	77.1	61.6	0.20	0.44	79.9	221	0.06	0.29
RNE 1-1	6.5	165	24.2	31.9	01 17 278	124 46 701		< b.g.	< b.g.	15.4	< b.g.	4.18	5.64	< b.g.	11.4	42.7	0.07	0.37	3.11	12.1	n.a.	0.02
NMG 1-1	7.2	350	25.7	28.5	01 16 953	124 43 779	4000 l/s	< b.g.	0.49	26.9	< b.g.	6.55	11.1	< b.g.	33.3	45.2	0.11	0.34	23.7	46.7	0.02	0.01
NMG 2-1	7.5	380	27.3	27.0	01 16 8	124 43 8	4000 l/s	< b.g.	0.50	25.9	< b.g.	7.78	9.88	< b.g.	42.6	50.2	0.09	0.39	26.3	51.6	0.04	n.a.
NMG 3-1	7.5	360	27.0	27.8	01 17 016	124 43 740	8000 l/s	< b.g.	0.51	26.3	< b.g.	7.52	10.2	< b.g.	41.3	49.2	0.09	0.39	26.3	50.4	0.05	n.a.
KM 1-1	2.1	2500			01 08 153	124 45 141	400m2	40.0	< b.g.	69.8	21.8	1.27	45.7	0.72	13.3	108	0.10	2.45	4.87	1008	0.05	0.72
KM 1-2	2.2	2510	43.6		01 08 153	124 45 141	400m2	48.8	< b.g.	71.0	24.7	0.81	48.4	0.76	14.4	108	0.10	1.08	2.60	1035	n.a.	0.60
KM 2-1	2.5	1600	20.6	21.7	01 08 560	124 45 190	1 l/s	15.4	< b.g.	26.5	3.33	1.04	5.29	< b.g.	7.80	47.9	0.07	1.03	2.56	329	n.a.	0.27
KM 3-1	6.2	160	19.7	20.7	01 08 56	124 45 19	5 l/s	< b.g.	< b.g.	17.5	< b.g.	1.70	5.48	< b.g.	8.06	35.0	< b.g.	0.34	1.86	25.5	n.a.	n.a.
KM 4-1	3.4	400	21.4	20.7	01 08 6	124 45 4	6 l/s	3.61	< b.g.	20.1	0.13	1.60	7.66	< b.g.	7.91	39.2	< b.g.	0.42	1.57	128	n.a.	0.28
KM 5-1	5.5		20.2	19.5	01 08 85	124 45 7	1 l/s	< b.g.	< b.g.	27.1	< b.g.	1.81	10.0	< b.g.	9.42	42.1	< b.g.			106		
KM 6-1	3.0	800	25.9	20.7	01 10 380	124 47 182	250 l/s	18.8	< b.g.	33.4	3.98	5.05	12.5	< b.g.	19.7	66.9	0.10	0.61	5.30	341	n.a.	0.79
KM 7-1	6.3	300	25.6	25.2	01 11 755	124 47 184	1000 l/s	< b.g.	< b.g.	27.0	< b.g.	4.55	10.7	< b.g.	20.5	45.9	0.07	0.50	5.65	107	0.03	0.12
MHW 1-1	6.0	1260	36.5	28.5	01 20 891	124 50 897	1 l/s	< b.g.	0.29	113	< b.g.	22.4	50.5	1.56	83.1	70.3	0.17	0.59	160	295	0.12	n.a.
MHW 2-1	6.5	420	24.5	28.9	01 23 96	124 52 88	50 l/s	0.48	< b.g.	33.1	< b.g.	8.39	12.6	< b.g.	30.5	47.9	0.10	0.94	57.3	73.2	0.05	0.92
MHW 3-1	3.5	1160	25.2	26.4	01 23 964	124 52 719		13.1	0.47	76.5	< b.g.	19.5	23.8	1.52	72.6	55.0	0.10	3.53	271	114	0.38	n.a.
TDS 2	2.6	1510	51.7	29.9	01 09 990	124 49 286	2500m2	0.82	3.70	55.1	2.97	21.9	14.2	0.34	113	152	0.15	1.42	104	463	0.2	0.16
TDO 1	6.5	270	25.3	26.1	01 17 214	124 54 848		< b.g.	< b.g.	16.7	< b.g.	3.74	9.89	< b.g.	25.9	6.66	0.06	0.34	18.4	23.8	0.02	n.a.
DB 1-1	6.7	400	30.0	29.3	01 02 480	124 40 406		< b.g.	< b.g.	29.4	< b.g.	4.90	23.7	< b.g.	26.5	26.3	0.12	0.31	9.65	20.3	n.a.	0.44
PL 1-1	6.5	120			01 15 9	124 50 5		< b.g.	< b.g.	10.1	< b.g.	2.90	4.91	< b.g.	7.34	15.8	< b.g.	0.26	3.61	11.9	n.a.	0.20
AMB 1-1	1.6	7200	49.8	23.4	00 44 978	124 25 268		189	2.90	167	43.0	3.15	72.4	3.32	92.0	173	< b.g.	1.97	94.3	3203	1.1	1.45
AMB 2-1	1.6	5770	82.0	23.4	00 44 978	124 25 268		172	2.73	168	36.4	2.48	69.2	3.23	88.3	176	< b.g.	2.08	86.6	3118	n.a.	n.a.
AMB 3-1	2.0	3430	50.9	25.3	00 44 911	124 25 319	5 l/s	16.6	0.4	239	3.03	5.95	46.6	2.00	75.8	130	0.08	1.68	11.4	1478	n.a.	1.55
AMB 4-1	1.6	8370	43.5	24.7	00 44 852	124 25 321	10 l/s	198	4.57	179	52.3	4.82	68.8	3.19	83.5	170	0.12	1.85	214	3144	n.a.	n.a.
AMB 5-1	1.7	6500	45.1	23.1	00 44 824	124 25 361	12 l/s	121	3.35	206	28.8	4.18	60.0	2.73	81.2	154	0.11	1.71	114	2546	n.a.	n.a.
AMB 6-1	6.0	150	27.0		00 45 408	124 25 354		< b.g.	< b.g.	13.3	< b.g.	3.71	2.84	< b.g.	9.10	50.7	< b.g.			49.9		
DTA 1-1	6.0	150						< b.g.	< b.g.	13.8	< b.g.	4.21	3.05	< b.g.	10.1	49.0	< b.g.	0.34	1.50	46.9	n.a.	0.05
MD 1-1	2.5	2260	23.0	22.7	00 42 950	124 24 074		56.1	2.58	141	11.4	6.93	24.8	0.86	49.0	65.5	0.21	1.24	105	904	0.14	1.60
TM 1-1	6.5	310	23.3	23.6	00 42 894	124 24 096	10 l/s	< b.g.	< b.g.	39.9	< b.g.	2.63	7.37	< b.g.	15.4	29.1	0.11	0.32	4.52	93.9	0.01	0.04
TM 2-1	7.0	120	22.1	30.0	00 43 209	124 24 746		< b.g.	< b.g.	11.9	< b.g.	1.98	3.98	< b.g.	7.51	24.1	< b.g.	0.30	1.48	14.9	0.02	0.01
KP 1-1	2.5	1970	23.3	26.2	00 42 814	124 24 024	600 l/s	45.0	2.28	122	8.82	6.21	21.5	0.59	43.5	58.3	0.18	1.15	96.4	715	0.10	3.20
TBG 1-1	6.7	210	24.4	30.0	00 42 317	124 23 391	1500 l/s	< b.g.	< b.g.	23.8	< b.g.	2.28	7.48	< b.g.	10.1	27.3	0.10	0.26	2.24	34.6	n.a.	0.20
KP 2-1	4.3	410	24.5	28.0	00 42 281	124 23 353	2500 l/s	2.33	0.43	44.2	< b.g.	3.28	10.4	< b.g.	18.0	33.2	0.12	0.22	18.1	154	0.04	1.16
TB 1-1	6.5	390	25.1	26.5	00 42 654	124 22 946		< b.g.	0.24	48.9	< b.g.	4.38	10.9	< b.g.	20.2	24.3	0.16	0.24	10.7	100	0.01	n.a.
KP 3-1	5.5	390	26.1	30.2	00 41	124 20	1200 l/s	1.20	0.51	42.5	< b.g.	5.65	13.6	< b.g.	23.4	26.2	0.14	0.22	19.2	108	0.02	0.25
M 4	7.0	470	27.4	25.9	00 39 990	124 18 671	6000 l/s	0.56	0.59	55.3	< b.g.	4.52	16.0	< b.g.	25.7	26.5	0.25	0.22	21.5	128	0.04	n.a.
DMoat	6.4	70	24.7	27.4	00 43 922	124 27 542		< b.g.	< b.g.	6.91	< b.g.	0.93	2.48	< b.g.	3.65	10.9	< b.g.	0.19	1.00	3.51	0.02	0.01
M 3	6.5	70	24.5	28.9	00 46 225	124 27 030		< b.g.	< b.g.	6.97	< b.g.	0.84	2.42	< b.g.	3.63	10.6	< b.g.	0.21	1.00	3.19	0.01	n.a.
DTD 1-1	6.5	80			00 48 2	124 19 6		< b.g.	< b.g.	5.40	< b.g.	1.58	3.26	< b.g.	5.67	11.1	< b.g.	0.22	1.67	1.02	n.a.	0.06
BW 1-1	6.7	850						< b.g.	2.49	59.6	0.65	24.6	31.8	1.22	86.0	75.5	0.16	0.25	56.7	76.0	0.05	1.98
DLFUM 1					01 16 150	124 49 330																
SP 8-1	7.0	310	27.0	32.7	01 12 128	124 47 052																
DT 1-1	6.0	30	24.3	24.5	00 43 421	124 26 594																
M 2	6.0				00 44 912	124 26 952																
MD 1-1A	2.5	2150	22.9	23.6	00 42 894	124 24 0																

RNE1-1, KM1-1/2 and KM2-1. The large differences between ISE and IC chloride concentrations were caused by the extra dilution of the samples for measurements with the Ion Chromatograph. Therefore, for these samples the analysis of the ISE were used to determine a final chloride concentration.

To determine the final sulphate concentrations the results of S measured with the ICP and the sulphate concentration measured with Ion Chromatography were used. The S of the ICP was recalculated to sulphate, supposed that (nearly) all the S was still sulphate. The recalculated sulphate concentration and the sulphate concentration of the IC were averaged. Only the ICP analysis were taken for the samples KM5-1 and AMB6-1, because they were not measured with Ion Chromatography. Furthermore, the ICP results were taken for the samples DL2-1, DL4-1, KM6-1, TDS2 and MD1-1, because these samples had a variation in sulphate concentration obtained with both methods of up to 30%, caused by the enormous (up to 100 times) dilution for the IC measurements. On the other hand, the IC analysis results were taken for sample DTD1-1, because the ICP did not detect S. In general the ICP analysis had given a few percent higher sulphate concentrations than the Ion Chromatography analysis, which was caused by the different ways of sulphate determination. The ICP detected all S in a sample, while Ion Chromatography detected only free sulphate.

The absence or low concentration of phosphate can be caused by a) a low concentration of phosphate; b) undetectable P, because phosphorus will be adsorbed on complexes at a pH of 7 (for 70%); This rapidly increases to 100% adsorption at lower pH (Sposito, Figure 8.4, 1989). Probably, phosphorus is bound to the walls of the flasks.

It can be concluded that the data set contains useful data, while the B, Ba, Mn, Sr, V, Y, Zn, F, P, Br and NO₃ concentrations must be taken indicative, because they are present in low concentrations.

3.14. Major, minor and trace element analysis of sediments by XRF

The major, minor and trace elements of the sediments were measured by XRF. The samples were prepared by crushing a small amount of sediment with a "tungsten-carbide mil". The crushed sediments were heated at 1000 °C, in order to lose all bound water, after which they were milled in a "tungsten-carbide mil" (5.000 g Flux 66/34 Lithium (tetra/meta) borate with 0.5000 g sample). In order to form glass beads, for the major and minor elements determination, the mixes were melted in Pt-cups in a furnace after adding five drops of LiF to the sample. Furthermore, two standards were prepared, to check the accuracy of the analysis. The sulphur mud rich sediments were not prepared, because they can give problems by heating over the 120 degrees. Next to the glass beads, tablets were made for the determination of trace elements. The dried sediment samples were mixed with an Elvacite solution and pressed in a tablet. If possible, 6 g sediment was used for the preparation, but otherwise less than 6 g was used.

The major and minor elements were analysed with a chromium tube, while the trace elements were measured with a chromium or rhodium tube. The measured major and minor elements were: Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti and P. These elements were recalculated to oxide percentage and given in Table 5 (Appendix II) for each sediment. The measured trace elements were: Co, Cs, Cu, Nb, Ni, Pb, Rb, Sr, Y, Zn, Zr, Ba, La, Sc and V, and are given in Table 6 (Appendix II).

Next to the chemical composition of the sediments, the LOI (loss on ignition) percentages of the sediments are given in Table 5. The LOI percentages were quite high with 3.75 to 23.3% and may indicate the weathered stage of the samples and/or the amount of sulphur. For an accurate measurement the LOI needs to be less than 1.5%. The LOI of 52% in sample

KM1-1 was caused by the high amount of native sulphur. The accuracy of the measurement was quite good, which can be concluded from the two standards (see Table 5). The measured and given composition of the granitic standard (GRAN-1) agreed with each other, while the basaltic standard (BN-02) showed more variation.

To obtain an useful data set for the major and minor elements, the chemical compositions of the sediments are given in two ways. Samples, which are labelled with A, were calculated by excluding the LOI percentage from the total of 100%. These data can be used to compare the trace element percentage with the major and minor oxide percentages in the sediments, because the amount of water, and possible carbonate and sulphur, were eliminated this way. In the second way, labelled with LOI, the samples were recalculated to 100%, including the LOI percentage, so this data can be used to compare the samples to each other.

The analysis of trace elements (Table 6) showed that Ni was only found in sample TM 2-1, while Cs was not found in any sediment sample. The accuracy of the trace element determination was good, based on the in duplicate measured sample KP1-1. The variation was less than a few percent for each element, but for V and Zr about 15%. In general, the element concentrations of Co, Nb, Ni, Pb and Rb were only a bit higher than the detection limit, and were therefore not accurate. The concentrations of Sr, Ba, Sc and V exceed the upper limit for an accurate detection in a few samples (see Table 6). The concentrations were recalculated with a parabolic calibration curve for Sr and Sc and with a linear calibration curve for V. The Ba content in sample DLFUM1 was measured again by XRF and by the use of the ICP (after solving the sample with HF), but the unexpected high concentration of 6% Ba was measured by all these techniques.

3.15. Mineral determination of sediments by XRD

The mineralogy of the sediment samples was determined by XRD. The samples were prepared by crushing a small amount sample in an agate cup. The crushed sample was placed on a sample holder. The results were adapted with a computer program. Possible and expected minerals were selected from the list of theoretically possible minerals, with the use of literature and work done with a optical microscope.

The mineralogy of the sediments are given in Table 7 (Appendix II). Quartz, α -cristobalite and sulphur are the most common minerals. Other common minerals are the Fe-minerals, like goethite, magnetite and hematite, and the minerals barite, kaolinite, pyrite and albite.

3.16. The mud pools and wells of Lahendong

The mud pools and mud wells in the Lahendong area were investigated briefly to make a possible classification. The pH, conductivity and temperature of the pools were measured and the colour and appearance of the pools were described. The pH-paper did not work well, because the mud was dark coloured, but the pH seems to be mainly lower than 2. In the field a classification of the mud pools and wells was made, based on the colour and appearance of the pools. In Table 8 (Appendix II) the measurements and descriptions for the different kind of pool are given.

3.17. Water analysis of the North Sulawesi samples done by MVO

Nearly all the samples were analysed by the MVO in Indonesia. The cations were analysed by the use of AAS, and Fe, SO₄ and Cl were analysed by a spectrophotometer. H₂S, NH₃ and chloride were analysed volumetrically. The analysis of H₂S and NH₃ was not accurate. The chemical composition of the North Sulawesi water samples, measured by the MVO, are given in Table 9 (Appendix II), except for the samples DL8-1, DL9-1, MHW2-1, MHW3-1, BW1-1

and the Lahendong samples, because they were not analysed.

In order to compare these results with the analysis done in Utrecht, ten samples which were analysed in Utrecht and in Indonesia are given in Table 10 (Appendix II). The main difference is the chloride concentration of the samples, which is higher for the measurements done by the MVO. The largest difference was observed for sample DMOat, (1 ppm Utrecht and 100 ppm MVO). An explanation for this large difference in chloride concentration had not been found yet. The sulphate concentrations were in the same order, but differed up to 50% for sample DL2-1. The concentrations of Al, Fe, K and Na were 1.5 to 4 times higher in the Utrecht analysis than in the MVO analysis. An explanation of the large difference between both analysis is not found yet. In this study the chemical compositions determined in Utrecht are used. However, the H_2S concentrations measured by the MVO is used for the SOLVEQ modelling (see section 5.2.1.).

4. Geochemical signatures of the North Sulawesi waters

4.1. Classification model

Hydrothermal or volcanic waters can be classified according to the content of sulphate, chloride and bicarbonate (Rowe *et al.*, 1995, Giggenbach 1988). In this study, the bicarbonate concentrations could not be measured. Therefore, a simplified model is used for the classification of the samples of Sulawesi, based on the models of Rowe and Giggenbach. The simplified model uses the chloride and sulphate concentrations and the pH. Samples with a pH lower than 5, were supposed to contain no bicarbonate. The model is given in Table 4.1.

Table 4.1
Classification model.

Type	pH-range	SO ₄ /Cl
Acid Sulphate (AS)	< 5.0	> 1.0
Acid Chloride (AC)	< 5.0	< 1.0
Neutral Sulphate (NS)	5.0 - 8.0	> 3.5
Neutral Chloride (NC)	5.0 - 8.0	< 3.5

The classification of the Sulawesi samples, according to the model presented in Table 4.1, is given in Table 4.2.

Table 4.2
Classification of the Sulawesi water samples.

Sample	Type	Sample	Type	Sample	Type	Sample	Type	Sample	Type
DL 1-1	AS	LA 2-1	AS	KM 4-1	AS	AMB 1-1	AS	KP 2-1	AS
DL 1-1A	AS	LA 3-1	NS	KM5-1	--	AMB 2-1	AS	TB 1-1	NS
DL 1-1B	AS	LH 2-1	AS	KM 6-1	AS	AMB 3-1	AS	KP 3-1	NS
DL 2-1	AS	RND 1-1	NC	KM 7-1	NS	AMB 4-1	AS	M 4	NS
DL 4-1	AS	RNE 1-1	NS	MHW 1-1	NC	AMB 5-1	AS	DMoat	NC
DL 5-1	NS	NMG 1-1	NC	MHW 2-1	NC	DTA 1-1	NS	M 3	NC
DL 6-1	AS	NMG 2-1	NC	MHW 3-1	AC	MD 1-1	AS	DTD 1-1	NC
DL 7-1	AS	NMG 3-1	NC	TDS 2	AS	TM 1-1	NS	BW 1-1	NC
DL 8-1	AS	KM 1-2	AS	TDO 1	NC	TM 2-1	NS		
DL 9-1	AS	KM 2-1	AS	DB 1-1	NC	KP 1-1	NS		
LA 1-1	NS	KM 3-1	NS	PL 1-1	NC	TBG 1-1	NS		

AS = acid sulphate
AC = acid chloride
NS = neutral sulphate
NC = neutral chloride
-- = not determinable

All the acid samples are 'acid sulphate' samples, except for MHW3-1, which is 'acid chloride'. The neutral samples are chloride or sulphate rich. For the neutral samples (M3, DMoat and DTD1-1) a model with a bicarbonate base is preferable, because these samples have very low contents of both sulphate and chloride (< 4 ppm).

4.2. Geochemical characteristics of the North Sulawesi locations

4.2.1. The most remarkable locations of North Sulawesi

The Ambang mountains have high sulphate concentrations, which go up to 3200 ppm. The

Kawah Masem crater lake contains 1000 ppm sulphate. The highest sulphate concentration was found in the small well, near the Danau Linow, DL2-1 (Photo 3, Appendix III), with a concentration of 1.5%. This sample contains the highest concentrations of nearly all elements. The Al concentration is 1500 ppm, while the Ambang samples have only 200 ppm and the Kawah Masem 45 ppm. The B content is comparable with the Ambang samples (3-5 ppm), while the Kawah Masem has no B. The iron content of sample DL2-1 is high compared to the Ambang samples (2400 and 3 - 52 ppm, respectively). The other concentrations of the elements measured are quite higher in DL2-1 compared to the Ambang samples, which, in their turn, are rich compared to the other Sulawesi samples. In contrast, the chloride concentration of DL2-1 is remarkably low, with 13 ppm.

The Ambang mountains are drained by the acid and ionic rich river Kali Putih, which has a discharge of 600 l/s, during the sampling period; At a constant discharge, this would lead to yearly transport of: 840 ton Al, 40 ton B, 170 ton Fe, 10 ton Mn, 3 ton Sr, 20 ton F, 1800 ton Cl and 13500 ton sulphate. From the Kali Putih 1200 l/s for irrigation at location KP3-1 is taken. This means that yearly 24 ton Al, 100 ton B, 4000 ton sulphate and more than 5 ton Sr are spread over this area by irrigation.

High chloride concentrations are found in the Ambang samples and in the samples taken on the flanks of the Mahawu volcano. MHW3-1 contains the highest chloride concentration (270 ppm) and is the only 'acid-chloride' water. The Mahawu samples probably are outlets of or contain water from the Mahawu crater lake. The high chloride and fluoride concentrations of the Mahawu samples, may be an indication for the volcanic activity of the Mahawu, which had its last eruption in 1977 (Simkin and Siebert, 1994).

The Royongan Ranoraindang (RND1-1) is a neutral river (pH 7). It is interesting that this river contains, in contrast to all the other neutral rivers, high concentrations of sulphate, chloride and cations. The rivers is comparable with the Kali Putih (KP1-1) and MHW3-1.

4.2.2. The acid Danau Linow and its active hydrothermal surroundings

In Table 4.3 the chemical composition are given of the Danau Linow (DL 1-1, DL 1-1A, DL 1-1B and DL 8-1), the input (DL9-1) and output (DL6-1, DL7-1) river of the lake and the yellow pool (DL2-1) and two small rivers (DL4-1, DL5-1), which are used for irrigation. These sample locations are indicated on Map 5 (Appendix I).

Table 4.3
Chemical composition of the Danau Linow and its surrounding waters.

Sample	Kind	pH	Ec μ S	Al ppm	B ppm	Ca ppm	Fe ppm	K ppm	Mg ppm	Mn ppm	Na ppm	Si ppm	F ppm	Cl ppm	SO ₄ ppm
DL 1-1	lake	2.6	1330	3.83	0.17	13.4	9.15	3.62	5.85	< b.g.	13.7	28.3	0.49	4.92	261
DL 1-1B	lake	2.4	1380	4.02	0.17	13.8	9.37	3.69	5.66	< b.g.	13.4	30.1	1.42	5.05	281
DL 8-1	lake	2.5	1410	4.37	0.17	14.0	9.44	3.92	6.06	< b.g.	14.3	29.3	0.70	5.04	293
DL 1-1A	lake	2.3	1370	2.57	< b.g.	7.77	5.10	2.10	3.15	< b.g.	7.80	17.0	1.71	5.48	309
DL 9-1	input	2.4	1480	27.2	0.19	21.5	37.0	3.99	12.9	0.14	16.7	62.6	0.77	4.64	503
DL 6-1	output	2.2	2170	27.4	0.53	32.5	19.8	5.17	13.3	0.24	24.6	43.8	1.99	39.6	587
DL 7-1	output	2.2	2310	32.5	0.68	39.1	22.9	5.96	16.0	0.53	25.9	51.6	1.55	37.3	662
DL 2-1	pool	2	6520	1494	5.12	419	2394	27.4	218	22.6	67.1	246	3.83	13.1	14762
DL 4-1	river	3.5	700	0.56	1.9	37.3	3.34	29.1	14.2	0.17	76	78.6	0.61	39.3	322
DL 5-1	6.5	6.5	150	< b.g.	< b.g.	13.49	< b.g.	2.813	6.16	< b.g.	8.216	24.95	0.78	2.549	20.427

< b.g. = below detection limit.

According to the analysis, it can be concluded that the composition of the Danau Linow is quite homogeneous, with the exception of sample DL1-1A. The cation analysis of DL1-1A is doubtful, because the dilution factor is not clear. It is most probable that the sample is four

times diluted, which would result in cation concentrations a bit higher than the other three Danau Linow samples. This might be due to degassing at location DL1-1A. Degassing can also contribute in extra SO_4 , Cl, F and cations. The more than twice higher concentration of fluoride in sample DL1-1A/B, might be also caused by degassing.

Next to degassing, river DL9-1 contributes to the chemical composition of the lake. The small river (3 l/s), which streams first through a fumarolic area, contains two to seven times higher concentrations of Al, Fe, Mg, Si and SO_4 , compared to the concentrations in the lake. The concentrations of the anions F and Cl are lower in the input river than in lake. This supports the hypothesis for gas input (HCl and HF, Philpotts 1990), near the samples DL1-1A/B.

In Table 2.1 and 2.2 (chapter 2) the chemical compositions are given of samples in the surroundings of the Danau Linow and of the lake, analysed around the beginning of this century. A comparison of these results with the results of this study is quite difficult, because the earlier measurements are given in total amounts instead of concentrations (see Table 2.1 and 2.2). If the volume measured was 1 litre the concentrations would be more than 20 times higher than measured in this study.

East of the Danau Linow, the water of a hot spring (DL3-1) mixes with a small neutral stream (Map 5, Appendix I and Photo 4, Appendix III). Sample DL4-1 is taken after the mixing of the waters. Around sample location DL4-1, two different colours of the precipitate are observed. It seems to be that the mixing of a different amount of neutral water has some influence on the colour of the precipitate. At a low water level (less mixing, low pH) the colour of the precipitate is green-blue, while at a higher water level (much mixing, higher pH) the colour will change to orange-red. Rowe (1995) has observed a comparable phenomenon and he mentioned a clear river at a pH lower than three, a greenish tinge coloured precipitate with a red-orange precipitate ($\text{Fe}(\text{OH})_3$) at the bottom at a pH between 3 and 5, and a translucent whitish-blue colour due to suspension of an amorphous milky-white precipitate, which is composed of aluminum, silica and oxygen with small amounts of sulphur and iron in neutral rivers. The orange-red precipitate of sample DL4-1 can be an iron precipitate, but it is unclear which mineral or mineral composition causes the green-blue colour.

In Figure 4.1 the profile of water is reproduced from DL9-1 to NMG1-1 via the outlet of the Danau Linow (DL1-1) and RND1-1. In Table 4.4 the chemical compositions are given of RND1-1 and NMG1-1.

The concentrations of Al, Ca, Fe, Mg, Na, Si and sulphate decrease sharply from the input river of the lake (DL9-1) to the lake DL1-1 (see Figure 4.1 and discussion above). The output river of the Danau Linow starts at sample location DL1-1. The more downstream samples DL6-1 and DL7-1, are at least three times enriched in the elements Al, B, Mn, F, Cl and SO_4 , compared to DL1-1 (Figure 4.1). The input is caused by degassing fumaroles and probably by a small (few litres per second) acid water from the south mountains. A sediment sample of DL6-1 shows the content of α -cristobalite, native sulphur and barite.

From this location (DL6-1 and DL7-1) to sample location RND1-1 the river is fifty times diluted by inlet rivers. The pH increases from 2.2 to 7.0 and the conductivity decreases from 6500 to 800 μS . Therefore, the enormous enrichment of the elements B, Ca, K, Mg, Na, Si and Cl is remarkable. The Al, Fe and sulphate concentrations are depleted enormously. The three or more times enrichment, may be caused by the inlet of ionic rich waters of the rice fields. The enrichment of Ca, K, Mg, Na and Cl may be explained with these waters, but the high B concentration may be better explained by an ionic rich spring. More downstream, the river is diluted from 500 l/s to 4000 l/s between the sample locations RND1-1 to NMG1-1.

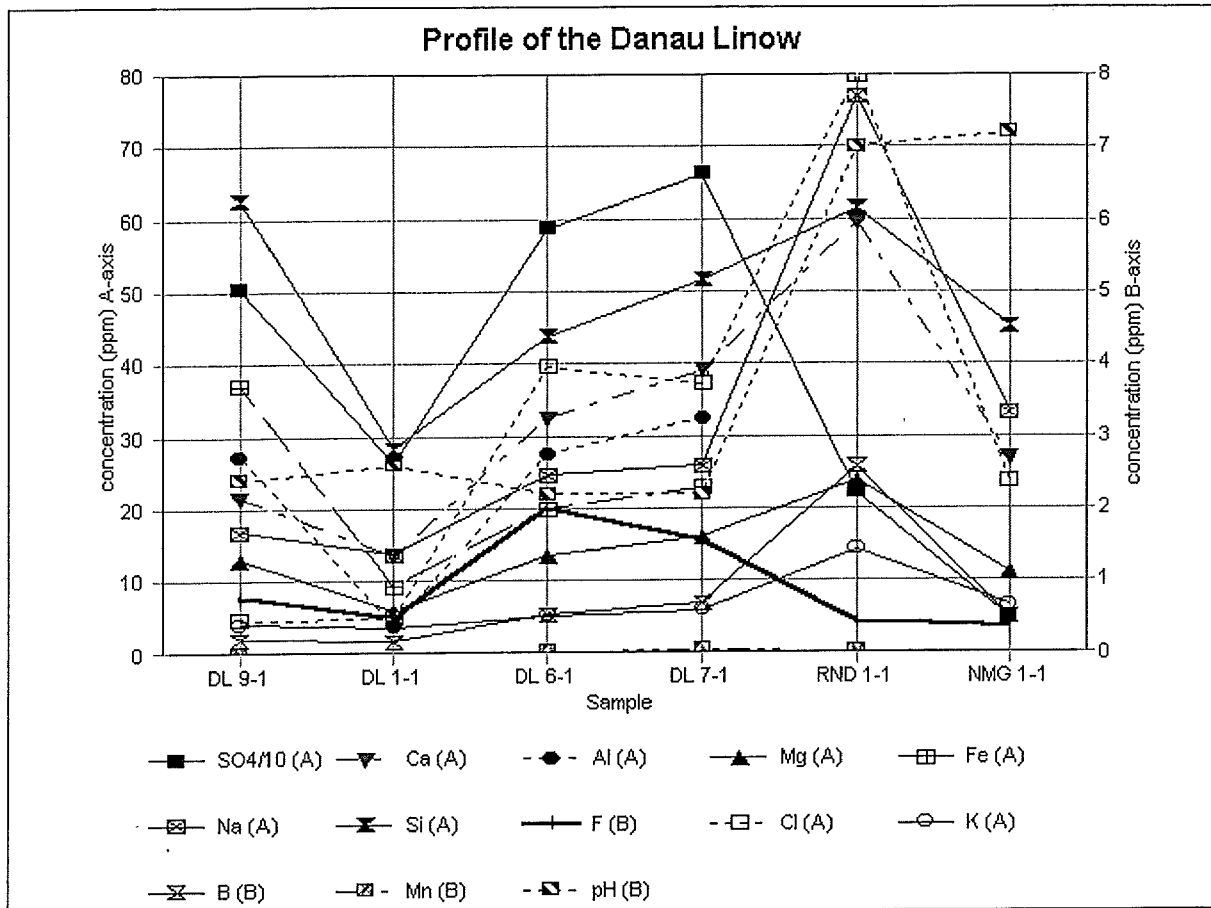


Figure 4.1 Profile of the water streaming from the acid input river, DL9-1, via the Danau Linow to the R. Nimanga. Concentrations in ppm.

A very interesting sample is the yellow pool in the centre of the rice field, east of the Danow Linow, which has the most extreme composition of all the North Sulawesi waters measured. The pool has a sulphate content of 1.5%, while the chloride concentration is extremely low with 13 ppm. The cation concentrations are very high. In contrast, sample DL5-1 is quite normal, because it has a pH of 6.5, a conductivity of 150 μ S and low ion concentrations (see Table 4.3). The small river DL5-1, east of the Danau Linow, does not enter the Danau Linow directly, but may possibly be an inlet.

A highly active fumarole, which degasses, is situated at the road between Tomohon and Sonder to the lake (DLFUM1, Map 5 Appendix I). A sediment sample of this fumarole contains about 6% Ba, which is quite high. Further, the Sr concentration is high with 1800 ppm. The oxide percentage of this sample (Table 5, Appendix II) shows that the sample is mainly composed of quartz (80%) and aluminium oxide (6%). There is no explanation found for the high Ba concentration in this sample. Sediments taken at the locations DL1-1 and DL1-1A contain high contents of quartz, 75 and 87% respectively. Sample DL1-1 contains native sulphur, and part of the silica oxide is present as α -cristobalite.

It can be concluded that the Danau Linow is an interesting lake, with fumaroles, degassing, active areas, mud volcanoes and (hot) pools. The lake is quite homogeneous, except for the gas inputs DL1-1A/B, where the F, Cl and sulphate concentrations are enriched. The most extreme composition is found in the yellow hot pool DL2-1. Sediments with the highest Ba and Sr concentrations (6% and 1800 ppm, respectively) are found in the large fumarole DLFUM1. It is recommended to investigate the flow of the river between DL7-1 and RND1-

1, because the enrichment elements, and the simultaneous discharge and pH increases, are not explained yet.

4.2.3. The weathered Lahendong area and its hydrothermally active rice fields and outlets

In the Lahendong area, waters of the rice fields and the outlet rivers of Lahendong were investigated. The chemical compositions of the rice field samples, the outlet rivers of the Lahendong and Danau Linow and the river R. Nimanga are presented in Table 4.4.

Table 4.4
Chemical composition of Lahendong samples and the discharge rivers.

Sample	pH	Ec μS	Al ppm	B ppm	Ca ppm	Fe ppm	K ppm	Mg ppm	Mn ppm	Na ppm	Si ppm	Sr ppm	F ppm	Cl ppm	SO ₄ ppm
LA 1-1	6.5	120	< b.g.	< b.g.	10.3	< b.g.	0.97	5.57	< b.g.	6.38	13.0	< b.g.	0.37	1.12	7.6
LA 2-1	3.6	240	0.25	< b.g.	7.12	2.83	0.36	4.35	< b.g.	6.93	12.1	< b.g.	0.28	0.97	59.1
LA 3-1	6.0	100	< b.g.	< b.g.	7.40	< b.g.	< b.g.	5.40	< b.g.	6.58	9.90	< b.g.	0.27	0.98	20.6
LH 2-1	2.5	1150	13.6	0.39	23.6	42.9	5.40	7.86	< b.g.	12.0	73.9	0.10	1.41	7.53	363
RND 1-1	7.0	800	< b.g.	2.58	59.5	< b.g.	14.3	23.8	0.19	77.1	61.6	0.20	0.44	79.9	221
RNE 1-1	6.5	165	< b.g.	< b.g.	15.4	< b.g.	4.18	5.64	< b.g.	11.4	42.7	0.07	0.37	3.11	121
NMG 1-1	7.2	350	< b.g.	0.49	26.9	< b.g.	6.55	11.1	< b.g.	33.3	45.2	0.11	0.34	23.7	46.7
NMG 2-1	7.5	380	< b.g.	0.50	25.9	< b.g.	7.78	9.88	< b.g.	42.6	50.2	0.09	0.39	26.3	51.6
NMG 3-1	7.5	360	< b.g.	0.51	26.3	< b.g.	7.52	10.2	< b.g.	41.3	49.2	0.09	0.39	26.3	50.4

< b.g. = below detection limit

Sample LA1-1 is the inlet stream in the rice fields of Lahendong. It is composed of rain water, and has therefore a low concentration of ions. The rice field water (LA3-1) is also very poor in ions. However, sample LA2-1, taken in a rice field below sample LA3-1, is enriched with Al, Fe, K, Si and SO₄, caused by a small fumarole, which also decreases the pH from 6 to 3.6. The influence of the small fumarole is not widespread, so only the surrounded rice field (5 * 4 m) is enriched in elements and has a decreased pH. The largest influence can be seen 20 cm around the fumarole, where the growth of rice was stopped. The red sediment in this rice field (sediment sample LA2-1A) contains twice the iron concentration compared to the white surface deposit sampled near the fumarole (LA2-1B), (Table 5, Appendix II). The concentrations of the trace elements in these samples are not remarkable. The high LOI of both samples (14 and 19 %) lets show the weathered state of these sediments.

An outlet river of the Lahendong, LH2-1, is acid (pH 2.5) and rich in chemical components, like Al, Fe, Si and SO₄. The float on the water LH2-1 looks like oil, and can be explained by the high content of iron. The sediment of this sample has also a high content of Fe₂O₃ (11%).

The neutral river RND1-1 (pH 7) has element concentrations comparable with acid samples, while the elements concentrations Cl, Ca, K, Mg, B and SO₄ are higher. As discussed in section 4.2.2., the origin of the enrichment of the river is unclear, and is therefore interesting to investigate. The river Sosoan Ranoesem (RNE1-1) is not acid and does not contain remarkable concentrations (Table 4.4). Probably, this river is acid in wet seasons if the Lahendong drains its water by this river. The NMG-samples did not have remarkable concentrations. The acid rivers of the Danau Linow, Lahendong and the Kawah Masem are enough diluted by neutral rivers or rain water at the location NMG (see section 2.3.1. and 2.4.1.).

It can be concluded that the Lahendong is an interesting weathered location, with mud pools, mud volcanoes and mud wells (see Table 8, Appendix II). The surrounded rice fields are small, but contain small fumaroles, which enrich the irrigation water with Al, Fe and SO₄. The outlet of the Lahendong (LH2-1) and the sample RND1-1 are interesting for a detailed

research, because these rivers contain high concentrations of the elements and are used by the local people.

4.2.4. The acid Kawah Masem crater lake and the acid river R. Maasem

The samples KM1-1 and KM1-2 (both of the Kawah Masem crater lake) differ in the elements concentrations of Al, Fe, K, Mg, Na, F and Cl (see Table 4.5). The difference may be due to the different way of sampling, temperature, rainfall and subsurface volcanic activity. The main difference can probably be explained by rainfall, temperature and the lightly degassing of the lake, which can increase the chemical components F and Cl.

Table 4.5
Chemical composition of the Kawah Masem crater lake and the river Royongan Maasem.

	pH	Ec μ S	Al ppm	B ppm	Ca ppm	Fe ppm	K ppm	Mg ppm	Mn ppm	Na ppm	Si ppm	Sr ppm	F ppm	Cl ppm	SO ₄ ppm
KM 1-1	2.1	2500	39.991	< b.g.	69.807	21.825	1.2667	45.673	0.7238	13.329	107.51	0.1017	2.4453	4.87	1008.12
KM 1-2	2.2	2510	48.844	< b.g.	71.018	24.739	0.81	48.378	0.76	14.369	108.29	0.1	1.08	2.6	1034.78
KM 2-1	2.5	1600	15.354	< b.g.	26.514	3.3252	1.0376	5.2866	< b.g.	7.7966	47.858	0.07	1.03	2.56	328.546
KM 3-1	6.2	160	< b.g.	< b.g.	17.469	< b.g.	1.697	5.4767	< b.g.	8.0582	34.999	< b.g.	0.3367	1.8595	25.4953
KM 4-1	3.4	400	3.6113	< b.g.	20.122	0.1287	1.6044	7.6641	< b.g.	7.9061	39.192	< b.g.	0.4219	1.57	127.565
KM 5-1	5.5	n.d.	< b.g.	< b.g.	27.092	< b.g.	1.8063	10.011	< b.g.	9.4227	42.056	< b.g.	n.d.	n.d.	105.9
KM 6-1	3	800	18.776	< b.g.	33.433	3.9764	5.0519	12.548	< b.g.	19.66	66.9	0.1	0.6093	5.3	341.4
KM 7-1	6.3	300	< b.g.	< b.g.	27.044	< b.g.	4.555	10.748	< b.g.	20.509	45.886	0.072	0.499	5.65	106.87

< b.g. = below detection limit.

n.d. = not determined.

A sediment sample of the Kawah Masem crater lake has no exceptional major, minor or trace element concentrations (Table 5 and 6, Appendix II). However, the LOI of this sample is 52%, which may be mainly due to the amount of sulphur and only for a small part to the weathered state of the sample. The XRD analysis, which shows the presence of native sulphur, and the smell and colour of the sample support this hypothesis.

The stream of the Royongan Maasem starts at KM2-1 at a small well, in an area covered with yellow precipitate. The chemical composition of the samples of the river is given in Table 4.5. The run off of the river is reproduced in Figure 4.2. In this figure the Kawah Masem crater lake is also included.

According to the major and minor element concentrations of KM1-2 (crater lake) and KM2-1 (spring), it must be concluded that the KM2-1 is not an outlet of the Kawah Masem crater lake, but an single spring. The chloride concentrations of the samples are in the same range. Therefore, dilution of crater lake water with meteoric water cannot explain the concentration found in the spring water. It is possible that the spring and the lake have a single origin deep in the earth. However, strong evidence for this hypothesis was not found. To further investigate this hypothesis isotope analysis should be used.

Downstream of KM2-1, KM3-1, a neutral water from the north, enters the river Royongan Maasem. After this join (KM4-1), the river bed is covered with red precipitate, for a few decade metres. The sediment sample KM4-1 contains 13% Fe₂O₃, which is quite high compared to the other North Sulawesi sediment samples measured. From Table 4.5 the sudden decrease of iron in the water phase can be seen. In chapter five a model to explain the sudden supersaturation of Fe will be presented (section 5.2.3.2.). For that reason, a good dilution factor of this mixing point is made, because field observations give a rough dilution factor of 1:5 (KM2-1:KM3-1). Calculations using the conservative element chloride didn't work, because the chloride concentration of sample KM4-1 is lower than that of the mixing waters

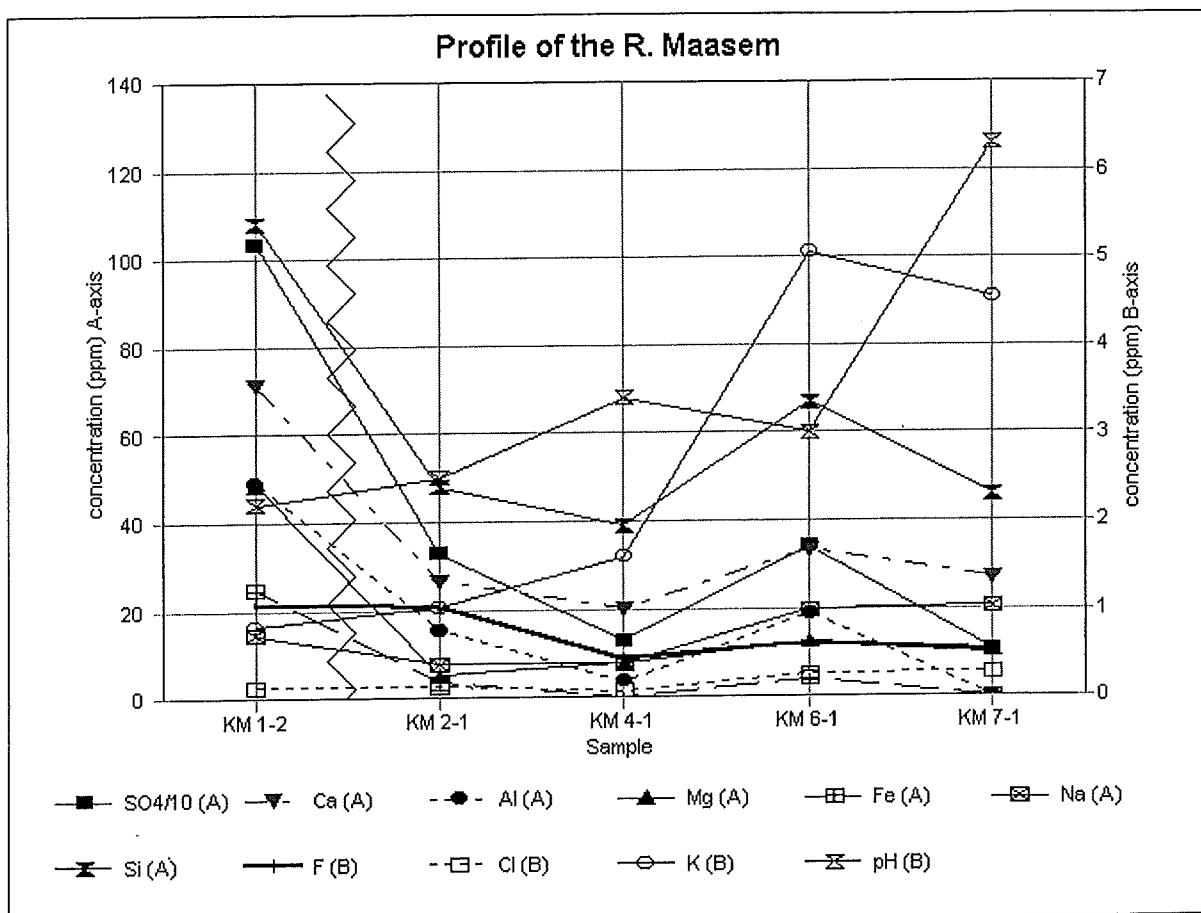


Figure 4.2 A profile of the river Royangan Maasem, starting at the well KM2-1. Concentrations in ppm.

(see Table 4.5). Therefore, the ratio 1:5 is taken, based at the field observations.

The very small (1 l/s) inlet KM5-1 enters the river after sample location KM4-1, but does not seriously affect the chemical composition of the R. Maasem, because it is a small inlet of rain water. However, the chemical composition of the river changes enormously between sample location KM4-1 and KM6-1. It was expected that the river would be diluted down stream, because many rivers enter the R. Maasem in this profile. However, the river is enriched for all ions, especially Al, Fe, K, Na, Cl and SO₄, and also the pH decreases from 4 to 3. An explanation for this enrichment can be the presence of a (highly) fumarolic active area, between the sample locations KM4-1 and KM6-1. This fumarolic area was not observed, but could be situated north east of sample KM5-1 at the north side of the river Maasem. At the climb to the Kawah Masem and along the river Maasem a rotten eggs smell was observed, which can support the hypothesis of a fumarolic field. Sample KM6-1 was taken in the rice fields, but the water is not directly used to irrigate. Downstream of KM6-1, the river water is used as washing water for people, cows and horses. It can be concluded that the Kawah Masem crater lake and its near surroundings are quite active and produce polluted water.

4.2.5. The chloride rich waters on the flank of the Mahawu volcano

The Mahawu is a quiet volcano, with only small fumarolic activity. On the flanks of the volcano neutral rivers stream like the Kuala Keketan (KK1-1), and an unnamed river (MA7-1). Further, the neutral (pH 6) spring MHW1-1 produces water with a high chloride concentration (160 ppm, see Table 4.6). The river MHW3-1 is also chloride rich, with 270 ppm, while the water is acid (pH 3.5, see Table 4.6). The high chloride concentrations of MHW1-1

and MHW3-1 and the high fluoride concentration of the latter suggest that both samples derive their water from the crater lake or a brine of the volcano, where chloride rich waters are produced. To test this hypothesis, a sample of the crater lake should be taken and isotope analysis should be performed.

According to Map 3 (Appendix I) the river MHW2-1 comes from near the crater, and has a quite normal composition and is neutral (pH 6.5). The river MHW3-1 starts 2 km below the top of the crater. Its water has a high concentration of Al, F, Cl and sulphate, while MHW2-1 has a lower ion concentrations, except for the start of this river near the top of the volcano/crater lake. In section 5.2.3.4., this difference will be investigated in more detail, with the modelling program SOLVEQ.

Table 4.6
Chemical composition of the waters, sampled on the flank of the Mahawu volcano.

	pH	Ec	Al	B	Ca	Fe	K	Mg	Mn	Na	Si	Sr	F	Cl	SO ₄
		μ S	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
MHW 1-1	6	1260	< b.g.	0.29	113.18	< b.g.	22.438	50.514	1.5615	83.071	70.29	0.168	0.5927	159.67	295.44
MHW 2-1	6.5	420	0.4785	< b.g.	33.148	< b.g.	8.3871	12.645	< b.g.	30.485	47.872	0.1006	0.939	57.267	73.185
MHW 3-1	3.5	1160	13.097	0.4744	76.535	< b.g.	19.544	23.811	1.5152	72.637	54.954	0.1	3.5327	270.5	114

< b.g. = below detection limit.

4.2.6. The neutral Tondano lake and its southern active hydrothermal area

The composition of the Tondano lake was deduced from its single outlet river. Only one sample was taken from this river. The chemical composition of the lake is quite normal (Table 3.1.a). Acid inlet rivers or degassing fumaroles were not observed along the lake, but local people mentioned degassing at the south of the lake. No statement can be given on the activity of the lake, because not much attention could be paid to degassing, during the field trip. However, the degassing or acid inlet rivers are not thought to have much influence on the lake composition, because the lake is not enriched in typical active hydrothermal elements.

In the south area of the Tondano lake, several small lakes are situated near sample location TDS2. The lakes or pools are quite warm ($>35^{\circ}\text{C}$) and some of them have temperatures of 50 to 80°C . The lakes are used as washing water, but the lake TDS2 was also used to drink by one of the locals for probably therapeutic purposes. This lake is quite active, which can be seen by the large turbulence of white particles in the clear water. The pH is low with 2 and the conductivity is high with $1500\ \mu\text{S}$. The water is rich in chloride (104 ppm) and sulphate (463 ppm), and also the cations B, Ca, Na and Si are present in high concentrations (see Table 3.1.a). No polythionates were found in the lake (see discussion in section 3.7). A sample of the lake sediments contains native sulphur, according to the XRD results (Table 7, Appendix II). Further, the sample contains the highest amount of Al_2O_3 (21%), which is present in the form kaolinite (Table 7). The iron probably exists in the form pyrite, according to the XRD analysis.

The results of this study are in accordance with Heringa (1895), who mentioned that the area south west of the Tondano lake is weak hydrothermally active, with mud pools, hot water pools and mud volcanoes. The hot lake TDS2 is a good example of this activity. The Tondano lake is less influenced by volcanic activity.

4.2.7. The highly fumarolic active Ambang mountains

The Ambang mountains are a hydrothermally active complex, with highly fumarolic activity and boiling springs. Water escapes from holes and (boiling) springs and finally forms a discharge river of this area, which downstream of the last sample locations AMB5-1, is named the Kali Putih (Map 4 and 10, Appendix I). The Ambang samples have, as mentioned, the

most extreme water compositions of all samples. The chemical water compositions of the Ambang samples, including the spring DTA1-1, are given in Table 4.7.

Table 4.7
Chemical composition of the Ambang mountains samples.

	pH	Ec	Al	B	Ca	Fe	K	Mg	Mn	Na	Si	Sr	F	Cl	SO ₄
		μS	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
AMB 1-1	1.6	7200	189.27	2.8957	167.43	42.994	3.148	72.412	3.3241	91.989	172.92	< b.g.	1.97	94.342	3202.8
AMB 2-1	1.6	5770	171.76	2.73	168.35	36.427	2.48	69.195	3.23	88.318	175.76	< b.g.	2.0847	86.63	3118.1
AMB 3-1	2	3430	16.58	0.4	239.25	3.03	5.95	46.61	2	75.76	129.65	0.08	1.6823	11.4	1478.4
AMB 4-1	1.6	8370	197.72	4.5702	179.29	52.264	4.82	68.839	3.19	83.467	170.11	0.12	1.846	213.9	3144.2
AMB 5-1	1.7	6500	120.79	3.35	205.56	28.773	4.1834	59.97	2.73	81.221	154.18	0.11	1.71	113.9	2545.7
AMB 6-1	6	150	< b.g.	< b.g.	13.322	< b.g.	3.7126	2.8435	< b.g.	9.0955	50.734	< b.g.	n.d.	n.d.	49.9
DTA 1-1	6	150	< b.g.	< b.g.	13.798	< b.g.	4.2112	3.0539	< b.g.	10.051	48.98	< b.g.	0.34	1.5	46.874

< b.g. = below detection limit.

n.d. = not determined.

The Utrecht team and the VSI team both have sampled a cool spring in the Ambang, which were named AMB6-1 and DTA1-1, respectively. Because the chemical compositions were quite the same, it can be concluded that both teams sampled the same spring. This is supported by their field descriptions. The water is used for drinking and cooking by campers.

The sediment samples of the Ambang, AMB2-1 and AMB3-1, were yellow grey, while AMB4-1 was lightly grey green. The high sulphur content of the sediment samples prevented a major and minor element analysis. Therefore only trace elements and mineralogic composition of the sediments were determined. Sample AMB3-1 has a remarkable Sr concentration of 540 ppm, while sample AMB2-1 has no extreme concentrations. Sample AMB4-1 has a remarkably high Sc concentration with 117 ppm compared to all other samples analysed. The XRD analysis shows that the yellow coloured sediment AMB2-1 contains mainly native sulphur and some α -cristobalite, while the samples AMB3-1 and AMB4-1 contain quartz, α -cristobalite, sulphur and anatase (see Table 7, Appendix II).

4.2.8. The acid discharge river of the Ambang, the Kali Putih

The first sample of the river Kali Putih taken downstream of AMB5-1 in this study, is MD1-1. The last sample taken is M4 (see Map 4, Appendix I). The chemical composition of the river samples and the secondary rivers are given in Table 4.8. In Figure 4.3 the run off of the Kali Putih from AMB5-1 to M4 is reproduced.

Table 4.8
Chemical compositions of the Kali Putih run off samples.

	pH	Ec	Al	B	Ca	Fe	K	Mg	Mn	Na	Si	Sr	F	Cl	SO ₄
		μS	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
MD 1-1	2.5	2260	56.149	2.5845	140.75	11.409	6.927	24.807	0.86	49.033	65.499	0.21	1.24	105.08	904
TM 1-1	6.5	310	< b.g.	< b.g.	39.902	< b.g.	2.6332	7.3699	< b.g.	15.351	29.072	0.1097	0.317	4.515	93.943
TM 2-1	7	120	< b.g.	< b.g.	11.913	< b.g.	1.9786	3.9805	< b.g.	7.5091	24.057	< b.g.	0.299	1.482	14.895
KP 1-1	2.5	1970	45.008	2.2761	122.43	8.8206	6.2133	21.514	0.59	43.493	58.286	0.1836	1.1467	96.35	715.36
TBG 1-1	6.7	210	< b.g.	< b.g.	23.792	< b.g.	2.285	7.4787	< b.g.	10.077	27.33	0.1012	0.26	2.24	34.618
KP 2-1	4.3	410	2.3285	0.4264	44.23	< b.g.	3.2769	10.42	< b.g.	18.018	33.196	0.1236	0.2233	18.08	154.42
TB 1-1	6.5	390	< b.g.	0.2355	48.89	< b.g.	4.3841	10.922	< b.g.	20.166	24.327	0.1602	0.24	10.67	100.37
KP 3-1	5.5	390	1.1956	0.5076	42.523	< b.g.	5.6518	13.565	< b.g.	23.382	26.174	0.1431	0.2167	19.208	108.23
M4	7	470	0.5592	0.5869	55.292	< b.g.	4.5166	15.987	< b.g.	25.738	26.462	0.25	0.2213	21.45	127.63

< b.g. = below detection limit.

All ion concentrations decreased from sample AMB5-1 to MD1-1, except for K, which increased. The large decrease may be caused by dilution of the river between AMB5-1 and

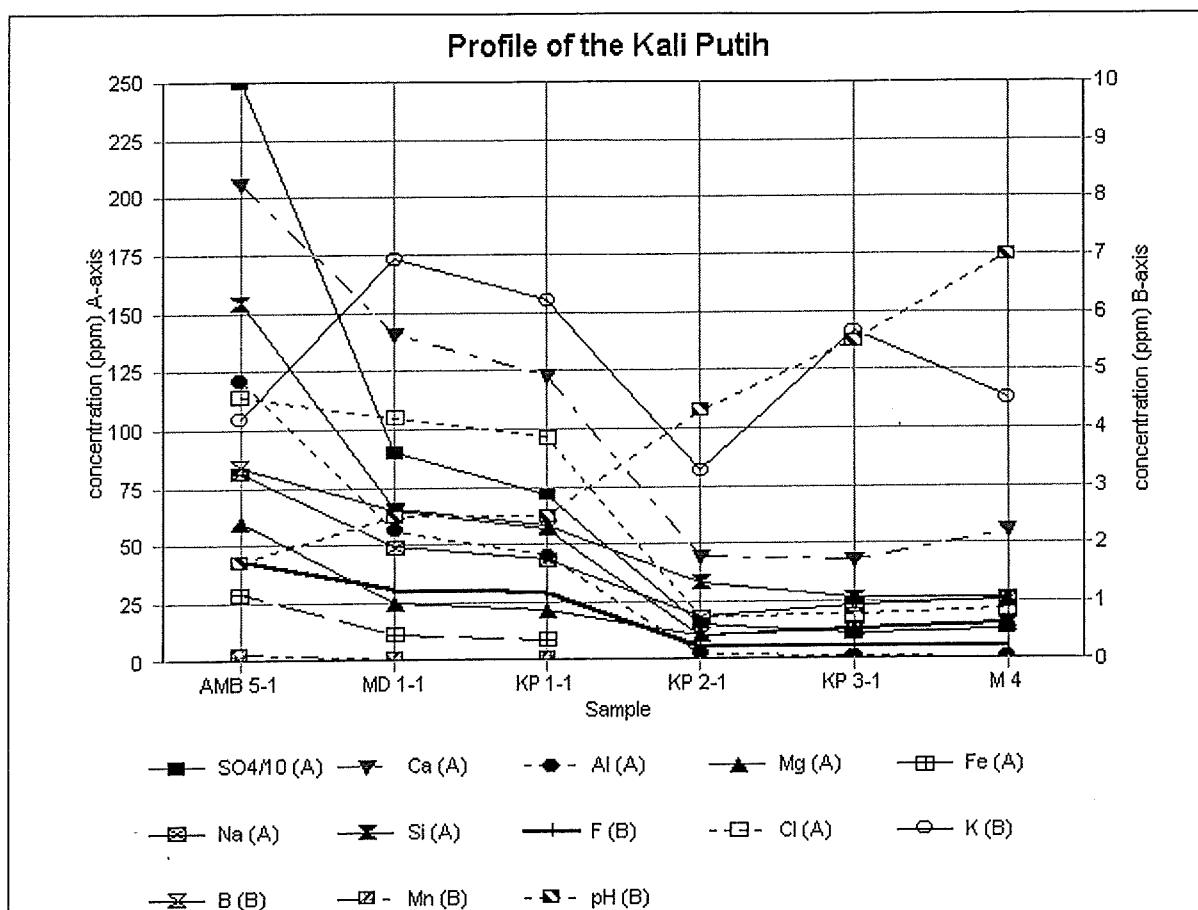


Figure 4.3 The profile of the river Kali Putih. Concentrations in ppm.

MD1-1. The chemical composition of the river is slightly decreased from MD1-1 to KP1-1, but the Al, Fe and SO_4 concentrations significantly decreased. Since in this part of the river only one small inlet TM1-1 enters the river, this should cause the significant decrease (see Map 11, Appendix I). It is remarkable that the small neutral inlet (10 l/s) has so much influence on the chemical composition of the Kali Putih river, which itself has a discharge of 600 l/s. The calculation of a dilution factor (taking chloride as conservative element) gives a dilution factor of 1:10.7 (TM1-1:MD1-1), while based on field observations a dilution factor of 1:60 (see Table 4.9) is expected. A dilution factor of about 1:60 can only be true, if elements co-precipitate with Al, Fe and sulphate. Other explanations of the depletion of ions from sample MD1-1 to KP1-1 are not available.

Table 4.9.
Mixing of the river T. Maayat and the Kali Putih (MD1-1).

dilution	pH	Ec μ S	Al ppm	B ppm	Ca ppm	Fe ppm	K ppm	Mg ppm	Na ppm	Si ppm	F ppm	Cl ppm	SO ₄ ppm
MD 1-1	2.5	2260	56.1493	2.58453	140.746	11.4094	6.92703	24.8072	49.0331	65.4994	1.24	105.075	904
TM 1-1	6.5	310	< b.g.	< b.g.	39.9018	< b.g.	2.63322	7.36989	15.3509	29.0719	0.317	4.515	93.9428
KP 1-1	2.5	1970	45.0082	2.27609	122.43	8.82065	6.21332	21.5142	43.4932	58.286	1.14667	96.35	715.359
TM:MD 1:10.7	25	2093	514	236	132	104	656	233	462	624	116	965	835
TM:MD 1:60	2.5	2228	55.2	2.54	139	11.2	6.86	24.5	48.5	64.9	1.23	103	891

<b.g. = below detection limit.

The most important dilution of the Kali Putih occurs by the combined rivers T. Lombiyawan and T. Tabongon that enter at sample location TBG1-1. These rivers causes a pH increase of

2.5 to 4.3 and the removal of Fe and Mn from solution. The dilution ratio is about 1:3 to 1:4 (KP1-1:TBG1-1), based on field observations, but if chloride is taken as conservative element a dilution factor of 1:5 is obtained (Table 4.10). It can be seen that in both cases no satisfying dilution factor is found, because of the large variations in the calculated combination of river and the chemical composition of sample KP2-1.

Table 4.10
Mixing of the river Kali Putih by the combined rivers T. Tabongan and T. Lombiyawan.

dilution	pH	Ec μ S	Al ppm	B ppm	Ca ppm	Fe ppm	K ppm	Mg ppm	Na ppm	Si ppm	F ppm	Cl ppm	SO ₄ ppm
KP 1-1	2.5	1970	45.0082	2.27609	122.43	8.82065	6.21332	21.5142	43.4932	58.286	1.14667	96.35	715.359
TBG 1-1	6.7	210	< b.g.	< b.g.	23.7917	< b.g.	2.28499	7.47869	10.0766	27.3295	0.26	2.24	34.6181
KP 2-1	4.3	410	2.32853	0.42641	44.2299	< b.g.	3.27688	10.4201	18.0184	33.1962	0.22333	18.08	154.418
KP:TBG 1:3.5	3.2	601	10	0.51	45.6	196	3.15	10.6	17.5	34.1	0.46	23.2	185
KP:TBG 1:5	3.3	508	760	38	405	149	295	987	157	326	41	181	150

<b.g. = below detection limit.

Finally, the chemical composition of all elements, except Si and SO₄, increases up to 50%, from KP2-1 to M4. Probably, discharge of rivers and waste water of the rice fields change the chemical composition of the river in this profile.

Sediment KP1-1 is mainly composed of the minerals quartz and α-cristobalite, while TM2-1 contains only quartz and some iron minerals (see Table 7, Appendix II). The sediment TM2-1 contains remarkably high concentrations of Ni, Zn, La and V compared to other samples analysed (see Table 6, Appendix II). This may support the hypothesis of a sudden precipitation (see discussion above), where other elements then Al and Fe are co-precipitated. The precipitation of Al and Fe may be supported by the high content of these elements in the oxide part of this sediment (see Table 5, Appendix II).

4.2.9. Geochemical signature of neutral lakes

In North Sulawesi mainly acid rivers and lakes were investigated, which are discussed in the sections above. In this section neutral lakes are discussed, which did not have a clear relation with other samples or areas in North Sulawesi. The chemical compositions of the neutral lakes are given in Table 4.11.

Table 4.11
Chemical composition of neutral lakes.

	pH	Ec μS	Al ppm	B ppm	Ca ppm	Fe ppm	K ppm	Mg ppm	Mn ppm	Na ppm	Si ppm	Sr ppm	F ppm	Cl ppm	SO ₄ ppm
DB 1-1	6.7	400	< b.g.	< b.g.	29.378	< b.g.	4.8969	23.668	< b.g.	26.529	26.319	0.1195	0.307	9.6467	20.288
PL 1-1	6.5	120	< b.g.	< b.g.	10.07	< b.g.	2.9038	4.9075	< b.g.	7.3353	15.83	< b.g.	0.256	3.6067	11.89
DMoat	6.4	70	< b.g.	< b.g.	6.9106	< b.g.	0.9295	2.4764	< b.g.	3.6518	10.949	< b.g.	0.1893	1.0047	3.5111
M 3	6.5	70	< b.g.	< b.g.	6.9666	< b.g.	0.8407	2.4236	< b.g.	3.6332	10.629	< b.g.	0.2127	0.998	3.1867
DTD 1-1	6.5	80	< b.g.	< b.g.	5.4016	< b.g.	1.5781	3.2602	< b.g.	5.6672	11.052	< b.g.	0.219	1.6667	1.02
BW 1-1	6.7	850	< b.g.	2.4894	59.587	0.6512	24.598	31.752	1.2208	86.022	75.451	0.1565	0.25	56.675	760

< b.g. = below detection limit.

The Danau Bulilin (DB1-1, Map 3, Appendix I) is a strangely shaped lake, with a pH of 6.7 and a conductivity of 400 μS. The ion concentrations are low and the water is used for drinking, washing and fishing.

The Danau Panolombian, PL1-1, is a small old crater lake, east of the Danau Linow (Map 5, Appendix I). The extremely low conductivity of this water is of 120 μS, together with the pH of 6.5 indicates that the lake is not influenced by volcanic activity, like degassing. This

hypothesis is further supported by the low ion concentrations.

The Danau Mooat probably is an old crater lake (Koperberg, 1928). Today, no volcanic activity is observed, and the chemical composition of the lake also does not indicate any volcanic activity. The lake seems to be homogeneous, because the samples DMOat and M3 have nearly the same chemical composition, while they were sampled at opposite locations at the lake.

North-west of the Ambang mountains a small lake Danau Tuduaog, DTD1-1 is situated. The water has a lightly yellow colour, and is very turbid. This lake is very poor in ion concentrations and therefore not interesting for further research.

The lake BW1-1 is quite interesting, because the conductivity is high with 850 μ S and the ion concentrations are very high compared to other neutral lakes and rivers, while the pH is just 6.7. The VSI had taken this sample of a lake, named Bangunan Wuwuk HS, which is situated in the Ambang mountain complex. Possibly, the Bangunan Wuwuk HS is the crater lake Danau Tabang, two kilometres north west of AMB1-1.

4.2.10. The chemical composition of red sediments and sediments of acid waters

A more detailed look to the chemical composition of sediments shows that red sediments contain much more iron oxides compared to the other sediment samples (Table 5 and 6, Appendix II). For example, sample KM4-1 (the red river), LA2-1A (near the fumarole in the rice field), LH2-1 (output of the Lahendong with floating iron) and TM2-1 (an inlet in the Kali Putih, causing red precipitate). Remarkably, the samples TM2-1 and KM4-1 (both at locations where neutral water mixes with acid water) are, next to a high iron concentration, enriched in Mn, Mg, Ca and Na oxides and trace elements like Co, Sr, Zn and V (mainly elements of the same period as iron, see the periodic system of the elements). It is therefore likely that these four trace elements co-precipitate with the sudden iron precipitation.

In general, North Sulawesi is constructed by andesitic products (Kemmerling, 1923) and it is expected that the samples have sediment samples with an andesitic composition. Therefore, it is remarkable that sediments of acid waters, like the Danau Linow and the Kali Putih, have a higher silica composition. The higher silica content of the Danau Linow and the Kali Putih sediments may be caused by the influence of acid water. Probably, precipitation of silica minerals occurs. Rowe (1995) mentioned that in acid rivers amorphous silica causes white coatings in vugs and fractures. This process may also explain why the Danau Linow and the Kali Putih show a white bedding.

In general, the sediment samples are poor in Mg, Ca and Na oxides. In most samples, the depletion of the rock-forming elements, such as Mg, Ca, Na, K and Al might be due to alteration.

4.3. A comparison of the chemical composition of Sulawesi waters with that of other waters descending from active geothermal areas, crater lakes or hot springs

The chemical composition of the Sulawesi samples is compared with that of samples taken at other locations in Indonesia or elsewhere in Table 4.12.

The compositions of the waters in the geothermal Province Guantacaste in Costa Rica is most like that of the Sulawesi samples. These waters have in general high sulphate and low chloride concentrations. The B concentration in the Sulawesi samples is quite high compared to other samples throughout the world. The crater lake Kawah Masem and the highly hydro-thermally active area of the Ambang do not have such extreme concentrations as the crater

lakes of the Poás Volcano in Costa Rica (Rowe *et al.*, 1992b), Kawah Ijen, Indonesia (Delmelle *et al.*, 1994) and the Mt Ruapehu, New Zealand. The rivers that originate from these crater lakes are in general more concentrated than the Sulawesi discharge rivers. The difference in chemical composition can be easily explained by the difference in volcanic activity. The Ijen, Poás Volcano, and Mt Ruapehu are highly active volcanoes, while the Ambang and Kawah Masem are much more quiet, and produce only a small amount of gases.

Giggenbach (1974 & 1992) and Deely (1996) mentioned the existence of Zn (1 to 3 ppm), Li (0 to 5 ppm) and V (8 to 17 ppm) in crater lakes, while these elements in Sulawesi, with detection limits of 0.15, 0.05 and 0.10 ppm respectively, were not found. In the river descending from the Ruapehu crater lake Deely (1996) found As, Cd, Cr, Cu, Li, Ni and Pb with concentrations up to 300 µg/l, Zn up to 600 µg/l, values which are too low to detect with ICP-AES. It is recommended to analyse the waters with the use of the ICP-MS to obtain good concentrations for trace elements.

5. Geochemical modelling of the North Sulawesi waters

5.1. Origin of the waters of North Sulawesi

As discussed in chapter four, nearly all the acid samples are rich in sulphate, except for sample MHW3-1, which is rich in chloride. Delmelle *et al.* (1994) mentioned the presence of high sulphate, chloride and fluoride concentrations in lakes or rivers, when magmatic volatiles (SO_2 , H_2S , HCl and HF) from a degassing magma are injected in the waters. However, the waters of the Kawah Masem, Danau Linow, Lahendong and Ambang contain mainly high sulphate and low chloride and fluoride concentrations. At these locations a sharp odour of rotten egg, which indicate the presence of H_2S (g), was observed. Rowe *et al.* (1995) mentioned that sulphate rich waters can originate from a low level degassing magma body. On the other hand, he mentioned that low-temperature (200 - 550 °C) fumaroles are extremely enriched with chloride and fluoride, because boiling of brines at depth causes mobilization of highly volatile HCl and HF in preference to relatively non-volatile H_2SO_4 . Thus, low temperature fumaroles that contain a significant brine component will be enriched with chloride relative to sulphur. In the investigated regions of Sulawesi, the fumaroles and waters, which are injected by gases, are not hot (< 100 °C) and did not show high halogenic components. It can be concluded that the hydrothermal waters of North Sulawesi did not derive directly of brines, but must have an other origin.

Slightly thermal acid sulphate springs, which are enriched with sulphate over chloride, show in the hydrothermal system of the Poás volcano, a Ca/SO_4 ratio of 0.1 to 0.2 (Rowe *et al.*, 1995). The samples around the Danau Linow, Kawah Masem and Ambang shows a Ca/SO_4 ratio below 0.1. Rowe supposed that the Ca is attributed by solution of gypsum, but if the ratio is lower than one, sulphate is not only derived by solution of gypsum, but also from oxidation of sulphur gases (SO_2 , H_2S , see discussion in paragraph 5.2.3.3) or weathering of native sulfur and alunite $[(\text{Na},\text{K})\text{Al}_3(\text{SO}_4)_2(\text{OH})_6]$. Native sulphur is abundant in zones of low temperature fumaroles (e.g. Ambang, Lahendong, Danau Linow and Kawah Masem) and is major constituent of recently formed lake sediments. Alunite can be found in old lake sediments (e.g. Kawah Masem crater lake) exposed in the walls of active craters (Rowe *et al.*, 1995). It can be concluded that oxidation or solution of degassing sulphur contributes mainly to the amount of sulphate in solution of the Sulawesi waters, because a) sulphur holding gases was observed; b) weathering of minerals is a very slow process and there is less time to get equilibrium if the waters flow away fast (e.g. in the Ambang), and c) the slow diffusion processes do not contribute to dissolution.

Rowe (1995) mentioned that if the water is not injected by halogen rich vapour, it can be injected by magmatic gases, like SO_2 , H_2S and CO_2 . Philpotts (1990) listed the magmatic gases, under which SO_2 , H_2S and CO_2 , and mentioned that chloride, fluoride and borium are only slightly present in magmatic gases. It can be concluded that in the light active hydrothermal areas of North Sulawesi waters mainly derive there sulphate content from oxidation and solution of injected sulphur gases, escaping from magma sources. The Kawah Masem derives its gases probably from a magmatic magma of the active volcano Soputan, which is situated west of the Kawah Masem.

The three samples, taken on the flanks of the Mahawu, are the only (acid) samples with a SO_4/Cl ratio below 2. This can be due to the fact that these waters derive their water from the Mahawu crater lake or from springs/fumaroles generated by the Mahawu. If the Mahawu is

an active volcano with low-temperature fumaroles, the crater lake of the Mahawu can be enriched with chloride. Observations shows that the Mahawu is degassing, but any temperature of the gases is unknown, and also the amount of degassing.

Rivers, descending from active hydrothermal areas, are enriched with Al, Fe and sulphate, but will be neutralized by water-rock reactions and by mixing with (bicarbonate) rain/river water. Rivers like the Kali Putih, the outlets of the Danau Linow and the Lahendong, and the Royongan Maasem will be diluted by neutral waters (see Map 3 and 4, Appendix I).

The samples TDO1, DMOat, M3, DTD1-1, DB1-1, PL1-1 and the rice field water of Lahendong have very low ion concentrations. These waters are mainly composed of rain water, and small dissolution of rocks and sediments. The Tondano lake and the rice field of the Lahendong are little polluted by small fumaroles.

5.2. Aqueous speciation and mineral saturation modelling

Analysis of the water samples gives only indications of the amount of an element in solution. However, elements in solution are present in several species, like aluminium can be in solution as free ion Al^{3+} , or as complex AlF^{2+} , $AlOH^{2+}$, $Al(OH)_2^+$ and Al-org. It is important to know in which species an ion is present in solution to a) predict precipitations and b) to determine the toxicity of elements. Al^{3+} is more toxic than aluminium bound by organic material. The program SOLVEQ is used for determining the aqueous speciation of the elements and mineral saturations. Before the results of modelling are discussed, an introduction to the program SOLVEQ is given.

5.2.1. Introduction to SOLVEQ

SOLVEQ is a computer program designed to calculate aqueous-mineral-gas equilibria (Spycher and Reed, 1990). Given a sample's temperature (in °C) and analytical chemistry (in this research in ppm), the program determines the activity of each aqueous species and calculates a saturation index for each possible mineral. To carry out these calculations SOLVEQ uses a database consisting of reaction stoichiometries, equilibrium constants for input species and minerals (Pasternack, 1993). SOLVEQ uses the Newton-Raphson method for the calculations (Reed, 1982). This method holds that geochemical processes involving composition changes, will be modelled by linking a series of discrete heterogeneous equilibrium calculations in which the bulk composition is changed incrementally from one calculation to the next (Reed, 1982).

Cation and anions move as solvation complex (surrounded by water molecules as an outer sphere complex) or bound by ligands forming complexes (inner-sphere) in solutions (Sposito, 1989). Which species of an ion is present in solution depends on pH, temperature, Eh, concentration of the ions and equilibrium with minerals. For aluminium in solution can be written:

$$Al_T = [Al^{3+}] + [AlOH^{2+}] + [Al(OH)_2^+] + [Al(OH)_4^-] + [AlSO_4^+] + [Al(SO_4)_2^-] + [AlF^{2+}] + [AlF_2^+] + [AlF_3] + [AlF_4^-] + [AlF_5^{2-}] + [AlL^{2+}] \quad (5.1)$$

where L is organic material and Al_T the total amount of aluminium in solution. (In Morel and Hering (1993) many possibly complexes are described.) Each complex can be described, by a conditional stability constant:

$$^{\circ}K_1 = [AlOH^{2+}]/[Al^{3+}][OH^-] \quad (5.2)$$

and

$$^{\circ}K_2 = [Al(OH)_2^+]/[Al^{3+}][OH^-]^2 \quad (5.3)$$

etc.

All the stability constant expressions have the concentration of the free-ion species, Al^{3+} , in common. Therefore, equation 5.1 can be rewritten in the form:

$$Al_T = [Al^{3+}] \{ 1 + ^{\circ}K_1[OH^-] + ^{\circ}K_2[OH^-]^2 + ^{\circ}K_3[OH^-]^3 + ^{\circ}K_4[SO_4^{2-}] + ^{\circ}K_5[SO_4^{2-}]^2 + ^{\circ}K_6[F^-] + ^{\circ}K_7[F^-]^2 + ^{\circ}K_8[F^-]^3 + ^{\circ}K_9[F^-]^4 + ^{\circ}K_{10}[F^-]^5 + ^{\circ}K_{11}[L^-] \}. \quad (5.4)$$

SOLVEQ uses for ['ion'] the molality of the ion multiplied with the activity coefficient of this aqueous species (Reed, 1982). With all the equilibrium constants, activity coefficients, molalities, pH and the total amount of aluminium the amount of each complex can be calculated. The element concentrations measured with ICP is supposed to be the total element concentrations.

Some reactions in an aqueous system involve the transfer of electrons. Therefore, the redox condition of a system must be determined from the amount of species of an redox couple. SOLVEQ uses the oxygen or the sulphur redox couple, which are given in Formula 5.5 and 5.6,



In the modelling system only one couple can be used. For acid sulphur rich waters the sulphur couple is used by giving the H_2S concentration. The oxygen couple is used for more neutral well mixed rivers, by giving an O_2 (aq) concentration.

SOLVEQ uses a saturation index for the mineral phase modelling, which is built up with a thermodynamic equilibrium constant (K_T) for a mineral precipitation reaction and by an ion activity product (Q) (Pasternack, 1993). The saturation index (SI) is defined by the following equation:

$$SI = \log [Q/K_T]. \quad (5.7)$$

If the SI value is greater than zero, the water is supersaturated with respect to the particular mineral and precipitation of the mineral is possible. If the SI value is less than zero, the water is under saturated and dissolution of the minerals is possible. A SI value equal to zero indicates equilibrium between water and the mineral.

The simulation calculation tries to represent natural processes. Several aspects, however, must be considered: a) the assumption that the natural system attains chemical equilibrium status; b) the quality and quantity of thermodynamic and analytical data and the input way of data in the program; c) the validity of the hypothesized geologic process being simulated

(Reed, 1982), and d) kinetic processes which play an important role in aqueous chemistry (Deely *et al.*, 1996). Of consideration b must be said that the absence of minor species, like metals, and the absence of bicarbonate data will have influence on the modelling results. The used H_2S data from the MVO (Table 9, Appendix II) must be taken with some care. It will be assumed that in neutral well mixed waters the O_2 redox couple is suitable. The last problem is the amount of discharge of cations and anions. Because the chloride concentration is too low, the sulphate concentration is mainly corrected in order to obtain a correct charge balance. Corrections of 50% of the total amount of sulphate, however, can occur (e.g. at sample AMB1-1). In paragraph 5.2.3.5 the use of H^+ is tried in order to correct the charge balance.

More details of the SOLVEQ program are described by Reed (1982), Reed and Spycher (1984) and Spycher and Reed (1990).

5.2.2. How to use SOLVEQ?

To run SOLVEQ, first the program GEOCAL is used to give the concentrations of the elements, the pH and the temperature. In this research for acid sulphate rich waters H_2S concentrations, measured by the MVO are used (see Table 9, Appendix II). For neutral well mixed water an O_2 (aq.) concentration of 0.0096 ppm is given (Morel and Hering, 1993). An increase or decrease of the oxide concentration with a factor of ten gives only a small change in redox potential and aqueous species percentages. Therefore, an O_2 concentration of 0.0096 ppm is useful.

The amount of bicarbonate in acid samples ($\text{pH} < 5$) is set to zero. For samples with a pH higher than 5 the bicarbonate concentration is also set on zero, because no good approximation can be made. In the samples RND1-1 and M4 100 ppm H_2CO_3 is added, to compare the SI and the amount of aqueous species with and without bicarbonate. The saturation index did not change significant, but new complexes are formed, like CaHCO_3^+ , MgHCO_3^+ and NaHCO_3 , but only a few percent of these complexes are formed in respect of the total cation concentration.

In the program GEOCAL the iron concentration measured with the use of the ICP is used. The program asked the Fe^{2+} concentration, but calculated the real Fe^{2+} and Fe^{3+} concentrations, based on the redox potential, which is determined with the use of H_2S or O_2 . The measured concentration of B is recalculated to H_3BO_3 before the concentration is given in the program GEOCAL. At the end of the program GEOCAL, the charge balance ion is set on sulphate, instead of the usually chloride ion. The possible species and the saturation of the minerals is given in a special output file. An example of the SOLVEQ output is given for sample DL2-1 (Appendix V).

5.2.3. Modelling results

The saturation of minerals of the water samples are given in log Q/K plots. The percentage of aqueous species for each element of 19 samples is given in Table 5.1. The totals of the aqueous species for each element are not always exactly 100%, which can be due to three facts: a) not all complexes are taken of an element, only the common and in reasonable concentrations presented complexes; b) the calculated values are round off, and this can cause significant differences for small concentrations, and c) in Table 5.1 are presented the percentages of complexes, while these complexes can contain two or more moles of an ion. For example the species AlF_2^+ contains two mol F^- . If these facts are taken in account, the results given in Table 5.1 are good and useful.

The silica minerals (chalcedony, cristobalite, quartz, and sometimes amorphous silica) are supersaturated in nearly all the modelled samples (see the log Q/K plots). This can explain

Table 5.1

Aqueous speciation of ten water samples.

	sample	AMB2-1	AMB1-1	AMB5-1	MD1-1	KP1-1	KP2-1	KP2-1	KP3-1	M4	KM4-1	DL1-1B	TDS 2	KM1-2	DL2-1	MHW3-1	DL4-1	RND1-1	KM6-1	DL7-1
	H ₂ S (ppm)	0.51	0.63	0.95	0.82	0.51	0.09	O ₂	O ₂	O ₂	0.04	1.4	0.05	0.25	0.13	0.05	0.95	O ₂	0.37	1.52
	T (C)	82	49.8	45.1	23	23.3	24.5	24.5	26.1	27.4	21.4	27.1	51.7	43.6	27	25.2	45	30.9	25.9	34.8
	pH	1.6	1.6	1.7	2.5	2.5	4.3	4.3	5.5	7	3.3	2.4	2.6	2.2	2	3.5	3.5	7	3	2.2
	Eh (V)	0.18	0.19	0.18	0.13	0.13	0.003	0.92	0.85	0.76	0.08	0.13	0.11	0.15	0.18	0.06	0.04	0.75	0.09	0.15
H ⁺	H ⁺	43.2	51.7	56.8	77.1	78.7	89.6	89.3	88.0	86.0	94.7	83.0	72.5	66.4	39.4	94.6	72.9	n.p.	84.6	73.5
	HSO ₄ ⁻	56.8	48.3	45.5	22.9	21.3	10.4	10.7	12.0	14.0	7.0	15.5	30.0	35.5	60.6	5.1	22.9	n.p.	14.6	24.5
SiO ₂	SiO ₂	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Cl ⁻	Cl ⁻	96.0	96.3	100	100	100	100	100	100	98.4	100	100	100	100	97.4	98.9	100	100	100	100
	HCl	0.3	0.3	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.0	0.0	0.0	0.1
	CaCl ⁺	0.9	0.5	0.6	0.4	0.3	0.2	0.2	0.2	0.2	0.1	0.1	0.3	0.3	0.4	0.3	0.2	0.2	0.1	0.1
	MgCl ⁺	0.5	0.3	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.1	0.2	0.3	0.1	0.1	0.1	0.1	0.1
F ⁻	F ⁻	0.0	0.0	0.0	0.0	0.0	0.4	0.4	3.3	96.4	0.3	0.4	20.0	0.0	0.0	0.1	9.1	95.4	0.1	0.0
	AlF ⁺⁺	100	100	100	100	98.4	96.7	96.7	79.8	0.0	95.8	85.3	6.5	98.2	100	90.7	31.3	n.d.	100	97.6
	AlF ₂ ⁺	0.2	0.2	0.3	0.4	0.4	1.3	1.3	8.3	0.1	2.1	6.9	29.3	0.5	0.1	3.5	28.4	n.d.	0.5	0.9
	AlF ₃	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.5	0.0	0.0	0.0	1.0	n.d.	0.0	0.0
	CaF ⁺	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.9	0.0	0.0	0.4	0.0	0.0	0.0	0.0	1.1	0.0	0.0
	MgF ⁺	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.5	0.0	0.0	1.0	0.0	0.0	0.0	0.0	3.5	0.0	0.0
Al ⁺⁺⁺	Al ⁺⁺⁺	46.9	35.7	35.6	38.6	39.4	46.5	46.5	8.6	0.0	47.4	24.7	0.2	35.0	19.6	49.0	2.6	n.d.	45.7	37.5
	AlF ⁺⁺	1.7	1.4	2.0	3.1	3.5	12.8	12.8	20.7	0.0	24.2	42.7	16.3	3.1	0.4	34.7	47.6	n.d.	4.6	6.7
	AlF ₂ ⁺	0.0	0.0	0.0	0.0	0.0	0.2	0.2	2.3	0.0	0.5	3.5	73.3	0.0	0.0	1.2	43.3	n.d.	0.0	0.1
	AlF ₃	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	11.3	0.0	0.0	0.0	1.5	n.d.	0.0	0.0
	AlOH ⁺⁺	0.4	0.0	0.0	0.1	0.1	6.2	6.2	20.2	0.0	0.5	0.0	0.0	0.1	0.0	0.9	0.2	n.d.	0.3	0.1
	Al(OH) ₂ ⁺	0.0	0.0	0.0	0.0	0.0	0.7	0.0	38.6	0.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	n.d.	0.0	0.0
	Al(OH) ₄ ⁻	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.1	100	0.0	0.0	0.0	0.0	0.0	0.0	0.0	n.d.	0.0	0.0
	AlSO ₄ ⁺	40.6	44.3	44.4	45.7	44.7	31.4	31.4	6.1	0.0	26.3	24.6	0.2	48.3	37.5	12.4	2.8	n.d.	42.9	45.8
	Al(SO ₄) ₂ ⁻	11.3	18.6	18.4	11.9	10.6	2.8	2.8	0.6	0.0	1.8	3.7	0.0	13.9	42.9	0.6	0.4	n.d.	6.0	10.8
Ca ⁺⁺	Ca ⁺⁺	73.8	66.7	65.4	74.3	76.7	85.5	85.5	81.8	85.7	89.4	79.4	71.4	66.7	50.9	94.7	77.4	80.0	80.7	72.4
	CaCl ⁺	0.5	0.3	0.4	0.3	0.3	0.1	0.1	0.1	0.1	0.0	0.0	0.6	0.0	0.0	1.4	0.2	0.3	0.0	0.1
	CaSO ₄	23.8	33.3	32.7	27.1	26.0	14.5	14.5	14.5	16.4	11.7	21.2	24.3	29.4	46.4	6.8	22.6	19.3	19.3	26.5
Fe ⁺⁺	Fe ⁺⁺	67.7	64.9	65.4	80.0	75.0	n.d.	n.d.	n.d.	n.d.	89.9	82.4	71.7	68.2	54.5	n.d.	76.7	n.d.	83.1	73.2
	FeSO ₄	32.3	35.1	34.6	24.5	22.5	n.d.	n.d.	n.d.	n.d.	9.8	18.8	28.3	31.8	43.2	n.d.	23.3	n.d.	18.3	26.8
K ⁺	K ⁺	82.8	92.3	85.5	94.4	100	98.8	98.8	100	99.0	97.6	98.9	98.2	95.2	88.7	100	98.6	97.3	100	100
	KHSO ₄	12.7	5.9	3.7	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.1	0.4	0.9	2.0	0.0	0.0	0.0	0.0	0.5
	KSO ₄ ⁻	3.1	4.2	3.9	2.2	2.1	0.8	0.8	0.9	0.9	0.6	1.4	2.1	2.9	9.4	0.4	1.6	1.3	1.2	2.3
Mg ⁺	Mg ⁺⁺	58.6	56.7	56.0	71.0	69.7	83.7	83.7	82.1	80.3	86.4	78.3	65.5	60.0	47.3	87.8	69.0	75.5	76.5	66.7
	MgCl ⁺	0.4	0.3	0.3	0.3	0.3	0.1	0.1	0.1	0.1	0.0	0.0	0.5	0.0	0.0	1.1	0.2	0.3	0.0	0.1
	MgSO ₄	41.4	43.3	44.0	31.0	29.2	16.7	16.7	17.9	19.7	13.6	25.2	36.2	39.5	52.7	11.4	31.0	23.5	23.5	33.3
Mn ⁺	Mn ⁺	67.8	65.6	66.0	75.0	75.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	72.6	68.6	54.8	92.9	77.4	80.0	n.d.	74.2
	MnCl ⁺	0.5	0.3	0.4	0.5	0.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.7	0.0	0.0	2.0	0.3	0.5	n.d.	0.2
	MnSO ₄	32.2	34.4	34.0	23.1	21.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	27.4	30.7	45.2	5.7	23.2	17.7	n.d.	25.8
Na ⁺	Na ⁺	97.4	97.5	97.1	100	100	100	100	100	100	100	100	100	98.4	93.3	96.9	100	97.1	98.8	100
	NaSO ₄ ⁻	1.8	2.8	2.7	1.7	1.6	0.6	0.6	0.7	0.7	0.4	1.0	1.3	1.9	7.0	0.3	1.1	0.9	0.9	1.6
S=	HS ⁻	0.0	0.0	0.0	0.0	0.0	0.2	n.d.	n.d.	n.d.	0.0	0.0	0.0	0.0	0.0	0.0	0.1	n.d.	0.0	0.0
	H ₂ S	100	100	100	100	100	100	n.d.	n.d.	n.d.	100	100	100	100	100	100	100	n.d.	100	100
SO ₄ =	SO ₄ =	12.0	24.5	29.7	60.6	61.6	84.2	84.2	85.0	87.0	84.6	73.7	66.0	46.9	27.6	73.3	81.8	81.2	74.3	55.7
	HSO ₄ ⁻	76.4	59.2	54.1	11.1	11.6	0.3	0.3	0.0	0.0	3.1	21.6	22.6	30.0	11.8	1.6	3.3	0.0	5.4	27.3
	CaSO ₄	1.8	2.9	4.6	9.6	9.1	8.4	8.4	8.0	10.0	4.2	1.9	6.4	4.1	3.0	10.8	6.4	9.1	4.6	3.0
	FeSO ₄	0.4	0.6	0.5	0.5	0.4	n.d.	n.d.	n.d.	n.d.	0.1	0.8	0.3	1.1	11.2	n.d.	0.4	n.d.	0.4	1.3
	MgSO ₄	2.2	2.7	3.0	3.1	3.0	3.8	3.8	5.0	5.7	2.3	1.5	4.0	6.1	2.8	6.5	5.5	7.2	3.4	2.5
	AlSO ₄ ⁺	4.7	6.3	5.4	9.7	8.8	1.4	1.4	0.1	0.0	1.9	0.1	0.0	6.7	12.4	5.1	0.0	n.d.	8.6	6.3
	Al(SO ₄) ₂ ⁻	1.3	2.7	2.2	2.5	2.1	0.1	0.1	0.0	0.0	0.1	0.1	0.0	1.9	14.1	0.2	0.0	n.d.	1.2	1.5
	KSO ₄ ⁻	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.2	0.0	0.0	0.2	0.4	0.2	0.0	0.0
	NaSO ₄ ⁻	0.1	0.2	0.3	0.4	0.3	0.2	0.2	0.3	0.4	0.1	0.2	1.2	0.1	0.1	0.8	1.1	1.0	0.2	0.2

n.p. = not possible to calculate

n.d. = no data

the high silica amount in the sediment samples of the Danau Linow and the Kali Putih (see paragraph 4.2.10.) Silica appears in solution for nearly 100% in the form SiO_2 and in a very small amount as silicic acid (see the SOLVEQ output example of sample DL2-1, Appendix V and Table 5.1). Borium is present in solution for 100% as H_3BO_3 .

Sample BW1-1 is modelled, but the large charge unbalance made it impossible to calculate the mineral saturation index or aqueous species of this sample. Comparable samples are not modelled, like sample DL1-1, because sample DL1-1B is modelled and AMB3-1 and AMB4-1 are not modelled, because other Ambang samples are modelled and these samples do not contribute to new insights.

5.2.3.1. Downstream changes of the Kali Putih river

The changes of aqueous species of elements in the profile AMB2-1, AMB1-1, MD1-1, KP1-1, KP2-1, KP3-1 and M4 are plotted in Figure 5.1 (only element changes) and Figures 5.2 to 5.7 (change of aqueous species). In this profile, the temperature, pH and redox state of the waters change. The influence of these changes on the aqueous species is investigated and is presented in Table 5.1 and Figures 5.2 to 5.7. In addition, the changes in the minerals saturation are presented in the Figures 5.8 to 5.17.

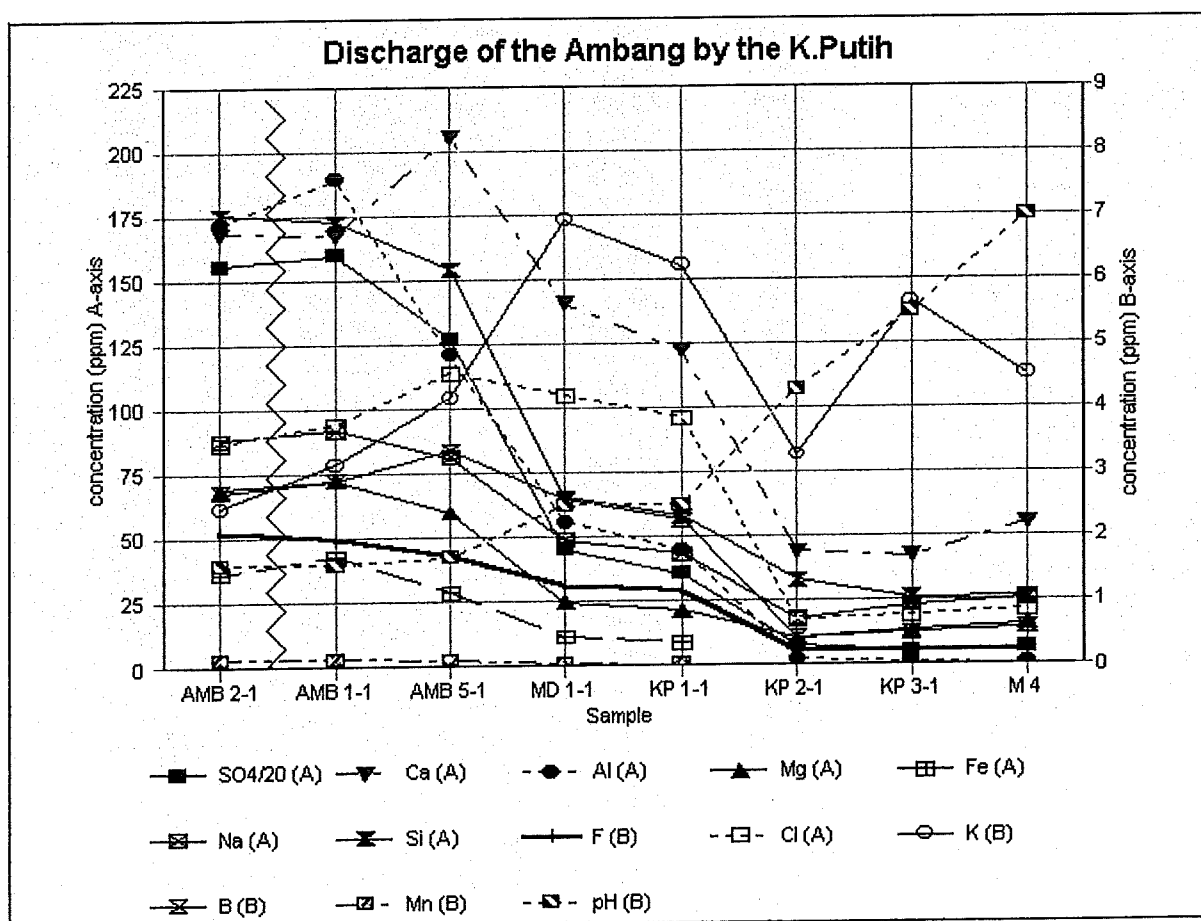


Figure 5.1 Profile of the river Kali Putih, starting in the Ambang mountains.

In general, chloride is mainly present in solution as free ion. Only in very acid waters ($\text{pH} < 3$) a small amount ($< 0.3\%$) of HCl is present. Chloride may also form Ca and Mg complexes, but no more than 1%. Fluoride exists mainly in the form AlF_2^{2+} (nearly 100%) and AlF_2^+ (maximum 1.3%), but the pH increases and the aluminium concentration decreases, fluoride

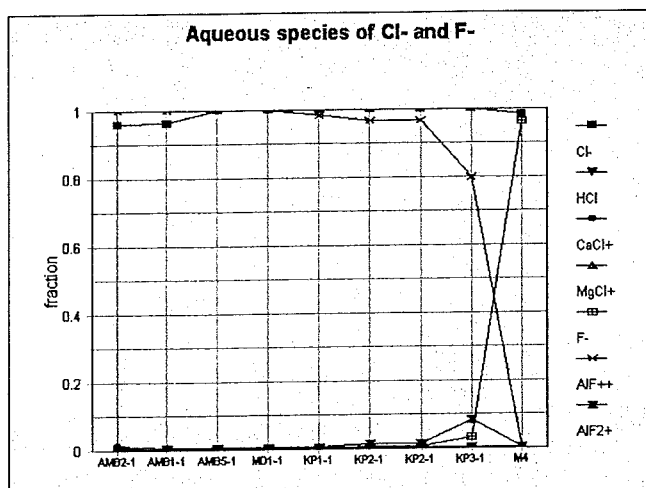


Figure 5.2. Profile of the aqueous species Cl and F.

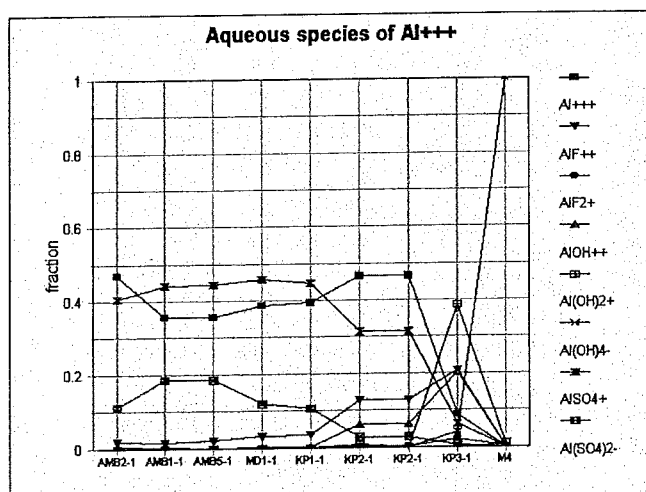


Figure 5.3. Profile of the aqueous species Al.

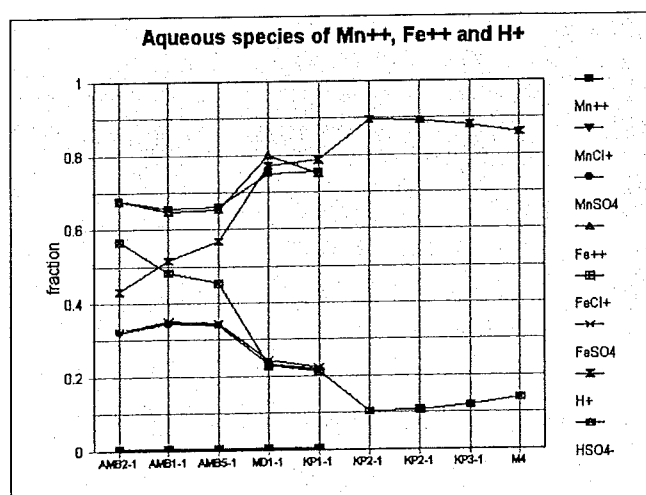


Figure 5.4. Profile of the aqueous species Mn, Fe and H.

is also present as free ion in solution, which can be clearly seen in Figure 5.2, where the free F concentration increases from KP3-1 to M4.

Aluminium exists for 35 to 45% as free ion, 30 to 45% as AlSO_4^+ , 3 to 20% as $\text{Al}(\text{SO}_4)_2^-$ and 1.5 to 20% as AlF^{2+} (see Table 5.1 and Figure 5.3). In the neutral waters, however, like KP3-1 (pH 5.5) and M4 (pH 7), aluminium is present as aluminium hydroxide complexes. In sample M4, fluoride is no longer bound to aluminium and all the aluminium is bound as $\text{Al}(\text{OH})_4^-$. It is remarkable, that in these neutral waters Al is still present, while Fe and Mn are removed from the solution (probably by precipitation). It seems to be that the aqueous species AlF^{2+} and aluminium hydroxides are quite stable and keep the aluminium in these complexes in solution, despite the high pH.

Other cations, including H^+ , move freely in solution competing with their sulphate complex. H^+ is present in acid water for 50% as free ion and for 50% as HSO_4^- , while the ratio changes with increasing pH and more H^+ is present in solution at the cost of HSO_4^- (see Figure 5.4). In this Figure, the ratio of free iron and manganese and their sulphate complexes are plotted. Next to a sulphate complex, Mn is bounded for a small percentage to chloride as MnCl^+ (0.4%). On the other hand, FeCl^+ is not significant present in solution. K, Ca and Mg move as free ions and as sulphate complex in solution, and the amount of free ions increases with increasing pH (Figure 5.5 and 5.6). Na is for nearly 100 % present as free ion. Only a small amount of NaSO_4^- will be formed (<3%).

Sulphate (Figure 5.7) exist mainly in two species, SO_4^{2-} and HSO_4^- and

to a smaller extent complexes in acid waters. With increasing pH, however, the amount of SO_4^{2-} , CaSO_4 and MgSO_4 increases to a maximum of 87, 10 and 6%, respectively. Up to a pH of 2.5, the percentage of the aluminium complexes increases to 12%, but this decreases to

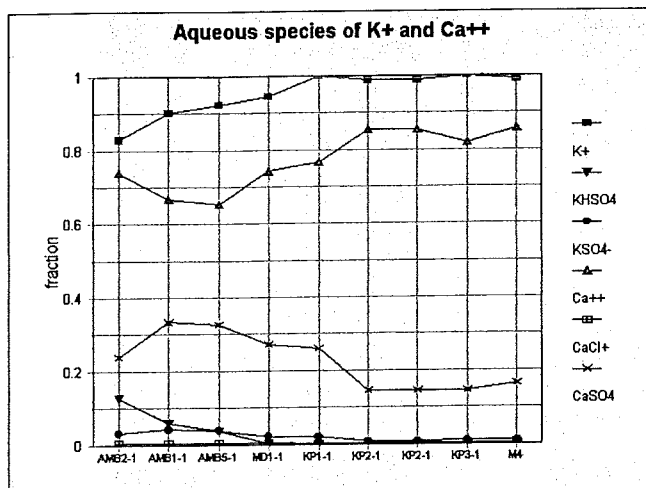


Figure 5.5. Profile of the aqueous species K and Ca.

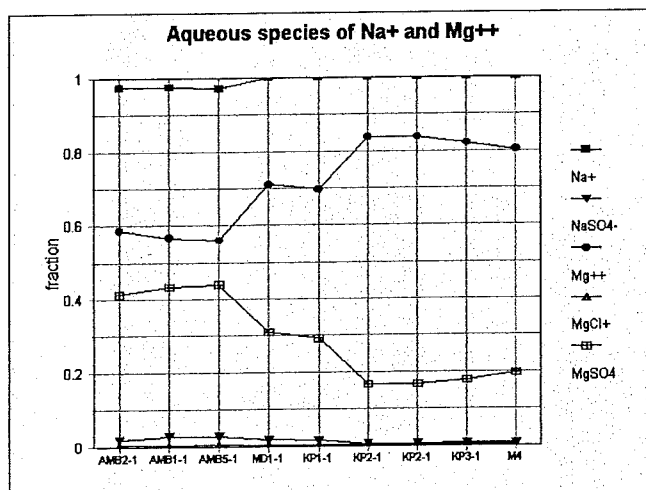


Figure 5.6. Profile of the aqueous species Na and Mg.

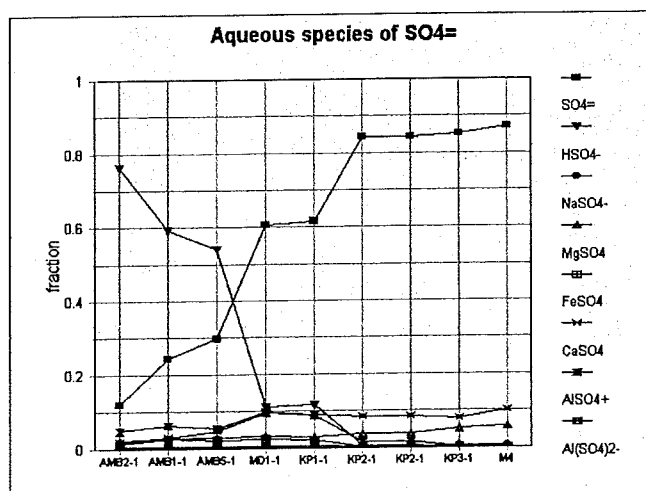


Figure 5.7. Profile of the aqueous species sulphate.

zero for higher pH's. Other sulphate complexes are present in a very small (<0.5%) amount (see Table 5.1). S^{2-} is present for 100% as H_2S in reducing conditions. In oxidizing conditions, H_2S is oxidized to sulphate (see section 5.2.3.3.).

In Figure 5.2 to 5.7, the aqueous species of sample KP2-1 are listed for reducing conditions (first) and for oxidizing conditions. The aqueous species does not show changes, but the saturation of minerals change considerably.

The saturation of minerals of the Ambang and Kali Putih samples are plotted in Figure 5.8 to 5.17. The saturation indices of the minerals are quite the same for the samples AMB1-1, AMB2-1 and AMB5-1. However, pyrite is slightly supersaturated at AMB2-1, while it is supersaturated in the other two samples. Further, native sulphur is only supersaturated in sample AMB5-1, which is mainly caused by the amount of H_2S . A decrease of the amount of injected H_2S causes a decrease in native sulphur saturation in sample AMB5-1, while it did not influence the ratio of aqueous species significantly.

The saturation of pyrite increases from sample AMB5-1 to KP1-1, while the saturation of native sulphur decreases, due to a decrease of H_2S . In general, Figure 5.11 (MD1-1) and Figure 5.12 (KP1-1) did not differ much with the Ambang samples (Figures 5.8 to 5.10). A significant change is observed at KP2-1. The river Kali Putih becomes diluted by the neutral Tubig Tabongon (TBG1-1, Map 4, Appendix I) and iron and manganese are removed from the solution. Therefore, iron minerals are not present in Figure 5.13. If sample

KP2-1 is modelled by adding 5 ppm Fe, pyrite is clearly supersaturated (Figure 5.14). The main difference between KP1-1 and KP2-1 is the supersaturation of clay minerals, K-feldspate, muscovite, gibbsite and kaolinite in sample KP2-1.

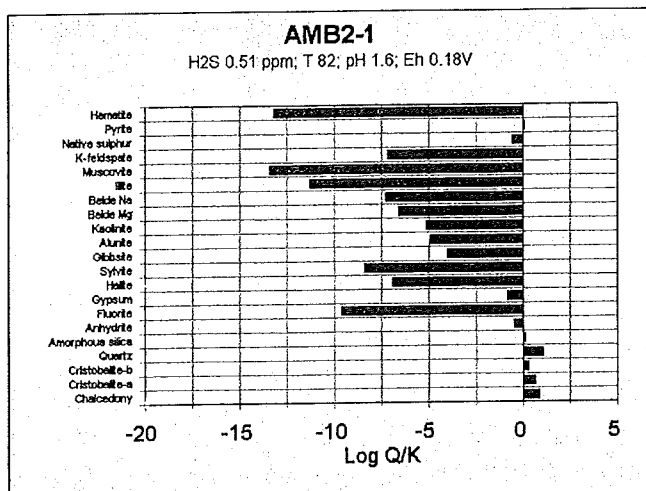


Figure 5.8. Mineral saturation index of sample AMB2-1.

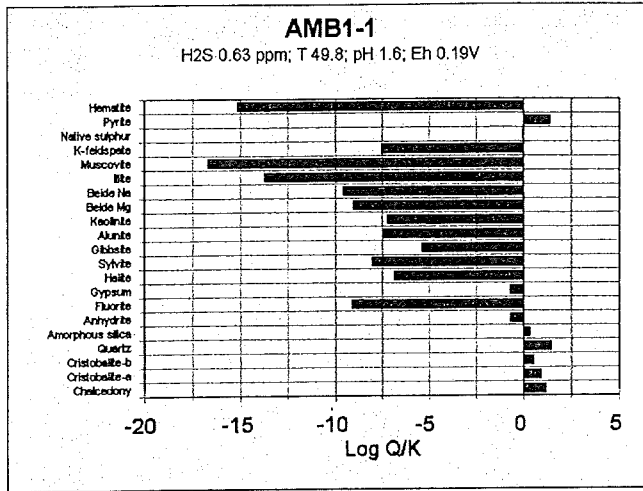


Figure 5.9. Mineral saturation index of sample AMB1-1.

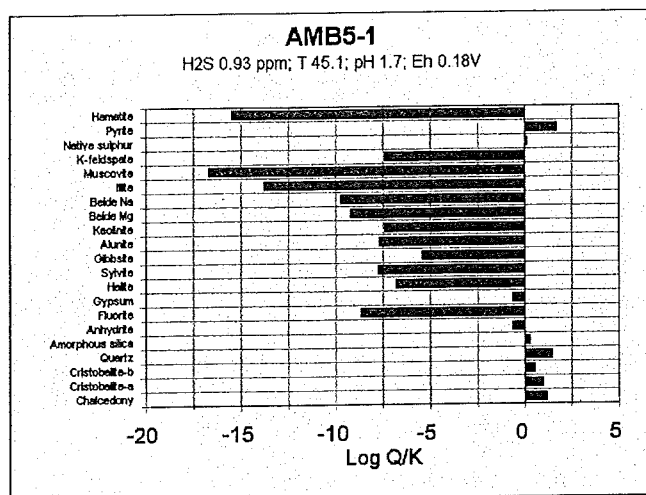


Figure 5.10. Mineral saturation index of sample AMB5-1.

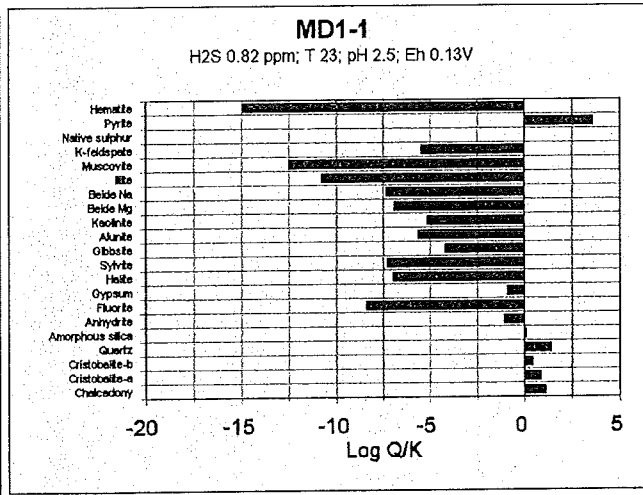


Figure 5.11. Mineral saturation index of sample MD1-1.

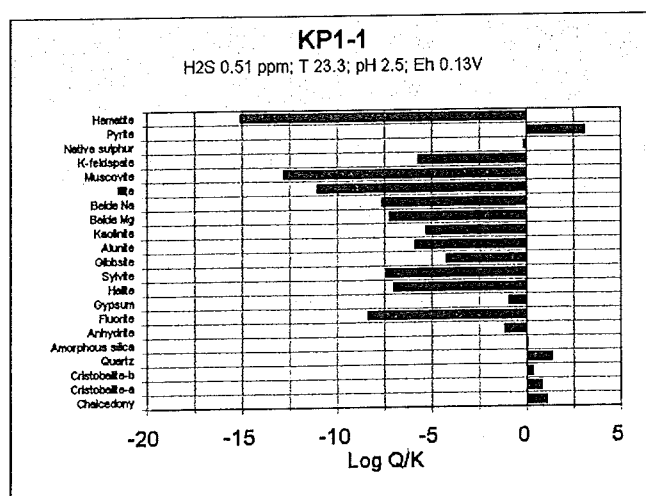


Figure 5.12. Mineral saturation index of sample KP1-1.

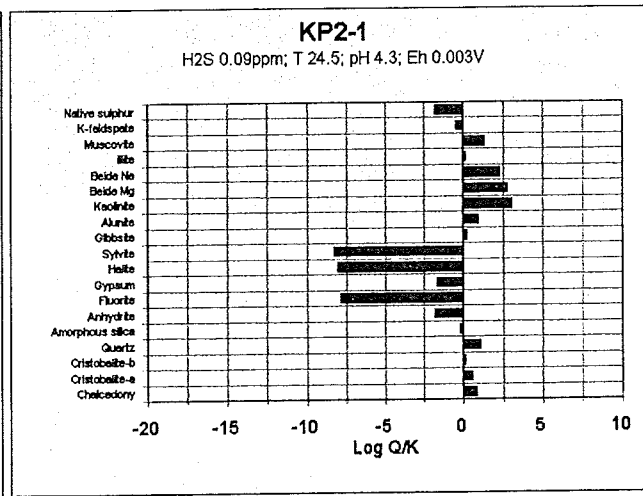


Figure 5.13. Mineral saturation index of sample KP2-1. (Under reducing conditions.)

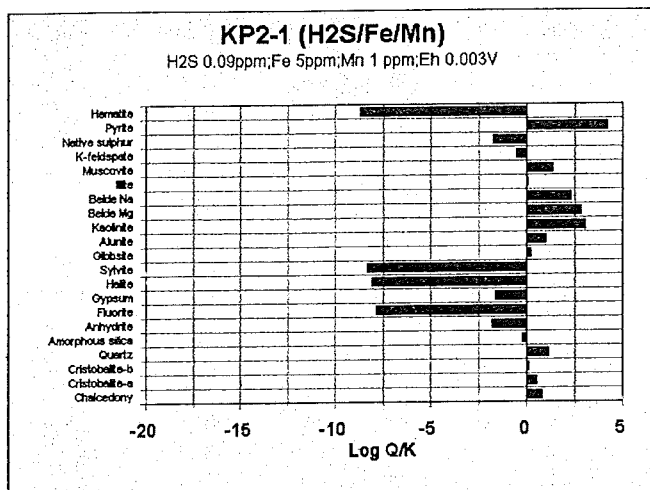


Figure 5.14. Mineral saturation index of sample KP2-1 (Under reducing conditions, with additional Fe and Mn).

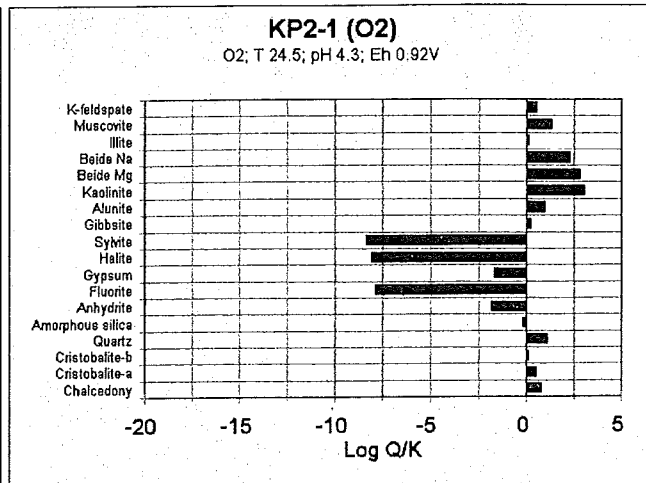


Figure 5.15. Mineral saturation index of sample KP2-1. (Under oxidizing conditions.)

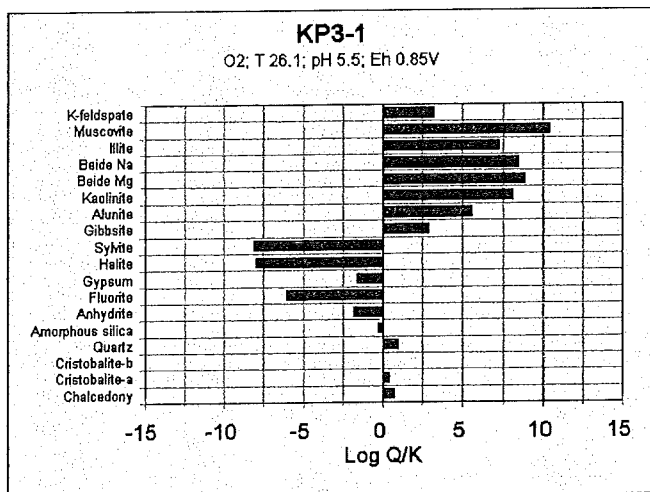


Figure 5.16. Mineral saturation index of sample KP3-1.

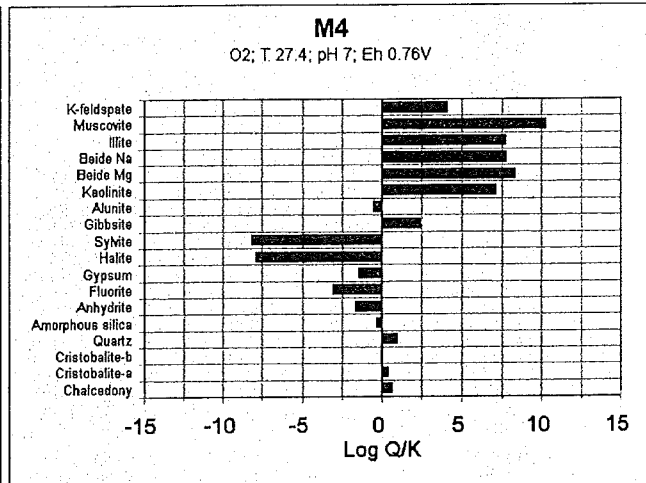


Figure 5.17. Mineral saturation index of sample M4.

Sample KP2-1 is also modelled with the presence of oxygen in stead of H₂S (see Figure 5.15 and 5.13, respectively). Main difference is the absence of native sulphur in Figure 5.15, which is caused by the absence of any H₂S in an oxidizing condition. K-feldspate is saturated in an oxide environment. Next to sample KP2-1, sample KP1-1 is modelled with oxide in stead of H₂S as redox couple, but only with extreme high oxide concentrations the results were valid, while at sample KP2-1 by an oxide concentration of 0,0096 ppm an valid model was constructed. This calculations support the possibility of an oxide rich KP2-1.

The supersaturation of clay minerals, K-feldspate, muscovite, kaolinite and gibbsite increases for the samples KP3-1 and M4. Alunite is under saturated in sample M4, while it is supersaturated in sample KP3-1 (see Figure 5.16 and 5.17). The chemical components of alunite decrease, but not enough to explain an difference in log Q/K of 6. An possible solution is that aluminium is not available for mineral forming, because, at this pH, it forms the Al(OH)₄⁻ complex.

It can be concluded that in general, cations move freely in solution, competing with their sulphate complex and to a smaller extent with their chloride complex. Furthermore, the amount of free cations increases with increasing pH. Fluoride is mainly present as AlF²⁺,

while chloride is present as free ion. Sulphate is mainly present as SO_4^{2-} and HSO_4^- , and to a smaller extent as cation complexes. The silica minerals are, in most cases, supersaturated. The saturation of native sulphur is primarily controlled by the amount of H_2S . Pyrite is supersaturated only in reducing conditions. With increasing pH of the Kali Putih clay minerals, feldspate and aluminium bearing minerals become supersaturated in these from origin acid river.

5.2.3.2. The mixing of KM2-1 and KM3-1 to KM4-1

The acid spring KM2-1 mixes with a neutral river KM3-1 (see paragraph 4.2.4). After this mixing, the river bottom is covered by red precipitate, probably the mineral hematite. The situation is modelled with SOLVEQ to predict or construct the precipitation of the red mineral. For the modelling, a H_2S concentration of 0.04 ppm is taken, assuming a dilution of 1:5 (KM2-1:KM3-1). First, the aqueous species (Table 5.1) and the saturation of minerals (Figure 5.18) are calculated with the redox couple H_2S . Thereafter, the saturation of minerals is calculated with the redox couple O_2 (Figure 5.19).

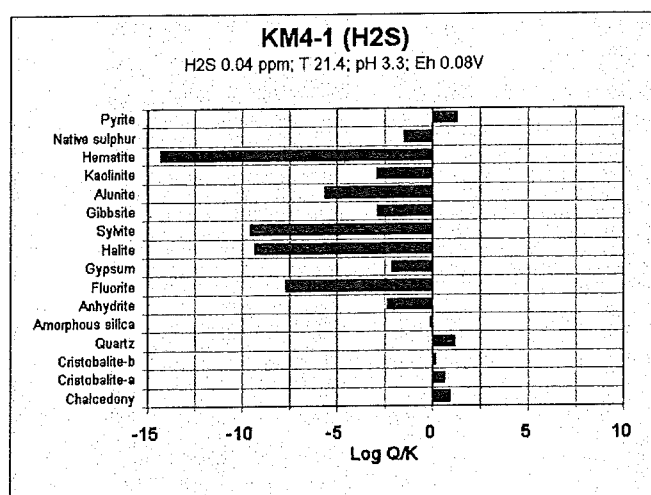


Figure 5.18. Mineral saturation index of sample KM4-1. (Under reducing conditions.)

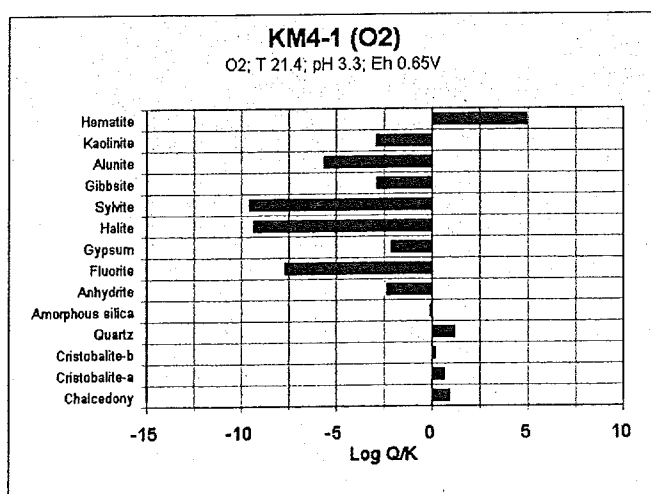


Figure 5.19. Mineral saturation index of sample KM4-1. (Under oxidizing conditions.)

Pyrite and native sulphur only exist in reducing conditions with H_2S (Figure 5.18). (They are therefore not present in Figure 5.19.) The main difference between both situations is the Eh: 0.08 V for reducing conditions and 0.65 V for oxidizing conditions. This causes large supersaturation of hematite from log Q/K of -14 for reducing conditions to +5 for oxidizing conditions. Eh-pH diagrams for sulphur and iron are used to explain this mechanism (Figure 5.20 and 5.21). Brookins (1988) made seven Eh-pH diagrams for iron, but the Fe-S-O-H system is the best according to this situation. Brookins took a S activity of 10^{-3} (roughly 32 ppm) and an activity of 10^{-6} (roughly 0.06 ppm) for iron. These concentrations are lower than measured. However, an increase of S or Fe will cause a slight shift of the not horizontal boundaries to the left side. Therefore, these diagrams are valuable for explaining a precipitation model. An increase in the activity of dissolved S will enlarge the stability field of native sulphur (Brookins, 1988).

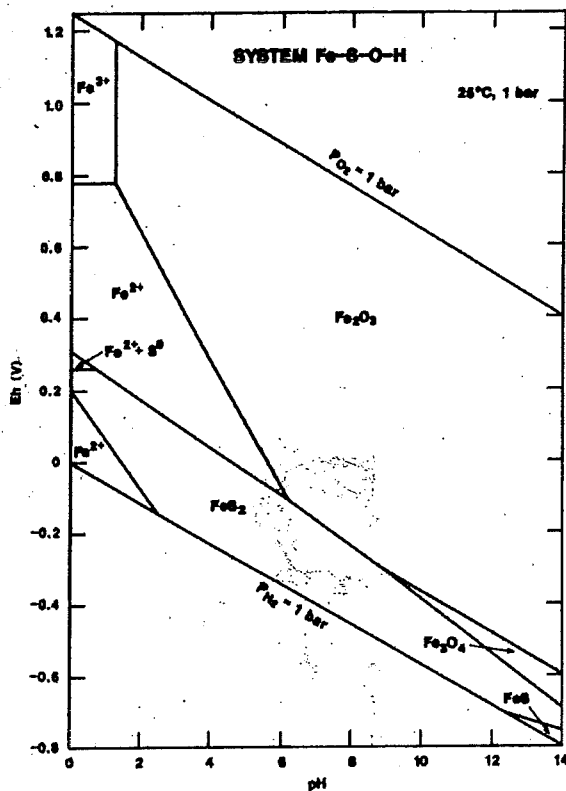


Figure 5.20. The Eh-pH diagram of a Fe-S-O-H system (Brookins, 1988).

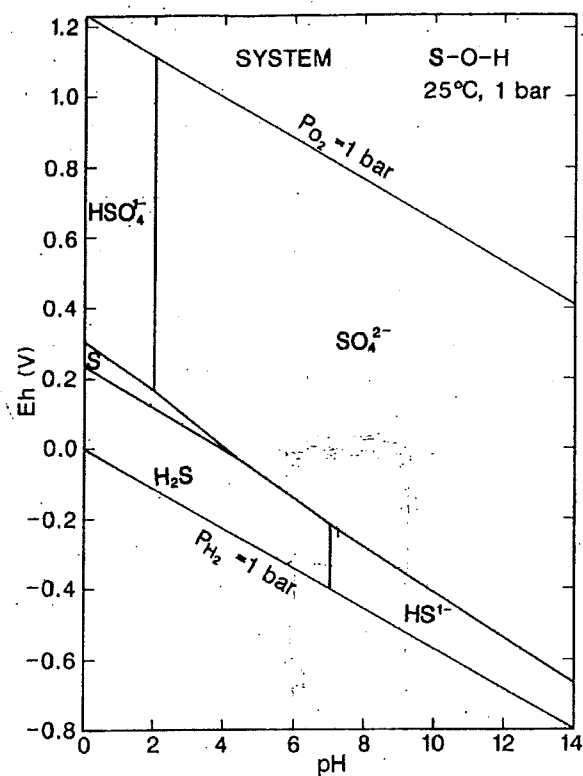
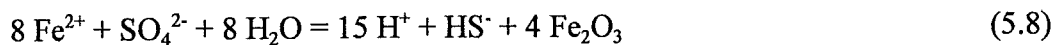


Figure 5.21. The Eh-pH diagram of a S-O-H system (Brookins, 1988).

At a pH of 3.3, pyrite is stable if the Eh is lower than of 0.09 V and hematite is stable if the Eh is higher than 0.39 V (Figure 5.20). A slight increase in Eh (from 0.09 V) will only make the pyrite instable and increase the amount of free Fe^{2+} . Fe^{3+} is only stable in very oxidic and acid environment ($\text{pH} < 1.5$). At a pH of 3.3 and an Eh of 0.08 V, native sulphur can be present, and sulphate is the major species in stead of HSO_4^- (see Table 5.1).

The general equation for the precipitation of hematite is given in the next reaction (this equation is also used in the SOLVEQ program):



(Delmelle *et al.*, 1994). The potential jump, caused by the change of the redox couple from H_2S to O_2 , causes a jump from the stability fields of pyrite and H_2S to the hematite and sulphate fields. Therefore, in oxidizing conditions, the HS^- concentration decreases significantly, while the sulphate concentration increases. This makes the formation of hematite more favourable (see Reaction 5.8).

5.2.3.3. The acid lakes and pH calculations

The Kawah Masem crater lake, the Danau Linow, the small lake TDS2 and the small pool in the rice field DL2-1, are acid lakes ($\text{pH} < 2.6$) and are supersaturated for the silica minerals and pyrite (Figures 5.22 to 5.25), except for TDS2, which is slightly under saturated in pyrite, which is caused by the small amount of iron in solution. On the other hand, TDS2 is supersaturated for barite (it is they only sample, which had a measurably concentration Ba, see Table 3.1.b). Native sulphur is slightly under saturated for these samples, but supersaturated for

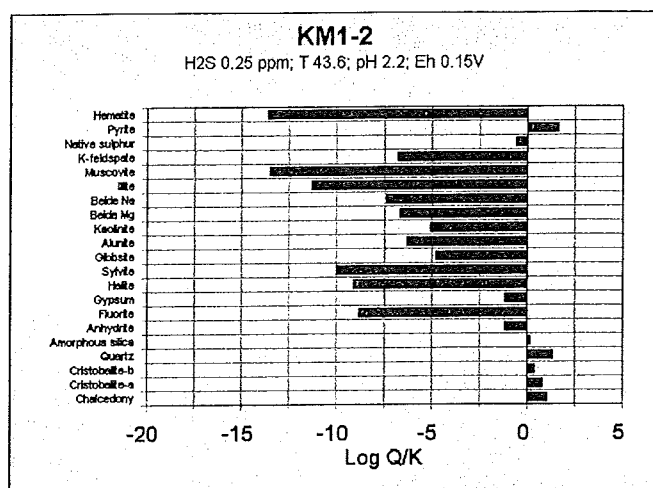


Figure 5.22. Mineral saturation index of sample KM1-2.

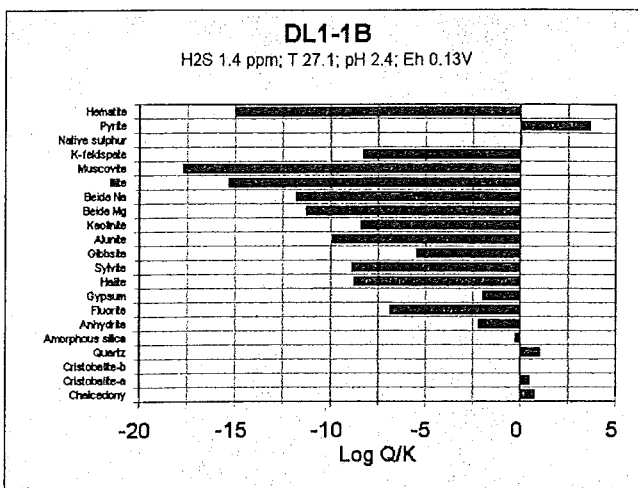


Figure 5.23. Mineral saturation index of sample DL1-1B.

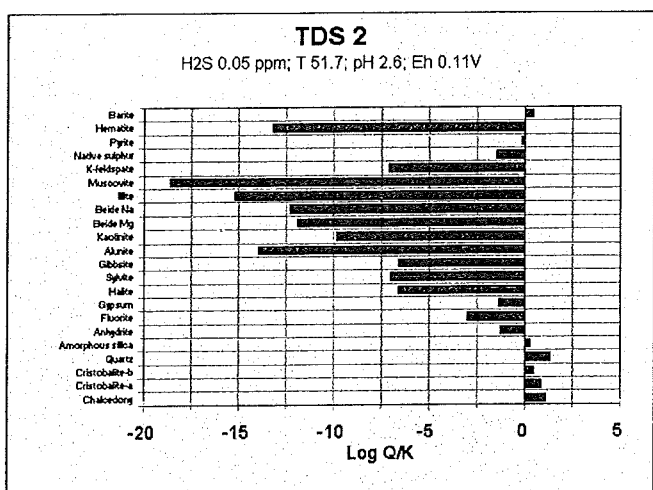


Figure 5.24. Mineral saturation index of sample TDS2.

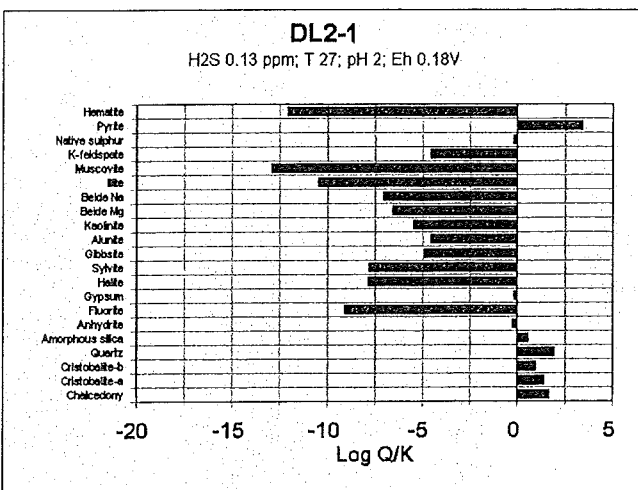
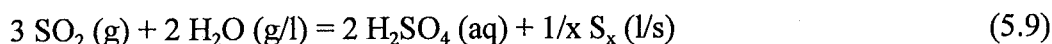
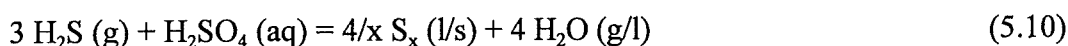


Figure 5.25. Mineral saturation index of sample DL2-1.

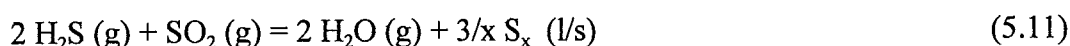
sample DL1-1B. The saturation of native sulphur is mainly controlled by the amount of injected SO_2 , which can be seen in the next reaction:



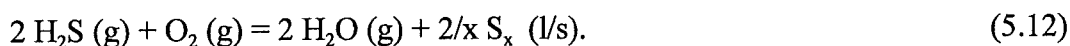
or indirectly, by first forming H_2S and sulphuric acid followed by:



(Oppenheimer, 1992). Any H_2S present can be oxidized to elemental sulphur by a variety of agents including SO_2 , O_2 , H_2O , H_2SO_4 and Fe^{3+} (Oppenheimer, 1992), e.g.:



and:



The degradation of polythionic acids can also contribute to the precipitation of sulphur (Takano and Watanuki, 1990), but is not likely in this area of low volcanic activity, with quite small inputs of S-containing gases.

An extra input of H_2S does not change the ratio of the aqueous species. With SOLVEQ H_2S concentration for which native sulphur is saturated can be calculated: for TDS2 the H_2S concentration should be at least 5 ppm, while 1.4 ppm causes in sample DL1-1B a small supersaturation ($\log Q/K = 0.07$). DL2-1 should have a H_2S concentration of 0.27 ppm, instead of the 0.13 ppm measured, in order to be supersaturated in native sulphur. Around these lakes elemental sulphur is found, while elemental sulphur is under saturated in the Kawah Masem crater lake, DL2-1 and TDS 2. Because an increase of H_2S and/or a change in the amount of SO_2 and sulphuric acid may cause a supersaturation of native sulphur, it is possible that at other times native sulphur becomes supersaturated and precipitates.

Gypsum and anhydrite are only at sample DL2-1 slightly under saturated, caused by the high amount of Ca (420 ppm), while at the other lakes these minerals are very under saturated, having Ca concentrations of 72 ppm or less.

The aqueous species of the four acid samples are quite different (see Table 5.1). Most differences are due to the amount of sulphate. DL1-1B, TDS2, KM1-2 and DL2-1 have sulphate concentration of 280, 465, 1035 and 14760 ppm, respectively. In general, with increasing sulphate concentration H^+ is more bound to SO_4^{2-} than as free ion. This phenomenon occurs also for the cations Ca, Fe, K, Mg, Mn and Na. This trend is also valuable for Al, but Al is first bound as a fluoride complex instead of a sulphate complex. Sample TDS2 has the remarkable complex AlF_3 in a concentration of 11.3% in comparison of Al ions and 4.5% for the F ion, which that 13.5% of total F is bounded in this complex (see Table 5.1). This complex is also found in sample DL4-1.

The pH of the samples can be calculated by the program SOLVEQ. This may be useful, because there are no good pH values of the acid samples, since the pH is only measured with pH-paper in the field. The pH calculations are done by selecting H^+ as the charge balance ion, assuming that the charge unbalance can be only compensated by H^+ . The results of the pH calculations are given in Table 5.2.

Table 5.2
Measured and calculated pH values of five samples.

Sample	pH calculated	pH measured
KM1-2	2.38	2
AMB1-1	1.92	1.6
DL1-1B	2.56	2.4
DL2-1	2.4	2
TDS2	2.72	2.6

The differences of the calculated and measured pH values seems to be small, but at a low pH the difference in H^+ concentration is quite big. For better pH results, the waters should be measured again in the field.

5.2.3.4. The chloride rich samples of the Mahawu

The three samples, sampled around the Mahawu volcano, show different $\log Q/K$ plots (see Figure 5.26 to 5.28). All three samples are (as usual) supersaturated for the silica minerals. Kaolinite is supersaturated in sample MHW3-1, while in sample MHW2-1 K-feldspate, muscovite, clay-minerals and Al-bearing minerals, like kaolinite, alunite and gibbsite are supersaturated. The supersaturation of clay minerals is typical for acid waters, that become

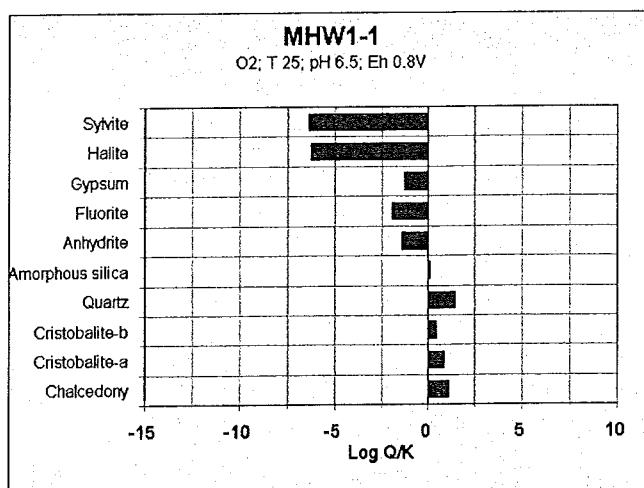


Figure 5.26. Mineral saturation index of sample MHW1-1.

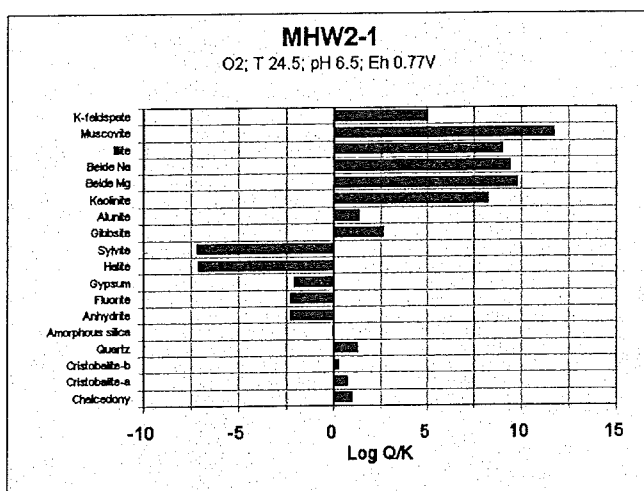


Figure 5.27. Mineral saturation index of sample MHW2-1.

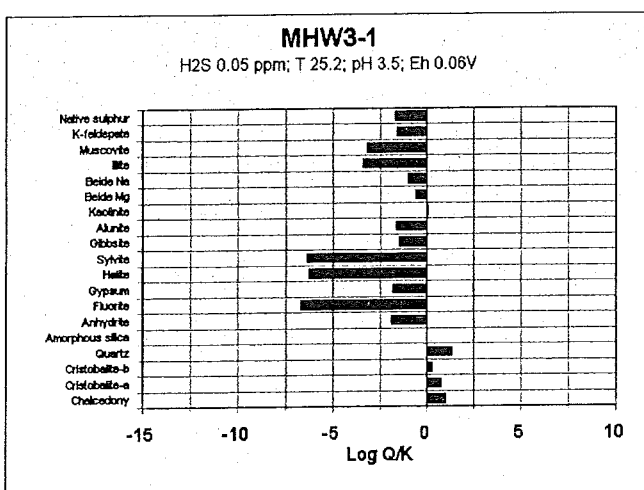


Figure 5.28. Mineral saturation index of sample MHW3-1.

diluted and oxidized. This phenomenon is also observed in sample KP3-1 (Figure 5.16) and M4 (Figure 5.17). The river MHW2-1 (Map 9, Appendix I), comes from nearly the top of the crater and can thus be expected to be acid or ion rich, if it drains the crater lake of the Mahawu. The river MHW2-1 However, the river is still neutral (pH = 6.5) at the sample location and does not have an ionic rich composition. This river is therefore not expected to drain the Mahawu crater lake. On the other hand, the supersaturation of K-feldspate, muscovite, clay-minerals and Al-bearing minerals may indicate that the origin of this river was acid, because this supersaturation pattern is characteristic for acid waters, which are diluted to a large extent. It can be concluded that MHW2-1 drains for a certain part the Mahawu crater or is enriched in ions by a hydrothermal spring of the Mahawu. This would also explain the name of the river of MHW2-1. The name of this river is Sosoan Saluesem, which indicates the acid character of the river ('esem' means acid in Indonesia). Possibly, the river becomes more acid or ion rich by variations of volcanic activity or seasons influences. The acid river Sosoan Rayow (MHW3-1) may originate from a spring or some other lower situated outflow.

5.2.3.5. Changes in redox, pH and temperature modelled on sample DL4-1

East of the Danau Linow, the water of an acid, hot spring (DL3-1) mixes with a small neutral stream (Map 5, Appendix I and Photo 4, Appendix III). Sample DL4-1 is taken after the mixing of the waters. This situation is used to

investigate the changes in mineral saturation, by varying the redox potential, pH and temperature. Although, the influence of the ion concentrations are not investigated directly, it is clear that in general an increase in ion concentration gives an increase in saturation of minerals in

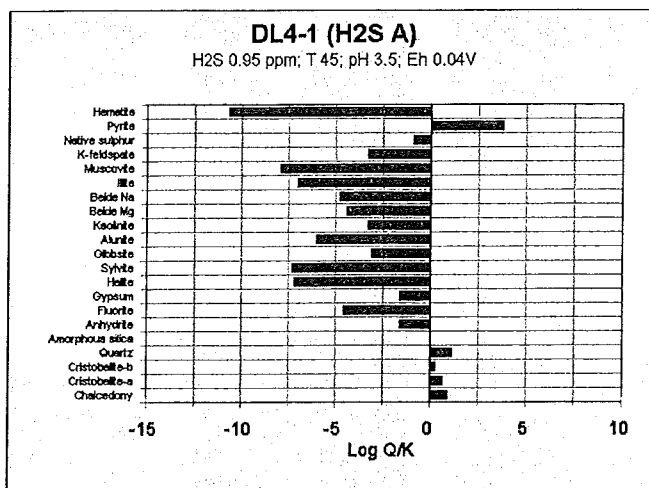


Figure 5.29. Mineral saturation index of sample DL4-1. (Under reducing conditions, 45 °C, pH 3.5).

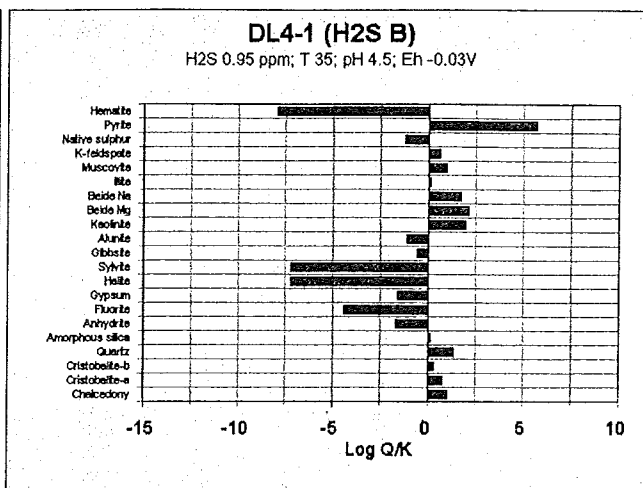


Figure 5.30. Mineral saturation index of sample DL4-1. (Under reducing conditions, 35 °C, pH 4.5).

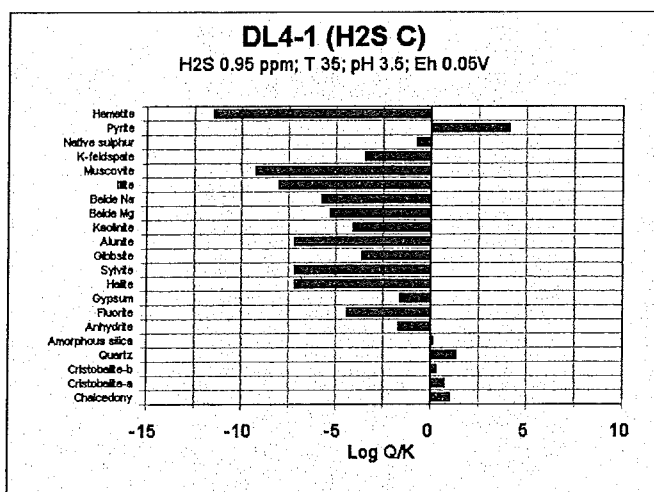


Figure 5.31. Mineral saturation index of sample DL4-1. (Under reducing conditions, 35 °C, pH 3.5).

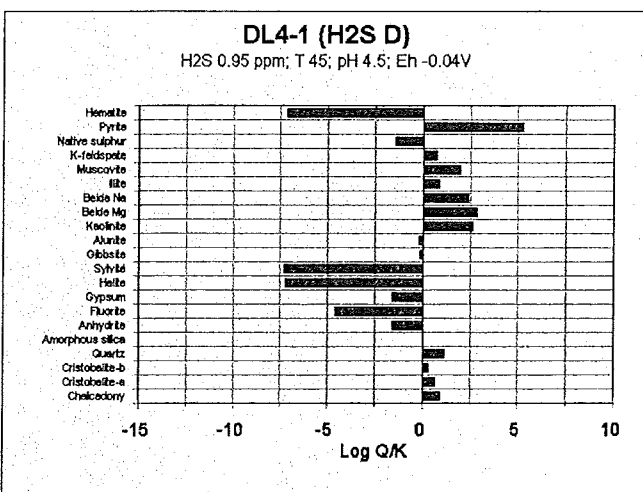


Figure 5.32. Mineral saturation index of sample DL4-1. (Under reducing conditions, 45 °C, pH 4.5).

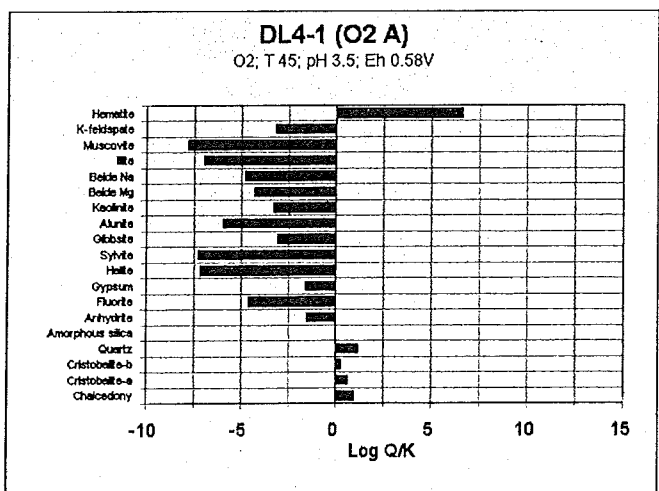


Figure 5.33. Mineral saturation index of sample DL4-1. (Under oxidizing conditions, 45 °C, pH 3.5).

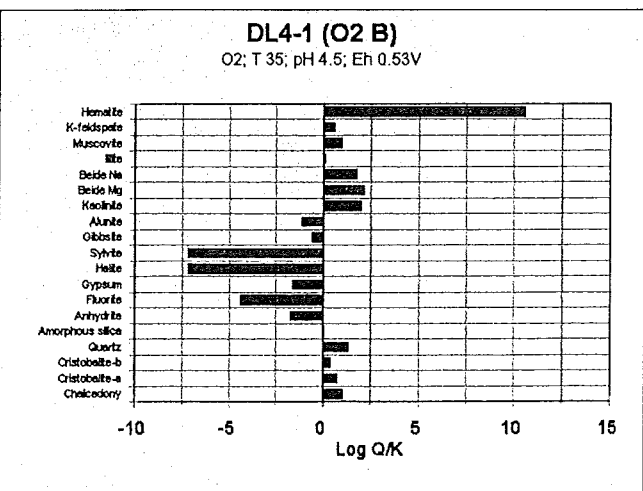


Figure 5.34. Mineral saturation index of sample DL4-1. (Under oxidizing conditions, 35 °C, pH 4.5).

the aquatic environment. In order to investigate the changes in mineral saturation, sample DL4-1 is modelled under different conditions. From these models mineral saturation plots are made (Figures 5.29 to 5.34). The redox condition is controlled in the first four plots by H_2S , while in the last two plots O_2 controlled the redox state. In Figure 5.29, 5.32 and 5.33, the original temperature of 45 °C is taken, while in the other three Figures a temperature of 35 °C is taken (a temperature, which can be possibly after dilution with cool water, which streams along the hot spring). In Figure 5.29, 5.31 and 5.33, the original pH of 3.5 is taken and for the other three Figures a pH of 4.5 is taken.

The influence of the redox potential, controlled by H_2S or O_2 , can be seen in Figure 5.29 versus 5.33 and Figure 5.30 versus 5.34. Main difference is the saturation of hematite, which is in anoxic conditions very under saturated and in oxidic conditions very supersaturated. This phenomenon is also observed at sample KM4-1, where hematite becomes supersaturated when the redox potential increases with 0.57V to 0.65V (section 5.2.3.2.). Pyrite and native sulphur are very under saturated if H_2S is not present in the water.

The influence of a temperature decrease of 10 °C on the mineral saturation is presented in Figure 5.29 versus 5.31 and Figure 5.32 versus 5.30 at a pH of 3.5 and 4.5, respectively. The silica minerals, pyrite and native sulphur show a small positive shift of log Q/K, they thus become more saturated by a temperature decrease. However, alunite, beidelite (Mg and Na), K-feldspate, gibbsite, hematite, illite, kaolinite and muscovite show a small negative shift in log Q/K. They thus become less saturated by a temperature decrease. These shifts occur at both pH values. A shift of the log Q/K, caused by a temperature change, can be mainly explained by a change in the thermodynamic equilibrium constant (log K), and to a smaller extent by a change in the ion activity product (log Q).

Finally, the influence on the mineral saturation, caused by a change in pH from 3.5 to 4.5, is investigated and presented in Figure 5.29 versus 5.32 and Figure 5.31 versus 5.30 with a temperature of 45 and 35 degrees, respectively. The changes are remarkable. Iron-bearing minerals, Al-bearing minerals, clay minerals and K-feldspate become more saturated and for most minerals supersaturated. This can be explained by the fact that the forming of (many) minerals is controlled by H^+ or OH^- , thus log Q changes significantly by a change of pH, while log K does not change.

The mineral saturation index given in Figure 5.29 is valid for the conditions of the sample DL4-1. The water of DL4-1 becomes diluted, which induces an increase of the pH and a decrease of the temperature. The mineral saturation index of this situation is given in Figure 5.30. If the dominant species H_2S disappears, the water becomes in equilibrium with air and oxygen the minerals saturation index of this situation is given in Figure 5.34. In this situation, magnetite (log Q/K = 5.27) and jarosite become supersaturated (these are not indicated in Figure 5.34).

It can be concluded that hematite and magnetite are mainly controlled by the redox conditions and become only saturated in an oxidizing condition at a low pH. Pyrite and native S can only be present if H_2S is dissolved in the water. A change in temperature causes for some minerals a small shift in the log Q/K (<1), which is mainly caused by a small change in the thermodynamic equilibrium constant (K). An increase of the pH causes a large positive shift of log Q/K (3-9), which is due to a change in the ion activity product (Q).

5.2.3.6. The ion rich, neutral river RND1-1

The sample RND1-1 is modelled to predict mineral saturations and aqueous species of ions of an ion rich, neutral sample. Because iron and aluminium are removed from the solution at the sample location RND1-1, it was not possible to predict the saturation of clay minerals and

aluminium bearing minerals, which could be used to determine the origin of this water, as is done with sample MHW2-1 (paragraph 5.2.3.4.). The saturation index of the minerals of this sample is given in Figure 5.35 and the aqueous species are given in Table 5.1. The most

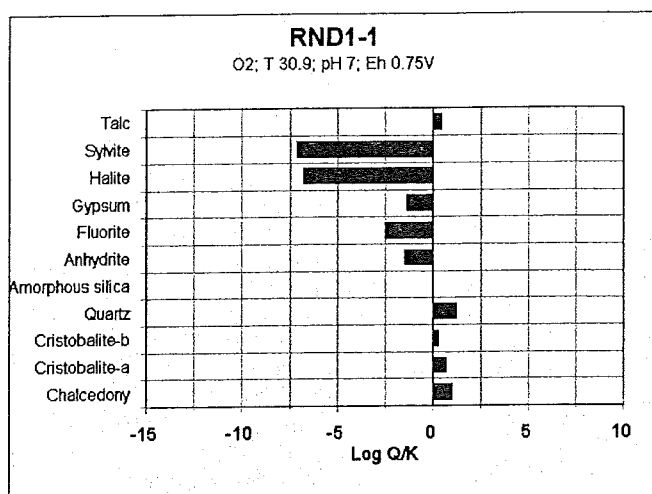


Figure 5.35. Mineral saturation index of sample RND1-1.

remarkable supersaturated mineral is talc [$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$], with a log Q/K of 0.42. This mineral becomes never supersaturated in the other samples of Sulawesi, only in the R. Nimanga samples (NMG), with a log Q/K of 1.8.

In the absence of aluminium, F exists for at least 95% as free ion (Table 5.1). In sample M4, F exists also for at least 95% as free ion, but in this sample Al is very strong bound as hydroxide complex. The cations in sample RND1-1 are mainly present as free ion or bound as sulphate complex. This is also the situation for acid waters, but in neutral waters more free cations can

be found. An addition of 100 ppm bicarbonate in the modelling system for this sample did not show a remarkable change of the aqueous species. The cations are present as free ions and form sulphate, chloride and bicarbonate complexes. The bicarbonate complexes, however, are only formed for a few percent of the total cation concentration.

5.2.4. Conclusions of the modelling with SOLVEQ

It can be concluded that the program SOLVEQ is an useful tool for the prediction of the aqueous species and mineral saturations in solution. The redox state of a water is mainly controlled by H_2S , or O_2 . If H_2S is present in solution, native sulphur and pyrite may become saturated. If O_2 is present, hematite and magnetite may become supersaturated. Thus, the formation of iron minerals and elemental sulphur are primarily dependent on the redox state of the water. The saturation of other minerals is primarily dependent on the pH, where an increase of the pH causes an increase at the saturation of minerals, and secondarily by the temperature of the water, which has a small influence on the thermodynamic equilibrium constant. An increase of the temperature, decreases the saturation of native sulphur, pyrite and silica minerals, while other minerals become more saturated. Waters, that have a acid origin, become supersaturated in K-feldspate, muscovite, clay-minerals and kaolinite if the redox potential and pH increase by dilution with neutral water.

The modelling of aqueous species shows that Si, B and S^{2-} are for 100% present as SiO_2 , H_3BO_3 and H_2S , respectively, under all conditions. Chloride is present for nearly 100% as free ion and only a few percent of CaCl^+ and MgCl^+ complexes have been formed. Cations are mainly present as free ion and as sulphate complex and in small amounts as chloride complex. However, the percentage of free ions increases with increasing pH. Fluoride exist as free ion in neutral waters in the absence of aluminium. In acid waters, however, fluoride exist mainly as AlF^{2+} and to a lesser extent as AlF_2^+ complex. Aluminium is present in solution as free ion, AlF^{2+} and as sulphate complex, while in neutral waters, aluminium is strongly bound in hydroxide complexes. Sulphate is mainly present as SO_4^{2-} and HSO_4^- and to a smaller extent as Ca, Fe, Mn and Al complexes.

6. Volcanic hazards from environmental pollution

6.1. Introduction to environmental pollution

The waters of North Sulawesi contain cations and anions in high concentrations. Some metals and anions may be toxic, if they exceed a certain level. Several institutions made guidelines to indicate when a metal or anion is toxic or can be supposed to be toxic. However, the toxicity of an element depends on many factors. The form of the element is very important. Is the element present in solution as free ion, complex ion or chelate ion or is it bound on a colloidal, precipitated or adsorbed? Is it organic or inorganic? Soluble or not? Further, the amount of other metals or anions may influence the toxicity: antagonism and synergism. In addition, factors like temperature, pH, redox conditions, light and salinity may have influence on the toxicity of metals. Finally, the kind of organism, which is infected by an exceeding amount of an element, determines the toxicity of an element. The stage in life when it is infected, the condition, age, sex and size of the organism are also important factors. Förstner and Wittmann (1979) concluded that many influences determine the toxicity of a metal. This makes it difficult to determine the toxicity of an element in a environment. The use of guidelines gives its own problems: the compatibility of the guidelines. The guidelines are made in the laboratory, with one or two variables, a few standard conditions and with mainly one organism. Despite of these complications, the risks of the use of North Sulawesi drinking, washing or irrigation water will be investigated.

Pollution of water can occur by geologic weathering, industrial processing of ores and metals, the use of metals and metal components, leaching of metals from garbage and solid waste dumps, deposition by air and by animal and human excretions, which contain heavy metals (Förstner and Wittmann, 1979). In this research, and thus in the investigated area of North Sulawesi, these aspects are not considered to be the source of pollution. No industrial activities, waste or excretions are observed in reasonable amounts. Further, geologic weathering is probably not the main source of metals in the waters, because these processes occur very slow, but it may contribute to a small amount of the metal concentrations. The main source is the volcanic activity, which increases the metal and anion concentrations in rivers, lakes, springs, wells and mud pools (section 5.1.).

6.1.1. Guidelines for safe water

In this study, several guidelines are used for the determination of the toxicity of the elements in the waters of North Sulawesi. In Table 6.1, the used guidelines are given, including the detection limit of the analysis.

The first norm is the Dutch environmental quality norm for surface water. The norm gives an indication for a Maximal Acceptable Add (MAA, in Dutch MTT) for surface water. The starting point in this guideline is the Maximal Acceptable Risk (MAR, in Dutch MTR), where no risk can be expected, or where, for carcinogenic elements, a chance of 10^{-6} to die can be predicted. From this MAR the background levels of common Dutch waters (AC) are subtracted; this leaves the MAA. The MAR is made in the laboratory for a common Dutch organism, in a pH range of 5.5 to 8. The MAA norm is not very useful in this discussion, because the background levels are not known. So the MAR guidelines will be more useful. To use the MAA in the right way, more calculations are needed, like the PAF calculation and the EPA method (Schallenberg, 1998). This is not done in this research.

Table 6.1
Guidelines for safe drinking, aquatic or irrigation water, in ppb.

Element	Detection Limit ICP	Dutch (a)	Canadian aquatic (b)	Canadian irrigation (c)	WHO 1993 (d)	CEC 1980 (e)	UK (f)	USA (g)
Al	150		5-100	5000	200*	50*		
B	150	500		500	300	1000	2000	1000
Ca	200					100,000*	250,000	
Fe	50		300	5000	300*	50*	200	50
K	300					10,000*		
Mg	50					30,000*	50,000	
Mn	50			200	500	20	50	50
Na	100				200,000*	20,000*		
P	400							
SO ₄	250	100,000			250,000*	25,000*		
Si	100							
Sr	50							
Ti	100							
F	100**	1500		1000	1500		1500	800-1700
Cl	100**	200,000		100,000	250,000*	25,000*		
Li	50			2500				
Be	50	0.16		100				
Ba	50	147			700	100	1000	
V	50	3.5		100				
Cr	50	8.5	2-20	100	50		50	50
Co	50	2.6		50				
Ni	50	1.8	25-150	200	20			
Cu	50	1.1	2-4	200	2000	100	3000	1000
Zn	100	6.6	30	1000-5000	3000*	100*	5000	5000
As	200	24	50	100	10		50	50
Se	200	5.3	1	20	10			
Cd	50				3		5	10
Pb	250	11	1-7	200	10		50	5
Sb	200				5			
Mo	50				70			
H ₂ S	50**				50*			
Br	100**							
NO ₃	100**				50,000	25,000	50,000	

*) Substances in drinking water that may give rise to complaints from consumers.

**) Estimated detection limits, measured with an ISE and IC.

blanco) no data.

a) Dutch quality guideline for environmental water (MAA), Schallenberg (1998).

b) Canadian norm for aquatic environmental water, Canadian Water Quality Guidelines (1995).

c) Canadian norm for irrigation water, Canadian Water Quality Guidelines (1995).

d) WHO guideline for safe drinking water, WHO (1993).

e) CEC guideline for safe drinking water, CEC (1980 and 1989).

f) Guideline and maximal acceptable concentrations for human consumption, made by the UK, Alloway (1997).

g) Guideline and maximal acceptable concentrations for human consumption, made by the USA, Alloway (1997).

The second norm is the Canadian Water Quality Guidelines (1995). This norm is made for the aquatic environment of Canadian waters. Next to this aquatic environmental norm, a guideline for safe irrigation water is made by Canadians (Canadian Water Quality Guidelines, 1995). This norm is made for irrigation water for the Canadian ecosystems, by using common vegetation of Canada. This norm can be used for irrigation waters of North Sulawesi. However, the irrigation situations differ and therefore some elements may be more or less toxic. Furthermore, the amount of irrigation water used, the amount of rainfall, climate, temperature, the soil and vegetation may differ in both situations. If bad irrigation water is used, problems of salt accumulation in the root-system, decrease of the permeability, and the accumulation of toxic minor and trace elements and pesticides can occur. It can be concluded that in comparison to the guidelines of irrigation water three aspects must be taken in account: a) the amount of water: how much water is irrigated and how much evaporates? This determines the amount of accumulation of ions, metals and toxic elements; b) the kind of growths, the sensitiveness of the growth can differ for the Canadian growth and the Indonesian, and c) the type of soil, which can drain water, or can bind ions. The Canadian guidelines are based on 1000 mm

irrigation water and on the resistance of trace elements in the upper 15 cm of the soil. The guidelines must prevent that within the first 100 years phytotoxicity is reached (Canadian Water Quality Guidelines, 1995). Because a lot of waters in North Sulawesi are used for irrigation, this norm will be used for these samples.

In addition, the World Health Organization (WHO, 1993) has made a guidelines for safe drinking water. For the most elements the guideline is the maximum for safe drinking water, but for Al, Ca, Cl, H₂S, Fe, Mg, K, Na, SO₄ and Zn the guideline is the maximum concentration that does not give rise to complaints from consumers. The most expected complaint is the bad taste of the water. A lot of Fe gives water a bad taste. In addition, Mn, Na, Cl and H₂S give the water a bad taste if they exceed the norm (CEC, 1989 and WHO, 1996). The fifth guideline, made by the CEC (Commission of the European Community, 1980), has the same two criteria of safe drinking water and the possibility of the rise of complaints. The next two guidelines of the UK and USA are listed in Table 6.1, and show the maximum acceptable concentrations for metals and inorganic pollutants in water for human consumption.

The guidelines made by the CEC are more stringent than the guidelines of the WHO (see Table 6.1). Differences in guidelines for drinking or aquatic water made it difficult to compare the waters of North Sulawesi with these guidelines. Which norm is the best or fits best with the Indonesian situation? In this research for irrigation water the Canadian norm for irrigation water is used. The Canadian norm for aquatic environment and the UK and USA guidelines are not used, because the WHO and CEC guideline are more stringent. The Dutch norm is not very useful, because a) the most norms for elements are elements which are not detected in this research and b) this norm is not valid for the purposes of the Dutch norm. Therefore, the WHO (1993) and the CEC (1980) norm will be used to determine whether the waters are suitable as drinking water or not.

6.1.2. Problems with the use of guidelines for safe water

As discussed, the guidelines may give problems when applying them with the chemical compositions of the samples, because the norms are made in other conditions than the situation of North Sulawesi. The water vary in pH, hardness, matrix, redox state and the amount organic material and the different behaviour of living organisms of (Western) Europe or Canada in respects of the organisms in this tropical area. In this paragraph, these aspects will be investigated in more detail.

6.1.2.1. Problems with pH and Eh

The pH which is used in the guidelines is mainly between 5.5 to 8. The samples, however, have pH values of 2.5 or lower. A pH decrease of one unit may lead to an increase of more than one order of magnitude in the concentration of certain metals, like Al and Be (Edmunds and Smedley, 1996). Changes in pH and also in redox conditions will affect the mobility of Fe, Mn, NO₃, Se, U and As (Edmunds and Smedley, 1996), which may increase the toxicity of these elements and the availability for organisms. The pH influences the speciation of elements in solution (as is discussed in chapter 5). Since the toxicity of an element depends on its speciation, changes in pH may cause changes in toxicity. It can be concluded that the differences of the pH in guidelines instead of the real situations has influence on the mobility, speciation and solubility of cations and anions and thus toxicity of the elements.

6.1.2.2. The influence of the hardness of water

The hardness of water is important for the solubility of metals and the toxicity of the elements. In soft water (0 - 60 mg/l CaCO₃) metals are more soluble, while in hard water (>120 mg/l

CaCO_3) a higher concentration of a metal is needed to become lethal (Edmunds and Smedley, 1996). It seems to be, that in hard water Ca and Mg compete stronger with heavy metals than in soft water (Edmunds and Smedley, 1996).

6.1.2.3. The organic compounds and aqueous species

In this research and in the guidelines no attention is given to organic material. The influence of organic material in tropical ecosystems is less investigated. Organic material can bound metals, which decreases the total amount of free metal ions. However, some organic materials can be more toxic, when they bound metals. The toxicity of unnatural organic compounds, which come in the ecosystems by the use of pesticides, fertilizers and industrial pollution, is much investigated in industrial countries.

The guidelines are made for dissolved cations and anions. However, free cations form complexes with sulphate, chloride, fluoride, hydroxides, carbonate and if available phosphate. Today, less research is done on the toxicity of several aqueous species and therefore it is difficult to make a good estimation of the dangers of the aqueous species, which are found with modeling. It can be concluded that the guidelines are in no way absolute, because the toxicity of a metal can change by the forming of complexes or species.

6.1.2.4. Bioaccumulation of elements in organisms

Except the guideline for irrigation water the norms are in general for in situ situations. However, metals can accumulate in organisms. This means that the concentration in the organism is higher than in the surroundings, especially for heavy or toxic metals. This accumulation can occur by diffusion processes and by the uptake via complex permeation, e.g. Cd crowd out Ca in the ATP-ase (Schallenberg, 1998). Other metals are taken up and are not thrust out, but are stored in the organism. Not all accumulations are directly fatal, but if aquatic micro biota is consumed by higher organisms (like fish and humans) it can become increasingly dangerous. The elements As, Be, Cr (VI), Cu, Pb, Ni, Se and Zn accumulate in organisms (Canadian Water Quality Guidelines, 1995), while for the elements Al, Co, F and V no accumulation data is found.

6.1.2.5. Laboratory situation versus field situation

As mentioned in paragraph 6.1.1., the guidelines are made by varying the concentrations of one element for one organism to investigate the toxicity of that element. However, rivers and lakes contain many elements in several concentrations and contain many organisms. It is unknown which correction must be made for the laboratory situation versus field situation. Because nature is a multivariate system, much research is needed to give a well-balanced correction factor. In laboratory studies, synergism and antagonism of elements are investigated and if possible, discussed in section 6.2. Synergism is the increase of the toxicity of an element caused by the influence of an other element and antagonism is the opposite process (e.g. see paragraph 6.1.2.2.).

6.1.2.6. Sensitivity of ecosystems

The next problem with the guidelines is the sensitiveness of different ecosystems for a given element concentrations. As known, the vegetation, biota, humans, soil and climate for Europe and Canada are different from that of Indonesia. The guidelines are made for the situations in the own country, although the WHO guideline may be expected to be more common. It keeps, therefore, still difficult to apply the guidelines with the Indonesian situation. Despite this, tropical systems are not necessarily more sensitive than ecosystems of temperate zones

(Schallenberg, 1998).

6.1.2.7. Adaption of organisms

Schallenberg (1998) mentioned the possibility of physiologic or genetic adaptation of organism by the constant exposure to polluted water. North Sulawesi is a lightly active hydrothermal area, which produces polluted water. Volcanic activity is recorded for at least 150 years ago, which is not a very long time for adaptation. However, the island is formed by mainly volcanic deposits, and North Sulawesi still is situated in an active hydrothermal arc. Therefore, it can be expected that for a long time volcanic waters are produced. However, the amount and ionic strength of these waters are unknown and therefore no serious predictions of the adaptation of organisms can be done. On the other hand, the rate of adaptation varies for each organism. Bacteria are more capable to adapt, but humans are relatively more resistant against toxic influences. It can be concluded that adaptations of organisms are possible in North Sulawesi, but much research must be done on the amount of adaptation and the change of the toxicity of the elements on organisms.

6.1.3. Dangers of undetected elements

In Table 6.1 the guidelines and the detection limits of the ICP-AES and the estimated detection limits for the determination of the anions F and Cl are given. The elements Ti, Li, Be, Cr, Co, Ni, Cu, As, Se, Cd, Pb, Sb, Mo and Hg are not detected with ICP-AES. However, this does not mean that the concentrations are per se below the detection limit. If the matrix of a sample is strong (which is the case in many Sulawesi samples) the detection limit of (trace) elements can be two to three times higher. Therefore, concentrations of metals in samples can be higher than the given detection limit and could then exceed a guideline, which is not expected if the metal concentration is lower than the detection limit.

It is remarkable that Br and Sr are never mentioned in any guideline. Förstner and Wittmann (1979) mentioned that these elements are noncritical for the toxicity and availability. However, it can be expected that waters polluted by volcanic activity, have elevated concentrations of these elements.

Schallenberg (1998) did research on the volcanic hazards of the polluted Banyuputih river, descending from the Ijen crater lake (East Java) and he concluded that potential toxic elements are Al, Be, Co, Cu, F, Mn, Ni, Pb, S, Cl, Se, V and Zn. He recommended the need of more research on Al, Zn, F and V. In this study, the volcanic waters of North Sulawesi did not contain the elements Be, Co, Cu, Ni, Pb, Se, V and Zn in measurable concentrations. It is recommended to analyse the trace elements in ppb concentrations with ICP-MS, to make a good estimation of the dangers of the volcanic waters of North Sulawesi.

6.1.4. Conclusions from the guidelines for safe water

The element concentrations of Al, B, Ca, Fe, K, Mg, Mn, Na, S (as SO₄), Si, F and Cl can be compared with the guidelines in Table 6.1 for safe water. The element concentrations of P, Ba, V and Zn can be compared with the safety guidelines, but only for a few samples (see Table 3.1.b.) The elements Ti, Li, Be, Cr, Co, Ni, Cu, As, Se, Cd, Pb, Sb, Mo and Hg are not further investigated, because they are not detected in the samples.

The Canadian Water Guideline for irrigation water should be used as norm for the irrigation waters in North Sulawesi. The WHO (1993) and CEC (1980) guidelines should be used to investigate the risks of drink, wash and surface waters. These norms are used despite the problems with compatibility. Differences between the laboratory and the field situation, like pH, hardness of water, adaptation of organisms, redox conditions, organic compounds,

aqueous species and bioaccumulation, are taken into account and discussed if possible in paragraph 6.2.

6.2. Discussion of dangers of elements in the Sulawesi samples

6.2.1. The use of the waters of North Sulawesi and the comparison with guidelines

The use of each samples is given in Table 6.2. The waters which are used as irrigation water, or are probably used as irrigation water, are compared with the Canadian guideline for irrigation water (Table 6.3). Drink, wash and fish waters are compared with guidelines of the WHO and CEC (Table 6.4). The WHO and CEC guidelines are also used for the determination of risks of surface waters, hot springs and acid rivers, which are not used, or of which no use is known (Table 6.5)

Table 6.2
The kind and use of the waters, sampled in North Sulawesi.

Sample	Kind	Used as	Sample	Kind	Used as
DL 1-1	lake	possible fishing water	MHW 1-1	spring	irrigation water
DL 1-1A	lake	possible fishing water	MHW 2-1	river	probably irrigation
DL 1-1B	lake	possible fishing water	MHW 3-1	river	probably irrigation
DL 2-1	pool	not used	TDS 2	hot lake	drinking water
DL 4-1	river	irrigation water	TDO 1	lake	probably irrigation
DL 5-1	river	unknown	DB 1-1	lake	fishing water
DL 6-1	river	not used	PL 1-1	lake	unknown
DL 7-1	river	not used	AMB 1-1	hot spring	not used
DL 8-1	lake	possible fishing water	AMB 2-1	hot spring	not used
DL 9-1	river	not used	AMB 3-1	river	not used
LA 1-1	river	irrigation water	AMB 4-1	river	not used
LA 2-1	pool	irrigation water	AMB 5-1	river	not used
LA 3-1	pool	irrigation water	DTA 1-1	cool spring	drinking water
LH 2-1	river	probably irrigation/wash	MD 1-1	river	not used
RND 1-1	river	probably irrigation	TM 1-1	river	irrigation water
RNE 1-1	river	probably irrigation	TM 2-1	river	irrigation water
NMG 1-1	river	probably irrigation	KP 1-1	river	not used
NMG 2-1	river	probably irrigation	TBG 1-1	river	probably irrigation
NMG 3-1	river	probably irrigation	KP 2-1	river	probably irrigation
KM 1-2	crater lake	not used	TB 1-1	river	not used
KM 2-1	spring	not used	KP 3-1	river	irrigation water
KM 3-1	river	drinking water	M 4	river	irrigation water
KM 4-1	river	not used	DMoat	lake	fishing water
KM 5-1	river	not used	M 3	river	fishing water
KM 6-1	river	probably irrigation	DTD 1-1	lake	unknown
KM 7-1	river	irrigation water	BW 1-1	lake	unknown

It must be said that only a few of the waters of North Sulawesi are used as drinking water. The samples KM3-1, TDS2 and DTA1-1 are certainly used as drinking water, but sample TDS2 only on one occasion. Rivers and surface waters are more used as fishing and washing water and probably as cooking water. In that case some waters can be dangerous. Furthermore, these waters are used as drinking water for cows and horses. Edmunds and Smedley (1996) mentioned that drinking water in developing countries are more dangerous because of the faecal pollution then by pollution from agriculture chemicals, like nitrate and pesticides.

Table 6.3

Comparison of the (possible) irrigation waters with the guideline for irrigation water.

	Al	B	Ca	Fe	K	Mg	Mn	Na	Si	F	Cl	SO ₄
Guideline (a)	5.00	0.50		5.00			0.20			1.00	100	
Irrigation												
DL 4-1	0.56	1.90	37.3	3.34	29.1	14.2	0.17	76.0	78.6	0.61	39.3	322
LA 1-1	< b.g.	< b.g.	10.3	< b.g.	0.97	5.57	< b.g.	6.38	13.0	0.37	1.12	7.6
LA 2-1	0.25	< b.g.	7.12	2.83	0.36	4.35	< b.g.	6.93	12.1	0.28	0.97	59.1
LA 3-1	< b.g.	< b.g.	7.40	< b.g.	< b.g.	5.40	< b.g.	6.58	9.90	0.27	0.98	20.6
KM 7-1	< b.g.	< b.g.	27.0	< b.g.	4.55	10.7	< b.g.	20.5	45.9	0.50	5.65	107
MHW 1-1	< b.g.	0.29	113	< b.g.	22.4	50.5	1.56	83.1	70.3	0.59	160	295
TM 1-1	< b.g.	< b.g.	39.9	< b.g.	2.63	7.37	< b.g.	15.4	29.1	0.32	4.52	93.9
TM 2-1	< b.g.	< b.g.	11.9	< b.g.	1.98	3.98	< b.g.	7.51	24.1	0.30	1.48	14.9
KP 3-1	1.20	0.51	42.5	< b.g.	5.65	13.6	< b.g.	23.4	26.2	0.22	19.2	108
M 4	0.56	0.59	55.3	< b.g.	4.52	16.0	< b.g.	25.7	26.5	0.22	21.5	128
Possibly irrigation water												
LH 2-1	13.6	0.39	23.6	42.9	5.40	7.86	< b.g.	12.0	73.9	1.41	7.53	363
RND 1-1	< b.g.	2.58	59.5	< b.g.	14.3	23.8	0.19	77.1	61.6	0.44	79.9	221
RNE 1-1	< b.g.	< b.g.	15.4	< b.g.	4.18	5.64	< b.g.	11.4	42.7	0.37	3.11	12.1
NMG 1-1	< b.g.	0.49	26.9	< b.g.	6.55	11.1	< b.g.	33.3	45.2	0.34	23.7	46.7
NMG 2-1	< b.g.	0.50	25.9	< b.g.	7.78	9.88	< b.g.	42.6	50.2	0.39	26.3	51.6
NMG 3-1	< b.g.	0.51	26.3	< b.g.	7.52	10.2	< b.g.	41.3	49.2	0.39	26.3	50.4
KM 6-1	18.8	< b.g.	33.4	3.98	5.05	12.5	< b.g.	19.7	66.9	0.61	5.30	341
MHW 2-1	0.48	< b.g.	33.1	< b.g.	8.39	12.6	< b.g.	30.5	47.9	0.94	57.3	73.2
MHW 3-1	13.1	0.47	76.5	< b.g.	19.5	23.8	1.52	72.6	55.0	3.53	271	114
TBG 1-1	< b.g.	< b.g.	23.8	< b.g.	2.28	7.48	< b.g.	10.1	27.3	0.26	2.24	34.6
KP 2-1	2.33	0.43	44.2	< b.g.	3.28	10.4	< b.g.	18.0	33.2	0.22	18.1	154

a) The Canadian guideline for irrigation water, Canadian Water Quality Guidelines (1995).

= concentration above the guideline

Table 6.4

Comparison of the drinking or surface waters with the guidelines of the WHO and the CEC.

	Al	B	Ca	Fe	K	Mg	Mn	Na	Si	F	Cl	SO ₄
Guidelines												
WHO (a)	0.20*	0.30		0.30*			0.50	200*			250*	250*
CEC (b)	0.05	1.00	100*	0.05*	10*	30*	0.02	20*		1.50	25*	25*
Drinking water												
KM 3-1	< b.g.	< b.g.	17.5	< b.g.	1.70	5.48	< b.g.	8.06	35.0	0.34	1.86	25.5
TDS 2	0.82	3.70	55.1	2.97	21.9	14.2	0.34	113	152	1.42	104	463
DTA 1-1	< b.g.	< b.g.	13.8	< b.g.	4.21	3.05	< b.g.	10.1	49.0	0.34	1.50	46.9
Possibly drink, fish or wash water												
DL 8-1	4.37	0.17	14.0	9.44	3.92	6.06	< b.g.	14.3	29.3	0.70	5.04	293
TDO 1	< b.g.	< b.g.	16.7	< b.g.	3.74	9.89	< b.g.	25.9	6.66	0.34	18.4	23.8
DB 1-1	< b.g.	< b.g.	29.4	< b.g.	4.90	23.7	< b.g.	26.5	26.3	0.31	9.65	20.3
DMoat	< b.g.	< b.g.	6.91	< b.g.	0.93	2.48	< b.g.	3.65	10.9	0.19	1.00	3.5
M 3	< b.g.	< b.g.	6.97	< b.g.	0.84	2.42	< b.g.	3.63	10.6	0.21	1.00	3.2

*) Substances in drinking water that may give rise to complaints from consumers.

a) Guideline for safe drinking water, WHO (1993).

b) Guidelines for safe drinking water, CEC (1980 and 1989).

= concentration above the guideline

Table 6.5

Not used or unknown use of water samples compared with the guidelines of WHO, CEC and irrigation water.

Guidelines	Al	B	Ca	Fe	K	Mg	Mn	Na	Si	F	Cl	SO ₄
WHO (a)	0.20*	0.30		0.30*			0.50	200*			250*	250*
CEC (b)	0.05	1.00	100	0.05*	10*	30*	0.02	20*		1.50	25*	25*
Irrigation (c)	5.00	0.50		5.00			0.20			1.00	100	
Not used waters												
DL 2-1	1494	5.12	419	2394	27.4	218	22.6	67.1	246	3.83	13.1	14762
DL 6-1	27.4	0.53	32.5	19.8	5.17	13.3	0.24	24.6	43.8	1.99	39.6	587
DL 7-1	32.5	0.68	39.1	22.9	5.96	16.0	0.53	25.9	51.6	1.55	37.3	662
DL 9-1	27.2	0.19	21.5	37.0	3.99	12.9	0.14	16.7	62.6	0.77	4.64	503
KM 1-2	48.8	< b.g.	71.0	24.7	0.81	48.4	0.76	14.4	108	1.08	2.60	1035
KM 2-1	15.4	< b.g.	26.5	3.33	1.04	5.29	< b.g.	7.80	47.9	1.03	2.56	329
KM 4-1	3.61	< b.g.	20.1	0.13	1.60	7.66	< b.g.	7.91	39.2	0.42	1.57	128
KM 5-1	< b.g.	< b.g.	27.1	< b.g.	1.81	10.0	< b.g.	9.42	42.1			106
AMB 1-1	189	2.90	167	43.0	3.15	72.4	3.32	92.0	173	1.97	94.3	3203
AMB 2-1	172	2.73	168	36.4	2.48	69.2	3.23	88.3	176	2.08	86.6	3118
AMB 3-1	16.6	0.4	239	3.03	5.95	46.6	2.00	75.8	130	1.68	11.4	1478
AMB 4-1	198	4.57	179	52.3	4.82	68.8	3.19	83.5	170	1.85	214	3144
AMB 5-1	121	3.35	206	28.8	4.18	60.0	2.73	81.2	154	1.71	114	2546
MD 1-1	56.1	2.58	141	11.4	6.93	24.8	0.86	49.0	65.5	1.24	105	904
KP 1-1	45.0	2.28	122	8.82	6.21	21.5	0.59	43.5	58.3	1.15	96.4	715
TB 1-1	< b.g.	0.24	48.9	< b.g.	4.38	10.9	< b.g.	20.2	24.3	0.24	10.7	100
Unknown use of the waters												
DL 5-1	< b.g.	< b.g.	13.5	< b.g.	2.81	6.16	< b.g.	8.22	25.0	0.78	2.55	20.4
PL 1-1	< b.g.	< b.g.	10.1	< b.g.	2.90	4.91	< b.g.	7.34	15.8	0.26	3.61	11.9
DTD 1-1	< b.g.	< b.g.	5.40	< b.g.	1.58	3.26	< b.g.	5.67	11.1	0.22	1.67	1.0
BW 1-1	< b.g.	2.49	59.6	0.65	24.6	31.8	1.22	86.0	75.5	0.25	56.7	76.0

*) Element concentrations in drinking water that may give rise to complaints from consumers.

a) Guideline for safe drinking water, WHO (1993).

b) Guidelines for safe drinking water, CEC (1980 and 1989).

c) Guideline for irrigation water, Canadian Water Quality Guideline (1995).

< b.g. = concentration above the guideline

The element concentrations, which exceed the guidelines are indicated with a grey colour in Table 6.3, 6.4 and 6.5. In Table 6.5, the element concentrations, which exceed the WHO and irrigation norm, and if this data is not available of the CEC, are indicated with grey.

6.2.2. Essential and non-essential elements for organisms

For most elements maximum acceptable levels are given values to prevent complication of health or death. However, many elements are essential for life of organisms, like the common elements Ca, K, Na, Mg, HCO₃, SO₄, Cl, NO₃ and Si (Edmunds and Smedley, 1996 and Förstner and Wittmann, 1979). Furthermore, F, P, Fe, Zn, Cu, Mn, I, V, Se, Co, Ni, Cr and Mo are essential for human or animal health. The elements Sr, Li, Ba, Rb, La, Be, Sc, Sn, Te and Nb are probably essential for health, but in very low concentrations (Edmunds and Smedley, 1996). The elements As, I, F and Se can give health problems, if the amount taken in is too low. The intake of these elements does not only come from water, what made it very complicated to find a relationship between trace elements and their water chemistry. Arsenic is essential to prevent grow retardation (Thornton, 1996). Iodine is essential to prevent endemic goitre (Edmunds and Smedley, 1996). Se is in very small amount essential to prevent muscular degeneration, impeded growth fertility, anaemia and liver disease (Edmunds and Smedley, 1996). Fluoride is discussed in paragraph 6.2.2.9. It can be concluded that a lot of elements are essential for organisms. However, especially trace elements can give seriously complaints if the concentration becomes too large.

6.2.3. The discussion of the risks of elements

6.2.3.1. pH

Acid water itself is not thought to be a health risk. However, many minerals are more soluble

in acid waters and therefore more toxic elements may be present in acidic water. The mobility of many elements increases in acidic waters (Edmunds and Smedley, 1996). On the other hand, a very low pH prevents normal living of organisms. For that reason, vegetation did not grow in rivers like the Kali Putih (KP1-1) and the R. Maasem (KM4-1).

The Canadian guideline gives an acceptable pH for aquatic life of 6.5. However, the sampled rivers and lakes have pH values far below 6.5. No aquatic life will be expected in waters with a pH of 3.7 or lower (Schallenberg, 1998). However, aquatic life is observed in the Danau Linow (pH is 2.5), where larvae of insects and probably fish were present. Schallenberg mentioned that only very adapted fishes persist at a pH of 3.7; therefore it can be concluded that the aquatic organisms, living in the acid Danau Linow, are adapted to this pH.

The solubility and mobility of toxic metals can be influenced by the pH. If water becomes more acid, metals (e.g. Al, Be, Cd and Pb) become more in solution and are more mobile. A low pH can also decrease the concentrations of elements like Ca and Mg, which can induce heart disease (Edmunds and Smedley, 1996). A decrease of Ca and Mg concentration induces a stronger competition or prevalence of heavy metals (see section 6.1.2.2.).

6.2.3.2. Aluminium

Aluminium exists, as discussed in chapter 5, in many complexes in the aqueous phase in acid waters. The free Al^{3+} and aluminium sulphate complexes are dominant. Aluminium fluoride complexes are formed in significant concentrations if much fluoride is in solution. The amount of Al bound on organic material, like humic acids, is not investigated, but could be significant. Information about the toxicity of aluminium complexes is not found. The WHO and the CEC guidelines set the maximum Al concentration at 200 and 50 ppb, respectively. These guidelines lay close to the detection limit of Al (150 ppb). It can be concluded that many samples exceed these guidelines, especially the samples which are related to (light) volcanic activity. The drinking waters (KM3-1 and DTA1-1) have Al concentration, which are lower than the detection limit. Sample TDS2 has an Al concentration of 820 ppb. This exceeds the guidelines of 200 and 50 ppb and therefore this concentration is dangerous.

The guideline for irrigation water shows a maximum acceptable Al concentration of 5 ppm. With this guideline the waters of DL4-1, LA2-1, MHW2-1, KP2-1, KP3-1 and M4 can be used as irrigation water with respect to the Al concentration. KM6-1 and MHW3-1 can give serious problems because they exceed the norm 4 and 3 times, respectively, but which complication to health can be expected?

The occurrence of high Al concentrations in drinking water has been linked to the development of Alzheimer's disease. However, only a small part of Al intake comes from drinking water. On the other hand, this form has a larger bioavailability and is therefore more harmful than other forms of Al intake, like food (Edmunds and Smedley, 1996). In general, the total Al intake per day is about 20 mg (WHO, 1996). The intake of Al can also cause a decrease of phosphate in human beings, but this is not directly toxic (CEC, 1989).

An Al concentration of 50 ppb is acutely toxic and causes death for some micro organisms (Schallenberg, 1998). A clear negative effect is observed on trouts by an Al concentration of 0.2 ppm (Peereboom and Reijnders, 1989). In general, high aluminium concentrations cause a decrease in fish and amphibian stock (Peereboom and Reijnders, 1989). Swedish research shows that eggs of fish eating birds (living near Al rich waters) are very small and have thin shells (Peereboom and Reijnders, 1989). An aluminium concentration of 0.1 ppm can cause growth retardation for very sensitive plants (Schallenberg, 1998). Roots of trees may be damaged by a high Al concentration in water (Peereboom and Reijnders, 1989).

6.2.3.3. Boron

Boron exist in the water phase mainly as the species H_3BO_3 . In principle, boron is not toxic for human beings (CEC, 1989) and influences on growth are not found; nevertheless, guidelines for boron have been made (Table 6.1). The WHO guideline for boron (300 ppb) is more stringent than the other guidelines (Table 6.1). The samples DL2-1, DL6-1, DL7-1, BW1-1, MD1-1, KP1-1 and the Ambang samples have B concentrations which goes up to 15 times the norm of 300 ppb. However, these samples are not used by the local people and therefore no risks are expected. Problems can be expected for sample TDS2, with a B concentration of 3700 ppb, because one man drank this water every day. The (probable) irrigation waters, DL4-1, RND1-1, NMG, KP3-1 and M4, have higher B concentrations than the norm of 500 ppb, but influences on growth by a exceeding boron concentration are not found (CEC, 1989).

6.2.3.4. Iron and manganese

Iron exists in acid, reducing water mainly as Fe^{2+} (65-90%) and FeSO_4 . In oxidizing waters iron is generally removed from solution by precipitation. Manganese is present as free ion or as MnCl (< 0.5%) and MnSO_4 (5-45%). Edmunds and Smedley (1996) mentioned that iron may form colloidal complexes and manganese is mainly adsorbed on particles, but this is not investigated in this study. There is limited evidence that Mn may be toxic at high concentrations (Edmunds and Smedley, 1996 and CEC, 1989). Despite this hypothesis, strong guidelines are made for manganese. The maximal concentration of manganese for irrigation water is 0.2 ppm for continuous use on every soil (Canadian Water Quality Guidelines, 1995). The irrigation waters MHW1-1 and MHW3-1 exceed the Mn guideline of 0.2 ppm with more than 1.3 ppm. No irrigation waters have iron concentrations above the guideline of 5 ppm. The use of irrigation waters is not risky in respect of these two elements.

The use of the drinking water TDS2 can be more risky, because this sample has an iron and manganese concentration above the guidelines for safe drinking water. In more detail, the concentrations may give rise to complaints from consumers, which should be mainly the taste of the water and the growing of some micro-organism in human beings. Iron holding waters taste like blood (CEC, 1989). The waters KM1-2, MD1-1, KP1-1 and the Ambang samples have higher concentrations of Mn and Fe than the guidelines (Table 6.5). However, they are not used and therefore no direct hazards for humans are expected. Furthermore, in the low active hydrothermal areas Danau Linow and Lahendong, waters have iron concentrations which exceed the guidelines. Most of these waters are not used, and if used no serious problems occur, because iron is not very toxic.

6.2.3.5. The non-toxic element potassium

Potassium exist in acid waters mainly as free ion (>85%) and to a lesser extent as potassium sulphate complexes. Only the CEC gives a guideline for (free) potassium. The K concentration of drinking water TDS2 exceeds this norm of 10 ppm, with 12 ppm (total concentration is 22 ppm). Problems are not expected, because potassium is an essential element and the other guidelines did not give any norms. Sample DL2-1 and BW1-1 also exceed the norm of 10 ppm, but these samples are not used and therefore not riskfull. Potassium is not a risky element in the waters of North Sulawesi.

6.2.3.6. The non-toxic element sodium

Sodium exists in the aqueous phase mainly as free ion and only for a few percent as sodium sulphate. The WHO guideline gives a value of 200 ppm and the CEC a value of 20 ppm before a rise of complaints can be expected. These complaints are mainly the bad taste of the

water, which can be caused by high (> 200 ppm) sodium concentrations (CEC, 1989). All the samples satisfy the WHO guideline, but many samples, also neutral rivers and lakes exceed the CEC guideline. The very stringent CEC norm for sodium is exceeded with a factor up to 5.5. However, no problems are expected with the use of the North Sulawesi water, because sodium is an essential element and the sodium concentration did not exceed the WHO guideline.

6.2.3.7. *The risks of sulphate*

Sulphate is mainly present as SO_4^{2-} and HSO_4^- and to a lesser extent as metal sulphate complexes. Information about dangers of sulphate complexes is not found; therefore it is difficult to make a good estimation about the risks of sulphate and its complexes. However, sulphate is not a very toxic complex, it is an essential element and in normal seawater sulphate concentration of 2700 ppm are found (WHO, 1996). The WHO made a guideline of 250 ppm, while the CEC has, as usual, a more stringent norm with 20 ppm, a norm which is not reachable for (these) natural systems. The drinking water TDS2 has a sulphate concentration of 460 ppm, twice the WHO guideline, and can give complaints if people drink too much of this water. For irrigation water, no guideline is made for sulphate. The use of irrigation water with high sulphate concentrations (> 300 ppm) are therefore not directly harmful. As expected, active hydrothermal areas, like the Danau Linow, Kawah Masem and the Ambang with the river Kali Putih, have sulphate concentrations far above the WHO guideline. The most waters exceed the guidelines 2 to 4 times, except for the Ambang samples which have sulphate concentrations of up to 13 times the guidelines.

6.2.3.8. *The risks of chloride*

Chloride exists as free anion in the aqueous phase. Chloride is a conservative element and does not form much complexes. The guideline of the WHO (for drinking and washing water) gives a norm of 250 ppm, which is not exceeded, while the stringent CEC norm of 25 ppm, is only exceeded by sample TDS2 (Table 6.4). In light active hydrothermal areas, only three 'not used' samples, exceed a chloride concentration of 100 ppm (AMB4-1, AMB5-1 and MD1-1). Problems are therefore not expected for drinking, washing and an used waters.

The irrigation guidelines give a value of 100 ppm for chloride, which is only exceeded by the samples MHW1-1 (160 ppm) and MHW3-1 (270 ppm). Sensitive growth must not be irrigated with water with higher concentrations than 100 ppm, because chloride, taken up by the roots, will be stored in the leaves. Excessive accumulation can cause leaf burning, chlorosis and mortality of twigs (Canadian Water Quality Guidelines, 1995). More chloride tolerate growth can be irrigated with chloride concentrations of up to 700 ppm. MHW1-1 and MHW3-1 exceed the norm of 100 ppm as irrigation water. It is unknown if rice, which is mainly cultivated in these areas, tolerate chloride concentrations of up to 270 ppm. However, most vegetables and cereals are not sensitive for high chloride concentrations. If citrus or avocados are cultivated in the area around sample MHW3-1, growth problems can be expected, because these plants are very sensitive for chloride (Canadian Water Quality Guidelines, 1995).

6.2.3.9. *Health and harmful aspects of fluoride*

Fluoride exists in acid waters mainly as aluminium complexes. The toxicity of these complexes is unknown. The guidelines of the USA give a norm of 800 to 1700 ppb for fluoride that is due to the activity of F, which decreases at lower temperatures (Alloway, 1997 and CEC, 1989). Fluoride is an essential element which is mainly necessary for dental health. Limited growth and decrease of fertility could be expected, if people do not get any fluoride.

When the fluoride concentration is higher than 0.5 ppm, dental caries can happen. Fluoride concentrations from 0.5 to 1.5 ppm promote dental health and result in healthy teeth. Higher fluoride concentrations induce dental fluorosis and from 4 ppm skeletal fluorosis (Edmunds and Smedley, 1996). The drinking waters are good for teeth, because the concentrations lay between 0.2 and 1.5 ppm. High fluoride concentrations are not expected, because dissolved Ca controls the F concentration. A Ca concentration of at least 40 ppm causes a maximum concentration of fluoride of 3 ppm (Edmunds and Smedley, 1996).

For irrigation waters the norm is more stringent than for drinking waters: 1 ppm for continuous use. Fluoride can damage the genetic material of roots or can damage seriously leaves of vegetation (Schallenberg, 1998). Sample MHW3-1 can give problems with growth, because it contains a fluoride concentration of 3.5 ppm.

6.2.3.10. The non-toxic elements calcium and magnesium

Calcium causes no problems in the waters of North Sulawesi. According to the CEC guideline, Ca can give rise to complaints from consumers if the concentration exceeds 100 ppm. The calcium concentration is higher than 100 ppm for the samples DL2-1, MD1-1, KP1-1 and the Ambang samples. These waters are, however, not used as drinking water.

The magnesium concentration in irrigation or drinking waters did not exceed the norm of 30 ppm (CEC, 1980). However, the magnesium concentration of the samples DL2-1, KM1-2 and the Ambang exceed this stringent norm. The exceeding is not more than 2.5 times in these waters. Because these waters are not used, no complaints are expected.

Ca and Mg are important components of the hardness of water. The WHO (1996) gives a norm of 10 to 500 mg/l calcium carbonate. Water with higher calcium carbonate concentrations (harder water) does not cause direct health problems, but the taste of these waters decreases (CEC, 1989). Influences of the hardness of water on the irrigated growth are not found.

6.2.3.11. The volcanic gas H_2S

The WHO gives a guideline for H_2S of 0.05 ppm. H_2S (g) is very toxic, but information about dangers of dissolved H_2S are not found. Waters with concentrations higher than 0.05 ppm are in general not used as drinking water, because they taste badly (CEC, 1989). The volcanic related waters in most cases have mostly H_2S concentrations which are higher than the norm (see Table 9, Appendix II for the H_2S concentrations). Because not all H_2S concentrations are reliable and since the risks of H_2S are unknown, no good indication can be made of the harmful effects of this component.

6.2.3.12. Silica, strontium, bromide and nitrate

For silica no guideline is made. Therefore, it can be expected that this element does not give any problems with health or growth of vegetation. Further, guidelines for the elements Sr and Br are absent. Probably, these elements are not expected to be present in high concentrations, or they are not (very) toxic. The Sr and Br concentrations reach a maximum of 0.25 and 1 ppm, respectively, in the North Sulawesi waters.

Nitrite and nitrate can give problems with health. Nitrite is more toxic than nitrate, but it is changed to nitrate in oxidizing conditions. The WHO guideline for nitrate is 50 ppm, whereas the nitrite concentration might not exceed the 3 ppm. Because the samples have no nitrate concentrations higher than 4 ppm (Table 9, Appendix II), no diseases or stomach cancers are expected, if water is the main intake of nitrate. As known, vegetables can contain high concentrations of nitrate, but this is not investigated in this study.

6.3. Possible hazards of various locations in North Sulawesi

6.3.1. The acid Danau Linow and its polluted surroundings

The Danau Linow has a too low pH to explain animal life. Very adapted fishes can live at a pH of 3.7. Enormous amounts of larvae are observed at the east side of this lake. Despite the high Al, Fe and sulphate concentrations the lake is not dangerous, if this water is not used as drinking water (see sample DL8-1 in Table 6.4). No real dangers are expected, if the outlet waters of the Danau Linow, DL6-1 and DL7-1, and the inlet river DL9-1, are not used as drinking water, which is not the case. The irrigation water DL4-1 gives no problems, despite the four times higher concentration of boron, because boron is not toxic.

Sample DL2-1, a white yellow pool within a rice field, has for nearly all elements to high concentrations to be called safe drinking or irrigation water. Fortunately, it is not used as drinking water. However, water can ooze through the walls of the sods, which causes a rise of the element concentrations in the surrounding rice field. This can give problems with the growth of the rice and if elements accumulate in this rice, it can give problems with human health. More research on this rice field is recommended, especially on the elements Al, B, Fe, Mn, F and sulphate.

6.3.2. The polluted rice fields in Lahendong and high concentration discharge rivers

Small fumaroles have polluted the rice fields south of the Lahendong area at a few locations. Sample LA2-1 is taken from an polluted rice field, but the increased concentration of Al and Fe may not give problems, because the concentration did not exceed the irrigation guidelines. The discharge river of the Lahendong, LH2-1, has high concentrations of Al, Fe and fluoride and exceeds the irrigation guideline for these elements. The use of this water is unknown, probably it only drains the Lahendong area. However, children washed themselves with this water and then the high sulphate concentration can give rise to complaints. The B concentration of the neutral river RND1-1 (2.6 ppm) was higher than the guideline (0.5 ppm). Problems are not expected, however, because boron is not toxic.

6.3.3. The acid Kawah Masem crater lake and the high aluminium concentration of the river R. Maasem

As expected, the Kawah Masem crater lake contains element concentrations which exceed the guidelines of safe drinking or irrigation water; especially the Al, Fe, Mg, Mn and sulphate concentrations (Table 6.5) are too high. However, the water of this crater lake is not used and therefore no risks are expected. Furthermore, no risks are expected for the water KM2-1, despite the high aluminium concentration, because this water is not used. Fortunately, the drinking water KM3-1 has no harmful concentrations of any element.

More downstream of the R. Maasem, a high concentration of aluminium in sample KM6-1 can give growth problems for vegetation, if this water is used as irrigation water, and for the animals, which use this water for washing and drinking. The local people did not drink the water of sample KM7-1, because they think that the water contains high sulphate concentrations. However, the sulphate concentration in this season is 110 ppm, while the WHO and CEC guidelines permit concentrations of 250 ppm and 25 ppm, respectively.

6.3.4. The polluted irrigation waters of the Mahawu volcano

MHW1-1 is certainly used as irrigation water, while the other two samples are probably used as irrigation water. MHW1-1 has too high Mn and Cl concentrations, 1.6 ppm instead of the recommended 0.2 ppm and 160 ppm instead of 100 ppm, respectively. A high Mn concentration can cause an accumulation in the vegetation. A high chloride concentration causes, in excessive concentrations, leave burning, chlorosis and mortality of twigs (Canadian Water Quality Guidelines, 1995). MHW2-1 can be used safely as irrigation water, but MHW3-1 has too high Al, Mn, F and Cl concentrations, which can decrease the grow of vegetation seriously and cause damage to roots and leaves.

6.3.5. The Tondano lake and the acid, polluted lake TDS2

The Tondano lake has element concentrations, which are below the guidelines for safe drinking water and therefore, it can be used safely as drink water (Table 6.4). More risks are expected at the hot lake TDS2, south of the Tondano lake. The water contains too high concentrations of Al, B, Fe and sulphate to be safe drinking water. The high aluminium concentration can promote Alzheimer disease, while the other elements may give rise to complaints.

6.3.6. The very polluted waters of the active hydrothermal Ambang mountains

The element concentrations in the samples AMB1-1 to AMB5-1, and BW1-1 exceed the guidelines many times (Table 6.5). However, no real risks are expected, because the waters of this lightly active hydrothermal area are not used. Fortunately, the drinking water of the spring DTA1-1 is not harmful; only the sulphate concentration exceeds the very stringent norm of the CEC, while it is still far below the WHO guideline (Table 6.4).

6.3.7. The polluted Kali Putih and its use for irrigation

The Kali Putih is the discharge river of the Ambang mountains and contains high element concentrations, which decrease on going downstream, after dilution by several rivers. The river is not used as irrigation water, fortunately, in the upper region of the Kali Putih, because the concentrations of Al, B, Fe, Mn, F and sulphate in sample MD1-1 and KP1-1 exceed the guidelines. It is unknown where the Kali Putih is used for irrigation; probably after the dilution with the T. Tabongon. However, it is sure that KP3-1 is used for irrigation. The water of the KP3-1 contains only a slightly too high boron concentration, according to the irrigation guideline (Table 6.3). Therefore, the irrigation water KP3-1 (and KP2-1, M4) can be used safely as irrigation water. However, if the concentration of Al and B become higher in other seasons, the waters must be used with some care.

The small inlet (TM1-1) from the sawas, which enters the Kali Putih at sample location MD1-1, has no element concentrations which exceed the safety guidelines. However, sediment analysis shows a remarkable high concentration of Ni, Zn, La and V in respect of the other sediments of North Sulawesi (paragraph 4.2.8.). Probably, the small river contains elevated concentrations of these elements, which could not be detected with ICP-AES, but could be harmful if they exceed the guidelines for safe water (Table 6.1).

It can be concluded that the irrigation waters taken from the Kali Putih are not directly harmful, but, ions can probably accumulate in these acid soils, because of the large amount of irrigation water used and the high amount which vaporizes in this tropical climate. On the other hand, this irrigation water is diluted by large amounts of rain.

6.4. Conclusions and recommendations

Guidelines are used to determine whether the element concentrations of the North Sulawesi samples exceed the safety norms or not and to predict harmful effects, when these waters are used as drinking, washing, fishing or irrigation water. The use of these guidelines, which are made for general use or specific areas, gives problems, because test conditions of the guidelines are different from that of the field situation. These differences can be present for the pH, Eh, ionic strength, hardness of water, the amount of bioaccumulation of elements in organisms, the adaptation of organisms and the kind of organisms. These differences between the field and laboratory situation makes it difficult to determine the real dangers of the volcanic waters to humans, animals and vegetation.

It can be concluded that aluminium is the most dangerous element in North Sulawesi, when its concentration exceeds the safety guidelines for drink or irrigation water. Alzheimer disease can occur if much water with high concentrations of Al is used as drinking water. High Al concentrations can also limit the growth of irrigated growth. Furthermore, aluminium can be harmful for aquatic biota and consumers of aquatic biota.

Boron exceeds the guideline in several irrigation waters, but clear risks are not expected, because boron is not very toxic. The concentrations of iron and manganese exceeded the guidelines mainly in the volcanic waters, however, clear dangers are not expected, because the main effect of elevated concentrations of iron and manganese is a bad taste of the water.

Because fluoride never exceeded the 1.5 ppm guideline in drinking waters, no dental risks are expected. Otherwise, concentrations up to 1 ppm can cause problems for lower organisms, like vegetation and micro-organisms. High chloride concentration can retard the growth of vegetation, or can give, in excessive concentrations, leaf burning, chlorosis and mortality of twigs. The toxicity of sulphate is low and therefore no large risks are expected. Moreover, waters with very high sulphate concentrations are seldom used.

The elements Ca, K, Mg, Na, Si, S(II), Sr, Br and the component nitrate are not harmful in the North Sulawesi samples. For a real risk analysis it is recommended to analyse elements like Ba, Be, Cr, Co, V, Ni, Cu, As, Se, Cd, Pb, Sb, Mo, Hg and Zn with ICP-MS, to compare these concentrations with the guidelines for safe drinking and irrigation water, with a main attention to Zn, Cu, Cd and Pb (Förstner and Wittmann, 1979).

In general, the waters of North Sulawesi are not dangerous, because they have low concentrations of harmful elements, like Al, B, Fe, Mn, F, Cl and sulphate. Moreover, waters which contain high concentrations of harmful elements are in most cases not used, like the Ambang waters, the Kawah Masem crater lake water, rivers around the Danau Linow and Lahendong and the upper part of the Kali Putih. The most extreme composition, found in sample DL2-1, is also not used, but if these water seeped through the soils of the pool the surrounded rice field becomes polluted. Large scale problems are thus not expected, only small scale problems, like small fumaroles in rice fields.

MHW1-1 and MHW3-1 can give problems if they are used as irrigation water, because they have high chloride and manganese concentrations and sample MHW3-1 also has high aluminium and fluoride concentrations. The use of water KM6-1 for irrigation and drinking will be dissuaded, because it contains too high aluminium, iron and sulphate concentrations. Further, the use of TDS2 as drinking water will be dissuaded, because it contains too high concentrations of Al, B, Fe and SO_4^{2-} . The use of the Danau Linow is unknown, but for safe water it contains too high concentrations of Al, Fe and sulphate. Despite these elevated concentrations and the pH, fish and larvae are still living. The use of the irrigation water KP3-1 is safe, but variations in the elements concentrations due to variations with the season can occur; then Al and B could exceed the guidelines.

7. Conclusions

The volcanic active area North Sulawesi was investigated in July 1997. Locations with hydrothermal activity that were visited for this study include: the Danau Linow and Lahendong, the Kawah Masem crater lake and its river R. Maasem, the southern area of the Tondano lake, Mahawu volcano and the Ambang mountains with Kali Putih river.

The waters of North Sulawesi can be subdivided into four groups: acid and neutral waters, with high or low sulphate or chloride concentrations. Of the acid waters, sample MHW3-1 from Mahawu is the only 'chloride rich' sample. High sulphate concentrations were found in the waters of Ambang and the Kawah Masem crater lake. A small pool near the Danau Linow (DL2-1) contains the highest sulphate concentration, and also has the highest concentrations of other elements, especially Al, Ca, Fe, Mg and Mn. A very low concentration of chloride forms an exception. The most remarkable neutral river is the Royongan Ranoraindang, which has sulphate, chloride and cations concentrations comparable to the acid rivers Kali Putih and Sosoan Rayon (MHW3-1).

The volcanic waters of North Sulawesi are mainly formed by rainwater, which is injected by magmatic gases, like SO_2 , H_2S , CO_2 and some HCl, and obtains high element concentrations by dissolution of minerals. The chloride-rich samples around the Mahawu probably derive their water from the Mahawu crater lake or from a chloride rich spring on the flank of the volcano. Waters with a very low content of ions are mainly composed of rainwater that may have interacted with rocks and minerals.

The modelling of the volcanic waters of North Sulawesi with SOLVEQ gives insight into the behaviour of aqueous species of elements and the degree of saturation of minerals in solution. Si, B and S^{2-} are completely present in the water phase as SiO_2 , H_3BO_3 and H_2S , respectively. Chloride is mainly present as free ion and slightly in complexes as CaCl^+ and MgCl^+ . Sulphate is mainly present as SO_4^{2-} and as HSO_4^- , and less in the Ca, Fe, Mn and Al complexes. The concentration of the SO_4^{2-} complex and free H^+ increases with increasing pH at the cost of HSO_4^- . Fluoride exists as free ion in neutral waters in the absence of aluminium, but in acid waters fluoride exists mainly as AlF^{2+} and less as AlF_2^+ complex. Aluminium exists in the acid waters as free ion, AlF^{2+} and sulphate complex, but in the neutral samples (KP3-1 and M4) aluminium is still in solution as hydroxide complexes. Cations are mainly present in solution as free ions and sulphate complexes, and less as chloride complexes. The percentage of free ions increases with increasing pH.

Mineral saturation modelling shows that all the waters are supersaturated in silica minerals, like chalcedony, cristobalite, quartz and sometimes amorphous silica. The redox state of the water is controlled by the amount of dissolved H_2S or O_2 . When the redox potential is controlled by H_2S , pyrite and native sulphur may be supersaturated, but when the redox potential is controlled by oxygen, pyrite and native sulphur cannot be present, while hematite may become supersaturated. Thus, the saturation of hematite, pyrite and native sulphur is vided dominated by the redox potential, while the saturation of other minerals is mainly dominated by the pH and to a lesser extent by temperature. Acid waters become supersaturated in K-feldspar, muscovite, clay-minerals and kaolinite, when they are diluted, and undergo a pH increase and an increase of Eh by change of the redox couple from H_2S to O_2 .

The waters of North Sulawesi have been compared with guidelines for safe drinking and irrigation water to investigate risks from the use of these waters. The most hazardous element

is aluminium, the values of which often exceed guideline values in many acid waters. Possible effects of toxic levels of aluminium include Alzheimer disease or limited growth of irrigated vegetation. Further, Al can be harmful for aquatic biota and consumers of aquatic biota. Other elements, like B, Fe, Mn, SO₄, F and Cl, exceed the guidelines only in a few occasions. Serious problems are not expected, because guideline values are not significantly exceeded. For final conclusions concerning the quality of hydrothermal waters in North Sulawesi, a formal toxicological risk assessment is recommended.

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Maps

Map 1A, 6, 7 and 9 are modified from G.L.L. Kemmerling (1923) De vulkanen van den Sangi-Archipel en van de Minahassa, Vulkanologische mededeelingen No. 5, maps XII - XVIII. Map 1B and 2 are modified from the Kleine Schoolatlas der gehele aarde, Bos, P.R. and Balen van, C.L., J.B. Wolters Groningen, 1965.

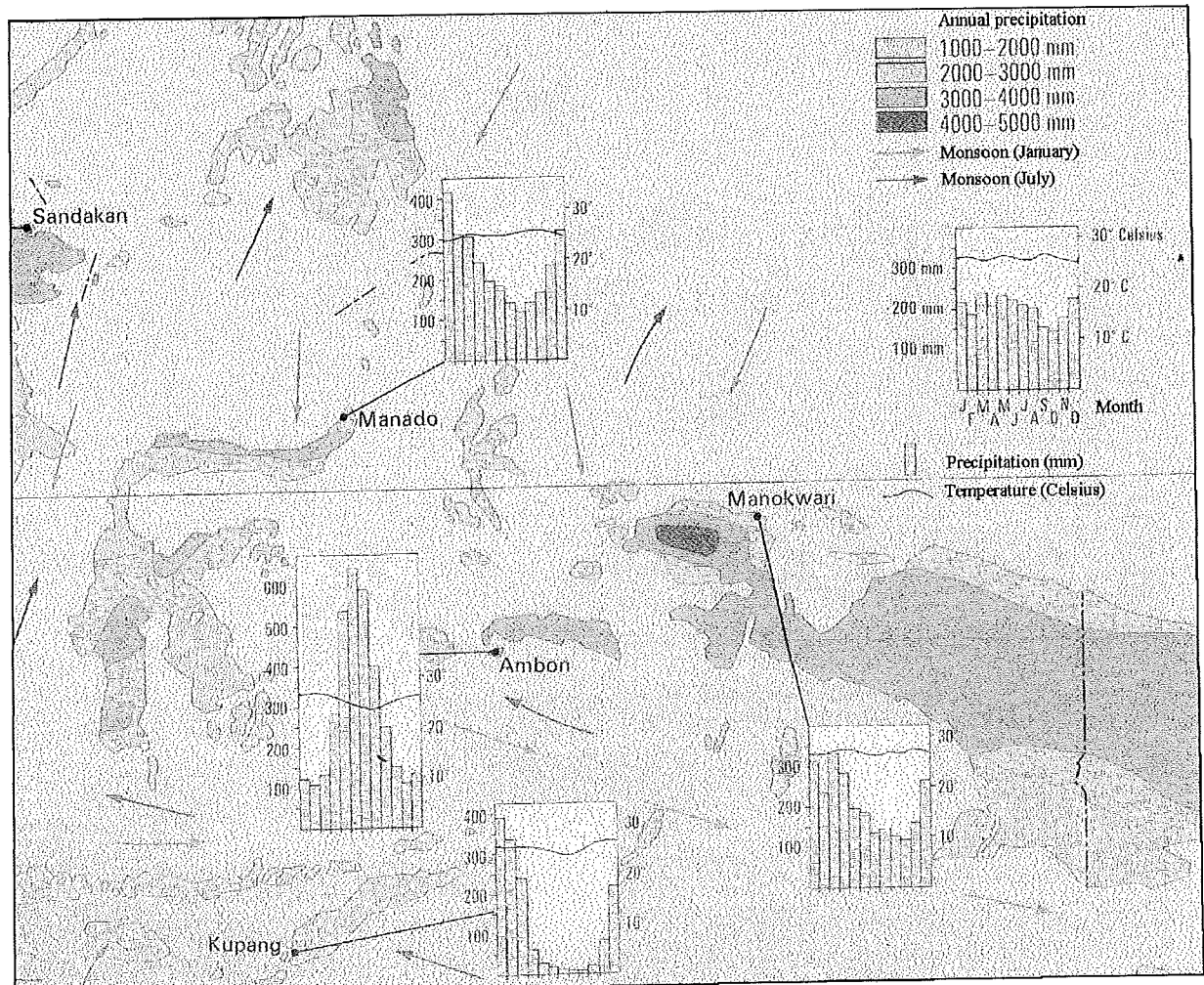
Map 3, 4, 5, 8, 10 and 11 are modified from the Peta Rupabumi Indonesia maps, first edition (1991), sheets Manado (2417-23), Langowan (2417-21), Tanawangko (2417-14), Bilalang (2316-64), Kotamobagu (2316-62), and Amurang (2417-12).

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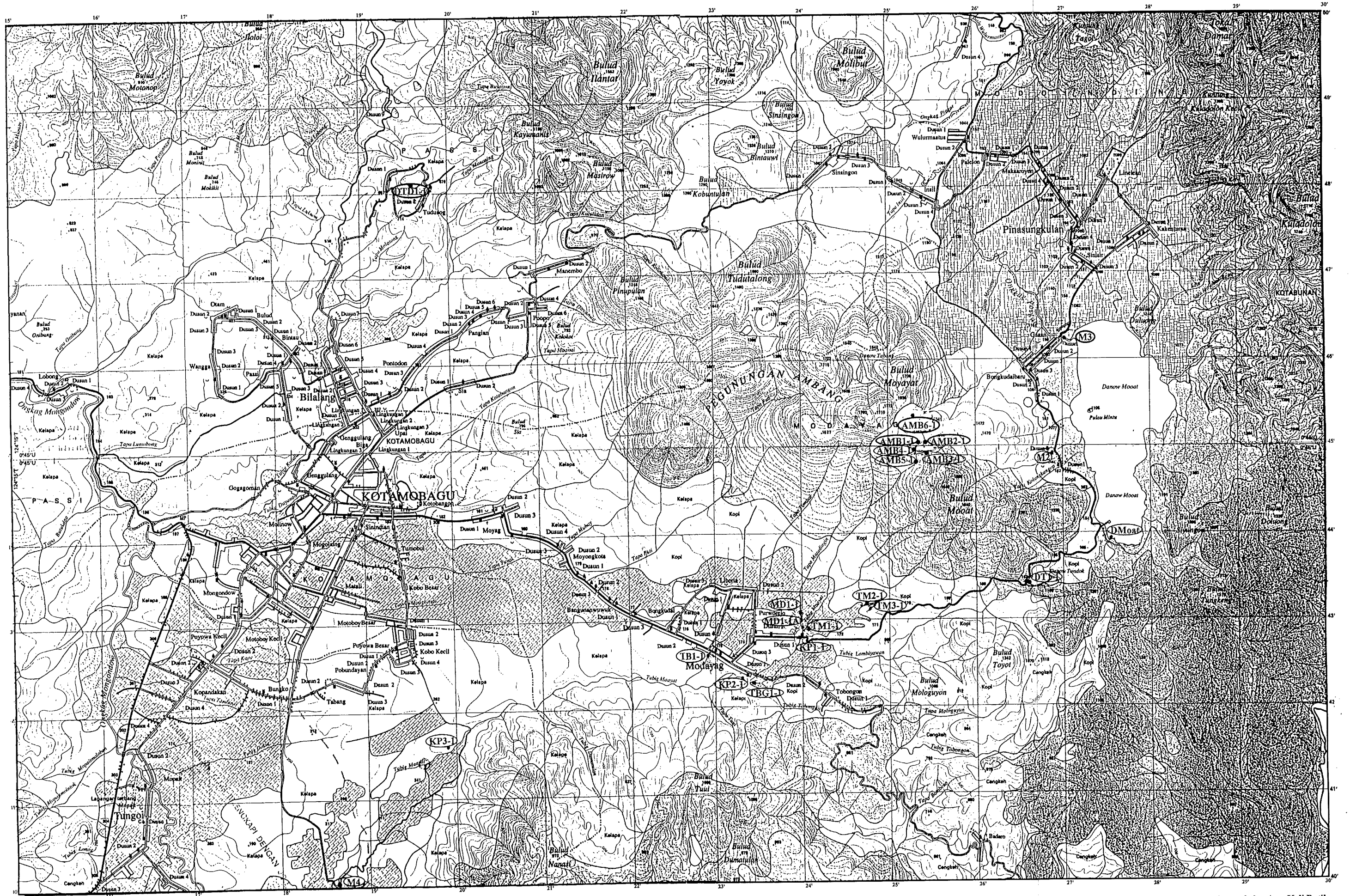
Appendix I

Maps of North Sulawesi



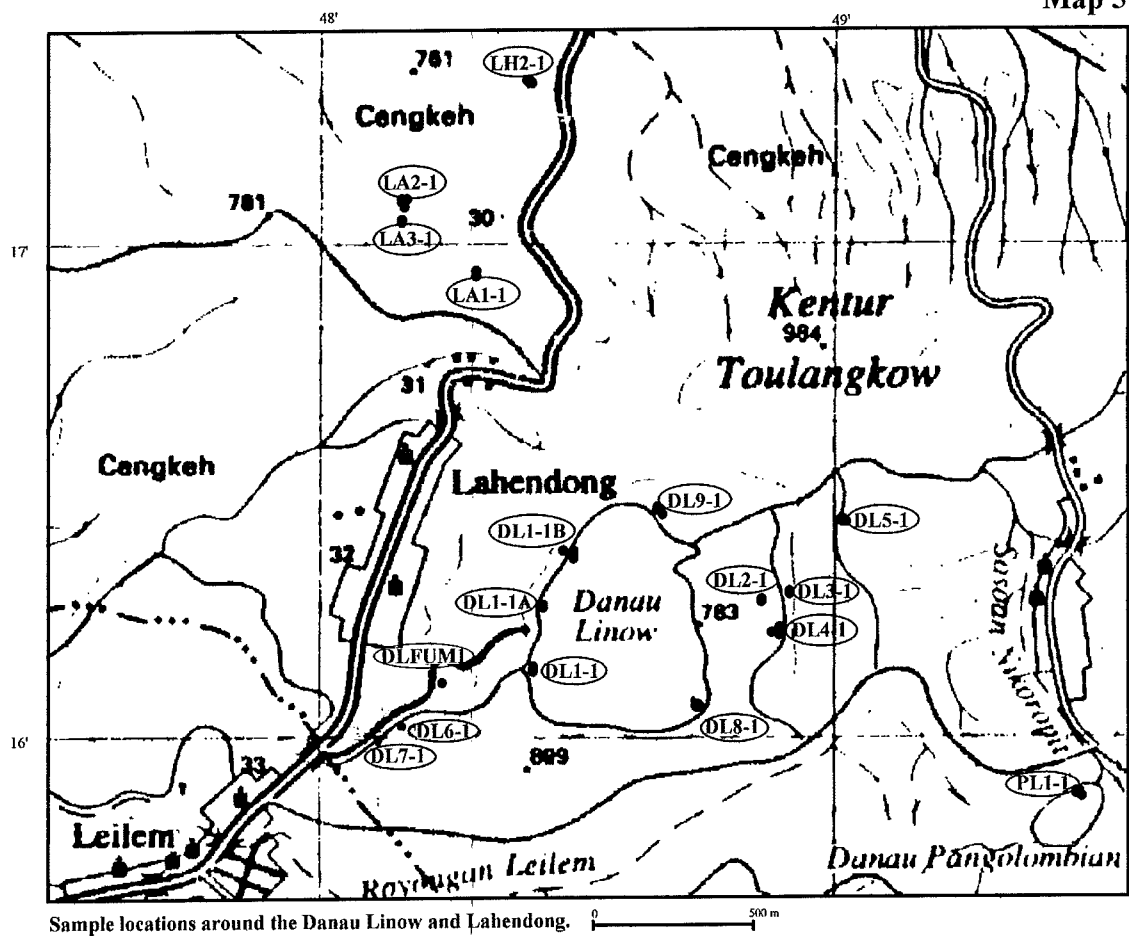
Climate map of east Indonesia.

Map 2



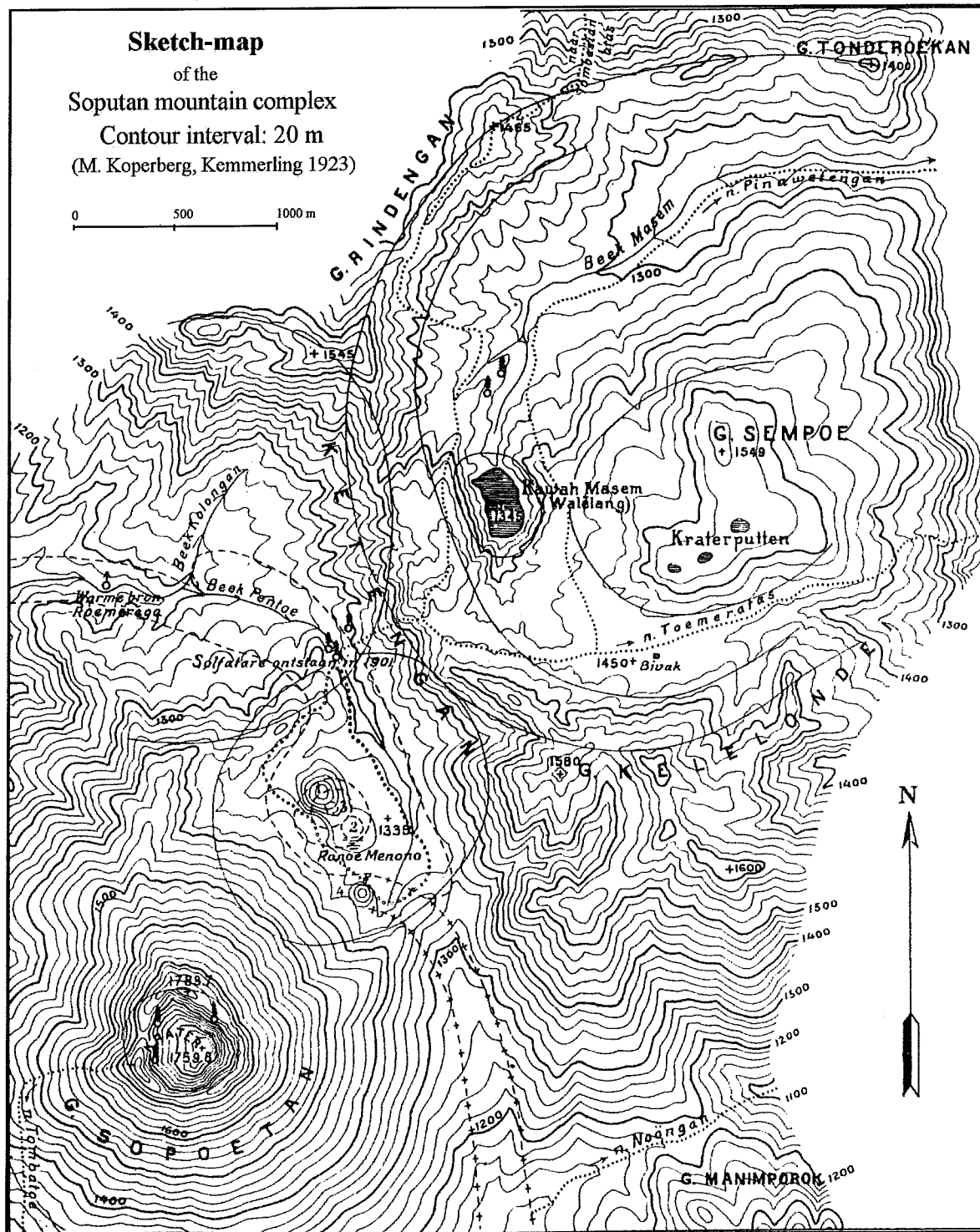
Keymap of the Ambang mountain complex and the river Kali Putih.
The sample locations are indicated on the map.

Map 5



Sample locations around the Danau Linow and Lahendong.

Map 6








♂ Fumaroles

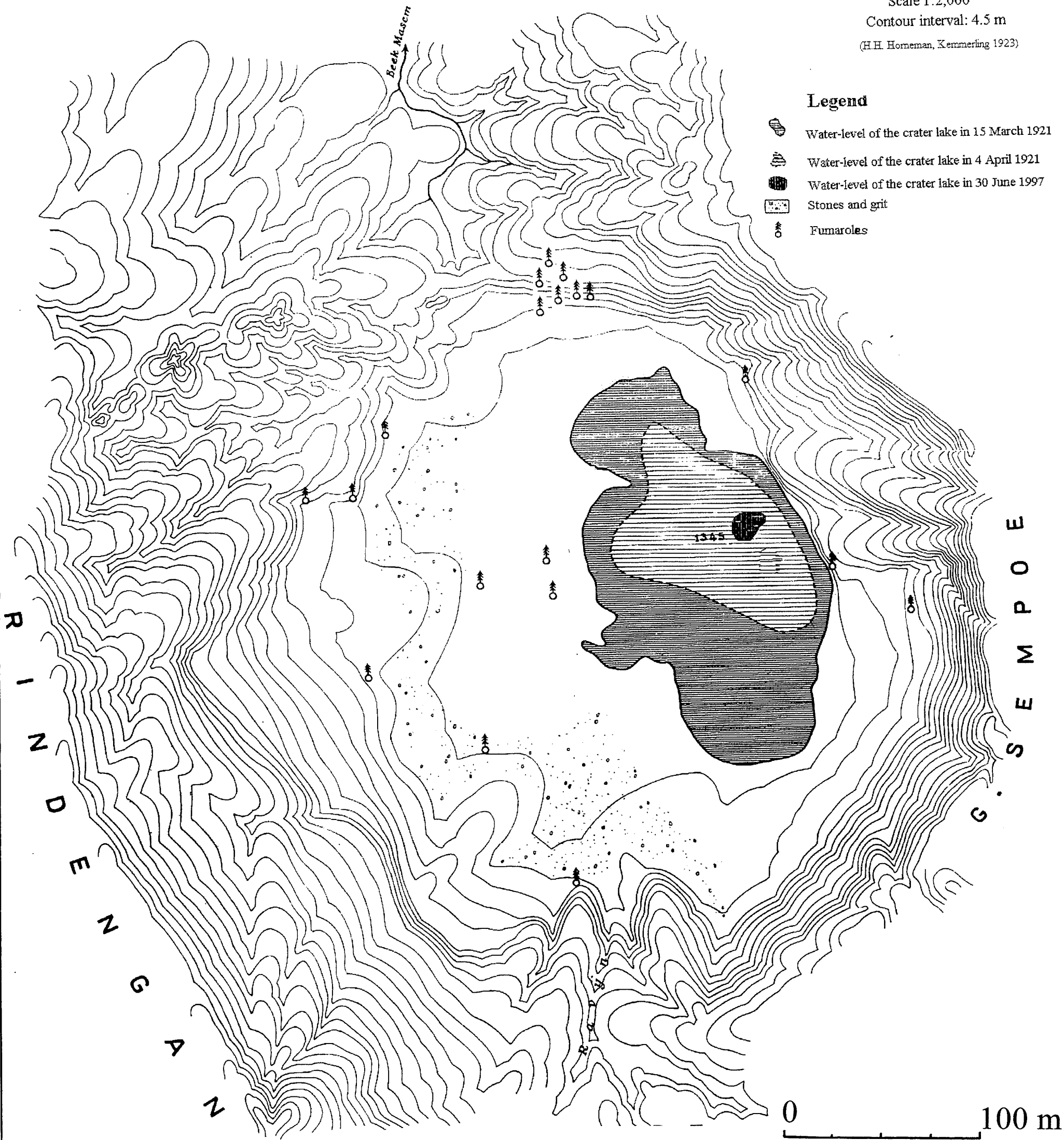
Sketch-map
of the
Kawah Masem crater

Scale 1:2,000
Contour interval: 4.5 m

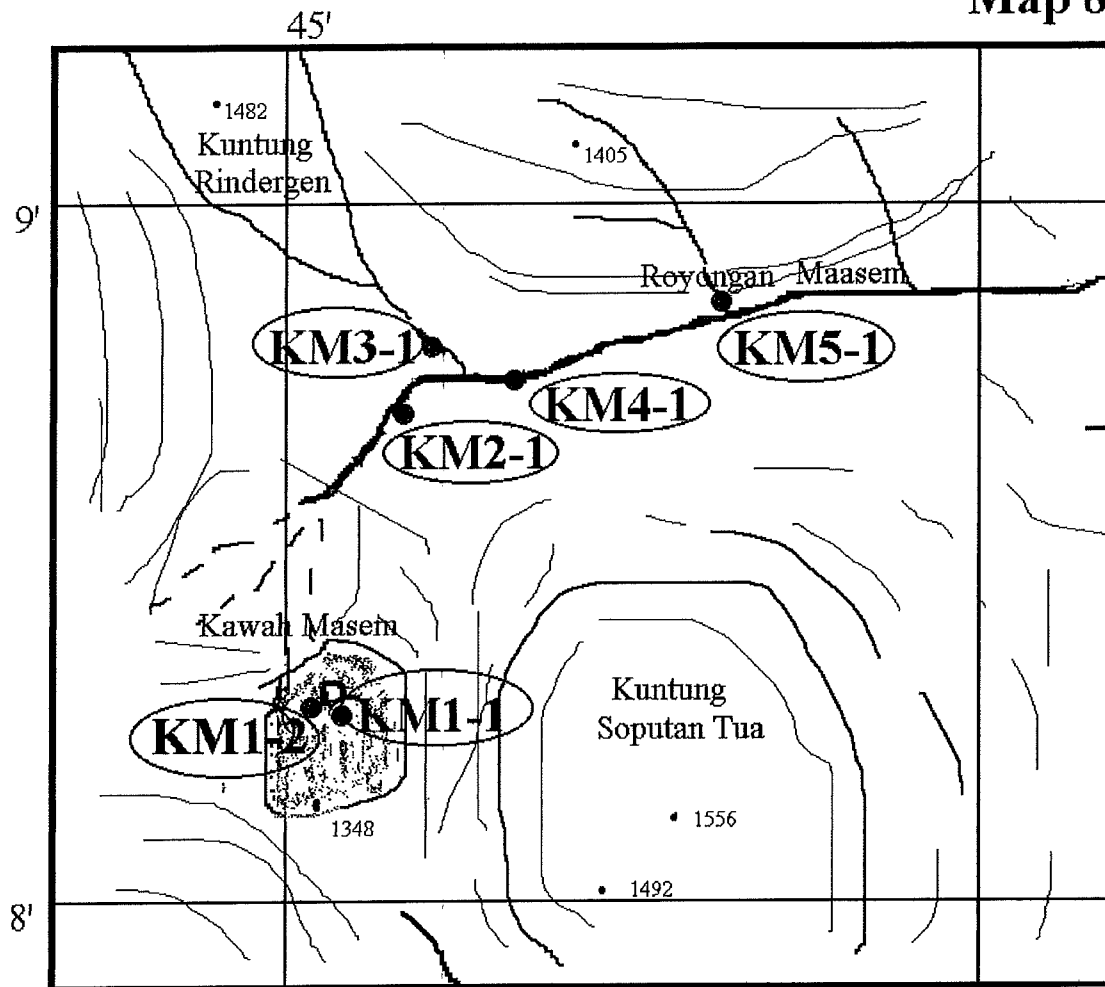
(H.H. Horneman, Kemmerling 1923)

Legend

-  Water-level of the crater lake in 15 March 1921
-  Water-level of the crater lake in 4 April 1921
-  Water-level of the crater lake in 30 June 1997
-  Stones and grit
-  Fumaroles



Map 8



Sample locations near the Kawah Masem.

46'

0 500 m

Sketch-map

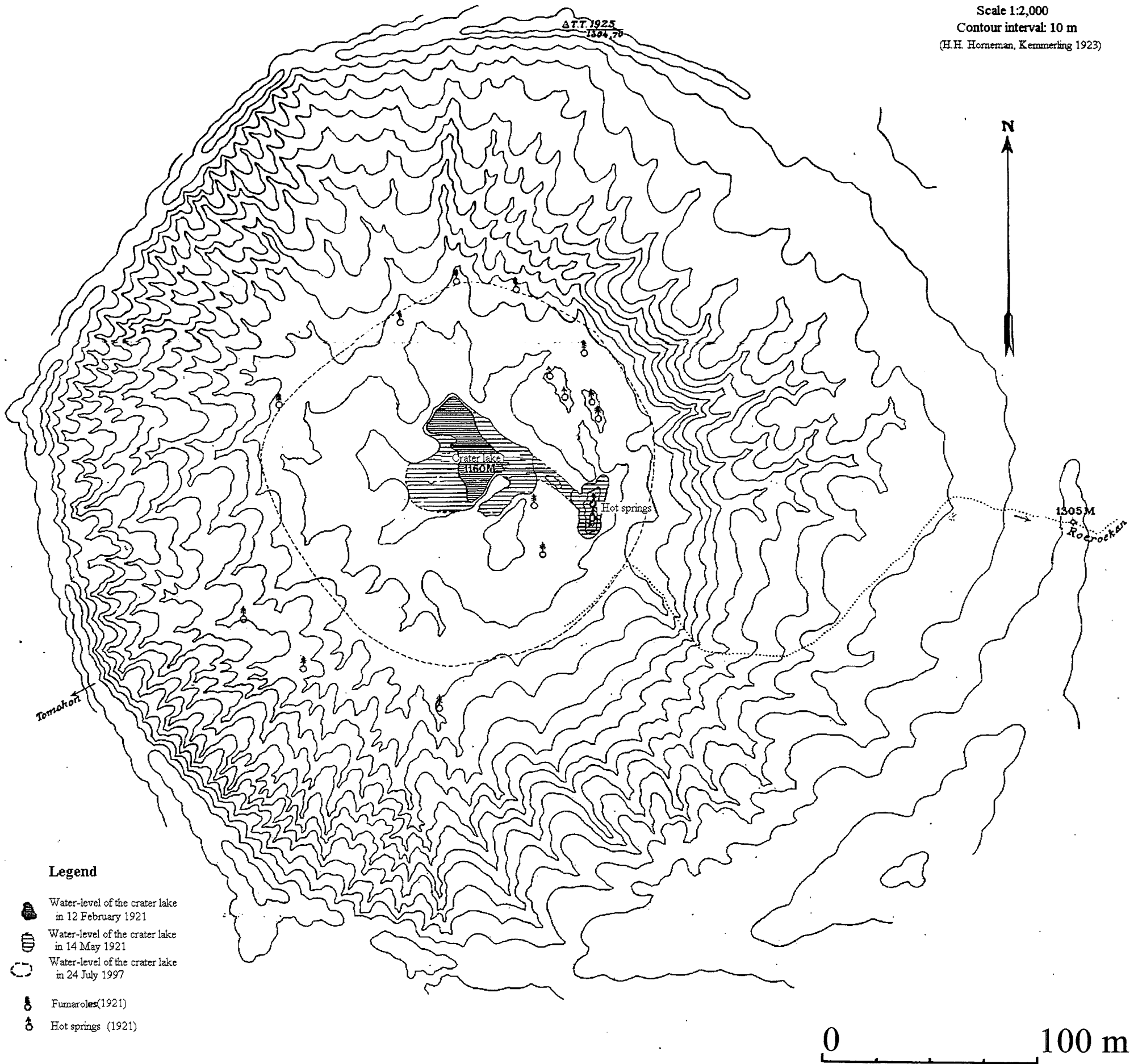
of the

G. Mahawu crater

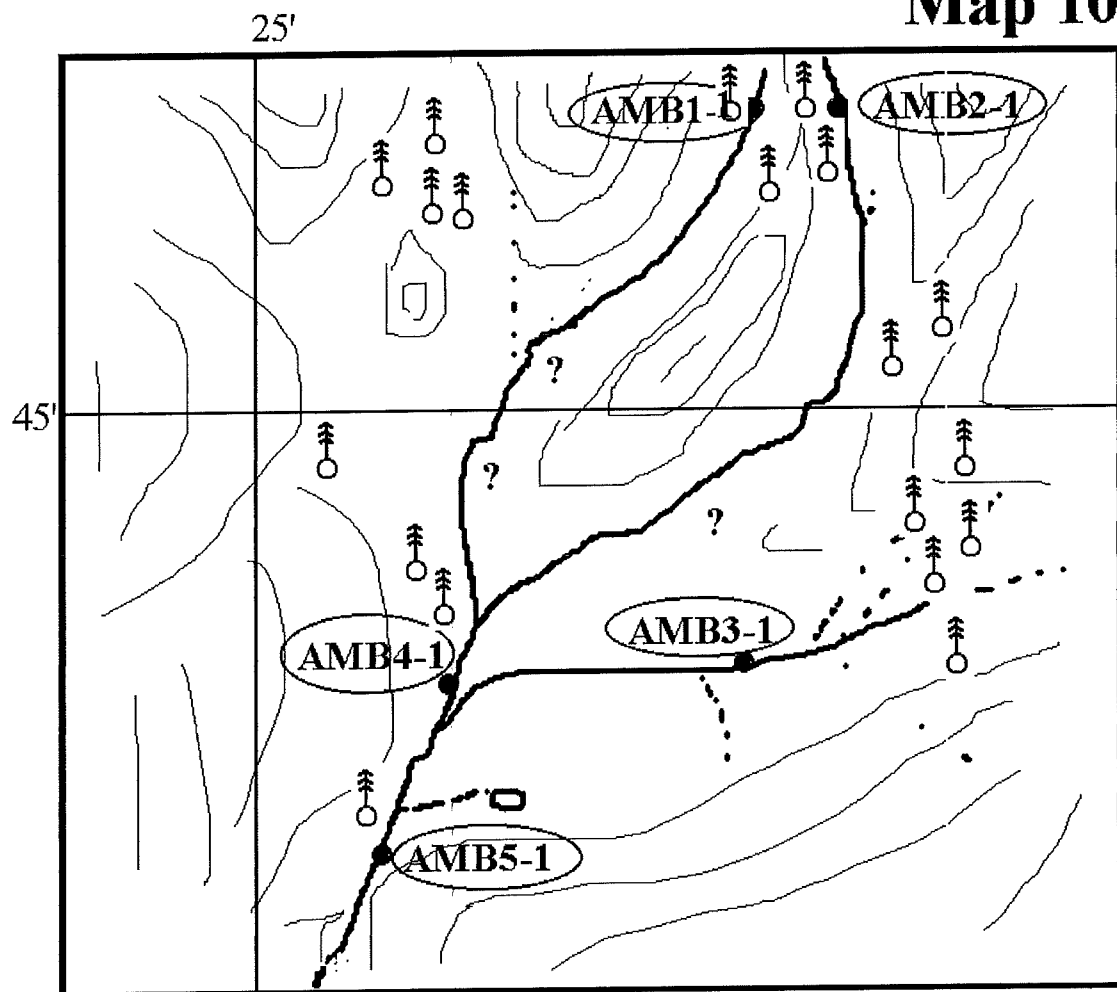
Scale 1:2,000

Contour interval: 10 m


(H.H. Horneman, Kemmerling 1923)



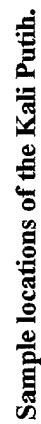
Map 10



Sample locations of the Ambang.

 Fumaroles and hot springs.

0 300 m



Kali Putih = Tapa Matanging and Tubig Maayat (from KP2-1)

Appendix II

Tables

Table 1

Variation in chemical composition of seven samples measured with the use of the ICP-AES (in ppm).

	added acid	dilution	Al	B	Ca	Fe	K	Mg	Mn	Na	S	Si
Detec. lim.			0.15	0.15	0.20	0.05	0.30	0.05	0.05	0.10	0.25	0.10
DL 1-1			3.86	0.17	13.5	9.19	3.61	5.85	< b.g.	13.8	92.5	28.6
DL 1-1			3.80	< b.g.	13.4	9.11	3.63	5.85	< b.g.	13.7	92.9	28.1
DL 4-1			0.63	2.06	37.7	3.68	30.0	14.7	0.17	79.5	107.7	76.8
DL 4-1		2x	0.49	1.74	36.9	3.00	28.2	13.6	< b.g.	72.5	107.2	80.5
DL 7-1			32.8	0.68	39.4	23.8	6.24	16.6	0.53	27.1	228.1	49.1
DL 7-1		3x	32.2	< b.g.	38.8	22.1	5.68	15.3	< b.g.	24.8	229.3	54.1
KM 1-1	NA		41.8	< b.g.	74.3	23.7	1.34	48.9	0.76	14.4	348.8	109.5
KM 1-1			39.6	< b.g.	69.3	22.2	1.27	45.3	0.66	13.7	326.5	103.2
KM 1-1			39.9	< b.g.	68.4	21.8	1.20	45.1	0.75	12.9	334.4	109.9
KM 1-1		4x	38.6	< b.g.	67.1	19.6	< b.g.	43.4	< b.g.	12.4	329.7	107.4
KP 1-1		3x	45.3	2.03	124.5	8.09	5.82	21.3	< b.g.	42.7	254.4	61.8
KP 1-1			43.3	2.25	117.9	8.69	5.98	20.5	0.58	41.1	239.2	57.6
KP 1-1	HCl		43.8	2.30	118.5	8.75	5.90	20.6	0.59	41.5	241.8	58.1
KP 1-1			45.9	2.39	125.2	9.28	6.63	22.5	0.58	45.8	250.5	56.7
KP 1-1			46.7	2.42	126.0	9.29	6.74	22.8	0.59	45.8	251.5	57.2
AMB 5-1			120.9	3.35	205.3	31.8	5.31	62.4	2.73	85.1	849.2	150.4
AMB 5-1		10x	120.7	< b.g.	205.8	25.7	3.06	57.6	< b.g.	77.3	889.1	157.9
AMB 6-1			< b.g.	< b.g.	13.3	< b.g.	3.92	3.01	< b.g.	9.53	15.8	48.3
AMB 6-1			< b.g.	< b.g.	13.8	< b.g.	3.81	2.91	< b.g.	9.16	17.5	53.9
AMB 6-1			< b.g.	< b.g.	13.0	< b.g.	3.55	2.72	< b.g.	8.64	16.2	50.1
AMB 6-1	HCl		< b.g.	< b.g.	13.1	< b.g.	3.57	2.73	< b.g.	9.05	17.2	50.7

NA = not acidified

= measured above the gauge line

< b.g. = below detection limit

Table 2

Anions concentrations measured with ion chromatograph (in ppm).

	F	Cl	Br	NO3	SO4
DL 1-1	n.a.	4.4	n.a.	0.26	245
DL 1-1A	0.18	4.6	0.13	0.85	309
DL 1-1B	0.11	3.7	0.08	1.6	270
DL 2-1	n.a.	14.2	0.90	1.2	6560
DL 4-1	n.a.	36.5	0.09	0.18	264
DL 5-1	n.a.	2.77	0.06	0.05	20.2
DL 6-1	n.a.	37.9	0.10	0.23	594
DL 7-1	n.a.	35.2	0.08	0.75	640
DL 8-1	n.a.	4.2	0.05	0.16	288
DL 9-1	n.a.	1.2	n.a.	0.30	488
LA 1-1	n.a.	0.88	n.a.	n.a.	7.4
LA 2-1	n.a.	0.15	0.01	0.14	57.2
LA 3-1	n.a.	0.72	n.a.	n.a.	19.8
LH 2-1	n.a.	2.8	0.17	1.3	343
RND 1-1	0.04	72.3	0.06	0.29	209
RNE 1-1	n.a.	n.a.	n.a.	0.02	12.0
NMG 1-1	n.a.	22.8	0.02	0.01	45.6
NMG 2-1	n.a.	25.2	0.04	n.a.	50.8
NMG 3-1	n.a.	25.2	0.05	n.a.	49.5
KM 1-1	n.a.	n.a.	0.05	0.72	1014
KM 1-2	n.a.	n.a.	n.a.	0.60	1016
KM 2-1	n.a.	0.25	n.a.	0.27	322
KM 3-1	n.a.	1.7	n.a.	n.a.	23.4
KM 4-1	n.a.	1.1	n.a.	0.28	121
KM 6-1	n.a.	3.8	n.a.	0.79	278
KM 7-1	n.a.	5.0	0.03	0.12	101
MHW 1-1	0.54	155	0.12	n.a.	282
MHW 2-1	n.a.	53.0	0.05	0.92	74.0
MHW 3-1	n.a.	232	0.38	n.a.	111
TDS 2	n.a.	97.8	0.20	0.16	373
TDO 1	n.a.	17.4	0.02	n.a.	22.2
DB 1-1	n.a.	8.5	n.a.	0.44	18.7
PL 1-1	n.a.	3.6	n.a.	0.20	12.0
AMB 1-1	n.a.	79.0	1.1	1.5	3080
AMB 2-1	n.a.	74.0	n.a.	n.a.	3000
AMB 3-1	n.a.	6.0	n.a.	1.6	1425
AMB 4-1	n.a.	189	n.a.	n.a.	3020
AMB 5-1	n.a.	100	n.a.	n.a.	2490
DTA 1-1	n.a.	1.3	n.a.	0.05	46.4
MD 1-1	n.a.	99.4	0.14	1.6	724
TM 1-1	n.a.	4.0	0.01	0.04	90.4
TM 2-1	n.a.	1.2	0.02	0.01	14.4
KP 1-1	n.a.	91.5	0.10	3.2	690
TBG 1-1	n.a.	2.1	n.a.	0.20	34.2
KP 2-1	n.a.	17	0.04	1.2	140
TB 1-1	n.a.	8.9	0.01	n.a.	94.4
KP 3-1	n.a.	18.3	0.02	0.25	105
M 4	n.a.	19.9	0.04	n.a.	120
DMoat	n.a.	0.7	0.02	0.01	3.9
M 3	n.a.	0.7	0.01	n.a.	3.3
DTD 1-1	n.a.	1.4	n.a.	0.06	1.0
BW 1-1	0.16	52.9	0.05	2.0	72.5

n.a. = not detected

Table 3

Fluoride concentrations measured with ISE.

sample	concentration ppm	standard deviation	number of measurements
DL 1-1	0.49	0.03	3
DL 1-1A	1.71	0.12	2
DL 1-1B	1.42	0.25	3
DL 2-1	3.83	0.48	3
DL 4-1	0.61	0.07	2
DL 5-1	0.78	0.40	2
DL 6-1	1.99	0.64	2
DL 7-1	1.55	0.40	3
DL 8-1	0.70	0.14	3
DL 9-1	0.77	0.04	2
LA 1-1	0.37	0.13	4
LA 2-1	0.28	0.02	2
LA 3-1	0.27	0.02	2
LH 2-1	1.41	0.04	2
RND 1-1	0.44	0.10	3
RNE 1-1	0.37	0.00	2
NMG 1-1	0.34	0.01	3
NMG 2-1	0.39	0.02	2
NMG 3-1	0.39	0.01	2
KM 1-1	2.45	0.95	3
KM 1-2	0.62	0.10	3
KM 1-2	1.53	0.28	3
KM 2-1	0.57	0.08	2
KM 2-1	1.31	0.18	2
KM 3-1	0.34	0.01	3
KM 4-1	0.42	0.12	3
KM 6-1	0.61	0.15	3
KM 7-1	0.50	0.04	2
MHW 1-1	0.59	0.19	3
MHW 2-1	0.94	0.63	2
MHW 3-1	3.53	0.96	3
TDS 2	1.42	0.68	4
TDO 1	0.34	0.14	4
DB 1-1	0.31	0.16	2
PL 1-1	0.26	0.13	2
AMB 1-1	1.97	0.92	3
AMB 2-1	2.08	0.43	3
AMB 3-1	1.68	0.27	3
AMB 4-1	1.85	0.35	3
AMB 5-1	1.71	0.16	2
DTA 1-1	0.34	0.02	2
MD 1-1	1.24	0.64	2
TM 1-1	0.32	0.00	2
TM 2-1	0.30	0.00	2
KP 1-1	1.15	0.16	3
TBG 1-1	0.26	0.17	2
KP 2-1	0.22	0.04	3
TB 1-1	0.24	0.13	2
KP 3-1	0.22	0.04	3
M 4	0.22	0.08	3
DMoat	0.19	0.06	3
M 3	0.21	0.09	3
DTD 1-1	0.22	0.07	2
BW 1-1	0.25	0.10	2

Table 4

Chloride concentrations measured with ISE.

sample	concentration ppm	standard deviation	number of measurements
DL 1-1	5.45	0.98	8
DL 1-1A	6.35	3.58	4
DL 1-1B	6.39	3.27	4
DL 2-1	11.9	2.40	4
DL 4-1	42.1	2.42	4
DL 5-1	2.33	0.57	6
DL 6-1	41.3	3.91	3
DL 7-1	39.3	2.97	3
DL 8-1	5.89	0.92	4
DL 9-1	4.64	0.94	4
LA 1-1	1.36	0.57	4
LA 2-1	0.97	0.79	4
LA 3-1	1.24	0.73	4
LH 2-1	7.53	3.16	10
RND 1-1	87.4	3.61	4
RNE 1-1	3.11	0.33	2
NMG 1-1	24.6	0.88	8
NMG 2-1	27.4	0.82	4
NMG 3-1	27.3	1.05	4
KM 1-1	4.87	2.15	6
KM 1-2	3.20	0.23	2
KM 1-2	2.00	0.42	2
KM 2-1	3.28	0.11	2
KM 2-1	1.83	0.48	2
KM 3-1	1.98	0.14	2
KM 4-1	2.06	0.14	2
KM 6-1	6.76	0.34	2
KM 7-1	6.30	0.40	2
MHW 1-1	196.5	12.5	4
MHW 2-1	61.5	2.52	6
MHW 3-1	308.5	16.9	4
TDS 2	109.8	6.24	4
TDO 1	19.4	1.47	4
DB 1-1	10.8	0.21	3
PL 1-1	3.57	1.10	3
AMB 1-1	108.7	6.29	8
AMB 2-1	99.3	7.95	4
AMB 3-1	16.8	1.13	2
AMB 4-1	238.8	12.2	4
AMB 5-1	127.7	2.99	4
DTA 1-1	1.65	0.30	3
MD 1-1	110.8	3.30	4
TM 1-1	5.06	0.25	2
TM 2-1	1.72	0.30	3
KP 1-1	101.2	3.61	8
TBG 1-1	2.38	0.33	3
KP 2-1	19.2	0.59	4
TB 1-1	12.5	0.88	3
KP 3-1	20.1	0.86	4
M 4	23.0	1.26	4
DMoat	1.27	0.69	3
M 3	1.30	0.73	3
DTD 1-1	1.89	0.26	3
BW 1-1	60.5	3.61	4

Table 5

Major and minor elements concentrations of the sediments, measured with XRF (in %).

		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	Total	LOI	total+loi
Detectie lim.		0.40	0.15	0.08	0.010	0.15	0.08	0.25	0.06	0.02	0.020	-	-	-
DL1-1	A	77.71	13.84	1.81	0.033	0.671	1.14	1.64	1.94	1.13	0.077	100.0	5.43	
DL1-1	LOI	73.49	13.09	1.72	0.031	0.635	1.08	1.55	1.83	1.07	0.072	94.6	5.43	100.0
DL1-1AD	A	90.83	6.23	0.84	<b.g.	0.180	0.22	<b.g.	0.46	1.06	0.051	99.9	6.22	
DL1-1AD	LOI	85.15	5.84	0.79	<b.g.	0.169	0.21	<b.g.	0.43	0.99	0.048	93.6	6.22	99.8
DLFUM1	A	88.67	7.10	1.77	<b.g.	0.244	0.35	<b.g.	0.38	1.12	0.100	99.7	11.01	
DLFUM1	LOI	78.90	6.32	1.57	<b.g.	0.217	0.31	<b.g.	0.34	0.99	0.089	88.7	11.01	99.8
LA2-1A	A	61.68	20.13	13.84	0.044	0.908	0.79	0.63	0.72	1.08	0.165	100.0	13.87	
LA2-1A	LOI	53.13	17.34	11.92	0.038	0.782	0.68	0.54	0.62	0.93	0.142	86.1	13.87	100.0
LA2-1B	A	69.39	18.80	7.12	0.035	0.790	0.85	0.86	0.87	1.14	0.154	100.0	18.70	
LA2-1B	LOI	56.41	15.28	5.79	0.029	0.642	0.69	0.70	0.71	0.93	0.125	81.3	18.70	100.0
LH2-1	A	61.87	20.76	11.90	0.082	1.106	1.30	0.72	0.66	1.46	0.136	100.0	11.27	
LH2-1	LOI	54.90	18.42	10.56	0.073	0.981	1.15	0.64	0.58	1.30	0.121	88.7	11.27	100.0
KM1-1	A	79.18	12.05	4.33	0.018	0.251	0.51	0.75	0.31	2.47	0.126	100.0	52.42	
KM1-1	LOI	37.67	5.73	2.06	0.008	0.120	0.24	0.36	0.15	1.18	0.060	47.6	52.42	100.0
KM4-1	A	50.50	17.85	13.58	0.187	5.571	8.86	2.10	0.35	0.89	0.102	100.0	3.74	
KM4-1	LOI	48.61	17.18	13.07	0.180	5.362	8.53	2.02	0.34	0.85	0.098	96.2	3.74	100.0
TDS2	A	60.54	26.71	8.33	0.033	0.453	1.43	0.61	0.54	1.18	0.178	100.0	23.28	
TDS2	LOI	46.44	20.49	6.39	0.025	0.348	1.10	0.47	0.41	0.91	0.137	76.7	23.28	100.0
KP1-1	A	76.19	11.75	4.00	0.073	1.502	2.66	1.87	1.03	0.84	0.094	100.0	5.64	
KP1-1	LOI	71.89	11.09	3.78	0.068	1.417	2.51	1.76	0.97	0.79	0.089	94.4	5.64	100.0
TM2-1	A	50.14	14.29	20.84	0.381	5.681	4.01	1.58	0.56	2.39	0.120	100.0	3.83	
TM2-1	LOI	48.22	13.74	20.04	0.366	5.463	3.86	1.52	0.54	2.30	0.115	96.2	3.83	100.0
BN-02	measured	51.98	16.90	9.47	0.171	5.681	10.70	2.91	0.72	0.95	0.113	99.6	0.40	100.0
BN-02	standard	52.74	17.31	9.17	0.158	5.610	10.35	2.98	0.73	0.92	0.120	100.1		
GRAN-1	measured	71.39	14.64	2.40	0.059	0.438	1.43	3.53	5.41	0.29	0.084	99.7	0.33	100.0
GRAN-1	standard	71.39	14.18	2.31	0.069	0.480	1.47	3.44	5.32	0.29	0.087	99.0		

<b.g. = below detection limit

Table 6

Trace elements concentrations of the sediments, measured with XRF (in ppm).

	Co	Cu	Nb	Ni	Pb	Rb	Sr	Y	Zn	Zr	Ba	La	Sc	V
Detection lim.	9	6	2	9	6	9	7	3	8	9	30	6	2	50
DL-1	<b.g.	8	7	<b.g.	8	44	85	24	24	198	251	17	20	125
DL 1-1 AD	<b.g.	15	6	<b.g.	12	14	56	20	17	164	176	48	17	77
DLFUM 1	10	66	3	<b.g.	10	12	1789	13	19	135	62000	13	7	250
LA 2-1 A	<b.g.	41	6	<b.g.	13	20	63	21	44	131	151	11	38	258
LA 2-1 B	<b.g.	32	6	<b.g.	12	21	67	17	36	140	152	11	31	191
LH 2-1	<b.g.	47	6	<b.g.	15	22	61	17	54	160	189	13	38	312
KM 1-1	10	50	5	<b.g.	27	<b.g.	108	4	20	67	77	<b.g.	7	61
KM 2-1	<b.g.	38	<b.g.	<b.g.	<b.g.	<b.g.	11	4	18	<b.g.	<b.g.	<b.g.	12	<b.g.
KM 4-1	23	57	<b.g.	<b.g.	<b.g.	12	229	15	60	51	73	<b.g.	28	318
TDS 2	10	47	6	<b.g.	13	10	189	17	43	167	267	14	26	111
AMB 2-1	10	39	<b.g.	<b.g.	<b.g.	23	9	<b.g.	19	11	<b.g.	<b.g.	<b.g.	<b.g.
AMB 3-1	11	37	5	<b.g.	<b.g.	10	538	<b.g.	20	107	149	9	21	<b.g.
AMB 4-1	<b.g.	22	4	<b.g.	12	14	117	6	18	77	158	95	117	<b.g.
KP 1-1	11	13	4	<b.g.	13	31	172	9	35	114	247	12	14	136
TM 2-1	44	51	7	16	11	22	183	20	139	132	235	134	31	563

= measured above gauge line

<b.g. = below detection limit

Minerals determined in the sediments with XRD.

Sample	quartz	cristobalite	sulphur	anatase	albite	other minerals
DL 1-1	X	X	X		X	anorthite zircon
DL 1-1 AD	X					
DL 4-1	X					natroalunite cuprospinel alunite
DL 6-1		X	X			barite
DLFUM 1	X					goethite
LH 2-1	X				X	kaolinite antigorite
KM 1-1	X	X	X			sphalerite halite minamiite
KM 2-1		X	X			
KM 4-1					X	magnesioferrite magnite
TDS 2	X		X		X	kaolinite pyrite
AMB 2-1		X	X			
AMB 3-1	X	X	X	X		pyrite
AMB 4-1	X	X	X	X		
KP 1-1	X	X				magnesioferrite barite enstatite
TM 2-1	X					stishovite chromite hematite enstatite
albite		(Na,Ca)Al(Si,Al) ₃ O ₈				
alunite		KAl ₃ (SO ₄) ₂ (OH) ₆				
anatase		TiO ₂				
anorthite		CaAl ₂ Si ₂ O ₈				
antigorite		Mg ₃ Si ₂ O ₅ (OH) ₄				
barite		BaSO ₄				
cristobalite		a-SiO ₂				
chromite		FeCr ₂ O ₄				
cuprospinel		CuFe ₂ O ₄				
enstatite		MgSiO ₃				
goethite		a-FeOOH				
halite		NaCl				
hematite		a-Fe ₂ O ₃				
kaolinite		(Si ₄)Al ₄ O ₁₀ (OH) ₈				
magnesioferrite		MgFe ₂ O ₄				
magnetite		Fe ₃ O ₄				
minamiite		(Na,Ca)Al ₃ (SO ₄) ₂				
natroalunite		NaAl ₃ (SO ₄) ₂ (OH) ₆				
pyrite		FeS ₂				
quartz		SiO ₂				
stishovite		SiO ₂				
sulphur		S				
zircon		ZrSiO ₄				

Table 8

Classification of and measurements on the mud pools and mud wells of Lahendong.

Type	Descriptions	Sample	Temperature (Celsius)	Conductivity (mS)
A	The light grey mud pool	1	72	6.5
	* Light grey mud pool, with bubbles.	2	55	3.0
	* Water seems to be clear.	3	68	4.8
	* The float has a light grey colour.	4	34	0.8
	* The sediment has a grey white colour.	5	47	4.6
		6	63	3.9
B	The black mud pool	1	85	3.4
	* Black (grey) pool, with bubbles.	2	93	3.9
	* Surrounded with white scale.			
	* Black sediment.			
	* The float is light grey coloured.			
C	The grey mud pool	1	91	1.7
	* Grey to dark grey water.			
	* Dark grey sediment.			
D	Brown, black mud pool	1	72	4.2
	* The water has a brown black colour.	2	82	3.9
	* Black sediment.	3	91	4.9
	* No float.	4	32	10.6
E	Light brown waterpool	1	50	8.5
	* Light brown water.			
	* Near bubbles the colour is black.			
	* Dark brown, grey sediment.			
	* The float has a light brown, grey colour.			

Table 9

Chemical composition of the Sulawesi samples, analysed by the MVO in Indonesia.

	Al	B	Ca	Fe	K	Mg	Mn	Na	SiO ₂	Cl	SO ₄	H ₂ S	NH ₃	Li
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
DL 1-1	2.32	0.03	13.4	6.21	1.33	4.80	0.22	7.88	25.4	93.2	315	1.45	2.65	0
DL 1-1A	2.31	0.04	9.35	5.75	1.18	4.02	0.15	6.23	23.6	55.8	204	1.39	2.26	0
DL 1-1B	2.34	0.03	9.91	6.19	1.34	4.41	0.24	6.83	24.8	87.1	204	0.32	1.86	0
DL 2-1	562	1.06	239	437	7.93	108	11.5	22.1	122	140	7174	0.13	46.3	0.018
DL 4-1	0	0.05	37.2	3.35	10.1	10.3	0.56	45.4	75.2	169	245	0.95	2.63	0.013
DL 5-1	0	0.04	10.0	0	0.85	4.49	0	4.3	24.3	86.3	17.4	0.76	2.20	0
DL 6-1	15.3	0.08	26.9	16.4	2.58	10.0	0.58	13.5	42.2	200	625	0.82	2.05	0.005
DL 7-1	17.6	0.07	32.6	21.5	3.02	12.2	0.75	14.1	49.0	198	679	1.52	2.16	0.003
LH 2-1	7.29	0.21	18.5	32.2	2.31	6.47	0.41	6.54	67.6	63.2	446	0	4.15	0
RND 1-1	0	0.99	84.8	0	6.27	16.4	0.56	47.8	54.8	188	169	0	3.07	0.011
RNE 1-1	0	0.10	11.6	0	0.96	4.32	0	5.85	42.2	88.5	12.4	0.51	2.16	0
NMG 1-1	0	0	22.3	0	3.38	8.54	0	20.0	45.7	110	24.5	0	4.48	0
NMG 2-1	0	0	21.0	0	4.19	7.17	0	23.5	48.0	187	38.0	0	2.26	0
NMG 3-1	0	0.08	21.4	0	4.01	7.40	0	23.1	46.6	111	32.6	0	5.76	0
KM 1-1	23.2	0.06	62.1	17.5	0.26	48.9	0.93	6.85	95.7	104	897	0.13	3.90	0
KM 1-2	28.8	0.07	64.6	18.8	0.27	53.5	0.97	7.49	100	91.0	1019	0.25	4.75	0
KM 2-1	9.16	0.07	21.0	2.96	0.22	4.32	0.10	4.24	44.2	n.d.	163	0	3.16	0
KM 3-1	0	0.07	14.0	0	0.48	4.38	0	4.50	30.4	n.d.	22.8	0.25	3.05	0
KM 4-1	2.59	0.15	15.4	0.65	0.43	5.86	0.12	4.44	35.1	111	139	0.51	2.34	0
KM 5-1	0	0.14	21.3	0	0.50	7.24	0.24	5.08	40.0	93.9	111	0.25	2.27	0
KM 6-1	11.2	0.21	29.3	3.49	2.52	9.61	0.37	11.5	60.2	n.d.	370	0.37	2.22	0
KM 7-1	0	0.16	21.4	0	1.90	7.53	0.24	10.7	42.1	92.9	98	0.63	2.24	0
MHW 1-1	0	0.14	142	0	7.93	50.6	1.66	51.5	64.9	245	287	0	2.40	0
TDS 2	0	0.48	132	2.68	8.41	11.1	0.68	69.8	137	163	140	0	3.51	0
TDO 1	0	0.10	14.4	0	1.70	7.46	0.10	13.9	2.50	109	18.5	0.51	2.56	0
DB 1-1	0	0.10	22.9	0	2.34	16.3	0	14.0	21.0	115	18.0	0	2.16	0
PL 1-1	0	0.07	9.57	0	0.86	4.19	0	4.43	15.8	84.3	11.0	0	2.16	0
AMB 1-1	122	0.23	211	35.0	2.08	69.4	2.61	60.3	151	223	3587	0.63	6.29	0.005
AMB 2-1	109	0.07	194	32.1	1.61	69.9	2.55	57.7	153	127	2935	0.51	4.54	0.005
AMB 3-1	9.97	0.04	250	2.84	4.10	45.3	1.78	45.3	117	138	1391	0.51	3.62	0.003
AMB 4-1	126	5.49	276	43.6	3.03	68.7	2.52	51.3	157	298	3370	0.22	4.10	0.008
AMB 5-1	102	1.12	177	25.6	3.30	57.4	2.22	48.7	140	252	2935	0.95	4.93	0.004
AMB 6-1	0	0.07	10.8	0	1.35	2.63	0	5.05	49.1	102	10.9	0.76	1.90	0
DTA 1-1	0	0.51	10.8	0	1.41	2.48	0	5.41	43.6	97.6	39.3	1.61	4.98	0
MD 1-1	33.5	0.15	229	12.7	3.83	17.7	0.91	29.5	60.7	157	880	0.82	2.34	0.003
TM 1-1	0	0.04	29.7	0	0.92	5.30	0.13	7.78	27.3	108	76.1	0	1.87	0
TM 2-1	0	0.02	8.81	0	0.57	3.12	0	3.84	22.8	91.6	15.0	0	2.42	0
KP 1-1	24.1	0.17	124	7.63	3.43	15.1	0.79	24.9	56.0	231	707	0.51	2.12	0.003
TBG 1-1	0	0.21	18.1	0	0.77	5.65	0	5.67	23.3	78.5	36.0	0	2.16	0
KP 2-1	0	0.06	35.5	0	1.28	7.48	0.24	9.08	32.0	171	152	1.40	2.16	0
TB 1-1	0	0.07	39.8	0	1.92	7.70	0.08	10.5	19.9	123	70.2	0	2.34	0
KP 3-1	0	0.03	38.1	0	2.75	10.4	0	13.5	23.4	147	111	1.20	2.05	0
M 4	0	0.67	58.6	0	1.99	11.1	0	13.2	24.3	105	100	0.57	n.d.	0
DMoat	0	0.03	5.60	0	0.16	2.11	0	2.40	9.52	100	3.53	7.88	2.34	0
M 3	0	1.12	5.19	0	0.15	2.05	0	1.99	9.75	65.0	1.36	7.88	2.05	0
DTD 1-1	0	0	5.07	0	0.39	2.69	0	2.85	9.90	110	0.54	0.82	2.49	0

n.d. = no data

0 = not found or below detection limit.

Table 10

Comparison of the chemical compositions of the North Sulawesi samples, analysed in Utrecht and Indonesia.

	Analyse done by	Al ppm	B ppm	Ca ppm	Fe ppm	K ppm	Mg ppm	Mn ppm	Na ppm	SiO ₂ ppm	Cl ppm	SO ₄ ppm
DL 1-1B	MVO	2.34	0.03	9.91	6.19	1.34	4.41	0.24	6.83	24.8	87.1	204
DL 1-1B	Utrecht	4.02	0.17	13.8	9.37	3.69	5.66	< b.g.	13.4	30.1	5.05	281
DL 2-1	MVO	562	1.06	239	437	7.93	108	11.5	22.1	122	140	7174
DL 2-1	Utrecht	1494	5.12	419	2394	27.4	218	22.6	67.1	246	13.1	14762
RND 1-1	MVO	< b.g.	0.99	84.8	< b.g.	6.27	16.4	0.56	47.8	54.8	188	169
RND 1-1	Utrecht	< b.g.	2.58	59.5	< b.g.	14.3	23.8	0.19	77.1	61.6	79.9	221
NMG 3-1	MVO	< b.g.	0.08	21.4	< b.g.	4.01	7.4	< b.g.	23.7	46.6	111	32.6
NMG 3-1	Utrecht	< b.g.	0.51	26.3	< b.g.	7.52	10.2	< b.g.	41.3	49.2	26.3	50.4
KM 1-2	MVO	28.8	0.07	64.6	18.8	0.27	53.5	0.97	7.49	100	91.0	1019
KM 1-2	Utrecht	48.8	< b.g.	71.0	24.7	0.81	48.4	0.76	14.4	108	2.60	1035
KM 4-1	MVO	2.59	0.15	15.4	0.65	0.43	5.86	0.12	4.44	35.1	111	139
KM 4-1	Utrecht	3.61	< b.g.	20.1	0.13	1.60	7.66	< b.g.	7.91	39.2	1.57	128
MHW 1-1	MVO	< b.g.	0.14	142	< b.g.	7.93	50.6	1.66	51.5	64.9	245	287
MHW 1-1	Utrecht	< b.g.	0.29	113	< b.g.	22.4	50.5	1.56	83.1	70.3	160	295
AMB 2-1	MVO	109	0.07	194	32.1	1.61	69.9	2.55	57.7	153	127	2935
AMB 2-1	Utrecht	172	2.73	168	36.4	2.48	69.2	3.23	88.3	176	86.6	3118
KP 1-1	MVO	24.1	0.17	124	7.63	3.43	15.1	0.79	24.9	56.0	231	707
KP 1-1	Utrecht	45.0	2.28	122	8.82	6.21	21.5	0.59	43.5	58.3	96.4	715
DMoat	MVO	< b.g.	0.03	5.60	< b.g.	0.16	2.11	< b.g.	2.40	9.52	100	3.53
DMoat	Utrecht	< b.g.	< b.g.	6.91	< b.g.	0.93	2.48	< b.g.	3.65	10.9	1.00	3.5

< b.g. = below detection limit.

Appendix III

Photos of North Sulawesi

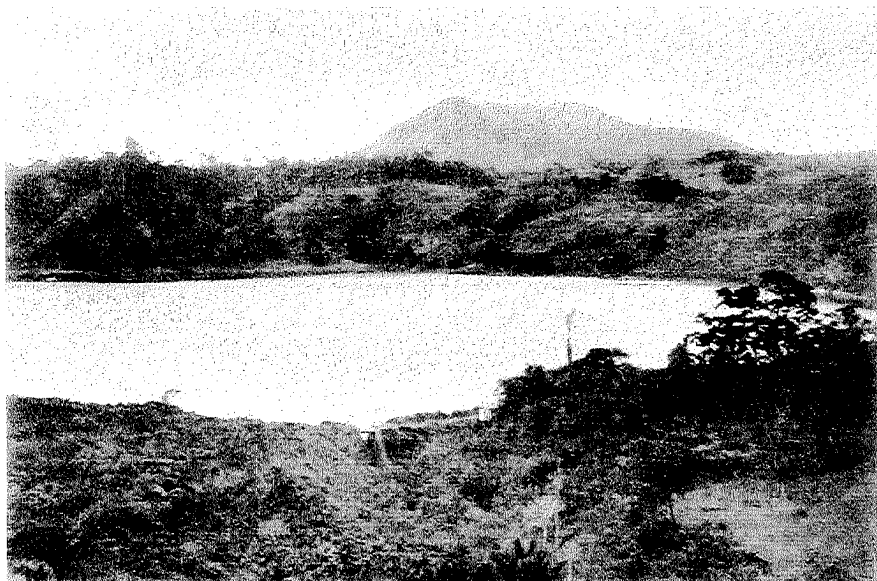


Photo 1. The crater lake Linow Lahendong, with the at the background the G. Tampoesoe, according to Kemmerling (1923).

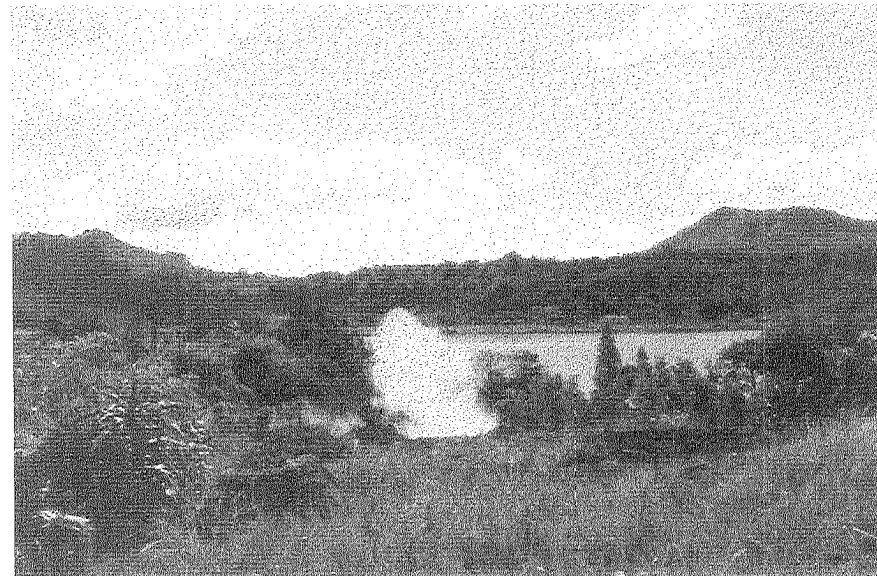


Photo 2. The Danau Linow, with at the background the G. Tampuso and at the foreground the fumarole DLFUM1.



Photo 3. The yellow, white pool DL2-1, with fumarolic activity.



Photo 4. The hot spring DL3-1 with at the foreground the neutral river DL4-1.



Photo 5. The acid Kawah Masem crater lake, with fumaroles at the background.



Photo 6. The Mahawu crater, with a crater lake and fumaroles.



Photo 7. High fumarolic activity at the Ambang mountains.



Photo 8. The Kali Putih, at the foreground the inlet for irrigation water, KP3-1.

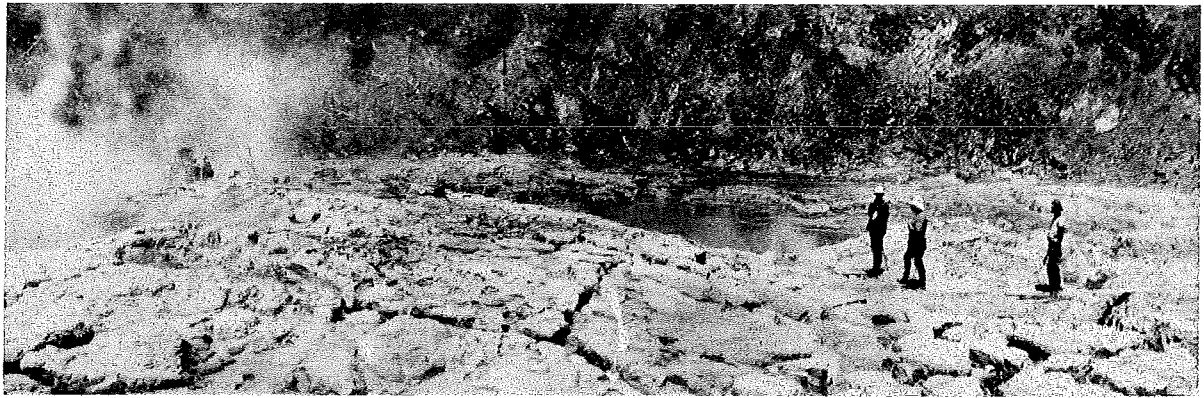


Photo 9. The inside of the Mahawu crater, the north side (Kemmerling, 1923).



Photo 10. The inside of the Mahawu crater, the west side (Kemmerling, 1923).

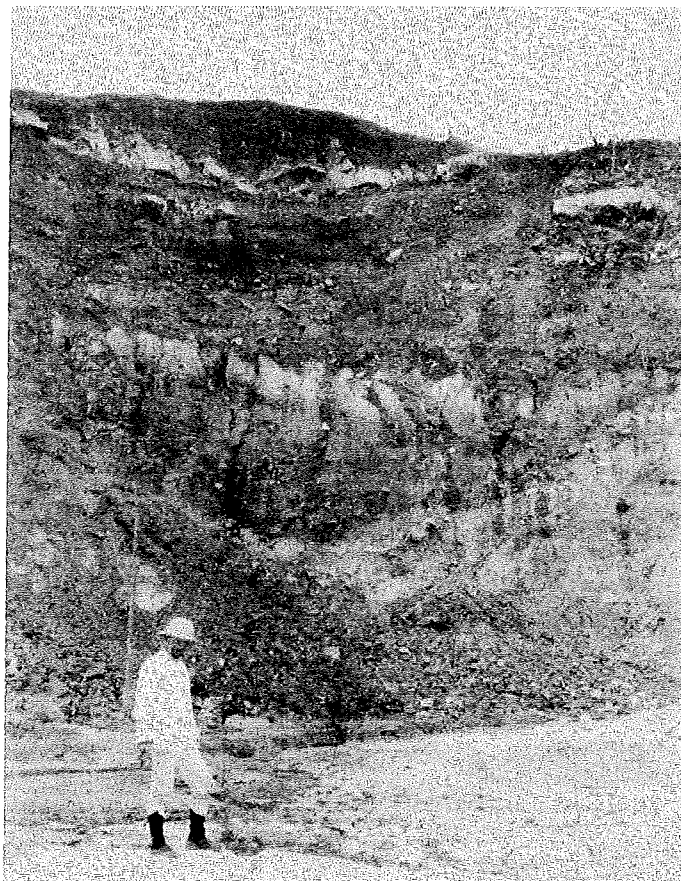


Photo 11. North east side of the Mahawu crater rim and bottom (Kemmerling, 1923).



Photo 12. The R. Maasem, sample location KM4-1.

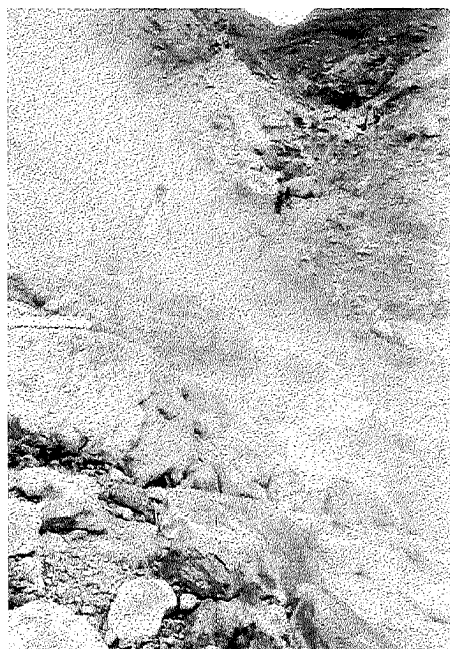


Photo 13. Sample location AMB2-1.



Photo 14. Sample location DL1-1. (Photo Drs. P. van Thienen)

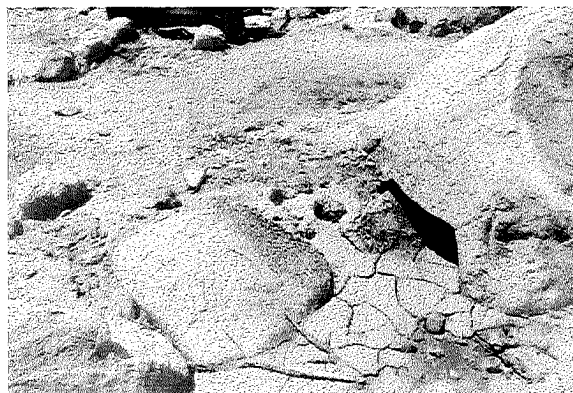


Photo 16. Mud volcano, near sample location DL6-1.



Photo 18. Mud volcanoes of Lahendong.



Photo 15. The large fumarole, DLFUM1.

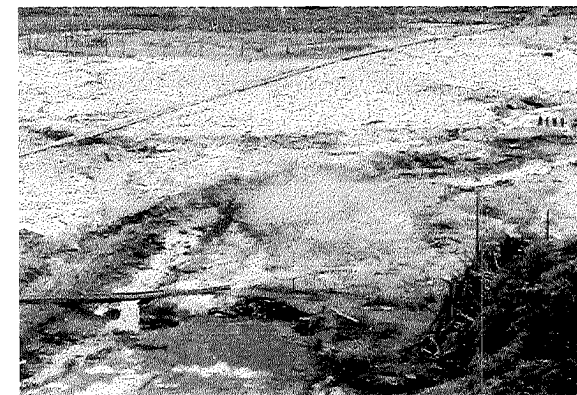


Photo 17. Mud volcano, near sample location DL9-1.

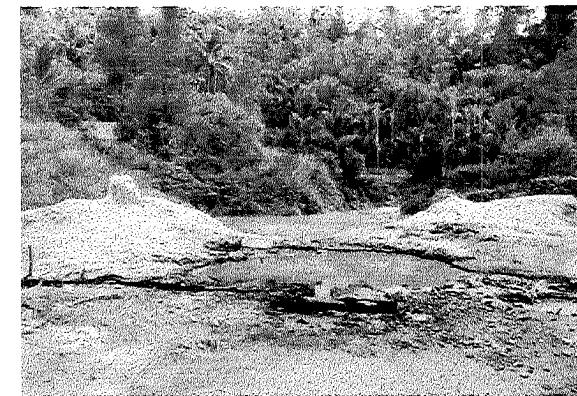


Photo 19. Mud/water pools of Lahendong.



Photo 20. Mud pools of Lahendong, with two outlets.



Photo 21. Mud volcanoes of Lahendong.

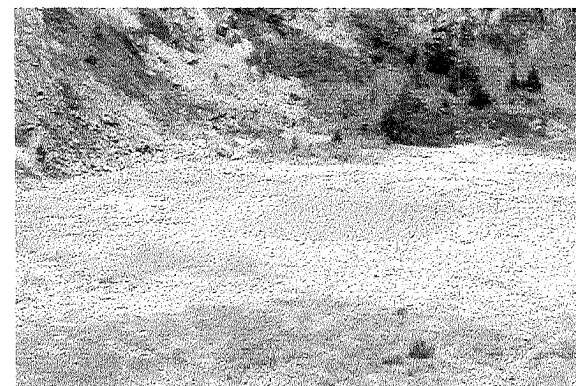


Photo 22. The Kawah Masem crater lake.



Photo 23. Weathered area, near sample KM2-1. (Photo Drs. P. van Thienen.)



Photo 24. The Mahawu crater.



Photo 25. Mud pools south of the lake of Tondano.



Photo 26. Sample location TDS2.

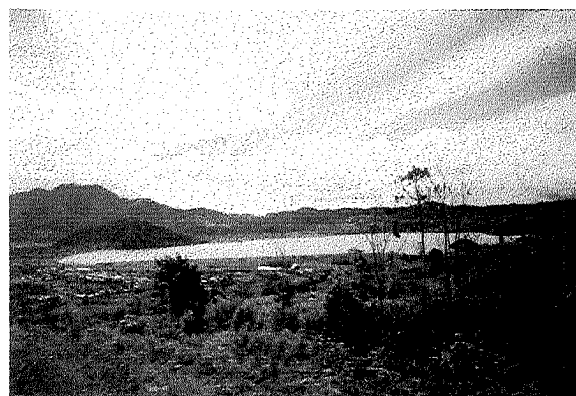


Photo 27. The Danow Moat. (Photo Drs. P. van Thienen.)

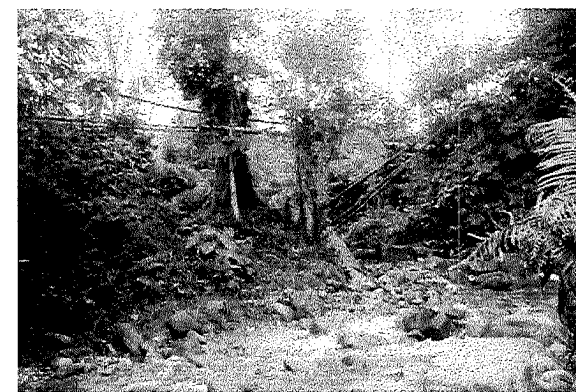


Photo 28. The Kali Putih at sample location MD1-1.

Appendix IV

Field report of sampling campaign of North Sulawesi

Appendix V

SOLVEQ-output of sample DL2-1

DL2-1

T: 27; pH 2.0

+++++

NO. OF LOOPS USED = 22 LOOP LIMIT = 40

Charge balance on SO4-- original Mtot value: .15367E+00

changed by: .98194E-02

TEMPERATURE: 27.00 DEGREES CENTIGRADE

Water: .9803(Kg.Liq.) 54,4133(Moles Liq.) 54.4133(Moles Total)

Activity = .9859

Stoichiometric Ionic Strength=.7184283E+00 Osmotic Coef.= .8159

Apparently NaCl is not the dominant solute,
thus Gamma(I) may be in error for this run

Ionic Strength = .2533144E+00 Calculated Alkalinity = .3012363E-03

Eh = .1779 V. (FROM HS- + 4H2O <=> 9H+ + SO4-- +8e-)

Na-K-Ca Source Temperature : 63. Deg.C. (Fournier & Truesdell, 1973)

SPECIES	MOLALITY	LOG(M)	ACTIVITY	LOG(A)	GAMMA
1 H+	.1309E-01	-1.8832	.1000E-01	-2.0000	.7642E+00
2 H2O			.9859E+00	-.0062	.9859E+00
3 Cl-	.3712E-03	-3.4304	.2687E-03	-3.5708	.7237E+00
4 SO4--	.4702E-01	-1.3278	.1457E-01	-1.8367	.3098E+00
5 HS-	.6196E-10	-10.2079	.4482E-10	-10.3485	.7234E+00
6 SiO2(aq)	.8934E-02	-2.0490	.8934E-02	-2.0490	.1000E+01
7 Al+++	.1079E-01	-1.9669	.9174E-03	-3.0375	.8501E-01
8 Ca++	.5578E-02	-2.2535	.1681E-02	-2.7743	.3014E+00
9 Mg++	.4311E-02	-2.3654	.1272E-02	-2.8956	.2950E+00
10 Fe++	.2431E-01	-1.6143	.7205E-02	-2.1423	.2964E+00
11 K+	.6343E-03	-3.1977	.4562E-03	-3.3408	.7192E+00
12 Na+	.2764E-02	-2.5585	.1990E-02	-2.7010	.7201E+00
13 Mn++	.2333E-03	-3.6321	.6942E-04	-4.1585	.2976E+00
14 Zn++	.6363E-05	-5.1964	.1886E-05	-5.7244	.2964E+00
15 F-	.8921E-08	-8.0496	.6556E-08	-8.1834	.7349E+00
16 HPO4--	.2213E-08	-8.6550	.6861E-09	-9.1636	.3100E+00
17 H3BO3	.4834E-03	-3.3157	.4834E-03	-3.3157	.1000E+01
18 AlF++	.2052E-03	-3.6878	.6135E-04	-4.2122	.2990E+00
19 AlF2+	.2271E-06	-6.6438	.1633E-06	-6.7869	.7192E+00
20 AlF3	.1358E-10	-10.8671	.1358E-10	-10.8671	.1000E+01
21 AlF4-	.3109E-16	-16.5074	.2250E-16	-16.6478	.7237E+00
22 AlF5--	.3516E-22	-22.4539	.1078E-22	-22.9675	.3065E+00
23 AlOH++	.3635E-05	-5.4395	.1087E-05	-5.9639	.2990E+00
24 Al(OH)2+	.1246E-08	-8.9044	.8964E-09	-9.0475	.7192E+00
25 Al(OH)4-	.1345E-16	-16.8712	.9736E-17	-17.0116	.7237E+00
26 AlSO4+	.2113E-01	-1.6751	.1520E-01	-1.8182	.7192E+00
27 AlSO4)2-	.2435E-01	-1.6134	.1762E-01	-1.7539	.7237E+00
28 CaCl+	.1728E-05	-5.7625	.1243E-05	-5.9056	.7192E+00
29 CaCl2	.3893E-10	-10.4097	.3893E-10	-10.4097	.1000E+01
30 CaF+	.2026E-09	-9.6933	.1457E-09	-9.8365	.7192E+00
31 CaOH+	.6830E-13	-13.1656	.4912E-13	-13.3087	.7192E+00
32 CaSO4	.5085E-02	-2.2937	.5085E-02	-2.2937	.1000E+01
33 HCl	.3747E-06	-6.4263	.3747E-06	-6.4263	.1000E+01
34 HF	.1002E-11	-11.9990	.1002E-11	-11.9990	.1000E+01
35 HF2-	.2920E-14	-14.5346	.2113E-14	-14.6750	.7237E+00
36 FeCl+	.2124E-05	-5.6728	.1528E-05	-5.8159	.7192E+00
37 FeCl2	.1271E-17	-17.8960	.1271E-17	-17.8960	.1000E+01
38 Fe3+	.8953E-11	-11.0480	.7805E-12	-12.1076	.8718E-01
39 FeCl++	.5047E-13	-13.2970	.1509E-13	-13.8213	.2990E+00
40 FeCl2+	.1002E-17	-17.9993	.7203E-18	-18.1425	.7192E+00
41 FeCl3	.6502E-21	-21.1870	.6502E-21	-21.1870	.1000E+01
42 FeCl4-	.2759E-26	-26.5593	.1996E-26	-26.6997	.7237E+00
43 FeF+	.1933E-08	-8.7138	.1390E-08	-8.8570	.7192E+00
44 FeF3	.4895E-22	-22.3102	.4895E-22	-22.3102	.1000E+01

45	FeF++	.4427E-13	-13.3538	.1324E-13	-13.8782	.2990E+00
46	FeF2+	.6254E-17	-17.2038	.4498E-17	-17.3470	.7192E+00
47	FeOH+	.7298E-10	-10.1368	.5249E-10	-10.2799	.7192E+00
48	Fe(OH)2	.3699E-19	-19.4319	.3699E-19	-19.4319	.1000E+01
49	Fe(OH)3	.2495E-17	-17.6029	.2495E-17	-17.6029	.1000E+01
50	Fe(OH)3-	.9203E-30	-30.0361	.6660E-30	-30.1765	.7237E+00
51	Fe(OH)4-	.8404E-25	-25.0755	.6082E-25	-25.2160	.7237E+00
52	FeSO4+	.3896E-09	-9.4093	.2802E-09	-9.5525	.7192E+00
53	FeSO4	.1942E-01	-1.7117	.1942E-01	-1.7117	.1000E+01
54	H2 aq.	.8422E-13	-13.0746	.8943E-13	-13.0485	.1062E+01
55	KCl	.4829E-08	-8.3162	.4829E-08	-8.3162	.1000E+01
56	KHSO4	.1354E-04	-4.8684	.1354E-04	-4.8684	.1000E+01
57	KSO4-	.6695E-04	-4.1742	.4845E-04	-4.3147	.7237E+00
58	MgCl+	.1307E-05	-5.8838	.9399E-06	-6.0269	.7192E+00
59	MgF+	.7639E-09	-9.1170	.5494E-09	-9.2601	.7192E+00
60	MgOH+	.3633E-12	-12.4397	.2613E-12	-12.5828	.7192E+00
61	MgSO4	.4835E-02	-2.3156	.4835E-02	-2.3156	.1000E+01
62	MnCl+	.1071E-06	-6.9702	.7703E-07	-7.1133	.7192E+00
63	MnCl2	.5586E-11	-11.2529	.5586E-11	-11.2529	.1000E+01
64	MnCl3-	.9769E-15	-15.0101	.7070E-15	-15.1506	.7237E+00
65	MnOH+	.2890E-12	-12.5390	.2079E-12	-12.6822	.7192E+00
66	MnSO4	.1863E-03	-3.7299	.1863E-03	-3.7299	.1000E+01
67	NaCl	.6136E-07	-7.2121	.6136E-07	-7.2121	.1000E+01
68	NaF	.1783E-11	-11.7487	.1783E-11	-11.7487	.1000E+01
69	NaHS	.7458E-14	-14.1274	.7458E-14	-14.1274	.1000E+01
70	NaOH	.4558E-15	-15.3412	.4558E-15	-15.3412	.1000E+01
71	NaSO4-	.2133E-03	-3.6710	.1544E-03	-3.8114	.7237E+00
72	O2 aq.	.3706E-65	-65.4311	.3935E-65	-65.4051	.1062E+01
73	OH-	.1603E-11	-11.7951	.1174E-11	-11.9304	.7322E+00
74	H2PO4-	.1458E-03	-3.8364	.1053E-03	-3.9777	.7222E+00
75	H3PO4	.1518E-03	-3.8186	.1518E-03	-3.8186	.1000E+01
76	PO4---	.2695E-18	-18.5694	.3132E-19	-19.5042	.1162E+00
77	S--	.1128E-24	-24.9477	.3457E-25	-25.4613	.3065E+00
78	H2S aq.	.3891E-05	-5.4099	.4132E-05	-5.3839	.1062E+01
79	HSO4-	.2010E-01	-1.6968	.1451E-01	-1.8384	.7217E+00
80	H2SiO4--	.1579E-18	-18.8016	.4839E-19	-19.3152	.3065E+00
81	H3SiO4-	.2628E-09	-9.5805	.1902E-09	-9.7209	.7237E+00
82	ZnCl+	.2030E-08	-8.6926	.1460E-08	-8.8357	.7192E+00
83	ZnCl2	.4466E-12	-12.3501	.4466E-12	-12.3501	.1000E+01
84	ZnCl3-	.1215E-15	-15.9154	.8794E-16	-16.0558	.7237E+00
85	ZnCl4=	.4160E-19	-19.3809	.1275E-19	-19.8945	.3065E+00
86	ZnF+	.2598E-12	-12.5853	.1869E-12	-12.7285	.7192E+00
87	Zn(HS)2	.3134E-13	-13.5039	.3134E-13	-13.5039	.1000E+01
88	Zn(HS)3-	.3137E-21	-21.5034	.2270E-21	-21.6439	.7237E+00
89	Zn(HS)4=	.5866E-33	-33.2317	.1798E-33	-33.7453	.3065E+00
90	ZnOH+	.1057E-10	-10.9758	.7604E-11	-11.1190	.7192E+00
91	ZnOH2	.8303E-20	-20.0808	.8303E-20	-20.0808	.1000E+01
92	ZnOH3-	.4553E-29	-29.3417	.3295E-29	-29.4821	.7237E+00
93	ZnOH4--	.1824E-39	-39.7389	.5592E-40	-40.2525	.3065E+00
94	ZnSO4	.5807E-05	-5.2360	.5807E-05	-5.2360	.1000E+01
95	H2BO3-	.4132E-10	-10.3838	.2984E-10	-10.5252	.7222E+00

SPECIES	MOLALITY	TOT MOLES	PPM	TOT MOLALITY	ALPHA
1 H+	.1309E-01	.3299E-01 CM	.332065E+02	.3365E-01	.388904
2 H2O	.1000E+01	.5441E+02	.979044E+06	.5551E+02	.018015
3 Cl-	.3712E-03	.3695E-03	.130836E+02	.3769E-03	.984853
4 SO4--	.4702E-01	.1635E+00 AD	.156856E+05	.1668E+00	.281901
5 HS-	.6196E-10	.3815E-05	.125997E+00	.3891E-05	.000016
6 SiO2(aq)	.8934E-02	.8758E-02	.525537E+03	.8934E-02	1.000000
7 Al+++	.1079E-01	.5537E-01	.149213E+04	.5649E-01	.191042
8 Ca++	.5578E-02	.1045E-01	.418475E+03	.1066E-01	.523044
9 Mg++	.4311E-02	.8967E-02	.217727E+03	.9147E-02	.471264
10 Fe++	.2431E-01	.4287E-01	.239100E+04	.4373E-01	.555829
11 K+	.6343E-03	.7007E-03	.273657E+02	.7148E-03	.887392

12 Na+	.2764E-02	.2919E-02	.670159E+02	.2977E-02	.928335
13 Mn++	.2333E-03	.4114E-03	.225717E+02	.4197E-03	.555873
14 Zn++	.6363E-05	.1193E-04	.779023E+00	.1217E-04	.522732
15 F-	.8921E-08	.2016E-03	.382520E+01	.2057E-03	.000043
16 HPO4--	.2213E-08	.2917E-03	.279649E+02	.2976E-03	.000007
17 H3BO3	.4834E-03	.4739E-03	.292633E+02	.4834E-03	1.000000

CM means total moles of that species was computed from input of its activity
AD means total moles of that species was adjusted for charge balance

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Note: for gases listed below, Log (fugacity of gas) = Log (Q/K)

This solution is SUPERSATURATED with the following minerals

MINERAL	LOG K	LOG Q	LOG Q/K
chalcedo	-3.70	-2.05	1.65
cristoba	-3.42	-2.05	1.37
cristo-a	-3.42	-2.05	1.37
cristo-b	-2.98	-2.05	.93
pyrite	-24.58	-21.21	3.37
quartz	-3.97	-2.05	1.92
silic-am	-2.70	-2.05	.65

This solution is UNDERSATURATED with the following minerals

MINERAL	LOG K	LOG Q	LOG Q/K
H2O gas	1.45	-.01	-1.46
H2 gas	8.34	-1.63	-9.97
H2S gas	-7.98	-12.35	-4.36
HCl gas	6.21	-5.57	-11.78
HF gas	.88	-10.18	-11.07
SO2 gas	3.04	-7.46	-10.49
S2 gas	-7.20	-21.43	-14.23
O2 gas	65.75	3.26	-62.49
akermani	44.84	-.56	-45.40
alabandi	-.44	-12.51	-12.07
albit-hi	4.34	-3.90	-8.23
albit-lo	3.03	-3.90	-6.93
alunite	.41	-4.16	-4.57
analcime	7.18	-1.85	-9.03
anal-dhy	11.85	-1.85	-13.70
andalusi	16.30	3.86	-12.45
andradit	50.07	2.84	-47.23
grossula	51.63	3.42	-48.21
anhydrit	-4.29	-4.61	-.32
annite	29.42	1.01	-28.41
anorthit	26.71	3.03	-23.68
apat-chl	-28.88	-38.93	-10.06
apat-flu	-33.76	-43.55	-9.79
apat-hyd	.12	-33.37	-33.49
anthophy	67.17	-8.71	-75.88
antigori	30.01	-1.07	-31.08
beide-Mg	6.10	-.46	-6.57
beide-Na	6.19	-.88	-7.07
boehmite	9.45	2.95	-6.50
brucite	16.31	1.09	-15.21
camin625	5.21	-4.46	-9.68
camin75	9.05	-4.19	-13.23
chrysoti	31.28	-.82	-32.09
clcl14/2	27.39	2.61	-24.78
dap14/2*	27.92	4.50	-23.42

clchl7a	71.19	5.23	-65.97
daph7a*	59.66	8.99	-50.67
clinozoi	43.38	5.15	-38.24
epid-ord	41.58	4.86	-36.72
cord-hyd	50.64	3.76	-46.88
cord-anh	53.10	3.76	-49.33
corundum	21.08	5.91	-15.17
diaspore	8.62	2.95	-5.67
diopside	20.80	-1.78	-22.58
hedenber	19.28	-1.03	-20.31
enstatit	11.36	-.95	-12.32
fayalite	18.87	1.65	-17.21
feldsp-K	.05	-4.54	-4.59
ferrosil	7.34	-.20	-7.54
fluorite	-10.02	-19.14	-9.12
forsteri	27.90	.15	-27.75
gehlenit	56.08	6.30	-49.79
gibbsite	7.85	2.94	-4.90
greenali	27.11	1.44	-25.67
grunerit*	49.14	-3.44	-52.57
gypsum	-4.45	-4.62	-.18
halite	1.61	-6.27	-7.88
hematite	17.47	5.33	-12.14
illite	9.60	-.92	-10.52
jadeite	8.62	-1.85	-10.47
jarosite	16.81	-5.03	-21.83
kalsilit	11.13	-.44	-11.57
kaolinit	7.26	1.80	-5.46
kerolite	23.50	-4.93	-28.43
laumonti	13.92	-1.09	-15.02
lime	32.37	1.22	-31.15
magnetit	27.70	7.18	-20.52
manganos	17.78	-.16	-17.94
margarit	41.58	8.93	-32.65
merwinit	67.73	.66	-67.07
micr-max	.05	-4.54	-4.59
monticel	29.51	.27	-29.25
muscovit	14.29	1.36	-12.92
paragoni	18.16	2.00	-16.16
pargas/2	51.10	1.34	-49.75
par/2Fe*	46.41	2.85	-43.56
periclas	21.30	1.10	-20.20
phlogopi	37.84	-1.25	-39.09
phlogo-F	16.49	-21.60	-38.09
portland	22.40	1.21	-21.19
prehnite	32.91	2.19	-30.72
pyrophyll	.94	-2.30	-3.23
px.Ca-Al	36.04	5.08	-30.97
pyrrhoti	-3.78	-10.49	-6.71
pyrrhot!	-3.89	-10.49	-6.60
rhodonit	9.65	-2.21	-11.86
rhodoni2	9.65	-2.21	-11.87
S native	-10.47	-10.71	-.25
sanid-hi	1.23	-4.54	-5.77
sepiolit	30.78	-7.94	-38.73
sphaleri	-11.32	-14.07	-2.75
spinel	37.94	7.00	-30.93
sylvite	.91	-6.91	-7.83
talc	21.36	-4.91	-26.27
minneso*	13.65	-2.65	-16.29
tremolit	61.15	-8.47	-69.61
Fe-actin	51.06	-4.70	-55.76
wairakit	18.27	-1.08	-19.36
wollasto	13.53	-.83	-14.36
wurtzite	-9.04	-14.07	-5.04
zoisite	43.43	5.15	-38.28