Review Articles

Natural Pollution Caused by the Extremely Acidic Crater Lake Kawah Ijen, East Java, Indonesia

Ansje J. Löhr[1]*, Thom A. Bogaard[2], Alex Heikens[3], Martin R. Hendriks[2], Sri Sumarti[4], Manfred J. Van Bergen[4], Cornelis A.M. Van Gestel[1], Nico M. Van Straalen[1], Pieter Z. Vroon[5] and Budi Widianarko[6]

[1] Institute of Ecological Science, Vrije Universiteit, De Boelelaan 1085, NL-1081 HV Amsterdam, The Netherlands
[2] Faculty of Geographical Sciences, Utrecht University, P.O. Box 80115, NL-3508 TC Utrecht, The Netherlands
[3] Institute for Risk Assessment Sciences (IRAS), Utrecht University, P.O. Box 80176, NL-3508 TD Utrecht, The Netherlands
[4] Faculty of Earth Sciences, Utrecht University, PO Box 80021, NL-3508 TA Utrecht, The Netherlands
[5] Institute of Earth Sciences, Vrije Universiteit, De Boelelaan 1085, NL-1081 HV Amsterdam, The Netherlands
[6] Faculty of Agricultural Technology, Soegijapranata Catholic University (UNIKA), Jl. Pawiyatan Luhur IV/1 Semarang 50234, Indonesia

* **Corresponding author** (ansje.lohr@ecology.falw.vu.nl)

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Abstract

Background, Aims and Scope. Lakes developing in volcano craters can become highly acidic through the influx of volcanic gases, yielding one of the chemically most extreme natural environments on earth. The Kawah Ijen crater lake in East Java (Indonesia) has a pH < 0.3. It is the source of the extremely acidic and metal-polluted river Banyupahit (45 km). The lake has a significant impact on the river ecosystem as well as on a densely populated area downstream, where agricultural fields are irrigated with water with a pH between 2.5 and 3.5.
The chemistry of the river water seemed to have changed over the past decade and the negative effect in the irrigation area increased. A multidisciplinary approach was used to investigate the altered situation and to get insight in the water chemistry and the hydrological processes influencing these alterations. Moreover, a first investigation of the effects of the low pH on ecosystem health and human health was performed.

Methods. Water samples were taken at different sites along the river and in the irrigation area. Sampling for macroinvertebrates was performed at the same sites. Samples of soil and crop were taken in the irrigation area. All samples were analysed for metals (using ICP-AES) and other elements, and concentrations were compared to local and international standards.

Results and Discussion. The river carries a very high load of SO_4, NH_4, PO_4, Cl, F, Fe, Cu, Pb, Zn, Al and other potentially toxic elements. Precipitation and discharge data over the period of 1980–2000 clearly show that the precipitation on the Ijen plateau influences water chemistry of the downstream river. Metal concentrations in the river water exceed the concentrations mentioned in Indonesian and international quality guidelines, even in the downstream river and the irrigation area. Some metal concentrations are extremely high, especially iron (up to 1,600 mg/l) and aluminium (up to 3,000 mg/l).
The food-webs in the acidic parts of the river are highly underdeveloped. No invertebrates were present in the extremely acidic water and, at pH 2.3, only chironomids were found. This also holds true for the river water with pH 3.3 in the downstream area.
Agricultural soils in the irrigation area have a pH of 3.9 compared to a pH of 7.0 for soils irrigated with neutral water. Decreased yields of cultivated crops are probably caused by the use of Al containing acidic irrigation water. Increased levels of metals (especially Cd, Co, Ni and Mn) are found in different foodstuffs, but still remain within acceptable ranges. Considering local residents' diets, Cd levels may lead to an increased risk for the human health. Fluoride exposure is of highest concern, with levels in drinking water exceeding guideline values and a lot of local residents suffering from dental fluorosis.

Conclusions, Recommendations and Outlook. In short, our data indicate that the Ijen crater lake presents a serious threat to the environment as well as human health and agricultural production.

Keywords: Acidic crater lake; ecosystem health; human health; Indonesia; low pH; metal pollution; water chemistry

Introduction

Volcanoes are a well-known source of catastrophic events. Worldwide, five hundred million people live in the vicinity of volcanoes [1] and are exposed to the dangers that are associated with eruptions. Considering the increasing population pressure in volcanic areas worldwide, the risk of exposure to volcanic activity relative to the number of people increases. Besides the direct threats to human life and property [2], volcanic processes can also be chronically hazardous to the surrounding environment. An extraordinary and hardly documented chemical hazard is related to the high levels of metals and other elements present in acidic crater lakes, which may threaten surface or groundwater around volcanoes.

Crater lakes in volcanic terrains fill depressions that are formed by explosive crater-forming excavation or caldera collapse, or result from blockage of common waterways by mudflows, lava flows, or ash deposits. These crater lakes are of varying size and usually exist in the central summit part of a volcano. About 12% of the volcanoes formed in the Holocene have a volcanic lake within their crater [3]. The water chemistry of crater lakes reflects the status of volcanic activity, and monitoring changes in lake volume, temperature, and chemistry may help to predict future eruptive events [4].

Crater lakes can become highly acidic by injection at the lake bottom of magmatic volatiles, such as SO_2, H_2S, HCl, and HF, yielding one of the chemically most extreme natural environments on earth [4]. Water-rock interactions at low pH enrich the water with rock-derived elements, such as Al, Fe, Mn, Mg, Ca, Na, K, and trace metals.

Through these processes, crater lakes accumulate a range of elements that normally occur at low natural concentration levels. Environmental consequences are limited when the lake water remains inside the crater. However, by distributing heavy metals and other elements in extremely high concentrations via water seepage, these acidic crater lakes can become a prime source of environmental pollution [4,5] as is seen by seepage into surface or groundwater at Patuha volcano in Indonesia [5], Ruapehu volcano in New Zealand [6], Poas volcano in Costa Rica [7] and Copahue volcano in Argentina [8]. The conditions arising from volcanic lake leachates resemble those in acidic mine drainage systems.

In this paper, an Indonesian river, the Banyupahit-Banyuputih, that contains extremely high levels of metal ions and other toxic chemicals, will be discussed. The pollution of this river has its origin in the extremely acidic crater lake, the Kawah Ijen in East Java, Indonesia and is a good example of a system where a lake-river connection causes the release of pollutants of volcanic origin [9,10].

The water has a great impact on the environment, not only near the volcano, on the Ijen plateau, but especially in the coastal plains downstream. Of special concern is the fact that polluted water is used in a large irrigation area with harmful consequences for agriculture and human health. The concern about the consequences has increased in the area during the last 10 years, when it seemed that the pH had decreased. Since a lot of people depend on the river water, it is important to get good insight in the processes underlying these changes. Therefore, current water chemistry data from the crater lake and the river was compared to former data, and also hydrological data over the last 20 years was investigated. Moreover, a first investigation in the area of the effects of the low pH on ecosystem and human health was performed.

1 The Ijen System

The Indonesian archipelago contains 129 active volcanoes, accounting for 13% of the world's active volcanoes. On Java there are 21 active volcanoes and seven crater lakes [11]. The Ijen complex is the most easterly situated volcanic complex of Java (**Fig. 1**). It consists of a group of stratovolcanoes constructed within the 15-km wide Ijen caldera. The area is subject to a tropical climate, characterised by dry and rainy seasons, with a much higher precipitation in the caldera than in the coastal areas. Rain intensities on a daily basis in the caldera can be as high as 100 mm.

Kawah Ijen is an active stratovolcano (2,346 m above sea level) located on the rim of the caldera, which contains a turquoise-coloured lake. It is one of the world's largest (30–40 x 10^6 m^3) natural reservoirs of extremely acidic (pH < 0.3) volcanic water and has a surface area of about 1,000 x 600 m and a

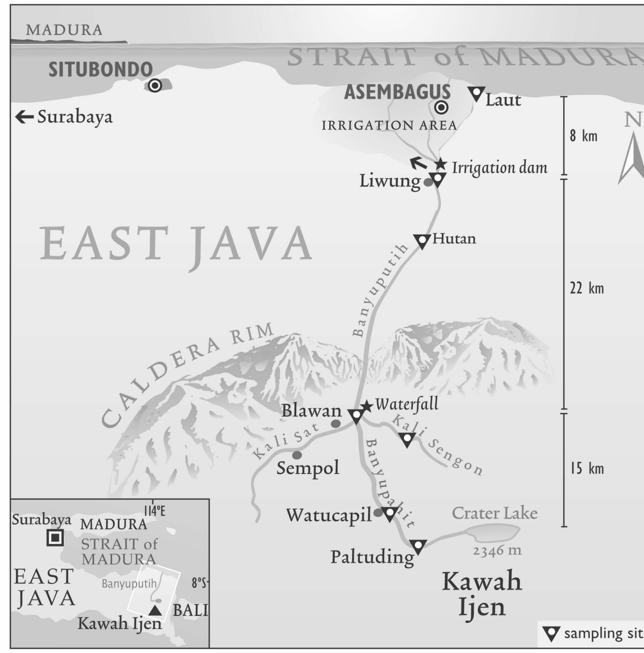

Fig. 1: Map of the Ijen ecosystem, showing the location of the Kawah Ijen crater lake, the Banyupahit-Banyuputih river and the Kali Sengon, and indicating the sampling sites along the rivers

maximum depth of 180 m [12]. The lake forms a potential danger in the case of an eruption and the area is designated a volcanic hazard. Of the 275 historical records of crater lake eruptions worldwide since 1796, six concern the Kawah Ijen [12]. A major eruption was in 1817, when a mud flow devastated the agricultural areas in the coastal plains of Banyuwangi and Asembagus, 45 km downstream from the lake [12]. Since then occasional phreatic and geyser-like activities have been reported and the volcano is continuously monitored by the Indonesian Directorate of Volcanological and Geological Hazard Mitigation. A dam was built on the western crater rim in 1921 in order to control the level of lake water and to block the influx of acidic water into the downstream areas. For several decades the sluices of the dam have not been used as the lake level remained below that of the dam. The acidic sulphur and chlorine rich water, though, leaks through the rock basement at several locations underneath the dam with a total discharge of about 50 l/s [9]. The acidic seepage water of the lake is input to the headwaters of a 45 km long river, the Banyupahit (Bitter River) which flows in a westward direction down the volcanic slopes underlain by basaltic-andesitic rocks through the settlements Paltuding and Watucapil. Two neutral rivers on the Ijen plateau mainly dilute the Banyupahit, the Kali Sat, after which the river is called Banyuputih (White River), and the Kali Sengon.

2 Water Characteristics and Changes over Time

Water chemistry samples were taken in the crater lake of Kawah Ijen in June 2000, and at five sites in the Banyupahit-Banyuputih river and in the neutral Kali Sengon river in December 2000. Samples were analysed and compared to data of the last ten years.

At each sampling site, pH and conductivity were measured in triplicate using a Multi-line P4 (WTW) aquatic field kit. Water samples were collected in triplicate in 1% HNO_3 rinsed polypropylene bottles; nitrate was measured using the cadmium reduction method (Hach method 8171); sulphate using the Sulfa Ver 4 method (USEPA method 375.4, Hach method 8051); chloride using the mercuric thiocyanate method (Hach method 8113); reactive phosphorus was measured using the molybdovanadate method (Hach method 8114).

To adjust pH < 2, 65% HNO_3 (Merck p.a.) was added to filtered samples for metal analysis and unfiltered samples for total organic carbon (TOC) determination. TOC was measured with a Dohrmann DC-190 TOC analyser; trace-elements by a HP4500 ICP-MS; major-elements (Ca, Al, Fe) by a Varian Liberty II ICP; F, Na and K with the Dionex DX120 ion chromatograph. Total suspended solids (TSS) were measured by filtering 500 ml of sample over a 0.22 µm pore-size filter. For the analysis of alkalinity and acidity, water samples were collected and stored at 4°C before analysis. Acidity was determined by titration to pH 8.3 (APHA 1995) with NaOH (Merck, Darmstadt, Germany, p.a., 99% pure). Alkalinity was measured by titration to a pH of 4.3 (APHA 1995) with H_2SO_4 (Merck, Darmstadt, Germany, p.a., 95.0% pure).

The pH of the crater lake is less than 0.3 (**Table 1**). The time interval needed for the lake water to travel through the crater wall is unknown. Observed variations in seepage water do not coincide with changes in lake water composition, possibly due to a considerable transfer time. Also significant variations of the water level have been observed due to seasonal fluctuations in rainfall. Paltuding, close to the origin, and Watucapil, 8 km downstream, in the most acidic stretch of the river have a pH of 0.7. Blawan is located on the Ijen plateau directly below the confluence of the neutral river Kali Sat with the Banyupahit, which shows a strong increase in pH up to 2.9. The neutral river Kali Sengon, with pH 7.7, confluences with the Banyuputih just before the waterfall, which is the edge of the caldera.

After leaving the caldera, the water flows in a northerly direction through a very steep canyon surrounded by high monsoon forest. The 60,000 ha of forest is the largest single expanse of forest on Java. Site Hutan, with pH 3.2, is located in the forest (not accessible by road) and was sampled in July 2001 during a 4-day expedition. Twenty km downstream of the caldera rim the river water is used for irrigation and household purposes in the Asembagus irrigation area. No further dilution is seen between the caldera rim and the irrigation dam at Liwung. The water used for irrigation in the Asembagus area still has a pH of approximately 3.3. Nearly all of the river water is led into the irrigation system at the village of Liwung. The original riverbed follows its way to the Strait of Madura and serves as an overflow discharge channel when flashfloods occur in the rainy season.

Conductivity of the water is closely related to pH and is extremely high at the most acidic sites, Paltuding and Watucapil, with values up to 110 mS/cm. The increase of pH over the first 20 km up to the waterfall is accompanied by a decrease of conductivity. Phosphate, chloride, sulphate, nitrate and ammonium concentrations are very high at the most acidic sites which are Paltuding and Watucapil (Table 1). Further downstream, at Blawan, Hutan and Liwung, concentrations of these compounds are one or two orders of magnitude lower. The lowest values for all measurements are found in the neutral Kali Sengon river. Acidity is very high at most acidic sites (around 500 mg $CaCO_3$/l) and decreases from 9.9 at Blawan to 4.7 mg $CaCO_3$/l at Liwung. Alkalinity in the Kali Sengon is 0.95 mg $CaCO_3$/l. The oxygen content is close to saturation at all sites. Total suspended solids (TSS) and total organic carbon (TOC) do not show a clear pattern. TSS is lowest at Blawan and highest at Liwung. TOC values vary between 1.92 mg/l and 6.43 mg/l in the Banyupahit, being lowest at Liwung and highest at Blawan. In the Kali Sengon, TOC is 5.07 mg/l. Observations in the laboratory suggest that the contribution of mineral and organic contents to TSS may vary significantly from one location to another.

It is very clear from the 2000 data that the Banyupahit has an increasing pH (pH 0.7–3.5) and decreasing level of volcanogenic elements with an increasing distance from its source (**Fig. 2**). The influx of water from tributaries and other sources within the caldera largely controls changes in pH and concentrations of dissolved elements. Decreasing concentrations are also caused by removal via mineral phases that precipitate, especially where the acidic water mixes with water from other sources. The Kali Sengon tributary has a

Table 1: Physicochemical characteristics of the Banyupahit-Banyuputih and Kali Sengon in 2000

Parameter	Kawah Ijen	Paltuding	Watucapil	Blawan	Hutan [1]	Liwung	Kali Sengon	WHO [2]
pH	0.17	0.72	0.65	2.88	3.20	3.27	7.71	–
Conductivity (ms/cm)	–	111	109	3.0	1.7	1.8	1.1	–
Nitrate (mg/l)	–	140	190	2.6	1.3	1.2	0.7	50
Phosphate (mg/l)	–	96.7	96.7	2.1	1.2	0.1	0.2	
Chloride (mg/l)	23380	8633	9400	237	186	183	69	250
Ammonium (mg/l)	–	22.3	21.3	0.8	–	1.2	0.1	–
Acidity	–	499	495	9.9	6.2	4.7	0.95 [3]	–

[1] measurements from July 2001
[2] WHO guideline values drinking water (1996)
[3] alkalinity (mg $CaCO_3$/l)

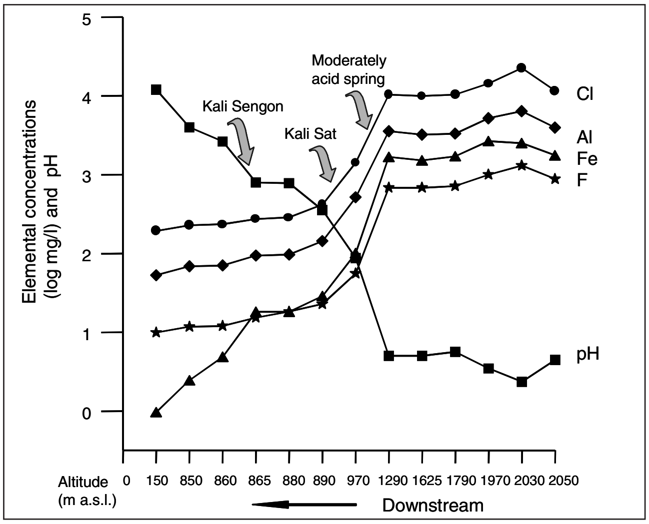

Fig. 2: Elemental concentrations in the Banyupahit-Banyuputih river system in 2000 plotted as a function of the altitude, starting with the crater lake on the right and moving to the downstream coastal plain (irrigation area) on the left. The positions of three major (moderately acidic and neutral) contributaries are indicated by arrows. (a.s.l.= above sea level)

neutral pH of 7.7 and low concentrations of virtually all elements. Nevertheless, somewhat elevated values for SO_4, Cl, F and conductivity point to a contribution of hydrothermal water from a local source close to the sampling site. Metal speciation calculations show that there are considerable variations in the distributions of Al and Fe species along the Banyupahit-Banyuputih [9]. For example, in the most acidic upstream part, aluminium occurs not only as Al^{3+}, but also as sulphate and fluoride ligands, due to the large SO_4 and F activities. The proportions of these species change downstream. Below the entrance of the Kali Sengon tributary, nearly all dissolved Al is present as fluoride complexes.

Metal concentrations (**Table 2**) all lie above the concentrations mentioned in the Indonesian Government Regulation for water used for irrigation and other agricultural purposes and the WHO guideline values for drinking water, even in the downstream river and the irrigation area. Some metal concentrations are extremely high, especially iron and aluminium. Concentrations are highest at most acidic sites and decrease with increasing pH, except for Mg and Ca. Only minor changes in the concentrations of metals are observed for Paltuding and

Table 2: Element concentrations in Kawah Ijen, Banypahit-Banyuputih and Kali Sengon in 1990, 1993, 1996 and December 2000 (all data in mg/l). Guideline values Indonesia: Indonesian Government Regulation No. 82 (14 Dec 2001) on 'Management of Water Quality and Water Pollution Control'; WHO guideline values drinking water (1996); 1990 data from [4]; 1993 and 1996 data from [9]; 2000 data own measurements (SD < 10% of the mean)

Parameter	Year	Kawah Ijen	Paltuding	Watucapil	Blawan	Liwung	Kali Sengon	Laut	Well	Guideline values Indonesian/WHO	
pH	1990	0.18	0.65	–	–	–	–	–	–		
	1993	< 0.02	0.91	–	4.55	5.12	–	–	–		
	1996	–	0.76	0.74	2.80	3.83	–	–	–		
	2000	0.17	0.72	0.65	2.88	3.27	7.71	–	–	6 – 9	
Ca	1990	1105	781	–	–	–	–	–	–		
	1993	–	384	–	93	103	–	–	–		
	1996	968	718	815	110	90	101	–	–		
	2000	690	697	704	108	101	110	313	–		
Al	1990	5490	3759	–	–	–	–	–	–		
	1993	–	1184	–	15	6.7	–	–	–		
	1996	5413	3163	3058	81	29	0.3	–	–		
	2000	5150	2735	2960	92	56	0.2	0.4	< 0.01		0.2
Fe	1990	1862	1836	–	–	–	–	–	–		
	1993	–	780	–	0.9	0.9	–	–	–		
	1996	2063	1511	1466	48	7.2	0.12	–	–		
	2000	1977	1566	1516	25	5.4	< 0.01	0.2	< 0.01		0.3
Cl	1990	–	–	–	–	–	–	–	–		
	1993	21218	4145	–	135	125	–	–	–		
	1996	22630	10323	9551	257	145	71	–	–		
	2000	23380	8633	9400	237	183	69	–	–		250
F	1990	1325	815	–	–	–	–	–	–		
	1993	–	283	–	12	11.0	–	–	–		
	1996	1045	473	480	15	8.0	< 1	–	–		
	2000	1266	497	494	18	11.2	1.8	3.4	>2.5	1.5	1.5
SO4	1990	59305	37715	–	–	–	–	–	–		
	1993	–	11996	–	346	293	–	–	–		
	1996	71309	35010	35856	774	442	166	–	–		
	2000	64750	31893	32086	846	551	250	4437	–		250
Na	1990	585	379	–	–	–	–	–	–		
	1993	–	190	–	32	45	32	–	–		
	1996	–	583	–	50	45	–	–	–		
	2000	1025	638	–	67	55	–	–	52.9		200
K	1990	1702	1306	–	–	–	–	–	–		
	1993	–	358	–	15	20	15	–	–		
	1996	–	859	–	22	18	–	–	–		
	2000	1113	743	–	30	20	–	–	–		
Cu	1990	0.4	0.80	–	–	–	–	–	–		
	1993	–	0.34	–	< 0.02	0.02	–	–	–		
	1996	–	0.70	–	0.11	0.01	–	–	–		
	2000	0.19	0.92	0.88	0.02	0.02	0.01	–	0.002	0.02	2
Zn	1990	4.0	2.7	–	–	–	–	–	–		
	1993	–	–	–	–	< 0.05	–	–	–		
	1996	–	3.6	–	0.14	< 0.05	–	–	–		
	2000	4.8	4.8	4.5	0.25	0.21	0.16	–	0.004	0.05	3
Pb	1990	–	–	–	–	–	–	–	–		
	1993	–	1.4	–	< 0.2	< 0.5	–	–	–		
	1996	–	2.4	–	< 0.5	< 0.5	–	–	–		
	2000	4.9	2.7	2.7	0.05	0.03	0.01	–	< 0.01	0.03	0.01

Watucapil. At Blawan, a strong decrease in element concentrations, together with a strong increase in pH, e.g. almost two orders of magnitude for Cl, can be seen. At the Laut site, at the end of the original riverbed at the mouth of the Banyuputih, the river water is extremely diluted by seawater.

Comparison with earlier findings (see Table 2) shows that chemistry and principal characteristics of the water of the lake and at the acidic sites of Paltuding and Watucapil have not significantly changed over the last seven to ten years. In Blawan and Liwung, though, there has been a clear increase in acidity in the last seven years. Also a strong increase in most element concentrations, especially aluminium, iron, sulphate, sodium, potassium and zinc, is observed over the last seven to ten years, confirming the strong influence of pH on water chemistry.

3 The Asembagus Irrigation Area: Impacts on Crops and Human Health

The irrigated coastal area near Asembagus has a surface of 3,564 hectare and hosts approximately 50,000 inhabitants. The agricultural land is mainly used for the cultivation of rice and sugar cane. The local people largely depend on the river for their water supplies, although most people use wells for their drinking water.

The amount of water available for irrigation is influenced by the base flow discharges of the Banyuputih. When Banyuputih discharges are high, the discharge inlet irrigation area at the Liwung dam can be maintained at a maximum of approximately 4 m^3/s, but when base flow discharges are low, as in the dry 1989–1999 decade, the irrigation inlet discharge will drop to a lower value of 3 m^3/s; in the latter case, both the pH and quality of the irrigation water are expected to decrease due to a reduction in fresh water contribution from the upstream Kali Sat and Kali Sengon tributaries [13].

Local farmers and irrigation authorities report a loss of rice yields over 70% in recent years, which could be attributed to an increase in acidity of the irrigation water (see Table 2). Hydrological data (**Fig. 3**) reveal that the total precipitation on the Ijen plateau has decreased in the last 20 years. In the period 1980–1989, the average precipitation was 2437 mm/y with an average of 143 rain days. Over the last ten years, though, from 1990–1999, the average precipitation was 1,447 mm/y with an average of 115 rain days. Fig. 3 shows, for the period 1989–1999, that the irrigation inlet discharges have been lower than before, thus indicating lower base flow conditions for this period.

Concern has risen about the long-term effects of polluted irrigation water on the quality of the soil in the irrigation area. Delmelle and Bernard [9] calculated a daily discharge of 150 tons of SO_4, 2.8 tons of F, 50 tons of Cl, 10 tons of Al, 34 tons of SiO_2, 0.42 tons of Mn, 0.035 tons of Ti and 0.004 tons of Cu into the irrigation network. The river water has already been used for irrigation purposes for at least 200 years. Therefore, large amounts of metals must have accumulated in the soils of the irrigation area. Results of a regional soil sampling campaign in 2001 [14] showed that the average soil pH (H_2O) at 0–20 cm depth was 3.9 (±0.2), while in adjacent reference areas, irrigated with neutral water, soil pH (H_2O) was 7.0 (±0.5). In the topsoil, levels of various elements (Mn, Ca and Mg) have decreased as compared to the reference areas. In contrast, the Al level has increased

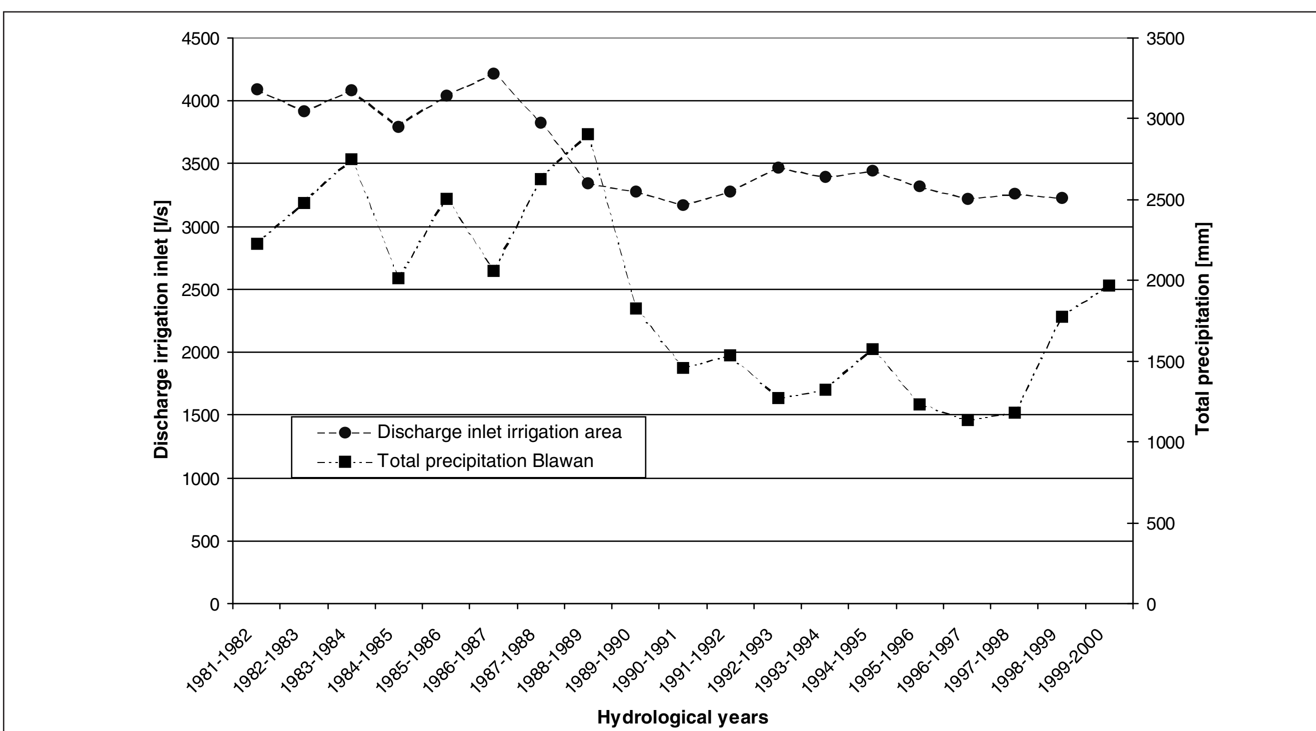

Fig. 3: Comparison of the discharge inlet irrigation area at Liwung dam and the precipitation totals in Blawan for the period 1980–2000 (data were kindly provided by the Asembagus Irrigation Office and Blawan coffee factory)

Table 3: Number of macroinvertebrate families found in the acidic Banyupahit-Banyuputih and the neutral Kali Sengon in 2000

Site	Paltuding/Watucapil	Blawan	Liwung	Kali Sengon
pH	0.72	2.88	3.27	7.71
Number of families	0	1	1	29

due to precipitation of Al originating from the irrigation water. If defined as a loss of basic cations and of acidic neutralizing capacity, the soils that received polluted irrigation water show an increased weathering rate. It is assumed that the composition of the pore water more or less resembles the irrigation water, since the soil pH is 3.9 everywhere and that of the irrigation water is 3.2.

Concentrations of Fe, Mn and especially Al exceeded the guideline values for irrigation water. Al is of major concern for the agricultural food production due to its phytotoxicity. In laboratory experiments with rice exposed to Al in solution culture, the threshold of toxicity was around 10 mg/l [15,16]. Aluminium concentrations in irrigation water in the Asembagus irrigation area by far exceeds this level (64 mg/l) and, in combination with the low soil pH, are probably responsible for the phytotoxicity.

In addition to crop loss, foodstuffs consumed from these areas could be hazardous to human health. In general, it is assumed that dissolved elements are available to plants and it is well known that the availability of many elements increases with decreasing pH [17,18]. Uptake and translocation of elements by plants, however, are both element and plant species specific. Intraspecies differences are also common [19,20]. This makes it difficult to predict elevated levels of elements in crops.

In 2000, edible parts of rice, maize, cassava root, cassava leaves, peanuts and sugar cane were collected from the areas irrigated with acidic water and from surrounding reference areas irrigated with neutral water. Increased levels of various elements, in particular Cd, Co, Ni and Mn, were found in a number of crops. Most levels were within acceptable ranges, but a hazardous exposure of humans to Cd cannot be fully excluded, considering the high consumption of rice and cassava root with increased levels of Cd [14].

Also fluoride constitutes a risk and excessive F exposure can weaken the structure of bone tissue and can cause dental fluorosis. Exposure to excess F occurs via drinking water, food, tea and natural food additives [21–24]. Fluoride concentrations in water wells in the Asembagus area on average contain fluoride concentrations > 2.5 mg/l (Table 2), exceeding the guideline value of 1.5 mg/l for F in drinking water [25].

Also increased levels of fluoride in the locally grown crops may be expected when irrigation water levels exceed guideline values for F by a factor 10. F uptake in plants highly depends on the speciation of F in the soil solution, which is in turn determined by soil pH and Al concentration in the soil solution [26,27]. In general, roots contain the highest levels and translocation to shoots seems to differ among species [25]. In the Asembagus area, dental fluorosis is observed among the majority of the local residents. In general, mild forms of dental fluorosis can be observed for concentrations of fluoride around 1.5 mg/l and skeletal fluorosis can occur above 4 mg/l [28].

4 Ecosystem Health

Several studies have documented the effects of a low pH on metal bioaccumulation and the toxicity of metals to macroinvertebrates [29]. Changes in diversity and abundance of macroinvertebrate species have been observed [30] and macroinvertebrate abundance and species richness decrease with decreasing pH [31]. Also leaf litter decomposition rate is suppressed under acidic conditions, leading to limited food resources [32]. Only a few species are capable of dealing with environments with a pH lower than 3.

Macroinvertebrates of the Banyupahit-Banyuputih were sampled along the acidity gradient using a hand net with mesh size 500 µm and five minutes effective sampling of all possible substrates in order to sample a representative community. Animals were sorted and fixed in 70% ethanol. Preliminary results show that the food-webs in the acidic parts of the river are highly underdeveloped (**Table 3**). No invertebrates were found in the extremely acidic water at Paltuding and Watucapil, although several invertebrates (Ephemeroptera, Trichoptera and chironomid larvae) were observed in small rain-fed pools with a pH of 4 in the riverbed, just alongside the main stream. These observations clearly prove that the acidity of the water, and the associated chemical composition, is prohibitive to the development of a normal macro-invertebrate community and that the absence of this community is not caused by the lack of colonising populations. In the moderately acidic site at Blawan, only chironomids were found in high abundance. Some other specimen of invertebrates were also found (water striders, diving beetles, leeches), but only very sparingly. This also holds for the river water with pH 3.0–3.5 in the downstream area (Liwung). This observation cannot be attributed to a low pH only, because macro-invertebrates are known to occur at corresponding pH conditions elsewhere [33]. It is therefore suspected that high contents of metals or other dissolved chemicals, such as nitrate, phosphate and sulphate, play an important role in limiting the development of aquatic animal life.

5 Conclusions

The Kawah Ijen crater lake, with its extremely low pH (< 0.3), is the source of a naturally metal-polluted river, the Banyupahit. Concentrations exceed quality guidelines and some metal concentrations are extremely high, especially iron and aluminium.

The river water used in the Asembagus irrigation area, 25 km downstream, exceeds the quality guidelines for irrigation water. Local farmers and irrigation authorities report loss of crop yields in recent years. These losses can be attributed to an increase in acidity of the irrigation water, which is related to the total precipitation on the Ijen plateau being significantly lower during the last ten years. Aluminium levels are often higher than the phytotoxicity threshold.

Ecological consequences of low pH, in combination with high metal concentrations, are clear in the river ecosystem where the food-webs are highly underdeveloped. Alteration in precipitation in the last twenty years has led to a lowered pH of the river water, although it is less clear if this precipitation has also led to the ongoing trend of a decrease in pH over the last ten years. Our data indicates that the Ijen crater lake presents a serious threat to the environment as well as to human health and agricultural production.

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