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## The Specific Nature of Chemical Composition of Water from Volcanic Lakes Based on Bali Case Study

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### Abstract

The research area was localized in the Indonesian Archipelago, at the latitude of eight and nine degrees S on the one of the Lesser Sunda group island provinces, Bali (563,3 km<sup>2</sup>). Two massive calderas (Mount Batur 1717 m above sea level.; Mount Sangiang 2093 m above sea level) are one of the most prominent landforms in the chain of volcanic mountain ranges of the Bali Island. Lake Batur (17,18 km<sup>2</sup>) and Batur Spring (which are part of the freshwater lake system of Mt. Batur caldera) and also Danau Bratan Lake (one of the unconnected lakes next to the Mt. Sangiang caldera), were selected for studies on the pollutants concentration levels in this volcanic area located in tropical climate. The research was aimed at determining the concentration of pollutants of natural (volcanic) and anthropogenic origin occurring in both lakes. The following parameters were determined: anions, metals, pH and conductivity. Based on the obtained dataset of initial studies it can be stated that the localization of aquatic ecosystems has the significant impact on the chemical composition of surface water.

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## 1. Introduction

Calderas are important features in all volcanic environments and are commonly the sites of geothermal activity and mineralisation. Descriptions of calderas, based on dominant composition of eruptives (basaltic, peralkaline, andesitic–dacitic, rhyolitic) can be used, and characteristics of each broad group are given. Styles of eruption may be effusive or explosive, with the former dominant in basaltic calderas, and the latter dominant in andesitic–dacitic, rhyolitic and peralkaline calderas [1]. The natural lakes have usually been formed by volcanic or tectonic activity. Caldera lakes were formed in the depressions of the collapsed walls of volcanoes. Good examples of caldera lakes are Batur, Bratan, Buyan and Tamblingan lakes in Bali. Crater lakes were formed in the extinct craters. Maninjau and Ranau lakes in Sumatra and Lake Segara Anak in Lombok are typical crater lakes as well as many of the small lakes in Java and Tigawarna Lake in Flores [2].

Bali is one of the Lesser Sunda group of island provinces in the Indonesian archipelago, lying between eight and nine degree south of the equator. Bali covers an area of 563.3 sq. km. Bali landscape is dominated by a chain of volcanic mountain ranges that consist of both active and dormant volcanoes. Bali highest mountain Mount Agung (3143 m) and Mount Batur (1717 m) in eastern Bali are the active volcanoes while Mount Batukau (2276 m) in the centre of Bali and Mount Merbuk (1385 m) in west Bali are the dormant ones. Bali has 18 volcanic peaks exceeding 1000 m above sea level and seven higher than 2000 m above sea level. Because these high peaks are typically cone-shaped, stream pattern is classified as the radial throughout system. Soils are generally andosols and, like in the rest of Bali, originate from very fertile, basic volcanic ejecta. It distinguishes them from the other volcanic regions where soils are sometimes unproductive due to high acidity. The two most prominent landforms of this system are the two massive calderas and four caldera lakes formed during ancient geological disasters. Both calderas have freshwater lake systems, the largest is Lake Batur (17.18 sq. km) in the Mt. Batur caldera. Mt. Sangiyang to the west has three smaller unconnected lakes Danau Buyan, Danau Bratan and Danau Tamblingan [3,4].

Geologically Bali is still active with two main active volcanic centers. A dangerous eruption is expected on average every 30-100 years. The last time both volcanoes erupted in May 1963 and fortunately no one was killed by the eruptions in Batur. Because Bali is situated in a highly active tectonic zone, seismic events are also common. Earthquakes that cause local slight to moderate damage to property occur on average every ten years. Massive earthquakes that cause loss of life are predicted to occur less often than once every 100 years. The most recent event of this nature, which cost hundreds of lives and measured 6.2 on the Richter Scale, was in 1976 [3,4]. Chemistry of the Indonesian equatorial lakes is largely unknown and it is strongly affected by biological and perhaps geothermal processes. This paper is an initial attempt at a regional assessment of different crater lakes chemical composition.

## 2. Experimental

### 2.1. Sampling

Water samples from two caldera lakes were collected in February 2013. To avoid losses of analytes to headspace, samplers were filled without a bubble of air. Then samples were transported to the laboratory and stored prior to analysis in the temperature of 4<sup>0</sup>C. In order to minimize the storage time the analysis was performed immediately after delivery of the samples to the laboratory. The research area was localized in the Indonesian Archipelago, at the latitude of eight and nine degrees S on the one of the Lesser Sunda group island provinces, Bali (563,3 km<sup>2</sup>). Two massive calderas (Mount Batur 1717 m a.s.l.; Mount Sangiyang 2093 m a.s.l.) are one of the most prominent landforms in the chain of volcanic mountain ranges of the Bali Island. Lake Batur (17,18 km<sup>2</sup>) and Batur Spring (which are part of the freshwater lake system of Mt. Batur caldera)

and also Bratan Lake (one of the unconnected lakes next to the Mt. Sangiyang caldera) were selected for studies on the pollutants concentration levels in this volcanic area located in the tropical climate (Table 1).

Table 1. Geochemical and petrological data of rocks and lakes characteristics

Buyan-Bratan Caldera	Batur Caldera
Lake Bratan, ordinate 1231 m above sea level, area 3,8 km <sup>2</sup> , maximum depth 22 m	Lake Batur, ordinate 1031 m above sea level, area 15,9 km <sup>2</sup> , maximum depth 88 m
Caldera volcanic activity earlier than around 500 ka. BP	Caldera volcanic activity around 500 ka. BP
No information about volcanic eruptions	28 volcanic eruptions (from 1804 to 2000)
Geochemical and petrological data of rocks :Geochemical analysis revealed that the rock composition of those edifices are in the wide range of SiO <sub>2</sub> concentration from 45% to 63% or from basaltic to andesitic. So far, only rocks collected from caldera rim have high SiO <sub>2</sub> concentration from 65 to 72% or from dacitic to rhyolitic composition. BBC is composed of similar mineral assemblage of plagioclase, pyroxene, magnetite and olivine.	Geochemical and petrological data of rocks :BC of the construction of a basaltic to andesitic stratovolcano. Magma erupted from Batur has wide range in composition, from basaltic to rhyolitic, indicating mature evolution of magma and progressive development of a shallow magmatic system resulted in catastrophic caldera-forming eruptions.
Bratan Lake: Bratan is the shallowest confined lake in Bali, but yet very heavily under the pressure of recreational activities, motor boating and other outdoor activities, hotels and restaurants. The temple of Pura Ulun Danu (goddess of the lake) is at the lake. There are several big outboard engines for a small (3.9 km <sup>2</sup> ) and shallow (22 meters) lake, the biggest with the power of more than 200 horsepower. Attention to this fact was already drawn 18 years ago. Some small-scale agriculture is maintained around the lake.	Batur Lake: Lake Batur is the largest and deepest confined lake in Bali, and its basin is a caldera. It is situated next to the volcano Gunung Batur. The most recent eruption happened in 1963. There is some small-scale agriculture around the lake, and an increasing number of guest houses is being built. The lake is also used for fishery. The volcano is a favored hiking area, and on the western shore, there is the oldest village in Bali, Trunyan. By now there have been no major man-caused threats to the lake.

## 2.2. Analytical methods

Table 2 presents analytical techniques employed to determine both the main and trace elements and the TOC parameter together with their metrological characteristics.

Table 2. Validation parameters, technical specifications used in the analytical procedures.

Parameters	LOD <sup>3</sup>	LOQ <sup>3</sup>	Measurement instrumentation	
Cations <sup>1</sup>	0.01	0.030	DIONEX 3000 chromatograph (DIONEX, USA)	column: Ion Pac® CS14 (3x250mm); suppressor: CSRS-300, 2mm, mobile phase: 38 mM metasulfonic acid, flow rate: 0.36 ml/min, detection: conductivity
Anions <sup>1</sup>	0.055-0.09	0.027-0.17		column: Ion Pac®AS22 (2x250 mm); suppressor: ASRS-300, 2mm, mobile phase: 4.5 mM CO <sub>3</sub> <sup>2-</sup> , 1.4 mM HCO <sub>3</sub> <sup>-</sup> , flow rate: 0.38ml/min, detection: conductivity
Metals <sup>2</sup>	0.0007	0.002	Elan DRC, PerkinElmer, USA gas fed to the atomizer→ Ar:0,98 l/min, plasma gas→ Ar: 15 l/min	

<sup>1</sup>[mg/L], <sup>2</sup>[µg/L], <sup>3</sup>Both the limit of detection (LOD) and the limit of quantitation (LOQ) were calculated based on the standard deviation of the response (s) and the slope of the calibration curve (b) according to the formulas: LOD = 3.3(s/b), LOQ = 10(s/b).

### 3. Results and discussion

Physical processes of the Indonesian equatorial lakes are largely unknown (weak Coriolis force and prevailing winds), and chemistry is strongly affected by biological and perhaps geothermal processes. The density structure is governed by small temperature gradients and relatively important gradients in total dissolved solids. The importance of biogenically driven stratification maintained by salinity gradient has also to be emphasized, as well as the deep thermal gradients, which may be adiabatic and stable. Water balance is dominated by seepage, rainfall and evaporation. The variations in the mixing depth caused by weather and depth of seasonal mixing may have an impact on the nutrient flux into the epilimnion zone [2].

Hydrochemical parameters for water samples obtained during conducted research for two different calderas are listed in Table 3.

Table 3. Average concentration of selected parameters determined in water samples from Batur and Bratan Lake.

Determined parameter [mg/l]	Batur Lake	Bratan Lake
pH [-]	8.54	7.00
<sup>1</sup> EC [ $\mu$ S/cm]	1730	27.9
Na <sup>+</sup>	287	3.40
K <sup>+</sup>	55.7	0.388
Mg <sup>+</sup>	26.9	1.87
Ca <sup>2+</sup>	18.2	0.082
SO <sub>4</sub> <sup>2-</sup>	394	1.85
F <sup>-</sup>	2.71	0.504
Cl <sup>-</sup>	165	1.15
Br <sup>-</sup>	0.723	0.118

<sup>1</sup>EC – Electrical conductivity

Electrical conductivity (EC) in the natural Indonesia lakes, which can be of the different types (caldera, tectonic, tectonic/volcanic, floodplain, semi-natural, landslide, volcanic/crater, crater) was usually at the range of 80-300  $\mu$ S/cm. Generally, the EC value decreases slightly with the increasing depth of the lake.

Alkaline cations, especially calcium and magnesium, appeared mainly as a result of the ions, contained in magma creating calderas, exchange processes and the reaction of magma erosion (CaO and MgO) [5]. Customarily calcium concentrations in the Indonesia lakes were from 1.9 to 35 mg/l. During conducted research the lowest concentration was determined in Bratan Lake (0.082 mg/l) while the highest one in Batur Lake (18.2 mg/l).

Table 4. Average concentration of selected parameters determined in water samples from Batur and Bratan Lake.

Determined parameter [ $\mu$ g/l]	Batur Lake	Bratan Lake	Determined parameter [ $\mu$ g/l]	Batur Lake	Bratan Lake
Li	423	<LOD	B	1440	53
Al	2.4	8.0	V	34.8	0.4
Cr	3.8	0.5	Mn	0.4	0.4
Cu	2.2	0.4	Zn	1.7	1.0
As	4.1	0.2	Se	0.94	<LOD
Rb	62.7	3.33	Sr	96	11
Mo	3.15	<LOD	Cs	3.13	0.04
Ba	11.2	2.2	U	0.113	<LOD
Be, Ag, Sb, Tl, Bi, Co, Ni, Cd, Sn, Pb	<LOD	<LOD			

In 1993 heavy metals (cadmium, chromium, copper, nickel and lead) were not detected in the Indonesian lakes [2]. Only zinc concentrations varied from undetectable in the natural lakes to 0.34 mg/l in Batur Lake [2]. At present the majority of metal ions, including heavy metals, are detected and determined (Table 4).

The chemical form of metals is modified by the environmental physicochemical factors such as pH value, presence of complexing ligands (humic acids, fulvoacids, chlorides, sulphates, carbonates or phosphates) and other metal ions as well. For the pH value of around 7 (for example in Bratan Lake) the heavy metals occur in the most accessible and toxic ionic form. Humic acids, fulvoacids, chlorides, sulphates, carbonates or phosphates can also create stable complexes with metals. Such considerations on the influence of pH on the presence of trace elements have been described for Ijen caldera (Indonesia) [6].

Elements such as V, Cr, Co, Ni, Cu, Rb, Sr, Mo, Cs, Ba, Pb or U, which were detected and determined in waters of Batur Lake, are also present in volcanic gas plumes and rock obtained from the substrate. The elements determined in water of the lakes situated in calderas are also present in minerals creating these calderas: Al (Plagioclase), Li (Pyroxene), V and Cr (Magnetite), Ni (Olivine). Hydrothermal fluids with element ratios that are different from those in host rocks either have precipitated secondary phases during their history or must have been formed by incongruent dissolution of volcanic rock during water–rock interaction. The main rock-derived elements in volcanic lake fluids from andesitic volcanoes are Na, Ca, K, Mg and Al, which are derived from the dissolution of volcanic glass, plagioclase, pyroxene and biotite or muscovite [5], [7], [8].

#### 4. Conclusions

The results of the first extensive study on the abundance of major, minor, trace elements and organic compounds in water from two different caldera lakes indicate that their chemistry is the results of important interactions among water, volcanic gases and host rocks.

The conducted researches show that water of both lakes differs diametrically for cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^+$ ,  $\text{Ca}^{2+}$ ) and anions ( $\text{SO}_4^{2-}$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ). The mentioned parameters are around 100 times higher in Batur Lake than in Bratan Lake. Similar differences are also for conductivity and pH. The comparison of concentration levels of trace elements in both lakes indicates that in Batur Lake they are from several to several hundred times higher than in Bratan Lake whereas the concentration levels in water of Batur Lake and Batur Spring are very similar.

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