# 東海大学大学院平成26年度博士論文

# Geochemical characterization of volcanic lakes: Implication for volcanic hazards monitoring/surveillance along the Cameroon Volcanic Line

(カメルーン火山列における災害監視活動を目 的とする火口湖の地球科学的特性解明)

## 指導 大場 武 教授

東海大学大学院総合理工学研究科 総合理工学専攻

Issa

Geochemical Characterization of Volcanic Lakes: Implications for Volcanic Hazards Monitoring and Surveillance along the Cameroon Volcanic Line (CVL)



By:

#### ISSA (ID: 1LTAD001)

Dissertation submitted as part fulfilment of the requirements for the degree of Doctor of Philosophy (PhD) in the Department of Chemistry, School of Science and Technology of Tokai University

Supervisor: Takeshi OHBA (Prof.)

Examining Committee:

Akira UEDA (Prof.) Maki TSUJIMURA (Prof.) Michio IWAOKA (Prof.) Osamu KANIE (Prof.) Rio KITA (Prof.) Takeshi OHBA (Prof.) Toyama University Tsukuba University Tokai University Tokai University Tokai University Tokai University

Geochemical characteristics of the CVL lakes

### Abstract

Lakes Nyos and Monoun gas explosions killed ca 1800 people. The danger stems from the accumulation in their bottom waters of magmatic  $CO_2$ . To avoid future deadly exhalation, the stored gas is currently being removed. Except those two, the Cameroon Volcanic Line (CVL) hosts ca 37 other lakes. Excluding other triggering mechanisms, saturation may entrain gas explosion from lakes Nyos and Monoun every ca 100 and 30-40 years respectively as demonstrated by recent geochemical studies. Still, there are no evidences of past events in the collective memory of the people who live near the lakes since centuries. The absence of traces may mean such events might have never occurred before. It is therefore thought that the catastrophes may have resulted from relatively recent seismic and/or volcanic activities which might have entrained significant gas to seep in the lakes. Due to such processes, gas release might migrate from lake to lake as supported by social studies which indicate that, in the Oku region, some ethnic groups might have also suffered lost and destruction from lakes. Accordingly, this study provides baseline data to encourage the implementation of multiparametric monitoring and surveillance of the CVL lakes. It investigates the physico-chemistry, stable isotope, diffuse gas emission and the effect of methane on the stability of the lakes Nyos and Monoun; seventeen lakes, ca 40% of 39 crater lakes are evaluated. Finally, for risks mitigation, it advocates for the setting up of a minimum volcanic lakes surveillance network.

Major ion chemistry indicates the lakes waters are almost devoid of sulfates and chlorides and rich in bicarbonate justifying their classification as neutralbicarbonates (NB) type-lakes. The bicarbonate dominance suggests the acidity for rock dissolution is provided by  $CO_2$ . The cations derive from water-rock interaction through rock-dominated alteration systems meaning, the mineralization processes is dominantly controlled by the hosting rocks. The fact that the water chemistry could be explained by specific geological formations supports the above assertion. Alike Nyos and Monoun, the other lakes also display thermally and physically stratified water columns the shape of which depends on seasons and mixing with exogenous water bodies. The waters were generally neutral and their conductivities were close to fresh waters. The <sup>18</sup>O and <sup>2</sup>H study also shows that, lakes waters are meteoric in origin and the water columns display stratified pattern with heavy isotope enriched epilimnia. It was also observed that, although the rain gets depleted northward, the lakes instead get more heavy isotopes enriched. Accordingly, the Adamaua lakes are the heaviest. Given that the mean annual temperature in the Adamaua is lower than that in the South, it was conclude that, the temperature-dependent isotopic fractionation might be reversed along the CVL. The lakes Nyos and Monoun bottom most waters were the most depleted in <sup>18</sup>O due to fractionation between water and  $CO_2$  molecules; the process would tend to enrich the gas. This finding could be used as a geochemical monitoring tool for gassy lakes since the induced <sup>18</sup>O depletion might imply concomitant  $CO_2$  increase. In addition to the physico-chemical and isotopic, the study also provides insights on diffuse gas (e.g: CO<sub>2</sub>) manifestation in lakes and soil.

During periods of quiescence, volcanogenic structures emit significant amount of volcanic gas to the atmosphere, especially  $CO_2$  whose impacts on the global climatic evolution is now well established. This study reports on diffuse gas surveys from 9 lakes  $(CO_2)$  and soil  $(CO_2, He, Ar, N_2)$  from Nyos valley and Mount Manenguba Caldera. Results showed that, besides lakes that emit  $CO_2$  (diffuse  $CO_2$ -positive lakes) to the atmosphere, there exist neutral (in equilibrium with atmosphere) and  $CO_2$  sinks lakes (consume atmospheric  $CO_2$ ). All taken, the surveyed lakes emit totally ca  $28 \pm 0.37$  t.d<sup>-1</sup> CO<sub>2</sub> to the atmosphere; Extrapolate to the 39 CVL lakes, the emission would amount to  $75\pm0.5$  t.d<sup>-1</sup>. In addition, to the surface generation of  $CO_2$  from precipitates, the gas removal operation at Nyos and Monoun, has released ca  $2.52\pm0.46\times10^8$  moles.Km<sup>-2</sup>.yr<sup>-1</sup> CO<sub>2</sub> to the atmosphere from January 2001 to March 2013 more than the double of the per land area amount (10<sup>8</sup> mol.Km<sup>-2</sup>.yr<sup>-1</sup>) released from the Yellowstone volcanic system in the USA. The soil emission would be ca  $578.1\pm 1.3$  t.d<sup>-1</sup>. Finally, at the global scale, the CVL hosts ca 5% of the volcanic lakes of the world and would contribute 0.023 % of the global CO<sub>2</sub> emission.

In addition to the diffuse emission, the  $CO_2$  concentration and its origin were also determined. Although in minor concentrations (0.56 mmoles/kg to 8.7 mmoles/kg), several lakes contain magmatic  $CO_2$  as evidenced by the  $\delta^{13}C$  values from -4.42 ‰ to -9.46 ‰ implying that magma continues to degas at depth thousands years after the last eruptive activities as confirmed by the Manenguba Caldera soil gas geochemistry. The ubiquitous presence of magma-derived  $CO_2$  in soil and in lakes implies that, future increase to seismic and/or volcanic activities might re-open vents allowing more gas to seep and dangerously accumulates in the lakes.

For hazards mitigation and risks management, it is recommended that, (1) a minimum surveillance network made up of suitably selected lakes be set up; (2) in addition to the seismic surveillance, gas-based monitoring system ( $CO_2$ , Helium, Radon...) could be established to enhance the volcanic activity predictability.

In addition to the study of volcanic gases, the work attempted to assess  $CH_4$  role on the stability of lakes Nyos and Monoun water columns. The results show that,  $CH_4$ concentration is slightly increasing. Given its lower solubility compared to  $CO_2$ , current  $CH_4$  increase rate may create instability in the lakes as recently argued for in the case of Lake Kivu which might release gas within the current century. In order to assess its effect, the study proposes a simple, rapid, accurate and cheap method to monitor  $CH_4$ .

Finally, in view to set up a minimum volcanic lakes surveillance network, the study attempted to identify the lakes having natural characteristics similar to lakes Nyos and Monoun. In addition to the data generated, depth and area, ca 24 parameters were used to group the lakes and subsequently identify the parameters that most account for the variance. The results highlighted the peculiarity of the gassy lakes. However, Lake Benakuma, the third deepest lake (after Nyos and Manenguba female) was identified as the one that most resembles the gassy lakes. Bicarbonate was the parameter that most accounted for the similarity/difference among the lakes.

### Abstract

論文題目:カメルーン火山列における災害監視活動を目的とする火口湖の地球化学的特 性解明

キーワード:カメルーン,ニオス湖,マヌン湖,自然災害,安定同位体,モニタリング

ニオス・マヌン湖のガス放出は 1800 人の犠牲をもたらした.災害の原因は湖に供給 されるマグマ起源の二酸化炭素(CO<sub>2</sub>)の蓄積であり,現在は除去されつつある.ニオ ス・マヌン湖以外に,カメルーン火山列(CVL)には 37 の火口湖が分布している.ガ ス放出の引き金がなければ,ニオス湖とマヌン湖ではそれぞれ 100 年,30~40 年で CO<sub>2</sub>が溶解度の限界に達してしまうと考えられている.湖の周辺には何百年も前から 人々が住んでいるが,過去には同様の災害が起きた証拠はない.したがって,ガスの放 出による災害は,比較的最近の地震の影響あるいは火山活動の結果,大量のガスが湖に 供給されたことが原因なのかも知れない.このように考えると,ガスの放出が起きた湖 は時代により移動したのかも知れない.民族学的な調査で明らかになったように,オク 火山地帯では,実際にいくつかの民族の集落が湖によって失われたらしい.そこで,本 研究では,CVL に分布する湖の,多項目監視活動の基礎となるデータを取得すること を目的とする.本研究では,37 の湖の 40%に相当する 17 の湖を研究対象とし,湖水 の物理化学,安定同位体比,拡散的ガス放出,メタンの影響について考察する.最後に 最低限必要な湖監視活動の取り組みについて提案を行う.

ニオス・マヌン湖の水の主要なイオンは炭酸水素イオンであり、硫酸イオン、塩化物 イオン濃度は極めて低い.炭酸水素イオンが陰イオンとして優勢であることは、湖水の 酸性は CO<sub>2</sub>の溶解によりもたらされたことを示している.湖水の陽イオンは岩石---水 作用で供給されると考えられる.水質が特定の地層により説明されることは上述の推定 を支持する.ニオス・マヌン湖と同様に、他の湖でも熱的あるいは物理的な性質に関し、 水の成層構造が存在し、その形は季節的に変化し、外来水の影響を受けている.概して 湖水は中性であり、電気伝導率は低く、淡水の特徴を示す.水の<sup>18</sup>O と D 濃度から、 湖水は天水起源であり、表層水はこれらの同位体について濃集した層構造が見られる. 一般に高緯度の天水は同位体比が低いが、CVL に沿った湖では、逆に高緯度の湖に同 位体比が高い傾向がみられ、北部のアダマワ湖では最高の同位体比を示した.アダマワ 湖の地域における降水量は南部よりも低く、蒸発にともなう同位体比分別の影響が大き いと考えられる.ニオス・マヌン湖の水は底部で最も 180 に乏しく,水と CO2 の間の 同位体分別が影響しているのかも知れない.水-CO2間では CO2 に 18O が分配し易い. このことは、ガスに富む湖の地球化学的監視活動に利用できる. すなわち、水の 180 の低下は、CO<sub>2</sub>の増加を意味するのかも知れない。湖水の物理化学および安定同位体 比に加え、本研究では、湖水と周辺土壌における拡散的放出ガスを追跡した、火山活動 が静穏な時期に火山体は相当量の火山ガス,特に CO<sub>2</sub> を放出し,これが地球の気候に 影響を与えることがよく知られている.本研究では 9 つの湖で湖水からの CO<sub>2</sub>の拡散 的放出とニオス谷とマゲンヌバ山カルデラにおける土壌ガス(CO<sub>2</sub>, He, Ar, N<sub>2</sub>)を調 査した. その結果, CO2 を放出する湖に加えてまったく放出がない湖, 逆に CO2 を吸 収する湖が見いだされた. 調査した湖から大気への放出量を総合すると 28 ton/day と なり, 39 の湖に外挿すると 75 ton/day となる. 土壌からの CO<sub>2</sub> 放出は, 578 ton/day であった. CVL には世界の火口湖の約 5%が存在し、全地球の CO2 放出量の 0.0035% が放出されていると考えられる. 拡散放出量に加え, 溶存 CO<sub>2</sub> の濃度とその起源につ いても調べた. 濃度は、 $0.56 \sim 8.7 \text{ mmol/kg}$  と低いものの、いくつかの湖では  $\delta^{13}$ C の 値が, -4.42 ‰~-9.46 ‰であり, マグマに起源する CO<sub>2</sub>を含んでいることを示した. マゲンヌバカルデラでは最後の噴火から数千年が過ぎているにも拘わらず依然としてマ グマの脱ガスが継続していることを暗示している.マグマ起源の CO<sub>2</sub> が土壌や湖水に |幅広く分布していることは,将来,地震活動や火山活動によりガスの通路が再開した場 合、多量のガスが放出され、湖水に蓄積する危険性がある.災害防止とリスク管理のた めに、以下のことが望まれる.1)特定の湖に対し、最低限の監視活動ネットワークを 構築する.2)地震観測ネットワークに加えて、ガス観測(CO<sub>2</sub>, He, ラドン等)に よる監視活動を行う.

火山ガスの研究に加え、ニオス・マヌン湖の水に溶存するメタン(CH<sub>4</sub>)の役割について調べた. CH<sub>4</sub>は CO<sub>2</sub>に比べて水に対する溶解度が低いために湖水成層構造の不安定化をもたらすかもしれない. アフリカ東部のキブ湖では、今世紀内に CH<sub>4</sub>による影響でガス放出があり得ると懸念されている. CH<sub>4</sub>の効果を評価するために本研究では現場で結果が得られるシンプルで迅速なモニタリング法を開発した.

最後に,必要最低限の火口湖モニタリングネットワークを構築するため,ニオス・マ ヌン湖に類似する特性を有する湖の探索を行った.調査で得たデータに加え,湖の深度 と面積を加え,24のパラメータで統計学的に類似性を評価し,どのパラメータが類似 性に寄与しているのか検討した.その結果,ニオス・マヌン湖のようなガス成分に富む 湖は特異であることが証明され,高深度のベナクマ湖はニオス・マヌン湖に類似性が最 も高いことが示された.類似性に最も寄与する湖水のパラメータは、炭酸水素イオン濃度であることが示された.

### Résumé

# « Les caractéristiques physico-chimiques et isotopiques des lacs volcaniques et leurs incidences sur le suivi et la surveillance des risques volcaniques le long de la Ligne Volcanique du Cameroun (CVL) »

L'accumulation de gaz carbonique d'origine magmatique et son exhalaison soudaine fut la cause des 1800 morts des catastrophes des lacs Nyos et Monoun. Celle du lac Nyos reste la catastrophe naturelle la plus mortelle (1784 morts) jamais enregistrée au Cameroun. Les deux lacs qui constituaient de véritables «bombes à retardement» en raison de leur propension à accumuler des gaz pour ensuite, quand les conditions sont réunies, exploser, sont en voie d'être purgés de leurs contenus mortels. En dehors de ces deux, la Ligne Volcanique du Cameroun (CVL) en héberge plus d'une trentaine. Si le vecteur de la mort est connu, le processus déclencheur, si l'on met de côté les conjectures, demeure encore une énigme. Toutefois, il est possible que l'exhalaison ait pu être spontanée, c'est-à-dire que les lacs auraient atteints la saturation avant d'exploser. En admettant que cela ait été le cas, alors les explosions de gaz aurait des périodes de retour d'environ 100 ans et de 30 à 40 respectivement pour les lacs Nyos et Monoun, comme le démontrent des études récentes. Cette fréquence théorique amène à nous poser la question : pourquoi n'existe-t-il pas des traces de tels évènements dans la mémoire des collectivités qui vivent prêt de ces lacs depuis des centenaires? En guise de réponse, on pourrait penser que l'exhalaison de gaz aurait été la conséquence d'une augmentation tu taux de recharge, elle-même résultant d'une augmentation correspondante de la volcanicité au cours des décades précédentes. Dans ce cas, on peut envisager ce type de processus migrant le long de la CVL comme le laisse penser des études sociologiques qui suggèrent que, dans le passé, des lacs auraient endeuillé certains groupes ethniques (e.g. : Bamessi, Oku) provoquant leur migration. C'est dans le souci de prévenir l'occurrence des drames du type Nyos outre part, que cette étude est menée avec pour objectif de générer les données de base pouvant servir à la surveillance des lacs volcaniques du Cameroun et par ricochet, d'évaluer les risques qu'ils posent afin d'en réduire, le cas échéant, les effets sur les populations. Le travail analyse des données sur la physico-chimie, les isotopes, l'émission des gaz diffus ( $CO_2$ , He, Ar, N<sub>2</sub>) et évalue les conséquences qu'une augmentation de la concentration en méthane pourrait entrainer sur la stabilité des lacs Nyos et Monoun ; au total, dix-sept, soit 40% des 39 lacs de cratères répertoires sont concernés.

Sur le plan de la chimie des majeurs, les résultats montrent que les lacs sont, en général, pauvres en sulfates et chlorures (absence des gaz volcaniques acides : HCl,  $H_2S$ ) et riches en bicarbonates ; ce qui conduit à les classifier comme des lacs de type Neutre-bicarbonatés (NB). La concentration élevée and bicarbonates suggèrent que l'acidité nécessaire à la dissolution des roches proviendrait du dioxyde de carbone (CO<sub>2</sub>). Le lessivage qui en résulte donne l'empreinte minérale spécifique des eaux de chaque lac. Au cours de ce processus de minéralisation, ce sont les roches

qui contrôlent la cinétique des réactions chimiques eaux - roches (water-rock interaction) au lieu des gaz, comme c'est le cas dans les zones volcaniques actives ; on dit alors que les systèmes d'altération sont à dominante géologique. Cette régulation de la géologie du volcan abritant les lacs se traduit souvent par une minéralisation spécifique des eaux.

Sur le plan de la physicochimie, les résultats montrent qu'à l'instar des lacs Nyos et Monoun, les autres lacs sont aussi stratifiés. La structure thermique et physicochimique des colonnes d'eau dépendent des saisons ainsi que du degré de mélange avec des eaux exogènes locales. Il convient de noter que les lacs ont en général un pH neutre et que la conductivité correspond à celle des eaux naturelle fraiches.

Parlant des isotopes, l'analyse du <sup>18</sup>O et <sup>2</sup>H suggère que les eaux des lacs proviennent des précipitations, et que les colonnes d'eau sont aussi stratifiées sur le plan isotopique avec des épilimnions généralement enrichis en isotopes lourds par rapport aux eaux des fonds (hypolimnions). Concernant la variation isotopique spatiale, il a été noté une particularité qui pourrait être propre aux lacs de la CVL. En effet, alors que, du Sud vers le Nord, les pluies (qui sont la source en eaux des lacs) s'appauvrissent progressivement en raison de l'effet de la latitude, celles des lacs s'enrichissent plutôt en isotopes lourds ; ce qui veut dire que les eaux des lacs de l'Adamaua sont en général les plus «lourdes». Cette tendance singulière suggère que l'effet du fractionnement isotopique dû à la température n'obéirait plus à la logique de la covariance (positive) entre les deux paramètres ; ceci se justifie par le fait que la température moyenne dans l'Adamaoua est inférieure à celle des zones côtières où les lacs sont comparativement pauvres en isotopes lourds. L'étude montre aussi que les eaux profondes riches an  $CO_2$  des lacs Nyos et Monoun sont les plus appauvries en oxygen-18 sans doute en raison du fractionnement isotopique entre les molécules d'eau et celles du  $CO_2$ ; cet échange tendrait à enrichir le gaz aux dépens de l'eau. Par conséquent, le résultat de ce processus pourrait servir d'outil de surveillance géochimique des lacs riches en  $CO_2$  car, un déficit croissant des eaux en oxygène-18 traduirait une augmentation conséquente des teneurs en gaz. En plus de la physico-chimie et des isotopes, l'étude s'intéresse aussi à la géochimie des émissions passive des gaz (e.g.  $CO_2$ ) dans les lacs et sur les sols.

Dans les zones non volcaniques, le dégazage passif se limite à la respiration des sols. Dans les zones actives, même en période de repos, les structures volcanogènes émettent dans l'atmosphère des quantités appréciables de gaz volcaniques, spécialement du  $CO_2$  dont les effets sur le climat et son caractère létal sont bien connus. Le présent travail analyse les résultats des mesures de  $CO_2$  diffus effectuées sur 9 lacs et celles du  $CO_2$ , He, Ar, et du N<sub>2</sub> réalisées sur les sols dans la vallée du Lac Nyos et dans la caldera du Mont Manenguba. Les résultats obtenus montrent que certains lacs sont en équilibre avec le  $CO_2$  atmosphérique, d'autres se comportent comme de réservoirs tandis une dernière catégorie émet effectivement du  $CO_2$  dans l'atmosphère. Il ressort du bilan que les 9 lacs étudiés émettraient environ  $28\pm 0.37$  t d<sup>-1</sup> ( $3.69 \pm 0.37$  Kt Km<sup>-2</sup> j<sup>-1</sup>)  $CO_2$  dans atmosphère. Et si l'on extrapole ces résultats aux 39 lacs volcaniques connus, cela représenterait un total d'environ  $75\pm 0.5$  t d<sup>-1</sup> (27.37 ± 0.5 Kt Km<sup>-2</sup> an<sup>-1</sup>) de CO<sub>2</sub>.

De Janvier 2001 et Mars 2013, en plus de  $CO_2$  généré par la décomposition des précipités carbonatés, la purge des lacs Nyos et Monoun aurait relâché dans l'atmosphère ca  $2.52\pm0.46\times10^8$ moles.Km<sup>-2</sup>.an<sup>-1</sup> CO<sub>2</sub>, plus du double d'émission spécifique (108 mol.Km<sup>-2</sup>.an<sup>-1</sup>) du système volcanique du Yellowstone aux USA. Quant aux émissions du sol, elles représenteraient ca 578± 1.30 t d<sup>-1</sup> (4.57 ± 1.30 Kt Km<sup>-2</sup> an<sup>-1</sup>).

A l'échèle globale, le Cameroun abrite environ 5% des lacs volcaniques répertoriés au monde. L'émission des lacs de la CVL représenterait 0.023 % des émissions globales de CO<sub>2</sub>; ce qui est considérable.

En plus du CO<sub>2</sub> diffus, la concentration des autres lacs en CO<sub>2</sub> ainsi que son origine ont fait l'objet de recherche. Bien qu'en teneurs négligeables (variant de 0.56 mmoles/kg a 8,7 mmoles/kg), plusieurs lacs de la CVL contiennent aussi du CO<sub>2</sub> d'origine magmatique comme en témoignent les valeurs du  $\delta^{13}C_{(CO2)}$  variant entre -4.42 ‰ et -9.46 ‰ prouvant que le dégazage magmatique se poursuit encore en profondeur longtemps après la fin des éruptions volcaniques le long de la ligne ; ce que confirme aussi d'ailleurs la géochimie des gaz du sol de la caldera du Mont Manenguba. La présence du CO<sub>2</sub> dans certains lacs et son omniprésence le long the la CVL viennent appuyer l'idée selon laquelle une augmentation de la sismicité et/ou de la volcanicité pourrait ré-ouvrir des diatrèmes sous-lacustres permettant ainsi à plus de gaz de s'infiltrer dans les lacs et par suite, probablement de s'y accumuler de façon dangereuse. Afin de prévenir et de réduire les impacts des risques encourus, l'étude recommande (1) la mise sur pied d'un réseau minimum de surveillance des lacs volcaniques et (2) qu'en plus de la surveillance sismique actuelle, que soit mis en place, un système de monitoring des gaz volcaniques tels que le CO<sub>2</sub>, Hélium et l'Argon (et pourquoi pas le Radon) dont la variation temporelle permet de mieux suivre la migration du magma. Parce que les volatiles sont les premières à transmettre les « messages » des activités se déroulant en profondeur, ceci permettrait non seulement de compléter, mais aussi de disposer de plusieurs paramètres d'interprétation utilement redondants afin d'améliorer l'efficacité de la surveillance volcanique actuelle.

En dehors des gaz volcanique, l'étude s'est aussi intéressée au méthane (CH<sub>4</sub>) dont la concentration bien que insignifiante pour l'instant, est en augmentation dans les lacs Nyos et Monoun. En raison de sa plus faible solubilité par rapport au CO<sub>2</sub>, le CH<sub>4</sub> a un potentiel de déstabilisation plus important des lacs gazeux. Cette vision corrobore les conclusions des études menées au Lac Kivu dont elles prédisent l'explosion au cours des 100 prochaines années si rien n'est fait pour enrayer l'augmentation du CH<sub>4</sub>. Bien que les teneurs en CH<sub>4</sub> soient négligeables, il a été proposé dans le cadre de cette étude, une méthode simple, rapide et surtout pas chère qui permettrait de suivre l'évolution du  $CH_4$  dans les lacs gazeux (Nyos, Monoun, Kivu etc.)

Pour terminer, afin de mettre sur pied un réseau minimum de surveillance, l'étude s'est attachée à identifier les lacs ayant des caractéristiques naturelles similaires aux lacs Nyos et Monoun. Pour ce faire, les données isotopiques, physico-chimiques et quelques paramètres morphométriques (tels la profondeur, la surface), soit au total 24 paramètres, ont été utilisés afin d'identifier statistiquement les lacs les plus représentatifs. Les résultats de l'analyse soulignent le caractère particulier et unique des lacs Nyos et Monoun. Toutefois elle a permis d'identifier le Lac Benakuma, le 3<sup>ème</sup> le plus profond (après les lacs Nyos et Manenguba Femelle) comme étant celui qui aurait le plus de similarité avec les lacs de références. Le bicarbonate a été identifié comme le paramètre ayant le plus d'influence sur la variance observée.

## Acknowledgment

This work is carried out in the framework of the project "Magmatic Fluids input in lakes Nyos and Monoun and Mitigation of Volcanic Hazards through Capacity Building in Cameroon" under the "Science and Technological Research Partnership for Sustainable Development" (SATREPS) program. The 5-years SATREPS project funded by the Japanese government through the Japanese International Cooperation Agency and the Japan Science and Technology (JICA and JST) on one hand, and counterpart funding from the Cameroon government via the Institute for Geological and Mining Research of the Ministry of Scientific Research and the Innovation (MINRESI/IRGM), aims at achieving safety and promote the social and economic rehabilitation of the Lakes Nyos and Monoun areas.

My close involvement in the monitoring of lakes Nyos and Monoun goes back to January 2001. Since then, I met many people, from broad horizon and origin, who endeavored to "tame" the gassy lakes. That commitment actually strengthened my faith in the humanity to come together when it comes to tackle common issues.

During my study, I receive support from many people. I sincerely appreciate the valuable advice and multiform assistance by Prof. Ohba Takeshi who supervised the present work. I have also benefited from unfailing support and lecturing by Minoru Kusakabe, Emeritus Professor of University of Okayama, who have been working on Lakes Nyos and Monoun for more than 25 years; his experience served me a lot.

I'm grateful to the Institute for Geological and Mining Research (IRGM), my employer, through the Director, Dr Hell Joseph and the Nyos and Monoun Degassing Project permanent secretary, Dr Tanyileke Gregory for their multiform support. May all my IRGM colleagues be thanked especially, Take Emmanuel, Kegny Willy who securely drove thousands of kilometers, to take the research team to the several lake sites.

I wish to acknowledge the moral support of several family members, notably Ousman Amrakai and his wife Kaltoum Mamat, Halilou Adam, Dairou Ibrahim, Hamidou Ibrahim, my in laws Rose and Daniel Fobella and my friends, Dr Sigha Nkamdjou, Dr Sighomnou Daniel and Idrissou. Many thanks to Oginuma Yu, Sakurai Mamoru and Michiko Sakurai, and Mayumi Oginuma for their unfailing supports to my daily life in Japan.

Finally, I would like to thank my beloved wife Nkengfac Yochembeng Fobella Samira who had enough tenacity and willpower to cope with difficulties in taking care of Midipings Noura, Naim, Zyad and Yacine our kids, during my absence. God bless all of you.

# Dedication

To all those who have worked and continue to do so with tenacity, courage and faith for the social and economic rehabilitation of Lake Nyos area

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### Study outline

The promotion of monitoring/surveillance policies is critical to forecast and reduce the impacts of natural hazards. In the case of volcanic lakes related risks, that goal can be achieved through a regular follow up of the time-running physico-chemical changes that might occur along the water column due to fluids transport in and or out of a lake system. The anomalous evolution of the monitored parameters could thus serve to predict impending hazard. The several parameters: the major ions, temperature, TDS, pH, dissolved O<sub>2</sub>, water isotopes, CO<sub>2</sub>, Ar, N<sub>2</sub> etc. generated in the present work could serve that goal. The work is subdivided into five chapters:

*Chapter one* Introduces the work, gives the general background, describes the study area and sets the objectives;

*Chapter two* classifies the lakes according to the global lakes nomenclature. It describes them from physical and chemical stand point and investigates the mineralization processes, evaluates the spatial variability of the parameters and assesses the influence of the control factors. Finally, it studies water isotopes (the inter/intra lake) identifies and evaluates the influence of environmental and morphometric parameters that control the isotopic variability *(Issa et al., 2014a. DOI: 10.4081/jlimnol.2014.966);* 

Chapter three gives a comprehensive overview on the occurrence, the features the geochemistry of diffuse  $CO_2$  emission from some lakes (water/atmosphere interface) and from soil, (*Issa et al., 2014b. DOI: 10.1016/j.jvolgeores.2014.07.001*). It evaluates the future impacts of the increase in CH<sub>4</sub> concentration on the stability of lakes Nyos and Monoun by using a cheap, rapid and accurate "on-site" method of measuring gas concentration in gassy lakes, (*Issa et al., 2013 Geochem. J. 47,349-362*)

Based on the several parameters generated, *chapter four* attempts to statistically group the lakes according to their shared natural characteristics and identifies the main parameters accounting for the observed similarities/differences among the

lakes. It is hoped that identification of lakes naturally similar to lakes Nyos and Monoun shall permit to choose the most representative that could make-up a minimum basic network for crater lakes monitoring surveillance/activities;

Finally, *Chapter five* summarizes the achievements and opens future perspective for volcanic lakes study in Cameroon.

# CHAPTER I Background, Objectives and description of the Study area

## I.1 Introduction

Based on estimate, the Earth would host *ca* 700 volcanic lakes (Perez et al., 2011) of which, ca 140 have been more or less documented (Delmelle and Bernard 2000). Holding to their peculiar setting, crater lakes constitute a worldwide attraction because of their beauty (Eagles 1997; Butler, 1991). Beside that merely aesthetic and recreational benefit, they act, at local and regional levels, as climate regulators, represent a source of biodiversity and in addition, play important economic roles such as, water source for domestic, and water reservoirs for hydroelectric power production and irrigation demands (http://www.env.go.jp/en/water/wq/lakes/why.html). Holding to their location and formation processes, volcanic lakes represent some kind of aerial extension of processes developing in the volcanic-hydrothermal systems. Viewed as the integrators of those processes, the study of a lake system can provide useful insights to understanding magma movements, associated processes and the message carried by their surface manifestations.

In a given area, the monitoring of fluids transport in and out of a volcanic lake system could help to trace the evolution of magmatic activities. The changes induced by those activities on the lake system dynamic (Ohba et al., 1994; Delmelle and Bernard, 2000; Takano et al., 2008) serves to forecast crater lakes related hazards. For example, when a volcanic eruption takes place beneath a volcanic lake, it can result, e.g. in lahars and avalanches (O'shea, 1954; Blong 1984; Badrudin, 1994), phreatic eruptions (Rowe et al., 1992; Christenson, 2000; Christenson et al., 2010). Beside above developments, spilling of acidic water from a volcanic lake can contaminate the surrounding hydrological network rendering the water not suitable for irrigation (Srivana et al., 1998; van Rotterdam-Los et al., 2008). In addition to the risks posed by water, release of gas, e.g.  $CO_2$  which constitutes the second most

abundant component of volcanic fluids after water (Padron et al., 2013) causes lethality (Allard et al., 1989; Freeth et al., 1987, 1991) and also has an influence on the climatic evolution. The multiform impacts of  $CO_2$  on the Earth dynamic in general and the current climatic change (Leavitt, 1982; Marty and Tolstikhin, 1998; Kerrick, 2001), in particular have received increasingly greater attention among geoscientists and the civil societies, in recent years.

### I.2. Background

The first significant fatalities related to diffuse CO<sub>2</sub> degassing occurred in Indonesia at the Dieng Plateau where, 179 people were trapped and killed by  $CO_2$ -pockets formed in low-lying and poor-air-circulated areas locally refer to as "Guat Jimat" (Allard et al., 1989). Such diffuse-degassing-prone areas also exists in Democratic Republic of Congo where they are called "mazutos" (means evil winds), considered, according to social beliefs, as evil environments where animals die mysteriously (Tuttle et al., 1990). Besides accumulating on land surface,  $CO_2$  can also seep and accumulate in lakes. That process lead, on the 21 August 1986, to the most spectacular CO<sub>2</sub> lethality (Baxter et al., 1986) when, a violent explosion of magmaoriginated CO<sub>2</sub> from Lake Nyos, located on the Cameroon Volcanic Line (CVL), killed *ca* 1800 people (Freeth et al., 1992, 1991; Kusakabe et al., 2000; Kling et al., 2005). That event was a large scale repetition of similar event that took place exactly two years before, on the 15 of August 1984 (Sigurdsson et al., 1987) at Lake Monoun, another volcanic lake, located *ca* 100km S-E wing fly, killing 37 people. Those events inaugurated a new type of geologic hazards spreading worldwide concerns on volcanic lakes (Christenson, 1994; Martini et al., 1994; Cabassi et al., 2013)

What triggered the unprecedented and the sudden exhalation of gas baptized *"limnic eruption"* (Halbwachs et al., 2004; Kusakabe et al., 2008) is still to be formally identified. However, several causes have been suggested such as intrinsic and/or exogenous disturbances (Rice 2000; Issa et al., 2013 and other references

Geochemical characteristics of the CVL lakes

therein) or volcanic activity (Tazieff et al., 1987; Chevrier 1990). After the catastrophes, follow-up surveys indicated that  $CO_2$  content of the lakes was increasing at a high rate (Evans et al., 1993). Therefore, to avert a repetition of gas explosion, it was recommended to artificially remove the dissolved gas from the lakes (Tietze, 1992; Kusakabe et al., 2000). Detailed description of the process and the technique can be found in Halbwachs et al., (2004). In brief, when gas-rich water from the bottom is uplifted towards shallower levels, it forms bubbles in the pipe due to decompression referred to as the "gas self-lifting" (Halbwachs et al., 1993; 2004; Yoshida et al., 2010). Then a mixture of gas and water flow is initiated and would continue until the gas partial pressure at the pipe intake is not enough to drive the ex-solution process. Feasibility of such operation was successfully experimented (Halbwachs and Sabroux 2001; Halbwachs et al., 1993) and gas removal started in January 2001 and January 2003 at Lakes Nyos and Monoun with one degassing pipe at each lake. The  $CO_2$ -TDS-rich bottom water is piped to the surface where the gas is harmlessly released to the atmosphere while water falls back onto the lake's surface. In January 2006, two additional pipes were installed at Lake Monoun to foster the gas removal. At Lake Nyos, numerical modeling indicated that the single pipe would soon be ineffective as natural gas input would balance the removal rate and draw down to safe  $CO_2$  levels in the lake would take several years (Kling et al., 2005). Consequently, two additional pipes were installed in March 2011 to make the lake safe within a reasonable timeframe. After 8 years of operation, the degassing pipes have stopped at Lake Monoun indicating the majority of the gas was vented out. At Lake Nyos, good progress has been made to lower the gas content and the degassing is still proceeding.

Based on geochemical studies, the limnic eruption is a cyclic phenomenon (Kling, 1987b; Tietze, 1992; Halbwachs et al., 1993, 2004; Schmidt et al., 2004). But it is not known for certain if such dramatic events have taken place in the past or are likely to reoccur along the CVL. A clear cut answer to that interrogation is difficult. However, geo-anthropologic studies suggest that such events might have taken

place in the past. In fact, there exist, among the many tribes living in the grassland in the corridor of the CVL, numerous myths about "maleficent" activities of lakes. The tales, often related to the cosmogony of the tribes, explain the migrations of ethnic groups after a body of water brought them death and destruction (Shanklin, 1992, Eby and Evans 2006). It is the case of the Bamessi, Kom and Oku ethnic groups in the Oku region located in the North-west (Shanklin 1992). The precedent historical evidences are further supported by the more than 20 years of geochemical study of Lake Monoun. In fact, barely 19 years after the 1984 gas explosion (2003), it was observed that, waters at about 60 m depth in Lake Monoun were almost saturated with  $CO_2$  (Kling et al., 2005; Kusakabe et al., 2008). According to Kusakabe et al., (2008), this situation might have resulted into gas exhalation within less than about 10 years if artificial gas removal had not been initiated implying a gas burst frequency of about 30-40 years for Lake Monoun. At Lake Nyos, the development of such a dangerous situation may take longer, about 100 years or so.

Surprisingly, there exists no sound trace of pass events in the collective memories among the population living in the Nyos and Monoun areas (Eby and Evans 2006). About 100 years represent relatively a short period on societal time scale to forget about such unique and probably deadly events as evidenced by the fact that, the  $17^{\rm th}$  century volcanic eruption of long Island off the coast of Papua New Guinea was somehow, well preserved in oral transmission (Blong 1984). The absence of clues substantiating pass catastrophic events in Nyos and Monoun areas may simply imply that: (1) gas accumulation is relatively a recent phenomenon; (2) the 1980s limnic eruptions would have resulted from tectonic events, which, might have created and/or re-opened sublacustrine vents/faults allowing gas to seep in the lakes or; (3) gas input rate has dramatically increased due to comparatively increase to magma degassing in recent years. So, geochemical and social studies suggest that, any of the *ca* 39 volcanic lakes (Kling 1987a) located of the CVL (Figure 1a), especially those that have the potential to accumulate harmful amount of gas (Freeth 1992), could experience the lakes Nyos and Monoun type events and/or another type of volcanic lake related hazards. Still, lakes Nyos and Monoun are unique and the circumstances required to onset such events are rather rare or unlikely (Kling et al., 1989). The debate remains open and the precedent evidences which tend to support a possible re-occurrence of volcanic lakes related urges for the setting up of a minimum monitoring and surveillance network for the volcanic lakes to prevent unnecessary and avoidable deaths and sorrows.

### I.3 Objective of the study

In Cameroon, the study of crater lakes started back in the early 20<sup>th</sup> century with the study by Hassert (1912) who reported bathymetric data for about eight lakes. In the 1970s ecology and biology of some crater lakes were reported (Corbet et al., 1973; Green et al., (1973). Georges Kling's PhD thesis subject was related to the limnology of tropical lakes and he incidentally studies CVL lakes on which he reported the physico-chemistry, biology and morphometry of 39 lakes (Kling 1987a). That study which coincided with the lakes Nyos and Monoun tragedies was the most comprehensive and was used to draw crucial and constructive remarks about the gas explosions.

The limnic eruption spur a worldwide survey of crater lakes, e.g. in Italy (Martini et al., 1994; Cabassi et al., 2013), in Indonesia (Christenson, 1994), in Costa Rica (CVL7 Workshop, Cabassi et al., in progress). In Cameroon very little had been undertaken so far to regularly check the status of the CVL lakes. Accordingly, general goal of this work is to provide a geochemical and physical baseline data in the perspective of setting up volcanic hazards forecasting and mitigation activities in Cameroon. It studies 17 lakes (Table I.1) and together with their physical, chemical and isotopic characteristics, it reports on the diffuse  $CO_2$  degassing so as to have a comprehensive understanding of its occurrence and the related threats. It is hoped that, this study constitutes a starting point to develop volcanic fluids geochemistry in Cameroon and promote volcanic risk reduction activities as aimed

by the project titled "Magmatic Fluids input in lakes Nyos and Monoun and Mitigation of Volcanic Hazards through Capacity Building in Cameroon" jointly funded by Japanese and Cameroonian governments under the frame work of the program "Science and Technological Research Partnership for Sustainable Development" (SATREPS).

In order to evaluate the environmental factors on their internal dynamic, the studied lakes were selected from diverse phytogeographical, climatological, geological and hydrological settings. Additionally, their size parameters such as area and depth were chosen so as to represent those of all the CVL lakes; especially, those having morphometric parameters similar to lakes Nyos were almost all included so as to permit comparative analysis between those and the one that have different size parameters (see Table I.1). Out of the 17 lakes, six had maximum depths greater than 100 m, 5 with a maximum depth greater than 50 m and the remaining were less than 50 m deep (see Table I.1). Lakes in the first group were chosen because their depths are similar to that of lakes Nyos and Monoun; thus, they are expected to share Monoun and Nyos characteristics such as stratification and the likelihood to store dangerous amount of gas. The second group may also feature same characteristics, but, probably to a lesser extent, and finally, the last group encompasses expected homogeneous and well-mixed lakes assumedly not potentially hazardous.

## I.4 Characteristics of the studied area

### I.4.1. The Cameroon Volcanic Line (CVL)

Cameroon is located on the coast of West Africa between 8° and 16° longitude East and 1.7° and 13° latitude North (Figure 1.1). It hosts *ca* 39 crater lakes grouped into three districts, the Adamau Lake District (Ad-LD), Bamenda Lake District (Bd-LD) and the South-west Lake District (SW-LD) (Kling, 1987b). All the lakes are located on the CVL (Figure 1.1), a 1600 km long chain of Cenozoic volcanoes, including the Mount Cameroun which erupted 3 times within the last 30 years (Tsafack et al., 2009). The geological makeup of the CVL comprises sedimentary, metamorphic, plutonic and several volcanic series (Noughier 1979; Fitton and Dunlop 1985).

The basement rock complex is a mixture of gneiss, granites and micaschists with an age of 2500 to 1800 Ma (Fitton and Dunlop 1985; Ngako et al., 2008). In the exception of Lake Idjagham, an astrobleme formed in sedimentary terrain in the Mamfe plain (Kling 1987a), all the lakes are hosted in volcanoes formed in trachytic and/or recent basaltic series overlain by pyroclastic materials.

Table I. 1. GPS position and some characteristics of the studied lakes: Depths and areas from Kling (1987). D is the distance from the Atlantic Ocean; avg. T and avg. P stand for averaged temperature and precipitation estimated from Fig 1.2a and b respectively. Heading "Type" refers to the hydrological setting: C= closed lakes, T-f= through flow lakes, H/T= Head or Terminal lakes. The last column refers to the abbreviated names of the lake.

L. District	Name	Lat	Long	Elev	Area	Depth	D	avg. T	Р	Type	
		(°)	(°)	(m asl)	(ha)	(m)	(km)	(°C)	(mm)		Abb.
SW-LD	Barombi Koto	4.28	9.16	106	140	5.5	42.1	24.5		T-f	BK
	Barombi Mbo	4.65	9.41	301	415	110	65.5	24.5		T-f	BM
	Debunscha	4.06	8.98	54	6	13.5	0.7	26.5	3500	$\mathbf{C}$	Db
	Manenguba Female	5.04	9.82	1920	22	168	127	23.5		H/T	M f
	Manenguba Male	5.04	9.82	1900	2	92	127	23.5		H/T	Mm
Bd-LD	Baleng	5.33	10.26	1374	8	52	235	23.5		С	Ba
	Benakuma	6.26	9.57	576	154	138	288	23.5		T-f	Be
	Idjagham	5.75	8.99	100	70	17	165	25.5		$\mathbf{C}$	Id
	Elum	6.20	10.02	960	50	35	251	22.5	2000	$\mathbf{C}$	El
	Nyos	6.27	10.18	1091	158	208	278	22.5		T-f	Ny
	Monoun	5.35	10.35	1080	53	96	241	23.5		T-f	Mo
	Wum	6.41	10.06	1177	45	124	266	22.5		T/H	Wu
	Oku	6.12	10.27	2227	243	52	259	19		С	Ok
Ad-LD	Baledjam Marbuwi	7.08	13.52	1180	20	104	614	21		С	B-m
	Ngaoundaba	7.13	13.69	1160	10	62	620	21	1500	H/T	Ng
	Baledjam (Ranch)	7.08	13.52	1249	25	13	636	21		$\mathbf{C}$	B- $r$
	Tizon	7.25	13.58	1160	8	48	612	21		С	Ti

#### I.4.2 Climate and vegetation

Figures 1.2. a, b and c summarize the meteorological and phyto-geographical characteristics of the studied area. The climate in Cameroon is governed by the North-South oscillations of two antagonist pressure cell systems (the St. Helena and Sahara anticyclones) that converge to form the Intertropical Convergence Zone (ITCZ) (Suchel 1987). The timing in the northward migration of the St. Helena anticyclone brings ocean-derived humid monsoon that favors precipitation across the country, whereas, the southward migration of the Azores derived wind from the Sahara anticyclone (Harmattan) installs the dry season over almost the whole territory (Sighomnou 2004).

Excluding local nuances, the Cameroonian territory can be subdivided into three climatological domains: The Atlantic coast, with a hot and humid climate, has mean annual temperature and rainfall of 26°C and 3000-4000 mm respectively (Figure 1.2 a, b). The relative humidity is about 89% throughout the year. On the Atlantic side of Mount Cameroon where rain falls almost continuously, the amount of annual precipitation reaches *ca* 12 000 mm (Fontes and Olivry 1976) (Figure 1.2 b). The vegetation cover is characterized by evergreen forest and mangroves (Letouzey 1968; 1985) (Figure 1.2 c). To the North, in the Adamau Plateau (mean elevation is *ca* 1500 m *asl.*), the mean temperature is 21°C, and the mean annual rainfall is *ca* 1500 mm (Figure 1.2a, b). The vegetation cover is of the sudano-Guinean type (White 1983). The area constitutes a transition between the green forest in the South and the savanna-steppe in the North (Figure 1.2 d).


Figure I. 1. Location of Cameroon in Africa showing the Cameroon Volcanic Line (CVL). The CVL is a ca 1600km long chain of volcanoes stretching from Pagalu in the Atlantic Ocean inside the continent to the Adamaua Plateau (Modified after Chako Tchamabe et al., 2013). It host ca 40 volcanic lakes grouped in the South-West Lake District (SW-LD), the Bamenda Lake District (Bd-LD) and the Adamaua Lake District (Ad-LD). CCSZ=Central Cameroon Shear Zone.

Between the coastal region and the Adamaua Plateau, lays the mountainous grassland with an altitude ranging from 700 to 2400 m *asl*. The mean temperature in the region is about 20°C (Figure 1.2a). The rainy season delivers about 2000 mm/yr. The evergreen highland type forest characterizes the vegetation in that region (Figure I. 2d). However, the vegetal cover has been significantly altered by human activities in that highly populated area (Letouzey 1968; 1985).

## I.4.3 Hydrology

The makeup of hydrographic network is directly linked to the tectonic structures (faults and fissures) which provide the river channels within the basement. The dense network of streams and rivers drain four major basins: Lake Chad, Niger, Congo and Sanaga. The first group of rivers, situated at the south west of Mount Cameroon drain directly into the Atlantic Ocean. Rivers at the east of Ngaoundéré Plateau drains into Lake Chad. The rest of the rivers (south of Ngaoundéré Plateau) constitute either the tributaries of rivers Niger or Sanaga. The lakes constitute integral part of that hydrological system.

Generally, lakes gain water by direct precipitation on their surface, by stream inflow or in some setting, through groundwater percolation. They lose water by evaporation, stream outflow and underground seepage. In the CVL lakes, the mass balance between these inflows/outflows results in change in storage which is reflected by a change in lake level of *ca* 1-2 m/yr as evidence by the visual landmark line on the walls of almost all the lakes.

Based on the hydrological setting, lakes can be grouped into three (Petterson et al., 1999): (1) topographically isolated and often enclosed lakes characterized by no or very limited topographic basin tributaries; they gain water mostly from direct rainfall. However, because of the permeable nature of the hosting rocks and the volcanic deposit surrounding them, some groundwater may be transferred across the topographic divides.



Figure I. 2. summary of the climatology and the phytogeography across the Cameroon Territory. (a) shows the temperature variation within the territory, (b) gives an over view of rainfall and (c) describes the phytogeography (a, b, and c modified after Sighomnou, 2004).

Of the 17 studied lakes, lakes Tizon, Baledjam Marbuwi, Baledjam (ranch), Oku, Elum, Debunscha, Idjagham, Baleng, more or less share the above characteristic. A second group, the through-flow lakes, grouping lakes Nyos, Monoun, Barombi Mbo, Benakuma, and Barombi Kotto, receives and loses water through inlets and outlet streams or rivulets and/or seepage located at the contacts between the basement rock or the lava flow and volcanic deposits. A third group is composed of terminal (Ngaoundaba, Manenguba Male and female) or head lakes (Wum). Terminal lakes refer to the ending point of one or several emissaries, whereas head lakes located upstream constitute the rise of perennial or ephemeral streams depending on the annual fluctuation of the level of the lake (see Table I.1).

## CHAPTER II - CHEMICAL, PHYSICAL AND THE ISOTOPIC CHARACTERISTICS OF THE LAKES AND MINERALIZATION PROCESS

# II.1. CHEMICAL AND PHYSICAL CHARACTERISTICS: INSIGHT INTO THE MINERALIZATION PROCESS

## **II.1.1 Introduction**

Hazardous events occur when, yet passive forces become suddenly active and destructive. But in many cases, before they get to a paroxysmal stage, processes that ultimately lead to catastrophes develop and intensify gradually in the course of time, allowing the upcoming events to be foreseen. Hazard consubstantially includes the idea of risk, which expresses the level of damages living beings or properties may suffer in affected areas (Scarpa and Tilling, 1996). Basic assumption to forecasting volcanic hazards is that, the monitoring of historical changes can give some clues to predict future behavior (Thorlakson, 1967) thus, permitting to reduce the risks. Although hazards associated with eruptions are apparent, volcanic lakes have an air of quietness and tranquility that hide their dynamics and inherent instability. Volcanic lakes represent a kind of open "window" through which deepseated magmatic/volcanic activities can be assessed. If regularly monitored, the induced lacustrine physico-chemical changes can be assesses and interpreted from hazard mitigation stand point.

## II.1.2 Objective of the study

In spite of the danger represented by volcanic lakes, the CVL lakes have been little studied. Volcanic monitoring-surveillance activities are either inexistent or poorly developed. Accordingly, the objective of this study is to provide physico-chemical baseline data that shall serve to set up a network for surveillance and forecasting volcanic lakes related hazards.

Volcanic lakes are dynamic and complex environments. Therefore, to understand them, it is strategically necessary to measure several parameters to be able to derive meaningful interpretations. Accordingly, this work reports on the major element chemistry (major ions) and the physical parameters (Conductivity, pH, dissolved Oxygen, Temperature) of 17 lakes. It uses common geochemical approaches to understand the processes that control the chemical composition of the lakes and its variability.

## II.1.3 Methods

Three field surveys were conducted in the dry season (March to Mai) 2012 and 2013 and in the rainy season in November December 2013. Table I.1 lists the lakes that have been sampled; their images taken from google Map can be found in appendix E. Together with the lakes, the surrounding and regional rivers (inlets and outlets) and ground water have also been sampled.

For the lakes, water was collected from the surface, mid depth and the bottom. Mid depth and bottom waters were sampled using a NISKIN bottle. Samples were filtered through  $0.45\mu$ m hydrophilic acetate syringe driven filters into in 50ml polyethylene bottles. The bottles were thoroughly rinsed (three times) with water to be sampled. Two aliquots were collected: one for anions and the second, which was acidified with HNO<sub>3</sub>, served for cations analysis. Bottles were filled to the top and firmly capped to avoid evaporation. During the 2012 field sampling, alkalinity expressed as bicarbonate concentration was determined on site by acid titration from the volume of 0.02 N H<sub>2</sub>SO<sub>4</sub> added to 10 ml of the sample to reach the endpoint titration, which was marked by a pH of *ca* 4.5. The curves obtained were analyzed by the Gran method (Drever, 2002; Appelo and Postma 2005). Conductivity normalized to 25°C (C<sub>25</sub>) and dissolved oxygen (mg/kg) were obtained using, either a hand conductivity/TDS/temperature meter (Hanna Instruments HI

Geochemical characteristics of the CVL lakes

98129 Tester), a hand pH-meter (SK-920PH, SATO), or a Conductivity Depth Temperature (CTD) profiler (SEABIRD or HYDRONAUT 316). TDS was either obtained by summing up elemental concentration expressed (in mg/kg) or given by the hand Conductivity/TDS/Temperature meter. Water analysis was carried at the Laboratory of Volcanology and Geochemistry in Tokai University. Cations: Na<sup>+</sup>, K<sup>+</sup> Ca<sup>2+</sup>, Mg<sup>2+</sup> and Fe<sup>2+</sup> were determined using atomic absorption spectrometer and/or ICP-MS iCAP Q (Thermo Scientific) and Si<sup>4+</sup> by ICP and expressed as SiO<sub>2</sub>. Sulfate, NO<sub>3</sub><sup>-</sup>, F<sup>-</sup>, PO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup> and NO<sub>2</sub> were determined by IC (Dionex ICS-900). The consistency of the analysis was checked using the geochemical software package AqQA; charge balance was within less than  $\pm 7\%$  (Appendix A, Figure A.1).

## II.1.4 Results and discussion

## II.1.4.1 Chemical and physical characteristics of the CVL lakes

The average chemical composition and the physical parameters of the lakes are given in Table II.1. Detailed composition of the lakes and that of the rivers and ground waters could be found in the appendix A.

## II.1.4.1.1 Chemical characteristics

a) Systematic of the lakes

Because they are hosted in craters, the physico-chemistry of volcanic lakes is controlled by the interaction between the volcanic volatiles and fluids on one hand and the nature of the hosting rocks with which they interact. That interaction is further enhanced by heat input from magma or solar radiation or hindered by mixing with local groundwater etc. Volcanic lakes are classified based on the nature and magnitude of magmatic volatiles input on which depend the degree of the leaching of the hosting rocks, thus their ionic composition. Based on their anionic content, volcanic lakes are classified in three types (Figure II.1): 1) The high acidic sulfate chlorite waters (ASC): These lakes experience good amount of discharge of acid bearing species, SO<sub>2</sub>, H<sub>2</sub>S, HCl and HF. The presence of those high acidifying species mainly originated from magma, shall generate high acidic sulfate chlorite waters (ASC) with pH varying between 0-2 in the example of Kawah Ijen (Delmelle and Bernard, 1994), Kusatsu Shirane (Ohba et al., 1994), Poàs (Rowe et al., 1995), Keli Mutu (Pasternack and Varekamp, 1994), le Ruapehu (Christenson, 2000). The disproportionation and hydrolysis of the magmatic SO<sub>2</sub> (e.g:  $4SO_2 + 4H_2O \rightarrow H_2S + 3H_2SO_4$ ) is the most significant process responsible for that acidity (Delmelle and Bernard, 1994; Rowe et al., 1995).

2) The neutral-bicarbonates (NB): In the course of time and with decreasing volcanic activities, the input of acidic magmatic fluids decreases and eventually ceases. The acidity for rock dissolution is then dominantly provided by dissolved  $CO_2$  which is converted to bicarbonate. These lakes which are almost devoid of sulfates and chlorides constitute the neutral-bicarbonates (NB) type in the example of lakes Nyos and Monoun in Cameroon.

3) The neutral-chloride (NC) lakes are "matured" environments where equilibrium between fluids and hosting rocks has been achieved; thus, almost no and/or negligible acidity is left (Sigurdsson, 1977; Aguilera et al., 2000). The neutralization process takes place by hydrolysis of the rock following, e.g.,  $3KAlSi_3O_8+ 2H^+ \rightarrow KAl_3Si_3O_{10}$  (OH)<sub>2</sub>+  $6SiO_2+ 2K^+$  (K-Feldspar to K-Mica). Examples of that type of lakes is la Soufrière (Sigurdsson, 1977), le Quilotoa (Aguilera et al., 2000) and the Kelud in Indonesia.

As stated above, lakes Nyos and Monoun are known to be  $CO_2$  active lakes and they accordingly classify as NB lakes. Unexpectedly, the rest of the studied lakes also cluster near the bicarbonate apex indicating the CVL lakes are all of NB-type (Fig II.1, data from Table II.1) stressing once more on the ubiquitous presence of diffuse  $CO_2$  along the CVL. The conversion of the  $CO_2$  to bicarbonate e.g.,  $CO_2 + H_2O \rightarrow$  $H_2CO_3 \rightarrow H^+ + HCO_3^-$  is the landmark of NB-type lakes. In those lakes, the degree of the mineralization processes, e.g.,  $CaAl_2$ -silicate + KAlSi<sub>3</sub>O<sub>8</sub>+ CO<sub>2</sub>+ H<sub>2</sub>O  $\rightarrow$  CaCO<sub>3</sub>+ KAl<sub>3</sub>Si<sub>3</sub>O<sub>10</sub> (OH)<sub>2</sub>+ nSiO<sub>2</sub> (Mazot, 2002) depends on the availability of rock matrix on one hand and the residence time of the circulating CO<sub>2</sub>-rich water on the other.

		pН	т	C <sub>25</sub>	TDSN	a +Mg	g 2+ Al	<sup>8+</sup> SiO <sub>2</sub>	K+	Ca <sup>2+</sup>	Mn <sup>2+</sup>	Fe <sup>2+</sup>	F	Cl-	NO2	Br <sup>.</sup>	NO <sup>3</sup>	PO <sub>4</sub> <sup>2</sup>	SO <sub>4</sub> <sup>2</sup>	HCO3-
L. Distric	t Lake		°C	µS/cm	n mg/l pj	om pp	om pp	mppm	ppn	nppm	ppm	ppm	ррт	ppm	ppm	ppm	ı ppm	ppm	ppm	ppm
	Barombi Kotto	9.0	28.8		174.3 19	9.6 8.	7 0.	1 14.6	4.3	10.9	0.0	0.2	0.3	5.7	na	0.0	na	na	na	110.0
	Barombi Mbo	6.8	27.3	93.55	67.97 2	.6 2.	8 na	a 14.8	2.1	1.3	na	5.9	0.1	0.9	na	na	na	na	0.1	37.25
SW-LD	Debunscha	9.0	29.8	82.20	25.70 3	.4 0.	5 0.	1 2.0	1.5	1.5	0.0	0.1	0.1	1.3	na	na	0.1	na	0.6	14.50
	Manenguba Male	7.8	19.3	73.07	130.1 8	.6 4.	7 0.	1 34.7	2.4	7.1	0.1	1.6	0.2	0.5	na	na	2.1	0.2	0.6	68.00
	Manenguba Female	e 6.6	20.4	54.78	39.91 1	.8 1.	4 na	a 9.8	0.6	1.4	na	2.3	0.0	0.4	na	na	3.0	na	0.0	21.08
	Baleng	7.7	24.9	275.2	215.4 15	5.7 6.	8 0.	1 40.2	5.3	21.8	0.2	1.7	0.4	1.5	na	na	0.1	na	0.4	121.5
	Benakuma	7.0	26.8	221.9	184.0 10	).0 3.	4 0.	1 31.6	2.9	10.8	1.8	17.7	0.6	0.6	na	0.0	0.1	0.3	0.3	104.0
	Wum	7.0	24.1	104.8	49.33 1	.6 3.	2 na	a 7.9	1.6	1.0	na	4.2	0.1	0.3	na	na	0.2	na	na	30.88
	Nyos	5.9	22.9	1000	1192 27	7.8 65	.6 na	a na	7.4	8.4	na	202	0.1	0.4	0.0	0.1	0.1	na	0.2	879.9
NW-LD	Monoun	6.8	22.7	827.2	1087 11	.6 9.	1 na	a na	2.9	4.0	na	304	0.1	1.2	0.0	0.0	2.0	na	0.7	751.6
	Elum	7.3	25.6	129.6	108.0 5	.1 3.	3 0.	1 20.2	1.9	5.6	0.3	8.3	0.1	0.3	na	na	0.1	0.2	0.0	62.50
	Oku	7.9	18.6	31.58	43.83 6	.0 1.	1 0.	1 3.1	1.3	2.7	0.1	0.1	0.1	0.4	0.0	0.0	0.1	0.2	0.7	28.00
	Idjagham	7.0	30.6	49.52	26.14 2	.6 0.	2 0.	1 1.8	1.3	1.1	0.1	2.1	0.0	0.3	na	na	0.1	0.1	0.1	16.50
	Ngaoundaba	7.2	22.1	260.4	118.3 5	.3 8.	6 na	a 26.6	1.1	1.4	na	3.2	0.1	0.6	0.0	na	6.5	na	na	67.15
Ad-LD	Tizon	7.5	21.9	281.0	196.4 11	.0 10	.8 na	a 34.1	7.4	7.3	na	0.7	0.5	1.1	na	na	5.5	0.1	0.1	119.7
	Baledjam M	7.1	22.4	197.0	186.9 7	.6 9.	9 0.	0 27.1	3.6	14.6	0.6	6.7	0.1	0.7	na	0.0	0.2	na	0.1	115.7
	Baledjam	6.9	22.6	237.0	112.3 4	.5 6.	2 0.	1 17.9	3.1	7.8	0.4	2.8	0.1	0.8	na	na	0.1	na	0.1	68.50

Table II. 1. Physico-chemical composition of the CVL lakes. Data collected in 2012, 2013 and 2014 (na= not analyzed, under detection limit; - not measured)



Figure II. 1. Lake Classification: ASC (Acidic-Sulfate-Chloride), NC (Neutral-Chloride) and NB (Neutral-Bicarbonate). All studied Cameroonian occupy the bicarbonate apex.

b) Source of mineral and process of mineralization in the CVL lakes

The ionic concentration of solutions involving water and surrounding rock is believed to be controlled by the relative importance of the water/rock (W/R) ratio implying, the dynamic of the system is under the dependence of acidic fluids supply and the availability of rock matrix.

In an open system, like dynamic geological systems, the concept of water/rock interaction is used to qualitatively evaluate which of the rocks or the fluids have a predominant control on its chemical evolution. Low W/R implies the interface between water and rocks is limited (relatively small fraction of rock is in contact with water) and conversely, high W/R would mean appreciable fraction of rocks is in contact with water. In one or the other case, this results in relatively mild or more or less intense rock leaching. In order to discriminate the respective importance of above on the chemical processes, the bottom waters which may better reflect the conditions in the volcanic-hydrothermal-sublacustrine systems were plotted in Figure II. 2 (Varekamp et al., 2000; data from Table II.1 and appendix A Table A.1). The PPRA was assumed to be the sum of the concentration of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> (Rouwet et al., 2014). The soda springs, characterized by relatively high dissolved CO<sub>2</sub> similar to the lakes bottom most water, have also been included in the graph. Lakes from other parts of the world (Japan and Indonesia) are also shown for comparison.

The CVL lakes plot in the rock dominated alteration systems (Figure II. 2) indicating the dominant control of hosting rocks. This implies that, the chemistry of the lakes is largely controlled by the availability of leachable rock matrix which in turn, is determined by their nature. This means the denser and harder the rock, limited is the water-rock interface, thus the interaction and vice-versa. In summary, the mineralization process would depend on the permeability/hardness of the hosting rocks and the residence time of the  $CO_2$ -rich water. That geological control on the chemistry of the lakes will be discussed in more details in the following.



Figure II. 2. The CVL lakes are all rock dominated alteration systems. Cr-lakes- Cameroonian lakes (Nyos, Monoun, Wum, Baleng, Barombi Mbo, Tizon, Ngaoundaba, Baledjam M, Baledjam Ranch, Oku, Idjagham, Benakuma, Maenguba Twin Lakes); JPN= Japan lakes (Yugama and Tamagawa); Indsia= Indonesian lakes (Papandayan, Ruapehu, Kawa Ijen) and Ssp= Cameroon Soda-springs (Ndibsi and Bare).

As the water-rock interaction process develops, the lakes shall move towards equilibrium; unless the systems receive "reactants" (recrystallization or redissolution of the products) for the disequilibrium to persist. Attainment of equilibrium (maturity) of hydrothermal systems could be evaluated by using the Na-K-Mg diagram of Giggenbach (Giggenbach 1997). For the same reasons as above, the bottom most waters were used for that evaluation (Figure II.3). All waters plot as "immature" with a maturity index (MI=0.315\*L<sub>km</sub>-L<sub>kn</sub> where L<sub>km</sub> and L<sub>kn</sub> represent the K-Mg and K-Na geothermometers, see Giggenbach, 1988) ranging from 0-0.66 confirming the "highly immature" nature of the waters; the systems are still progressing towards water-rock equilibrium.

a) The major ions chemistry

## Anionic abundance

Anions are dominated by the presence of carbonates species (Table II.1) especially bicarbonate with relative abundance varying from 73-to 97% (average=96%) and contribute 80-93% the charge balance ( $\Sigma$ Cat almost equal the HCO<sub>3</sub> on equivalent basis).

The overall bicarbonate-type characteristic of the lakes was further broken down using the piper diagram plot (Appendix A, Figure A.2). The plot indicates that, 41%, 35% of the lakes waters are of Fe-HCO<sub>3</sub><sup>-</sup> and Mg-HCO<sub>3</sub><sup>-</sup> types. Majority of lakes in the North-west Lake District (70%) are of Fe-HCO<sub>3</sub><sup>-</sup> in the exception of lakes Oku and Wum. The latter and Lake Manenguba Male (SW-LD) distinguish themselves with waters type similar to the Adamaua lakes which are of Mg-HCO<sub>3</sub><sup>-</sup> type. As will be discussed later, the isotopic signature of Lake Wum is also similar to that of the lakes of the Adamaua Lake District. Overall, more than 75% of the CVL lakes contain waters of Fe-Mg-HCO<sub>3</sub><sup>-</sup> type. Noteworthy, besides containing the same type of water, the lakes in the Adamaua Lake District are also distinguished by high nitrate and phosphate concentrations which likely originate from intensive rearing in the region.

## Cationic abundance

Depending on the lithology, cations are variably dominated by Na Mg, Ca, Fe, K, except in lakes Nyos and Monoun where Fe is the most abundant especially in the hypolimnia. Alkaline earth elements might have greater proportion in lakes located in trachytic dominated terrain while alkaline elements may constitute the most abundant elements in those hosted in basaltic dominated terrains. A clear relationship between the geology and the solution composition is difficult to draw given the lack of specific information on the chemistry of the lake hosting geological formations. However, because a given lake is located in a given hydrological watershed, it may act as integrator of the different salient contributed from weathering in the catchment and rock leaching within. Thus, a relationship between the broad regional geology and the chemistry of the lake can be established. This view is consistent with the work by Le Marechal (1976) who found that chemistry of soda springs along the CVL can be explained by a specific association of rock type.

## The control of the geology on the mineralization

Mineral in the lakes derive from the attack by the dissolved  $CO_2$  on the hosting rocks as already stated above. This observation is confirmed by the positive correlation between the Conductivity normalized at 25°C ( $C_{25}$ ) and  $HCO_3$  shown in Figure II.4. Beyond, it may also portray the influence of evaporation on the chemical composition of the lakes. This assertion is supported by the fact that, salient content and the conductivity of the lakes increase as the ratio between the precipitation and the evaporation (P/E) decreases when moving from the South towards the North and/or where the precipitations are abundant. Accordingly, low cations content lakes are found either in high altitude (Lake Oku) or near the



Figure II. 3. Plot of the lakes in the so called "Giggenbach diagram" (Giggenbach, 1997). The dotted green line indicates the full equilibrium and the blue is the boundary between partially equilibrated fluids and immature one. The lakes plot as immature waters.



Figure II. 4. C<sub>25</sub> vs HCO<sub>3</sub><sup>-</sup> for all the lakes. Inset represents enlargement of the indicated area (Ny= Nyos; Mo= Monoun).

coastal region (Lakes Debunscha and Idjagham) where annual precipitations attain values greater than 3000 mm. Except lakes Nyos and Monoun, high conductivity lakes are found in the Adamaua Lake District in the Northern region of Adamaua. In order to explain the influence of the lithology on the cationic composition, the average composition in the five rock matrix forming minerals Ca, Na, K, Mg and Fe of the lakes and the average composition of the basement and the volcanic rocks along the CVL were plotted in Figure II.5. The average composition of the basement and the volcanic rocks was obtained from data in Sato et al., (1990), Fitton and Dunlop, (1985), Marzolli et al., (2000) Kagou et al., (2001), Aka et al., (2008) and Djouka Fonkwe et al., (2008).

Besides delineating the predominant path for water-rock interaction, Figure II.5 clarifies the relationship between the lakes and a given formation or association of formations.

Three domains of dominant specific rocks type and associated water chemistry can be identified:

*Domain 1:* the process of mineralization is influenced by the volcanic formation (such as basalt) and pyroclastic ejecta riming the lakes or volcanic products previously deposited in the diatremes as in the case of Lake Nyos (Tuttle et al., 1992). The resulting waters have greater proportion of Mg-Fe and subsidiary Ca compared to the alkali.

*Domain 2:* the substratum might be of granitoide-type (e.g. Wum, Elum) where water chemistry is chiefly dominated by K and Na and subsidiary by Ca with low Mg and Fe.

*Domain 3:* it encompasses the waters where both the basement and volcanic formations may contribute to the cationic concentration. The relative elemental abundance is variably dominated by all four cations.



Figure II. 5. Plot of the chemical composition of the surface, mid depth and bottom waters for each lake showing the relationship between the five major rock matrix forming elements and the 3 domains where a given type of formation or association of formations control the lakes chemistry. Domain 1 and 2 are where the volcanic and the basement formations respectively predominantly contribute to the mineralization. Domain 3 is where water is simultaneously in contact with the basement and volcanic.

In order to understand the chemical evolution of the systems, and assuming equilibrium is maintained between the solution (secondary minerals) and the rocks, the lake waters were evaluated by the use of the thermodynamics of mineral stability diagrams (Drever, 2002) (Figure II.6 and Figure II.7). In the log  $aH_4SiO_4$  vs log ( $aNa^+/aH^+$ ), most of the waters plot in the Kaolinite - Na-smectite stability field and on the log( $aH_4SiO_4$ ) vs log( $aK^+/aH^+$ ) most of the lakes plot in the Kaolinite stability field and few in the k-feldspar (Figure II.6 and Figure II.7). The general reactions that control the lake water chemistry were inferred. The primary minerals such as albite, muscovite and alkaline bearing primary minerals (anorthite, enstatite etc.) are converted preferentially to kaolinite following for example (Drever, 2002; Mazot, 2002; Ako, 2010; Anazawa et al., 2013 pers. com): Albite to Kaolinite

NaAl
$$Si_3O_8 + \frac{9}{2}H_2O + H^+ \rightarrow Na^+ + 2H_4SiO_4 + \frac{1}{2}Al_2Si_2O_5(OH)_4$$

Muscovite to Kaolinite:

$$KAl_{2}(AlSi_{3})O_{10}(OH)_{2} + \frac{3}{2}H_{2}O + H^{+} \rightarrow K^{+} + \frac{3}{2}Al_{2}Si_{2}O_{5}(OH)_{4}$$

Anortite to Kaolinite:

$$CaAl_2Si_2O_8 + H_2O + 2H^+ \rightarrow Ca^+ + Al_2Si_2O_5(OH)_4$$

On the other hand, ferromagnesian could be converted to brucite and goethite: Enstatite to brucite:

$$Mg_2Si_2O_6 + 6H_2O \rightarrow 2Mg(OH)_2 + 2H_4SiO_4$$

Ferrosilite to goethite:

$$Fe_2Si_2O_6 + 6H_2O \rightarrow 2Fe(OH)_2 + 2H_4SiO_4$$



Figure II. 6. Chemical composition of CVL lakes in relation to the Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> mineral system (Drever, 2002). Lake waters are expected to be stably in equilibrium with Kaolinite.



Figure II. 7. Chemical composition of CVL lakes in relation to the K2O-Al2O3-SiO2 mineral system (Drever, 2002). Lake waters are expected to be dominantly and stably coexisting with equilibrium with Kaolinite.

#### II.1.4.2 Conductivity, pH, dissolved O2 and Temperature

Average conductivity ( $C_{25}$ ), pH, dissolved oxygen and temperature of the lakes have been taken either from Table II.1 or from CTD one-meter-step wise averaged data listed in appendix B Table B.1 to Table B.12.

One of the features of the gassy Lakes Nyos and Monoun is their permanent stratification. Similarly, the other CVL lakes also display stratified water columns (Figure II.8) having mainly 2 water masses as in other tropical lakes (Hutchinson, 1957). The epilimnetic waters are generally characterized by a low conductivity compared to the hypolimnia. In addition to the distinct epilimnion and hypolimnion, some lakes, in the example of Lake Ngaoundaba and Barombi Mbo display some micro layering (Figure II.8) like in lakes Nyos and Monoun.

The low conductivity observed in Lake Idjagham with surface  $C_{25}$  of 7  $\mu$ S/cm (average= 51  $\mu$ S/cm), Oku with surface C<sub>25</sub>=27  $\mu$ S/cm (average (45  $\mu$ S/cm), Manenguba Female with surface  $C_{25}=37 \ \mu\text{S/cm}$  (average=57  $\mu\text{S/cm}$ ) suggest the concern lakes are weakly mineralized. This is consistent with the above observation concerning the coastal and high altitude lakes. The low conductivity is similar to that of lakes located in high rainfall areas or on resistant bedrocks in tropical and temperate regions (Hutchinson, 1957; Imboden and Wuest, 1978; Kling, 1987a). All taken, lakes in the Adamaua Lake District show the highest mineral contents with average  $C_{25}>250\mu$ S/cm compared to those located in the southern part of the country. Taken individually however, the Lake Manenguba Male had the highest  $C_{25}$  with bottom water  $C_{25}=524 \mu$ S/cm. The Lake Manenguba Male and the Female which are located side by side on the same caldera are differently mineralized; the Female had low mineralized water with only  $C_{25}=113 \mu$ S/cm proving the geological influence on their chemical composition. In fact, the Female is carved in the granites although the Male is partly sited in basaltic formations. The difference in the chemical and physical composition of the two lakes may also imply that, they have distinct hydrothermal systems and that there minimal or no material transport between them.

The pH is also in the range of that of fresh waters. The lakes in the Ad-LD had slightly alkaline pH (about 8), although the remaining were circumneutral (6.32 <pH< 7.3) except lakes Nyos and Monoun bottom waters, which are known to have slightly acidic (pH=5.92) due to the dissolved  $CO_2(H_2CO_3)$ . The highest pH (9.86) was observed in Lake Benakuma which also presents the largest chemical gradient. All the epilimnia were found to contain oxygen. Its concentration rapidly depletes from the surface to about 10m to 15m on average. The *chemoclines* are generally located at that depth. Lake Oku had the lowest temperature (18°C) while the highest temperature was observed in Lake Barombi Mbo (28.5°C).

Thermal stratification is a common phenomenon in lakes and oceans (Beadle, 1981). But its persistence over season may depend on meteorological conditions. Strong and permanent stratification is believed to favor gas accumulation in lakes (Kling et al., 1987, Halbwachs et al., 2004 and in ref elsewhere therein). Figure II.9 exemplifies the temperature profiles for five chosen lakes; the profiles were taken during the rainy and dry seasons.

The temperature of surface water during the dry season were generally greater that in the wet season. It can be observed, in the exception of Lake Barombi Mbo that, the thermoclines have slightly subsided by 2·3m from April 2013 (dry season) to December 2013 (rainy season). The effect of daily temperature variation on water column is evidenced by the Jan-2014 profile taken early in the morning in lake Barombi Mbo profile which shows an inverse temperature gradient. That daily thermal inversion had also been observed by Kling (1987a) in that lake. Worth of note, the hypolimnetic temperature increased by about 0.6°C from April 2013 to the 5<sup>th</sup> January 2014 probably indicating heat input from depth or that, it was returning to its status after it overturned in late November-2012 during which it might have possibly lost heat. Beside the clear influence of seasonal and daily factors such as the convective mixing (work of the wind) and conductive cooling (Spiegel et al., 1986; Price et al., 1986), admixture with local water bodies may also contribute to shaping the water column structure as will be discussed in the following chapter.



Figure II. 8. Layering of the water columns as exemplified by some chosen lakes. Although some lakes may present micro layers, in general, the water columns show two main layers.



Figure II. 9. The influence of season on the water column structuring. The April profile represents the dry season and the Dec January the rainy season. The influence of daily conditions on the lakes is well exemplified by the case of Lake Barombi Mbo which features an inverse thermal gradient early in the morning.

## II.1.5 Conclusion

Devoid of sulfates and chlorides the CVL lakes contain high concentration of bicarbonates that classifies them as Neutral-Bicarbonates type (NB) lakes. Magmatic  $CO_2$  provides the necessary acidity for rock dissolution to the alteration systems identified as rock-dominated, based on the chemical composition of the bottom most waters which indicate the lake waters are immature and still evolving towards water-rock equilibrium. The lithology is the dominant factor determining the cationic content of the lakes. Based on the physical parameters, it was observed that, the water columns generally present two distinct water masses. That structure is influenced by the seasons and other physical processes such as convective and conductive mixing or input of local waters.

# II.2 FACTORS CONTROLING THE VARIATIONS OF $\delta^{18}\mathrm{O}$ AND $\delta\mathrm{D}$ IN THE LAKES

(Issa et al., 2014a. 818O and 8D variations in some volcanic lakes on the Cameroon Volcanic Line (West-Africa): generating isotopic baseline data for volcano monitoring and surveillance in Cameroon. J. Limnol.DOI: 10.4081/jlimnol.2014.966)

## **II.2.1 Introduction**

In addition to the physicochemical information provided in the precedent section, this section aims at providing a comprehensive overview on the isotopic characteristics of the CVL lakes (Table I.1). It assesses the spatial and intrinsic isotopic variability and attempts to identify the parameters that control that variability. Previous work on stable isotopes of water encompassed 5 lakes (Tanyileke et al., 1996; Kling et al., 1987; Kusakabe et al., 1989; Nagao et al., 2010). Only the last two reported isotopic profiles of lakes Nyos, Monoun and Wum without further discussing their variation.

Water isotopes study can provide useful information on the dynamic of a volcanic lake (Rowe et al., 1992). For example, in response to inflow of fluids with distinct  $\delta^{18}$ O/ $\delta$ D composition, the isotopic composition of lake water may undergo some changes. Those signals could be, in some cases, reasonably linked up to the origin of the ensuing fluids. For example, the rise and subsequent mixing of connate, formation (Tyler et al., 2001) or magmatic fluids (Giggenbach, 1997) with lake water may produce chemical and/or isotopic anomalies due to their specific isotopic composition (Varekamp and Kreulen, 2000). To be able to decipher and interpret such changes from hazards management standpoint, it is essential to understand the reservoir dynamic, especially the mechanisms that control its evolution (Brown et al., 1989; Ohba et al., 1994). In the case of the Nyos and Monoun gas explosions, the sinking of cold parcel of water in the peak of the rainy season was thought to be one of the triggering causes (Kling et al., 1987b). Given that rain water has specific isotopic finger print, it might have been possible to detect the sinking of that parcel of water by the use of isotopes.

## II.2.2. Method

### II.2.2.1 Sampling

The isotopes incorporated into the water molecules (18O and 2H) have been extensively used to trace processes that govern the hydrodynamic and water balance of lakes (Fontes et al., 1970; Gat 1995; 2010 and other references therein). The variation in isotopic content due to interaction between a lake and exogenous waters can be deciphered, and their origin may also be constrained. Qualitative and quantitative evaluations of the evaporative and/or degree of mixing effect on open water bodies such as lakes are complex, and their assessment requires that the control parameters be accurately estimated. Unfortunately, together with climatological information, which, in this study is regional rather than site specific, important lake parameters such as volume, inflow/outflow rates are also lacking. Available morphometric, climatologic and hydrological parameters of the studied lakes are listed in Table I.1. Despite above drawbacks, the work provides valuable understanding of some features of the CVL lakes that will serve for future studies. To our knowledge, if we exclude reviews (e.g. IAEA 1981; Fontes and Edmond 1989; Gat 1996, the list is not exhaustive), this study is the first that discusses isotopes in more than 15 lakes at once. In addition to the fairly large number of lakes, their varied phytogeographical, hydrological, and geological setting constitutes another incentive.

During the 2012 and 2013 dry seasons, we conducted 2 sampling campaigns, from March to May. Lakes were surveyed from 4° 6'7"N; 8 58'58"E in the SW-LD to 7°8'4"N; 13°52'15"E in the Ad-LD (Figure II.10). Precipitation events were sampled at Yaoundé, Bertoua, Ngaoundéré and Garoua. During the 2012-2013 rainy seasons,

18 occasional rainfalls were collected from 12 sites. Table II.2 gives a list of all the samples.

Seventeen lakes were surveyed (Figure II.10): Tizon, Ngaoundaba, Baledjam Marbuwi and Baledjam (Ranch) in the Ad-LD, Monoun, Baleng, Nyos, Wum, Elum, Benakuma, Oku and Idjagham in the Bd-LD and, Manenguba Female, Manenguba Male, Barombi Mbo, Barombi Kotto and Debunscha in SW-LD. Water was collected from the surface, mid-depth and the bottom; the mid depth and bottom waters were sampled using a NISKIN bottle. Twenty nine water samples were collected from shallow wells, boreholes, soda springs, springs and outlet / inlet streams in 2012 and 2013 (Table II.4). After sampling, water was filtered through 45 $\mu$ m hydrophilic acetate syringe driven filters in newly purchased 50 ml high density polyethylene bottles which were rinsed three times with water to be sampled prior to collection. Bottles were filled to the top and firmly capped to avoid evaporation. The sampled waters were analyzed within one month using a Cavity Ringdown Spectrometer L-2120-i (PICCARO) in the Laboratory of Volcanology and Geochemistry of Tokai University. The analytical precision was  $\pm 0.4$  ‰ and  $\pm 0.3$ ‰ for  $\delta$ D and  $\delta^{18}$ O respectively.

#### II.2.2.2 Approach to water isotopes studies

The study of the fractionation of natural occurring stable isotopes of water provides information on a great variety of important bio-geochemical processes occurring in various environments (Faure 1986).

The correlation between  $\delta^{18}$ O and  $\delta$ D in precipitations on a global scale is now well understood (Craig et al., 1961) and known as the Global Meteoric Water line (GMWL) which, is often used to evaluate and constrain sources and the processes affecting water isotope variation in a given system. However, because the stable isotopes composition in precipitation in a given region may reflect specific meteorological and physical conditions, they are better described by a local derivative often referred to as Local Meteoric Water Line (LMWL). Several studies on water isotopes in Cameroon had been carried using the GMWL.

In a recent study, Garcin et al., (2012) constructed a Cameroon Meteoric Water Line (CMWL) that they used in their work. The equation of the line was  $\delta D=8.3\delta^{18}O+14.2$ . However, it was noted that, the data they used did not cover the entire Cameroonian territory.

This study attempts to establish a more representative water line for Cameroon precipitations by using data that better covers the territory. In addition to data obtained during this work, we utilized literature data (Fontes and Olivry, 1976; Njitchoua et al., 1995; Njitchoua and Ngounou Ngatcha 1997; Gonfiantini 2001; Ako et al., 2009; Ako 2011; Garcin et al., 2012), the weighted average of isotopes of Ndjamena in Chad (IAEA, 2007) to supplement existing data in the northern semi-arid region and data from Mbonu and Travi (1994) in the Joss Plateau in Nigeria, to better constrain the isotopic composition of rainfall in the neighboring Adamaua Plateau where we had only 2 samples; the two areas being climatologically similar. Water isotopes were expressed in the usual " $\delta$ " notation in ‰ relatively to Vienna standard mean ocean water (V-SMOW) according to:  $\delta(\%_0) = \left(\frac{R_{Sample}}{R_{SMOW}} - 1\right) * 1000$ , where  $R_{Sample}$  and  $R_{SMOW}$  refer to  ${}^{18}O/{}^{16}O$  and  ${}^{2}H/{}^{1}H$  ratios (Craig, 1961).

## II.2.3 Results and discussion

## II.2.3.1 The Cameroon Meteoric Water Line (CMWL)

Several studies on water isotopes in Cameroon had been carried out using the Global Meteoric Water Line (GMWL) (Craig, 1961). However, because the stable isotopes composition of precipitation in a given region may reflect specific meteorological and physical conditions, they are better described by a local derivative often referred to as Local Meteoric Water Line (LMWL). In a recent study, Garcin et al., (2012) proposed a Cameroon Meteoric Water Line (CMWL). The

equation of the line was  $\delta D=8.3\delta^{18}O+14.2$ . However, it was noted that, the data they used did not cover the entire Cameroonian territory.



Figure II. 10. Map of Cameroon showing locations where precipitations were sampled (solid circles) and the studied lakes (open diamond). The Lake Districts are also indicated.

Table II. 2. Isotope ratios in precipitations with name of locations and source (\* column): 1=this study; 2=Ako (2010); 3=Njitchoua and Ngounou Ngatcha (1997); 4= Njitchoua et al. (1995); 5=Gonfiantini et al. (2001); 6= Garcin et al. (2012); 7=Mbonu and Travi (1994); 8=IAEA; 9=Kusakabe et al. (1989).

Site	Date	δD	δ18Ο	*	Site	Date	δD	δ <sup>18</sup> Ο	*	Site	Date	δD	δ18O	*
Fontem	May-12	1.06	-1.64	1	Yaoundé		27.2	1.30	6	Garoua		-49.4	-7.31	4
Monoun	Apr-12	12.9	-0.62	1	Yaoundé		1.80	-1.87	6	Garoua		-70.4	-10.2	4
Nyos	May-12	10.9	-1.12	1	Yaoundé		10.6	-0.97	6	Garoua		-66.3	-6.43	4
Buea		5.82	-0.72	<b>2</b>	Yaoundé		-13.4	-3.39	6	Garoua		-58.9	-8.98	4
Buea		6.19	-0.81	<b>2</b>	Yaoundé		2.30	-2.08	6	Garoua		-45.8	-6.71	4
Buea		-19.3	-3.69	<b>2</b>	Yaoundé		-0.90	-3.18	6	Garoua		-26.8	-2.82	4
Buea		-37.9	-6.05	<b>2</b>	Yaoundé	Mar-13	-3.86	-3.57	1	Garoua		-5.8	-1.61	4
Muyuka		-20.1	-3.56	2	Yaoundé	Mar-13	3.00	-2.50	1	Garoua		-12.1	-1.78	4
Muyuka		-1.56	-1.29	2	Yaoundé	May-13	25.6	2.33	1	Garoua		1.3	-0.65	4
Limbe		-5.07	-2.61	<b>2</b>	Yaoundé	May-13	-36.0	-7.27	1	Garoua		-36.6	-5.64	4
Limbe		7.89	-0.60	2	Yaoundé	Apr-13	11.0	-0.44	1	Garoua		-34.0	-4.84	4
Limbe		-22.4	-3.54	2	Yaoundé	Apr-13	9.81	-3.99	1	Garoua		-22.5	-3.86	4
Ndjamena		-22.5	-4.10	8	Yaoundé	Apr-13	-1.03	-2.62	1	Garoua		-22	-4.17	4
Diamare		-30.6	-4.20	8	Debunsc		-5.50	-3.03	6	Garoua		-34.7	-4.86	4
Bakingele		-15.0	-3.02	<b>5</b>	Debunsc		-7.50	-2.94	6	Garoua		-30.5	-4.83	4
Idenau		-25.4	-3.58	<b>5</b>	Debunsc		-3.60	-2.99	6	Garoua		-3.8	-1.72	4
Idenau	May-13	5.13	-2.61	1	Debunsc		-9.10	-3.28	6	Garoua		-25.8	-4.50	4
Brasseries		-24.1	-3.70	<b>5</b>	Debunsc		-16.3	-4.17	6	Garoua		-10.3	-1.57	4
Upper farm		-27.7	-5.00	<b>5</b>	Debunsc		-20.3	-4.37	6	Garoua		-16.1	-3.51	4
Foret		-22.8	-4.22	<b>5</b>	Debunsc		-9.5	-3.49	6	Garoua		-39.3	-6.47	4
Foret SW		-34.7	-5.60	<b>5</b>	Debunsc		-18.7	-4.33	6	Garoua		-11.8	-1.84	4
Station VHF	,	-46.5	-6.90	<b>5</b>	Debunsc		-16.0	-3.85	6	Garoua		-12.8	-3.42	4
Vsant Nord		-44.6	-7.06	<b>5</b>	Debunsc		-12.9	-4.08	6	Garoua		-36.3	-6.45	4
Foret Buea		-39.7	-6.57	<b>5</b>	Banguem		1.90	-1.95	6	Garoua	Oct-12	21.6	-1.18	1
SWBP		-44.6	-7.60	<b>5</b>	Banguem		13.4	-0.56	6	Garoua	Aug-12	-0.69	-2.02	1
Bottle Peak		-55.4	-8.02	<b>5</b>	Banguem	May-13	-19.4	-5.76	1	Benakum	Apr-13	35.6	3.85	1
Summit BP		-60.9	-8.69	<b>5</b>	Mt.Man		0.60	-2.20	6	Mbomba	Apr-13	6.70	-2.48	1
Summit BP		-64.6	-9.52	<b>5</b>	Mt Man	Apr-13	-7.87	-4.65	1	Meigang	Apr-13	24.2	-0.94	1
Yaoundé		-58.6	-9.32	6	M. Darlé		17.6	1.13	6	Bertoua	Apr-13	6.3	-1.53	1
Yaoundé		0.50	-2.24	6	Garoua		-46.2	-6.37	4	Bamenda	Sep-86	10.4	-4.00	9
Yaoundé		-1.40	-2.24	6	Garoua		-37.8	-5.22	4	Bamenda	Apr-13	21.5	0.16	1
Yaoundé		-1.00	-2.13	6	Garoua		-27.3	-3.48	4	Ngdéré	Jun-13	17.8	-0.37	1
Yaoundé		-5.40	-2.73	6	Garoua		-73.8	-8.46	4	P.Joss	88-99	-18.8	-3.85	7

Consequently, this study attempts to establish a more representative water line for Cameroon precipitations by using data that better covers the territory.

Ninety eight data points (Table II.2) were used to construct a meteoric water line for precipitations in Cameroon. Figure II.11 depicts the  $\delta$  D- $\delta$  <sup>18</sup>O relationship for rain events across the country with a least square line equation  $\delta$ D=8.6 $\delta$ <sup>18</sup>O + 15.2. The correlation coefficient r<sup>2</sup>=0.88 indicates the reasonably good quality of the fit; the narrow 95% confident band delineated by dotted lines suggests that the statistical parameters of the population (mean, Std, variance) are well constrained by the sampled data.

The new CWML is not decisively different from that reported by Garcin et al., (2012). However, the slight increase to the intercept and to the slope values compared to the previous meteoric line may reflect a better territorial repartition of the sampled rain events. The slope is slightly greater than 8 indicating the rainfall events mostly occur under slight 18-oxygen enrichment during the descent of the droplets. The 5.2 ‰ excess in <sup>2</sup>H compared to the GMWL indicates the influence on the <sup>2</sup>H fractionation of the continental derived air masses composed of mixing of the continental-derived air winds which integrate the southern high evapotranspiration dominated air masses and the dry desert derived air masses originating from the Sahara.

#### II.2.3.2 Variation in the isotopic ratios

a) The intra-lake variation and the relationship of lakes with local water bodies.

In the SW-LD,  $\delta^{18}$ O in surface water varies from -0.8‰ to +5.5 ‰ (mean= +3.2‰, n=5) and  $\delta$ D from -21.1‰ to +9.2‰ (mean= -2‰, n=5). At mid-depth, values vary from -0.4 to +3.8‰ (mean= +2.1 n=3) and  $\delta$ D from -27.8‰ to +2.2‰ (mean= -11.4‰, n=3) and finally, isotope values in bottom waters vary from -1.8‰ to +3.8‰ (mean= +1.8‰, n=4) and  $\delta$ D from -27.6‰ to +1.1‰ (mean= -8.7‰, n=4). In the Bd-LD,  $\delta^{18}$ O in surface water vary from -0.8‰ to +6.5 ‰ (mean= +2.8‰, n=8) and  $\delta$ D from -

16.6‰ to +17.1‰ (mean= +11.3‰, n=8). At mid-depth,  $\delta^{18}$ O values vary from -2‰ to +5.8‰ (mean= +0.6, n=4) and  $\delta$ D from -18‰ to +12‰ (mean= -6.7‰, n=4) and finally in bottom waters  $\delta^{18}$ O values vary from -2.2‰ to +5.9‰ (mean= +3.3‰, n=8) and  $\delta$ D from -22‰ to +13‰ (mean= +12‰, n=8).

Finally, in the Ad-LD,  $\delta^{18}$ O in surface water vary from +4.0‰ to +10.6 ‰ (mean=+6.6, n=4) and  $\delta$ D from +12.6‰ to +31.7‰ (mean=+19.3, n=4). At mid-depth,  $\delta^{18}$ O values vary from +4.2‰ to +9.4‰ (mean=+6.4, n=3) and  $\delta$ D from +9.8‰ to +26.7‰ (mean=+14.5‰, n=4) and in bottom waters,  $\delta^{18}$ O values vary from +4.2‰ to +9.3‰ (mean=+5.8‰, n=4) and  $\delta$ D from +10‰ to +27‰ (mean=+15‰, n=4).

In order to describe the intra-lake isotopic variation,  $\delta^{18}$ O and  $\delta$ D values for the three (for lakes >50 m deep) and two (for lakes <50 m deep) sampled depths have been plotted as a function of depth (Figure II.12).

Two important remarks about the lakes can be done: the first one is that, all the lakes, in the exception of Lake Oku (Figure II.12c and d) and to a lesser extent, lakes Barombi Mbo (SW-LD) and Baledjam Marbuwi (B-m) in the Ad-LD, are isotopically stratified.

They present at least 2 distinct layers and, secondly, irrespective of their location, even lakes <15m deep are stratified contrary to the observation that shallow lakes and swamps have, generally, homogeneous water columns (Gonfiantini, 1986). The epilimnia are generally more heavy isotopes enriched than the hypolimnetic waters. Compared to other areas, the  $\delta^{18}$ O profiles of the CVL lakes have similar shapes as those found in water content in Saharan dunes (Coplen et al., 2001). However, they have reverse isotopic gradient compared to the  $\delta^{18}$ O-profiles of lakes Malawi and Tanganyika (Gonfiantini, 1986) which are also isotopically stratified.

The isotopic profiles above might not thoroughly depict the actual structure of the water columns of the lakes because only three depths were sampled as mentioned above. Consequently, the isotopic gradient may be positioned at shallower depth. Secondly, due to the limited number of sampled depths, sub-layers and micro-layers (e.g. lakes Nyos and Monoun) may not appear. However, the profiles in Figure II.12



Figure II. 11. The Cameroon Meteoric Water Line (CMWL) derived from 97 isotopic ratios distributed across the Cameroonian territory (Red line). The 95% confidence band is also shown in dotted line.
may be regarded as describing the overall (bulk) physical structure of the water columns.

Chemical or thermal stratification in lakes is generally driven by density difference between the layers. In subtropical areas, almost all deep lakes are thermally stratified because of the solar radiation energy input to the surface water. Some like lakes Nyos and Monoun are both thermally and chemically permanently stratified (Evans et al., 1994; Kling et al., 1987 and other reference therein). At this stage, whether the observed stratification is seasonal or permanent remains a subject of investigation.

In the following, the discussion of the isotopic characteristics of the lakes is done from the South to the North starting with the South-west Lake District, the Bamenda Lake District then the Adamaua Lake District.

The South-west Lake District comprises five lakes. However Figure II.12a and b present the profiles of only four lakes because only one sample was collected from mid-depth at Lake Barombi Koto which is less than 5 m deep (see Table I.1). Of the 4 lakes, Barombi Mbo (BM) is the most enriched in heavy isotopes followed by Manenguba Female (Mf), which, in turn, is <sup>18</sup>O heavier than Lake Debunscha (Db), although the latter is comparatively more enriched in <sup>2</sup>H. The Lake Manenguba male (Mm) has the lightest waters and exhibits the strongest isotopic gradient. In addition to that peculiarity, the  $\delta^{18}$ O and  $\delta$ D in the Mm do not co-vary throughout the depth range: while  $\delta^{18}$ O profile is marked by a positive isotopic gradient from the surface to *ca* 45 m (remember that the depth might not be the exact location of the gradient as explained above) and then reverses towards the bottom, the  $\delta$ D instead shows a negative gradient downwards to the same depth and then remains stable.

Differences in the isotopic distribution along the water column in the lakes are common. However, the twin lakes Manenguba Female and the Manenguba Male, are located about 200 m apart on the same caldera (Figure II.13) and they experience the same meteorological conditions. Why are they isotopic ally so different? The marked difference in their isotopic composition can be tentatively ascribed to their morphometry (Jones and Imbers, 2009) and/or their biotopes (Petit, Differences in the isotopic distribution along the water column in the lakes are common. However, the twin lakes Manenguba Female and the Manenguba Male, are located about 200 m apart (Figure II.13) and they experience the same meteorological conditions. Why are they isotopic ally so different? The marked difference in their isotopic composition can be tentatively ascribed to their morphometry (Jones and Imbers, 2009) and/or their biotopes (Petit, 1936).

First, the relative isotopic enrichment of the Manenguba Female may be due to the fact that, the lake is large and open, therefore, it may suffer more evaporation, mainly from wind (Birge, 1916; Garwood et al., 1985) as compared to the Manenguba Male which, is located 20 m lower at 1900m *asl.*, in a deep crater with high walls. That setting may contributes to relatively shield it from the work of the wind.

The second explicative argument is related to their colors (Figure II.13), which can reveal nutrient load, algal growth etc. In fact, the green color displayed by crater lakes is often attributed to chemical reactions triggered by volcanic gas activity that drives nutrient-rich water to the surface (Tiwu Nuwa Muri Koo Fai Lake, Keli Mutu volcano, Indonesia) and/or to high nutrients content and/or algal growth (Morris and Hargreaves 1997). Since the Manenguba area is not volcanically active, we think that the green color of the Manenguba Male may be due to the presence of algae. As has been observed by Pushkar et al. (2008), depending on the metabolic cycles of micro-organisms involved, bioorganic processes (e.g. respiration and photosynthesis) can induce a negative shift in <sup>18</sup>O composition of a lake; this may be the case of the Lake Manenguba Male.



Figure II. 12. Isotopic profiles: a and b (SW-LD: Mm=Manenguba male; Mf= Manenguba female; Db=Debunscha; BM=Barombi Mbo), c and d (Bd-LD: Mo=Monoun; Ny= Nyos; Be= Benakuma; Ba= Baleng; El= Elum; Ok= Oku; Id= Idjagham; Wu= Wum), e and f (Ad-LD: B-m=Baledjam Marbuwi; B-r= Baledjam ranch; Ng=Ngaoundaba; Ti= Tizon). All the lakes, except Oku, Baledjam and Barombi Mbo are more or less stratified with heavy isotopes enriched surface waters. Even shallow lakes (>15m) are stratified. The largest gradient between surface and bottom waters is observed in Lake Benakuma. Lake Baledjam Marbuwi is distinguished by a hypolimion being more enriched than epilimnion. Gassy lakes Nyos and Monoun are the most depleted.

Lakes Barombi Mbo (BM) located *ca* 60 km wing fly to the south-west of Mount Manenguba at ca 301 m *asl.*, is the largest crater lake in Cameroon (Chako Tchamabe et al., 2013). The lake is *ca* 100 m deep. Alike Lake Baledjam Marbuwi in the Adamaua Lake District, its  $\delta^{18}$ O and  $\delta$ D profiles indicate its water column is almost isotopically homogeneous (Figure II.12a, b) compared to lakes with similar depths such as lakes Benakuma (Be) and Wum (Wu) in the Bamenda Lake District or the Manenguba twin lakes (see Table I.1). At present, it is difficult to say if the Lake Barombi Mbo always features a homogenous water column. However, it is assumed that, the observed isotopic distribution along the water column may be due to the fact the overturn the lake Mbo underwent several months before the survey.

Finally, the Lake Debunscha (Db) is located few hundreds of meters from the Atlantic Ocean at *ca* 54 m *asl*. Given the *ca* 12000mm/year rainfall (see Figure I.2b) it receives (the precipitation amount is almost equal to its depth=13 m), its water column was expected to be isotopically homogenous with isotopic composition similar to that of the precipitations (means  $\delta^{18}O= -3.6\%$ ,  $\delta D=-11.9\%$ ). But, surprisingly, the lake shows a clearly stratified feature suggesting that, the high humidity and the expected rapid cycling of isotopes near the coast due to the frequent precipitations seem to have minimal effect on the isotopic composition of that lake. Instead, the lake water undergoes noticeable isotopic fractionation, especially the isotopic enrichment of the surface water ( $\delta^{18}O=3.1\%$ ,  $\delta D=0.1\%$ ) which, may solely result from wind-driven evaporation.

The Bamenda Lake District is located to the North of the South-west Lake District. As pointed out above, all the lakes in that district, in the exception of Lake Oku (Ok, see Figure II.12c, d) show weak to relatively strong isotopic stratification. The lake Oku is located in the highlands at *ca* 2227 m *asl*. The area is characterized by small daily temperature amplitude variation (Letouzey, 1985) which, together with the size of the lake (52 m deep only, see Table I.1), may contribute to maintain a homogenous water column structure through internal mixing.



Figure II. 13. View of the twin lakes Manenguba and the Manenguba caldera' geological setting composed of two structures: the Elengum volcano and the Eboga volcano, the most recent formed (0.51 Ma) hosts the caldera. The Female Lake is the largest and the male has a green color and is hosted in a deep crater with high walls. In spite of their proximity, the two lakes feature different isotopic composition

The Lake Benakuma, (Be), (Figure II.12c, d), (the third deepest lake of the CVL after lakes Nyos and Manenguba female) and to a lesser extent, the Lake Baleng, shows the strongest isotopic gradients among the CVL lakes. That feature may limit material transport between the epilimnion and the hypolimnion. The hypolimnetic water has an isotopic signature markedly different from that of the isotopic composition of the present days rainfall ( $\delta^{18}O=3.8\%$ ,  $\delta D=35.6\%$ ); it is thus assumed that the water in the bottom of the lake may have been rapidly recharged under cold conditions.

Among the lakes of the Bamenda Lake District, lakes Nyos and Monoun are of particular significance since they have been the theater of catastrophic gas explosions.

Their isotopic profiles (Table II.3; Figure II.14) indicate that their water column has several micro-layers separated by weak isotopic gradients. They also have the lowest isotopic values, which is similar to that of local ground water implying extensive hydraulic connectivity among the two reservoirs. The CO<sub>2</sub>-rich bottom waters are even more depleted probably due to isotopic fractionation between CO<sub>2</sub> and water molecules, which will tend to enrich the carbon dioxide and deplete the water in <sup>18</sup>O, modifying their initial compositions as predicted by  $\alpha_{CO2-H2O} = ca.$  1.041 (Bottinga and Craig, 1968; Brenninkmeijor et al., 1983).

The enrichment/impoverishment factor of specie 2 relatively to specie 1 is expressed as:  $\alpha_{2(1)=}$  (R<sub>1</sub>/R<sub>2</sub> - 1) x 1000 where R<sub>1</sub> and R<sub>2</sub> are the <sup>13</sup>C/<sup>12</sup>C of specie 1 and 2 respectively. In terms of  $\delta$  notation  $\epsilon_{2(1)}=(\delta_1 - \delta_2)/(1 + 0.001 \times \delta_2)$ .

Since the use of water isotopes for hazard surveillance is the avowed purpose of this study, it is important to show that noticeable changes in the isotopic distribution along the water column can be detected. Therefore, isotopic data from literature for the years 2012, 2010 and 1989 (Sasaki et al., 2012 pers. com.; Nagao et al., 2010 and Kusakabe et al., 1989 respectively) have been plotted as a function of depth (Figure II.14) to show the changes occurred to the water column structure since 1986 At Lake Nyos, the 1986 profile which has been taken several months after the

Geochemical characteristics of the CVL lakes

gas burst is the most depleted. Then, the surface waters evolved towards higher isotopic values and attained equilibrium since 1999. The isotopically enriched middepth water may represent a mixture of pre-catastrophe waters and rain since, the gas explosion occurred in the heart of the rainy season. The process of replenishment by the surface water inflow which assumedly started after the event continued even three years after. The deepest water got heavier in 2012, probably under the double effect of  $CO_2$  removal and ground water inflow.

At Lake Monoun, the 1999 profile shows the lowest  $\delta^{18}$ O values. Although the surface layer thickness (*ca* 18m), was maintained throughout the observation period, reflecting constant volume of water inflow (e.g. from River Panke), its  $\delta^{18}$ O became more enriched, possibly due to variation in inflow/evaporation ratio. An isotope-concentration anomalous layer was developed at depth between 60 m and 85 m suggesting the inflow of fluids with comparatively positive isotopic composition. At the bottom meanwhile, the isotopic composition did not change much since 1986.

The  $\delta^{18}$ O profile vs time shows that, anomalies created by inflow fluids can be traced, and their origin may also be constrained. In lakes Nyos and Monoun, the water column structure is controlled by the Total Dissolved Solid (TDS) which increase from the surface towards the bottom (Evans et al., 1994; Kusakabe et al., 2008; Issa et al., 2013). In contrast, the  $\delta^{18}$ O concentrations instead decrease towards the bottom implying TDS do not influence  $\delta^{18}$ O concentrations or that, the isotopic fractionation between water and dissolved CO<sub>2</sub> has preponderant effect compared to the dissolved salt (Gat, 1995). Assuming the latter observation is not valid, the independent variation of the <sup>18</sup>O vary makes it a useful tool to trace inflows in the case of the gassy lakes and hopefully for the other lakes.

Finally, the lakes in the Adamaua Lake District (Ad-LD) are among all, the heaviest with average  $\delta^{18}O$  and  $\delta D$  greater than 6.1‰ and 16.7‰ respectively (Figure II.12e, f). Lake Tizon is distinguished by the highest isotopic ratios ( $\delta^{18}O$ =9.8 and  $\delta D$ =28.6‰).

Sampling site	Date	Depth	dD	d <sup>18</sup> O	Sampling site	Date	Depth	dD	d18O
Lake Nyos	Mar-12	0	-6.0	-1.6	Lake Monoun	Mar-12	-30	-18.1	-3.7
		-5	-6.0	-1.8			-50	-19.3	-4.3
		-10	-7.2	-2.0			-55	-19.0	-4.0
		-15	-7.4	-2.0			-60	-17.9	-3.7
		-20	-7.6	-2.0			-70	-18.1	-3.6
		-25	-7.6	-2.1			-75	-19.0	-3.9
		-30	-7.6	-2.0			-80	-19.8	-4.0
		-50	-8.0	-2.1			-82	-20.6	-4.0
		-70	-7.8	-2.1			-85	-20.6	-4.2
		-80	-8.5	-2.2			-87	-20.7	-4.2
		-90	-9.9	-2.3			-90	-20.6	-4.2
		-100	-9.9	-2.4			-93	-20.6	-4.1
		-120	-10.2	-2.4			-95	-21.0	-4.2
		-130	-10.1	-2.5			-97	-21.2	-4.2
		-140	-10.3	-2.5			-98	-21.3	-4.2
		-150	-10.6	-2.5			-98.5	-21.5	-4.2
		-160	-10.7	-2.8					
		-170	-11.2	-2.7					
		-176	-10.3	-2.5					
		-180	-10.3	-2.4					
		-184	-10.2	-2.4					
		-188	-10.1	-2.4					
		-190	-10.2	-2.5					
		-192	-10.1	-2.4					
		-194	-10.0	-2.5					
		-198	-9.8	-2.6					
		-200	-9.9	-2.5					
		-201	-9.8	-2.6					
		-202	-9.9	-2.6					
		-203	-9.8	-2.5					
		-204	-9.9	-2.6					
		-205	-10.2	-2.6					
		-206	-10.2	-2.5					
		-206.5	-10.2	-2.5					
		-207	-10.1	-2.6					
		-208	-10.6	-2.7					
		-209	-10.5	-2.6					
		-209.5	-10.9	-2.6					

Table II. 3. Isotopic profiles of Lakes Nyos and Monoun (2012)



Figure II. 14.  $\delta^{18}O$  profiles of lakes Nyos and Monoun. Although elemental profiles, exemplified by TDS, increase from the surface to the bottom,  $\delta^{18}O$  instead shows negative gradient.  $CO_2$ -rich bottom waters are the most depleted probably due to isotopic fractionation between  $CO_2$  and water

As mentioned above, the Lake Baledjam Marbuwi (B-m) is the only one that displays  $\delta^{18}$ O enriched bottom water as compared to the surface water.

b) Effect of mixing with local water bodies (precipitations, rivers and ground water)

In order to qualitatively evaluate and constrain the isotopic contribution of the present day's precipitations to the lakes isotopic composition, we have plotted in Figure II.15, the lakes average isotopic composition and the mean composition of precipitations from each region. The Local Evaporative Line (LEL) of each Lake District and the CMWL are also shown. The local evaporative lines have been back-extrapolated to intersect with the Cameroon Meteoric Water line in order to theoretically constrain the isotopic composition of the evaporating water bodies from each Lake District (Gat, 1995; Kebede, 2004; Henderson and Shuman, 2010).

From Figure II.15 one can note a marked mismatch, especially in the case of the South-west Lake District, between the theoretical graphical prediction and the measured isotopic signature of the source rain. Usually, in order to assess the degree of mixing with the local ground and the surface waters, we have plotted the lakes isotopic composition with the averaged isotopic composition of local ground water and inlet/outlet rivers in Figure II.16 (Darling et al., 1996; Ayenew, 1998; Chernet, 1998; Mckienze et al., 2001; Kebede et al., 2002; Delalande et al., 2008; Gat, 2010).

Figure II.16 indicates that, the regional surface and ground have almost similar isotopic signature from the South to the Adamaua Plateau. The lakes in the South-west Lake District plot slightly away from the regional water bodies. This may indicate that they have limited connectivity with local hydrogeological systems or that, they may be hydraulically connected to several and different aquifer systems. For example, the Lake Manenguba male bottom water has similar isotopic composition as the inlet spring (Mm inlet:  $\delta^{18}O= -2.3\%$  and  $\delta D= -29.5\%$ , see Table II.4) indicating the two water bodies probably tap from the same aquifer system. Its

heavy isotope depleted nature suggests that, the water was recharged under low temperature and high humidity conditions.

The surface water seems to result from mixing of rain ( $\delta^{18}O$ =-5.8‰), ground water ( $\delta^{18}O$  = -2.3‰) and water from a different aquifer system which has  $\delta^{18}O$  = -0.9‰ comparable to the isotopic composition of the Mf inlet spring (see Table II.4). In the case of the Mf, its isotopic composition compares with neither its inlet nor the any of the sampled ground water. Its water seems to derive from the mixing of waters from different origin. In summary, the Lake Manenguba Male and Manenguba female contain water resulting from the mixing of the several local aquifer systems; the Mf water seems to have undergone relatively higher evaporation due its setting as explained above.

In the case of Lake Barombi Mbo, its water is remarkably heavy isotopes enriched relatively to the inlets (BM inlet 1, 2 and 3, see Table II.4) with mean  $\delta^{18}O = 0.4\%$ ,  $\delta D = 12.0\%$  and the regional ground water (Kumba Gw, Barombi Koto GW and Bar. Village) with mean isotopic composition of  $\delta^{18}O = 0.3\%$ ,  $\delta D = 12.8\%$ .

Alike the lakes Manenguba Female and Debunscha, the difference in the isotopic ratio between the lake on one hand and the and the inflows and ground water on the other hand may signify that the contribution of the emissary to the shaping of the isotopic composition of the lake is limited. In fact, the Barombi Mbo has been harnessed to supply drinking water to the neighboring city of Kumba. The majority of the water contributed to the lake by the inlets might be abstracted for that purpose.

In the exception of lakes Wum, Idjagham and Oku, the majority of the lakes in the Bamenda Lake District cluster with the ground and surface water indicating extensive hydraulic connectivity. By plotting slightly away, Lakes Oku seems to tap water from aquifer with different isotopic composition from the one the water of which was sampled with  $\delta D$ =-26.0‰ and  $\delta^{18}O$  -1.9‰ significantly different from that of the lake  $\delta^{18}O$ =4.1‰,  $\delta D$ =2.8‰ (see Table II. 4).



Figure II. 15. Plot of regional isotopic ratios of precipitation and mean isotopic composition of the lakes. The Local evaporative Lines (dotted lines: purple for the Adamaua Lake District; green for the Bamenda Lake District and red for the South-west Lake District) have been back extrapolated to intersect with Cameroon Meteoric Water Line in order to theoretically constrain the isotopic composition of the source rain. There's an obvious mismatch between the measured isotopic composition of each region and the graphically predicted values. (Circled): N-W=North-West (Bd-LD), S-W= South-West (SW-LD), Ad=Adamaua (Ad-LD) and F-N= Far-North



Figure II. 16. Graph of the mean isotopic composition of the lakes and that of the regional groundwater and surface. Water source: SW=Stream water, GW= ground water.

This is also the case of lakes Wum and Idjagham which have isotopic composition markedly different from that of the sampled ground waters with isotopic ratios of  $\delta D$ =-9.3‰ and  $\delta^{18}O$ =0.6‰; and  $\delta D$ =-10.3‰ and  $\delta^{18}O$ =0.8‰ respectively.

Finally, by plotting further away, the lakes in the Ad-LD are the ones that show the highest isotopic difference with local ground and surface waters implying very limited interaction. Unless, the climate-driven isotopic fractionation processes (Drever, 2002 and other references therein) masks the lake-groundwater-surface waters relationship in that LD.

Besides the mixing effect with local water bodies, another important factor can account for the present isotopic composition of the lakes. The long-term evaporation-mixing-subsidence processes may also contribute to the shaping of the isotopic distribution along the water columns. In fact, in the case strong stratification does not prevent material transport between layers, temperature variation between day and night time induces downward circulation (Rowe, 1992) of water from the isotopically more positive epilimnion, towards the hypolimnetic water strata during the nights. In the long run, depending on the residence time, the subsidence will result into isotopic enrichment of the lake as compared to the local ground water. Such process could be envisaged for example, in the case of the BM which is minimally or not stratified.

	Ground and surface water			Lakes								
L. District	Site	Date	δD	$\delta^{18}O$	L. District Name		Date	Depth (m)	δD	$\delta^{18}O$	mean	mean
	Db Gw	May-13	-2.8	1.0		Barombi Koto		0	9.3	5.5		
	BKGw	Apr-13	-14.3	0.1		Debunscha		0	0.1	3.1		
	BM  Gw	Nov-12	-16.0	-0.3		Debunscha	May-13	10	-1.1	2.4	-0.5	2.8
	BM Vi	Nov-12	-8.2	1.3		Manenguba Male		0	-21.5	-0.8		
(BM)	Inlet 1	Nov-12	-15.0	-0.3		Manenguba Male		45	-27.7	-0.4		
	Inlet 2	Nov-12	-15.1	-0.1	SW-LD	Manenguba Male		90	-28.4	-1.8	-25.9	-1.0
	Inlet 3	Nov-12	-15.2	-0.5		Manenguba Female	May-12	0	-1.5	3.8		
	Inlet 3	Apr-12	-7.4	1.3		Manenguba Female		75	-6.5	3.0		
SW-LD	Inlet 1	Apr-12	-9.4	1.2		Manenguba Female		149	-7.2	2.9	-5.1	3.2
	Inlet 2	Apr-12	-9.9	1.0		Barombi Mbo		0	3.4	4.1		
	Ndi.Gw	Apr-12	-22.0	-0.2		Barombi Mbo		50	1.6	3.8		
	Tap 1	Apr-12	-27.8	-0.9		Barombi Mbo		98	1.2	3.8	2.1	3.9
	Tap 2	Apr-12	-28.1	-0.9		Baleng	Apr-13	0	1.2	1.6		
(Mm)	Inlet-a	May-12	-29.5	-2.3		Baleng		50	-8.7	-0.8	-3.7	0.4
( <i>Mf</i> )	Inlet-b	May-12	-26.2	-0.9		Benakuma	Apr-13	0	3.6	1.2		
	Evam1	May-12	-24.1	-0.4		Benakuma		70	-12.2	-2.0		
	Evam2.	May-12	-23.9	-0.6		Benakuma		130	-12.3	-2.2	-6.9	-1.0
	Mboue	May-12	-26.8	-0.9		Oku	May-13	0	2.7	4.1		
	Bal. Gw	Apr-13	-17.7	-0.2	Bd-LD	Oku		49	3.0	4.1	2.8	4.1
	Bef. Gw	Apr-13	-9.3	0.6		Idjagham	May-13	0	10.0	5.8		
	Ok. Gw	May-13	-26.0	-1.9		Idjagham		15	8.5	5.5	9.3	5.7
Bd-LD	Idj. Gw	May-13	-10.3	0.8		Elum	Apr-13	0	3.4	0.7		
	Mo.	Mar-13	-18.4	-2.3		Elum		34	1.4	0.4	2.4	0.6
	$Mo.\ Gw$	Mar-13	-20.4	-2.9		Wum	Apr-12	0	16.7	6.5		
	Riv.Pan	Mar-13	-11.3	-1.9		Wum		60	12.8	5.8		
	Tiz.Gw	Apr-13	-13.7	0.3		Wum		126	12.6	5.9	14.0	6.1
	Dib.Gw	Apr-13	-16.0	0.0		Ngaoundaba	Apr-12	0	13.9	6.5		
						Ngaoundaba		25	9.9	5.8		
						Ngaoundaba		49	9.8	5.7	11.2	6.0
						Tizon	Apr-12	0	32.3	10.6		
Ad-LD						Tizon		20	26.8	9.4		
					Ad-LD	Tizon		42	26.8	9.3	28.6	9.8
						Baledjam Marbuwi		0	12.8	4.0		
						Baledjam Marbuwi		40	12.5	4.2		
						Baledjam Marbuwi		100	10.4	4.1	11.9	4.1
						Baledjam (Ranch)		0	16.9	5.2		
						Baledjam (Ranch)		11	13.3	4.1	15.1	4.7

Table II. 4. Isotopic composition of groundwater, rivers and lakes

c) Spatial variation in isotopic composition and evaluation of the control parameters

In order to evaluate the influence of the geographical location on the isotopic composition of the lakes, the surface, mid and bottom isotopic ratios were averaged to yield a representative isotopic composition for each lake (Table II.4). The values were plotted in the conventional  $\delta D \cdot \delta^{18}O$  space together with the CMWL and presented in Figure II.17. Since we are evaluating crater lakes which may have some connections with the hydrothermal systems, the fields for metamorphic and magmatic waters (Taylor, 1979; Giggenbach, 1992) have also been included in the graph. The lakes plot to the right of the CMWL along a least square line  $\delta D$ = 3.86<sup>18</sup>O -10.2, r<sup>2</sup>=0.82 (designated hereafter as Lakes Water Line LWL) indicating significant isotopic enrichment. That remarkable displacement in the  $\delta O^{18}$ - $\delta D$  space of the African lakes compared to lakes in other parts of the world was already noted during the early surveys of stable isotopes variation in hydrological cycle (Gat, 1995). The slope of the Lake Water Line (3.8) falls in the expected interval of 3.5-6.5 (Dincer, 1968; Kebede, 2004) predicted for evaporating open water bodies. However, much lower than that for Ethiopian lakes (5.2 to 6.4) and other lakes in Eastern (Turkana) and or Central Africa like Lake Chad (Fontes et al., 1970). A second noteworthy indication is that, in contrast to the northwards impoverishment of rains in heavy isotopes due to the latitude effect (Dansgaard, 1964, Gat, 2010), the lakes instead get more enriched as one move inland.

In order to theoretically evaluate the latitudinal evaporative effects on each group of lakes, we base our analysis on the Local evaporative Lines (Figure II.15). Their slopes decrease from 5.4 in the South-west Lake District, to 2.9 in the Adamaua Lake District passing through the value of 3.3 in the Bamenda Lake District. The values of the slopes of the 2 Southern-most lake districts fall in the theoretical interval of evaporating open water bodies. In contrast, that of the Adamaua Lake District falls out of that range and even approaches that of high temperature fluids (Figure II.17) encountered in arc volcanic regions (Taran et al., 1989; Giggenbach, 1992) suggesting a more severe evaporative effect. Given that in the Adamaua Lake District the mean temperature is ca 20°C, much lower than in the southern lake districts (24-26°C), the observed trend signifies that, temperature dependence isotopic fractionation might be reversed along the CVL. A possible explanation to that behavior would be attributed to the difference in the humidity between the South and the Northern region. Contrary to the Adamaua Lake District, which is covered by sparse vegetation of pre-savanna-type (Figure I.2d) and characterized by low ambient humidity, dense evergreen vegetation prevails in the southern lake districts. It is therefore conceivable that, the intense evapotranspiration contributes to reduce the isotopic transport (equilibrium and/or, diffusive and/or turbulent transport) among the reservoirs by maintaining high atmospheric humidity (>85%) throughout the year. Parallel to the increase in the values of the slopes, d-excess also increase from -20 in the South-west Lake District to -7.5 in the Bamenda Lake District and attain -1 in the Adamaua Lake District. This testifies the influence of increasingly dryer conditions marked by a decreasing precipitation/evaporation ratio (Sighomnou, 2004). As already indicated above, Lake Wum, Idjagham and Oku in the Bamenda Lake District plot among those of the Adamaua Lake District (Figure II.16) suggesting that, in addition to the climatologic control, interaction between the lakes and their immediate environments such as hydrological setting (Cabassi et al., 2013) and intrinsic parameters (such as size, depth, sheltering from wind...), cannot be ignored in the shaping of the isotopic composition of the CVL lakes.



Figure II. 17. Plot of averaged isotopic composition of the lakes in the  $\delta^{18}O$ -  $\delta D$  space. Metamorphic and magmatic fields (Taylor 1979) are shown. Line representing high temperature ( $350^{\circ}C \leq T \leq 400^{\circ}C$ ) gas from arc-volcanic areas (data from Mazot, (2002)) is also shown together with isotopic composition of water having  $66^{\circ}C \leq T \leq 94^{\circ}C$  (triangles). The lakes are remarkably shifted to the right of the CMWL indicating evaporation effects.

#### II.2.3.3 Quantification of the influence of some parameters

Thorough evaluation of the influence of a given parameter on a lake dynamic requires detailed and precise information. Although the information used in this work is broad and not specific to each lake, in the following, we attempt to quantify the effect of five selected parameters on the isotopic composition of the CVL lakes. The estimated average temperature, the altitude, the maximum depth, the distance from the coast and the hydrological setting (data from Table I.1) have been plotted as a function of  $\delta^{18}$ O and displayed in Figure II.18. The plots are characterized by a correlation coefficient of r<sup>2</sup><0.15. The scattering of the  $\delta^{18}$ O values indicates no or very weak correlation with afore mentioned parameters.

Among all the parameters, the mean regional temperature and altitude seem to play the least role in the isotopic composition of the lakes (Figure 2.18a and b). In contrast, Figure 2.18c suggests the depth may have comparatively a greater and discernible influence. Among all, the distance from the coast had a quantifiable effect and it has been estimated that the lakes get more enrichment by +0.6%/100km as one move from the South to the North (Figure II.18d). Although not quantifiable, Figure II.17e which shows the  $\delta^{18}$ O-hydrolgical setting, indicates that the closed lakes have the most positive isotopic values (e.g: Lake Tizon the isotopically heaviest lake) compared to the others, especially the through-flow lakes. The observation is consistent with the fact that the mixing of surface inflows, which are in general heavy isotopes depleted, contributes to lower the isotopic concentration of the lakes contrary to closed lakes from which evaporation removes lighter isotopes without subsequent replenishment.

Though the study has qualitatively described and attempted to quantify the effect of some factors that could explain the actual isotopic signature of the lakes, more accurate information on those factors are necessary to hierarchize their respective effect. The work indicates that, the variation in isotopic content due to interaction between a lake and exogenous waters can be reasonably deciphered, and the origin of the exogenous waters identified if accurate and sufficient information on the climatology, geology and the hydrology is available. Although complex, the availability of such parameters could permit to qualitatively and quantitatively evaluate the evaporative and/or degree of mixing effect on open water bodies such as a lake. For example, Henderson and Shuman (2010) have proposed a polynomial that integrates climatological, hydrological geographical settings to explain the isotopic signature of lakes in the western USA. Jones and Imbers (2009) quantified the relationship between isotopic composition and size parameters of lakes. In the absence of geothermic heat, evaporation is mainly controlled by ambient temperature, dependent factors such as latitude, altitude, climate, humidity wind, (Patalas, 1984; Imberger, 1985) and intrinsic parameters. As shown above, deciphering the influence of each given parameter is possible.



Figure II. 18. Plot of some control parameters as a function of  $\delta^{18}O$ . Temperature (a) and the altitude (b) seem not to play a remarkable role in controlling the isotopic composition of the lakes. Depth (c), distance from the coast (d) and hydrological setting (e) show extremely weak, however, discernible control. (T-f= Through-flow lakes; H/T= Head or Terminal lakes; C= Closed lakes)

## **II.2.4** Conclusion

Seventeen lakes, 47% out of 38 more or less documented volcanic lakes located on the CVL, have been isotopically characterized. To our knowledge, if we exclude reviews (e.g. IAEA, 1981; Fontes and Edmond, 1989; Gat, 1996, the list is not exhaustive), this study is the first that discusses isotopes in about 20 lakes. The results indicate that, irrespective of their location, size parameters or hydrological setting, the CVL lakes have been found to be isotopically stratified with heavy isotope enriched epilimnia compared to the hypolimnetic waters. In several lakes, the isotopic gradient between surface and bottom waters was significantly large indicating the concerned lakes might be meromictic. Whether the stratification is permanent or seasonal remains a matter of investigation. That clarification is necessary because, permanent stratification might favor the accumulation of gas in lakes in the example of lakes Nyos and Monoun. An attempt has been made to qualitatively and quantitatively evaluate the effect of some parameters on the lakes' isotopic variation. However, none of them has been found to play a predominant role. Consequently, in the absence of accurate information on those parameters, it is assumed that, the interplay of the factors may contribute to shape the isotopic composition of the lakes. The present study constitutes a starting point for isotopes study in the CVL lakes. It provides a much needed snapshot of their present status in order to monitor the subsequent changes that might occur to their water columns (Rowe et al., 1992). Prospectively, the study of almost half gives a possibility to draw significant inferences on the isotopic characteristic of the other lakes that have not been studied. This may be useful for the setting up of a minimum monitoring/surveillance network for those volcanic lakes.

# CHAPTER III- GEOCHEMISTRY OF DIFFUSE GAS ALONG THE CVL AND THE ASSESSMENT OF THE EFFECT OF METHANE ON THE STABILITY OF LAKES NYOS AND MONOUN WATER COLUMNS

III.1 Diffuse gas emission from some volcanogenic structures of the Cameroon Volcanic Line (CVL): Implication for natural disaster prevention and global carbon cycle.

(Issa et al., 2014b. Diffuse Gas emission from some Diffuse Diffusion Structures of the Cameroon Volcanic Line (CVL): Implication for the prevention of CO<sub>2</sub> related hazards. J.Volcanol. Geotherm. Res. DOI: 10.1016/j.jvolgeores.2014.07.001)

## **III.1.1 Introduction**

Of the magmatic fluids,  $CO_2$  gas constitutes the second most abundant component after water (Stopler and Holloway, 1988). This makes it a suitable geochemical tracer for volcanoes monitoring. On the other hand, because of its multiform impacts on the Earth dynamic in general and on the bio-ecosystems in particular, the studies on its origin and source-sink balance estimations have received increasingly greater interest among geoscientists and the civil society. Since several decades,  $CO_2$  has been widely studied especially to understand volcanic eruption processes (Hernandez et al., 2001a; 2001b) and subsequently to evaluate (1) its effect on current climate change (Leavitt, 1982; Marty and Tolstikhin, 1998; Kerrick, 2001) and (2) to assess its hazardous potential both during volcanic crisis and in periods of quiescence. During quiescent periods, migration  $CO_2$  from the Earth interior to the superficial envelopes takes place along crustal weaknesses (Mazot et al., 2011) and feature on the Earth as fumaroles ground water systems, mud volcanoes, soda or accumulates in crater lakes. That type of accumulation lead to a violent release of  $CO_2$  from Lake Nyos in August 1986 killing *ca* 1700 people (Freeth and Kay, 1987; 1991; Sigvaldason, 1989; Kusakabe et al., 2000; Kling et al., 2005). To avert repetition of gas explosion, the artificial removal of gas started in January 2001 and January 2003 at Lakes Nyos and Monoun with one degassing pipe at each lake. In January 2006, two additional degassing pipes were installed at Lake Monoun to foster the gas removal., At Lake Nyos, numerical modeling (Kling et al., 2005) indicated that the single pipe would be soon be ineffective as natural gas input would balance the removal rate and draw down to safe level would take several years. Consequently, two additional degassing pipes were installed in March 2011 to make the lake safe in reasonable time.

Beyond the fatale side,  $CO_2$  constitutes one of the driving forces of climatic processes. Whether the current increase in Earth temperature results solely from its internal dynamic or not is a matter of debate. However, as climate Science and the Earth's climate have continued to evolve over recent decades, increasing evidence of anthropogenic influences on climate change has been found. Correspondingly, the Inter-governmental Panel on Climate Change (IPCC) has made more definitive statements about human impacts on climate. Now, it is a fact that, since the industrialization era, the Earth's temperature has increased concomitantly with the atmospheric  $CO_2$  concentration, primarily due to the combined effect of combustion of fossil fuels whose demands will continue to increase in the future (Nathan and Nocera, 2006) and removal of forests. That increase in the atmospheric  $CO_2$  concentration has reduced the radiation to the space of the long wave energy emitted from the surface of the Earth itself increasing thereby the greenhouse effect, which in turn drives the current climatic disorder.  $CO_2$  has been notoriously known as the most important greenhouse gas after water vapor (IPPC, 2007). Thus, humankind has dramatically altered the chemical composition of the global atmosphere with substantial implications for climate marked by extreme climatic events. The frequent occurrence of extreme meteorological events has increased the awareness vis-à-vis human-induced climatic forcing and called for the control and reduction of the anthropogenic emission of green-house gases to the atmosphere (Kyoto Protocol, 1997) in order to, in the long run, reverse the current climatic trend.

The implementation of policies deemed to control the impact of anthropogenic  $CO_2$ would require that, the identification of the sources and the quantification of the component of the naturally emitted  $CO_2$  is adequately and accurately determined, and the total output accurately estimated. However, current reports on global estimates of CO<sub>2</sub> degassing vary by an order of magnitude (Etiope and Klusman, 2002; Morner and Etiope, 2002). Given that, on geological time, only silicate weathering would balance the global CO<sub>2</sub> emission, on one hand and, considering the estimate of the total  $CO_2$  output, it appeared that all sources have not yet been accounted for. Therefore, the search for the missing source has fostered the inventory of the CO<sub>2</sub> output from tectonically controlled CO<sub>2</sub> degassing structures regrouped under the appellation of diffuse degassing structures (DDS) (Duarte et al., 2008; Chiodini and Frondini, 2001) to quantify their contribution to the global carbon cycle and also to serve as proxies for volcanic activities surveillance (Chiodini et al., 1998; 2005). The diffuse degassing structures encompass among others, volcanic areas characterized by sustained passive CO<sub>2</sub> degassing and crater lakes.

## III.1.2 Objective of the study

In spite of the deadly gas explosions occurred in the middle of 1980s and its cyclic nature (Kling et al., 1989; Tietze, 1992, Halbwachs et al., 1993), the frequent eruptions of Mount Cameroon and the existence of numerous gassy springs which prove that the CVL is still an active volcanic environment (Hard, 2005), volcanic surveillance/forecasting activities remain poorly developed (Issa et al., 2013) in Cameroon, especially multi-parametric assessment of the evolution of volcanic edifices. Accordingly, this study attempts to:

1) Provide basic and a comprehensive insight on the aerial (Soil/- water/atmosphere interfaces) manifestation of the passive emission of CO<sub>2</sub> along the CVL on one hand,

and on the other, (b) to check the lakes for containing  $CO_2$  or not. Besides, the study of other magmatic gases such as noble gases He and Ar are also studied to understand the origin and the mechanism controlling gas emission (shallow or deep origin). The information generated shall hopefully serve as baseline data for risk/mitigation activities in connection with  $CO_2$ -related hazards along the CVL.

2) Estimate the contribution to the global carbon cycle of the CVL volcanic lakes which represent about ca 30% of the 113 to 138 more less document volcanic lakes worldwide (Delmelle and Bernard, 2000; Perez et al., 2011).

## III.1.3 Material and Method

Different types of Earth degassing require widely different methods of measurement and of investigation e.g. Eddy covariance (Kanemasu et al., 1974; Parkinson, 1981) and the infrared analyzing methods such as the accumulation chamber technique (Chiodini et al., 1998; 2008; Sorey et al., 1998). Combined with stable isotopes, those techniques provide constrains on both the origin (Chiodini et al., 2008) and the estimate of the total  $CO_2$  output from volcanic areas (Werner and Brantley, 2003). Tremendous advances have been made in both the techniques and estimation of total diffuse  $CO_2$  output from several environments (Kling et al., 1991; Bergfeld et al., 2001; Chiodini et al., 2008; Nemesio et al., 2011). However, in recent years, the portable flux meter known as the accumulation chamber (AC) method (Chiodini et al., 1998) has been widely used to measure diffuse gas at soil/atmosphere and water/atmosphere interfaces (Photo 3.1) (Kling et al., 1991; Mazot, 2002; Nemesio et al., 2011; Mazot et al., 2011). Thorough description of the instrument can be found in Chiodini et al. (1998) and in the portable flux meter handbook (*www.westsystems.com*).

In brief, the accumulation chamber system comprises (1) an inverted circular chamber with a volume of  $6.231 \times 10^{-3}$  m<sup>3</sup> and an internal height and diameter of 0.198 m and 0.2 m respectively, (2) a non-dispersive infra-red gas analyzer (IRGA) LI-COR 820 (measuring range of 0-20,000 ppm, accuracy of 4% of reading), (3) an

Geochemical characteristics of the CVL lakes

in-built peristaltic pump (0.01 L s<sup>-1</sup>) that ensures the circulation of the gas in a close loop circuit, from chamber-analyzer-chamber via a small inner diameter (4.3 to 4 mm) RILSAN and SILICON tubing and, (4) a fan mounted inside the chamber that ensures the homogenization of the gas before entering the analyzer. The operation of the system and the data storing is ensured by a human interface device, a palmtop computer, also refer to as PDA (Personal Digital Assistant). The locations and the temperatures of the surveyed points were recorded by a GPS (Garmin *GPSmap 62s)* and a hand thermometer (SATO SK-1110) respectively. The CO<sub>2</sub> flux was computed on the basis of the measured CO<sub>2</sub> concentration increment inside the AC with time (dC<sub>CO2</sub> / d*t*). Initially, the type of the AC (B) was configured on the PDA so as to obtain the flux directly in moles per square meter per day (mol.m<sup>-2</sup>d<sup>-1</sup>) instead of the slopes of the fitting curves.

Using the MK-sampler (Kusakabe et al., 2000) the bottom most waters of lakes Ngaoundaba, Baledjam Marbuwi, Benakuma, Barombi Mbo and Manenguba Male were fixed fixed *in-situ* into 60 ml plastic syringes containing initially 10ml of potassium hydroxide (10M KOH) solution to check and if possible, determine the  $CO_2$  concentration. Upon retrieval, the syringes were capped, tapped and securely stored in aluminum bags to avoid atmospheric contamination. Subsequently, the total carbonate was determined by the micro-diffusion technique (Conway, 1958). Afterwards, depending on the *in-situ* pH, the dissolved  $CO_2$  gas ( $CO_2$ aq) concentration was obtained by subtracting the titrated  $HCO_3^-$  and/or  $CO_3^2$  from the total carbonate. For the determination of the  $\delta^{13}$ C of the gas, the bottom waters were instead fixed in syringes an initial volume of 10ml of saturated barium hydroxide  $(Ba(OH)_2)$  solution following the same procedure. The obtained precipitates were washed using  $CO_2$ -free water following procedure by Kusakabe (2001). The precipitates were then decomposed by reaction with phosphoric acid on a high vacuum line. The evolved  $CO_2$  was cryogenically collected in a multi-trap using liquid nitrogen and purified through standard trap. Finally, the  $CO_2$  was

collected in a glass for stable isotope mass spectrometry (precision  $\pm$  0.03‰) at Toyama University.

The soil gas surveys were carried near Lake Nyos (January 2009), in the valley located at the north-eastern side and at a 3.5 km diameter caldera on the Mount Manenguba (9°42' and 10°10' E and 4°49' and 5°15'N) at 2 411 m *asl.* (Figure III.1). The Manenguba volcano hosts about 70 strombolian cones and three crater lakes two of which (Manenguba twin lakes) occur within the Eboga formations (Kagou et al., 2001). The lakes are underlined by two N20-40° and N110-130° faults system (Kagou et al., 2001).

Beside the  $CO_2$ -flux measurement, gas samples were collected at several locations for the determination of its composition (Photo 3.2).

The soil gas sampling was done by inserting a stainless steel probe to *ca* 40 cm into the soil. A 60 ml plastic syringe was then used to suck and collect the gas into glass tubes. First of all, two needles were inserted in the sampling tube septum; one of which was used to introduce the gas and the second was used as exhaust designed to flush the tube. About 50 ml of gas from the syringe was injected into the tube to make it free of previous gas; then, the exhaust syringe was removed and the about 10 ml of gas remaining in the syringe was collected in the glass tube. The gas samples were analyzed for  $\delta^{13}$ C, He, N<sub>2</sub>, O<sub>2</sub>, <sup>40</sup>Ar and <sup>36</sup>Ar and CO<sub>2</sub> by a Quadrupole Mass Spectrometer (QMS; Pfeiffer Omnistar 422) in the Instituto Tecnologico y de Energias Renovables (ITER) in the Canary Islands (Spain).

The total output from lakes Tizon, Ngaoundaba, Baledjam, Manenguba Female and Baleng was obtained by simply multiplying the arithmetic mean value of the  $CO_2$ -flux by the surveyed area (Cardellini et al., 2003). For the remaining lakes and the soil  $CO_2$ , the mapping and the total output were elaborated using the now widely adopted sequential Gaussian simulation (sGs) algorithm (Deutsh and Journel, 1998) and the graphical statistical analysis method (GSA) (Sinclair, 1974).



Figure III. 1. Geology of the Mt Manenguba and its caldera showing the two major formations (the Elengum and the Eboga which belt the volcano). Two major faults underline the caldera. The Map shows tha Manenguba twin lakes (M·m=Lake Manenguba male and F·f= Lake Manenguba female). The area surveyed for diffuse gas emission in red (SA=surveyed Area). (Modified after Kagou et al., 2001).



Photo III 1 CO2-flux measurement at water/air interface (Lake Barombi Mbo). The AC was adapted



Photo III. 2 Soil CO2-flux measurement and gas sampling at Mt Manenguba Caldera

The sGs has been widely used to estimate the total  $CO_2$  output. The technique is suitable since the total  $CO_2$  output can be given with an uncertainty which is of great importance in the case of volcanoes monitoring/surveillance activities. The sGs needs the sampled population to study has a multi-Gaussian distribution meaning the population is normally distributed. Since the flux data are generally positively skewed, the data have first of all to be transformed into a normal distribution which the software will use instead of the experimental data. At the end of the operation, the data are back-transformed into the original data. The modelling of the experimental variogram is the second step after the sample site had been suitably divided into grid. Then a simple kriging estimate and variance, computed according to the variogram model of normal scores, are used to define a Gaussian conditional cumulative distribution function at each location. A random value is drawn from the conditional cumulative distribution as one "reasonable" simulated value for that location. Once a value is simulated, it is added to the data set and can be used together with the original data to estimate the variable at the next locations of the grid. The simulation proceeds to the next grid location and loop until all nodes are simulated. The *n* equiprobable realizations simulated should have the same statistics as the experimental data (Chiodini et al., 2008; Mazot, 2002; Cardelini et al., 2003; Padron et al., 2013 and other references therein). One hundred simulations were performed and the total  $CO_2$  output was computed as their averaged outputs.

## III.1.4 Results and discussion

Totally, 756ha representing about 37% of the 2035ha occupied by the volcanic lakes was surveyed (Table III.1).

Depending on whether a lake is in equilibrium, contributes or is an atmospheric  $CO_2$  sink, they have been grouped into two: group 1 comprises the Diffuse  $CO_2$  nonactive and group 2 the Diffuse  $CO_2$ -active lakes. The later has been further divided

Table III. 1.  $CO_2$  flux  $(t.d^{-1})$  measured at the surface of 9 volcanic lakes of the CVL. Soil  $CO_2$ -flux data from Nyos valley and from Mt Manenguba caldera have also been included. The 2009 data in italic were taken from Nemesio et al., (2010). The surveyed lakes areas are also given. In the column "Group", 1 refer to diffuse  $CO_2$ -non active lakes (in equilibrium with atmosphere); 2-1 refer to lakes which consume atmospheric  $CO_2$  and finally, 2-2 refers to the lakes which release  $CO_2$  to the atmosphere "-" not measured

	Lake	Jan-09	Ap-Mar-12	Ap-Mar 13	Dec13-Jan 14	Area (ha)	Group
SW-LD	Barombi Mbo	-	-13	-	-0.87 (±2.3)	415	2-1
	Man Female	-	0	-	-	22	1
Bd-LD	Monoun	19.13 (±0.1)	2.79 (±0.08)	-	21.8 (±0.7)	53	2-2
	Nyos	16.69 (±0.1)	122.9 (±2.0)	-	224 (±4.2)	158	2-2
	Wum		-1.5	-	-	45	2-1
Ad-LD	Tizon	-	-0.1	-	-	8	1
	Ngaoundaba	-	0.6	-	-	10	2-2
	Baledjam R	-	-	0	-	25	1
	Baledjam M	-	-	0	-	20	1
NW-LD	Nyos valley	2.13 (±0.2)	-	-		0.17	
SW-LD	Man. Caldera		-	-	26.9 (±1.4)	38.5	

into 2 sub-groups: the sub-group 2-1 comprising the Diffuse  $CO_2$ -positive relate to lakes that contribute  $CO_2$  to the atmosphere and the sub-group 2-2 constituted of the Diffuse  $CO_2$ -negative lakes which consume atmospheric  $CO_2$  (Diffuse  $CO_2$ -phagic) (Table III.1).

#### III.1.4.1.The Diffuse CO<sub>2</sub>-non-active lakes

Four lakes, Manenguba Female, Baleng, Baledjam Marbuwi, Baledjam and Tizon covering about 75ha (10% of the surveyed area), were found to be almost in equilibrium with atmospheric CO<sub>2</sub> (Table 1). Lake Baledjam Marbuwi bottom most water contains 2.97mmol/kg of CO<sub>2</sub> of magmatic origin with  $\delta^{13}C$ =-4.4 ‰ vs PDB (Table III.2). That value is comparable to that of lake Nyos  $\delta^{13}C$ =-3.4 ‰ however much heavier compared to the  $\delta^{13}C$ =-6.8 ‰ reported for Lake Monoun (Kling *et al.,* 1987b; Kusakabe and Sano, 1992). The lake is 100 m deep (see Table III.1) and could develop the potential to accumulate gas.

Although there is no discernable surface manifestation, it is however obvious that volcanic and/or magmatic  $CO_2$  seeps into that lake. This might be the indication that, a lake could contain  $CO_2$  but the gas may not freely diffuse at the surface, consequently it may tend to accumulate. Although the  $CO_2$  concentration in Lake Baledjam Marbuwi is very small compared to the maximum  $CO_2$  concentration of about 155mml/kg or 350mmol/kg in lakes Monoun and Nyos respectively (Kusakabe et al., 2008), it is advisable to check the remaining ones for containing or not  $CO_2$ .

#### III.1.4.2 The Diffuse CO<sub>2</sub>-active lakes

## a) CO<sub>2</sub>-phagic lakes

 $CO_2$ -flux has always been reported as efflux, meaning that the gas is emitted from the medium to the atmosphere in the positive or expected direction. During flux measurements however, the direction of the emission and the flux is therefore negative (Toutain et al., 2002) or could be termed "ifflux" (in- direction). In the case that the total ifflux is larger than the efflux output, the DDS may act as a  $CO_2$  sink.

Although scarce, lakes Wum and Barombi Mbo (BM), the largest volcanic lake in Cameroon, are weak  $CO_2$  sinks. The two lakes occupy 460 ha (about 61% of the surveyed area) and draw on average about -7.7 t.d<sup>-1</sup> of  $CO_2$  from the atmosphere (Table III.1). The total  $CO_2$  drawn from the atmosphere by the Lake Barombi Mbo was -13t.d<sup>-1</sup> in 2012; that rate decreased to -0.87 t.d<sup>-1</sup> in January 2014. Its bottom water contains 8.75mmol/l of  $CO_2$  the origin of which was not determined because the sample collected for  $\delta^{13}C$  yielded too small precipitate to evolve sufficient  $CO_2$  for the mass spectrometry.

Table III. 2.  $CO_2$  concentration and  $\delta^{13}C$  of bottom waters in some lakes. The sampling depths are also indicated.

Lake	Depth (m)	CO2 (mmol kg <sup>-1</sup> )	δ <sup>18</sup> C (‰ VPDB)	SD (VPDB ‰)
Ngaoundaba	67	0.56	-7.17	0.00
Baledjam M	100	2.97	-4.42	0.04
Benakuma	135	0.2	-6.55	0.00
Barombi Mbo	100	8.75	-	-
Manenguba Male	98	1.08	-9.46	0.03

The change with time of the CO<sub>2</sub>-flux at Lake Barombi Mbo may suggest some seasonal and or daily influence. In fact, the 2012 survey was carried during the dry season (April-May) whereas the second survey was conducted just at the end of the rainy season. Unless the above variation resulted from the overturn that the lake experienced in December-2012, several months before the first CO<sub>2</sub>-flux survey. In the case of Lake Wum, the samples collected for  $\delta^{13}$ C determination was unfortunately lost during laboratory manipulation. However, judging from the effervescence observed during the sampling of deep water, the lake may also contain gas.

## b) The diffused $CO_2$ -positive lakes

Three lakes, Ngaoundaba in the Adamaua Lake District, and the gassy lakes Nyos and Monoun in the Bamenda Lake District make up this sub-group (Table III.1). Lakes Nyos and Monoun bottom waters are known to contain high  $CO_2$  concentration (Kling et al., 2005; Issa et al., 2013). Lake Ngaoundaba also contains 0.56 mmol/L  $CO_2$  with  $\delta^{13}C$  of -7.17‰ vs PDB (Table III.2) value close to magmatic however, it seems that the sample was air contaminate during transport and/or laboratory handling. Its bottom water contains 0.56 mmol/L  $CO_2$ , which is very small. The three lakes cover an area of 221 ha, about 30% of the surveyed area. In 2012, Lake Ngaoundaba output was estimated at 0.6 t.d<sup>-1</sup> of  $CO_2$ . Lake Monoun and Nyos emissions were estimated at 14.6t.d<sup>-1</sup> and 121td<sup>-1</sup> respectively on average over the period January 2009- December 2013 (Table III.1). In all, the three lakes contribute about 136.2t.d<sup>-1</sup>  $CO_2$  to the atmosphere.

In shallow lakes, the gas degassing at the floor is apparent and can be measured at the lake (e.g: Lake Taal (Philippine), Hernandez et al, 2013, pers. Com. CVL8; Lake Laacher See (Germany), Maussen et al., 2013, pers. Com. CVL8). In contrast, in the deep gassy lakes, whether the surface degassing is connected or not to the degassing or accumulated gas at the bottom remains unclear, as explained above. Before the degassing was initiated at lakes Nyos and Monoun, the surface  $CO_2$  concentration
was assumed to be similar to the atmospheric concentration (Kusakabe et al., 2000, 2008). The absence of a gradient suggested there was minor and/or no surface diffuse  $CO_2$ -degassing. However, the result obtained in this study suggests the gassy lakes may release  $CO_2$  gas to the atmosphere. The magnitude of the output seem not to be controlled exclusively by the material transport across the water columns but also by a different mechanism as will be discussed in the following.

## III.1.4.3 Time Variation in diffuse CO<sub>2</sub> emission from lakes Nyos and Monoun.

Despite the material transport between layers was assumed to be almost inexistent due to the strong stratification (Kling et al., 1987, Kusakabe et al., 2000), the first CO<sub>2</sub>-flux measurement was conducted at those lakes Nyos and Monoun to serve as geochemical monitoring tool. It was hoped that little but however, discernable lake surface degassing that could be reasonably linked to the gas input dynamic could be measured. It was therefore thought that the mapping would reveal some high flux areas expectedly located at the vertical of the gas recharge sources at the lake floors. Figure 3.2 shows the spatial distribution of the flux for years 2012 and 2013 at Lake Nyos, Monoun and Barombi Mbo. It can be noted that, the high emission areas are not only located in the high-CO<sub>2</sub>-content central basin near the degassing pipes, but also, are randomly distributed in CO<sub>2</sub>-free shallow areas and near the shore line. Similarly, the high diffusion spots at Lake Monoun are also randomly distributed across the lake surface. At this stage, based on the variation and the relatively high surface diffuse  $CO_2$  output, it was concluded that, there may material transport across the water column and secondly, using the flux maps to locate the gas recharge points at the bottom was difficult. However, one question remained. Why the diffuse  $CO_2$  output evolved over time since 2009? Was it in response to the variation in the gas recharge rate?

Figure 3.3 represents the variation with time of the diffuse  $CO_2$  output from lakes Monoun and Nyos. The gas output from Lake Nyos had remarkably increased from 16.69t.d<sup>-1</sup> in 2009 (Nemesio et al., 2011) to 112.5t.d<sup>-1</sup> in 2012 finally to 224t.d<sup>-1</sup> in 2013 whereas at Lake Monoun the output instead decreased from 19.3 t.d<sup>-1</sup> in 2009 (Perez et al., 2011) to 2.9t.d<sup>-1</sup> in 2012 and then increased to 21.9t.d<sup>-1</sup> in 2013. It can be noted that the 2013 output value is similar to that of 2009. Given that hydrothermal-sublacustrine system beneath the lakes is not that active to entrain such significant and rapid changes, especially in the case of Lake Nyos, the cause of the variation should be looked for elsewhere.

At Lake Nyos, the 2009-flux was done when one degassing pipe of small inner diameter was operating. From our observation, the high  $CO_2$ -TDS-rich ejected at the surface of the lake did not alter much the surface water color. As explained above, to accelerate the gas extraction from the lake, two pipes of larger inner diameter were installed and went operational in March 2011. A drastic change to the surface water coloration and turbidity were then observed. The red coloration was attributed to the oxidation of Fe originating from anoxic bottom waters when it comes into contact with atmospheric oxygen. The increase in the water turbidity resulted from the suspended matter derived from the precipitation of the different Fe-bearing species.

It can be noted that the flux output had also concomitantly increased. Consequently, it was evident that the increase in the  $CO_2$ -flux output was influenced by the installation of the last two degassing pipes (Figure III.3). Thus, it was believed that the variation in the diffuse  $CO_2$  output is due to the amount of the high  $CO_2$ -TDS-rich water ejected at the lake surface. Tuttle et al., (1992) reported that frustule siderite at the bottom of Lake Nyos. It is therefore assumed that, the majority of the measured  $CO_2$  diffusing at the surface was produced by the oxidation of siderite to goethite and/or hematite following:



Figure III. 2. Spatial distribution of CO2 emitted from lakes Nyos, Barombi Mbo and Monoun. Judging from the Nyos distribution maps, high CO2 output locations change randomly with time. This means, it may not be possible to locate recharge sources at the bottom of the lakes as was one of the one of the aims of the flux survey.



Figure III. 3. Time variation in  $CO_2$ -flux output  $(t.d^{-1})$  at lakes Monoun and Nyos. Reference dates for the degassing related to the degassing operation are indicated. The addition of two pipes at Lake Nyos from March 2011was deemed to accelerate the gas removal and make the lake safe within reasonable timeframe.

• 
$$2FeCO_3 + \frac{1}{2}O_2 + H_2O \rightarrow 2FeOOH + 2CO_2$$
  
 $2FeCO_3 + \frac{1}{2}O_2 \rightarrow Fe_2O_3 + 2CO_2$ 

At Lake Monoun, the gas piping had almost stopped when the 2009 survey was carried. Consequently, the flux measured may more or less represent the "natural"  $CO_2$ -flux output from that lake. The 2013 output value confirms that view and it is thought that the 2012 measurement may have been affected by some unknown artifacts.

## III.1.4.4 The Soil gas geochemistry

Table III.3 gives a statistical summary of the diffuse soil gas data obtained at the Mt Manenguba caldera, the detailed data can be found in Appendix C Table C.1. Helium is given as  $\Delta$ He and was calculated as the difference between soil He and the He atmospheric value of 5240ppb (Gluekauf, 1946; Padron et al., 2013).

In order to decipher the process that drives the  $CO_2$  emission, we plotted the temperature against the flux (Figure III.4). The results indicate that the two parameters are not correlated suggesting that the soil gas emission at the Manenguba calderas is driven by diffusion rather than advection like in sustained volcanic activity areas (Allard et al., 1991; Hernandez et al., 2001a, 2001b) such as in the volcanic-hydrothermal systems in Greece, USA and Italy (Brombach et al., 2001; Gerlach et al., 2001; Werner and Brantley, 2003; Werner et al., 2000; Frondini et al., 2004). In those areas, the degassing is driven by the ascent of hot hydrothermal fluids from which, upon condensation, thermal energy is released and the non-condensable components such as  $CO_2$  ex-solves and diffuses at the surface resulting into a positive correlation between the flux and the temperature. The temperature against  $\Delta$ He plot also supports the above view (Figure III.4). The composition of the gas indicates that about 20% of the samples had He value similar or less than atmospheric value of 5240ppb suggesting their He content is of

atmospheric origin and/or the sampled points are probably located in the low diffusivity areas as will be discussed later on.

In aseismic or non-volcanically active areas, the soil  $CO_2$  is often a mixture of atmospheric and biogenic  $CO_2$  (Cerling et al., 1991). In volcanically active and/or quiescent areas, a third component of magmatic origin, also contributes to the soil  $CO_2$  emission. The Manenguba soil  $CO_2$  had a mean  $\delta^{13}C$  ( $CO_2$ ) of -8.6% vs. PDB (see Table III.3). That value is lighter than that of the typical magmatic-volcanic  $CO_2$  whose mean  $\delta^{13}C$  values range between  $\delta^{13}C$  ( $CO_2$ )=-5‰ vs. PDB (Shimoke et al., 2002) and 6.5‰ vs. PDB (Javoy et al., 1978).

It is however heavier than the mean biogenic ( $\delta^{13}$ C (CO<sub>2</sub>)=-27‰ vs. PDB (Shimoke et al., 2002) or -20.6‰ vs. PDB (Padron et al., 2013). To represent the biogenic end member, we have taken the average value between the two  $\delta^{13}$ C (CO<sub>2</sub>)=-23.8. In order to determine the origin of the CO<sub>2</sub> and the associated He, we have plotted in Figure III.5 the CO<sub>2</sub> concentration against the  $\delta^{13}$ C<sub>(CO2</sub>) together with the three end members represented by the Magmatic-volcanic, biogenic and atmospheric characterized by nowadays CO<sub>2</sub>=380ppm and  $\delta^{13}$ C (CO<sub>2</sub>)=-8‰ vs. PDB. The data cluster near the volcanic-magmatic corner indicating a clear and dominant deep seated contribution to the soil CO<sub>2</sub> at the Manenguba caldera with very minor biogenic and atmospheric addition.

In order to discriminate and quantify the relative contribution of each reservoir, the method by Sinclair (1974) was applied. Figure III.6 presents the normal probability plots for the whole population and its statistically distinct subsets designated PI, PII and PIII. They were determined by locating the two inflexion points on the curve representing the whole population. The 3 populations represent 9.3%, 49% and 41.7% respectively of the total population. They are characterized by mean diffuse  $CO_2$  emission of  $4.5g.m^2d^{-1}$ ,  $33.1m^2d^{-1}$  and  $129g.m^2d^{-1}$  respectively. The three populations have almost similar  $\delta^{13}C_{(CO2)}$  signatures (-8.6‰, -9‰ and-8.3‰, see Table III.3).



Figure III. 4. Relationship between temperature and CO<sub>2</sub>-flux and excess He for the Manenguba caldera soil gas. Mean average temperature is also shown.



Figure III. 5. Soil  $CO_2$  concentration and  $\delta^{13}C$   $CO_2$  of Manenguba soil  $CO_2$ -flux in relationship with  $CO_2$  signature of Volcanic, Atmospheric and Biogenic end-members. Arrows show the direction of mixing pattern with the dominant volcanic originated  $CO_2$ .

It can be noted that the PI which is often considered as "background" mainly deriving from biogenic source and the PIII considered as deriving from deep seated processes, have the same  $\delta^{13}$ C values. The values approach the upper limit of the biogenic  $\delta^{13}$ C range (-34.5% to -8.8%; Maberly et al., 1992) however locates out. The Population II which is supposed to be a mixture of the background and the deep seated originated CO<sub>2</sub> has the lightest  $\delta^{13}$ C signature. Consequently, it is thought that the bimodal distribution of the population is not due to their origin, but is instead determined by the diffusion rate through the media. In fact, the survey was carried few days after the end of the rainy season. The low flux CO<sub>2</sub> values representing population II seem to be dominantly located in the south-western and the north-eastern side of the surveyed area (Figure III.7). The soil in the south-western side shows a hardened surface assumedly due to an accumulation of salt in the shallow horizon. The vegetation is scare and seems to have been killed by some undefined processes. In the north-eastern side, the soil was still wet and it is well known that water-filled pores reduce the diffusion of the gas (Evans et al., 2001).

Deep seated derive argon which has distinct  ${}^{40}$ Ar/ ${}^{36}$ Ar (about 40000 for MORB) from that of the atmosphere could be used to trace the origin of deep derived gases. Padron et al., (2013) used Air and MORB (Mid Ocean Ridge Basalt) Argon-Nitrogen signatures as end-member to avail the origin of the argon in soil from Timnafaya volcano in Canary Islands. The N<sub>2</sub> was used because, according to Marty, 1995 and Graham, 2002, its concentration correlates with  ${}^{40}$ Ar in the MORB, this with the  ${}^{40}$ Ar/ ${}^{36}$ Ar. The Manenguba soil gas had argon isotopic mean ratio  ${}^{40}$ Ar/ ${}^{36}$ Ar of 297 much similar to the atmospheric ratio (298±0.31, Pujol et al., 2013) however remarkably lower than the ca 1650 value reported for the CVL upper mantle (Barfod *et al.*, 1999) suggesting no mantle contribution. The plot of the Manenguba caldera soil N<sub>2</sub>/Ar<sup>36</sup> vs  ${}^{40}$ Ar/ ${}^{36}$ Ar plot (Figure III.8) indicates a dominant atmospheric source for the two gases as the data cluster near the Air-end-member.



Figure III. 6. Normal probability plot of soil flux which discriminates three populations (I, II, III) with respectively 9.3%, 4% and 41.7% of the total population.



Figure III. 7. Spatial distribution of the soil  $CO_2$  emission. The swampy and hardened soil areas were characterized by low diffuse  $CO_2$  emission.

When the plot is enlarged, two other mixing patterns are revealed: One pattern characterized by  $N_2/^{36}Ar$  enrichment and a second follows the Air-MORB mixing line with however  $N_2/^{36}Ar$  and  $^{40}Ar/_{36}Ar$  lower than atmospheric (Figure III.8). The first mixing pattern may indicate addition of  $N_2$  from biogenic/organic, especially from manure, since the place is known to host cattle rearing activity. The second pattern shows a decrease in both ratios suggesting a low diffusion for the gas and low  $N_2$  in areas where the vegetation is scarce and the surface of the soil was hardened as explained above or, alternatively the conversion of  $N_2$  to nitrate or uptake in biosynthesis.

Based on  $\delta^{13}$ C signature and the He data, the total CO<sub>2</sub> was assumed to overwhelmingly derive from magma. Therefore, without subtracting any background contribution (which, we believed, might have been very minor) the total output from the caldera was estimated at 26.9 t.d<sup>-1</sup> for the about 38.5ha area that had been surveyed (Table III.1). Extrapolating to the whole caldera (8.2km<sup>2</sup>) would yield 573t.d<sup>-1</sup>. From Nyos valley, the total output was estimated at 2.13 t.d<sup>-1</sup> of CO<sub>2</sub> (Table III.1).

The deep seated origin of the diffuse soil  $CO_2$  at Manenguba caldera suggests that emplaced magma is still degassing several thousands of years after the third and last volcanic activity occurred from 0.56 to 0 Ma which erected the Eboga volcano and the caldera (see Figure III.1) (Kagou et al., 2001). Consequently, the Mt Manenguba caldera could represent one of the suitable sites where a gas-flux-based system for volcanic activity monitoring could be carried on the CVL.

Finally, although diffuse gas surveys have shown to be good geological tools by revealing the structural setting of the surveyed areas (Chiodini et al., 2005; Gerlach et al., 2001; Frondini et al., 2004; Mazot et al., 2011). The caldera is underlain by several faults (Kagou et al., 2001; see Figure III.1). However, our survey did not reveal any of the faults.



Figure III. 8. <sup>40</sup>Ar/<sup>36</sup>Ar vs  $N_2$ /<sup>36</sup>Ar for Mt Manenguba soil data together with two end-members Air and MORB.

#### III.1.4.5 The total CO<sub>2</sub> output

The 9 surveyed lakes cover an area of 756 ha and emit on average about  $28 \pm 0.37$  t.d<sup>-1</sup> CO<sub>2</sub> to the atmosphere. The surveyed area represents about 24% of the 2035ha occupied by volcanic lakes in Cameroon. If we extrapolate, all the CVL lakes would release about 75.00 ± 0.5 t.d<sup>-1</sup> CO<sub>2</sub> to the atmosphere. The CO<sub>2</sub> emission from the soil would amount to about 578.1 t.d<sup>-1</sup>. Totally, an estimate of 31.10 ± 0.43 Kt.km<sup>2</sup>.yr<sup>-1</sup> of CO<sub>2</sub> is released from the surveyed diffuse diffusion structures (DDSs). Compared to the output from volcanic lakes worldwide, the CO<sub>2</sub> emission from Cameroon volcanic lakes is less than that observed in Indonesia, New-Zealand, Mexico or Japan, whereas, it is more than two order of magnitude greater than the output from Philippines and Costa Rica located in volcanically active area (see Table III.4; Figure III.9).

However, it should be mentioned that, the  $CO_2$ -flux from Indonesia (Kelud), New Zealand (Ruapehu) and Mexico (El Chichon) was carried only in one lake. Thus, the total output from those countries may not represent the real estimate of the emission from crater lakes. It is also the case of the total output from Cameroonian volcanic lakes since, part of the diffuse CO<sub>2</sub>-output from lakes Nyos and Monoun may be due to from the on-going gas removal operation which, it should be mentioned, has released about 2.52±0.46x10<sup>8</sup> moles.Km<sup>-2</sup>.yr<sup>-1</sup> CO<sub>2</sub> to the atmosphere from January 2001 to March 2013 more than the double of the per land area amount (10<sup>8</sup> mol.Km<sup>-2</sup>.yr<sup>-1</sup>) released from the Yellowstone volcanic system in the USA (Werner and Brantley, 2003). Given that the  $CO_2$  emission from those lakes is evidently influenced by the on-going gas removal operation, the total emission from Cameroonian volcanic lakes would need to be refined. Still, Cameroon hosts about 5 % of the number of volcanic lakes in the world and the emission from those lakes would represent 0.023 % of the global  $CO_2$  emission (117 Mt.yr<sup>-1</sup>, Pérez et al., 2011) Finally, the results show that, in order to obtain an accurate estimate of the global CO<sub>2</sub>-flux from crater an extensive surveys would be needed because not all volcanic lakes release  $CO_2$  to the atmosphere, but some may instead act as  $CO_2$  sinks, as shown above. More importantly, gas degassing from shallow active lakes should not hide the possibility that, some deep lakes that contain dissolved gas may not emit  $CO_2$  to the atmosphere.



Figure III. 9. Visual representation of the diffuse  $CO_2$  emission from volcanic lakes worldwide. The output from Cameroon CVL lakes is more than double the output from certain volcanically active areas such as in Costa Rica or Philippines (data from Perez et al., 2010).

	Parameter	Range	Mean	SD	
	Flux	-13.9 to 380.8	70.1	70.7	
	$\mathrm{CO}_2$ (ppm)	14071 - 910268	163202	178316	
Р	$\Delta He (ppb)$	-425 to 1713	332	449	
	$\delta^{13}$ C (‰ vs PDB)	-12.2 to -6.6	-8.6	1.2	
	Т (°С)	15.5 - 27.5	19.5	1.6	
	Flux	-13.9 to 10.7	4.5	7.1	
	$\mathrm{CO}_2$ (ppm)	15000-192000	56000	38000	
PI	$\Delta He (ppb)$	-196 to 894	349	770.7	
	$\delta^{13}$ C (‰ vs PDB)	-10.5 to -8.3	-9	0.9	
	Т (°С)	18.3 - 21.3	19.2	1.1	
	Flux	11.5 - 54.2	33.1	13.2	
	$\mathrm{CO}_2$ (ppm)	14070-579630	145090	130730	
ΡП	$\Delta He (ppb)$	-248 to 1614	683	1317	
	$\delta^{13}$ C (‰ vs PDB)	-11.7 to -6.6	-8.3	1.1	
	Т (°С)	15.5 - 22.5	19.1	1.6	
	Flux	56 - 380.1	129.4	76	
	$\mathrm{CO}_2$ (ppm)	21150-910268	199200	218360	
РШ	$\Delta He (ppb)$	-422 to 1713	645.5	1507	
	$\delta^{13}$ C (‰ vs PDB)	-12.2 to -6.6	-8.9	1.3	
	T (°C)	17.7 - 27.5	19.7	1.6	

Table III. 3. Statistical summary of soil gas data and temperature measured at Mt Manenguba Caldera

Country	Lakes	SD	Soil	$\mathbf{SD}$	Lakes*	$\mathbf{SD}$
Cameroon	27.37	$\pm 0.5$	4.57	±1.3	3.69	±0.37
Costa Rica	10.78	$\pm 0.21$				
Ecuador	2.92	$\pm 0.14$				
Elsalvador	0.48	nd				
France	0.01	nd				
Germany	1.52	$\pm 0.07$				
Guatemala	0.39	$\pm 0.03$				
Indonesia	232.27	nd				
Japan	44.32	$\pm 1.56$				
Mexico	139.54	$\pm 6.81$				
New Zealand	159.90	nd				
Nicaragua	4.38	$\pm 0.07$				
Philippines	10.94	$\pm 0.24$	1323.33	±0.03		

Table III. 4. Per land diffuse  $CO_2$  emission from volcanic lakes and calderas worldwide. (Column Lakes\* refer to the total amount from the surveyed area. (data compiled from this study and Perez et al., 2010).

## **III.1.5** Conclusion

This study indicates that the diffuse  $CO_2$  emission from Cameroonian volcanic lakes may not be negligible and compares with the emission from lakes located in volcanically active areas. It has also shown that, besides emitting  $CO_2$  to the atmosphere, other volcanic lakes may act as  $CO_2$  sinks. The study also revealed that, some lakes contain little but however, discernable amount of magmatic  $CO_2$ suggesting volcanic activity and/or magma degassing still persist a depth and influence the sub-lacustrine systems confirming the view that the CVL is a sustained  $CO_2$  degassing environment. This finding comes to support the view that, an increase to volcanic activities and/or tectonic sublacustrine vents could entrain more  $CO_2$  to seep into the lakes increasing thereby their likelihood to release the gas to the atmosphere.

The soil  $CO_2$ -flux survey conducted at the Mount Manenguba caldera indicates that the soil gas originates from magma suggesting that emplaced magma continues to degas several hundred thousand years after the last volcanic crisis which took place between 0.52-0 Ma. For the sake of hazard prevention, together with the regular physicochemical monitoring of the lakes, the Manenguba caldera could represent one of the sites where a gas-flux-based system could be set up for volcanic activity monitoring/surveillance along the CVL. This is of prime importance given that, the occurrence of the lakes Nyos and Monoun type catastrophes cannot be completely ruled out in other areas of the CVL as suggested by the geochemical and social studies.

# III. 2. Assessment of the effect of Methane on the stability of lakes Nyos and Monoun water columns

(This section was published in the Geochemical Journal (Issa et al., 2013. Geochem. J. 47, 349-362) under the title "Contribution of Methane to the Total Gas Pressure in Deep waters in lakes Nyos and Monoun". The Tables and Figures numbering were modified to fit this text)

# **III.2.1 Introduction**

Several causes have been suggested to have triggered the mid-1980s explosive release of gas (Freeth and Kay., 1987; Sigurdsson, *et al.*, 1987; Kling *et al.*, 1987a; Kusakabe *et al.*, 1989; Lockwood and Rubin, 1989), mainly magmatic  $CO_2$  (Sigurdsson 1987; Kusakabe *et al.*, 1989; Allard *et al.*, 1989) from lakes Nyos and Monoun. Among those, the meteorological forces and rock-falls (Kling *et al.*, 1987a; Sigurdsson *et al.*, 1987), gradual gas accumulation (Kusakabe *et al.*, 2008) and volcanic activities (Tazieff *et al.*, 1987; Chevrier, 1990) have been proposed as potential triggering mechanisms. Lake Nyos occupies an area of 1.58 Km<sup>2</sup> and is 210 m deep as against 0.31 Km<sup>2</sup> and a maximum depth of 100 m for Lake Monoun. The latter is made up of three basins; the largest basin contains high concentrations of gas.

Nevertheless, irrespective of the trigger, it is apparent that the total gas pressure played a key role in the magnitude of the eruption. Beside the proposed potential causes above,  $CH_4$  was also believed to initiate a *limnic eruption* (Evans *et al.*, 1994). The possibility that  $CH_4$  destabilizes the lakes has never been carefully examined though such a risk cannot be discarded completely. For example, there were concerns that the volcanic eruption of Nyiragongo might trigger a  $CH_4$ - $CO_2$  massive gas exhalation from Lake Kivu (which contains very high quantities of dissolved  $CO_2$  and dominantly biogenic  $CH_4$ ) with unpredictable consequences (Tietze *et. al.*, 1980; Wauthier, *et al.*, 2002; Schmid *et al.*, 2005; Pasche *et al.*, 2011). Together with the potential forcing mechanism, Pasche, *et al.*, (2011) proposed that an endogenic catastrophic scenario stemming from  $CH_4$  accumulation is probable by ~2100 because  $CH_4$  concentrations in the lake have increased by up to 15% in the last 30 years. Given the precedent arguments, this work attempts to document the potential threat that continuous increase in  $CH_4$  might pose, by assessing its evolution and evaluating its contribution to the total gas pressure.

Much has been done during the last two and half decades to understand the Cameroonian gassy lakes in terms of hazards prevention (Freeth and Kay., 1987; Kling *et al.*, 1987b; Sigurdsson *et al.*, 1987; Tazieff *et al.*, 1987; Lockwood and Rubin, 1989; Tietze, 1992; Evans *et al.*, 1994; Kusakabe *et al.*, 2000; Halbwachs *et al.*, 2001). To assess the CH<sub>4</sub> hazardous potential, three field surveys were conducted at the lakes in January and December 2007 and January 2011. Specific goals were (1) to measure concentrations of all detectable gas species, and (2) to evaluate their contribution to the total dissolved gas pressure and saturation level using a new technique derived from the modification of the method used by Yoshida *et al.*, (2010). A portable gas-analyser (refer to as GA, hereafter) was used for measuring the dissolved gas composition.

# III.2.2 Materials and methods

Apparatus used for the field sampling constituted of an IR-based portable biogas analyser, a hose of suitable length, a separator and other devices as in Yoshida *et al.*, (2010). The apparatus serves to measure all parameters necessary to determine the gas concentrations and pressures. Using the Henry Law's approach, we converted the dissolved gas concentrations to their partial pressures. Polynomial fitting parameters for  $\log K_{\rm H}(t)$  have been taken from Taran, (2005).

## III.2.2.1 General description of the material and sampling techniques

Since the mid-1980s disasters at lakes Nyos and Monoun, several techniques have been used to determine the concentrations and subsequently estimate the gas content in the lake water. Those techniques were partially laboratory dependent; they include gas collection in pre-evacuated steel cylinders (Nojiri *et al.*, 1993; Evans *et al*, 1994) and *in-situ* fixation of  $CO_2$  species (Kusakabe *et al.*, 2000). Another technique based on self-gas lifting principles, the "Flute De Pan" (FDP) was used to estimate gas/water ratio (Halbwachs et al., 1993, Halbwachs and Sabroux, 2001). Recently, the Flute-De-Pan method was coupled with another apparatus used to study non-condensable volatiles in hydrothermal systems to precisely measure  $CO_2$  in the lakes (Yoshida *et al.*, 2010). In brief, a hose of a small inner diameter (e.g. 12 mm) is deployed from the surface into the gas-rich bottom waters. Then the water contained in the hose is sucked to the surface to initiate the flow of the water-gas mixture. Once the hose is primed, the mixture flows spontaneously driven by the gas phase exsolution (gas self-lifting) permitting the gas and water phases to be sampled using adequate apparatus. The process is selfsustaining and sampling from deeper to shallower depths can be executed until the releasing gas volume is not enough to drive the process. In this study, an *on-site* analytical apparatus was integrated in the system to estimate the volume proportion of the different gas species. Subsequently, the concentrations of the gases have been converted into their respective partial pressures to evaluate their contribution to the total gas pressure (TGP) and saturation level.

Once the biphasic fluid is brought to the surface, the mixture is directed into a separator. Determination of  $CO_2$  concentrations was done following Yoshida *et al.*, (2010) (Figure III.10; Photo III.3). For the  $CH_4$  analysis, a module consisting of an inverted 4 L bottle (separator), a bucket and a portable gas analyser (Geotechnical Instrument model GA2000) was used (Figure III.10, Photo III.4). As the water-gas



Photo III. 3 System for gas volume and determination of parameters necessary for gas volume calculation (lake water temperature measured using hand thermometer, gas pressure is measured by inbuilt manometer, temperature of gas is obtained by gas meter inbuilt thermometer).



Photo III. 4 The GA is connected to the inverted separator to analyze the gas. Sampling and analysis of  $CH_4$  and  $CO_2$ 

mixture is directed into the separator, its mouth is submerged and maintained under water, inside the bucket so as to allow gas to build up while avoiding atmospheric contamination. A glass tube fitted with a silicone rubber tube was inserted in the separator to let the gas escape and flow towards the Gas Analyser (Figure III.10, Photo 3.4).

## III.2.2.2 The Biogas analyser

The Gas Analyser uses a dynamic flow system to perform analysis. CH<sub>4</sub> is analysed by dual beam infrared absorption and  $CO_2$  by infrared absorption at specific wavelength. Although the GA was calibrated in the factory, CH<sub>4</sub> and CO<sub>2</sub> channels can be also user calibrated. The calibration can be done using gas mixtures with predetermined concentrations. For  $CH_4$  measurements, the GA is calibrated using a certified methane mixture and it gives correct readings if there are no other hydrocarbons (e.g. ethane, propane...). If there are other hydrocarbons present, the  $CH_4$  reading will be higher (never lower) than the actual methane concentration being monitored. For carbon dioxide, since it is analysed at specific wavelength, readings is not affected by any other gases present in the sample. Factory calibrated limits of  $CO_2$  and  $CH_4$  readings are below 65 % with an accuracy of  $\pm 0.5$ . The  $CH_4$ sensor has been auto-zeroed so that, a purge in clean air will display "zero" value. For  $CO_2$ , after similar operation, the GA should display its atmospheric value of 0.039 %. This configuration permits the user to check for eventual drift in the course of sampling. Relative gas concentrations are given in per cent volume (hereafter referred to as  $%CH_4$  or  $%CO_2$ ). Response time is basically ~ 20 seconds. During the measurements, the GA was regularly purged in clean air to ensure sensors have not been contaminated with previous sample and that the apparatus remained correctly calibrated. For thorough description of the use of the Gas Analyser, refer to user manual at http://www.keison.co.uk/products/geotechnical/GA2000Manual.,pdf.

## III.2.2.3 Sampling and analysis of CH<sub>4</sub> and CO<sub>2</sub>

When a two phase fluid flows in a pipe, each phase is subjected to specific friction. In the case of the Flute-De-Pan technique, as the fluid-gas mixture ascends, pressure reduces hence allowing the gas phase to come out of solution and escapes towards the surface more rapidly than the water. The consequence of such differential flow is that the measured liquid phase and gas phase may likely not represent *in-situ* values. To minimize the effects of these inconveniences, sufficient time (~10 minutes) was allocated to stabilize gas-water-mixture regime to achieve a steady state that reflects *in-situ* conditions prior to record parameters or to collect samples.

We first measured the necessary parameters (gas flow rate, gas and water volumes, water temperatures, gas temperature, and line pressure) to determine the total volume of gas  $(V_t)$  exsolved. Once  $V_t$  has been determined, CO<sub>2</sub> and CH<sub>4</sub> concentrations in water can be obtained as describe in the appendix by using the additional information concerning their volume proportion provided by the Gas Analyser.

The Flute-De-Pan-Gas-Analyser measurements were conducted in January and December 2007. More recently, in January 2011, gas was sampled in Pyrex glass tubes with stopcocks at lakes Nyos and Monoun by connecting the tube directly to the Flute-De-Pan line following Nagao *et al.*, (2010); this sampling technique permits to collect contamination-free gas samples. Twelve samples were collected at Lake Nyos at depths below 170 m where the gas self-lifting capability declines significantly making it impossible to sample shallower depths. Lake Monoun was not sampled in January 2011because gas concentration was not enough to drive the FDP. Gas samples collected in Pyrex glass were analysed at Hokkaido University using a continuous-flow gas chromatograph (Agilent 6890) for determination of CH<sub>4</sub> concentrations following Hirota *et al.*, (2010). Analytical precision was better than 5%.



Figure III. 10. Diagram presenting the technique for on-site  $CH_4$  analysis using the GA; the inset window shows the  $CO_2$  measuring system used in Yoshida et al., (2010). Arrows (bold) indicate flow path of water/gas mixture and dashed arrows indicate gas flow paths.  $CO_2$  and  $CH_4$  measurements were performed alternatively because the GA could not be directly connected to the volumetric gas meter outlet at the moment  $CO_2$  was measured.

#### III.2.2.4 Computation of CH<sub>4</sub> and CO<sub>2</sub> concentrations

Calculation of the dissolved gas concentrations was derived from Yoshida *et al.*, (2010). But that work's target was the determination of concentrations of  $CO_2$  only assuming it is the only gas present in the lakes. Although  $CO_2$  constitutes the overwhelmingly dominant specie, the lakes also contain other gases (Evans *et al.*, 1994; Kling *et al.*, 2005) contributing to the total gas pressure and whose effect on the stability of the water column may not be negligible.

Procedure to obtain the total volume  $(V_t)$  of CO<sub>2</sub> dissolved in a given amount of water has been thoroughly described in Yoshida *et al.*, (2010). The total dissolved gas volume is defined as:  $V_t = V + V_r$  where V represents the corrected (for water vapour contribution to the internal pressure of the measuring line) volume  $V_1$  given by the gas flow meter and  $V_r$  is the residual volume of gas that remains dissolved in the liquid phase at barometric pressure. Compare to Yoshida *et al.*, (2010), the modifications introduced here concern (a) the formulation of a single equation to calculate  $V_t$  in a single-step and, (b) the possibility to use the volume fraction of each gas to compute its individual concentration (see Appendix D-1 and D-2 computational details)

It should be noted that the method was directly implemented without checking for reproducibility. However, the results will be subsequently compared to the total gas pressure profiles (TGP) obtained using a gas pressure probe to check for the applicability of the method. The Total Gas Pressures have been measured using a silicone rubber gas probe. Measurement consists of deploying the probe at target depths and, let gas diffuse into it through the semi-permeable membrane. The gas then flows through a capillary tube to a pressure gauge where the pressure is measured. Pressures are recorded when they are stably displayed after allocating approximately one hour for the probe to equilibrate with *in-situ* conditions (see Evans *et al.*, (1993) for details.

## III.2.3 Results and discussion

Yoshida *et al.*, (2010) has shown that  $CO_2$  concentrations they obtained were in a good agreement with the 2006 data obtained by the syringe method (Kusakabe *et al.*, 2000). Therefore, we believed that Flute-De-Pan/Gas meter/Gas Analyser technique will have the advantage to qualitatively enhance the monitoring of the gassy lakes.

# III.2.3.1 GA gas readings

The Gas Analyser fraction readings in per cent volume of  $CO_2$  and  $CH_4$  are shown in Table III.5. Because  $CO_2$  concentrations in the lakes fall out of Gas Analyser calibrated range (OR=Out of Range), the volume fractions of  $CO_2$  (referred to as %\*CO<sub>2</sub>) in the last columns were obtained as the difference between 100% and %CH<sub>4</sub> under the assumption that lakes contain only methane and carbon dioxide. At Lake Monoun, since CH<sub>4</sub> concentrations at 91.5 m and 93 m did not vary, the same volume fraction value (in italic) was assigned to 92 m depth (see Table III.5).

Relative CH<sub>4</sub> volume fractions at Lake Monoun range from 2.6% to 1.5% (Table III.5), for an average value of ~2% for depth below 91 m. At Lake Nyos the CH<sub>4</sub> fractions range from 0.2 to 1% in depth between 120 and 207 m, for an average of 0.46 %. These proportions are similar to those reported previously (Evans *et al.*, 1994; Kling *et al.*, 2005). It is noteworthy that the volume proportion of CH<sub>4</sub> at Lake Nyos is lower than that of Lake Monoun, which appears to be more productive in terms of CH<sub>4</sub>, probably due to its phytogeographical and hydrological settings. In fact, the lake is a through flow lake which occurs in the Panke River channel; the river which drains a highly anthropogenized catchment area (27 Km<sup>2</sup>) collects quantity of organic and human detritus which may serve as the primary material for the methane production. Reversely, Lake Nyos has a smaller catchment (area 8 Km<sup>2</sup>) and is topographically isolated and less anthropogenized. The biogenic production of CH<sub>4</sub> comprises microbial reduction of CO<sub>2</sub> and thermogenic decay of

organic matter. Although not thoroughly investigated yet, the origin of  $CH_4$  in lakes Nyos and Monoun has been thought to be biogenic (Evans *et al.*, 1994, Kling *et al.*, 2005).

## III.2.3.2 CH<sub>4</sub> increase rates and profiles

Calculated dissolved  $CH_4$  and  $CO_2$  concentrations are shown in Tables III.6 and III.7 for lakes Nyos and Monoun respectively. They originate from four different methods: Laboratory analysis and GA (superscript by (a)), interpolation (superscript (b)) and literature indicated by superscript (c) (Kling *et al.*, 2005). Interpolation was done by carefully following the time evolutionary trend displayed by the previous data on one hand, and by observing if the derived values depict the general profile of gas in the lakes as shown by 2011-CH<sub>4</sub> profile in Figure III.11 on the other hand.

The shape of the 2011-CH<sub>4</sub> profile (Figure III.11) looks much like CO<sub>2</sub> profiles published in literature (e.g. Kling *et al.*, 2005, Kusakabe *et al.*, 2008); CH<sub>4</sub> concentrations decrease from 1109  $\mu$ mol/L at 170 m to 1026  $\mu$ moles/L at 175 m depth, and then, increase to 1154  $\mu$ mol/L at about 185 m depth where the lower *chemocline* is located (Kusakabe *et al.*, 2008). Concentrations then decrease again to a minimum of 814  $\mu$ moles/L at 200 m before sharply increasing down to ~209 m depth where its concentration reaches 2555  $\mu$ moles/L.

Finally, another decrease from 209 m depth to 2010  $\mu$ moles/L is observed. The shape of the profile seems to be quite complex. However, it might be divided into three sections corresponding to Layers II, III and IV described by Kusakabe *et al.*, (2008).

# III.2.3.3 The CH₄ increase rates

To illustrate the time evolution before and during degassing,  $CH_4$  concentrations in Tables III.6 and 3.7 (Nyos and Monoun) and  $CH_4$  content below 170 m depth (Lake Nyos) and 91 m depth (Lake Monoun) (Table III.8) are plotted as a function of time from March 1992 to January 2011 (Lake Nyos) and from 1992 to December 2007 for

Table III. 5. GA readings of  $CO_2$  and  $CH_4$ . Due to GA limited range \*% $CO_2$  (in the last columns) were obtained as 1- % $CH_4$  =% $CO_2$ . Values in italic were interpolated assuming concentration between 93 m and 91.5 m does not significantly vary. OR=out of range.

		Nyos					Monoun		
	Depth	Vol. fract	Vol. fract	Vol. fract		Depth	Vol. fract	Vol. fract	Vol. fract
Date	(m)	%CH4	%CO2	*%CO2	Date	(m)	%CH4	%CO <sub>2</sub>	*%CO2
27- Dec-07	-120	0.003	OR	0.997	21-Dec-	-91.5	0.015	OR	0.985
Dec 07	-160	0.004	OR	0.996	07	-92.0	0.015	OR	0.985
	-170	0.005	OR	0.995		-93.0	0.015	OR	0.985
	-180	0.006	OR	0.994		-94.0	0.015	OR	0.985
	-190	0.005	OR	0.995		-95.0	0.02	OR	0.98
	-192	0.005	OR	0.995		-96.0	0.021	OR	0.979
	-194	0.005	OR	0.995		-97.0	0.022	OR	0.978
	-198	0.004	OR	0.996		-98.0	0.024	OR	0.976
	-200	0.003	OR	0.997		-98.5	0.026	OR	0.974
	-204	0.003	OR	0.997		-99.0	0.026	OR	0.974
	-208	0.002	OR	0.998		-	-	-	-
	-209	0.01	OR	0.990		-	-	-	-



Figure III. 11. CH<sub>4</sub> concentration profile in 2011. The shape is similar to that of CO<sub>2</sub> profile (Yoshida et al., 2010; Kusakabe et al., 2008).

Lake Monoun (Figure III.12 and Figure III.13). Time variation in CH<sub>4</sub> concentrations at chosen depths is shown in Figure III.12(a, b); Figure III.12 (c) shows average change in concentrations below 171 m depth and Figure III.12 (d) illustrates the changes in total CH<sub>4</sub> content below 171 m depth in comparison to the variation in CO<sub>2</sub> content at Lake Nyos. Figure III.12(a, b) illustrate time variation in CH<sub>4</sub> concentrations below 91 m depth and Figure III.13(d) shows the variation with time in CH<sub>4</sub> content below 91 m depth compared to the time changes in CO<sub>2</sub> content at Lake Monoun. CO<sub>2</sub> content data have been taken from Kusakabe *et al.*, (2008). Figure III.12 (d) and Figure III.13 (d) demonstrate the constant decrease in CO<sub>2</sub> since the degassing started in 2001 (Lake Nyos) and 2003 (Lake Monoun). The extraction rate by one pipe at Lake Nyos is very slow while at Lake Monoun, three pipes have drastically lowered the gas content. Meantime the estimated total amount of CH<sub>4</sub> continued to increase.

Similar to CO<sub>2</sub>, highest concentrations of CH<sub>4</sub>, 7333  $\mu$ mol/L (Lake Nyos, Jan 2004) and 3956  $\mu$ mol/L (Lake Monoun, Dec 2007), were also observed near the bottom of the lakes below the lower *chemocline*. The most important finding is that CH<sub>4</sub> concentration in both lakes has been increasing since 1992 and continued even during gas removal. Figure III.12d and Figure III.13d show the changes with time in the total CH<sub>4</sub> content estimated using bathymetric data published by Kling *et al.*, (2005) and average concentrations.

Methane concentrations have increased by 7.7  $\mu$ moles/kg/yr and 16.9  $\mu$ moles/kg/yr at 183 m and 206 m depth respectively at Lake Nyos. The estimated total amount of CH<sub>4</sub> in the lake increased by 0.17 x10<sup>6</sup> moles/yr from 19.2x10<sup>6</sup> moles to 51.2x10<sup>6</sup> moles; over a period of ~19 years (1992-2001), this represents a 62.5% increase relatively to the methane content observed in 1992 as against 39.20% (from 3.061±0.057 giga-moles to 4.261±0.065 giga-moles (Kusakabe *et al.*, 2008) for CO<sub>2</sub> during the pre-degassing period in layer III (near the bottom of the lake).



Figure III. 12. Lake Nyos. Increase of CH4 concentrations in lake water since 1992 (a and b). CH4 concentration at depths below 171 m have been averaged and plotted vs time and presented in (c); the average concentration for each year was multiplied by the volume of the lake below 171 m to yield gas content for that year; the gas content in each year has been plotted vs time to show the variation in CH4 below 171 m depth (d). For comparison, change with time in CH4, CO2 content variation is also shown. CO2 content data have been taken from Kusakabe et al., (2008). The solid lines are the regression lines that best describe  $CH_4$  increase with time. Bracketed values are considered outliers and have not been taken into account in the regression.

At lake Monoun, CH<sub>4</sub> concentrations increased by 42.9  $\mu$ moles/kg/yr and 48.4  $\mu$ moles/kg/yr at 69 m and 95 m depth respectively. The total CH<sub>4</sub> content of the lake increased by 0.015x10<sup>6</sup> moles/yr from 2.7x10<sup>6</sup> moles to 3.9x10<sup>6</sup> moles which, represents an increase rate of ~0.9x10<sup>6</sup> moles/yr below 91 m depth over a period of ~14 years (1992-2007) that to say, an increase of ~30% relatively to the CH<sub>4</sub> content of the lake in 1992, compared to 29.14% (from 366±11 mega-moles to 404±13 mega-moles (Kusakabe *et al.*, 2008) for CO<sub>2</sub>, during the pre-degassing period in layer III. The highest increase in CH<sub>4</sub> is observed close to the bottom at both lakes. CH<sub>4</sub> concentrations increased faster in Lake Monoun than in Lake Nyos. This observation is in agreement with the fact that Lake Monoun might experience significant importation of organic matter which constitutes the primary material for CH<sub>4</sub> production as pointed out above.

In relative values,  $CH_4$  concentration increases rapidly, more rapid that  $CO_2$  as has been shown above. The present  $CH_4$  build up is a subject of concern since it is less soluble that  $CO_2$  and, might tend to strip the latter out (Evans *et al.*, 1994): when gas saturation is attained and/or if any external disturbance that goes deep enough to uplift water parcel upward where it can attain saturation,  $CH_4$  is likely to be the one to come out of solution first. While escaping, it may entrain  $CO_2$  resulting in massive gas eruption.

Therefore, it is important to quantify and qualify the  $CH_4$  increase and evaluate the consequences these changes might entrain in the future and propose solution. Increase in  $CH_4$  during the continuous gas extraction (since 2001 at Nyos and 2003 at Monoun) is quite puzzling; the observed syn-degassing augment in methane concentration could be tentatively explained by the fact that  $CH_4$  removal rate is balanced and further exceeded by enhance bio-methanogenesis (Kling *et al.*, 2005) and/or, additional supply from the hydrothermal-sublacustrine system through water-rock interaction (Etiope and Guslam, 2002; Chiodini *et al.*, 2004, 2005; Etiope, 2005). Whatever its source, the  $CH_4$  concentration in the lakes must be closely monitored.

	Jan-11	Dec-07		Jan-06	Jan-04	Jan-03	Jan-01	Oct-01	Nov-00	Nov-99	Apr-98	Mar-92
Depth (m)	CH4	CH4	CO2	$CH_4$	CH4	CH4	CH4	$CH_4$	CH4	CH₄	CH4	CH₄
-76		-		-	-	-	-	-	-	-	$348^{b}$	$325^{\rm b}$
-99		-		-	-	-	-	$416^{\mathrm{b}}$	-	-	$426^{\rm b}$	$340^{\rm b}$
-137		-		$795^{\rm b}$	-	-	$799^{\mathrm{b}}$	-	-	-	$638^{b}$	$430^{\rm b}$
-171	1093	-		$1118^{b}$	$1134{}^{\mathrm{c}}$	$1051^{ m c}$	$928^{ m c}$	-	-	-	$847^{ m c}$	$564^{ m c}$
-183	1115	-		$1567 {}^{\mathrm{b}}$	1600 c	$1542^{ m c}$	$1514{}^{\mathrm{c}}$	$1526^{ m c}$	$1266^{b}$	$1442^{ m c}$	$1230^{\circ}$	$704^{ m c}$
-191	1044	$726^{\mathrm{a}}$		$2689^{b}$	$2257^{ m c}$	$2459^{\circ}$	-	-	-	$2024^{ m c}$	1941 <sup>c</sup>	$864^{ m c}$
-198	853	$794^{\mathrm{a}}$		$2223^{\rm b}$	$2252^{ m c}$	$2653^{\rm b}$	2578 °	$2062^{\mathrm{c}}$	$2012^{\rm b}$	1976 °	1829 °	$1064^{\rm c}$
-206	1506	-		$3184^{\text{ b}}$	$2418^{\circ}$	$2516^{ m c}$	$1748^{\circ}$	$2344{ m c}$	-	$2084^{ m c}$	$2520^{ m c}$	$1591^{ m c}$
208	2555	$3694^{\mathrm{a}}$		$3775^{\mathrm{b}}$	-	-	$2504^{\mathrm{b}}$	-	-	-	-	-
210	2362				7330 °							
Average	1504	217997	1014	2193	2832	2044	1679	1587	1639	1882	1222	735

Table III. 6.  $CH_4$  and  $CO_2$  concentrations ( $\mu$ mol/kg) at certain depths (Lake Nyos). Concentrations of  $CO_2$  obtained as described in the text.



Figure III. 13. Lake Monoun. Increase of  $CH_4$  concentrations (a and b).  $CH_4$  concentration at depths below 91 m have been averaged and plotted vs time and presented in (c); the average concentration for each year was multiplied by the volume of the lake below 91 m to yield gas content for that year; the gas content in each year has been plotted vs time to show the variation in  $CH_4$  below 91 m depth (d). For comparison with time change in  $CH_4$ , variation in  $CO_2$  content is also shown.  $CO_2$  content data have been taken from Kusakabe et al., (2008). The solid lines are the regression lines that best describe  $CH_4$  increase with time.

#### III.2.3.4 Total gas pressure (TGP)

Data obtained in January and December-2007 are shown in Table III.10 and their profiles displayed in Figure III.14. It is the first time that Total Gas Pressure profiles for the lakes are published. The shapes of the profiles are similar to those of  $CO_2$  in literature (Halbwachs *et al.*, 2004; Kusakabe *et al.*, 2008; Kling, *et al.*, 2005) justifying the predominance of that gas in the lakes. The gas profiles for Lake Monoun obtained in January and

December 2007 indicate that the total gas pressure has been remarkably lowered.

Over the period referenced above (about one year), gas pressure has decreased by ~40% at 80 m depth and subordinately declined by ~31% at 72 m. Nevertheless, at deepest waters, the gas pressure was decreased by only 9%. The relatively minor decrease at the bottom most waters can be attributed to the layering of the water column (Kusakabe *et al.*, 2008) on one hand and, is inherent to the piping process on another. In fact, pipes suck water laterally instead of vertically; it follows that when the layer at the intake located at depth d is exhausted, it is replaced at the intake by the one above it located at  $d \cdot x$  m. The process progressive entrains the subsidence of the whole water column above the piping point. This explains why gas removal is more remarkable to layers above the intake manifold than to that lying below it.

A comparative view of Total Gas Profiles and gas partial pressures profiles plotted for similar depths are shown in Figure III.15 and Figure III.16 for lakes Nyos and Monoun respectively. For reference, the saturation lines (hydrostatic pressures) for each lake have also been included. Given that total gas pressures were not measured at Lake Nyos in Dec 2007, gas partial pressures were instead plotted together with the total gas pressure measured in January 2007 of the same year for comparison.



Figure III. 14. Total gas pressure profiles at lakes Nyos (a) in January 2007and Monoun in January and December 2007 (b). Dashed line refers to saturation level.

Table I	111.	7.	$CH_4$	and	CO2	conce	ntration	5 (µ1	mol/kg	) at	certain	depths	(Lake	Monoun).	CO 2	obtained	as
describ	ed	in t	he te	ext. "	a″= d	ata fro	от GA, '	b″=i	nterpo	lated	d and "C	"= Kling	et al.,	(2005).			

-	Dec-07		Jan-06	Jan-04	Jan-03	Jan-01	Nov-99	Apr-98	Mar-92
Depth (m)	$CH_4$	$CO_2$	$CH_4$	$CH_4$	$CH_4$	$CH_4$	$CH_4$	$CH_4$	$CH_4$
-46	-		$1651^{\rm b}$		$1656^{\mathrm{b}}$	-	$1484^{b}$	$1409^{b}$	$1071^{\text{ b}}$
-61	-		$2786^{\mathrm{b}}$	$2622^{ m c}$	$2462^{\mathrm{c}}$	$2593^{b}$	$2384^{ m c}$	$2213^{\circ}$	$2172^{\rm b}$
-69	-		$3647  {}^{\mathrm{b}}$	$2745^{ m c}$	$2857^{ m c}$	-	$2520^{ m c}$	2803 °	2118 °
-79	-		$4245^{\mathrm{b}}$			$3742^{b}$	$2496^{ m c}$		
-80	-		$2587 {}^{\mathrm{b}}$	$2885^{ m c}$	$2474^{ m c}$	-	$2496^{b}$	$2227^{ m c}$	2166 °
91		88210							
92		101600							
-93	2120 a	141300	$5207^{\mathrm{b}}$	-	-	$3977  {}^{\mathrm{b}}$	-	-	-
94	$2975^{\mathrm{a}}$	148700	$5283^{\mathrm{b}}$	-	-	$4079^{b}$	-	-	-
-95	$3173^{a}$	151100	$5394^{\text{ b}}$	$3948^{ m c}$	$3682^{ m c}$	3939°	$3449^{\circ}$	$3385 {}^{\mathrm{c}}$	$2724^{ m c}$
96	$3329^{a}$	151300	-	-	-	-	-	-	-
97	3646ª	151900	-	-	-	-	-	-	-
-98	3931 ª	151100	-	-	-	-	-	-	-
98.5	3956	152100	-	-	-	-	-	-	-
99	3956	152100	-	-	-	-	-	-	-
Average	3050	137479	3850	3050	2626	3666	2472	2407	2050



Figure III. 15. Lake Nyos  $CH_4$ ,  $CO_2$  and  $(CO_2+CH_4)$  partial pressures vs depth measured in Dec. 2007 are plotted with the total pressure ( $P_{gas}$ ) obtained in January 2007.  $P_{CH4}+P_{CO2}$  in Dec 2007 are lower than the total pressure in Jan 2007 reflecting the gas removal from January to December 2007.



Figure III. 16. Lake Monoun.  $P_{CH4}$ ,  $P_{CO2}$ , partial pressures and  $P_{CO2}+P_{CH4}$  vs depth plotted with total gas pressure (TGP) obtained using the probe in Dec 2007. Note the perfect agreement between  $P_{CH4}$  + $P_{CO2}$  and TGP obtained using the probe. Dashed line refer to saturation level

#### III.2.3.5 Computation of CO<sub>2</sub> and CH<sub>4</sub> partial pressures and contribution of CH<sub>4</sub> to TGP

Explosive phenomena related to volatile substances occur when, confined, their pressures (concentrations) exceed a threshold limit. In the case of the gas eruptions from lakes Nyos and Monoun, one of the possible causes is that the hydrostatic pressure was not enough to hold the gas any longer (saturation) leading to the drama. During the last two decades, great emphasis has been put to monitor  $CO_2$  in the water columns of the lakes. Because methane is the second most abundant gas in the lakes with a tendency to increase rapidly and given its significant contribution to the total gas pressure, it is essential that its effect on water column be carefully evaluated. That evaluation could be done by converting the concentrations of dissolved gases into *in-situ* pressures. The gas partial pressures were calculated using the Henry law's approach. The temperature dependence of Henry Law's constant for  $CO_2$  and  $CH_4$  were taken from Taran (2005). Temperatures for target depths were taken from Table III.9. Gas partial pressures were calculated as shown in the appendix. The pressures values and their profiles for Lake Nyos are shown in Table III.9 and Figure III.15. The  $CH_4$  and  $CO_2$  partial pressures for December 2007 and for depths below 91 m and 120 m for lakes Monoun and Nyos respectively are given in Table III.9. Note that the limited interval of depths over which the calculation was done is impose by the gas-self lifting: the Flute-De-Pan related techniques take advantage of the gas self-lifting principles, but unfortunately, it is also its weakness when it comes to sample depths where gas concentration is not enough to drive the process.

The pressures values and their profiles for Lake Nyos are shown in Table III.9 and Figure III.15. All three profiles ( $P_{gas}$ ,  $P_{CO2}$ ,  $P_{CH4+CO2}$ ) run down almost vertically, with a slight positive gradient down to 207 m depth. Within that depth range, concentrations vary from 307.8 µmoles/kg at 120 m to 3694 µmoles/kg where they represent on average ~0.4 mol% relatively to the total gas concentration and contribute ~4.7 mol% to the total gas pressure. Below 207 m, a sharp positive
pressure gradient is observed down to 210 m; in that interval, CH<sub>4</sub> makes up ~0.6 mol%. If we integrate into our data set the 2004 value of 7330 µmoles/kg (see Table III.3) representing the concentration at 210 m depth reported by Kling *et al.*, (2005), the concentration will amount on average to ~5500 µmol/kg for bottom most waters. Methane would then contribute ~18.6 % to TGP and 13 % of the saturation level at depth below 207 m. At Lake Monoun, the pressure attained 2.9 atm below 98 m depth (Table III.9, Figure III.16). This is more than half of CO<sub>2</sub> partial pressure (CH<sub>4</sub>= 2.88 atm and CO<sub>2</sub>=4.65 atm). Overall, CH<sub>4</sub> contribution to the Total Gas Pressure below 93 m represents more than one third, ~37 %, although its average concentrations is only ~2.2 mol %.

Based on results presented above, the CH<sub>4</sub> concentrations near the lake bottoms might double every  $\sim 20$  years. In the case of Lake Monoun, if we hypothesized the degassing shall stabilize the  $CO_2$  concentrations at current level, and methane continues to increase at depth below 96 m according to above estimated rates, its quantity will triple in the next 50 years.  $CH_4$  will then contribute ~5.6 atm to total gas pressure, slightly more than the current  $CO_2$  partial pressure and a half of hydrostatic pressure. More importantly, the sum of the  $CO_2$  and  $CH_4$  partial pressures shall attain saturation level. In Lake Nyos, attainment of similarly conditions may require longer time but is likely to occur within a century. These observations are based on the current "methanation" of the lakes. Lake Monoun is likely to be the first potential candidate because of continuous sedimentation of organic waste which constitutes primary material for  $CH_4$  production. Whatever the case, the evolution of methane must be closely monitored because of its remarkable contribution to the total gas pressure. Kusakabe et al., (2008) have shown that, barely 20 years after the gas burst at Lake Monoun, waters at 50-58 m depth have almost attained saturation in 2003. If we admit that saturation was the cause of the 1980s gas burst, Kusakabe et al., (2008)'s observation suggests that gas may be exhaled from that lake every 25-35 years period or so. One would never know the  $CH_4$  concentrations and the role it played during the 1980s deadly events.

Table III. 8.  $CH_4$  content of the lakes estimated using bathymetric data by Kling et al., (2005). Concentrations in mega moles

	Jan-11	Dec-07	Jan-06	Jan-04	Jan-03	Jan-01	Oct-01	Nov-00	Nov-99	Apr-98	Mar-92
L. Nyos	51.2	74.1	48.6	61.7	41.0	37.2	39.6	32.9	37.7	35.5	19.2
L. Monoun	-	3.9	-	4.0	3.7	4.0	-	-	3.5	3.4	2.7

Table III. 9.  $CO_2$ ,  $CH_4$  partial pressures ( $P_{CO2}$ ,  $P_{CH4}$ ), and  $P_{CO2}$ +  $P_{CH4}$ . Temperatures of depths of interest were taken from CTD (Conductivity, Temperature and Depth profiler) data.

		Nyos						Monoun			
	Depth	Т	$\mathbf{P}_{\mathbf{CH4}}$	$\mathbf{P}_{\mathbf{CO2}}$	PCH4+PCO2		Depth	Т	$\mathbf{P}_{\mathbf{CH4}}$	$\mathbf{P}_{\mathbf{CO2}}$	PCH4+PCO2
Date	(m)	°C	atm	atm	atm	Date	(m)	°C	atm	atm	atm
Dec-07	-120	23.1	0.21	2.93	3.14	Dec-07	-91.0	23.0	-	2.51	-
	-160	23.5	0.40	4.16	4.56		-92.0	23.4	-	2.92	-
	-180	23.7	0.59	4.11	4.70		-93.0	23.7	1.47	4.09	5.56
	-191	24	0.51	4.24	4.75		-94.0	24.0	2.08	4.34	6.42
	-192	24.2	0.57	4.78	5.35		-95.0	24.2	2.22	4.43	6.65
	-198	24.4	0.56	5.86	6.42		-96.0	24.5	2.34	4.45	6.79
	-200	24.8	0.47	6.57	7.04		-97.0	24.5	2.56	4.49	7.05
	-204	25.2	0.70	9.8	10.50		-98.0	24.6	2.77	4.48	7.25
	-208	25.5	0.53	11.2	11.73		-98.5	24.8	2.80	4.53	7.35

However, it is obvious that gas saturation might be reached much more rapidly if  $CH_4$  continues to increase, likely reducing the periodicity of catastrophic gas exhalation.

If subsequent surveys confirm enhanced methanogenesis, then device such as the one proposed by Yoshida *et al.*, (2010) must be put in place without delay to prevent any gas build up. The proposed system that will pump the bottom most water to the surface will use a solar energy driven pump which will be inserted in the present pipes. The system is projected to be robust and almost maintenance-free.

The proposal to set up a new device to continuously remove gas from the bottom of the lakes, thus preventing any gas build up is of a great importance. It is well known that populations living in hazardous volcanic areas quickly return to their settlement once hazard menace ends. That is mainly due to the fact that the shortterm threat posed by volcanoes related structures is strongly balanced by the volcanism over geologic time (Mason et al., 2004) and even at human scale time, we would say. Concerning that assertion, displaced populations of Nyos area do not constitute an exception; in search of good grazing lands and fertile soils, they have started to return on their lands after more than 25 years of exile. After the mid-1980s trauma, the population needs to live in a safer place for them to reconstruct their socio-cultural and economic environment. Because now people living near crater lakes fear repetition of lakes Nyos and Monoun syndrome, they live in kind of permanent psychological unrest judging from the frequency at which, several uncommon events related to some cater lakes (e.g. Lake Barombi Mbo in the 1940s and 2012; Lake Oku in 2010 and Lake Wum in 2001) (Issa et al., 2011. IRGM *internal report*) have been reported to authorities for investigation.

	Monoun		Nyos	
Date	7-Jan	7-Dec	Date	Jan-07
Depth (m)	TGP (atm)	TGP (atm)	Depth (m)	TGP (atm)
5	1.14		18	0.78
10	0.91		43	0.77
20	0.8	0.79	59	1.08
30	0.81	0.79	62	1.64
40		0.8	66	2.15
49		0.83	77	2.48
50	0.9		103	3.08
58	2.27		118	3.66
60		0.88	138	4.41
64	2.92		150	4.77
65		1.04	162	5.05
67		1.2	168	5.19
68		1.41	180	5.78
69		1.71	184	6.14
71		1.98	188	6.92
72	3.28	2.28	192	8.62
78	3.99		194	9.96
80	5.62	3	196	12.2
88	5.87	3.48	203	15.44
90		3.66		
91		3.92		
92		4.94		
93	6.68	6.06		
94		6.14		
95		7.32		

Table III. 10. Total gas pressure (TGP) measured using the probe at Nyos (Jan 2007) and Monoun (Jan and Dec 2007).

#### III.2.4 Conclusion

Several techniques have been jointly used in this study to determine  $CO_2$  and  $CH_4$ concentrations and their partial pressures. Subsequently, their respective contributions to total gas pressure in gassy lakes Nyos and Monoun have been assessed. The possible risks that increase in  $CH_4$  might entrain in the future have been highlighted and some solutions advised to evaluate and pre-empt the risks posed to the population. The study has also shown that with relatively little apparatus mobilization, it is possible to evaluate the effect of each gas species in the lakes. The GA that was used in this study is designed to analyse,  $CO_2$ ,  $CH_4$  and  $O_2$ . In addition to these three gases, the lakes also contain  $N_2$  and  $H_2S$ ; by using a suitable gas analyser, it will be possible to evaluate more precisely the effect of each gas. The method is laboratory analysis free, therefore cheap and suitable for developing countries where the prohibitive costs of analytical apparatus induced by volcanoes monitoring/surveillance watch systems constitutes the major obstacle to setting up observatories and hazards surveillance policies (Scarpa and Tilling, 1996). In consequence, the promotion of the type of techniques used in this study and in Yoshida *et al.*, (2010) could foster the setting up of surveillance networks in those countries, thereby reducing the risks from volcanoes related structures. The use of a new technique to evaluate the status of the gassy lakes Nyos and Monoun was the central goal of this study. The quite good overlap of estimated  $P_{\rm CO2}$ + $P_{\rm CH4}$  and TGP profiles measured by the gas pressure probe is a good testimony of the applicability of the method. The apparent mismatch observed between  $P_{CH4}$  +  $P_{CO2}$  and TGP profiles concerning Lake Nyos rather reflects the lowering of the pressure due to gas removal between January 2007 when the probe was done and Dec 2007 when methane was measured.

# CHAPTER IV- Grouping of the lakes according to their natural characteristics

### **IV.1 Introduction**

Earth scientists often study phenomena which are infinite and often spatially widely dispersed. Consequently, in order to have an overall view and summarize their findings, they increasingly rely on statistics (Isaaks and Srivastava, 1989; Wackernagel, 1995). Because of the infinite and complex nature of natural processes, an earth scientist is bound to study only a small fraction of a considered phenomenon (McKillup and Darby Dyar, 2010). Subsequently, he can try to generalize his findings and draw final inferences that describe the process (es) underlying the phenomenon. There exist several techniques, especially graphical displays. Bivariate data can be easily, conveniently and comprehensively displayed on a two-dimensional space. As the number of parameters increases, the exercise is difficult and it becomes almost impossible to graphically display the information in a comprehensive way. Two to 3 variable displayed in a two or three dimensional graph can be easily read and understood. However, as the number of dimensions increases, it becomes increasingly difficult to display all the variables in a graph. For example, how will it be possible to tell which lakes share similar natural properties by looking on the more than 20 parameters that have been generated in this study?

The difficulty to graphically portray and summarize and compare multivariate data can be alleviated if the redundancy among the data can be used (Goovaeerts, 1997). Multivariate analysis do this by reducing multiple data sampled at various sites to 1, 2 or 3 statistics or measures while retaining as much information as possible about each (McKillup and Darby Dyar, 2010). This can permit to compare several sampling sites. Two methods exist to simplify the visualization of multivariate data: variables oriented method (R-mode analysis) such as Principal Component Analysis (PCA) and sampling unit oriented (Q-mode analysis) method such as the cluster analysis.

## IV.2 Objective

Risk reduction is the overall goal of this work. The goal can be achieved by setting up a monitoring/surveillance activity for the Cameroonian volcanic lakes. Given that it is difficult and even useless to regularly monitor all the lakes, it is necessary to identify those that have similar natural characteristics so as to objectively select from each family the representative lake(s) that would make up a basic monitoring/surveillance network. Accordingly, the geochemical, isotopic and physical data generated on the about 40% (17 lakes) of the 39 volcanic lakes will be used o group them hosted by the CVL.

# IV.3 Method

We used the Q-mode analysis, the sampling site oriented and the R-mode analysis, the variable-oriented analysis in order to group the lakes in families of similar natural characteristics and identify the variables that most account for the similarities and the differences among them. The Q-mode analysis summarizes multivariate data by calculating a single measure or statistic that helps to appreciate the similarities and/or dissimilarity among sampling units, in our case the studied lakes. Based on the several parameters of each sampling site, the method calculates a measure such as the Euclidian distance ( $d_e$ ) that would help to quantify the similarity/dissimilarity among two sampling sites A and B. For example, if we consider a site A with coordinates 9 and 6 units on an Y<sub>1</sub> axis and 13 and 11 units on an Y<sub>2</sub> axis. The values represent for example the concentrations of two elements. The distance between A and B in a two dimensional space would be the hypotenuse of the triangle as shown in Figure IV.1. The smaller the distance, the higher the similarity between two given sampling sites and vice-versa.

In general in a p dimensional space:  $d_e = \sqrt{\sum_{i=1}^{p} (Y_{iA} - Y_{iB})^2}$  where  $Y_1, Y_2, \dots Y_p$  are the number of dimensions. For four sampling sites for example, a matrix of similarity/dissimilarity is constructed between pairs of sites. Based on the Euclidian distance, the sites could be positioned on a two dimensional graph. The exercise becomes difficult for p>3. However, statistical packages do that by placing the sampling units entirely randomly to correspond to the calculated Euclidian distances. This is done iteratively to find the position that better fits the actual position of the sites relatively to each other (Goovaerts, 1997; McKillup and Darby Dyar, 2010).

The hierarchical clustering which can be graphically portrayed by a graph named dendogram was used. The criterion of nearest neighbor was applied. Lakes Nyos and Monoun, the prototype of dangerous lakes are used as reference for the grouping.

To identify the parameters that most influence the resemblance/dissemblance among the lakes, the R-mode analysis, variable oriented principal component (PCA) was used. Alike the cluster analysis, the PCA works to reduce the number of variables by using the redundancy among them. It identifies the highly correlated variable with each other and combines them to derive a new statistic (or new variables) that still retain the maximum information on the original variables, thus the sampling sites (McKillup and Darby Dyar, 2010). For example, if we plot two variables taken from several sites, the points in the scatter plot can be enclosed by a boundary. In the case the variables are highly correlated, the boundary would be an ellipse with a long axis (also major axis) and short (minor axis) drawn halfway and perpendicular to the long axis. So instead of two variables, the variance among the sites can be described by the information combined in only one variable which describes the location of the sites about the major axis ( or the minor one) also called Principal Component 1 (PC1). The lengths of the axis are called vectors and their scalars eigenvalues.



Figure IV. 1. Euclidian distance  $(d_e)$  between sampling sites A and B in a two dimensional space. The formula for the calculation of  $d_e$  is also shown

If the variables are highly correlated, the major axis will have a large eigenvalue and the second a small value. In contrast if the variables are not well correlated, the boundary would be more circular and the axis would have similar eigenvalues. For example, for n variables, the PCA will calculate n new axis with their eigenvalues for the n objects in n dimensional space extracting n PCAs (PCA1, PCA2....PCAn) The PCAs can be highly or not correlated to the original variables. The correlation values which vary between 0 and 1 are also called loadings.

The analysis was performed by the package statistiXL, a Microsoft Excel Add-ins using the twenty four parameters selected from Tables II.1, Table II.2 and Table II.3:

- 1) morphometric (Depth and area),
- 2) physical (pH, T, Cond, TDS),
- 3) isotopic ( $\delta^{18}$ O and  $^{2}$ H),
- chemical (Na<sup>+</sup>, Mg <sup>2+</sup>, Al<sup>3+</sup>, Si, K<sup>+</sup>, Ca<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>2</sub>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>)

## IV.4 Results and discussion

## IV.4.1. Dissimilarities and similarities among the lakes

Table IV.1 gives a quantitative measure of the similarity between each pair of lakes. Taken two by two, the similarity/dissimilarity scores vary from 0.06 to 0.98 units. Since the strategy used to classify the sampling sites was the "nearest neighbor", the 0.06 index indicates the concerned two lakes represented by lakes Nyos and Monoun have similar characteristics. The dendogram (Figure IV.2), a tree-like diagram similar to that used in describing genealogy, also clearly separates the two lakes from the others which are grouped together with internal dissimilarity scores ranging from 0.11 to 0.84. The lowest similarity score between the other lakes and Nyos and Monoun is 0.77 (Nyos-Monoun/Benakuma). That large dissimilarity highlights the peculiarity of the gassy lakes Nyos and Monoun relatively to the

other lakes. Taken one by one, the Lake Benakuma is the lake that most resembles lakes Nyos and Monoun whereas the largest dissimilarity is observed is observed between those two lakes and lakes Debunscha and Idjagham with 0.98 and 0.94 scores respectively (Table IV.1). The large dissemblance between lakes Nyos and Monoun on one hand and Lake Idjagham is justified since the latter is an astrobleme (Kling, 1987) instead of a volcanic lake.

In order to classify the lakes into fewer groups, we have taken the similarity/dissimilarity measure unit (U) for each lake. We have devised a similarity  $S_m$ , calculated as  $S_m$ =100-U/0.5\*100 where 0.5 is the maximum U on the similarity/dissimilarity axis (see Figure 4.2). Based on obtained  $S_m$ , 3 groups of lakes characterized by mean  $S_m$ =73%,  $S_m$ =48% and  $S_m$ =24% were defined. Although that criterion may seem arbitrary, it is assumed that a lake which has on average >70% of the characteristic of the reference lakes suggest somewhat a close resemblance.

All the lakes in the Adamaua region (Ad-LD) classify in Group I with two lakes from the North-West region, Baleng and Benakuma. Group II comprises 2 lakes from the Bamenda Lake District and two from the South-West (SW-LD), the Manenguba twin lakes the monitoring of which could bear some interests because they are located in a caldera which experiences noticeable magmatic degassing as discussed in the previous chapter.



Figure IV. 2. The reference lakes Nyos and Monoun and the groups. Group I in circle, Group II in diamond, Group III in rectangle. Assumedly, the origin of the lakes is volcanism; Fluids-Rocks interaction gives them their properties.

Table IV. 1. Univariate distance matrix between sampled lakes. (BK= Barombi Kotto, BM= Barombi Mbo, Db= Debunscha, Mm= Manenguba Male, Mf= Manenguba Female, Ba= Baleng, Be= Benakuma, Wu= Wum, Ny= Nyos, Mo= Monoun, El= Elum, Ok= Oku, Id= Idjagham, Ng= Ngaoundaba, Ti= Tizon, B-m=Baledjam Marbuwi, B-r= Baledjam ranch).

	BK	BM	Db	Mm	Mf	Ba	Be	Wu	Ny	Мо	El	Ok	Id	Ng	Ti	B-m	B-r
BK	0.00	·			·												
BM	0.51																
Db	0.70	0.79															
Mm	0.52	0.45	0.77														
Mf	0.70	0.51	0.62	0.39													
Ba	0.48	0.54	0.81	0.38	0.62												
Be	0.41	0.39	0.85	0.42	0.55	0.16											
Wu	0.61	0.37	0.69	0.36	0.27	0.44	0.40										
Ny	0.89	0.87	0.98	0.90	0.92	0.82	0.77	0.89									
Mo	0.91	0.90	0.98	0.90	0.94	0.83	0.81	0.90	0.06								
El	0.40	0.40	0.72	0.27	0.50	0.28	0.31	0.25	0.87	0.88							
Ok	0.44	0.32	0.67	0.58	0.49	0.67	0.54	0.47	0.92	0.94	0.52						
Id	0.55	0.51	0.50	0.52	0.39	0.64	0.61	0.35	0.94	0.94	0.41	0.42					
Ng	0.58	0.51	0.79	0.38	0.59	0.23	0.34	0.39	0.83	0.84	0.28	0.64	0.59				
Ti	0.44	0.52	0.79	0.36	0.60	0.11	0.22	0.39	0.84	0.85	0.24	0.64	0.59	0.19			
B-m	0.48	0.47	0.82	0.36	0.54	0.11	0.13	0.36	0.81	0.81	0.27	0.65	0.62	0.27	0.15		
B-r	0.50	0.47	0.73	0.37	0.55	0.24	0.32	0.31	0.87	0.88	0.19	0.61	0.47	0.19	0.17	0.23	0.00



Figure IV. 3. Six components which explain > 80% of the total variance were retained. PC5 and PC6 which explain less than 10% of the total variance were not taken into consideration in the analysis.

Finally, lakes in the South-west Lake District have little resemblance with lakes Nyos and Monoun. Lake Barombi Mbo, the largest volcanic lake in Cameroon belongs to that group. If the criterion for choosing a lake for monitoring/surveillance network depends only on relatively significant resemblance with lakes Nyos and Monoun, then the Barombi Mbo would not feature in that list. However, given that, due to unknown reasons the Barombi Mbo overturns frequently, it would be interesting to include it in a monitoring network to determine the cause of its behavior.

Since the cluster analysis, does not indicate the parameters that most accounted for the variance among the lakes, the variable-oriented analysis was used to determine that or those variables.

Lake	Lake district	U	S	$S_m$	Group
Tizon	Ad-LD	0.11	78		
Baleng	NW-LD	0.11	78		
Baledjam Marbuwi	Ad-LD	0.11	78	73	Ι
Benakuma	NW-LD	0.13	74		
Baledjam ranch	Ad-LD	0.17	66		
Ngaoundaba	Ad-LD	0.19	62		
Elum	NW-LD	0.25	50		
Wum	NW-LD	0.25	50	48	II
Manenguba Female	SW-LD	0.27	46		
Manenguba Male	SW-LD	0.27	46		
Idjagham	SW-LD	0.35	30		
Oku	NW-LD	0.32	36	24	III
Barombi Mbo	SW-LD	0.32	36		
Barombi Kotto	SW-LD	0.4	20		
Debunscha	SW-LD	0.5	0		

Table IV. 2. Grouping of the lakes based on their similarity/dissimilarity with lakes Nyos and Monoun

#### IV.4.2. Parameters that most influence the similarity/dissimilarity among the lakes

All the PCAs were extracted and six which explain more than 80% (Figure 4.4) of the variance and having eigenvalues greater than 1 (Table IV. 3, Figure 4.3) were retained for the analysis. However, PC4, PC5 and PC6 which have low correlation with about 10 variables (Table IV.4) were considered not significant in the explanation of the variance among the lakes. PC1 and PC2 with and eigenvalues of 8.3 and 3.6 (Table IV.3) explain almost half (49.6%) of the variance and are the most important components. Ten variables, with loads > 0.6, show high correlation with PC1 and four with PC2. Bicarbonate had the largest load on PC1 (Table IV. 4, Figure 4.4) indicating thereby the important role of dissolved CO<sub>2</sub> on the dynamic of the lakes. TDS and C<sub>25</sub> which represent the bulk chemical composition of the lakes, also heavily load on PC1. Majority of the major ions loads on PC1 and PC2 suggesting the two components may represent the water-rock interaction. The isotopes, the depth, area, pH and the temperature seem not to be decisive in explaining the similarities and differences among the lakes.

Finally  $HCO_3^{-}$ , TDS,  $C_{25}$ ,  $Br^{-}$  and Fe are in order, the variables that most account for the similarity/dissimilarities among the lakes. For unclear reasons, although marginal in the chemical composition of the lakes,  $Br^{-}$  unexpectedly had a significant load (0.95) on PC1 (Table IV. 4).

Table IV. 3. Variance by each PCA and cumulative variance explained.

Value	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6
Eigenvalue	8.3	3.6	2.6	2.4	1.8	1.4
% of Var.	34.7	14.8	10.7	10.1	7.7	5.8
<b>Cum. %</b>	34.7	49.5	60.3	70.4	78.0	83.8



Figure IV. 4. Plot of PC1 vs PCA2 (explain ca 34.70 % and 14.8 % of the total variance). The graphical representations of the contributions of the original variables to both PC1 and PC2 are also shown. Circled are variable that most account for the variance.

Table IV. 4. Component loadings are the correlations between the original variable and the principal component and indicate roughly the relative contributions/importance of each variable in each principal component

Variable	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6
Depth	0.62	-0.03	-0.39	-0.10	0.42	0.17
Area	0.11	-0.12	0.30	0.12	0.51	0.56
pH	-0.51	0.22	0.58	-0.03	-0.25	0.08
Ť	0.05	0.15	0.50	0.53	0.35	-0.32
δ18O	-0.56	-0.37	-0.19	0.56	-0.29	0.26
${}^{2}\mathrm{H}$	-0.55	-0.13	-0.25	0.61	-0.19	0.26
$C_{25}$	0.96	-0.11	-0.11	0.03	-0.11	-0.07
TDS	0.98	-0.11	0.02	0.02	-0.09	-0.06
Na +	0.81	0.35	0.19	0.18	-0.30	0.17
Mg <sup>2+</sup>	0.81	-0.02	-0.14	0.22	0.04	0.23
Al <sup>8+</sup>	-0.31	0.58	0.59	-0.20	-0.14	0.00
$SiO_2$	-0.34	0.73	-0.44	-0.17	-0.17	0.01
K+	0.60	0.48	-0.17	0.34	-0.33	0.25
Ca <sup>2+</sup>	0.32	0.85	-0.08	0.04	-0.09	0.06
Mn <sup>2+</sup>	-0.07	0.67	-0.28	-0.19	0.41	0.05
Fe <sup>2+</sup>	0.92	-0.18	0.09	-0.06	-0.11	-0.16
F-	-0.03	0.80	-0.26	0.03	0.08	0.10
Cl	0.07	0.29	0.61	0.51	-0.28	-0.03
NO <sub>2</sub>	0.06	-0.27	0.35	-0.45	-0.09	0.66
Br <sup>.</sup>	0.95	0.02	0.02	0.16	0.03	0.16
NO3-	-0.08	-0.22	-0.48	-0.04	-0.60	-0.15
PO4 <sup>2-</sup>	-0.23	-0.03	0.01	-0.58	-0.37	0.31
$SO_{4^{2}}$	0.61	-0.04	0.32	-0.55	-0.20	-0.19
HCO3 <sup>-</sup>	0.98	-0.12	0.02	0.03	-0.08	-0.04

#### **IV.5** Conclusion

Based on collected parameters, the CVL lakes (17) have been statistically classified in groups of similar natural characteristics. The results confirm the high resemblance between lakes Nyos and Lake Monoun with a very low dissimilarity score (0.06). But also, they have revealed the quite big difference between those lakes and the others with dissimilarity score ranging from 0.98 to 0.77. In spite that remarkable dissimilarity, lakes Benakuma, the third largest and deepest volcanic lake in Cameroon was the most resembling Nyos and Monoun. That lake was followed by lakes in the Adamaua Lake District and the Manenguba twin lakes.

The monitoring of the latter two may bear some interests because they are located in a caldera which experiences noticeable magmatic degassing as discussed in the previous chapter.

The clustering also indicates that the two coastal lakes, Idjagham and Debunscha and lakes shallower than such as Lake Barombi Kotto have the highest dissimilarity scores thus can be assumed not hazardous; those lakes with Lake Barombi Mbo form the group III. The latter has, for undetermined reason, the peculiarity to overturn frequently. Therefore, it is suggest that Lake Barombi Mbo could be listed among the lakes that would be selected for the setting up of a minimum monitoring/surveillance activity for the CVL lakes. Among the parameters,  $HCO_3$ , TDS,  $C_{25}$ , Br<sup>-</sup> and Fe are in order, the variables that most account for the variance among the lakes. For unclear reasons, although marginal in the chemical composition of the lakes, Br<sup>-</sup> unexpectedly had a significant influence on the grouping.

### CHAPTER V GENERAL CONCLUSION

Because of its latitudinal and geological setting, the CVL is very diverse from the meteorological, hydrological and geological stand point. That diverse setting is also reflected on the chemical, isotopic and physical properties of the CVL lakes.

From the anionic point of view, the lakes water is overwhelmingly dominated by the presence of bicarbonate resulting from the titration of the hosting rocks by the dissolved  $CO_2$  which provides the necessary acidity for the process. The chemical processes develop in a rock dominated alteration system, if we assume that lake waters have some similarities with hydrothermal waters circulating in the sublacustrine system. Consequently, the cationic composition of the lakes reflects the nature of the hosting rocks: Lake water in basaltic or trachytic terrain was marked by greater proportion of alkali Earth and those in granitic geologic formations were instead found to contain more alkaline elements. Overall the lakes generally had physical properties similar to natural waters. The pH was close to neutral or slightly alkaline in the example of the lakes in the Adamaua Lake District. The conductivity was < 600µS/cm, except lakes Nyos and Monoun which are known to have high conductivity >1500  $\mu$ S/cm. The conductivity and the temperature profiles indicate that all the lakes, including the shallowest (>15m deep) were stratified and that, the water column structuring depend on the seasons and the daily temperature variation. Noteworthy, the uppermost 10 to 15 m of the water column contained discernable oxygen concentration whereas the bottom waters were anoxic. This implies that mixing between epilimnia and the hypolimnia is limited and probably scarce. The water isotopes study showed that, irrespective of their location and size parameters and hydrological setting, the CVL lakes were isotopically stratified with heavy isotope enriched epilimnia compare to the hypolimnetic waters. Against the depletion in heavy isotopes in the precipitations as one move from the South to the North, the lakes instead get more enriched. However, high altitude lakes of the Bamenda Lake District do not follow that general trend. None of the

morphometric, geographic and hydrological setting plays a prominent role in shaping the isotopic composition of the lakes. Rather, it is suggested that the interplay of all the factors control their isotopic composition.

Carbon dioxide was investigated given its implication in some deadly events along the CVL. Several lakes were found to contain low but discernable concentration of magmatic CO<sub>2</sub>. This suggests that a residual volcanic activity still continues and feeds gas into those lakes. The study on the diffuse CO<sub>2</sub>-flux was conducted at water/atmosphere interface at several lakes. The results indicate that, the lakes emit about 127.35 $\pm$ 3.2t.d-1 CO<sub>2</sub> to the atmosphere from the about 756 ha surveyed area. Extrapolating to all the CVL lakes, a total amount of 342.8t.d<sup>-1</sup> of CO<sub>2</sub> would be contributed to the atmosphere from the about 2035ha occupied by volcanic lakes in Cameroon. However, that estimate was believed to represent only the period where lakes Nyos and Monoun are under degassing process because the observed CO<sub>2</sub> emission results from the oxidation of siderite brought to the surface by the degassing pipes.

The diffuse  $CO_2$  flux was also conducted at soil/atmosphere interface at Mount Manenguba caldera. The 13-carbon values indicate that the  $CO_2$  originates from magma emplaced magma continues to degas 0.56Ma after the last volcanic activity. The Manenguba caldera could represent a suitable site where volcanic activity monitoring could be conducted using a  $CO_2$ -flux based system.

a minimum network for Finally. in order to  $\mathbf{set}$ up volcanic lakes monitoring/surveillance activities, the 24 parameters generated were used to group the lakes in families having similar natural characteristics. The results confirm the high resemblance between lakes Nyos and Lake Monoun. But also, they have revealed the quite remarkable difference between those lakes and the others. In spite of that dissimilarity, Lake Benakuma, the third largest and deepest volcanic lake in Cameroon was the most resembling Nyos and Monoun followed by lakes in the Adamaua Lake District and the Manenguba twin lakes which may be interesting sites to monitor due to the noticeable magmatic degassing. Among the parameters,  $HCO_3^-$ , TDS,  $C_{25}$ ,  $Br^-$  and Fe are in order, the variables that most account for the variance among the lakes.

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		Depth	Η	Т	C <sub>25</sub>	TDS	Na	Mg Al	SiO <sub>2</sub>	K+	Ca	Mn	Fe	F	Cl.	NO <sub>2</sub>	Br <sup>-</sup>	NO	PO <sub>4</sub>	$SO_4$	HCO <sub>3</sub>
LD	Lake	m		°C	μS/cn	1 mg/l	ppm	ppm ppn	ıppm	ppm	ppm	ppm	ppm	ı ppm	ppm	ppm	ppm	ı ppm	і ррш	ррт	ppm
	Bar.Koto	0	9.0	28.8		174	19.6	8.68 0.11	14.6	4.27	10.9	0.01	0.21	0.26	5.74	na	0.02	na	na	na	110
	Bar. Mbo	0		28.5	52.7	51.2	2.79	2.74 na	12.8	2.34	1.26	na	0.12	0.07	0.79	na	na	na	na	0.14	28.1
		50		26.7	81.9	58.2	2.58	2.84 na	13.6	1.98	1.29	na	3.89	0.07	0.79	na	na	na	na	na	31.2
		98		26.8	146	94.5	2.57	2.87 na	18.0	2.03	1.43	na	13.8	0.07	1.27	na	na	na	na	0.04	52.5
	Debunscha	0	9.6	30.8	-	24.1	3.26	$0.51\ 0.09$	9 1.79	1.50	1.15	0.01	0.20	0.04	1.01	na	na	0.03	na	0.51	14.0
		10	8.4	28.7	-	27.3	3.56	$0.55\ 0.09$	2.20	1.58	1.76	0.02	0.06	0.14	1.57	na	na	0.13	na	0.63	15.0
SW-LD	Man.Male	0	8.2	20.8	10.3	138	13.5	$4.70\ 0.14$	35.1	2.50	7.06	0.01	0.04	0.11	0.47	na	na	na	na	0.18	74.0
		45	7.4	18.0	105	117	5.92	4.56 0.03	334.1	2.19	6.82	0.09	0.53	0.12	0.52	na	na	0.55	na	0.76	61.0
		90	7.8	19.1	104	135	6.48	4.88 0.07	35.0	2.65	7.47	0.20	4.13	0.23	0.59	na	na	3.61	0.23	0.90	69.0
	Man. Female	0	5.8	22.1	37.5	30.1	1.85	1.27 na	8.68	0.44	1.33	na	0.07	0.03	0.43	na	na	na	na	0.03	16.0
		75		19.5	59.0	43.2	1.76	1.48 na	10.2	0.90	1.40	na	2.93	0.03	0.52	na	na	2.97	na	0.01	21.0
		149		19.5	67.8	46.4	1.78	1.57 na	10.6	0.41	1.48	na	3.83	0.04	0.39	na	na	na	na	0.04	26.3
	Baleng	10	8.0	26.3	215	194	16.6	5.95 0.08	3 34.1	5.58	19.8	0.01	0.05	0.31	1.78	na	na	0.07	na	na	110
		50	7.5	23.5	336	237	14.8	$7.55\ 0.14$	46.3	4.92	23.8	0.44	3.40	0.40	1.26	na	na	0.09	na	0.42	133
	Benakuma	0	7.8	29.3	63.3	81.7	8.67	1.89 0.06	3 18.2	2.23	5.37	0.01	0.08	0.25	0.49	na	na	0.12	0.08	0.22	44
		70	6.6	25.4	284	222	9.85	4.10 0.06	3 38.1	2.77	13.3	2.97	23.0	0.69	0.55	na	na	0.10	0.56	na	126
	***	130	6.7	25.8	319	248	11.4	4.24 0.06	3 38.7	3.68	13.8	2.51	29.9	0.93	0.67	na	0.02	0.15	na	0.37	142
	Wum	0	8.8	27.3	46.6	36.6	1.54	3.07 na	6.92	1.23	1.02	na	na	0.05	0.27	na	na	0.21	na	na	22.3
		60 100	~ ~	22.4	75.3	51.2	1.60	3.24 na	8.14	1.77	1.04	na	3.83	0.06	0.28	na	na	na	na	na	31.3
	N.T.	120	8.0	22.5	192	60.2	1.62	3.28 na	8.50	1.77	1.06	na	4.51	0.06	0.28	na	na	na	na	na	39.1
DIID	Nyos	10	6.9	22.0	114	91.3	3.41	11.3 na	na	1.61	1.2	na	0.6	0.066	0.17	0.01	0.01	0.26	na	0.00	/12.1
Ba-LD		110	0.0 7 7	22.6	733	578	53.6 96.9	3.63 na	na	13.1	10.3	na	89.5	0.084	0.38	0.01	0.03	0.02	na	0.06	407
	Monoun	210	0.0 7.0	24.3	2100	2906	26.3	182 na	na	1.34	13.6	na	1 90	0.162	1.04	0.00	0.12	0.01	na	0.44	2160
	wonoun	40	1.9	20.0	202	44.0	0.99 6 91	0.00 na	na	2.10	2.0	na	25.1	0.140	1.04	0.01	0.00	0.00	na	0.10	20.00
		40	6.0	22.5	202	3065	91 Q	97.9 no	no	4.20	6.8	no	874	0.142	1 79	0.00	0.00	2.00	na	1.85	2124
	Elum	0	77	26.9	60.1	71.8	1 79	3 03 0 10	167	1.20	4.56	0.01	0.29	0.07	0.30	0.00 na	0.00	0.03	ina	0.04	40.0
	Lium	34	7.0	24.2	199	144	5 41	3 51 0 11	23.8	2.01	6.59	0.67	16.3	0.07	0.25	na	na	0.00	0.16	0.04	85.0
	Oku	0	8.0	18.8	27.2	30.9	3 69	1 09 0 08	3 0 80	1.33	2.48	0.01	0.19	0.08	0.40	na	na	0.14	0.10 2 na	0.60	20.0
	onu	- 49	7.9	18.3	35.9	56.7	8.33	1.20 0.09	) 5.34	1.23	2.86	0.28	0.02	0.03	0.45	0.02	0.01	0.02	0.15	0.71	36.0
	Idiagham	0	8.4	31.2	7.1	14.0	1.80	0.16 0.08	3 0.83	1.00	0.55	0.01	0.00	0.04	0.27	na	na	0.08	0.07	0.10	9.0
		15	5.6	30.0	92.0	38.3	3.35	0.29 0.04	2.74	1.52	1.64	0.11	4.10	0.03	0.30	na	na	na	0.06	0.10	24.0
	Ngba	0	7.9	26.3	141	106	5.32	8.69 na	27.2	1.09	1.37	na	0.06	0.12	0.69	0.02	na	0.78	na	na	61.1
	0	25	6.9	20.1	172	115	5.21	8.34 na	26.1	1.12	1.07	na	1.80	0.11	0.48	0.01	na	na	na	na	70.9
		49	6.7	20.0	468	133	5.36	8.65 na	26.4	1.11	1.83	na	7.72	0.12	0.52	na	na	12.3	na	na	69.5
	Tizon	0	8.5	25.0	254	202	11.3	11.1 na	35.0	8.22	8.77	na	0.07	0.49	1.43	na	na	na	0.08	0.06	126
		20	7.1	20.4	269	197	11.0	10.8 na	34.7	7.35	7.09	na	0.92	0.45	0.94	na	na	5.60	0.17	na	118
Ad-LD		42	6.7	20.3	320	190	10.6	10.6 na	32.7	6.67	6.09	na	1.01	0.45	0.95	na	na	5.50	0.15	na	115
	Baledjam M	0		-		154	7.72	9.40 0.07	24.6	3.35	13.6	0.01	0.08	0.12	0.60	na	na	0.17	na	0.07	94.0
		40		-		157	7.12	9.10 0.04	1 23.0	3.53	13.5	0.25	0.14	0.14	0.57	na	na	0.09	na	0.08	99.0
		100		-		250	7.85	11.1 0.03	33.6	4.04	16.8	1.48	19.8	0.16	0.99	na	0.02	0.35	na	0.20	154
	Baledjam	0		24.0		106	6.15	$5.72\ 0.05$	517.3	3.81	7.30	0.01	0.15	0.08	0.64	na	na	0.15	na	0.05	65.0
		11		21.2		118	2.80	6.73 0.06	318.4	2.41	8.40	0.78	5.42	0.13	0.90	na	na	0.12	na	0.08	72.0
		Ground and	l str	ream	waters	9															
	Barombi Mbo	inlet 1				137	6.05	9.09 0.01	46.5	2.20	4.22	0.00	0.04	0.14	1.42	na	0.00	0.55	0.33	0.94	65.4
		Inlet 2				136	5.32	7.70 0.01	46.4	1.81	4.12	0.00	0.01	0.09	0.50	na	0.00	0.51	0.08	0.43	68.9
		Inlet 3				115	6.15	$5.64\ 0.01$	41.6	2.30	5.35	0.00	0.12	0.19	1.76	na	0.00	0.85	0.23	1.89	48.4
		Bor. Vil)				74.2	3.47	4.02 na	19.7	5.16	0.98	na	0.42	0.08	1.23	0.01	na	na	na	0.65	38.4
		well				89.5	5.22	$3.15\ 0.03$	3 33.7	1.92	4.19	0.01	na	0.05	0.90	na	na	0.10	na	2.28	38.0
SW-LD	Bar. Koto	well	7.9	27.6		377	19.5	33.2 0.04	165.1	5.07	40.1	0.23	0.05	0.42	37.8	na	0.11	0.57	na	80.5	94.0
	Debunscha.	spring				43.6	2.38	1.49 0.16	6 11.9	1.20	3.92	0.01	0.12	0.09	2.94	na	na	na	na	1.36	18.0
	Man. Male	Inlet	7.5	18.8		110	5.95	$3.35\ 0.04$	131.7	2.20	8.11	0.01	0.05	0.11	0.46	na	na	na	0.06	0.49	58.0
	Man Female	inlet				101	8.32	3.91 na	38.6	1.87	1.07	na	0.14	0.14	1.22	na	na	0.03	0.20	0.39	44.8
	Mt Manenguba	Bor.				81.6	5.03	3.92 na	34.0	0.85	1.00	na	0.05	0.11	0.52	na	na	na	0.12	0.45	35.5
		Riv Mbwe				86.0	5.17	4.38 na	34.2	1.04	1.13	na	0.03	0.10	0.52	0.01	na	na	0.14	0.45	38.9
1		Ndib S. sp.				588	36.5	16.6 na	112	45.0	30.1	na	1.40	2.17	2.60	0.04	na	na	na	na	341
		Bare S sp.				67.9	3.94	3.58 na	31.2	0.31	0.99	na	0.04	0.06	0.23	na	na	na	0.46	na	27.1
	Monoun.	welll				88.2	9.73	3.11 0.07	8.27	2.44	6.18	0.01	0.04	0.07	0.57	na	na	1.22	na	0.43	56.0
1	Monoun.	spring				106	8.56	$4.85\ 0.07$	13.42	22.10	9.44	0.01	0.05	0.10	2.12	0.05	na	5.53	na	0.24	59.0

Table A. 1: Detailed physico-chemical composition of the lakes, groundwater and rivers

Bd-LD	Monoun.	Riv. Panke		158	18.01	$3.74\ 0.12\ 19.10\ 5.05$	7.23	0.29 2.49 0.11	2.12	na na	0.10 na	0.87 99.0
	Elum	Bor.	$6.9\ 22.5$	200	9.33	$5.83\ 0.03\ 49.78\ 16.71$	19.38	0.01 na 0.37	12.45	na na	$6.43\ 0.47$	$0.95\ 78.0$
	Wum	Bor.		101	3.84	$5.25\ 0.02\ 34.06\ 1.41$	6.65	0.01 na 0.09	0.56	na na	$0.22\ 0.04$	$0.54\ 48.0$
	Oku	Bor.	$8.5\ 21.0$	83.1	3.05	$4.27\ 0.05\ 21.03\ 1.82$	6.11	$0.01 \ 0.04 \ 0.05$	0.56	na 0.02	3.34 na	$0.73\ 42.0$
	Idjagham	well	$7.0 \ 30.2$	38.4	2.59	$0.79\; 0.03\; 7.07\;\; 2.29$	4.78	$0.06 \ 0.10 \ 0.01$	2.10	na na	12.1 na	0.48 6.0
Ad-LD	Tizon area	spring	$6.2\ 25.3$	118	4.53	$4.25\ 0.11\ 29.27\ 1.54$	8.47	$0.01\ 0.03\ 0.54$	0.88	0.18 na	0.53 na	$0.75\ 67.0$
	Baledjam (Dibi)	Bor.	$6.6\ 24.5$	89.9	5.63	$2.14\ 0.01\ 39.26\ 3.35$	3.92	0.01 na 0.13	0.12	na na	0.04 na	$0.31\ 35.0$



Figure A.1: Graph showing the consistency of the analysis



**Figure** A 2: Water typology: more than 75% of waters are of Fe-Mg-HCO<sub>3</sub><sup>-</sup> type. All the Adamaua lakes are of Mg-HCO<sub>3</sub>-type and 41% of Bamenda lakes district are of Fe-HCO<sub>3</sub><sup>-</sup> type

## Appendix B

One meter stepwise averaged CTD data

Table B.1 : Nyos CTD 2012

Depth		C <sub>25</sub>	O <sub>2</sub>	pН	Eh	# Avg.	Depth	Т	C <sub>25</sub>	O <sub>2</sub>	pН	Eh	# Avg.
(m)		(µS/cm)	(mg/kg)				(m)	(° C)	(µS/cm)	(mg/kg)			
0	21.81	447.1	5.15	7.89	162.0	30	53	21.70	149.8	2.42	6.59	181.7	3
1	24.5	231.8	6.69	7.39	156.3	157	54	21.70	149.4	2.43	6.59	181.8	3
2	24.09	231.5	6.64	7.33	159.2	21	55	21.70	149.9	2.43	6.59	181.8	5
3	23.88	230.6	6.63	7.31	159.9	20	56	21.70	149.9	2.39	6.58	182.2	5
4	23.47	219.7	6.57	7.26	161.5	13	57	21.70	149.8	2.37	6.58	182.3	4
5	23.22	212.8	6.47	7.24	162.1	8	58	21.70	149.7	2.36	6.57	182.5	6
6	22.69	197.8	6.23	7.21	162.2	10	59	21.70	149.7	2.33	6.57	182.7	6
7	22.4	189.2	5.58	7.15	163.4	8	60	21.70	149.9	2.33	6.56	183.0	5
8	22.28	185.1	5.40	7.11	164.4	7	61	21.70	149.8	2.33	6.56	183.2	3
9	22.15	180.4	5.30	7.08	165.3	4	62	21.70	150.4	2.32	6.54	184.0	2
10	22.07	178.1	5.16	7.06	166.0	6	63	21.70	150.6	2.28	6.53	184.5	2
11	21.99	175.1	5.06	7.04	166.7	5	64	21.71	151.5	2.22	6.52	184.7	2
12	21.9	171.3	4.91	7.02	166.9	6	65	21.71	152.3	2.12	6.51	185.2	2
13	21.86	171.1	4.75	7.00	167.9	4	66	21.71	152.7	1.99	6.49	185.7	2
14	21.84	169.7	4.77	6.98	168.1	6	67	21.72	154.3	1.87	6.47	186.1	1
15	21.82	167.9	4.65	6.97	168.5	7	68	21.73	156.3	1.72	6.45	186.2	2
16	21.8	165.4	4.49	6.94	169.4	4	69	21.74	161.6	1.42	6.41	130.4	2
17	21.79	163.4	4.33	6.93	169.8	6	70	21.76	168.2	1.08	6.35	83.00	2
18	21.8	162.9	4.18	6.90	171.1	2	71	21.77	174.2	0.88	6.30	69.70	1
19	21.8	162.1	4.05	6.90	170.6	8	72	21.78	180.6	0.75	6.24	62.45	2
20	21.8	160.8	3.85	6.87	171.4	5	73	21.79	186.5	0.65	6.19	57.20	1
21	21.8	158.8	3.80	6.86	172.0	4	74	21.82	205.6	0.58	6.13	54.80	2
22	21.7	157.0	3.63	6.85	172.1	7	75	21.85	228.6	0.51	6.03	51.65	2
23	21.7	156.4	3.45	6.83	172.7	6	76	21.90	252.7	0.43	5.91	46.27	7
24	21.7	154.6	3.36	6.81	173.5	5	77	21.94	275.7	0.40	5.82	42.03	9
25	21.7	152.8	3.28	6.79	174.2	3	78	21.98	298.2	0.36	5.75	36.60	11
26	21.7	151.8	3.19	6.78	174.6	4	79	21.99	314.7	0.41	5.71	32.57	3
27	21.7	151.5	3.03	6.77	174.7	5	80	22.01	328.2	0.41	5.70	30.65	2
28	21.7	151.3	2.90	6.75	175.3	6	81	22.05	382.2	0.40	5.64	29.83	3
29	21.7	151.1	2.86	6.74	175.8	4	82	22.10	425.0	0.39	5.60	28.40	2
30	21.7	150.8	2.84	6.73	176.3	3	83	22.12	452.1	0.39	5.58	26.70	2
31	21.7	150.4	2.80	6.72	176.7	4	84	22.15	502.9	0.38	5.55	25.50	2
32	21.7	150.1	2.73	6.71	176.8	4	85	22.21	551.9	0.38	5.52	23.43	3
33	21.7	150.4	2.64	6.70	177.0	6	86	22.24	579.8	0.39	5.51	20.50	3
34	21.7	149.9	2.61	6.69	177.5	3	87	22.27	615.4	0.40	5.50	17.67	3
35	21.7	149.3	2.63	6.68	177.9	3	88	22.31	640.6	0.41	5.49	14.73	3
36	21.7	149.3	2.66	6.68	177.8	3	89	22.35	656.3	0.41	5.48	12.00	2

37	21.7	149.1	2.68	6.68	178.2	5	90	22.37	666.8	0.41	5.47	9.95	2
38	21.7	149.2	2.68	6.67	178.3	4	91	22.40	684.8	0.42	5.47	7.95	2
39	21.7	148.8	2.68	6.67	178.5	4	92	22.42	690.5	0.42	5.46	5.85	2
40	21.7	149.2	2.67	6.66	178.8	3	93	22.43	692.1	0.43	5.46	3.80	2
41	21.7	149.3	2.67	6.66	179.0	4	94	22.43	693.2	0.43	5.46	1.80	2
42	21.7	149.4	2.64	6.65	179.3	3	95	22.45	699.2	0.43	5.46	0.50	1
43	21.7	149.5	2.61	6.65	179.5	4	96	22.49	722.3	0.43	5.45	-0.60	2
44	21.70	149.3	2.60	6.64	179.6	3	97	22.52	728.4	0.43	5.44	-2.50	2
45	21.70	149.5	2.59	6.63	180.2	2	98	22.53	729.6	0.43	5.43	-4.10	1
46	21.70	149.6	2.58	6.63	180.5	2	99	22.53	730.8	0.43	5.43	-5.55	2
47	21.70	149.7	2.56	6.62	180.6	3	100	22.54	733.1	0.43	5.43	-7.00	1
48	21.70	150.0	2.53	6.62	180.6	4	101	22.56	735.7	0.43	5.43	-8.40	2
49	21.70	149.7	2.49	6.62	180.8	4	102	22.57	738.5	0.43	5.43	-9.70	1
50	21.70	149.8	2.45	6.61	180.7	6	103	22.58	741.3	0.43	5.42	-11.05	2
51	21.70	149.9	2.43	6.61	181.1	5	104	22.60	744.7	0.43	5.42	-12.70	2
52	21.70	149.9	2.42	6.60	181.6	5	105	22.62	748.1	0.43	5.41	-13.80	1

Table B.1 : Nyos CTD 2012 (continued)

Depth	т	$C_{25}$	O <sub>2</sub>	pН	Eh	# Avg.	Depth	Т	$C_{25}$	O2	pН	Eh	# Avg.
(m)	(° C)	(µS/cm)	(mg/kg)				(m)	(° C)	(µS/cm)	(mg/kg)			
106	22.64	750.0	0.43	5.41	-15.05	2	159	23.41	967.6	0.60	5.30	-83.84	5
107	22.65	752.1	0.43	5.40	-16.40	1	160	23.42	970.2	0.60	5.29	-84.80	6
108	22.66	754.6	0.43	5.40	-17.55	2	161	23.44	974.5	0.60	5.29	-86.01	7
109	22.67	757.1	0.43	5.40	-19.20	2	162	23.45	978.6	0.60	5.29	-87.18	6
110	22.69	758.7	0.43	5.40	-20.80	2	163	23.46	981.5	0.61	5.29	-88.30	6
111	22.71	762.4	0.43	5.40	-22.30	2	164	23.47	982.6	0.61	5.29	-89.33	7
112	22.74	765.8	0.43	5.39	-23.75	2	165	23.47	984.8	0.61	5.29	-90.25	4
113	22.76	769.2	0.43	5.39	-25.05	2	166	23.48	989.3	0.62	5.29	-90.80	3
114	22.78	772.2	0.43	5.39	-26.40	2	167	23.50	991.4	0.62	5.29	-91.53	6
115	22.80	773.5	0.43	5.38	-28.15	4	168	23.51	994.4	0.62	5.29	-92.74	9
116	22.82	779.0	0.43	5.38	-30.27	3	169	23.52	997.0	0.63	5.29	-94.20	12
117	22.83	781.7	0.43	5.38	-32.07	3	170	23.53	999.6	0.63	5.29	-95.65	11
118	22.84	784.3	0.43	5.37	-33.45	2	171	23.54	1003	0.64	5.29	-96.96	10
119	22.86	788.4	0.43	5.37	-34.55	2	172	23.55	1005	0.64	5.29	-98.08	8
120	22.88	793.7	0.43	5.36	-35.40	1	173	23.56	1009	0.64	5.29	-99.29	12
121	22.89	798.0	0.43	5.36	-36.00	1	174	23.57	1011	0.64	5.29	-100.5	8
122	22.91	802.4	0.43	5.36	-37.00	2	175	23.58	1013	0.64	5.29	-101.6	12
123	22.93	806.9	0.43	5.36	-38.00	1	176	23.59	1016	0.64	5.29	-102.6	6
124	22.94	810.9	0.43	5.36	-38.90	2	177	23.60	1019	0.64	5.29	-103.2	6
125	22.96	815.2	0.43	5.36	-40.84	5	178	23.61	1020	0.64	5.28	-103.9	6

126	22.98	819.2	0.43	5.36	-43.78 <i>8</i>	179	23.62 1024	4 0.64	5.29	-104.6	7
127	23.00	828.0	0.44	5.36	-47.24 8	180	23.63 1020	6 0.64	5.29	-105.4	8
128	23.02	832.4	0.44	5.35	-49.85 4	181	23.65 1028	3 0.64	5.28	-106.1	6
129	23.04	838.4	0.44	5.35	-51.30 <i>3</i>	182	23.66 1030	0.64	5.28	-106.7	8
130	23.06	843.6	0.44	5.34	-52.40 <i>2</i>	183	23.67 1032	2 0.64	5.28	-107.2	5
131	23.07	848.0	0.44	5.34	-53.35 <i>2</i>	184	$23.67 \ 1034$	4 0.64	5.28	-107.7	6
132	23.08	851.5	0.44	5.34	-54.20 <i>2</i>	185	23.68 103	5 0.64	5.28	-108.2	7
133	23.10	856.5	0.44	5.34	-55.00 2	186	23.69 1038	3 0.64	5.28	-108.7	7
134	23.11	860.5	0.45	5.34	-55.80 2	187	23.71 1043	3 0.63	5.28	-109.1	5
135	23.12	865.7	0.45	5.34	-56.80 3	188	23.72 1040	6 0.63	5.28	-109.5	4
136	23.14	872.0	0.45	5.33	-57.70 <i>2</i>	189	23.74 1049	0.63	5.28	-109.9	5
137	23.15	876.9	0.45	5.33	-58.45 2	190	23.76 105	5 0.63	5.28	-110.3	6
138	23.17	881.9	0.45	5.33	-59.33 <i>3</i>	191	23.79 1063	0.63	5.27	-110.7	6
139	23.18	885.6	0.45	5.33	-60.25 <i>2</i>	192	23.82 1068	5 0.63	5.27	-111.1	7
140	23.19	889.1	0.46	5.32	-60.95 <i>2</i>	193	23.83 1064	4 0.64	5.26	-111.7	$\mathcal{G}$
141	23.21	894.3	0.46	5.32	-62.00 4	194	23.83 1063	0.64	5.26	-112.5	7
142	23.22	901.1	0.46	5.32	<b>-</b> 63.30 4	195	23.86 106'	0.64	5.25	-112.5	6
143	23.24	908.7	0.47	5.32	-64.25 <i>2</i>	196	23.89 1072	2 0.64	5.25	-112.6	7
144	23.25	912.9	0.47	5.32	-65.10 <i>3</i>	197	23.93 1074	4 0.64	5.24	-112.7	6
145	23.27	917.9	0.47	5.31	-66.10 <i>3</i>	198	23.96 107	0.65	5.23	-112.6	5
146	23.28	921.6	0.47	5.31	-67.25 4	199	24.00 1082	0.65	5.23	-112.6	10
147	23.29	925.7	0.48	5.31	-68.23 <i>3</i>	200	24.03 108	5 0.65	5.22	-112.7	6
148	23.30	929.6	0.48	5.31	-69.52 <i>6</i>	201	24.07 1090	0.65	5.21	-112.7	5
149	23.31	933.3	0.53	5.31	-71.17 7	202	24.09 1094	4 0.66	5.21	-112.7	6
150	23.32	936.9	0.57	5.31	-73.30 <i>9</i>	203	24.12 1099	0.66	5.20	-112.7	8
151	23.33	939.3	0.59	5.31	-75.08 5	204	24.17 1104	4 0.66	5.19	-112.6	5
152	23.34	943.1	0.59	5.30	-75.90 <i>3</i>	205	24.21 1110	0.66	5.19	-112.6	5
153	23.35	947.4	0.59	5.30	-76.55 $2$	206	24.30 112	0.67	5.18	-112.4	$\mathcal{G}$
154	23.36	951.3	0.59	5.30	-77.10 2	207	24.48 1178	5 0.67	5.17	-111.7	7
155	23.37	954.1	0.59	5.30	-78.27 7	208	24.67 127	0.67	5.15	-110.7	$\mathbf{\mathbf{\mathbf{6}}}$
156	23.38	957.4	0.59	5.30	-80.09 10	209	24.84 142	0.68	5.16	-109.6	4
157	23.39	960.7	0.59	5.30	-81.76 7	210	24.94 2089	0.69	5.31	-105.8	7
158	23.40	964.7	0.60	5.30	-82.95 6						

Table B.2 : Nyos CTD 2013

Depth	Т	C <sub>25</sub>	<b>O</b> 2	pН	Eh	# Avg.	Depth	Т	C <sub>25</sub>	O <sub>2</sub>	pН	Eh	#Avg.
(m)	(° C)	(µS/cm)	(mg/kg)				(m)	(° C)	(µS/cm)	(mg/kg)			
0	24.78	252.4	6.70	7.28	122.9	5	52	21.87	176.3	1.89	6.68	137.8	19
1	24.53	251.2	6.44	7.22	123.6	12	53	21.86	174.3	1.78	6.66	138.1	14
2	24.31	251.2	6.16	7.11	124.8	12	54	21.84	172.1	1.70	6.64	138.2	16
3	24.04	245.1	5.90	6.98	122.5	10	55	21.83	170.3	1.59	6.62	138.4	17
4	23.27	226.5	5.53	6.97	82.94	11	56	21.82	168.8	1.48	6.60	138.4	15
<b>5</b>	22.97	218.9	5.11	6.97	81.15	11	57	21.81	166.2	1.37	6.58	138.5	18
6	22.62	212.7	4.79	6.96	92.43	12	58	21.80	163.7	1.21	6.55	138.6	15
7	22.19	205.5	4.38	6.94	100.4	12	59	21.79	162.0	1.08	6.53	138.6	16
8	22.06	202.6	4.06	6.92	106.0	12	60	21.79	161.0	1.00	6.51	138.5	18
9	22.02	201.0	3.80	6.90	110.2	13	61	21.78	159.7	0.92	6.50	138.3	15
10	22.01	200.6	3.71	6.90	113.7	13	62	21.77	158.3	0.85	6.48	138.2	15
11	22.00	199.8	3.62	6.89	116.3	10	63	21.77	156.7	0.76	6.45	138.2	17
12	22.00	199.5	3.60	6.89	118.4	12	64	21.77	155.7	0.65	6.42	138.4	16
13	22.00	199.2	3.54	6.88	120.2	12	65	21.77	155.6	0.63	6.40	138.4	14
14	21.99	199.1	3.54	6.88	121.8	11	66	21.77	155.6	0.61	6.39	138.4	13
15	21.99	198.9	3.58	6.88	123.1	10	67	21.77	157.6	0.61	6.38	138.5	19
16	21.99	198.6	3.58	6.88	124.1	10	68	21.77	157.5	0.60	6.36	138.5	17
17	21.99	198.5	3.52	6.88	125.1	13	69	21.77	157.0	0.60	6.33	138.6	15
18	21.99	198.5	3.47	6.88	126.2	16	70	21.77	157.3	0.60	6.31	138.8	15
19	21.98	198.0	3.44	6.88	127.1	13	71	21.78	157.7	0.60	6.29	139.1	17
20	21.98	197.6	3.31	6.87	127.8	15	72	21.78	158.1	0.60	6.27	139.4	14
21	21.98	197.2	3.27	6.87	128.5	13	73	21.78	158.6	0.59	6.26	139.6	15
22	21.98	197.1	3.24	6.87	129.0	11	74	21.78	160.1	0.59	6.24	139.9	16
23	21.98	196.5	3.17	6.86	129.5	13	75	21.79	161.3	0.59	6.23	139.8	16
24	21.98	196.4	3.18	6.86	130.0	14	76	21.79	162.2	0.59	6.21	136.3	14
25	21.98	196.5	3.17	6.86	130.4	16	77	21.80	164.9	0.58	6.16	128.3	15
26	21.98	196.4	3.13	6.86	130.7	15	78	21.81	170.0	0.58	6.11	102.8	14
27	21.98	196.5	3.17	6.86	131.1	13	79	21.82	174.7	0.59	6.07	80.47	15
28	21.97	195.8	3.18	6.86	131.5	10	80	21.83	177.4	0.59	6.05	69.34	17
29	21.97	195.5	3.13	6.86	131.8	12	81	21.83	179.9	0.59	6.03	62.60	15
30	21.97	195.2	3.12	6.86	132.1	14	82	21.84	183.5	0.59	6.01	57.68	13
31	21.96	194.4	3.07	6.85	132.4	16	83	21.85	189.9	0.59	5.98	52.57	16
32	21.96	194.0	2.93	6.85	132.7	14	84	21.86	200.0	0.59	5.94	47.91	16
33	21.96	193.8	2.93	6.84	133.1	14	85	21.89	220.7	0.60	5.88	44.15	14
34	21.96	193.5	2.92	6.84	133.3	19	86	21.90	231.5	0.60	5.85	41.04	14
35	21.95	192.9	2.89	6.84	133.6	13	88	21.95	272.1	0.60	5.77	38.10	14
36	21.95	192.3	2.85	6.83	133.8	14	89	21.97	287.1	0.61	5.74	37.21	11
37	21.95	191.7	2.82	6.83	134.1	14	90	21.99	309.8	0.61	5.71	36.93	12

38	21.94	191.1	2.65	6.82	134.2	14	91	22.01	324.8	0.61	5.69	36.08	16
39	21.94	190.7	2.59	6.82	134.5	15	92	22.06	366.6	0.61	5.65	32.63	18
40	21.94	190.0	2.54	6.81	134.7	16	93	22.10	410.2	0.62	5.61	21.54	16
41	21.94	189.4	2.53	6.81	135.2	16	94	22.14	455.8	0.63	5.58	3.79	14
42	21.93	188.5	2.53	6.80	135.4	15	95	22.17	486.3	0.64	5.56	-14.20	13
44	21.92	187.2	2.37	6.78	136.0	17	96	22.20	519.1	0.65	5.54	-27.71	11
45	21.92	186.5	2.32	6.78	136.2	15	97	22.23	546.7	0.66	5.53	-39.65	11
46	21.91	185.2	2.27	6.76	136.5	14	98	22.26	574.4	0.67	5.52	-50.81	14
47	21.91	184.2	2.20	6.75	136.7	15	99	22.31	616.0	0.68	5.50	-58.66	14
48	21.90	183.0	2.16	6.74	136.9	23	100	22.33	637.6	0.72	5.50	-65.11	16
49	21.90	182.1	2.14	6.73	137.3	22	101	22.36	649.6	0.60	5.49	-72.07	20
50	21.89	180.7	2.10	6.72	137.5	16	102	22.37	657.9	0.65	5.49	-77.81	17
51	21.88	179.3	2.03	6.71	137.7	16	103	22.40	672.3	0.65	5.48	-82.50	16

Table B.2 (continued)

Depth	Т	C <sub>25</sub>	<b>O</b> <sub>2</sub>	pН	Eh	# Avg.	Depth	Т	C <sub>25</sub>	O2	pН	Eh	# Avg.
(m)	(° C)	(µS/cm)	(mg/kg)				(m)	(° C)	(µS/cm)	(mg/kg)			
104	22.42	684.5	0.65	5.48	-86.51	19	157	23.25	912.2	0.61	5.33	-137.7	15
105	22.44	691.8	0.66	5.47	-90.24	16	158	23.26	917.4	0.61	5.32	-138.0	12
106	22.45	695.0	0.67	5.47	-93.13	13	159	23.27	921.9	0.61	5.32	-138.1	13
107	22.47	698.2	0.67	5.47	-95.41	14	160	23.28	926.0	0.61	5.32	-138.2	13
108	22.51	716.1	0.66	5.46	-98.09	14	161	23.29	930.2	0.61	5.32	-138.0	12
109	22.54	729.0	0.66	5.45	-100.7	17	162	23.31	934.9	0.61	5.32	-137.8	12
110	22.55	733.2	0.66	5.45	-103.3	17	163	23.32	937.7	0.61	5.31	-137.5	12
111	22.56	736.1	0.65	5.44	-106.0	16	164	23.33	940.3	0.61	5.31	-137.3	12
112	22.58	739.7	0.65	5.44	-107.8	15	165	23.33	942.9	0.61	5.31	-137.4	17
113	22.60	743.5	0.65	5.44	-109.5	20	166	23.34	946.3	0.61	5.31	-137.8	19
114	22.61	746.6	0.65	5.44	-111.5	22	167	23.36	950.8	0.61	5.31	-137.8	18
115	22.62	750.2	0.65	5.43	-113.3	18	168	23.37	955.6	0.61	5.31	-137.3	17
116	22.64	753.1	0.65	5.43	-115.0	22	169	23.38	959.4	0.61	5.31	-137.0	17
117	22.66	756.3	0.64	5.42	-116.8	21	170	23.39	963.6	0.61	5.31	-136.9	21
118	22.67	758.9	0.64	5.42	-118.1	17	171	23.40	966.6	0.61	5.30	-136.7	17
119	22.68	762.0	0.63	5.42	-119.3	16	172	23.41	969.9	0.61	5.30	-136.5	18
120	22.69	764.1	0.64	5.42	-120.4	18	173	23.42	972.7	0.61	5.30	-136.5	19
121	22.70	765.6	0.63	5.42	-121.4	19	174	23.43	976.8	0.61	5.30	-136.4	16
122	22.71	767.9	0.62	5.41	-122.3	19	176	23.46	984.8	0.61	5.29	-136.4	16
123	22.73	771.2	0.62	5.41	-123.2	17	177	23.47	986.9	0.61	5.29	-136.5	15
124	22.74	774.4	0.62	5.41	-124.2	20	178	23.48	987.9	0.61	5.29	-136.6	15
125	22.76	777.0	0.62	5.41	-125.0	21	179	23.49	991.7	0.61	5.29	-137.2	18
126	22.77	780.1	0.61	5.40	-125.8	15	180	23.49	991.0	0.61	5.29	-137.0	13
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127	22.78	782.7	0.61	5.40	-126.5	15	181	23.51	995.6	0.61	5.29	-136.5	12
128	22.80	785.6	0.61	5.40	-127.4	14	182	23.52	1001	0.60	5.29	-136.3	13
129	22.82	790.5	0.61	5.39	-128.9	15	183	23.53	1004	0.60	5.29	-136.2	13
130	22.85	794.2	0.61	5.39	-130.4	15	184	23.54	1007	0.60	5.29	-136.2	18
132	22.88	799.4	0.61	5.38	-133.1	14	185	23.55	1009	0.60	5.28	-136.0	20
133	22.90	804.0	0.60	5.38	-134.3	15	186	23.56	1010	0.60	5.28	-135.8	15
134	22.91	806.8	0.60	5.38	-134.7	16	187	23.57	1013	0.61	5.28	-135.6	13
135	22.93	811.8	0.60	5.38	-135.0	15	188	23.59	1020	0.60	5.28	-135.6	13
136	22.95	818.2	0.60	5.37	-134.8	15	189	23.61	1025	0.60	5.28	-135.6	12
137	22.97	821.5	0.60	5.37	-134.3	13	190	23.62	1027	0.60	5.28	-135.6	13
138	22.98	825.3	0.60	5.37	-133.8	13	191	23.63	1029	0.60	5.28	-135.6	14
139	23.00	829.8	0.60	5.37	-133.5	16	192	23.64	1031	0.60	5.27	-135.6	13
140	23.02	835.1	0.60	5.36	-133.4	15	193	23.65	1034	0.61	5.27	-135.7	13
141	23.03	840.5	0.60	5.36	-133.4	13	194	23.67	1039	0.60	5.27	-135.7	12
142	23.05	846.0	0.60	5.36	-133.4	18	195	23.69	1042	0.60	5.27	-135.7	13
143	23.06	849.8	0.61	5.35	-133.2	18	196	23.70	1045	0.61	5.27	-135.8	15
144	23.08	854.6	0.61	5.35	-133.5	17	197	23.72	1047	0.61	5.26	-135.8	16
145	23.09	857.1	0.61	5.35	-133.8	14	198	23.75	1054	0.61	5.26	-135.8	14
146	23.10	861.3	0.60	5.35	-133.8	14	199	23.76	1056	0.61	5.26	-135.8	14
147	23.12	866.2	0.60	5.35	-133.8	16	200	23.77	1058	0.61	5.26	-135.9	15
148	23.14	872.1	0.60	5.34	-133.7	13	201	23.78	1059	0.61	5.25	-135.8	16
149	23.15	876.2	0.61	5.34	-133.7	12	202	23.80	1065	0.61	5.25	-135.7	18
150	23.16	882.9	0.61	5.34	-133.8	13	203	23.83	1074	0.61	5.25	-135.8	20
151	23.17	886.2	0.61	5.34	-133.9	14	204	23.90	1110	0.61	5.26	-135.9	21
152	23.18	889.2	0.61	5.34	-134.2	15	205	23.96	1153	0.61	5.27	-136.7	20
153	23.20	894.0	0.61	5.33	-135.0	16	206	24.01	1197	0.61	5.28	-137.6	19
154	23.21	898.4	0.61	5.33	-135.9	17	207	24.09	1289	0.62	5.30	-139.1	21
155	23.22	902.1	0.61	5.33	-136.6	15	208	24.15	1636	0.62	5.39	-139.5	26
156	23.24	906.6	0.61	5.33	-137.2	16	209	24.26	2155	0.61	5.45	-141.1	75

Table B.3 : CTD Monoun April-2012

Depth	Т	C <sub>25</sub>	O <sub>2</sub>	pН	Eh	# Avg.	Depth	Т	$C_{25}$	O <sub>2</sub>	pН	Eh	# Avg.
(m)	(° C)	(µS/cm)	(mg/kg)				(m)	(° C)	(µS/cm)	(mg/kg)			
0	25.00	105.5	4.22	7.94	-35.70	102	50	19.70	179.4	0.03	6.56	-114.0	13
1	25.00	125.1	4.08	7.71	-20.13	83	51	19.75	206.8	0.03	6.53	-112.7	13
2	24.78	125.1	3.60	7.68	-9.875	40	52	19.76	209.9	0.03	6.53	-113.8	13
3	24.10	124.7	3.32	7.53	-2.422	9	53	19.80	229.3	0.03	6.52	-113.3	13
4	23.33	124.3	2.22	7.26	2.256	9	54	19.87	261.7	0.04	6.50	-112.6	15
<b>5</b>	22.14	129.4	1.11	7.03	5.555	11	55	19.98	322.3	0.04	6.46	-110.7	16
6	20.94	140.7	0.46	6.79	-6.323	13	56	20.00	334.4	0.04	6.46	-111.2	15

7	20.36	146.2	0.24	6.65	-30.01	14	57	20.00	334.9	0.05	6.47	-111.8	16
8	20.19	147.8	0.13	6.58	-41.80	13	58	20.03	349.9	0.05	6.47	-111.6	16
9	20.11	147.0	0.09	6.56	-51.59	14	59	20.04	354.4	0.05	6.47	-111.9	12
10	20.06	147.8	0.07	6.56	-60.88	12	60	20.06	363.9	0.05	6.46	-111.7	13
11	20.01	147.8	0.06	6.56	-67.99	17	61	20.09	376.5	0.05	6.45	-111.5	14
12	19.96	146.9	0.05	6.57	-73.37	13	62	20.09	377.8	0.06	6.45	-111.8	13
13	19.93	146.3	0.05	6.59	-77.39	13	63	20.13	394.9	0.06	6.43	-111.0	14
14	19.88	145.0	0.04	6.60	-81.03	14	64	20.15	405.3	0.06	6.42	-110.7	14
15	19.83	143.5	0.03	6.62	-84.28	15	65	20.21	423.5	0.06	6.39	-109.9	15
16	19.77	142.9	0.03	6.63	-87.24	16	66	20.26	442.7	0.06	6.37	-109.1	12
17	19.76	145.5	0.03	6.63	-89.57	15	67	20.32	461.5	0.06	6.35	-108.5	16
18	19.72	147.0	0.03	6.63	-91.61	13	68	20.37	478.2	0.06	6.33	-108.0	17
19	19.69	148.2	0.03	6.62	-93.41	15	69	20.43	499.3	0.07	6.31	-107.2	16
20	19.68	148.3	0.03	6.63	-95.15	16	70	20.49	521.2	0.07	6.28	-106.3	15
21	19.67	148.6	0.03	6.62	-96.55	13	71	20.56	546.2	0.07	6.26	-105.4	17
22	19.66	149.1	0.03	6.62	-97.58	11	72	20.63	582.9	0.08	6.23	-104.0	16
23	19.65	149.8	0.03	6.62	-98.50	11	73	20.72	639.6	0.08	6.19	-102.1	14
<b>24</b>	19.64	149.5	0.03	6.62	-99.30	12	74	20.79	685.2	0.08	6.16	-100.8	12
25	19.63	148.6	0.03	6.61	-99.97	13	75	20.89	764.2	0.09	6.11	-98.56	14
26	19.62	148.5	0.03	6.61	-100.5	15	76	21.01	844.9	0.10	6.07	-96.52	14
27	19.62	148.7	0.03	6.60	-101.3	17	77	21.13	939.7	0.11	6.03	-94.52	17
28	19.62	149.1	0.03	6.60	-101.8	12	78	21.28	1050	0.12	5.98	-92.31	18
29	19.62	151.5	0.03	6.58	-101.7	14	79	21.45	1173	0.13	5.93	-89.97	18
30	19.63	153.7	0.03	6.57	-101.7	14	80	21.65	1342	0.14	5.87	-86.85	18
31	19.63	155.5	0.03	6.56	-102.2	17	81	21.97	1631	0.16	5.77	-81.41	17
32	19.64	158.0	0.03	6.55	-102.7	13	82	22.07	1683	0.17	5.75	-81.42	16
33	19.65	162.2	0.03	6.55	-103.4	17	83	22.09	1694	0.15	5.75	-82.12	17
34	19.66	164.6	0.03	6.55	-104.1	14	84	22.12	1698	0.13	5.75	-82.78	17
35	19.69	176.7	0.03	6.53	-104.2	13	85	22.14	1702	0.12	5.75	-83.60	16
36	19.70	178.3	0.04	6.54	-105.7	17	86	22.15	1705	0.11	5.75	-84.38	13
37	19.70	178.3	0.04	6.55	-106.6	18	87	22.16	1708	0.10	5.75	-85.12	15
38	19.70	178.3	0.04	6.56	-107.5	14	88	22.17	1709	0.09	5.75	-85.83	15
39	19.70	178.4	0.04	6.56	-108.2	15	89	22.17	1711	0.08	5.75	-86.55	14
40	19.70	178.4	0.04	6.56	-108.9	14	90	22.19	1716	0.07	5.75	-87.32	13
41	19.70	178.4	0.03	6.56	-109.6	16	91	22.23	1727	0.07	5.76	-88.33	17
42	19.70	178.5	0.03	6.56	-110.2	15	92	22.35	1788	0.07	5.77	-90.14	13
43	19.70	178.5	0.03	6.56	-110.8	14	93	22.61	1917	0.07	5.78	-94.45	19
44	19.70	178.7	0.03	6.56	-111.3	13	94	22.78	2006	0.06	5.79	-99.26	31
45	19.70	178.9	0.03	6.56	-111.7	12	95	23.02	2169	0.06	5.81	-105.4	29
46	19.70	178.8	0.03	6.56	-112.2	12	96	23.21	2288	0.06	5.82	-110.7	23
47	19.70	178.8	0.03	6.56	-112.7	14	97	23.43	2664	0.06	5.90	-126.2	29
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48	$19.70\ 178.7$	0.03	6.56	-113.2 15	98	23.53	3110	0.05	5.95	-152.2 5
49	$19.70\ 178.8$	0.03	6.56	-113.6 13	-					

## Table B.4 : CTD Monoun Dec- 2013

Depth	Т	C <sub>25</sub>	O2	pН	Eh	# Avg.	Depth	Т	C <sub>25</sub>	O2	pН	Eh	# Avg.
(m)	(° C)	(µS/cm)	(mg/kg)				(m)	(° C)	(µS/cm)	(mg/kg)			
1	24.75	130.1	104.6	7.48	31.87	6	50	19.82	215.9	0.65	6.56	-146.3	11
2	24.24	129.3	93.41	7.43	38.57	6	51	19.83	219.7	0.61	6.55	-146.3	9
3	23.64	128.8	35.93	7.35	45.21	7	52	19.85	227.9	0.58	6.53	-146.0	12
4	22.71	136.3	29.03	7.19	26.91	9	53	19.87	238.2	0.54	6.51	-145.5	10
5	21.58	146.3	13.38	6.96	-43.62	9	54	19.90	255.0	0.50	6.48	-144.1	11
6	21.00	147.8	7.92	6.84	-68.26	9	55	19.93	271.3	0.48	6.44	-143.0	12
7	20.67	146.9	5.69	6.76	-77.54	12	56	19.97	287.0	0.46	6.42	-143.0	15
8	20.55	146.9	4.86	6.70	-82.74	14	57	19.99	296.7	0.46	6.41	-143.5	13
9	20.51	149.0	4.01	6.66	-83.01	11	58	20.02	312.5	0.44	6.40	-144.1	12
10	20.46	147.0	3.61	6.66	-92.24	11	59	20.05	326.5	0.43	6.40	-144.9	15
11	20.41	144.6	3.41	6.66	-98.11	12	60	20.10	348.6	0.42	6.38	-145.2	14
12	20.39	143.5	3.23	6.66	-101.8	10	61	20.14	360.7	0.47	6.37	-145.6	15
13	20.35	142.6	3.07	6.67	-105.0	11	62	20.17	371.8	0.49	6.36	-145.6	14
14	20.31	142.4	2.94	6.67	-108.3	13	63	20.21	381.7	0.46	6.35	-145.6	16
15	20.27	142.3	2.95	6.68	-111.8	12	64	20.22	386.3	0.42	6.34	-146.0	16
16	20.22	144.2	2.75	6.67	-114.5	12	65	20.24	392.4	0.40	6.34	-146.2	17
17	20.19	146.2	2.66	6.68	-117.5	13	66	20.28	406.7	0.36	6.32	-145.7	12
18	20.17	147.1	2.55	6.68	-120.0	11	67	20.31	415.4	0.38	6.30	-145.7	17
19	20.14	151.5	2.49	6.67	-121.9	11	68	20.34	428.7	0.37	6.29	-145.2	10
20	20.11	155.1	2.33	6.67	-124.7	11	69	20.42	452.3	0.37	6.26	-143.9	15
21	20.08	157.7	2.13	6.67	-127.2	12	70	20.49	476.5	0.36	6.23	-142.9	13
22	20.06	159.2	2.02	6.67	-129.3	13	71	20.55	498.0	0.37	6.20	-142.0	11
23	20.03	164.5	2.03	6.67	-131.2	12	72	20.61	519.5	0.37	6.18	-141.1	12
24	19.99	171.8	1.80	6.66	-133.4	9	73	20.68	547.3	0.36	6.15	-139.9	13
25	19.94	180.5	1.56	6.66	-136.0	11	74	20.76	578.4	0.37	6.12	-138.7	12
26	19.89	186.4	1.47	6.66	-138.3	13	75	20.86	620.7	0.39	6.08	-137.1	11
27	19.86	188.7	1.49	6.67	-140.2	13	76	21.03	694.4	0.40	6.02	-133.9	12
28	19.85	189.6	1.51	6.68	-141.3	11	77	21.20	769.4	0.45	5.96	-131.3	14
29	19.83	190.1	1.35	6.67	-141.9	12	78	21.36	833.2	0.48	5.91	-129.2	14
30	19.81	190.5	1.26	6.67	-142.3	11	79	21.61	950.8	0.50	5.83	-124.6	17
31	19.80	191.1	1.30	6.67	-142.5	11	80	21.91	1249	0.59	5.68	-116.4	15
32	19.79	191.7	1.30	6.66	-142.7	12	81	22.07	1393	0.71	5.62	-115.2	12
33	19.78	192.4	1.26	6.65	-142.7	15	82	22.10	1404	0.75	5.62	-115.9	15
34	19.77	193.1	1.18	6.65	-142.9	14	83	22.12	1407	0.71	5.61	-116.4	16
35	19.77	193.9	1.17	6.63	-142.5	13	84	22.13	1409	0.69	5.61	-117.0	20

Geochemical characteristics of the CVL lakes

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36	$19.77 \ 195.7$	1.07	6.62	-142.3 <i>11</i>	85	22.14	1412	0.65	5.61	-117.7 <i>21</i>
37	$19.77 \ 196.9$	1.05	6.61	-142.6 <i>13</i>	86	22.15	1415	0.61	5.61	-118.1 20
38	$19.77 \ 199.0$	0.96	6.60	-142.7 <i>13</i>	87	22.15	1418	0.60	5.61	-118.5 <i>18</i>
39	$19.77 \ 200.4$	0.94	6.60	-142.9 14	88	22.16	1423	0.56	5.61	-119.3 <i>17</i>
40	$19.78\ 201.0$	0.89	6.59	-143.2 <i>13</i>	89	22.16	1426	0.55	5.61	-119.8 14
41	$19.78\ 201.9$	0.87	6.59	-143.5 <i>11</i>	90	22.17	1429	0.53	5.61	-120.3 <i>15</i>
42	$19.78\ 202.8$	0.86	6.58	-143.8 <i>10</i>	91	22.17	1429	0.52	5.61	-120.6 <i>25</i>
43	$19.78\ 203.4$	0.87	6.58	-144.1 <i>13</i>	92	22.17	1430	0.51	5.61	-120.9 <i>15</i>
44	$19.79\ 204.4$	0.87	6.58	-144.3 <i>12</i>	93	22.25	1455	0.52	5.62	-122.4 <i>20</i>
45	$19.79\ 205.3$	0.79	6.57	-144.6 10	94	22.52	1614	0.63	5.66	-129.1 17
46	$19.79\ 206.0$	0.76	6.57	-145.1 <i>12</i>	95	22.85	1768	0.58	5.68	-136.7 <i>17</i>
47	$19.80 \ 207.1$	0.72	6.57	-145.6 <i>11</i>	96	23.13	1896	0.57	5.69	-143.1 14
48	19.80 208.8	0.68	6.57	-145.9 <i>12</i>	97	23.35	2018	0.57	5.71	-149.4 21
49	19.81 211.5	0.66	6.56	-146.0 <i>10</i>	98	23.58	2175	0.56	5.74	-159.6 17

Table B.5 : CTD L. Benakuma April 2013

Depth	ιT	C <sub>25</sub>	# Avg.	Depth	T	C <sub>25</sub>	# Avg.	Depth	Т	C <sub>25</sub>	# Avg.	Depth	Т	C <sub>25</sub>	# Avg.
(m)	(° C)	(µS/cm)	)	(m)	(° C)	(µS/cm)		(m)	(° C)	(µS/cm)		(m)	(° C)	(µS/cm)	
0	28.73	63.30	4	44	24.39	229.9	3	88	24.18	294.5	2	132	24.16	317.8	2
1	28.65	63.28	4	45	24.38	233.5	3	89	24.18	295.2	3	133	24.16	318.8	3
2	28.59	63.18	6	46	24.36	235.9	2	90	24.18	296.5	2	134	24.16	319.8	2
3	28.54	63.09	5	47	24.36	239.3	5	91	24.18	297.3	2	135	24.16	321.0	2
4	28.51	63.15	5	48	24.34	243.2	3	92	24.17	298.0	2	136	24.16	322.8	2
<b>5</b>	28.49	62.96	9	49	24.32	247.6	3	93	24.17	298.6	2	137	24.16	323.5	2
6	28.46	62.99	5	50	24.31	251.1	3	94	24.17	299.5	3	138	24.16	324.7	3
7	28.43	63.11	3	51	24.30	254.3	4	95	24.17	300.6	2	139	24.16	324.6	2
8	28.35	63.14	4	52	24.29	257.4	4	96	24.17	301.0	2	140	24.16	325.4	13
9	28.27	63.14	3	53	24.28	260.9	3	97	24.17	301.7	3				
10	27.88	63.47	4	54	24.27	263.8	3	98	24.17	301.9	2				
11	27.38	63.86	3	55	24.26	265.8	3	99	24.17	302.3	3				
12	27.00	64.01	4	56	24.25	267.6	2	100	24.17	302.8	3				
13	26.79	64.02	3	57	24.25	268.9	4	101	24.17	303.1	3				
14	26.63	63.91	3	58	24.24	270.3	3	102	24.17	303.4	3				
15	26.43	63.97	4	59	24.24	271.3	3	103	24.17	304.2	3				
16	26.31	64.04	2	60	24.24	272.6	3	104	24.17	271.1	3				
17	26.23	63.95	4	61	24.23	274.0	3	105	24.17	306.0	3				
18	26.15	63.93	3	62	24.23	275.5	3	106	24.17	306.0	3				
19	26.08	64.42	4	63	24.22	276.9	3	107	24.17	306.8	3				
20	26.03	65.16	4	64	24.22	278.4	2	108	24.17	307.2	4				
21	26.00	65.70	4	65	24.21	279.5	3	109	24.17	307.7	3				
22	25.97	65.78	2	66	24.21	280.7	2	110	24.16	308.1	3				

23	25.94	65.78	3	67	24.21	281.9	3	111	$24.16 \ 308.7$	3
24	25.86	65.47	3	68	24.20	282.8	3	112	$24.16 \ 309.7$	4
25	25.74	72.44	3	69	24.20	283.3	3	113	$24.16 \ 310.4$	3
26	25.67	76.23	2	70	24.20	283.5	3	114	24.16 310.3	3
27	25.51	85.20	3	71	24.20	283.9	2	115	$24.16 \ 310.4$	4
28	25.35	99.36	2	72	24.20	284.3	3	116	$24.16 \ 311.2$	4
29	25.24	107.6	3	73	24.20	285.0	2	117	$24.16 \ 311.7$	4
30	25.13	116.1	3	74	24.20	285.6	3	118	$24.16 \ 312.1$	5
31	25.01	128.0	2	75	24.19	286.5	2	119	$24.16 \ 312.4$	5
32	24.89	143.2	3	76	24.19	286.8	2	120	$24.16 \ 312.5$	5
33	24.80	157.8	3	77	24.19	287.0	2	121	$24.16 \ 313.2$	3
34	24.72	170.2	3	78	24.19	287.8	3	122	$24.16 \ 313.9$	4
35	24.69	175.4	3	79	24.19	288.6	2	123	$24.16 \ 314.6$	3
36	24.65	179.2	3	80	24.19	288.9	3	124	$24.16 \ 314.9$	5
37	24.61	188.1	3	81	24.19	289.8	2	125	$24.16 \ 315.4$	5
38	24.56	195.2	3	82	24.19	290.1	2	126	$24.16 \ 316.3$	4
39	24.51	204.2	3	83	24.19	291.6	3	127	$24.16 \ 316.7$	3
40	24.47	213.1	3	84	24.18	292.7	2	128	$24.16 \ 316.9$	8
41	24.44	218.7	3	85	24.18	293.3	2	129	$24.16 \ 317.0$	3
42	24.42	222.5	2	86	24.18	293.7	3	130	$24.16 \ 317.4$	3
43	24.41	226.4	3	87	24.18	293.8	2	131	$24.16 \ 317.6$	2

Depth	Temp	Cond	O <sub>2</sub>	pH	Eh	Depth	Temp	Cond	O <sub>2</sub>	pH	Eh
(m)	(°C)	(µS/cm)	mg/L			(m)	(°C)	(µS/cm)	mg/L		
1	27.6	57.7	9.0	7.3	112.8	68	24.2	289	0.2	6.4	-102
2	27.5	57.8	8.7	7.4	107.5	69	24.2	290	0.2	6.4	-103
3	27.5	57.8	8.7	7.4	105.3	70	24.2	291	0.2	6.4	-104
4	27.4	57.7	8.8	7.4	103.7	71	24.2	292	0.2	6.4	-105
5	27.4	57.7	8.8	7.4	102.3	72	24.2	293	0.2	6.4	-106
6	27.4	57.7	8.8	7.4	101.0	73	24.2	294	0.2	6.4	-107
7	27.4	57.8	8.9	7.4	99.8	74	24.2	294	0.2	6.4	-108
8	27.4	57.7	9.0	7.5	98.7	75	24.2	295	0.2	6.4	-109
9	27.4	57.7	9.0	7.5	97.7	76	24.2	295	0.1	6.4	-110
10	27.4	57.8	9.0	7.5	95.4	77	24.2	295	0.2	6.4	-110
11	27.4	57.8	9.0	7.5	93.6	78	24.2	296	0.1	6.4	-111
12	27.4	57.9	9.1	7.5	93.2	79	24.2	297	0.1	6.4	-112
13	27.4	57.8	9.1	7.5	92.5	80	24.2	298	0.2	6.4	-113
14	27.4	57.7	9.2	7.5	92.0	81	24.2	298	0.2	6.4	-113
15	27.4	57.8	9.2	7.5	91.5	82	24.2	299	0.2	6.4	-114

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16	27.4	57.8	9.2	7.5	91.0	83	24.2	300	0.1	6.4	-114
17	27.3	58.2	9.3	7.5	91.8	84	24.2	300	0.1	6.4	-115
18	27.0	59.7	7.7	7.3	94.9	85	24.2	301	0.1	6.4	-116
19	26.9	60.4	5.0	7.2	97.3	86	24.2	302	0.1	6.4	-116
20	26.8	61.3	3.1	7.1	99.3	87	24.2	303	0.2	6.4	-117
21	26.6	62.1	1.9	7.0	101	88	24.2	304	0.1	6.4	-118
22	26.4	65.4	1.2	6.9	104	89	24.2	304	0.1	6.4	-119
23	26.2	69.1	0.8	6.8	107	90	24.2	304	0.1	6.4	-120
24	26.0	78.6	0.6	6.7	110	91	24.2	305	0.1	6.4	-120
25	25.7	97.5	0.4	6.6	115	92	24.2	305	0.1	6.4	-121
26	25.5	111	0.4	6.6	117	93	24.2	306	0.1	6.4	-121
27	25.3	123	0.3	6.5	116	94	24.2	305	0.1	6.4	-122
28	25.2	134	0.2	6.5	82.3	95	24.2	306	0.1	6.4	-122
29	25.1	143	0.2	6.5	50.5	96	24.2	307	0.1	6.4	-123
30	25.0	151	0.2	6.5	30.0	97	24.2	307	0.1	6.4	-123
31	24.9	162	0.1	6.5	18.6	98	24.2	308	0.1	6.4	-123
32	24.8	173	0.1	6.4	12.5	99	24.2	308	0.1	6.4	-124
33	24.7	180	0.1	6.4	6.3	100	24.2	308	0.1	6.4	-124
34	24.7	188	0.1	6.4	1.3	101	24.2	308	0.1	6.4	-125
35	24.6	197	0.1	6.4	-3.0	102	24.2	309	0.1	6.4	-125
36	24.6	204	0.1	6.4	-6.9	103	24.2	310	0.1	6.4	-125
37	24.5	211	0.2	6.4	-11.6	104	24.2	310	0.1	6.4	-126
38	24.5	218	0.1	6.4	-20.7	105	24.2	311	0.1	6.4	-126
39	24.5	222	0.1	6.4	-29.2	106	24.2	311	0.1	6.4	-126
40	24.4	228	0.1	6.4	-35.9	107	24.2	311	0.1	6.4	-127
41	24.4	232	0.1	6.4	-41.6	108	24.2	312	0.1	6.4	-127
42	24.4	236	0.1	6.4	-47.6	109	24.2	312	0.1	6.4	-127
43	24.4	242	0.2	6.4	-52.3	110	24.2	312	0.1	6.4	-128
44	24.3	246	0.1	6.4	-56.9	111	24.2	313	0.1	6.4	-128
45	24.3	250	0.2	6.4	-61.3	112	24.2	314	0.1	6.4	-128
46	24.3	252	0.2	6.4	-63.5	113	24.2	315	0.1	6.4	-129
47	24.3	255	0.1	6.4	-64.7	114	24.2	315	0.1	6.4	-129
48	24.3	257	0.1	6.4	-67.8	115	24.2	315	0.1	6.4	-129
49	24.3	261	0.2	6.4	-70.6	116	24.2	316	0.1	6.4	-130
50	24.3	263	0.2	6.4	-73.2	117	24.2	316	0.1	6.4	-130
51	24.3	264	0.1	6.4	-76.0	118	24.2	317	0.1	6.4	-130
52	24.3	266	0.2	6.4	-78.2	119	24.2	318	0.1	6.3	-130
53	24.3	269	0.1	6.4	-80.2	120	24.2	319	0.1	6.3	-131
54	24.3	271	0.1	6.4	-82.1	121	24.2	319	0.1	6.3	-131
55	24.2	272	0.2	6.4	-84.0	122	24.2	320	0.1	6.3	-131
56	24.2	273	0.2	6.4	-86.0	123	24.2	320	0.1	6.3	-132

57	24.2	275	0.1	6.4	-87.8	124	24.2	321	0.1	6.3	-132
58	24.2	276	0.2	6.4	-89.4	125	24.2	321	0.1	6.3	-132
59	24.2	277	0.2	6.4	-90.9	126	24.2	321	0.1	6.3	-132
60	24.2	279	0.2	6.4	-92.5	127	24.2	321	0.1	6.3	-133
61	24.2	281	0.2	6.4	-93.9	128	24.2	322	0.1	6.3	-133
62	24.2	282	0.2	6.4	-95.2	129	24.2	322	0.1	6.3	-133
63	24.2	284	0.1	6.4	-96.5	130	24.2	323	0.1	6.3	-133
64	24.2	285	0.1	6.4	-97.5	131	24.2	324	0.1	6.3	-134
65	24.2	286	0.2	6.4	-98.7	132	24.2	325	0.1	6.3	-134
66	24.2	288	0.2	6.4	-99.9	133	24.2	327	0.1	6.3	-134
67	24.2	288	0.2	6.4	-101	134	24.2	378	0.1	6.3	-131

Table B.7 : CTDs

	Elum	Apri	1		Idjag	gham	(May	7			Lake	Baleng,	Apri	1	
	2013				2013	)					2013				
Dept h	Т	C <sub>25</sub>	# Avg.	Dept h	т	C25	# Avg.	Dept h	т	C <sub>25</sub>	# Avg.	Depth	Т	C <sub>25</sub>	# Avg.
 (m)	(° C)	(µS/cm)	8	(m)	- (° C)	(μS/cm)		(m)	(° C)	(µS/cm )		(m)	(° C)	(µS/cm )	8
0	26.8	60.1	7	0	31.4	7.09	6	0	25.7	7215	6	44	22.7	301	2
1	26.7	60.1	$\mathcal{G}$	1	31.3	7.11	11	1	25.7	7214	12	45	22.7	301	2
2	26.7	60.2	9	2	31.3	7.03	3	2	25.6	5214	11	46	22.7	301	2
3	26.7	60.2	8	3	31.3	7.08	3	3	25.6	5214	9	47	22.7	301	3
4	26.7	60.1	11	4	31.2	6.98	2	4	25.5	5214	8	48	22.7	301	4
<b>5</b>	26.6	60.2	10	<b>5</b>	31.2	6.98	3	5	25.5	5214	<b>5</b>	49	22.7	301	17
6	26.0	61.6	7	6	31.1	6.99	2	6	25.4	1215	4	50	22.7	301	6
7	24.8	63.1	11	7	31.0	7.04	5	7	24.9	9219	3	51	22.7	301	8
8	24.3	64.0	9	8	31.0	7.08	5	8	24.3	3220	3	52	22.7	302	7
9	24.1	65.7	10	9	30.9	7.25	3	9	24.1	220	3	53	22.7	302	6
10	24.0	65.7	$\mathcal{9}$	10	30.7	8.12	3	10	23.8	3220	<b>5</b>	54	22.7	303	<b>5</b>
11	23.9	65.7	$\mathcal{G}$	11	30.5	11.0	3	11	23.7	7220	4	55	22.7	307	<b>5</b>
12	23.9	65.6	11	12	30.2	14.9	$\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{$	12	23.5	5221	9	56	22.7	336	13
13	23.8	65.7	11	13	29.9	24.5	6	13	23.3	3222	3				
14	23.8	67.8	11	14	29.8	34.3	4	14	23.2	2224	<b>5</b>				
15	23.7	71.1	8	15	29.7	37.8	4	15	23.1	226	4				
16	23.6	74.4	7	16	29.7	48.5	5	16	23.0	) 228	4				
17	23.5	82.7	10	17	29.5	91.9	6	17	22.9	9232	4				
18	23.3	89.9	9					18	22.8	0.235	3				
19	23.2	100	7					19	22.9	9238	3				
20	23.2	107	10					20	22.8	3242	3				
21	23.1	113	13					21	22.8	3244	2				
22	23.1	119	10					22	22.8	3247	<b>5</b>				
23	23.1	123	12					23	22.8	3253	3				
24	23.1	127	12					24	22.8	3260	3				
25	23.1	133	14					25	22.8	3265	3				
26	23.1	135	9					26	22.7	7273	3				

27	23.1	139	11	27	22.7280	11
28	23.1	144	12	28	22.7287	3
29	23.1	149	11	29	22.7292	3
30	23.1	153	11	30	22.7294	4
31	23.1	156	12	31	22.7297	3
32	23.1	159	11	32	22.7299	3
33	23.1	161	11	33	22.7300	3
34	23.1	163	11	34	22.7300	3
35	23.1	199	16	35	22.7301	3
				36	22.7301	2
				37	22.7301	3
				38	22.7301	2
				39	22.7301	3
				40	22.7301	3
				41	22.7301.0	3
				42	22.7301.2	2
				43	22.7301.1	3

Table B.8 : CTD Lake Oku taken in 2011 (July) and 2013 (May)

Depth	Т	$C_{25}$	# Avg.	Depth	Т	C <sub>25</sub>	# Avg.
(m)	(° C)	(µS/cm)		(m)	(° C)	(µS/cm)	
0	18.9	27.52	4	0	19.4	27.22	4
1	18.8	27.57	7	1	19.4	27.17	9
2	18.8	27.54	8	2	19.4	27.23	7
3	18.8	27.56	8	3	19.4	27.20	6
4	18.8	27.50	9	4	19.4	27.21	7
5	18.7	27.50	7	5	19.4	27.23	7
6	18.7	27.49	9	6	19.4	27.23	9
7	18.7	27.51	8	7	19.4	27.13	7
8	18.7	27.47	9	8	19.3	27.28	5
9	18.7	27.52	9	9	19.3	27.26	4
10	18.7	27.56	9	10	19.3	27.36	5
11	18.7	27.48	8	11	19.3	27.18	6
12	18.7	27.50	7	12	19.2	27.33	6
13	18.7	27.50	7	13	19.1	27.31	6
14	18.7	27.48	7	14	19.1	27.28	5
15	18.7	27.62	7	15	19.1	27.27	4
16	18.7	27.44	7	16	19.1	27.30	5
17	18.7	27.47	6	17	19.0	27.34	7
18	18.7	27.51	7	18	19.0	27.32	5
19	18.7	27.50	7	19	19.0	27.34	5
20	18.7	27.52	5	20	19.0	27.22	5
21	18.7	27.44	7	21	18.9	27.44	5
22	18.7	27.50	8	22	18.8	27.49	4
23	18.7	27.45	8	23	18.7	27.62	5
24	18.7	27.56	7	24	18.6	27.70	4
25	18.7	27.54	8	25	18.6	27.70	4
26	18.7	27.52	8	26	18.5	27.72	4
27	18.7	27.55	7	27	18.5	27.84	4

28	18.7	27.54	9	28	18.5	27.81	4	
29	18.7	27.57	8	29	18.5	27.91	4	
30	18.7	27.57	8	30	18.5	27.97	4	
31	18.7	27.65	$\mathcal{G}$	31	18.4	28.12	4	
32	18.7	27.72	$\mathcal{G}$	32	18.4	28.22	4	
33	18.6	28.24	$\mathcal{G}$	33	18.4	28.34	5	
34	18.5	28.70	8	34	18.4	28.35	5	
35	18.5	29.05	8	35	18.4	28.48	4	
36	18.4	29.74	8	36	18.4	28.43	5	
37	18.3	30.34	7	37	18.4	28.73	5	
38	18.3	30.76	10	38	18.4	29.05	5	
39	18.3	30.94	7	39	18.4	29.04	5	
40	18.3	31.02	9	40	18.4	29.12	<b>6</b>	
41	18.3	31.32	8	41	18.4	29.14	5	
42	18.3	67.27	10	42	18.4	29.16	6	
				43	18.4	29.31	4	
				44	18.4	29.53	4	
				45	18.4	29.88	5	
				46	18.4	30.11	4	
				47	18.4	30.34	6	
				48	18.4	35.93	5	

Table B.9 : CTD data f	for The Manenguba	twin lakes
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	Manenguba Female (May 2012)										1	Manengub	a Male (Ma	ay 2013)					
Deptl	ıТ	C <sub>25</sub>	# Avg	Depth	Т	C <sub>25</sub>	# Avg.	Depth	ъT	C <sub>25</sub>	# Avg.	Depth	ιT	C <sub>25</sub>	# Avg.	Depth	Т	C <sub>25</sub>	# Avg.
(m)	(° C)	(µS/cm)	)	(m)	(° C)	(µS/cm)	)	(m)	(° C)	(µS/cm)		(m)	(° C)	(µS/cm)		(m)	(° C)	(µS/cm	)
0	22.1	37.5	2	46	19.6	47.0	4	92	19.5	65.1	5	0	20.13	103	1	47	17.2	105	4
1	22.1	37.6	2	47	19.6	48.1	3	93	19.5	65.1	3	1	18.58	101	1	48	17.2	105	6
2	22.1	37.5	1	48	19.6	48.6	3	94	19.5	65.4	3	2	17.93	102	1	49	17.2	105	3
3	22.0	37.4	2	49	19.6	49.0	3	95	19.5	65.5	5	3	17.59	102	2	50	17.2	105	3
4	22.0	37.5	1	50	19.6	49.6	3	96	19.5	65.7	5	4	17.50	103	7	51	17.2	105	3
5	22.0	37.5	$\mathcal{L}$	51	19.6	50.1	2	97	19.5	65.7	3	<b>5</b>	17.27	104	4	52	17.2	105	3
6	22.0	37.7	1	52	19.6	50.2	2	98	19.5	65.7	5	6	17.21	105	4	53	17.2	105	4
7	22.0	37.3	$\mathcal{2}$	53	19.6	50.6	4	99	19.5	65.7	6	7	17.19	106	6	54	17.2	105	3
8	21.8	37.4	$\mathcal{2}$	54	19.6	51.1	3	100	19.5	65.9	5	8	17.18	106	6	55	17.2	105	4
9	21.4	37.4	$\mathcal{2}$	55	19.6	51.4	4	101	19.5	66.2	5	9	17.18	106	4	56	17.2	105	3
10	20.8	37.4	$\mathcal{2}$	56	19.6	51.8	3	102	19.5	66.2	4	10	17.17	106	6	57	17.2	105	3
11	20.5	37.4	2	57	19.6	52.4	4	103	19.5	66.3	5	11	17.17	105	3	58	17.2	105	4
12	20.3	37.1	$\mathcal{L}$	58	19.6	53.0	3	104	19.5	66.4	4	12	17.16	106	4	59	17.2	105	3
13	20.2	37.2	$\mathcal{L}$	59	19.6	53.6	3	105	19.5	66.4	5	13	17.17	106	3	60	17.2	105	3
14	20.1	37.0	1	60	19.6	54.1	4	106	19.5	66.6	5	14	17.16	105	3	61	17.2	104	4
15	20.1	37.0	$\mathcal{L}$	61	19.6	54.6	4	107	19.5	66.7	5	15	17.16	105	3	62	17.2	104	3
16	20.0	37.1	1	62	19.6	55.2	4	108	19.5	66.8	4	16	17.16	105	3	63	17.2	104	4
17	19.9	37.1	3	63	19.6	55.8	3	109	19.5	66.9	4	17	17.16	105	3	64	17.2	104	3
18	19.9	37.0	$\mathcal{L}$	64	19.6	56.2	4	110	19.5	67.0	4	18	17.16	105	2	65	17.2	104	5
19	19.8	37.0	$\mathcal{2}$	65	19.6	56.6	4	111	19.5	67.1	6	19	17.16	105	2	66	17.2	104	3
20	19.8	37.0	3	66	19.6	57.0	4	112	19.5	67.3	4	20	17.16	105	3	67	17.2	104	5
21	19.8	36.9	$\mathcal{2}$	67	19.6	57.5	3	113	19.5	67.3	4	21	17.16	105	3	68	17.2	104	4
22	19.8	37.0	3	68	19.6	57.7	5	114	19.5	67.3	6	22	17.16	105	3	69	17.2	104	5
23	19.7	36.9	4	69	19.5	58.0	4	115	19.5	67.2	5	23	17.16	105	3	70	17.2	104	3
24	19.7	36.9	4	70	19.5	59.0	4	116	19.5	67.3	6	24	17.16	105	3	71	17.2	104	3
25	19.7	37.3	4	71	19.5	59.7	5	117	19.5	67.3	6	25	17.16	105	3	72	17.2	104	5
26	19.7	37.3	3	72	19.5	60.1	7	118	19.5	67.4	4	26	17.16	105	4	73	17.2	104	2
27	19.7	37.6	7	73	19.5	60.7	5	119	19.5	67.4	6	27	17.16	105	3	74	17.2	104	3
28	19.7	37.9	3	74	19.5	60.9	5	120	19.5	67.5	5	28	17.16	105	4	75	17.2	104	3
29	19.7	38.1	$\mathcal{2}$	75	19.5	61.1	5	121	19.5	67.5	6	29	17.16	105	3	76	17.2	104	2
30	19.7	38.0	3	76	19.5	61.4	5	122	19.5	67.6	5	30	17.16	105	4	77	17.2	104	3
31	19.7	38.7	$\mathcal{2}$	77	19.5	61.9	4	123	19.5	67.7	4	31	17.16	105	4	78	17.2	104	3
32	19.7	39.0	$\mathcal{2}$	78	19.5	61.9	4	124	19.5	67.6	4	32	17.16	105	4	79	17.2	104	2
33	19.7	39.2	3	79	19.5	62.2	4	125	19.5	67.7	5	33	17.16	105	5	80	17.2	104	3
34	19.7	39.7	2	80	19.5	62.4	4	126	19.5	67.7	5	34	17.16	105	4	81	17.2	104	3
35	19.7	40.0	3	81	19.5	62.7	4	127	19.5	67.7	6	35	17.16	105	6	82	17.2	104	3
36	19.7	40.2	3	82	19.5	63.1	4	128	19.5	67.8	5	36	17.16	105	7	83	17.2	104	3

37	19.7	40.8	4	83	19.5	63.5	4	129	19.5	67.7	4	37	17.16	105	5	84	17.2	104	3
38	19.7	41.8	2	84	19.5	63.6	5	130	19.5	67.8	4	38	17.16	105	3	85	17.2	104	4
39	19.7	42.1	3	85	19.5	63.7	3	131	19.5	67.7	7	39	17.16	105	4	86	17.2	104	2
40	19.7	42.4	2	86	19.5	63.7	3	132	19.5	67.7	7	40	17.16	105	3	87	17.2	104	3
41	19.7	42.8	4	87	19.5	63.8	4	133	19.5	67.7	6	41	17.16	105	4	88	17.2	104	3
42	19.6	43.4	3	88	19.5	63.9	5	134	19.5	67.7	6	42	17.16	105	3	89	17.2	104	4
43	19.6	44.1	2	89	19.5	64.1	5	135	19.5	67.8	9	43	17.16	105	3	90	17.2	165	4
44	19.6	45.2	2	90	19.5	64.4	4	136	19.5	67.8	13	44	17.16	105	4	91	17.4	498	4
45	19.6	46.0	3	91	19.5	64.6	5					45	17.16	105	3	92	17.4	576	1
												46	17.16	105	3				

Table B.2 : L Manenguba Female, Dec-2013

Dept	hTemj	o Cond	02	pН	Eh l	DepthTem	p Cond	02	pН	$\mathbf{E}\mathbf{h}$	Dept	hTem	o Cond	02	pН	Eh
(m)	(°C)	(µS/cm	n) mg/]	L	(	m) (°C)	(µS/cn	1) mg/.	L		(m)	(°C)	(µS/cm	n) mg/	L	
1	20.0	125.1	8.3	7.0	111.4	55 19.6	151.4	0.1	6.5	-54.2	109	19.5	153.7	0.1	6.5	-101.3
2	20.0	128.0	8.1	7.0	111.1	56 19.6	151.6	0.1	6.5	-56.0	110	19.5	153.5	0.1	6.5	-101.6
3	20.0	130.0	8.1	7.1	111.45	57 19.6	151.7	0.1	6.5	-57.5	111	19.5	153.5	0.1	6.5	-102.0
4	20.0	131.7	8.1	7.1	111.95	58 19.6	151.7	0.1	6.5	-59.6	112	19.5	153.5	0.1	6.5	-102.4
5	20.0	133.3	8.1	7.1	112.35	59 19.6	151.8	0.1	6.5	-61.4	113	19.5	153.5	0.1	6.5	-103.0
6	20.0	134.6	8.1	7.1	112.46	60 19.6	151.9	0.1	6.5	-63.0	114	19.5	153.6	0.1	6.5	-103.3
7	20.0	135.8	8.1	7.1	112.56	61 19.6	152.2	0.1	6.5	-64.5	115	19.5	153.7	0.1	6.5	-103.7
8	20.0	136.7	8.1	7.1	112.96	62 19.6	152.0	0.1	6.5	-65.5	116	19.5	153.7	0.1	6.5	-104.0
9	20.0	137.4	8.1	7.1	113.36	33 19.6	151.9	0.1	6.5	-66.7	117	19.5	153.8	0.1	6.5	-104.5
10	20.0	138.4	8.0	7.1	113.66	64 19.6	152.2	0.1	6.5	-68.4	118	19.5	153.7	0.1	6.5	-104.7
11	19.9	139.3	7.9	7.1	113.86	65 19.6	152.1	0.1	6.5	-69.7	119	19.5	153.7	0.1	6.5	-105.0
12	19.9	140.0	7.7	7.1	114.26	66 19.6	152.3	0.1	6.5	-71.3	120	19.5	153.7	0.1	6.5	-105.3
13	19.9	140.8	7.1	7.0	115.36	67 19.6	152.3	0.1	6.5	-72.8	121	19.5	153.8	0.1	6.4	-105.5
14	19.9	141.4	6.0	7.0	115.86	68 19.6	152.3	0.1	6.5	-74.1	122	19.5	153.6	0.1	6.4	-105.8
15	19.9	142.1	4.7	7.0	116.56	69 19.5	152.4	0.1	6.5	-75.3	123	19.5	153.6	0.1	6.5	-106.2
16	19.8	142.8	3.7	6.9	116.97	70 19.5	152.5	0.1	6.5	-76.4	124	19.5	153.7	0.1	6.4	-106.3
17	19.8	143.5	2.8	6.9	117.57	1 19.5	152.5	0.1	6.5	-77.5	125	19.5	153.8	0.1	6.5	-106.7
18	19.8	144.3	2.4	6.9	117.97	19.5	152.7	0.1	6.5	-78.6	126	19.5	153.7	0.1	6.4	-107.0
19	19.7	144.5	2.2	6.8	118.2	73 19.5	152.6	0.1	6.5	-79.4	127	19.5	153.7	0.1	6.4	-107.2
20	19.7	145.1	1.9	6.8	118.67	74 19.5	152.6	0.1	6.5	-80.5	128	19.5	153.8	0.1	6.4	-107.6
21	19.7	145.3	1.6	6.8	118.87	75 19.5	152.7	0.1	6.5	-81.4	129	19.5	153.7	0.1	6.4	-107.7
22	19.7	145.8	1.3	6.8	118.67	76 19.5	152.7	0.1	6.5	-82.4	130	19.5	153.7	0.1	6.4	-108.0
23	19.7	146.3	1.0	6.8	118.4	77 19.5	152.8	0.1	6.5	-83.2	131	19.5	153.9	0.1	6.4	-108.4
24	19.7	146.4	0.7	6.7	118.67	78 19.5	152.9	0.1	6.5	-83.9	132	19.5	153.9	0.1	6.4	-108.6
25	19.7	146.8	0.4	6.7	118.87	79 19.5	153.0	0.1	6.5	-84.8	133	19.5	153.8	0.1	6.4	-108.9
26	19.7	147.2	0.2	6.7	118.98	30 19.5	153.0	0.1	6.5	-85.5	134	19.5	154.0	0.1	6.4	-109.1
27	19.7	147.6	0.1	6.7	117.48	81 19.5	153.1	0.1	6.5	-86.1	135	19.5	153.8	0.1	6.4	-109.4
28	19.7	147.6	0.1	6.6	114.08	32 19.5	153.1	0.1	6.5	-87.0	136	19.5	153.9	0.1	6.4	-109.5
29	19.7	147.9	0.1	6.6	108.88	33 19.5	153.1	0.1	6.5	-87.8	137	19.5	153.9	0.1	6.4	-109.9
30	19.7	148.1	0.1	6.6	102.38	34 19.5	153.1	0.1	6.5	-88.6	138	19.5	153.9	0.1	6.4	-110.3
31	19.7	148.4	0.1	6.6	93.3 8	35 19.5	153.0	0.1	6.5	-89.1	139	19.5	153.9	0.1	6.4	-110.4
32	19.7	148.5	0.1	6.6	84.1 8	36 19.5	153.2	0.1	6.5	-89.7	140	19.5	154.0	0.1	6.4	-110.8
33	19.7	148.7	0.0	6.6	67.2 8	37 19.5	152.9	0.1	6.5	-90.3	141	19.5	153.9	0.1	6.4	-111.1
34	19.7	148.6	0.1	6.6	51.3 8	38 19.5	153.2	0.1	6.5	-91.0	142	19.5	153.9	0.1	6.4	-111.3
35	19.7	149.0	0.1	6.5	37.4 8	39 19.5	153.3	0.1	6.5	-91.4	143	19.5	153.9	0.1	6.4	-111.4
36	19.7	149.4	0.1	6.5	25.3	90 19.5	153.2	0.1	6.5	-92.0	144	19.5	154.0	0.1	6.4	-111.7
37	19.7	149.4	0.0	6.5	16.1	91 19.5	153.3	0.1	6.5	-92.6	145	19.5	154.0	0.1	6.4	-111.9
38	19.7	149.5	0.0	6.5	8.2	92 19.5	153.3	0.1	6.5	-92.9	146	19.5	154.0	0.1	6.4	-112.0
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39	19.7	149.8	0.0	6.5	0.9	93	19.5	153.2	0.1	6.5	-93.5	147	19.5	154.0	0.1	6.4	-112.4
40	19.6	149.7	0.0	6.5	-5.0	94	19.5	153.3	0.1	6.5	-93.9	148	19.5	154.0	0.1	6.4	-112.6
41	19.6	149.9	0.1	6.5	-10.4	95	19.5	153.4	0.1	6.5	-94.3	149	19.5	154.1	0.1	6.4	-112.9
42	19.6	150.2	0.1	6.5	-15.1	96	19.5	153.3	0.1	6.5	-94.9	150	19.5	154.1	0.1	6.4	-113.0
43	19.6	150.3	0.1	6.5	-19.2	97	19.5	153.4	0.1	6.5	-95.4	151	19.5	154.1	0.1	6.4	-113.2
44	19.6	150.3	0.1	6.5	-23.1	98	19.5	153.4	0.1	6.5	-96.0	152	19.5	154.2	0.1	6.4	-113.2
45	19.6	150.3	0.1	6.5	-26.7	99	19.5	153.4	0.1	6.5	-96.4	153	19.5	154.1	0.1	6.4	-113.4
46	19.6	150.5	0.1	6.5	-30.3	100	19.5	153.4	0.1	6.5	-97.0	154	19.5	154.1	0.1	6.4	-113.8
47	19.6	150.6	0.1	6.5	-33.6	101	19.5	153.4	0.1	6.5	-97.5	155	19.5	154.3	0.1	6.4	-114.2
48	19.6	151.0	0.1	6.5	-36.7	102	19.5	153.5	0.1	6.5	-98.0	156	19.5	154.1	0.1	6.4	-114.3
49	19.6	150.9	0.1	6.5	-40.0	103	19.5	153.4	0.1	6.5	-98.4	157	19.5	154.1	0.1	6.4	-114.5
50	19.6	151.1	0.1	6.5	-42.2	104	19.5	153.5	0.1	6.5	-99.0	158	19.5	154.3	0.1	6.4	-114.8
51	19.6	151.2	0.1	6.5	-44.9	105	19.5	153.5	0.1	6.5	-99.6	159	19.5	154.2	0.1	6.4	-115.1
52	19.6	151.2	0.1	6.5	-47.7	106	19.5	153.5	0.1	6.5	-99.8	160	19.5	154.3	0.1	6.4	-115.3
53	19.6	151.3	0.1	6.5	-49.9	107	19.5	153.6	0.1	6.5	-100.4	161	19.5	154.3	0.1	6.4	-115.7
54	19.6	151.5	0.1	6.5	-52.2	108	19.5	153.5	0.1	6.5	-100.7	162	19.5	154.3	0.1	6.4	-115.9
												163	19.5	159.1	0.1	6.3	-107.2

Table B.3 : Lake Manenguba Male, Dec-2013

Depth	Temp	Cond	<b>O</b> <sub>2</sub>	pН	Eh	Depth	Temp	Cond	<b>O</b> <sub>2</sub>	pН	Eh
(m)	(°C)	(µS/cm)	mg/L	-		(m)	(°C)	(µS/cm)	mg/L	-	
1	18.4	129.8	11.8	8.4	87.8	47	17.2	155.7	0.1	6.6	87.4
2	18.3	134.4	12.1	8.4	87.2	48	17.2	155.7	0.1	6.6	88.0
3	18.2	137.8	12.2	8.2	89.0	49	17.2	155.7	0.1	6.6	88.5
4	17.7	141.7	11.9	7.9	92.9	50	17.2	155.5	0.1	6.6	88.8
5	17.4	144.3	9.3	7.7	95.2	51	17.2	155.5	0.1	6.6	89.4
6	17.3	146.8	5.7	7.5	97.4	52	17.2	155.6	0.1	6.6	89.9
7	17.2	148.0	3.8	7.3	98.9	53	17.2	155.7	0.1	6.6	90.0
8	17.2	148.8	2.9	7.3	100.0	54	17.2	155.8	0.1	6.6	90.2
9	17.2	150.0	2.3	7.2	100.8	55	17.2	155.7	0.1	6.6	90.4
10	17.2	151.0	2.0	7.1	101.6	56	17.2	155.6	0.1	6.6	90.2
11	17.2	151.4	1.9	7.0	102.3	57	17.2	155.4	0.1	6.6	90.3
12	17.2	152.0	1.9	7.0	103.5	58	17.2	155.3	0.2	6.6	90.5
13	17.2	152.6	1.5	6.9	104.4	59	17.2	155.1	0.2	6.6	90.8
14	17.2	153.0	1.2	6.9	103.3	60	17.2	155.2	0.2	6.6	91.5
15	17.2	153.5	0.7	6.8	102.3	61	17.2	155.0	0.2	6.6	91.5
16	17.2	153.5	0.5	6.8	102.4	62	17.2	154.9	0.2	6.6	91.7
17	17.2	153.8	0.5	6.8	103.6	63	17.2	154.9	0.2	6.6	91.7
18	17.2	154.2	0.4	6.7	103.7	64	17.1	155.0	0.2	6.6	92.2
19	17.2	154.4	0.3	6.7	103.8	65	17.1	154.7	0.2	6.6	92.0
20	17.2	154.6	0.2	6.7	104.2	66	17.1	154.5	0.2	6.6	92.2
21	17.2	154.7	0.2	6.7	104.1	67	17.1	154.5	0.2	6.6	92.7
22	17.2	154.9	0.2	6.7	104.2	68	17.1	154.6	0.2	6.6	92.8
23	17.2	155.3	0.1	6.7	104.1	69	17.1	154.7	0.2	6.6	93.2
24	17.2	155.3	0.1	6.7	103.7	70	17.1	154.0	0.2	6.6	92.8
25	17.2	155.5	0.1	6.7	100.8	71	17.2	153.9	0.2	6.6	92.9
26	17.2	155.6	0.0	6.7	97.7	72	17.1	153.8	0.2	6.6	93.1
27	17.2	155.6	0.0	6.7	93.3	73	17.2	153.8	0.2	6.6	93.2
28	17.2	155.5	0.0	6.6	89.0	74	17.1	153.7	0.2	6.6	93.2
29	17.2	155.6	0.0	6.6	85.8	75	17.2	153.6	0.3	6.6	93.3
30	17.2	155.9	0.0	6.6	83.0	76	17.1	153.4	0.3	6.6	93.4
31	17.2	155.7	0.0	6.6	80.6	77	17.1	153.3	0.3	6.6	93.4
32	17.2	155.9	0.0	6.6	78.3	78	17.2	153.2	0.3	6.6	93.5
33	17.2	155.9	0.0	6.6	77.6	79	17.1	152.9	0.3	6.6	93.5
34	17.2	155.9	0.0	6.6	76.3	80	17.1	152.7	0.4	6.6	93.6
35	17.2	155.9	0.0	6.6	75.7	81	17.1	152.3	0.4	6.6	93.6
36	17.2	155.9	0.0	6.6	76.1	82	17.1	152.1	0.4	6.6	93.9
37	17.2	156.0	0.0	6.6	77.8	83	17.1	152.1	0.4	6.6	93.9
38	17.2	156.0	0.0	6.6	79.1	84	17.1	152.0	0.4	6.6	94.0
39	17.2	155.9	0.0	6.6	80.7	85	17.1	151.8	0.4	6.6	94.0
40	17.2	155.9	0.0	6.6	82.4	86	17.1	151.7	0.4	6.6	94.1
41	17.2	155.9	0.0	6.6	83.6	87	17.1	151.5	0.4	6.6	94.0
42	17.1	155.9	0.1	6.6	84.6	88	17.1	151.1	0.4	6.6	93.7
43	17.1	155.8	0.1	6.6	85.3	89	17.2	150.8	0.4	6.6	91.7
44	17.2	155.9	0.1	6.6	86.1	90	17.2	150.0 150.4	0.3	6.4	-14 4
45	17.2	155.8	0.1	6.6	86.9	91	17.3	150.1	0.2	64	-63 1
46	17.2	155.7	0.1	6.6	87.0	92	17.4	160.6	0.2	6.2	-79.0

Table B.3 :	CTD L	ake Baı	rombi	Mbo
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		Apr- 1	.3		·		·			Jan-14					
Dept	hT C <sub>25</sub>	# Avg	Dept	hT C <sub>25</sub>	# Avg.	Deptl	nTemj	p Cond	02	pH Eh	Dept	hTem	p Cond	02	pH Eh
(m)	(° C)(µS/cm	D)	(m)	(° C) (µS/cm	l)	(m)	(°C)	(µS/cm	)mg/I		(m)	(°C)	(µS/cm	) mg/]	
0	$28.5\ 52.65$	4	52.0	26.7382.29	5	1	27.9	59.4	9.2	7.2165.3	51	26.4	95.8	0.0	6.5-86.3
1	$28.3\ 52.48$	5	53.0	26.7382.18	3	2	28.6	77.7	8.6	7.9173.5	52	26.4	96.2	0.0	6.5 - 87.2
2	$28.2\ 52.29$	7	54.0	26.7382.29	4	3	28.6	67.5	8.7	8.0170.3	53	26.4	96.3	0.0	6.5 - 88.2
3	$28.1\ 52.33$	5	55.0	26.7382.12	3	4	28.6	83.9	8.8	8.0168.0	54	26.4	96.7	0.0	6.5 - 88.8
4	$28.1\ 52.33$	3	56.0	26.7382.07	3	5	28.6	82.8	8.8	8.0165.5	55	26.4	97.2	0.0	6.5 - 89.6
<b>5</b>	$28.0\ 52.42$	2	57.0	26.7381.97	4	6	28.6	83.0	8.7	8.0162.8	56	26.4	97.5	0.0	6.5 - 90.4
6	$28.0\ 52.62$	4	58.0	26.7381.96	4	7	28.6	83.7	8.8	8.0160.8	57	26.4	97.9	0.0	6.5 - 91.1
7	$27.9\ 54.13$	3	59.0	26.7382.22	4	8	28.6	84.3	8.6	8.0158.8	58	26.4	98.0	0.0	6.5-91.9
8	$27.6\ 62.07$	2	60.0	26.7382.82	4	9	28.2	85.1	8.2	7.8161.9	59	26.4	98.3	0.0	6.5 - 92.7
9	$27.2\ 73.61$	2	61.0	26.7383.04	4	10	27.9	86.4	5.0	7.4165.7	60	26.4	98.5	0.0	6.5 - 93.2
10	$27.0\ 76.39$	1	62.0	26.7383.19	4	11	27.8	86.4	2.5	7.1166.0	61	26.4	98.3	0.0	6.5 - 93.7
11	$27.0\ 77.18$	3	63.0	26.7383.11	5	12	27.5	87.1	1.2	6.9166.0	62	26.4	98.2	0.0	6.5 - 94.2
12	$27.0\ 77.63$	4	64.0	26.7383.17	4	13	27.1	92.5	0.7	6.8156.2	63	26.4	97.9	0.0	6.5 - 94.6
13	$26.9\ 79.55$	3	65.0	26.7383.43	2	14	26.9	95.4	0.4	6.7125.4	64	26.4	98.1	0.0	6.5 - 95.3
14	$26.8\ 80.54$	2	66.0	26.7383.51	2	15	26.7	97.3	0.3	6.672.1	65	26.4	98.0	0.0	6.5 - 95.7
15	$26.8\ 81.11$	2	67.0	26.7383.58	3	16	26.6	99.4	0.3	6.610.7	66	26.4	97.7	0.0	6.5 - 96.3
16	$26.8\ 81.75$	2	68.0	26.7383.72	2	17	26.6	98.9	0.2	6.6-11.8	67	26.4	82.4	0.0	6.5 - 96.4
17	$26.8\ 82.06$	4	69.0	26.7383.41	2	18	26.5	98.1	0.2	6.5-23.8	68	26.4	94.8	0.0	6.5-97.0
18	$26.7\ 82.09$	3	70.0	26.7383.41	2	19	26.5	97.8	0.2	6.5 - 31.5	69	26.4	96.6	0.0	6.5 - 97.2
19	$26.7\ 81.72$	2	71.0	26.7383.46	3	20	26.5	98.0	0.1	6.5 - 37.4	70	26.4	97.7	0.0	6.5 - 97.7
20	$26.7\ 81.29$	4	72.0	26.7383.35	3	21	26.5	98.6	0.1	6.5 - 41.8	71	26.4	97.2	0.0	6.5 - 98.0
21	$26.7\ 80.66$	2	73.0	26.7383.34	3	22	26.5	98.4	0.1	6.5 - 46.3	72	26.4	97.0	0.0	6.5 - 98.3
22	$26.7\ 80.35$	1	74.0	26.7383.29	4	23	26.4	99.3	0.1	6.5 - 49.8	73	26.4	97.1	0.0	6.5 - 98.7
23	$26.7\ 80.38$	4	75.0	26.7383.34	3	24	26.4	98.8	0.1	6.5 - 52.6	74	26.4	96.8	0.0	6.5 - 99.2
24	$26.7\ 80.19$	3	76.0	26.7384.00	3	25	26.4	98.8	0.1	6.5 - 55.3	75	26.4	97.7	0.0	6.5 - 99.5
25	$26.7\ 79.94$	5	77.0	26.7384.24	4	26	26.4	98.6	0.1	6.5 - 57.5	76	26.4	98.2	0.0	6.5 - 99.9
26	$26.7\ 79.78$	3	78.0	26.7384.39	4	27	26.4	98.4	0.1	6.5 - 59.4	77	26.4	98.2	0.0	6.5-100.3
27	$26.7\ 79.78$	3	79.0	26.7384.26	3	28	26.4	98.4	0.0	6.5 - 61.2	78	26.4	98.2	0.0	6.5 - 100.8
28	$26.7\ 79.66$	4	80.0	26.7384.70	4	29	26.4	98.3	0.0	6.5-63.0	79	26.4	98.1	0.0	6.5 - 101.2
29	$26.7\ 79.58$	2	81.0	26.7386.11	4	30	26.4	98.4	0.0	6.5 - 64.8	80	26.4	98.1	0.0	6.5-101.5
30	$26.7\ 79.58$	2	82.0	26.7387.31	3	31	26.4	96.3	0.0	6.5 - 66.2	81	26.4	98.9	0.0	6.5-102.3
31	$26.7\ 79.68$	3	83.0	26.7387.98	4	32	26.4	96.5	0.0	6.5 - 67.7	82	26.4	99.0	0.0	6.5 - 102.7
32	$26.7\ 79.65$	4	84.0	26.7388.70	3	33	26.4	97.0	0.0	6.5-69.3	83	26.4	98.8	0.0	6.5-103.1
33	$26.7\ 79.58$	3	85.0	26.7388.83	4	34	26.4	96.8	0.0	6.5-70.6	84	26.4	98.7	0.0	6.5-103.6
34	$26.7\ 79.42$	3	86.0	26.7389.74	4	35	26.4	97.0	0.0	6.5-71.9	85	26.4	98.8	0.0	6.5-104.2
35	$26.7\ 79.32$	3	87.0	26.7390.68	6	36	26.4	96.9	0.0	6.5-73.6	86	26.4	98.8	0.0	6.5-104.6
36	$26.7\ 79.31$	4	88.0	26.7391.69	4	37	26.4	96.8	0.0	6.5 - 74.9	87	26.4	98.5	0.0	6.5-105.0

37	$26.7\ 79.35$	4	89.0	26.7494.29	4	38	26.4	96.9	0.0	6.5 - 76.1	88	26.4	98.5	0.0	6.5 - 105.2
38	$26.7\ 79.49$	2	90.0	26.7498.61	4	39	26.4	96.8	0.0	6.5 - 76.8	89	26.4	95.5	0.0	6.5 - 105.5
39	$26.7\ 79.49$	4	91.0	26.74102.2	3	40	26.4	95.9	0.0	6.5 - 77.6	90	26.4	95.0	0.0	6.5-106.0
40	$26.7\ 79.77$	3	92.0	26.74104.8	2	41	26.4	95.4	0.0	6.5 - 78.7	91	26.4	97.1	0.0	6.5 - 106.3
41	$26.7\ 79.84$	5	93.0	26.75113.0	4	42	26.4	97.0	0.0	6.5 - 79.8	92	26.4	92.9	0.0	6.5-106.6
42	$26.7\ 79.97$	3	94.0	26.75115.6	5	43	26.4	97.0	0.0	6.5 - 80.7	93	26.4	93.8	0.0	6.5 - 106.8
43	$26.7\ 80.17$	3	95.0	26.75117.3	4	44	26.4	96.9	0.0	6.5 - 81.5	94	26.5	97.9	0.0	6.5-106.3
44	$26.7\ 80.44$	4	96.0	26.75118.6	3	45	26.4	96.7	0.0	6.5 - 82.4	95	26.5	102.3	0.0	6.5-106.9
45	$26.7\ 80.71$	5	97.0	26.75120.9	3	46	26.4	96.4	0.0	6.5 - 82.9	96	26.5	108.6	0.0	6.5-108.3
46	$26.7\ 80.72$	3	98.0	26.75123.4	2	47	26.4	96.5	0.0	6.5-83.6	97	26.5	120.6	0.0	6.5-110.7
47	$26.7\ 81.08$	3	99.0	26.75124.4	3	48	26.4	96.4	0.0	6.5 - 84.3	98	26.5	136.5	0.0	6.5-116.4
48	$26.7\ 81.15$	2	100.0	26.75124.8	3	49	26.4	96.7	0.0	6.5 - 84.9	99	26.5	154.2	0.0	6.6 - 125.4
49	$26.7\ 81.38$	3	101.0	26.75125.0	4	50	26.4	95.9	0.0	6.5-85.5	100	26.5	168.4	0.0	6.7-137.5
50	$26.7\ 81.48$	3	102.0	26.76127.7	3						101	26.5	267.6	0.0	6.7-176.3
51	$26.7\ 81.89$	5	103.0	26.76146.1	4						•				

L. Nga	ounda	ıba, April	2013				L. Tizo	on, April 2013					
Depth	Т	C <sub>25</sub>	O2	pН	Eh	# Avg.	Depth	Т	C <sub>25</sub>	O <sub>2</sub>	pН	Eh	# Avg.
(m)	(° C)	(µS/cm)	(mg/kg)				(m)	(° C)	(µS/cm)	(mg/kg)			
0	26.3	141	13.7	7.9	19.6	4	0	25.0	254	15.0	8.5	-48.8	3
1	25.9	141	12.9	7.9	17.4	10	1	24.9	252	14.3	8.6	-48.8	5
2	25.6	141	12.3	7.9	16.4	5	2	24.9	255	13.4	8.6	-48.1	4
3	25.4	141	12.1	7.9	16.0	6	3	24.9	256	12.8	8.6	-47.3	5
4	25.2	141	11.7	7.9	15.8	7	4	24.8	255	12.6	8.6	-46.5	4
<b>5</b>	24.5	140	11.3	7.7	18.7	5	5	24.8	256	12.4	8.6	-45.4	3
6	23.4	140	10.9	7.6	21.6	5	6	23.4	255	12.3	8.2	-37.1	6
7	22.5	141	10.0	7.5	24.7	4	7	21.9	254	10.3	7.9	-31.6	5
8	22.1	141	8.2	7.3	25.9	5	8	21.5	251	7.3	7.7	-30.3	6
9	21.8	140	6.2	7.2	26.8	5	9	21.1	250	4.5	7.5	-28.8	8
10	21.4	139	4.6	7.2	27.2	4	10	20.8	255	2.8	7.5	-27.6	7
11	21.1	139	3.6	7.1	28.3	3	11	20.8	254	2.1	7.4	-27.1	3
12	20.9	140	2.8	7.1	29.5	4	12	20.7	253	1.6	7.4	-28.0	6
13	20.8	141	2.0	7.1	30.3	4	13	20.7	253	1.3	7.4	-31.8	6
14	20.7	142	1.5	7.1	31.4	5	14	20.6	255	1.0	7.3	-43.1	7
15	20.6	144	1.1	7.0	32.3	3	15	20.6	259	0.9	7.2	-55.3	5
16	20.5	147	0.9	7.0	33.5	5	16	20.5	262	0.7	7.2	-64.5	6
17	20.4	149	0.7	7.0	34.4	4	17	20.5	265	0.7	7.1	-74.2	7
18	20.4	152	0.5	7.0	35.7	4	18	20.4	266	0.6	7.1	-82.7	6
19	20.3	154	0.4	7.0	36.3	4	19	20.4	266	0.6	7.1	-90	6
20	20.3	157	0.4	6.9	36.5	5	20	20.4	269	0.6	7.1	-96	7
21	20.2	160	0.3	6.9	30.4	4	21	20.4	271	0.5	7.1	-101	5
22	20.2	165	0.3	6.9	4.2	5	22	20.4	275	0.5	7.2	-104	7
23	20.1	168	0.2	6.8	-28.0	4	23	20.4	275	0.5	7.2	-107	6
24	20.1	170	0.2	6.8	-46.4	4	24	20.4	275	0.5	7.2	-109	6
25	20.1	172	0.2	6.8	-61.3	5	25	20.4	276	0.4	7.2	-111	6
26	20.0	174	0.2	6.9	-72.9	4	26	20.4	276	0.4	7.2	-112	6
27	20.0	174	0.2	6.9	-78.8	4	27	20.4	276	0.4	7.1	-113	6
28	20.0	175	0.1	6.9	-85.4	5	28	20.4	276	0.4	7.2	-115	5
29	20.0	177	0.1	6.9	-90.1	3	29	20.4	276	0.4	7.2	-116	5
30	20.0	177	0.1	6.9	-93.8	5	30	20.4	275	0.4	7.2	-117	6
31	20.0	178	0.1	6.9	-96.5	4	31	20.4	275	0.3	7.2	-118	5
32	20.0	178	0.1	6.9	-99.2	4	32	20.4	274	0.3	7.2	-119	6
33	20.0	179	0.1	6.9	-102	5	33	20.4	271	0.3	7.2	-120	4
34	20.0	180	0.1	6.9	-105	4	34	20.4	268	0.3	7.1	-120	3
35	20.0	182	0.1	6.9	-107	6	35	20.4	267	0.3	7.1	-121	5
36	20.0	185	0.1	6.9	-111	7	36	20.3	272	0.3	7.1	-122	3

Table B.44 : CTD for lakes in Adamaua Lake District

37	20.0	186	0.1	7.0	-113	5	37	20.3	273	0.3	7.1	-123	4
38	20.0	188	0.1	6.9	-115	5	38	20.3	277	0.3	7.1	-123	3
39	20.0	189	0.1	7.0	-118	6	39	20.3	278	0.3	7.1	-124	6
40	20.0	190	0.1	7.0	-120	6	40	20.3	281	0.3	7.1	-125	4
41	20.0	191	0.1	7.0	-122	6	41	20.3	284	0.3	7.0	-126	5
42	20.0	195	0.1	7.0	-124	6	42	20.3	288	0.2	7.0	-126	3
43	20.0	199	0.1	7.0	-126	5	43	20.3	320	0.2	6.7	-121	13
44	20.0	201	0.1	7.0	-128	6							
45	20.0	203	0.1	7.0	-130	5							
46	20.0	206	0.1	7.0	-132	5							
47	20.0	211	0.1	7.0	-133	3							
48	20.0	216	0.1	7.0	-135	4							
49	20.0	220	0.1	7.0	-137	4							
50	20.0	223	0.1	7.0	-140	5							
51	20.0	233	0.1	7.0	-144	8							
52	20.0	237	0.1	7.0	-148	6							
53	20.0	241	0.1	7.1	-152	8							
54	20.0	246	0.1	7.1	-155	6							
55	20.0	248	0.1	7.1	-159	6							
56	20.0	250	0.1	7.1	-161	6							
57	20.0	250	0.1	7.1	-164	7							
58	20.0	252	0.1	7.1	-166	5							
59	20.0	254	0.1	7.1	-167	5							
60	20.0	254	0.1	7.1	-169	5							
61	20.0	255	0.1	7.1	-170	5							
62	20.0	468	0.1	6.7	-156	4							

## **APPENDIX C**

Chemical composition of the soil gas from Mount Manenguba
Sampling site	d <sup>13</sup> C(co2) ‰ vs.PDB	SD ‰ vs.PDB	He (ppm)	<sup>36</sup> Ar (ppm)	<sup>40</sup> Ar (ppm)	CO2 (%)	$N_2$
							(%)
Mt Manenguba	-8.66	0.02	5.46	31	9106	3.5	77.23
	-8.93	0.08	5.92	32	9558	3.1	77.84
	-9.69	0.82	4.99	30	8862	1.8	78.09
	-6.56	0.03	5.76	31	9426	4.0	78.53
	-8.46	0.03	6.13	32	9614	1.2	78.54
	-8.05	0.03	6.14	33	9555	2.7	77.81
	-6.99	0.04	5.38	31	8933	0.9	78.18
	-8.23	0.03	6.85	32	9519	2.1	78.16
	-8.26	0.04	5.98	32	9540	1.3	78.17
	-8.60	0.03	5.91	32	9510	1.7	77.94
	-8.48	0.03	5.40	30	8881	4.8	77.16
	-8.60	0.17	6.04	32	9568	0.4	78.03
	-8.39	0.04	6.27	33	9607	4.2	78.72
	-9.34	0.03	5.24	30	8957	2.4	78.26
	-8.77	0.04	6.95	34	9794	9.1	80.85
	-7.81	0.05	5.18	31	8876	1.3	77.99
	-7.24	0.04	6.17	32	9575	4.1	78.31
	-10.48	0.05	5.29	31	9343	5.3	80.21
	-8.56	0.04	4.84	30	9046	1.4	78.17
	-8.16	0.03	5.25	31	9291	1.4	77.93
	-10.64	0.06	5.41	31	9335	0.9	78.16
	-10.82	0.05	5.19	31	9382	0.5	78.27
	-7.30	0.03	5.12	32	9364	1.5	78.12
	-8.05	0.04	5.46	32	9373	7.9	79.61
	-9.39	0.08	5.13	31	9431	0.9	78.28
	-7.60	0.02	5.08	32	9424	0.8	78.40
	-8.91	0.03	5.29	31	9332	0.8	78.64
	-9.01	0.04	5.04	31	9385	1.0	78.56
	-9.15	0.05	5.04	32	9447	0.4	78.32
	-10.38	0.08	5.04	31	9400	0.3	78.28
	-9.86	0.04	4.82	31	9220	0.5	78.30
	-10.49	0.07	5.04	32	9434	0.3	78.22
	-9.44	0.04	5.01	32	9404	0.6	78.37
	-7.34	0.03	5.05	32	9411	0.7	78.39
	-8.04	0.06	-	-	•	2.6	78.65
	-8.41	0.03	5.11	31	9216	0.6	79.38
	-10.91	0.04	5.70	33	9750	19	80.81
	-9.95	0.07	5.84	32	9615	5.8	79.75
	-10.91	0.05	5.51	32	9297	0.7	78.27
	-7 15	0.05	5.51	32	9322	2.6	78.37
	-6 59	0.03	5.69	32	9452	1.6	78.04
	-7 55	0.04	5.67	32	9431	0.5	78.30
	-7 57	0.05	5.43	31	9358	0.0	78.17
	-7.34	0.03	5.64	39	9300	0.4	78.17
	1.04	0.00	0.04	04	3030	0.7	10.11

Table C.5: The soil gas composition of the Manenguba caldera

Geochemical characteristics of the CVL lakes

1.20	0.10	0.45	1	192	1.78	0.66	
-8.63	0.06	5.57	32	9391	1.63	78.35	
-12.20	0.02	4.82	30	8862	0.14	77.16	
-6.56	0.82	6.95	34	9794	9.10	80.85	
-7.14	0.03	5.79	32	9574	0.8	78.42	
-7.26	0.02	5.75	32	9403	1.1	78.05	
-8.67	0.03	5.69	32	9482	0.6	77.96	
-7.04	0.12	5.74	32	9458	0.3	78.02	
-11.67	0.08	5.60	32	9493	0.3	78.02	
-12.20	0.02	5.67	32	9472	1.6	78.01	
-8.52	0.07	5.61	32	9470	2.4	78.28	
-8.41	0.03	5.49	32	9570	1.2	79.57	
-9.46	0.10	5.10	31	9164	0.2	78.04	
-8.10	0.05	5.44	32	9429	0.4	78.00	
-8.65	0.02	5.32	31	9228	0.5	77.98	
-8.45	0.03	5.55	32	9408	0.6	78.01	
-7.85	0.04	5.50	32	9452	0.4	78.10	
-7.79	0.12	6.68	32	9454	0.2	78.08	
-8.74	0.02	5.56	31	9483	1.0	78.22	
-8.45	0.07	5.38	31	9358	0.3	78.11	
-8.19	0.03	6.01	32	9459	1.2	78.07	
-8.07	0.22	5.87	32	9479	0.1	78.09	
-8.33	0.03	5.84	32	9468	0.6	78.01	
-8.48	0.10	5.85	32	9464	0.7	77.93	
-8.95	0.03	5.88	32	9472	0.7	78.21	
-8.20	0.03	5.80	32	9448	1.1	78.23	
	-8.20 -8.95 -8.48 -8.33 -8.07 -8.19 -8.45 -8.74 -7.79 -7.85 -8.45 -8.65 -8.10 -9.46 -8.41 -8.52 -12.20 -11.67 -7.04 -8.67 -7.26 -7.14 -6.56 -12.20 -8.63 1.20	-8.20 $0.03$ $-8.95$ $0.03$ $-8.95$ $0.03$ $-8.48$ $0.10$ $-8.33$ $0.03$ $-8.07$ $0.22$ $-8.19$ $0.03$ $-8.45$ $0.07$ $-8.45$ $0.07$ $-8.74$ $0.02$ $-7.79$ $0.12$ $-7.85$ $0.04$ $-8.45$ $0.03$ $-8.65$ $0.02$ $-8.10$ $0.05$ $-9.46$ $0.10$ $-8.41$ $0.03$ $-8.52$ $0.07$ $-12.20$ $0.02$ $-11.67$ $0.08$ $-7.04$ $0.12$ $-8.67$ $0.03$ $-7.26$ $0.02$ $-7.14$ $0.03$ $-6.56$ $0.82$ $-12.20$ $0.02$ $-8.63$ $0.06$ $1.20$ $0.10$	-8.20 $0.03$ $5.80$ $-8.95$ $0.03$ $5.88$ $-8.48$ $0.10$ $5.85$ $-8.33$ $0.03$ $5.84$ $-8.07$ $0.22$ $5.87$ $-8.19$ $0.03$ $6.01$ $-8.45$ $0.07$ $5.38$ $-8.74$ $0.02$ $5.56$ $-7.79$ $0.12$ $6.68$ $-7.85$ $0.04$ $5.50$ $-8.45$ $0.03$ $5.55$ $-8.65$ $0.02$ $5.32$ $-8.10$ $0.05$ $5.44$ $-9.46$ $0.10$ $5.10$ $-8.41$ $0.03$ $5.49$ $-8.52$ $0.07$ $5.61$ $-12.20$ $0.02$ $5.67$ $-11.67$ $0.08$ $5.60$ $-7.04$ $0.12$ $5.74$ $-8.67$ $0.03$ $5.69$ $-7.26$ $0.02$ $5.75$ $-7.14$ $0.03$ $5.79$ $-6.56$ $0.82$ $6.95$ $-12.20$ $0.02$ $4.82$ $-8.63$ $0.06$ $5.57$ $1.20$ $0.10$ $0.45$	-8.20       0.03       5.80       32         -8.95       0.03       5.88       32         -8.48       0.10       5.85       32         -8.33       0.03       5.84       32         -8.07       0.22       5.87       32         -8.19       0.03       6.01       32         -8.45       0.07       5.38       31         -8.74       0.02       5.56       31         -7.79       0.12       6.68       32         -7.85       0.04       5.50       32         -8.45       0.03       5.55       32         -8.65       0.02       5.32       31         -8.45       0.03       5.55       32         -8.65       0.02       5.32       31         -8.45       0.03       5.44       32         -9.46       0.10       5.10       31         -8.41       0.03       5.49       32         -8.52       0.07       5.61       32         -12.20       0.02       5.67       32         -7.04       0.12       5.74       32         -8.67       0.03       5.69	-8.20       0.03       5.80       32       9448         -8.95       0.03       5.88       32       9472         -8.48       0.10       5.85       32       9464         -8.33       0.03       5.84       32       9468         -8.07       0.22       5.87       32       9479         -8.19       0.03       6.01       32       9459         -8.45       0.07       5.38       31       9358         -8.74       0.02       5.56       31       9483         -7.79       0.12       6.68       32       9454         -7.85       0.04       5.50       32       9452         -8.45       0.03       5.55       32       9408         -8.65       0.02       5.32       31       9228         -8.45       0.03       5.44       32       9429         -9.46       0.10       5.10       31       9164         -8.41       0.03       5.49       32       9570         -8.52       0.07       5.61       32       9472         -11.67       0.08       5.60       32       9493         -7.04 <td>-8.20<math>0.03</math><math>5.80</math><math>32</math><math>9448</math><math>1.1</math><math>-8.95</math><math>0.03</math><math>5.88</math><math>32</math><math>9472</math><math>0.7</math><math>-8.48</math><math>0.10</math><math>5.85</math><math>32</math><math>9464</math><math>0.7</math><math>-8.33</math><math>0.03</math><math>5.84</math><math>32</math><math>9468</math><math>0.6</math><math>-8.07</math><math>0.22</math><math>5.87</math><math>32</math><math>9479</math><math>0.1</math><math>-8.19</math><math>0.03</math><math>6.01</math><math>32</math><math>9459</math><math>1.2</math><math>-8.45</math><math>0.07</math><math>5.38</math><math>31</math><math>9358</math><math>0.3</math><math>-8.74</math><math>0.02</math><math>5.56</math><math>31</math><math>9483</math><math>1.0</math><math>-7.79</math><math>0.12</math><math>6.68</math><math>32</math><math>9454</math><math>0.2</math><math>-7.85</math><math>0.04</math><math>5.50</math><math>32</math><math>9452</math><math>0.4</math><math>-8.45</math><math>0.03</math><math>5.55</math><math>32</math><math>9408</math><math>0.6</math><math>-8.65</math><math>0.02</math><math>5.32</math><math>31</math><math>9228</math><math>0.5</math><math>-8.10</math><math>0.05</math><math>5.44</math><math>32</math><math>9429</math><math>0.4</math><math>-9.46</math><math>0.10</math><math>5.10</math><math>31</math><math>9164</math><math>0.2</math><math>-8.41</math><math>0.03</math><math>5.49</math><math>32</math><math>9570</math><math>1.2</math><math>-8.52</math><math>0.07</math><math>5.61</math><math>32</math><math>9470</math><math>2.4</math><math>-12.20</math><math>0.02</math><math>5.67</math><math>32</math><math>9448</math><math>0.3</math><math>-7.04</math><math>0.12</math><math>5.75</math><math>32</math><math>9443</math><math>0.3</math><math>-7.26</math><math>0.02</math><math>5.75</math><math>32</math><math>9403</math><math>1.1</math><math>-7.14</math><math>0.03</math><math>5.79</math><math>32</math><math>9574</math><math>0.8</math><math>-7.26</math><math>0.02</math><math>5.75</math><math>32</math><math>9391</math><math>1.63</math><td>-8.20       0.03       5.80       32       9448       1.1       78.23         -8.95       0.03       5.88       32       9472       0.7       78.21         -8.48       0.10       5.85       32       9464       0.7       77.93         -8.33       0.03       5.84       32       9468       0.6       78.01         -8.07       0.22       5.87       32       9479       0.1       78.09         -8.19       0.03       6.01       32       9459       1.2       78.07         -8.45       0.07       5.38       31       9358       0.3       78.11         -8.74       0.02       5.56       31       9483       1.0       78.22         -7.79       0.12       6.68       32       9454       0.2       78.08         -7.85       0.04       5.50       32       9408       0.6       78.01         -8.45       0.03       5.55       32       9408       0.6       78.01         -8.45       0.03       5.44       32       9429       0.4       78.04         -8.45       0.02       5.67       32       9470       2.4       7</td></td>	-8.20 $0.03$ $5.80$ $32$ $9448$ $1.1$ $-8.95$ $0.03$ $5.88$ $32$ $9472$ $0.7$ $-8.48$ $0.10$ $5.85$ $32$ $9464$ $0.7$ $-8.33$ $0.03$ $5.84$ $32$ $9468$ $0.6$ $-8.07$ $0.22$ $5.87$ $32$ $9479$ $0.1$ $-8.19$ $0.03$ $6.01$ $32$ $9459$ $1.2$ $-8.45$ $0.07$ $5.38$ $31$ $9358$ $0.3$ $-8.74$ $0.02$ $5.56$ $31$ $9483$ $1.0$ $-7.79$ $0.12$ $6.68$ $32$ $9454$ $0.2$ $-7.85$ $0.04$ $5.50$ $32$ $9452$ $0.4$ $-8.45$ $0.03$ $5.55$ $32$ $9408$ $0.6$ $-8.65$ $0.02$ $5.32$ $31$ $9228$ $0.5$ $-8.10$ $0.05$ $5.44$ $32$ $9429$ $0.4$ $-9.46$ $0.10$ $5.10$ $31$ $9164$ $0.2$ $-8.41$ $0.03$ $5.49$ $32$ $9570$ $1.2$ $-8.52$ $0.07$ $5.61$ $32$ $9470$ $2.4$ $-12.20$ $0.02$ $5.67$ $32$ $9448$ $0.3$ $-7.04$ $0.12$ $5.75$ $32$ $9443$ $0.3$ $-7.26$ $0.02$ $5.75$ $32$ $9403$ $1.1$ $-7.14$ $0.03$ $5.79$ $32$ $9574$ $0.8$ $-7.26$ $0.02$ $5.75$ $32$ $9391$ $1.63$ <td>-8.20       0.03       5.80       32       9448       1.1       78.23         -8.95       0.03       5.88       32       9472       0.7       78.21         -8.48       0.10       5.85       32       9464       0.7       77.93         -8.33       0.03       5.84       32       9468       0.6       78.01         -8.07       0.22       5.87       32       9479       0.1       78.09         -8.19       0.03       6.01       32       9459       1.2       78.07         -8.45       0.07       5.38       31       9358       0.3       78.11         -8.74       0.02       5.56       31       9483       1.0       78.22         -7.79       0.12       6.68       32       9454       0.2       78.08         -7.85       0.04       5.50       32       9408       0.6       78.01         -8.45       0.03       5.55       32       9408       0.6       78.01         -8.45       0.03       5.44       32       9429       0.4       78.04         -8.45       0.02       5.67       32       9470       2.4       7</td>	-8.20       0.03       5.80       32       9448       1.1       78.23         -8.95       0.03       5.88       32       9472       0.7       78.21         -8.48       0.10       5.85       32       9464       0.7       77.93         -8.33       0.03       5.84       32       9468       0.6       78.01         -8.07       0.22       5.87       32       9479       0.1       78.09         -8.19       0.03       6.01       32       9459       1.2       78.07         -8.45       0.07       5.38       31       9358       0.3       78.11         -8.74       0.02       5.56       31       9483       1.0       78.22         -7.79       0.12       6.68       32       9454       0.2       78.08         -7.85       0.04       5.50       32       9408       0.6       78.01         -8.45       0.03       5.55       32       9408       0.6       78.01         -8.45       0.03       5.44       32       9429       0.4       78.04         -8.45       0.02       5.67       32       9470       2.4       7

## APPENDIX D

Calculation methods of the gas pressure using Henry's law and the virial Eqs. of states

## Appendix D-1

Step by step demonstration of how to compute  $\mathrm{CH}_4$  and  $\mathrm{CO}_2$  concentrations using the biogas method

1) Calculation steps of CO<sub>2</sub> and CH<sub>4</sub> concentrations. The concentration values are taken from Tables 2 and 3.

$$V_t = \left[ V_1 * \frac{T_0}{T_{gas}} * \frac{P_i - P_{H_2O}}{P_0} + V_{H_2O} * \frac{P_i - P_{H_2O}}{P_0} * \left( \% CO_2 * S_{CO_2} + \% CH_4 * S_{CH_4} \right) \right] (A \ 1)$$

where the first term (A 1a) calculates the volume of the dissolved gas corrected for the water vapour pressure V and the second (A 1b) computes the volume of the remaining dissolved gas in separated water  $V_r$ :

$$V = V_1 * \frac{T_0}{T_{gas}} * \frac{P_i - P_{H_2O}}{P_0}$$
(A 1a)

$$V_r = V_{H_2O} * \frac{P_i - P_{H_2O}}{P_0} * \left( \% CO_2 * S_{CO_2} + \% CH_4 * S_{CH_4} \right)$$
(A 1b)

 $P_{H_2O}$ ,  $S_{CO_2}$  and  $S_{CH_4}$  are obtained using the following equations:

$$P_{H_2O} = 9*10^{-4} T_{H_2O}^3 - 0.0107 T_{H_2O}^2 + 0.7316 T_{H_2O} + 6.11$$
 (A 2)

$$S_{CO_2} = 6*10^{-4} T_{H_2O}^2 - 0.0493 T_{H_2O} + 1.6948$$
(A 3)

$$S_{CH_4} = 10^{-5} T_{H_2O}^2 - 0.0013 T_{H_2O} + 0.0568$$
 (A 4)

Parameters used in A 1 to A 4 are as follow:

- 1)  $V_t$  is the total volume STP representing gas/water ratio at a given sampled depth (L);
- 2)  $V_{H_2O}$  is the volume of liquid phase collected in the separator (L);
- 3)  $V_1$  is the volume of gas obtained as difference between initial and final index readings of the gas flow-meter and volume  $V_{H_2O}$  of water in the separator ( $\Delta$ index- $V_{H_2O}$ ) (L);
- 4) *V* is the volume STP obtained after correcting  $V_1$  (L);
- 5)  $V_r$  is the residual gas remaining in water in equilibrium with the internal pressure of the measuring line (Pi) corrected for water vapour contribution (L);
- 6)  $T_0 = 273 \text{ (K)};$
- 7)  $T_{gas}$  gas temperature given by the gas meter inbuilt thermometer (K);
- 8)  $P_0 = \text{atmospheric pressure at sea level (1013 hPa);}$
- 9)  $P_i$  is the internal pressure of the measuring line calculated as:  $P_i = P_a + P_m$  (hPa) where,  $P_m$  is the pressure reading given by the manometer and  $P_a$  is the barometric pressure (~887.64 hPa) at the level of the lakes (*ca* 1100 m asl.);

- 10)  $P_{H_2O}$  is the water vapour pressure in the system calculated following Eq. 2 (Wilhelm *et al.*, 1976). Temperature (°C) of water measured by a hand thermometer at the outlet of the FDP;
- 11)  $S_{CO_2}$  is carbon dioxide solubility calculated following Eq. 3 (Wilhelm *et al.*, 1976); water temperatures (°C) was measured by a hand thermometer at the outlet of the FDP (cm<sup>3</sup>/cm<sup>3</sup>);
- 12)  $S_{CH_4}$  is methane solubility calculated following Eq. 4 (Wilhelm et al., 1976); water temperatures (°C) was measured by a hand thermometer at the outlet of the FDP (cm<sup>3</sup>/cm<sup>3</sup>)

Once  $V_t$  is obtained, the concentrations of the dissolved CO<sub>2</sub> and CH<sub>4</sub> are calculated using (1) and (2) where %CO<sub>2</sub> and %CH<sub>4</sub> are their volume concentrations in mole %, assuming water density is 1kg/L.

$$[CO_2] = \frac{1}{V_{H2O}} \left[ V_t * \frac{\% CO_2}{22.4} \right] * 1000 \qquad (\mu \text{mol/kg}) \tag{A5}$$

$$[CO_2] = \frac{1}{V_{H2O}} \left[ V_t * \frac{\% CH_4}{22.4} \right] * 1000 \quad (\mu \text{mol/kg}) \tag{A6}$$

13) Calculation of partial pressures using Henry law's constant  $P_i = K_{Hi} * X_i$  (A7) Where  $K_H (CH_4) = 10^{(4.37103+0.01096t-8.49689*10^{-5}t^2 + 2.09817*10^{-7}t^3 - 1.92689*10^{-10}t^4)}$  (A 7a)  $K_H (CO_2) = 10^{(2.89612+0.01502t-8.80542*10^{-5}t^2 + 2.07454*10^{-7}t^3 - 1.87966*10^{-10}t^4)}$  (A 7b) in atm/mole fraction (Taran, 2005); The mole fraction X:  $X = \frac{C}{55.51}$  (A 7c)

where C is gas concentration in mol/kg

## Appendix D-2

Alternatively, the virial equations of state can be used instead of the Henry' law.  $C_{i} = K_{0} * f_{i} * e^{\frac{(1-P)*v_{i}}{RT}}$ (Eq. 1) The fugacity of the specie *i* may be obtained from Eq. 7 as  $f_{i} = \frac{C_{i}}{K_{0}*e^{\frac{(1-P)*v_{i}}{RT}}}$ (Eq. 2)

Where  $K_0$  is a function of the salinity S and temperature T (Eq. 9). (Temperatures for depths of interest were taken from CTD profiles).

$$\ln K_0 = A_1 + \frac{A_2 100}{T} + \frac{A_3 \ln T}{100} + S_{\%o} \left[ B_1 + \frac{B_2 T}{100} + B_3 \left( \frac{T}{100} \right)^2 \right]$$
(Eq.3)

The CO<sub>2</sub> pressure p may be calculated as follow:

$$\ln\left(\frac{f}{p}\right) = B(T)^* \frac{P}{RT}; \text{ And } \frac{f}{p} = e^{B(T)^* \frac{P}{RT}}$$
(Eq.4)

Dividing Eq.8 by Eq.10 and solving for p yields:

$$\mathbf{p} = \frac{C_i * e^{\frac{B(T) * P}{RT}}}{K_0 * e^{\frac{(1-P) * v_i}{RT}}},$$

finally,

$$p = \frac{C_i}{K_0} * e^{\frac{B(T)*P + (P-1)*v_i}{RT}}$$
(Eq. 5)

where B(T) is a function only of temperature:

$$B(T) = -1636.75 + 12.0408T - 3.27957 * 10^{-2}T^{2} + 3.16528 * 10^{-5}T^{3}$$
(Eq.6)

Parameters used in equations above are defined as below:

- 14)  $C_i$  is the concentration of gas i (mole/kg);
- 15)  $v_i$  represent partial molar volumes (cm<sup>3</sup>/cm<sup>3</sup>);
- 16) P is the pressure at the liquid-gas interface; P= P<sub>a</sub>+ρgz (Pa as above, ρ density of water, g is the gravity acceleration, z is depth (atm);
- 17) p is CO<sub>2</sub> partial pressure (atm);
- 18) T is temperature obtained from CTD data (K);
- 19)  $K_0$  is the solubility constant in mole.liter<sup>-1</sup>.atm<sup>-1</sup>;
- 20)  $f_i$  is the fugacity of the gas (atm);
- 21) S is salinity calculated using TDS (‰);
- 22)  $A_n$  and  $B_n$  are constants (Weiss, 1974; Wilhelm *et al.*, 1977);
- 23) R is the gas constant;
- 24) B(T) is the virial coefficient.

## **APPENDIX E**

(Images were downloaded from Google Earth. For size parameters, location, hydrological setting, and climatology, refer to Table II.1)



Figure D.1 Lakes of the Adamaua Lake District



Figure D 2: The Lake of the South-West Lake District



Figure D 3: Lake of the Bamenda Lake District

Geochemical characteristics of the CVL lakes



Figure D.6: Lake of the Bamenda Lake District