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Isotopic Data for Inferring Groundwater Dynamics in Cagayan De Oro City, Philippines

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A groundwater study was conducted in Cagayan de Oro City (CDO) located in the north-central part of Mindanao, the Philippines using isotopic techniques. The study identifies the recharge sources of the groundwater in the city and estimates the groundwater age and groundwater recharge rate. Monthly integrated samplings of rainfall were conducted in three locations of varying altitudes from October 2012 to March 2015. Groundwater samples from production wells and shallow wells were also collected within the same period at least twice, during the dry and the wet seasons. The samples were analyzed for their stable isotopic compositions and groundwater in selected deep wells was dated using tritium-helium dating. A meteoric water line of $\delta D = (8.26 \pm 0.21)\ \delta^{18}O + (11.56 \pm 1.88)$ was calculated using the precipitation-weighted reduced major axis (PWRMA) method. Isotopic compositions of groundwater show that local precipitation recharges the shallow aquifer. An interaction exists between the shallow and deep aquifer possibly due to the absence of a well-defined multilayer aquifer based on available lithological profiles. Coastal shallow wells appear to be recharged from 35–80 meters above sea level (masl), while deep wells appear to be recharged from 200–300 masl. A recharge rate of 380 mm/yr was estimated, which is more than 20% of the average annual rainfall and twice the estimated recharge using the precipitation-based method.

Keywords: groundwater age, isotope hydrology, radioactive isotopes, recharge rate, stable isotopes

INTRODUCTION

Background and Objectives

Groundwater provides the bulk of the water supply in the Philippines, especially in areas outside Metro Manila (WB 2004). Over the last decades, the population in the Philippines has increased dramatically leading to an increase in water demand. This has led to increased exploitation of groundwater, with it being easily available and requiring little treatment. As early as 1991, the Japan International Cooperation Agency (JICA) has listed nine major cities in the Philippines (*i.e.* Metro Manila, Davao City, Baguio City, Angeles City, Bacolod City, Iloilo City, Zamboanga City, Cebu City, and CDO) as water-critical areas (JICA 1998). In CDO, the demand for water has increased over the last decades due to population expansion and the growth of industrial activities. From 3.3 million m^3/mo in 2000, the groundwater extraction

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rate increased to 4.7 million m^3/mo in 2011 (Palanca-Tan 2011). It is suspected that the city is overexploiting its aquifers as manifested in the drop in the groundwater level of some production wells in recent years. Of the 250 listed operating wells within the city in the Local Water Utilities Administration database, only 67 have permits in the records of the National Water Resources Board (NWRB), the country's water regulating body. Sustainable use of water resources with sufficient understanding of groundwater recharge and flow is, therefore, essential for future management of the city's groundwater resources.

CDO is located in the north-central part of Mindanao in the southern side of the Philippines (Figure 1). The city supports a population of 675,950 according to the last census of the Philippine Statistics Authority (PSA) in 2015 (PSA 2017). The annual average temperature is about 26.7 °C. Based on the Modified Coronas Climate Classification, CDO falls under the Type III climate. This type is characterized by not very pronounced seasons, which are relatively dry from December–April and wet during the rest of the year. It has an average monthly rainfall of 140 mm based on a 35-yr data of the Philippine Atmospheric, Geophysical and Astronomical Services Administration from 1977–2012 at Lumbia Airport gauging station (NWRB 2016). Annual average rainfall based on the same data is 1699.1 ± 309.1 mm. A radial network of 12 river systems originating from Mt. Kitanglad, an extinct volcanic center in Bukidnon, flows into the city towards the bay. The major river system is the CDO River, which has an average inter-annual discharge rate of 54 $m^3\ s^{-1}$.

In order to develop an effective water management policy, it is necessary to understand the behavior and dynamics of groundwater. Published studies conducted on the groundwater systems of CDO have focused mostly on the threats and factors affecting the city's groundwater resources (Palanca-Tan and Bautista 2003; Palanca-Tan 2011). Most of the data on the city's water resources are also not available due to issues in data ownership. In this case, the use of isotopic techniques provides a relatively inexpensive tool for the characterization of flow systems where there is a scarcity of hydrogeological information (Yasuhara *et al.* 1993). Although the use of isotopes of water (oxygen-18, ^{18}O; deuterium, ^{2}H; tritium, ^{3}H) has long been proven to provide substantial information on the behavior of aquifers (Clark and Fritz 1997; IAEA and UNESCO 2003; Charideh and Zakhem 2010), studies in the Philippines using the technique are relatively sparse. Most of these studies have applied the technique in geothermal environs (Alvis-Isidro *et al*. 1993; Gerardo *et al.* 1993; Gerardo-Abaya 2005). Some studies in the country using the technique on groundwater assessment remain unpublished as detailed in the International Atomic Energy Agency (IAEA) database (IAEA 2008).

Specifically, the study objectives are: (1) to identify the sources of recharge, and (2) to estimate the recharge rate of groundwater in CDO. In this study, we provide a comprehensive analysis of groundwater resources in CDO through the use of several isotopic tracers (oxygen and hydrogen). This multi-tracer approach has been used to determine the origin and residence time of groundwater (Bouchaou *et al.* 2009; Cartwright and Morgenstern 2012, 2016; Davisson *et al.* 1999; Gusyev *et al.* 2019; Harrington *et al.* 2002; McGuire *et al.* 2002; Palmer *et al.* 2007; Plummer *et al.* 2001; Ravikumar and Somashekar 2011; Subyani 2004). Tritium-helium dating was also applied for the first time in the Philippines through this study. Tritium-helium dating has been applied in several hydrological studies to determine groundwater age (Hinkle 2009; McMahon *et al.* 2011; Shapiro *et al.* 1998; Solomon and Sudicky 1991; Solomon *et al.* 1995; Szabo *et al.* 1996). While classical techniques are still important in hydrological studies, we demonstrate in this study that isotope data provide important supplemental information for studying groundwater recharge processes and residence time.

Geological and Hydrogeological Settings

CDO is located in the central coast of northern Mindanao and lies between the latitude 8°14′ to 8°31′5" N and longitude 124°27′ to 124°49′ E (Figure 1). It has an area of about 57,000 ha and is geographically nestled between the central coastline of Macajalar Bay to the north and the plateaus and mountains of the provinces of Bukidnon and Lanao del Norte to the south. It is bounded by the municipalities of Opol on the west and Tagoloan to the east.

The city is located in a small alluvial plain formed by the CDO River. This alluvial plain is extended with a long and narrow belt along the Macajalar Bay. Another alluvial plain with a fairly wide area is located along the Iponan River. The lowland is relatively flat with an elevation of not more than 10 masl. The hinterland surrounding the plain is occupied by a hill-top terrace of vast area with elevation ranging from 100–150 m. The top of the terrace is made of relatively flat land surrounded by steep cliffs. In the eastern part of the city, a vast mountainous area – dissected by many small streams – towers from 400–500 masl. This mountainous area is made of limestone. Hilly terrace and slope areas with high elevation are continuously distributed near the seashore. The city is drained by 12 river systems which originate from the slopes of Mt. Kitanglad in Bukidnon Province. These rivers form collectively five major watersheds – from west to east, these are the Iponan, Cagayan Oro, Culambog, Cugman-Agusan, and Alae watersheds (NWRB 2016). About 28% of the city has a slope of 0–8%. This is concentrated on the narrow coastal plains, the alluvial plains of Cagayan and Iponan Rivers, and in the upland terraces. The remaining land has a slope of more than 8%.

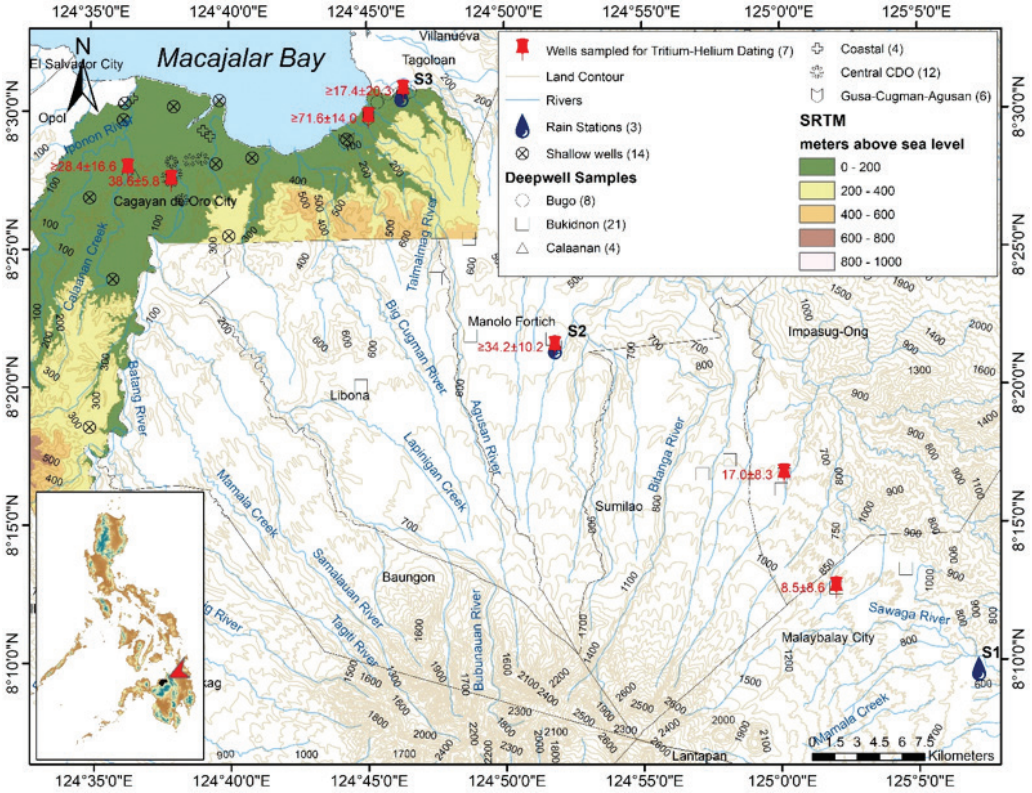

Figure 1. Site map showing boundaries of CDO, the adjacent towns and the sampling sites.

Geologically, the area is formed by six different formations. The quaternary alluvium (QAl) is deposited in the narrow areas along the CDO and Iponan Rivers and extending to the east of the city. This formation is made of silt, sand and gravel, and boulders. The Cagayan Terrace Gravel (CT) of Pleistocene to Holocene and Quaternary eras is distributed on both sides of the CDO River, forming hilly areas with elevation ranging from 100–150 m between the top of the terrace and riverbank. This formation has numerous boulders in the terrace basement consisting of gravel, sandstone, and shale. The Bukidnon Formation (BF) of Late Pliocene to Pleistocene eras is mainly distributed in the eastern part of the city and in the hinterland of the CT formation. It forms a hilly area with a high elevation of 250–300 m as well as a fairly flat top area. The formation consists mainly of tuffaceous sandstone, agglomerate, pebbly sandstone, and conglomerate. The Indahag Limestone (IL) of early to late Pliocene era is mainly distributed in the southern part of the city for a wide area. It is made up of corral rubbles and sandy limestone. The Opol Formation (OF) of the Miocene era is mainly distributed on the west side of the Iponan River beyond the city area. It is composed of conglomerate, pebbly sandstone, agglomerate and tuff. The Schist of the Mesozoic era is distributed in the mountainous area to the east of the city. This area has an elevation of about 500 m and is fairly dissected.

The majority of the city's deep wells are distributed in the narrow alluvial sediment area along the CDO and Iponan Rivers, and a small plain east of the city in Barangay Bugo. Of these well fields, the most productive are those distributed in the alluvial area of CDO River. Based on available lithological logs, the formation layers along this well field consist of sand and gravel with interspersed layers of clay. Known to locals as Macasandig formation, the aquifer yields an average of 7,100 m^3/d per well (JICA 1998). Lithological logs also show almost similar formation layers on the well fields distributed in the alluvial plains of Iponan River and on the small plain east of the city in Barangay Bugo. Other minor well fields are distributed along the coastal stretch of Gusa-Cugman-Agusan, and along the coastal area near the mouth of the CDO River. Groundwater flow models made by the NWRB show that recharge of groundwater in the city occurs through the IL and CT formations. The groundwater flows northward towards the bay (NWRB 2016).

MATERIALS AND METHODS

Sample Collection

Precipitation in the study area was sampled on a monthly basis between October 2012 to February 2015 in Barangay

Bugo, CDO (labeled S3 in Figure 1) and in two locations in Bukidnon Province (labeled S1 and S2, respectively). The rain collector was fabricated using an enclosed 5-gal water bottle fitted with a big funnel having a diameter of 30.5 cm. Thermal insulation was wrapped around the collector. Paraffin oil was also added inside the bottle to minimize evaporation. At the end of each sampling, the total volume of rainwater collected was recorded. Samples for stable isotopes analysis were collected using double-capped 20-ml polyethylene (PE) bottles that are fully filled with no headspace and immediately sealed tight to prevent exchange with the atmosphere. These were stored in a temperature and humidity-controlled room away from direct sunlight until ready for analysis.

Groundwater samplings were conducted at least twice, once during the dry season and another during the wet season. Samples were collected from production wells and shallow wells (*e.g.* handpump) within CDO and Bukidnon Province. Sampling locations are shown in Figure 1. In total, 55 samples were collected from production wells and 14 samples from shallow wells.

Groundwater samples were collected from production wells through a faucet directly connected to the well's discharge pipe or through a bypass discharge pipe. For shallow wells (*e.g.* handpumps), they are pumped manually by hand. Water was allowed to continuously flow while the conductivity, pH, and temperature were measured. Samples for stable isotopes analysis were collected using double-capped 20-ml PE bottles that are fully filled with no headspace and immediately sealed tight to prevent exchange with the atmosphere. The samples were stored in a temperature- and humidity-controlled room away from direct sunlight until ready for analysis.

A separate sampling was conducted in August 2013 for the collection of samples for tritium-helium dating samples from seven selected production wells – three from Bukidnon Province and four from CDO. Samples for helium and other noble gases analyses were collected by flushing the water sample through annealed copper tubes, which are then pinched-off at both ends to prevent atmospheric contamination. The volume of the water samples inside the copper tubes is around 40 ml (Visser *et al.* 2014). Samples for tritium analysis were separately collected in double-capped 1-L PE bottles that are fully filled with no headspace and immediately sealed tight to prevent exchange with the atmosphere.

Stable Isotopes Analysis

Laser spectrometry of hydrogen and oxygen isotopes in water was performed at the International Atomic Energy Agency Isotope Hydrology Laboratory (IAEA-IHL), Vienna, Austria following the method described by Wassenaar *et al.* (2014). Isotopic compositions are given as δ values, the relative deviations with respect to the standard value, the Vienna Standard Mean Ocean Water. Signifying *R* as the abundance ratio of the isotopic species, *i.e.* $^{2}H/^{1}H$ or $^{18}O/^{16}O$, δ is defined by:

$$\delta = \left[\left(\frac{R_{sample}}{R_{standard}}\right) - 1\right] x\ 1000 \qquad (1)$$

where δ is reported in ‰ (per mille, equivalent to 10^{-3}). For deuterium-hydrogen ($^{2}H/^{1}H$), δD is used; for $^{18}O/^{16}O$, the notation is $\delta^{18}O$. The reported maximum uncertainty of each measurement is ± 0.2‰ for $\delta^{18}O$, and ± 1.5‰ for δD.

The regression analysis of δD and $\delta^{18}O$ in precipitation were determined by the method of PWRMA (Crawford *et al.* 2014), which was called as local meteoric water line (LMWL, $\delta D = a*\delta^{18}O + b$; Craig 1961). The parameters a and b were determined by the following equations:

$$a = \frac{\sum_{i=1}^{n} w_i (y_i - \bar{y}_w)^2}{\sum_{i=1}^{n} w_i (x_i - \bar{x}_w)^2} \qquad (2)$$

$$b = \bar{y}_w - a * \bar{x}_w \qquad (3)$$

where

$$\bar{y}_w = \sum_{i=1}^{n} w_i y_i \qquad (4)$$

and

$$\bar{x}_w = \sum_{i=1}^{n} w_i x_i \qquad (5)$$

The w_i, y_i, and x_i refers to the fraction of monthly precipitation amount "p_i" to the total precipitation, δD and $\delta^{18}O$, respectively.

Tritium and Noble Gas Analyses

Concentrations of helium and other noble gases (*e.g.* Ne, Ar, Kr, and Xe) were determined at the IAEA-IHL, Vienna, Austria as described in Visser *et al.* (2014). Technical specifications of the instrument used are described in Matsumoto *et al*. (2017). Gases dissolved in the water samples inside the copper tube were extracted using a vacuum manifold. The extracted gases were inlet to a cryogenic and chemical getter cleanup system followed by analysis using a sector-field mass spectrometer for helium isotopes and a quadrupole mass spectrometer for ^{20}Ne,

^{40}Ar, and ^{84}Kr isotopes (Stolp *et al.* 2010). Tritium samples were analyzed at the HYDRSYS LABOR Analytical Laboratory Ltd., Budapest, Hungary. Enrichment factors of 15–16 were obtained, with a limit of detection of 0.5 TU at a 95% confidence interval.

Tritium-Helium Dating

The ^{3}H/^{3}H age is defined as:

$$Age = \lambda^{-1} ln\left(\frac{[^3He]_{Tritiogenic}}{[^3H]} + 1\right) \quad (6)$$

where λ is the ^{3}H decay constant (= 0.05626 y^{-1}; Lucas and Unterweger 2000), $[^3He]_{tritiogenic}$ is the amount of ^{3}He derived from tritium decay, and [^{3}H] is the amount of tritium. The $[^3He]_{tritiogenic}$ is estimated by separating it from the total [^{3}He] dissolved in the groundwater, which has a number of sources noted as follows:

$$[^3He_{tot}] = [^3He_{eq}] + [^3He_{exc}] + [^3He_{terr}] + [^3He_{tritiogenic}] \quad (7)$$

where $[^3He_{eq}]$ = ^{3}He in solubility equilibrium with the atmosphere, $^3He_{exc}$ = ^{3}He due to excess air, and $^3He_{terr}$ = terrigenic ^{3}He (nucleogenic ^{3}He together with mantle ^{3}He). In Equation 7, only $^3He_{tot}$ and $^3He_{eq}$ are determined through measurements. $^3He_{exc}$ and $^3He_{terr}$ (if present in the sample) were determined by using measurements of ^{4}He and Ne ($^3He_{terr}$). The total ^{4}He concentration measured in a groundwater sample can be written as:

$$[^4He_{tot}] = [^3He_{eq}] + [^4He_{exc}] + [^4He_{terr}] \quad (8)$$

where $^4He_{tot}$ = total measured ^{4}He concentration in the groundwater sample, $^4He_{eq}$ = ^{4}He concentration in solubility equilibrium with the atmosphere, $^4He_{exc}$ = ^{4}He concentration caused by excess air, and $^4He_{terr}$ = terrigenic ^{4}He concentration (radiogenic ^{4}He plus mantle ^{4}He). If no terrigenic helium is contained in the groundwater sample, $^3He_{trit}$ can be calculated by:

$$[^3He_{tritiogenic}] = 4.021E14\left[\frac{^4He_{tot} * (R_{tot} - R_{atm}) + {}^4He_{eq} * R_{atm} * (1-\alpha)}{\frac{1-S}{1000}}\right] \quad (9)$$

where R_{tot} = measured ^{3}He/^{4}He ratio of the sample, R_{atm} = ^{3}He/^{4}He ratio of air (1.384*10^{-6}), α = solubility isotope effect (ca. 0.983)), and S = salinity in ‰. The conversion factor for ^{3}He from cm^{3}STPg^{-1} to TU is 4.021*10^{14}/[(1–S)/1000)] TU/cm^{3}STPg^{-1}.

Based on the calculated groundwater ages, the recharge rate was estimated using the formula (Cartwright *et al.* 2017):

$$\bar{R} = \left(\frac{\theta H \ln(\frac{H}{H-z})}{\tau_z}\right) \quad (10)$$

where $\bar{R}$ is the recharge rate (mm yr^{-1}), θ is the porosity of the aquifer, H is the thickness of the aquifer, z is the depth of screen below the water table (calculated by subtracting the static water level from depth to top of well opening), and τ_z is the groundwater age from tritium-helium dating.

RESULTS AND DISCUSSION

Isotopic Compositions (δD and δ^{18}O) of Precipitation

The ^{18}O and deuterium composition of the precipitation samples collected from the three stations are summarized in Table 1. The δ^{18}O range from –14.81 to –4.59 per mil while the δD values ranged from –109.2 to –25.97 per mil.

Mostly, the isotopic signatures of collected rainwater samples during post-monsoon (December–April) season are relatively more enriched in heavier isotopes (*i.e.* δD and δ^{18}O are more positive) than the isotopic signatures of collected rainwater samples during monsoon (May–November) season. The behavior may be attributed to the shift in the prevailing winds systems in the Philippines between the Southwest monsoon, which usually prevails from July to September, and the Northeast monsoon, which prevails from November to February (Estoque *et al.* 2000). Gerardo-Abaya (2005) reported similar behavior in isotope data in rainwater samples collected from different parts of the Philippines. The phenomenon also reflects the effect of rain amount (*i.e.* "amount effect") to the isotopic composition of the rainwater. A higher volume of rainwater was collected during the monsoon season than during the post-monsoon season in this study.

The LMWLs calculated based on PWRMA method were δD = (8.26 ± 0.21) δ^{18}O + (11.56 ± 1.88), δD = (8.18 ± 0.26) δ^{18}O + (11.10 ± 2.28), and δD = (7.88 ± 0.0.30) δ^{18}O + (7.74 ± 2.71) for stations S3, S2, and S1, respectively. While S3 and S2 show almost similar meteoric water lines, S1's meteoric water line significantly differs from the other two, possibly due to its different topographic features of the neighboring catchment and its higher elevation.

Table 1. Stable isotopic composition of monthly precipitation samples collected from the three rain sampling stations.

Station name	Location	Altitude (masl)[a]	n	Total rainfall amount (mm)	Isotope Range				Weighted means		Deuterium excess
					$\delta^{18}O$, ‰		$\delta^{2}H$, ‰		$\delta^{18}O$, ‰	$\delta^{2}H$, ‰	
					Min.	Max.	Min.	Max.			
S1	8.16096, 125.11923	658	13	1700.60	–11.67	–2.28	–86.56	–21.12	–8.63	–61.10	7.96
S2	8.35625, 124.863417	570	13	1144.78	–11.9	–4.59	–85.71	–25.97	–8.48	–58.20	9.61
S3	8.50885, 124.7711	18	16	1315.26	–14.81	–5.13	–109.2	–28.2	–8.46	–58.36	9.36

The isotopic signatures of the rain samples were also used to calculate the isotopic lapse rate based on the altitude effect. Months during which a high amount of rainwater was collected, specifically July– September, were selected for this purpose (Figure 2). A lapse rate of $\delta^{18}O = –0.0034\ h – 7.14$ was calculated, where h is the altitude or recharge. This indicates a decrease of –0.34 ‰ in $\delta^{18}O$ per 100-m altitude. The value is more than the global average isotopic lapse rate of –0.28 ‰ $\delta^{18}O$/100m (Poage and Chamberlain 2001). Reported lapse rates for $\delta^{18}O$ and $\delta^{2}H$ worldwide lie within the ranges of −0.1 to −0.6 ‰ × 100 m^{-1} and −0.5 to −4 ‰ × 100 m^{-1}, respectively (Windhorst *et al.* 2013). The large lapse rate may be related to the orographic steepness of the study area.

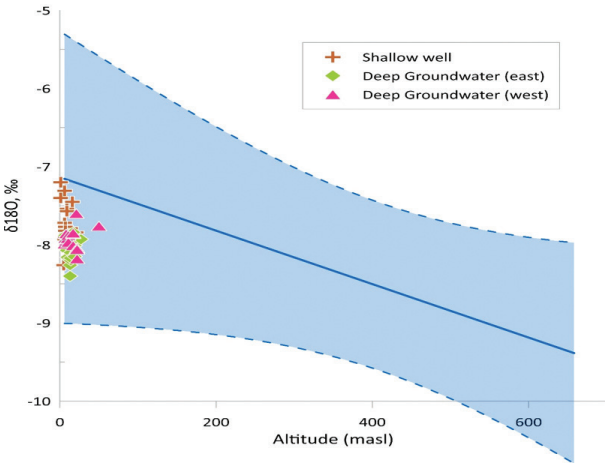

Figure 2. Estimation of the altitude of recharge of groundwater using the isotopic lapse rate calculated based on $\delta^{18}O$ of rainwater samples collected for the months of June – September.

Isotopic Composition of Groundwater Samples

Isotopic values of deep groundwater samples from Bukidnon Province varied from –9.19 to –7.87 ‰ for $\delta^{18}O$ and –63.63 to –53.24 ‰ for δD. On the other hand, isotopic values of deep groundwater samples from CDO ranged from –8.4 to –6.58 ‰ for $\delta^{18}O$ and –54.66 to –46.7 ‰ for δD (Figure 3). Groundwater samples from

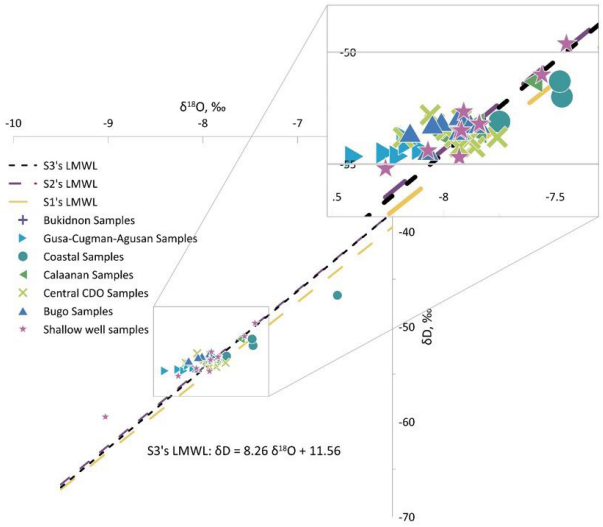

Figure 3. The relationship between δD and $\delta^{18}O$ of groundwater samples plotted on the LMWLs.

Bukidnon Province showed high variation, with samples from higher altitude having lower isotopic values than samples having a lower altitude. In contrast, groundwater samples from CDO showed minimal variation except for groundwater samples from the coastal well field, which have the highest isotopic values. Some samples from the same well field have isotopic values that deviated from the LMWL, possibly indicating mixing with intruding seawater as these samples also exhibit higher electric conductivity (> 2000 µS/cm) than samples from the nearest well field (*i.e.* Central CDO).

Shallow groundwater samples have isotopic values ranging from –9.03 to –7.45 ‰ for $\delta^{18}O$ and –59.50 to –49.63 ‰ for δD. The samples show distinct isotopic values, with samples at lower altitudes having higher isotopic values than the samples in higher altitudes. This strongly indicates recharge from local precipitation.

Although in general, groundwater samples from CDO have higher isotopic values than groundwater samples from Bukidnon, it is observed that isotopic values of some

groundwater samples from Bugo and Gusa-Cugman-Agusan well fields overlap with the isotopic values of groundwater samples from the downstream section of Bukidnon Province. These groundwater samples are in the towns of Libona and Manolo Fortich, which are adjacent to the southern border of CDO. Based on models from previous groundwater assessment studies of the NWRB, the groundwater in the eastern section of CDO is recharged within these parts through the BF (NWRB 2016).

Isotopic signatures of some shallow well samples also overlap with isotopic signatures of deep groundwater samples, suggesting an interconnection between the shallow and deeper aquifer. Based on the general lithological profiles in the study area, it seems that a well-defined multilayer does not exist. It may be possible that the aquifer in the area is a large aquifer interspersed with clay layers in some area but this needs to be further verified.

The altitudes of the recharge of the groundwater were estimated using the previously calculated isotopic lapse rate (Figure 2). Average $\delta^{18}O$ of the collected groundwater samples were substituted to the isotopic lapse rate to estimate the altitude of the recharge zones (Paternoster *et al.* 2008). Based on the available data, shallow wells near the coast are recharged from 35–80 masl, while inland shallow wells (more than 3 km from the coast) range from 100–200 masl. The groundwater in the production wells (*i.e.* deep groundwater) is estimated to be recharged at 200–400 masl. This is the same altitude as the CT, IL, and BF previously identified by groundwater flow models of NWRB as the recharge zones in CDO (Figure 4).

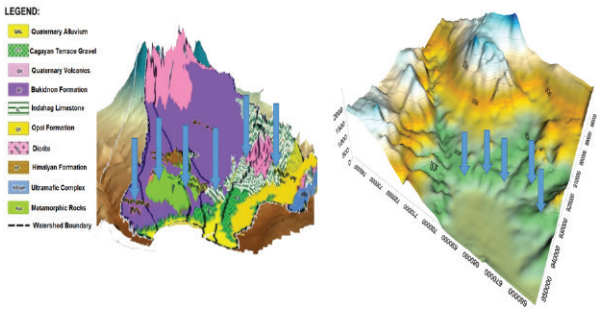

Figure 4. Front-view 3D images of the study area looking from Macajalar Bay. The arrows point to the inferred recharge zones based on the estimated altitudes of recharge.

Groundwater Ages

Groundwater ages determined by the $^3H/^3He$ dating technique were calculated with the assumption that there is no contribution of terrigenic helium from the mantle (Table 2). This is valid to some degree since Mt. Kitanglad is already extinct and the study area is mostly underlain by QAI. Low levels of tritium (< 0.5 TU; *i.e.* the LLD of

Table 2. Summary of measured noble gas and tritium concentrations, and calculated $^3H/^3He$ ages. Numbers in red are the lower limit of calculated ages due to low concentration of tritium (*i.e.* below LLD; LLD = 0.5 TU). The Chi^2 measures the fitness of the model to the measured values – the lower the number, the better is the fit.

Sampling site	He (cm³STP/g)	Error	Ne (cm³STP/g)	Error	Ar (cm³STP/g)	Error	Kr (cm³STP/g)	Error	Xe (cm³STP/g	Error	$^3He/^4He$	Error
Kihare Well, Manolo Fortich, Bukidnon	4.75E–08	6.65E–10	1.90E–07	2.00E–09	3.11E–04	5.67E–06	6.63E–08	1.96E–09	1.00E–08	1.66E–09	1.49E–06	2.70E–08
BSWM Well, Malaybalay City, Bukidnon	5.32E–08	7.37E–10	2.12E–07	2.27E–09	3.06E–04	5.51E–06	6.27E—08	1.78E–09	8.32E–09	3.76E–10	1.38E–06	1.84E–08
Kibangan Pump, Impasug-ong, Bukidnon	1.83E–07	2.53E–09	8.42E–07	9.39E–09	6.86E–04	1.21E–05	1.13E–07	3.34E–09	1.41E–08	7.01E–10	1.40E–06	1.56E–08
COWD PS #14, CDO	4.96E–08	6.76E–10	1.93E–07	2.07E–09	2.96E–04	5.30E–06	6.12E–08	1.93E–09	8.38E–09	6.18E–10	1.68E–06	3.96E–08
COWD PS #23, CDO	5.71E–08	8.31E–10	1.94E–07	2.16E–09	2.97E–04	5.24E–06	6.57E–08	1.96E–09	9.50E–09	4.64E–10	2.35E–06	2.67E–08
COWD PS#21, CDO	4.84E–08	7.17E–10	1.92E–07	2.13E–09	2.85E–04	5.00E–06	6.16E–08	1.84E–09	8.84E–09	4.31E–10	1.40E–06	1.63E–08
COWD PS#10, CDO	6.99E–08	1.00E–09	2.79E–07	3.06E–09	3.80E–04	6.69E–06	7.84E–08	2.36E–09	1.02E–08	5.05E–10	1.43E–06	1.56E–08

the analytical laboratory) prevented reliable age dating for four groundwater samples. The $^3H/^3He$ ages of the groundwaters ranged from 8.5 to > 71.6 yr. There is no discernible trend in $^3H/^3He$ age with depth, which may be related to the large distances between the wells sampled in this investigation (Figure 5).

The consistency of the estimated $^3H/^3He$ ages was checked against the rain tritium history. This is done by summing the observed ^3H and tritiogenic ^3He for each sample, in tritium units, and plotting these against the recharge year (observation year minus the $^3H/^3He$ age). There are no existing continuous rain tritium records for the Philippines except in 1961, 1964–1966, and 2000 onwards. The nearest Global Network of Precipitation stations with rain tritium records since the 1960s are Hong Kong, China; Jakarta, Indonesia; and Tokyo, Japan (IAEA and WMO 2018). The recently reconstructed rain tritium history of Tokyo, Japan from 1950–2018 was used by scaling it to 0.18 for the anthropogenic period (1963–1979) and 0.53 for the remaining years (Gusyev *et al.* 2016, 2019; Chatterjee *et al.* 2019). The comparison shown in Figure 6 indicates a reasonable agreement between estimated tritium in the recharge rain and actual rain measurements except for some samples, which have low tritium concentrations (< 0.5 TU). One of these samples has a recharge year prior to the 1950s. Groundwater with recharge year prior to 1950 is not representative of actual recharge year but is an artifact of mixing. The other samples are affected by mixing with younger groundwater (Price *et al.* 2003). This is notably exhibited by the well with depths of below 40 m but with groundwater age of at least 17.4 yr. This supports the earlier assumption of the absence of a well-defined multilayer aquifer or the presence of a large interconnected aquifer where young and old components mix.

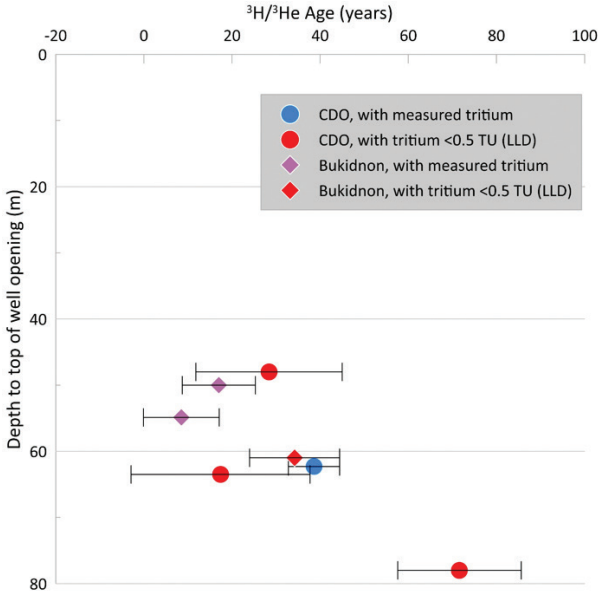

Figure 5. The $^3H/^3He$ age (years) of groundwater sites with sampling depth.

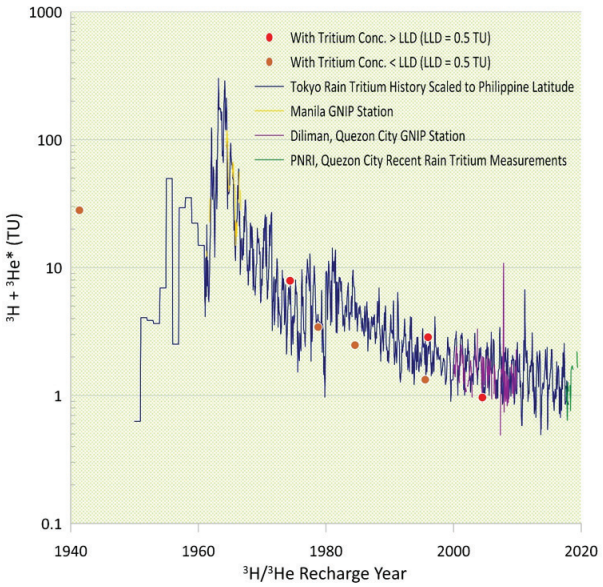

Figure 6. The sum of ^3H and tritiogenic ^3He in groundwater samples as a function of the recharge year. The blue line represents the tritium measurements measured in Tokyo, Japan scaled to Philippine Latitude at 0.18 for the anthropogenic years (1963–1979) and 0.53 for the remaining years. The yellow, violet, and green lines represent the tritium concentrations measured in Manila in 1961, and 1964–1966; Diliman, Quezon City in 2000–2009; and Philippine Nuclear Research Institute, Quezon City in 2017 onwards. The recharge year of groundwater sites prior to 1950 is not representative of the actual recharge year but is an artifact of mixing. Some groundwater samples, specifically those with < LLD tritium concentrations, do not match tritium in rain, possibly due to dispersion and mixing processes.

Recharge Rate

The recharge rate was estimated from the groundwater sample with measured tritium (*e.g.* COWD Deepwell No. 14), which is located in the Macasandig Aquifer. Water in this well has an apparent age of 38.6 ± 5.8 yr. The average porosity of 0.30 ± 0.15 was assumed for the aquifer due to its high contents of mixed sand and gravel. The well has its topmost screen at 62.03 meters below ground level (mbgl) and has a static water level of 17.52 mbgl. Although the NWRB estimated the shallow aquifer in the study area to be 10–40 m thick, there is no estimation for the thickness of the deeper aquifer. However, at certain places, the aquifer has been drilled up to 255 m. Assuming this number to be the maximum thickness of the aquifer, a recharge rate of 380 ± 52 mm/yr was calculated, which corresponds to at least 19% of the annual average rainfall in the city. This is more than twice the recharge rate estimated by NWRB using their

precipitation-based method, which assumes that only 10% of the annual average rainfall (*i.e.* 156 mm/yr) is recharged into the aquifer (NWRB 2016).

The high recharge rate may be due to the presence of fractured zones, particularly in the IL, which is identified by the NWRB as a recharge area of groundwater in the study area. Average recharge estimates from hydrogeological studies of tropical limestone aquifers typically lie within the range of 20–30% of annual rainfall (Vacher and Quinn 1997).

CONCLUSION

Groundwater in CDO is mainly of meteoric origin. Shallow groundwater is recharged by local precipitation, as manifested in its strong isotopic gradient relative to the distance from the coast and altitude. The deep groundwater is recharged on the downhill side of Bukidnon near its boundary with CDO. Isotopic signatures of the shallow and deep groundwater show an interaction between the shallow and deep aquifer, possibly due to the absence of a well-defined multilayer aquifer based on available lithological profiles. It is possible that the aquifer in the study area is a large aquifer that is interspersed only with clay layers in some areas.

Based on available data and the calculated isotopic lapse rate, shallow wells near the coast appear to be recharged from 35–80 masl. Deep groundwater is recharged from 200–300 masl. This is the same altitude as the IL, CT, and BF, which were identified by the NWRB as the possible recharge zones of groundwater in CDO.

A recharge rate of 380 mm/yr was calculated for CDO, which corresponds to more than 20% of the annual average rainfall in the city. This is twice the recharge rate calculated by the NWRB using their precipitation-based method, which assumes that 10% of the annual average rainfall is recharged to the aquifers. The high recharge rate is attributed to the presence of fractured zones in the recharge area, which acts as preferential flow paths.

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REFERENCES

AL CHARIDEH AR, ABOU ZAKHEM B. 2010. Distribution of tritium and stable isotopes in precipitation in Syria. Hydrolog Sci J 55(5): 832–843.

ALVIS-ISIDRO RR, SOLAÑA RR, D'AMORE F, NUTI S, GONFIANTINI R. 1993. Hydrology of the Greater Tongonan Geothermal System, Philippines, as deduced from geochemical and isotopic data. Geothermics 22(5/6): 435–449.

BOUCHAOU L, MICHELOT JL, QURTOBI M, ZINE N, GAYE CB, AGGARWAL PK, MARAH H, ZEROUALI A, TALEB H, VENGOSH A. 2009. Origin and residence time of groundwater in the Tadla basin (Morocco) using multiple isotopic and geochemical tools. J Hydrol 379: 323–338. DOI: 10.1016/j.jhydrol.2009.10.019.

CARTWRIGHT I, MORGENSTERN U. 2012. Constraining groundwater recharge and the rate of geochemical processes using tritium and major ion geochemistry: Ovens catchment, southeast Australia. J Hydrol 475: 137–149.

CARTWRIGHT I, MORGENSTERN U. 2016. Using tritium to document the mean transit time and sources of water contributing to a chain-of-ponds river system: implications for resource protection. Ap Geochem 75: 9–19.

CARTWRIGHT I, CENDON D, CURRELL M, MEREDITH K. 2017. A review of radioactive isotopes and other residence time tracers in understanding groundwater recharge: possibilities, challenges, and limitations. J Hydrol 555: 797–811.

CHATTERJEE S, GUSYEV MA, SINHA UK, MOHOKAR HV, DASH A. 2019. Understanding water circulation with tritium tracer in the Tural-Rajwadi geothermal area, India. Ap Geochem 109: 104373. DOI: 10.1016/j.apgeochem.2019.104373.

CLARK I, FRITZ P. 1997. Environmental Isotopes in Hydrogeology. Boca Raton, FL: Lewis Publishers. 328p.

CRAIG H. 1961. Isotopic variations in meteoric waters. Science (133): 1702–1703.

CRAWFORD J, HUGHES CE, LYKOUDIS SP. 2014. Alternative least squares methods for determining the meteoric water line, demonstrated using GNIP data. J Hydrol 519: 2331–2340. DOI: 10.1016/j.jhydrol.2014.10.033.

DAVISSON ML, SMITH DK, KENNEALLY J, ROSE TP. 1999. Isotope hydrology of southern Nevada groundwater: stable isotopes and radiocarbon. Water Resour Res 35: 279–94.

ESTOQUE MA, STA. MARIA MV, VILLARIN JT. 2000. Climatology of rainfall and wind for the Philippine-South China sea region: 1. monthly variations [Scientific Report]. Climate Studies Division, Manila Observatory, Quezon City, Philippines.

GERARDO JY, NUTI S, D'AMORE F, SEASTRES JS, GONFIANTINI R. 1993. Isotopic Evidence for Magmatic and Meteoric Water Recharge and the Processes Affecting the Reservoir Fluids in the Palinpinon Geothermal System, Philippines. Geothermics 22(5/6): 521–533.

GERARDO-ABAYA J. 2005. Determination of recharge from stable isotope data to the hydrological systems in the Southern Negros Geothermal Field and its environs, Philippines. In: Proceedings of World Geothermal Congress 2005; 2005 Apr 24–29; Antalya, Turkey. p. 1–8.

GUSYEV MA, MORGENSTERN U, STEWART MK, YAMANAZAKI Y, KASHIWAYA K, NISHIHARA T, KURIBAYASHI D, SAWANO H, IWAMI Y. 2016. Application of tritium in precipitation and baseflow in Japan: a case study of groundwater transit times and storage in Hokkaido watersheds. Hydrol Earth Syst Sci 20: 3043–3058.

GUSYEV MA, MORGENSTERN U, NISHIHARA T, HAYASHI T, AKATA N, ICHIYANAGI K, SUGIMOTO A, HASEGAWA A, STEWART MK. 2019. Evaluating anthropogenic and environmental tritium effects using precipitation and Hokkaido snowpack at selected coastal locations in Asia. Sci Tot Env 659: 1307–1321.

HARRINGTON GA, COOK PG, HERCZEG A. 2002. Spatial and Temporal Variability of Ground Water Recharge in Central Australia: A Tracer Approach. Ground Water 40(5): 518–528.

HINKLE SR. 2009. Tritium/helium-3 apparent ages of shallow ground water, Portland Basin, Oregon, 1997–98. US Geol Surv Sci Invest Rep 2009-5057. 8p.

[IAEA] International Atomic Energy Agency. 2008. Philippines. In: Atlas of Isotope Hydrology – Asia and the Pacific. Vienna: IAEA. p. 93–111.

[IAEA] International Atomic Energy Agency, [UNESCO] United Nations Educational, Scientific and Cultural Organization. 2003. Tracers and Transport. In: Environmental Isotopes in the Hydrological Cycle Principles and Applications, Volume IV. Mook WG ed. Vienna: IAEA. p. 327–331.

[IAEA] International Atomic Energy Agency, [WMO] World Meteorological Organization. 2018. Global Network of Isotopes in Precipitation. The GNIP Database. Retrieved on 28 Oct 2018 from http://www.iaea.org/water

[JICA] Japan International Cooperation Agency. 1998. Water resources development plans for selected major cities. In: Master plan on water resources management in the Republic of the Philippines. Tokyo, Japan: JICA. p. 6–3 .

LUCAS LL, UNTERWEGER MP. 2000. Comprehensive Review and Critical Evaluation of the Half-Life of Tritium. Journal of Research of the National Institute of Standards and Technology 105(4): 541.

MATSUMOTO T, SOLOMON DK, ARAGUÁS- ARAGUÁS L, AGGARWAL P. 2017. The IAEA's coordinated research project on "estimation of groundwater recharge and discharge by using the Tritium, Helium-3 dating technique": in lieu of a preface. *Geochemical Journal 51(*5): 385–390. DOI: 10.2343/geochemj.2.0500

MCGUIRE KJ, DEWALLE DR, GBUREK WJ. 2002. Evaluation of mean residence time in subsurface waters using oxygen-18 fluctuations during drought conditions in the mid-Appalachians. J Hydrol. 261: 132–149.

MCMAHON PB, PLUMMER LN, BOHLKE JK, SHAPIRO SD, HINKLE SR. 2011. A comparison of recharge rates in aquifers of the United States based on groundwater-age data. Hydrogeol J 19: 779–800.

[NWRB] National Water Resources Board. 2016. Development of Groundwater Management Plan (GMP) for highly urbanized water constraint cities; specifically, for Cagayan de Oro and surrounding areas. Quezon City, Philippines.

PALANCA-TAN R. 2011. Designing a Raw Water Fee Scheme for Groundwater Extraction in Cagayan de Oro, Philippines [Technical Report]. Singapore: Economy and Environment Program for Southeast Asia.

PALANCA-TAN R, BAUTISTA GM. 2003. Metering and a Water Permit Scheme for Groundwater Use in Cagayan de Oro [Research Report 2003-RR8]. Singapore: Economy and Environment Program for Southeast Asia.

PALMER PC, GANNETT MW, HINKLE SR. 2007. Isotopic characterization of three groundwater recharge sources and inferences for selected aquifers in the upper Klamath Basin of Oregon and California, USA. J Hydrol 336: 17–29.

PATERNOSTER M, LIOTTA M, FAVARA R. 2008. Stable isotope ratios in meteoric recharge and groundwater at Mt. Vulture volcano, southern Italy. J Hydrol 348: 87–97.

PLUMMER LN, BUSENBERG E, BOHLKE JK, NELMS DL, MICHEL RL, SCHLOSSER P. 2001. Groundwater residence times in Shenandoah National

Park, Blue Ridge Mountains, Virginia, USA: a multi-tracer approach. Chem Geo 179: 93–111.

POAGE MA, CHAMBERLAIN CP. 2001. Empirical relationships between elevation and the stable isotope composition of precipitation and surface waters: considerations for studies of paleoelevation change. Am J Sci 301: 1–15.

[PSA] Philippine Statistics Authority. 2017. Population and Housing. In: 2017 Philippine Statistical Yearbook. Manila, Philippines. p. 1–8.

PRICE RM, TOP Z, HAPPELL D, SWARK PK. 2003. Use of tritium and helium to define groundwater flow conditions in Everglades National Park. Water Resour Res 39(9): 1267–1278. DOI: 10.1029/2002WR001929

RAVIKUMAR P, SOMASHEKAR RK. 2011. Environmental Tritium (3H) and hydrochemical investigations to evaluate groundwater in Varahi and Markandeya river basins, Karnataka, India. J Env Rad 102: 153–162.

SHAPIRO SD, ROWE G, SCHLOSSER P, LUDIN A, STUTE M. 1998. Tritium-helium 3 dating under complex conditions in hydraulically stressed areas of a buried-valley aquifer. Water Resour Res 34(5): 1165–1180.

SOLOMON DK, SUDICKY EA. 1991. Tritium and helium-3 isotope ratios for direct estimation of spatial variations in groundwater recharge. Water Resou Res 27(9): 2309–2319.

SOLOMON DK, POREDA RJ, COOK PG, HUNT A. 1995. Site characterization using 3H/3He ground water ages, Cape Cod, MA. Ground Water 33(6): 988–996.

STOLP BJ, SOLOMON DK, SUCKOW A, VITVAR T, RANK DK, AGGARWAL PK, HAN LF. 2010. Age dating base flow at springs and gaining streams using helium 3 and tritium: FischaDagnitz system, southern Vienna Basin, Austria. Water Resour Res 46: W07503. DOI: 10.1029/2009WR008006

SUBYANI AM. 2004. Use of chloride-mass balance and environmental isotopes for evaluation of groundwater recharge in the alluvial aquifer, Wadi Tharad, western Saudi Arabia. Envi Geo 46: 741–749.

SZABO Z, RICE DE, PLUMMER LN, BUSENBERG E, DRENKARD S, SCHLOSSER P. 1996. Age dating of shallow groundwater with chlorofluorocarbons, tritium/helium 3, and flow path analysis, southern New Jersey coastal plain. Water Resour Res 32(4): 1023–1038.

VACHER HL, QUINN TM. 1997. Geology and hydrogeology of carbonate islands. Dev Sedimentol 54: 948.

VISSER A, FOURRÈ E, BARBECOT F, AQUILINA L, LABASQUE T, VERGNAUD V, ESSER BK. 2014. Intercomparison of tritium and noble gases analyses, $^{3}H/^{3}He$ ages and derived parameters excess air and recharge temperature. Applied Geochem 50: 130–141. DOI: 10.1016/j.apgeochem.2014.03.005

WASSENAAR L, COHEN TB, AGGARWAL P. 2014. Approaches for Achieving Long-Term Accuracy and Precision of $\delta^{18}O$ and $\delta^{2}H$ for Waters Analyzed using Laser Absorption Spectrometers. Environ Sci Technol 48(2): 1123–1131.

WINDHORST D, WALTZ T, TIMBE E, FREDE HG, BREUER L. 2013. Impact of elevation and weather patterns on the isotopic composition of precipitation in a tropical montane rainforest. Hydrol Earth Syst Sci 17: 409–419.

[WB] World Bank. 2004. Philippines – Environment monitor 2004. Washington, DC. p. 1–6.

YASUHARA M, MARUI A, KAZAHAYA K, SUZUKI Y, TAKAYAMA S. 1993. A study of groundwater flow systems in volcanic media: Isotopic evidence for when recharge occurs in Mt. Yatsugatake, central Japan. In: Selected Papers on Hydrogeology, Vol. 4. Sakura Y ed. Hannover, Germany: Verlag Heinz Heise. p. 185–194.