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 δD = (8.26 ± 0.21) δ¹⁸O + (11.56 ± 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 m³/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 (NWWRB), 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 (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, O; deuterium, D; tritium, H$^3$) 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; Davison et al. 1999; Gussyev et al. 2019; Harrington et al. 2002; McGuire et al. 2002; Palmer et al. 2007; Plummer et al. 2001; Ravikumar and Somasekhar 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; McGuire et al. 2002; 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 coastal 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, Culumbo, Cugman-Agusan, and Alae watersheds (NWWRB 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%.
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 tube 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:

$$\delta = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$$  \hspace{1cm} (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 δ$^{18}$O. The reported maximum uncertainty of each measurement is ± 0.2‰ for δ$^{18}$O, and ± 1.5‰ for δD.

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

$$a = \frac{\sum_{i=1}^{n} w_{i} (y_{i} - \bar{y}_{w})^{2}}{\sum_{i=1}^{n} w_{i} (x_{i} - \bar{x}_{w})^{2}}$$  \hspace{1cm} (2)

$$b = \bar{y}_{w} - a * \bar{x}_{w}$$  \hspace{1cm} (3)

where

$$\bar{y}_{w} = \frac{\sum_{i=1}^{n} w_{i} y_{i}}{\sum_{i=1}^{n} w_{i}}$$  \hspace{1cm} (4)

and

$$\bar{x}_{w} = \frac{\sum_{i=1}^{n} w_{i} x_{i}}{\sum_{i=1}^{n} w_{i}}$$  \hspace{1cm} (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 δ$^{18}$O, respectively.

**Tritium and Noble Gas Analyses**

Concentrations of helium and other noble gases (e.g., Ne, Ar, K, 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 HYDRYS 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:

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

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

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

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

$$[^{4}He]_{\text{tot}} = [^{4}He]_{\text{eq}} + [^{4}He]_{\text{exc}} + [^{4}He]_{\text{terr}} \quad (8)$$

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

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

where $R_{\text{tot}}$ = measured $^{3}He/^{4}He$ ratio of the sample, $R_{\text{atm}}$ = $^{3}He/^{4}He$ ratio of air (1.384$\times10^{6}$), $\alpha$ = solubility isotope effect (ca. 0.983), and $S$ = salinity in %. The conversion factor for $^{3}He$ from cm$^{3}$STP g$^{-1}$ to TU is 4.021$\times10^{14}$/[(1$ - $S)/1000)] TU/cm$^{3}$STP g$^{-1}$.

Based on the calculated groundwater ages, the recharge rate was estimated using the formula (Cartwright et al. 2017):
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 $\delta^2H$ worldwide lie within the ranges of $-0.1$ to $-0.6$ ‰ $\times 100 \text{ m}^{-1}$ and $-0.5$ to $-4$ ‰ $\times 100 \text{ m}^{-1}$, respectively (Windhorst et al. 2013). The large lapse rate may be related to the orographic steepness of the study area.

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

<table>
<thead>
<tr>
<th>Station name</th>
<th>Location</th>
<th>Altitude (masl)</th>
<th>n</th>
<th>Total rainfall amount (mm)</th>
<th>Isotope Range</th>
<th>Weighted means</th>
<th>Deuterium excess</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\delta^{18}O$, ‰</td>
<td>$\delta^2H$, ‰</td>
<td>$\delta^{18}O$, ‰</td>
</tr>
<tr>
<td>S1</td>
<td>8.16096, 125.11923</td>
<td>658</td>
<td>13</td>
<td>1700.60</td>
<td>-11.67</td>
<td>-2.28</td>
<td>-86.56</td>
</tr>
</tbody>
</table>

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 $\delta^2H$. 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 $\delta^2H$ (Figure 3). Groundwater samples from 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 ($> 2000 \mu S/cm$) 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 $\delta^2H$. 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 δ^{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/^4He 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...
the analytical laboratory) prevented reliable age dating for four groundwater samples. The \(^3\text{H}/\text{He}\) ages of the groundwaters ranged from 8.5 to > 71.6 yr. There is no discernible trend in \(^3\text{H}/\text{He}\) 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 \(^3\text{H}/\text{He}\) ages was checked against the rain tritium history. This is done by summing the observed \(^3\text{H}\) and tritiogenic \(^3\text{He}\) for each sample, in tritium units, and plotting these against the recharge year (observation year minus the \(^3\text{H}/\text{He}\) 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.

**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

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**Figure 5.** The \(^3\text{H}/\text{He}\) age (years) of groundwater sites with sampling depth.

**Figure 6.** The sum of \(^3\text{H}\) and tritiogenic \(^3\text{He}\) 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, Quezon City and Philippine Nuclear Research Institute, Quezon City in 2000 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.
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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