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Groundwater Residence Time Modelling in the Aquifers of the Ampasindava Peninsula, Northwestern of Madagascar

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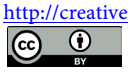

Abstract

This study concerns the use of isotope techniques to assess groundwater resource management in mining area. The objective of the study is first to estimate the groundwater residence time in the peninsula of Ampasindava and secondly to determine the relationship between wastewater from mining activity and groundwater resource in the study area by using environmental isotopes. It will contribute to clarifying the impact of the mining activity waste water on the groundwater in the study area. The stable isotopes of oxygen and hydrogen were used to understand groundwater recharge process and its origin. Tritium was used to estimate the groundwater residence time and hydrochemical tools helped identify the groundwater chemical facies. A simulation based on mathematical model was applied to estimate the groundwater residence time using the tritium concentration value of each groundwater sample. As results, the groundwater geochemical characteristics in the Ampasindava peninsula show two different water types. This assumption was confirmed by the isotope signature of the water samples. The results of the simulation run under exponential and dispersion models showed higher values of groundwater age for the spring waters compared to the groundwater age using a piston flow model. It suggests that spring waters are older than groundwater in the alluvium plains. The spring water seems to be protected from rare earth mining exploitation pollution. On the contrary, the mining exploitation could be a source of contamination of the groundwater in the alluvium plain.

Subject Areas

Environmental Sciences, Geology

Keywords

Isotopes, Groundwater, Model, Age, Madagascar

1. Introduction

The peninsula of Ampasindava is located in the northwestern coastal boarder of Madagascar, district of Ambanja in the province of Antsiranana at about 590 km from Antananarivo the country capital. The geographical coordinates are centered in E47˚12'30" and S13˚47'30" (**Figure 1**). The region is well known for its outstanding biodiversity and the underground wealth. This area has also a great potential of natural resources, terrestrial as well as under the sea. In recent years, a mining company has settled the exploitation of rare earth elements in this area. The mining activities are sources of toxic contamination that can degrade the water quality and destroy the marine ecosystem. Therefore, a system for safeguarding the environment must be considered to protect the marine ecosystem and the water resource in this coastal zone area. It is in this perspective that the researchers from "Centre National de Recherche Océanographique-CNRO" and "Institut national des Sciences et Techniques Nucléaires-INSTN Madagascar" have jointly designed a project to set up a monitoring station for marine pollution fight and the coastal zone preservation. The applied method is based on the use of the isotopic techniques to determine the mechanism of recharge and the process of groundwater mineralization.

The stable isotopes present in water (δ^2H, δ^{18}O) have been used extensively to evaluate the hydrological processes on the basis of parameters such as evaporation, precipitation, mixing, and residence time [1].

Both hydrochemical and isotopic information have been used to interpret the origin and the groundwater recharge, refine estimates of time scales of recharge and ground-water flow, decipher reactive processes, provide paleohydrological information, and calibrate groundwater flow models [2].

Radiogenic isotopes, such as radioactive carbon-14 (half-life: 5730 years) and tritium (half-life: 12.32 years) are useful to determine relative groundwater residence times over short (<50 years) to long (up to ~30 to 50 ka) timescales [3] [4]. Tritium measurement was used to identify water samples that were recharged approximately post-1950, or to identify water samples that contain fractions of post-1950 (Plummer *et al.*, 2004) [5]. Estimated groundwater ages can help validate or refute assumptions made about groundwater flow based on chemical and isotopic data or results of groundwater flow modelling.

Groundwater dating has also been used to extract information on rates of geochemical and microbiological processes in aquifers, to classify hydrogeologic environments on the basis of contamination potential [6], to retrieve historical records of contaminant loading to aquifers [7] [8] [9] and to estimate remediation times for contaminated groundwater systems.

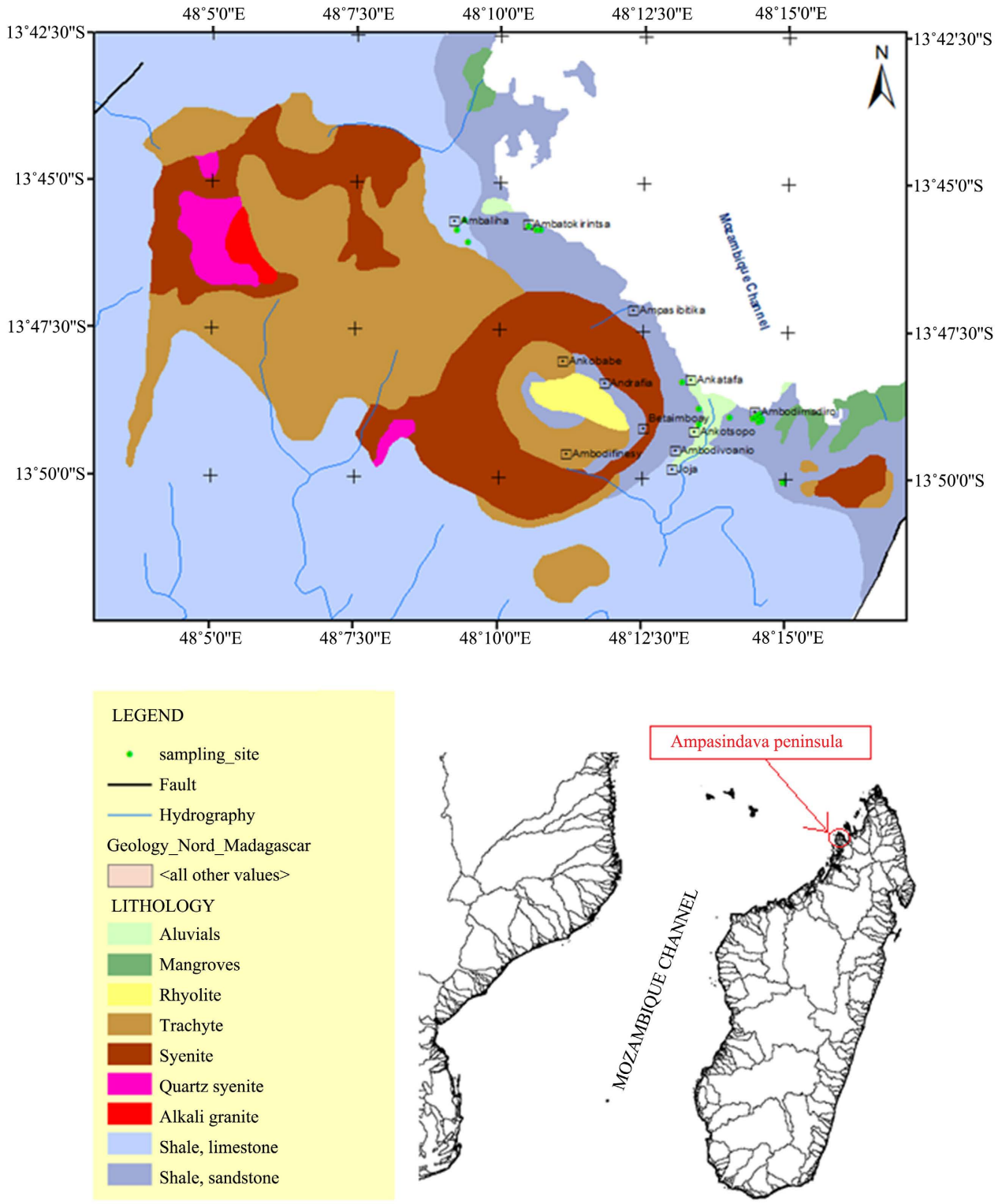

Figure 1. Localization and geological map of Ampasindava peninsula.

This research work aims to assess the impact of rare earth elements exploitation on the water resources in the coastal zone of Ampasindava peninsula. The main objectives are: 1) to characterize groundwater and determine their origin;

2) to estimate the groundwater residence time along the flow paths. The obtained results allow us to identify the main sources of groundwater contamination and to predict the influence of the mining exploitation on the water resources in the study site.

1.1. Climate

The northwestern region of Madagascar is generally dominated by the warm and humid tropical climate [10]. Local air temperature varies from 18˚C to 33.8˚C. In this part, the average monthly rainfall precipitation is more than 950 mm up to 2000 mm during the abundant rainfall between November and March and less than 20 mm between July and October according to the meteorological service in Antananarivo.

1.2. Regional Geological Setting

The northwestern part of Madagascar is characterized by the alkaline annular intrusion composed by several massifs and the mineralization in rare earth elements [11]. This region is dominated by Mesozoic sediments that were deposited in a predominantly marine environment and include mudstone, siltstone, limestone, sandstone and marl.

In the late Cenozoic, the central and northern parts of Madagascar were subject to uplift and rifting that resulted in the development of horst and graben structures. This extensional regime was also accompanied by intra-continental volcanism and the location of numerous igneous complexes, including several cones that occurred along a roughly linear southeast-northwest trending zone between the Nosy Be archipelago and Antongil Bay. The chronology of the location of the igneous complexes is poorly constrained, but thought to have occurred between the Eocene and Late Miocene (Ganzeev and Grechishchev, 2003; Melluso *et al.*, 2007) [12] [13].

The igneous rocks are significantly diverse and range in composition from mafic-ultramafic (olivine melilitite, olivine nephelinite, basanite, tephrite, alkali basalt and hawaiite) to intermediate (tephritic phonolite and phonolite) to acidic (quartz trachyte and rhyolite) (**Figure 2**).

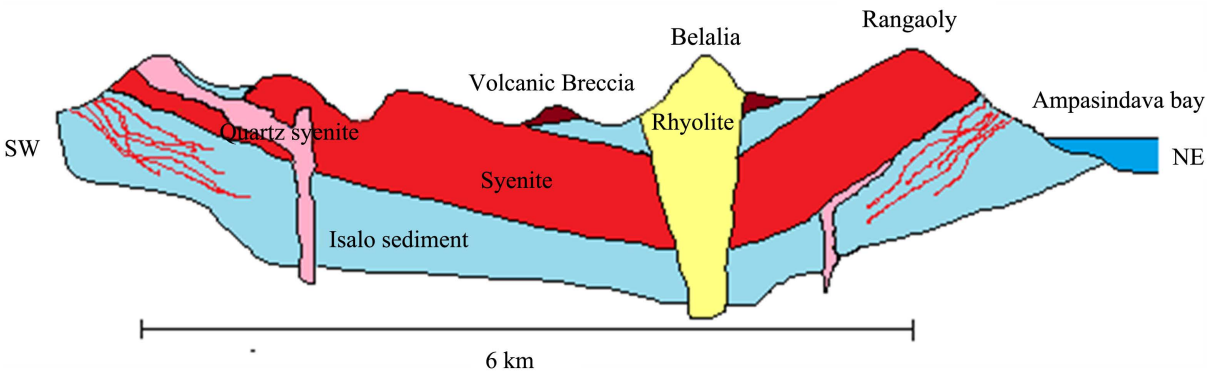

Figure 2. Schematic cross section of Ambatohimirahavavy of the igneous (Source: OMNIS).

1.3. Overview of Geology of Ampasindava Peninsula

1.3.1. Lithology

In the Ampasindava peninsula (**Figure 1**), the marine Permo-Trias characterises to the Sakamena continental group whereas the Lias and Dogger appear in mixed subsidence facies formed by fine to coarse sandstone layers, [14]. Sedimentary formations have been affected by post-Liasic eruptive intrusions represented by alkaline granites, syenites, nephelinic syenites, rhyolites, phonolites and basalts.

1.3.2. Global Tectonics

The intrusions of Nosy Be-Ampasindava (Ambohimirahavavy, Ampasibitika, massif of Manongarivo, Lokobe, Nosy Komba) present either an annular or semi-annular structure separated by ring-dykes, which are generally discordant with the host rocks, either a structure in cylindrical necks or in elongated blades, or still in intrusions spread out in subconcordance with the host rock as the ring-sills of Manongarivo [15]. Eruptive activity occurred in the province of Ampasindava during the Miocene. The general tectonic map of Madagascar shows that the Ampasindava volcano-plutonic massifs are aligned along a large NW-SE fault [11]. The latter author expressed the presence of a recent rift (terminal and current Miocene) which corresponds to the reactivation of the old faults of the African rift in the sedimentary basins of the west coast of Madagascar. This leads to the development of a fault system in this NW-SE direction.

1.4. Hydrogeological Setting

Groundwater in the Ampansidava peninsula is flowing through the hydrogeological system of Antsiranana sedimentary basin. The surface water in the sedimentary zone of the upper catchment is chemical of good quality (freshwater with average mineralization), but more or less charged with clay particles from lateritic origin in the lower watercourses. The best quality groundwater is generally located at a depth greater than 20 m in the porous formations (consolidated sandy and sandstone) or fractured (basalts).

The aquifers in the region of Antsiranana consist of arenas, sandstones and fractured basement which allow a relatively good flow rate for exploitation.

Three aquifer types can be mentioned in the peninsula of Ampasindava:

- Groundwater in the fractured basement is flowing above the healthy basement in a transition zone with the weathering horizon. Generally, the fissured aquifer is a free surface groundwater with low mineralization [16].
- The groundwater of alteration is often found in the grained arenas zone called arenas groundwater. Their lithology is mainly composed of sandy clay. The aquifer is free surface groundwater captured by dug well or borehole with a depth between 4 m and 15 m and the water static level varies from 2 m to 3 m. The layer thickness is about 5 m and the groundwater is fresh with low mineralization.
- The alluvium plain groundwater is recharged by the slow drainage by gravity

from the aquifer of alterite and by the superficial groundwater flow from ta hill with high slope. The upper superficially alluvium is covered by clay and limestone where infiltration can be held because of their low thickness (less than 2 m). The static water table level is less than 2 m and can reach up to 1 m during the flood period, during which the water is not good for drinking. Otherwise, the groundwater of inter collinear alluvium which flows at as bottom has relatively limited flow rate and is therefore not appropriate for exploitation.

2. Sampling and Methods

2.1. Field Measurements

In June 2018, 19 samples were collected as part of a reconnaissance ground water study of the Ampasindava peninsula. Physico-chemical parameters (such as temperature, electrical conductivity and pH values) of spring, dug well and river waters were determined in-situ using multimeter HQ40d. Bicarbonate content was measured by titration with 0.16 N H_2SO_4 using Hach digital titrator.

The samples were then analyzed for chemical and environmental isotope measurements (^{18}O, ^{2}H and ^{3}H).

2.2. Laboratory Analysis

The chemical analyses were carried out at the Isotope Hydrology Laboratory of INSTN-Madagascar by Ion chromatography method using ICs 1101 ion chromatograph.

The determination of isotope composition oxygen-18 and deuterium were made using a Laser absorption spectrometer Picarro L-2101i. Oxygen-18 and deuterium results are reported as parts per thousand (‰) with respect to V-SMOW using the (δ) notation where:

$$\delta_{sample} = \frac{R_{sample} - R_{standard}}{R_{standard}} * 1000 \quad (1)$$

where R_{sample} is the isotopic ratio of $^{18}O/^{16}O$ or $^{2}H/^{1}H$ in the sample, and $R_{standard}$ is the isotopic ratio of the international standard. The analytical precision of $\delta^{18}O$ and $\delta^{2}H$ are respectively 0.2‰ and 2.0‰.

Tritium analyses were performed with a Tri-Carb 3170 TR/SL in an obscure counting laboratory. Electrolytic enrichment and liquid scintillation decay counting methods were used [17] [18]. Enriched samples were mixed 1:1 by volume with a QuickSafe 40 Low Level Tritium cocktail. The results are reported in Tritium in units (TU) relative to the NIST 4926E standard with a typical error of ±0.50 TU. The detection limit for ^{3}H measurement in the laboratory is about 0.08 TU.

The tritium activity content of water was calculated according to the following relation.

$$A(t) = \frac{A_{std} * N_{sample}}{Z * N_{std}} * D \quad (2)$$

where:

A_{std} = Activity of standard (TU).

N_{std} = Net count of standard (cpm).

N_{sample} = Net count of sample (cpm).

Z = Enrichment factor of each cell.

D = Radioactive decay $e^{-\lambda t}$.

2.3. Calculating the Apparent Age

The results of tritium in groundwater samples are applied to estimate the recent groundwater residence time for each aquifer [19]. The groundwater age can be determined using mathematical model based on exponential distribution function [20]. The simulated tritium output curves are calculated by the integral convolution. Then, the calculation of tritium output curves was performed using a program model developed by the International Atomic Energy Agency [21].

$$c_{out}(t) = \int_{-\infty}^{t} c_{in}(t') \cdot f(t-t') \mathrm{d}t' \tag{3}$$

For Piston Flow Model (PFM), the response function is given by the well-known Dirac function δ:

$$f(t') = \delta(t-t'-\tau) \tag{4}$$

For Exponential Model (EM), we assume that there is no tracer exchange between the flow lines and we then obtain the following response function:

$$f(t-t') = \frac{1}{\tau} \cdot e^{-\frac{t-t'}{\tau}} \tag{5}$$

In the dispersion model (DM), the one-dimensional solution of a flow mode following a dispersion equation for a semi-infinite medium is used as a response function [22]:

$$f(t-t') = \frac{1/\tau}{\sqrt{4\pi\delta\frac{t-t'}{\tau}}} \cdot \frac{1}{\frac{t-t'}{\tau}} \cdot \exp\left[-\frac{\left(1-\frac{t-t'}{\tau}\right)^2}{4\delta\frac{t-t'}{\tau}}\right] \tag{6}$$

3. Results and Discussion

3.1. Hydrochemical Characteristics

The concentrations of major ions for all samples are plotted onto a trilinear diagram [23] to reveal the hydrochemical characteristics of the different groundwaters and understand their evolution along their flow paths (**Figure 3**). The hydrochemical facies of water samples show that two main groups of groundwaters predominate in the peninsula of Ampasindava. Fresh groundwater at high altitude and mixing of fresh and saline water intrusion are found in the samples collected along the coastal aquifer.

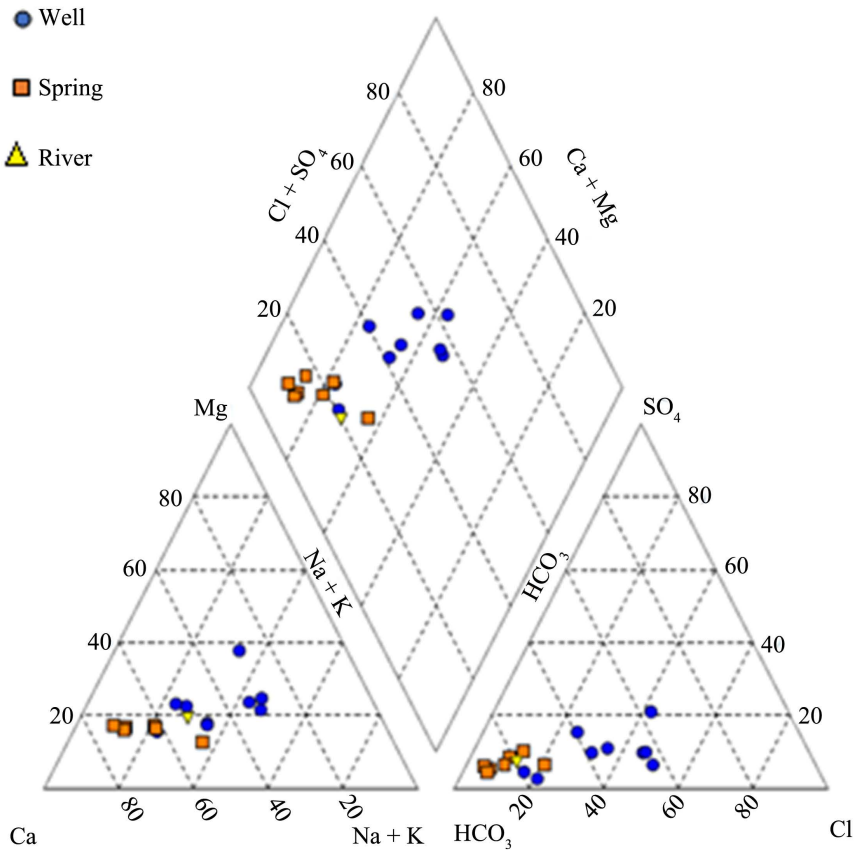

Figure 3. Hydrochemical facies of all water samples.

The fresh groundwaters in the peninsula of Ampasindava are mainly of Ca-HCO_3 and Ca-Na-(Mg)-HCO_3 water types with low Cl^- and SO_4^{2-} concentrations and electrical conductivity values varying from 142.62 µS/cm to 885 µS/cm. These groundwaters are weakly mineralized because they are not affected by several sources of contamination sources. These samples are collected from springs and dug wells. The pH and temperature values of these samples are homogenous varying respectively from 7.41 to 8.67 and from 27.7˚C to 29˚C (Table 1). The temperature values of groundwater are relatively high, close to the mean annual temperature of the region. Calcite or dolomite dissolution and carbonate silicate weathering could be a major source of mineralization of groundwater because rock-water interaction occurs along the flow paths in the fractured aquifer.

The mixture of fresh and saline waters is of Ca-Na-(Mg)-HCO_3-Cl or Na-Ca-Mg-Cl-HCO_3 water types with lower SO_4^{2-} concentration. The Electrical Conductivity values vary from 147.62 µS/cm to 1593.25 µS/cm. The groundwater flowing in the alluvium plain is characterized by Na-Ca-Mg-Cl-HCO_3 facies. They are more mineralized compared to the groundwater with Ca-Na-HCO_3-Cl types. pH values range from 7.84 to 8.89, and the temperature varies from 27˚C to 30˚C. The water temperatures are close to the local air temperature of the rainfall period. This is an indication that they can be influenced by evaporation

Table 1. Field and laboratory measurements.

Sample Code	Temp. (˚C)	pH	EC (µS/cm)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	^{3}H (TU)
GW01	29.3	7.77	259.77	−4.25	−22.4	-
GW02	28.4	7.96	357.53	−4.19	−21.7	0.09
GW03	28.3	7.89	178.85	−4.83	−21.3	0.88
GW04	28.0	7.78	185.69	−4.28	−22.8	0.28
GW05	27.7	7.55	142.06	−4.24	−22.0	0.08
GW06	27.0	7.84	125.62	−3.90	−20.0	2.18
GW07	28.9	7.41	396.30	−4.33	−23.1	0.09
GW08	28.4	7.47	601.73	−4.81	−25.4	0.25
GW09	27.3	8.18	239.98	−3.37	−16.7	2.88
GW10	27.4	8.41	204.24	−3.67	−18.5	1.92
GW11	28.9	8.63	147.31	−4.21	−22.1	1.75
GW12	28.2	8.89	332.77	−4.2	−22.6	2.02
GW13	30.9	7.86	866.87	−4.04	−20.8	0.82
GW14	30.0	7.93	1593.25	−4.07	−21.6	0.84
GW15	28.8	8.67	883.22	−4.61	−24.4	0.33
SW01	27.5	8.22	153.87	−4.07	−20.2	1.68
SW02	26.0	8.22	113.00	−4.25	−19.63	-
SW03	22.0	8.22	89.7	−4.05	−21.69	-

during infiltration. These waters undergo various types of contamination such as marine intrusion and anthropogenic activities (mining exploitation, agricultural activities). The other source of groundwater mineralization in this zone could be the dissolution of evaporite minerals or ion exchange process knowing that the major geological formation present in the Ampasindava coastal boarder is formed by clay sandstone and limestone.

3.2. Isotopic Results

The groundwater from springs samples stable isotopic composition vary respectively from −4.83‰ to −4.07‰ for $\delta^{18}O$ and from −25.4‰ to −20.2‰ for $\delta^{2}H$. These samples are relatively enriched compared to the annual isotope composition of rainfall in Antananarivo with respective $\delta^{18}O$ and $\delta^{2}H$ mean values of −4.90‰ and −25.1‰. The tritium activity is relatively low and ranges from 0.08 TU to 0.33 TU whereas the mean tritium activity in precipitation is close to 2.44 TU.

The wells groundwater collected along the coast have a relatively narrow range of $\delta^{18}O$ and $\delta^{2}H$ which are −4.21‰ to 3.37‰ and −22.1‰ to 16.7‰ re-

spectively. They are more enriched compared to the spring samples which are close evaporation. Tritium values are higher and range from 0.88 TU to 2.88 TU suggesting recent recharge of groundwater.

The river samples isotope composition vary from −4.5‰ to −4.07‰ and from −22.4‰ to −20.2‰ respectively for $\delta^{18}O$ and $\delta^{2}H$ which are close to the isotopic composition of the groundwater. It would mean that interconnection between surface water and groundwater in this zone may occur. The average river tritium value is 1.68 TU.

3.3. Groundwater Origin and Recharge Process

The environmental isotopes of $\delta^{18}O$ and $\delta^{2}H$ are excellent tracers for determining the origin of groundwater and widely used for studying the groundwater recharge, migration pathways and mixing of waters from different sources [24] [25]. The isotopes use plays on important role for the evaluation of the groundwater sources [24] [26] [27] [28] [29]. Stable isotopes of $\delta^{18}O$ and $\delta^{2}H$ in groundwater of an active hydrological cycle are derived from and reflect the initial isotopic composition of recharging rainwater in an active hydrological cycle.

Within the coordinate system of $\delta^{18}O$ vs $\delta^{2}H$ (**Figure 4**), it is possible to discern a meteoric line, the slope of which is characteristic of a certain hydrological system [30].

The isotope composition of the river samples varies respectively from −4.5‰ to −4.07‰ for $\delta^{18}O$ and from −22.4‰ to −20.2‰ for $\delta^{2}H$ which are close to the isotopic composition of the groundwater. It might mean that interconnection between surface water and groundwater in this zone occurs.

The samples lie between the Global Meteoric Water Line [31] and the Local meteoric water line plots of Antananarivo (dash line) of which equation line are $\delta^{2}H = 8\delta^{18}O + 10.3$ and $\delta^{2}H = 8.22\delta^{18}O + 15$, respectively. The spring samples are isotopically more depleted compared to the groundwater samples. A slight evaporation of groundwater samples seems to occur according to the groundwater samples plots line which is less than that of the local meteoric water line in

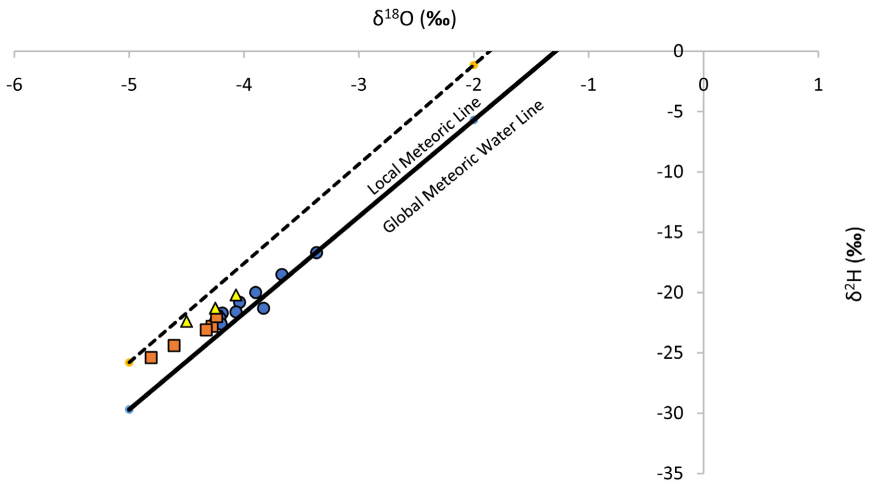

Figure 4. Isotope composition of all samples.

Antananarivo. The evaporation of the samples indicates that the rainwater may infiltrate slowly into the aquifer and that the recharging meteoric water remains somehow relatively long into the surficial aquifers, whereas the spring waters are affected by the altitude effect because of their depleted isotope composition.

Groundwater samples investigated from the dug well in the coastal area plot along a line of which with equation $\delta^2H = 6.15\delta^{18}O + 4.32$, which would mean that rainfall undergoes a slight evaporation before infiltration into the saturated zone.

Groundwater derived exclusively from pre-atomic bomb precipitation would have a maximum tritium concentration of 0.8 TU by the early 1990's if the maximum pre-atomic bomb estimate of 8 TU in atmospheric precipitation is used [32]. In this study, all spring waters have tritium content less than 0.5 TU. This value may show an aquifer recharge from pre-atomic bomb precipitation. These waters are depleted in $\delta^{18}O$ suggesting a recharge from precipitation with low temperature (**Figure 5**).

For groundwater with tritium concentrations greater than 0.8 TU, a fraction of the above the mentioned rainwater could have recharged the aquifer system since 1952. The dug well ground water which have tritium concentrations greater than 0.8 TU are found along the coastal parts of the study area and may indicate that post-1953 rainfalls has recharged in the alluvium aquifer system. These waters are more enriched in ^{18}O compared to the other groundwaters which are affected by the altitude effect. It means that the recharge temperature is higher than that of spring waters. This temperature greater than 30˚C is characteristic of semi-arid climate in coastal zone suggesting that the aquifer recharge occurs from direct infiltration of precipitation during the rainfall season. Tritium concentrations, although generally low, are very close to current levels of precipitation and show that modern recharging occurs [33].

3.4. Groundwater Dating Using Tritium

The groundwater age or its residence time is defined as the time elapsed since

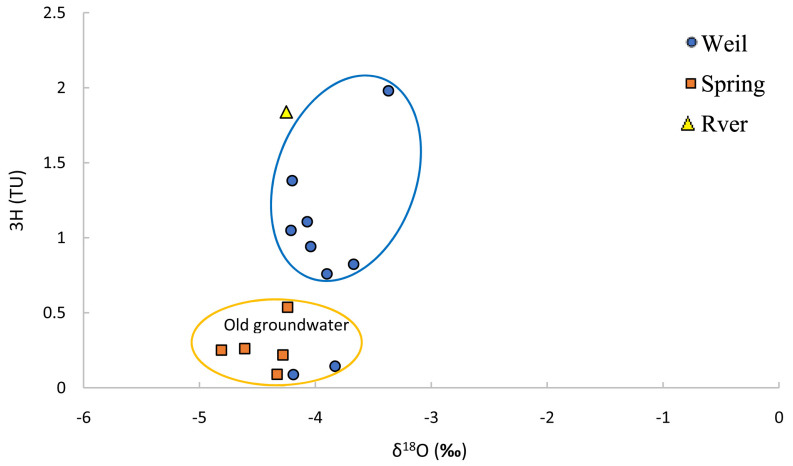

Figure 5. Relation between $\delta^{18}O$-^3H.

the water parcel had its last contact with the atmosphere. Water in shallow aquifers can range from days to decades in age, while old groundwater may have residence times from 10^3 to 10^7 years. Groundwater renewal or recharge is unknown for most aquifers or associated with great uncertainties as a result of the difficulties in its quantification [34].

In the last 50 years, the groundwater renewability has become an important component of groundwater resources assessment, as it is necessary to understand the groundwater circulation and implement the sustainable use of groundwater resources [35]. It is essential to estimate the age of groundwater in this study area to evaluate the groundwater renewability and aquifer vulnerability to pollution. In this study, the groundwater age has been determined by quantitative tritium measurement in groundwater samples since most of groundwaters have been recently recharged by rainfalls.

3.5. Input Function for ^{3}H in Groundwater

Several studies have been undertaken to estimate the mean residence time of groundwater in aquifers of different hydrogeological zones using tritium techniques. With the same objective, a mathematical model with dispersion, piston and exponential distribution functions, coupled with the hypothesis of a completely mixed reservoir, was applied to the study area. Practically, this method has proved to be satisfactory for two-dimensional groundwater flow of unlimited planar aquifer [19] [21]. For the Ampasindava peninsula study area, the required tritium input function for this simulation was taken from available tritium records at Antananarivo station which is 590 km far from the study area, which is the closest IAEA network station to the study area. The ealier missing tritum data of Antananarivo station during 1958-2020 were estimated from logarithmic correlation (r^2 = 0.864) [36] between Antananarivo and Vienna (Austria) stations which have globally the longest tritium records.

The simulated tritium output curves (**Figure 6**) were calculated using the convolution integral (Equation (3)). Then, the calculation of tritium output curves was performed using a program model developed by the IAEA [20].

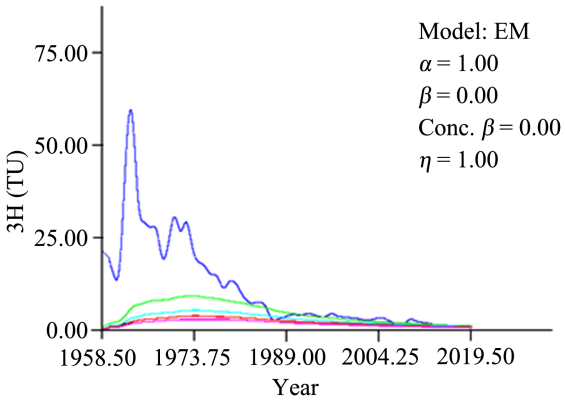

Figure 6. Calculated tritium output curves for different mean residence times with exponential model.

3.6. Simulation of Groundwater Age

Three models like EM, DM and PFM were used to simulate groundwater ages in the peninsula of Ampasindava according to the hydrogeological formation in the study site.

Table 2 below shows the result of simulated groundwater residence time in the peninsula of Ampasindava while considering three mathematical models with constant values of β, P_d and η.

The EM and DM models were applied to spring waters, the values of P_d and η are respectively 0.8 for DM model and 1.00 for EM model to all samples. The sigma value varies from 0.0005 to 0.0375 and there is no significant difference between the simulated groundwater residence times for the two models, except

Table 2. Calculated values of groundwater age.

Code	Type	Model	β	P_d	η	^{3}H (TU)	Sigma (TU)	Age (years)
W01	Well	-	-	-	-	-	-	-
W02	Spring	EM DM	0.0 0.0	- 0.8	1.00	0.08	0.0023 0.0039	800 430
W03	Well	EM DM	0.0 0.0	- 0.8	1.00	0.14	0.0012 0.0072	460 350
W04	Spring	EM DM	0.0	- 0.8	1.00	0.22	0.0020 0.0150	280 275
W05	Spring	EM	0.0	-	1.00	0.54	0.0375	90
W06	Well	PFM EM	- 0.0	- -	- 1.00	0.76	0.0025 0.0059	3.2 2.5
W07	Spring	-	-	-	-	-	-	-
W08	Spring	EM DM	0.0 -	- 0:8	1.00	0.25	0.0005 0.0128	240 250
W09	Well	PFM EM	- 0.0	- -	1.00	1.98	0.1296 0.9800	9.00 16.5
W10	Well	PFM EM	0.0 0.0	- -	- 1.00	0.82	0.0803 0.0039	9.8 4.00
W11	Well	PFM EM	0.0 0.0	- -	- 1.00	1.05	0.0422 0.0900	9.6 14.0
W12	Well	PFM EM	- 0.0		1.00	1.38	0.0506 0.4264	9.4 16.0
W13	Well	PFM EM	- 0.0	- -	- 1.00	0.94	0.0326 0.0012	5.2 11.5
W14	Well	PFM EM	- 0.0	- -	- 1.00	1.11	0.0178 0.1462	9.6 16.5
W15	Spring	EM DM	0.0 0.0	- 0.8	1.00 -	0.26	0.0011 0.0068	230 230

for W02. This point is located at the coastal board like the W015 water point. The geological structure of the site shows that the spring waters come out of a fractured aquifer enhanced by the existence of fault in the area zone. According to their tritium activity, the mean residence time of the latter aquifer groundwater varies from 90 up to 480 years. It would mean that the spring waters are issued from relatively old and long pathways groundwater.

For the dug well waters, EM and PFM models were applied. The output results show a slightly difference of sigma values and the simulated groundwater ages obtained differs strongly between the two models. Generally, the simulated groundwater age from the PFM model is lower than with the EM model. For the PFM model, the simulated mean groundwater age varies from 3.2 to 9.6 years while it varies from 2.5 to 16.5 years for the EM model. This would suggest that the groundwater in the alluvium plain of the coastal zone in Ampasindava is recharged from recent precipitation not far from the boarder ocean.

3.7. Rare Earth Exploitation on Groundwater Resources in Ampasindava Peninsula

The rare earth exploitation project in the Ampasindava peninsula started more than ten years ago. However, this project has created a disastrous impact on over thousands of hectares of natural spaces, in particular an extremely toxic pollution which threatens the livelihoods of the neighbouring populations as well as the exceptional terrestrial and marine biodiversity of the region [37].

According to the estimated groundwater age, in the alluvium plain groundwater is the most vulnerable and there is a greater risk of contamination by the rare earth exploitation project. Actually, the mining zone is located at high altitude in the peninsula; therefore the waste water runs off into the river and drains into the aquifer in the alluvium plain. Besides, the spring groundwaters are less threatened by the exploitation contamination because their recharge area is relatively far from the peninsula.

4. Conclusions

The Ampasindava peninsula groundwater is mainly recharged by meteoric water during the rainy season. This water is fresh with a dominant of Ca-HCO_3 facies type. The groundwater flows out of springs in the fractured with an isotope composition close to that of Antananarivo during the summer period suggesting that they are recharged by direct rainfall infiltration from inland precipitation which isotope composition of $\delta^{18}O$ and $\delta^{2}H$ which varies respectively from −4.83‰ to 4.24‰ and −22.0‰ to −21.3‰. It is relatively old groundwater according to the tritium concentration value which is less than 0.22 TU. It is not affected by any source of contamination.

The alluvium groundwater is enriched with isotope composition of $\delta^{18}O$ and $\delta^{2}H$ which vary respectively from −4.19‰ to −3.07‰ and −21.7‰ to −16.7‰, suggesting local rainfall precipitation recharge with somehow significant evaporation before infiltration into unsaturated zone. Nevertheless, some other com-

ponents are to be taken into account into the recharge mechanism. In fact, the isotope composition of the river is close to the isotope composition of the alluvium plain groundwater, meaning that the river water may also drain into this aquifer. Besides, the alluvium groundwater is more mineralized than the other types of waters, with a mixed fresh-saline water facies. This might suggest some contamination from several sources, thus justifying the increase of the groundwater electrical conductivity. In particular, the relatively high concentration of sodium and chloride could be explained by the saline water intrusion or anthropic activities impacts. And according to the tritium results, the above mentioned groundwater corresponds to mixed old and modern waters of which tritium concentration value ranges from 0.75 TU to 1.98 TU.

A simulation based on mathematical model was used to estimate the age of groundwater in the Ampasindava peninsula. According to the geological formation of the aquifer, three mathematical models such as EM, DM and PFM were applied with a computer program to estimate the age of each groundwater sample. On the one hand, the results of the simulation run under EM and DM models applied to the spring water samples show similar values of groundwater age with a slight variation of sigma value. Thus, the springs groundwater mean residence time varies from 90 up to 480 years with a range of sigma around 0.0001 TU. On the other hand, the EM and PFM models were applied to the groundwater samples collected in the alluvium plain. The results show different residence time values and different sigma values. As, for the PFM model, the simulated mean groundwater age varies from 3.2 to 9.6 years on one side and the simulated groundwater age from the EM model varies from 2.5 to 16.5 years on the other side. Therefore, one can infer that the spring water is not influenced by the rare earth mining exploitation project, whereas the alluvium plain groundwater may undergo a probable risk of contamination from the latter mining exploitation.

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Conflicts of Interest

The authors declare no conflicts of interest.

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