[RADIOCARBON, VOL 31, NO. 3, 1989, P 926–933]

^{14}C ANALYSES OF GROUNDWATER FROM THE BOTUCATU AQUIFER SYSTEM IN BRAZIL

ANNKARIN AURELIA KIMMELMANN E SILVA
ALDO DA CUNHA REBOUÇAS
Universidade de São Paulo, Instituto de Geociências, São Paulo, Brazil
and
MARIA MARLUCIA FREITAS SANTIAGO
Universidade Federal do Ceará, Departamento de Física, Fortaleza, Brazil

ABSTRACT. Measurements of ^{14}C activity as well as determinations of the stable isotope composition (^{18}O, ^{2}H and ^{13}C) of groundwater samples were made to investigate the flow path, origin, recharge and age of the Botucatu Aquifer System in Brazil, between 1984 and 1987. The stable oxygen isotope composition reflects infiltration during several climatic recharge conditions. Measured ^{14}C activities range from 0.4 to 94.2% modern. $\delta^{13}C$ values enable us to distinguish two groundwater types of different origins. There is a gradual increase of ^{14}C ages from the outcrop area towards the central part of the basin, associated with a progression of the confining conditions. Anomalous fluoride contents seem to be correlated with high ^{14}C ages of the groundwater. The reliability of the ^{14}C data is discussed.

INTRODUCTION

The aim of the study on the groundwater of the Botucatu Aquifer System in the Brazilian part of the Paraná Basin was to apply hydrochemical and environmental isotope techniques (^{18}O, ^{2}H, ^{13}C and ^{14}C) to investigate the age structure, origin and flow path within the huge aquifer.

The Botucatu Aquifer System (Fig 1) is the most important aquifer of the Paraná Basin covering 818,000km^2 of Brazilian territory. Over 90% of the aquifer is confined by basalt flows; it is unconfined along the border of the basin. The thickness of the formation increases towards the center of the basin. The aquifer consists of silty-clayish sandstones of fluvial origin, called the Pirambóia Formation. The upper part is the Botucatu Formation of eolian origin, consisting of fine to medium sandstones. Both formations are of Mesozoic age and represent the basis of São Bento Group. They are intercalated between the Permian layers of the Passa Dois Group and the basalt flows of the Serra Geral Formation.

The fundamental hydrogeologic characteristics of the Botucatu Aquifer are: average thickness, 300m, hydraulic conductivity, 10^{-4} to 10^{-5}m/s, effective porosity, 10 to 20%, storage coefficient, 10^{-3} to 10^{-6}, average transmissivity, 10^{-3}m^2/s.

The potentiometric surface of the water shows characteristics of artesianism in the central part of the basin. There, the groundwater level is ca 400m above sea level in the tropical northern part reaching 100m in the subtropical southern part of the Paraná Basin (Rebouças, 1976). Today groundwater is recharged by direct infiltration of rainwater in the outcrop area, which is ca 98,000km^2. Groundwater flows from the border of the basin towards its central part, in the direction of the dip of the geological

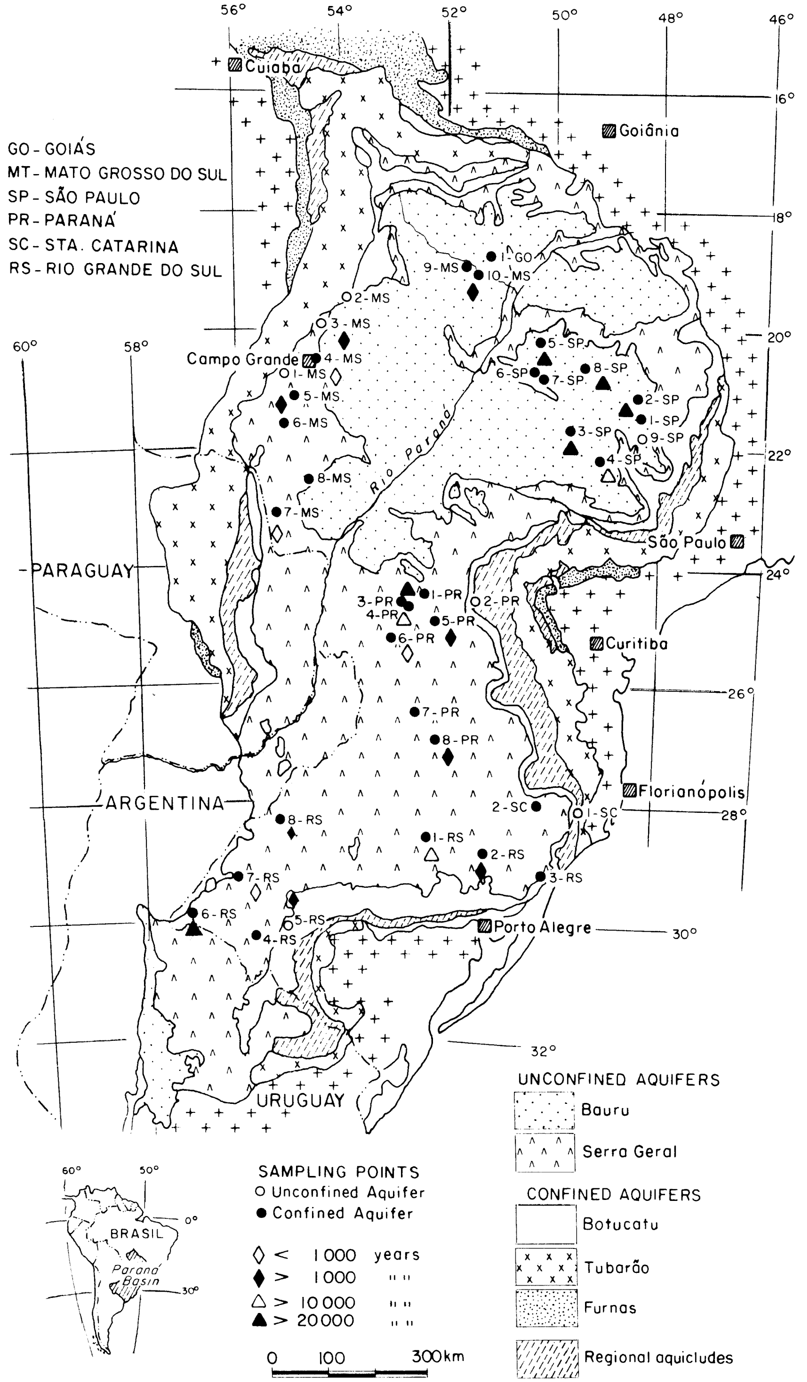

Fig 1. Geographic distribution of the calculated groundwater ages of the Botucatu Aquifer System in the Brazilian part of the Paraná Basin

units. With increasing travel time, the hydrostatic pressure increases, due to the increasing load of the basalt and other layers. Because of the large geothermal gradient, the system contains important heat resources. It also has great drinking water potential because of the high yield of suitable chemical and bacteriological properties. The demand increases with the growth of the population.

EXPERIMENTAL METHODS

Between 1984 and 1987 the groundwater samples for physical, chemical and isotopic analyses were collected from free-flowing and pumped deep wells, located in the unconfined and confined areas of the aquifer. The depths of the wells range from 75–1325m.

The ^{14}C samples were precipitated dissolved inorganic carbon (DIC) from groundwater. $BaCl_2.2H_2O$, $Ba(OH)_2$ solution and a flocculant "Praestol" were used in the field. Large amounts of water up to 400L were used, due to the low bicarbonate content. The specific ^{14}C activity of DIC was measured at the Radiocarbon Laboratory of the Federal University of Ceará in Fortaleza, Brazil (FZ). Acetylene was used as counting gas for two proportional low-level counters operating in anticoincidence. The NBS oxalic acid standard was used as reference. Three ^{14}C determinations were made at the Radiocarbon Laboratory of the Niedersächsisches Landesamt für Bodenforschung in Hannover, Federal Republic of Germany (HV).

$\delta^{13}C$ determinations were made with a Micromass 602 C mass spectrometer at the Laboratory for Stable Isotopes at CENA-USP in Piracicaba.

RESULTS AND DISCUSSIONS

The specific ^{14}C activity of the DIC samples ranges from 0.4 to 94.2% modern carbon (Table 1). The ^{14}C ages T were calculated using the formula

$$T = 8033 \ln \frac{A_0}{A} \qquad (1)$$

where A_0 is 0.95 times the ^{14}C activity of the NBS oxalic acid and A the measured ^{14}C activity of the sample. The ^{14}C ages are compiled in Table 1. Figure 1 shows the geographic distribution of the ranges of the ^{14}C ages.

At the border of the basin, the groundwater is young, sometimes mixed with some older water. In the central part, there is a zone with ages exceeding 30,000 yr, ranging from the northern part of the basin at Jales (well 5-SP) via São José do Rio Preto (well 8-SP), Lins (well 3-SP) until Cornélio Procopio (well 3-PR). The gradual increase of the ^{14}C ages from the outcrop area at the border towards the center of the basin may be interpreted as groundwater flow, although the great distances of the sampling sites do not enable us to interpolate the ^{14}C ages.

According to the $^{13}C/^{14}C$ relationship (Fig 2), two groundwater types can be distinguished. Most of the groundwater is recharged in areas where non-carbonaceous sediments exist. The $\delta^{13}C$ values start with –17 to –20‰ and increase to an equilibrium value of ca –11‰ ("maturation line") (Geyh & Michel, 1982). The other type is recharged in areas of carbonaceous sed-

TABLE 1

^{14}C ages, well depths and fluoride contents of Botucatu Aquifer System groundwater

No.	Sample no.	Code	Site	Depth (m)	^{14}C (% mod)	Age (BP)	F (mg/L)
1	FZ–383	2–SP	Monte Alto	581	0.4±0.6	>35,500	0.15
2	FZ–384	3–SP	Lins	1042	0.4±0.8	>33,200	2.04
3	HV–14208	4–SP	Bauru	291	11.0±0.8	17,700±710	0.14
4	FZ–420	5–SP	Jales	1323	1.5±0.8	>33,200	1.45
5	FZ–423	7–SP	Araçatuba	1200	7.1±0.8	$21,216^{+915}_{-820}$	1.34
6	FZ–424	8–SP	S J R Preto	1136	1.7±0.7	$32,500^{+4500}_{-2500}$	1.18
7	FZ–398	3–MS	Corguinho	150	67.8±0.5	3125± 55	nd*
8	FZ–339	4–MS	Campo Grande	144	93.3±0.6	560± 50	nd*
9	FZ–400	5–MS	Sidrolândia	95	87.1±0.8	1100± 70	nd*
10	FZ–401	7–MS	Amambaí	150	94.2±0.7	480± 60	nd*
11	FZ–422	10–MS	Cassilândia	215	75.1±0.7	2304± 80	0.33
12	FZ–443	1–PR	Cambará	220	33.9±0.5	8685± 30	0.39
13	FZ–444	3–PR	Corn Procópio	1070	0.8±0.5	>37,000	0.93
14	FZ–445	4–PR	Corn Procópio	1000	19.1±1.0	13,307±130	0.41
15	HV–14562	4–PR	Corn Procópio	1000	27.0±1.0	10,485±290	0.41
16	FZ–446	5–PR	S Cec Pavão	338	54.7±0.7	4840±100	0.27
17	FZ–447	6–PR	Grandes Rios	170	103.0±0.5	Modern	nd*
18	FZ–448	8–PR	Cruz Machado	248	9.1±0.5	19,260±400	0.35
19	HV–14563	8–PR	Cruz Machado	248	30.8±0.5	9450±200	0.35
20	FZ–449	1–RS	Encantado	224	27.6±0.5	10,355± 60	1.19
21	FZ–450	2–RS	Feliz	127	59.1±0.7	3225± 90	0.43
22	FZ–451	5–RS	S Franc Assis	99	65.9±0.7	3350± 80	0.11
23	FZ–452	6–RS	Uruguaiana	200	10.9±0.4	17,830±300	0.62
24	FZ–453	7–RS	Itaqui	**	92.2±0.7	650± 60	0.42
25	FZ–454	8–RS	S L Gonzaga	**	61.9±0.6	3850± 90	0.16

*Not detected

**Unavailable

iments starting with –12‰ and approaching –6‰. These values may also be due to CO_2 formed by C4 plants. This difference may correspond to a difference in age of maximum, 5000 years for the first type and 0 for the second. Thus, an age correction seems unnecessary.

There is a clear shift of the $\delta^{18}0$ values (Table 2) before and after ca 10,000 years, reflecting a change of climate or an increase of temperature. The $\delta^{18}0$ and δD values (Table 2) lie on the meteoric waterline.

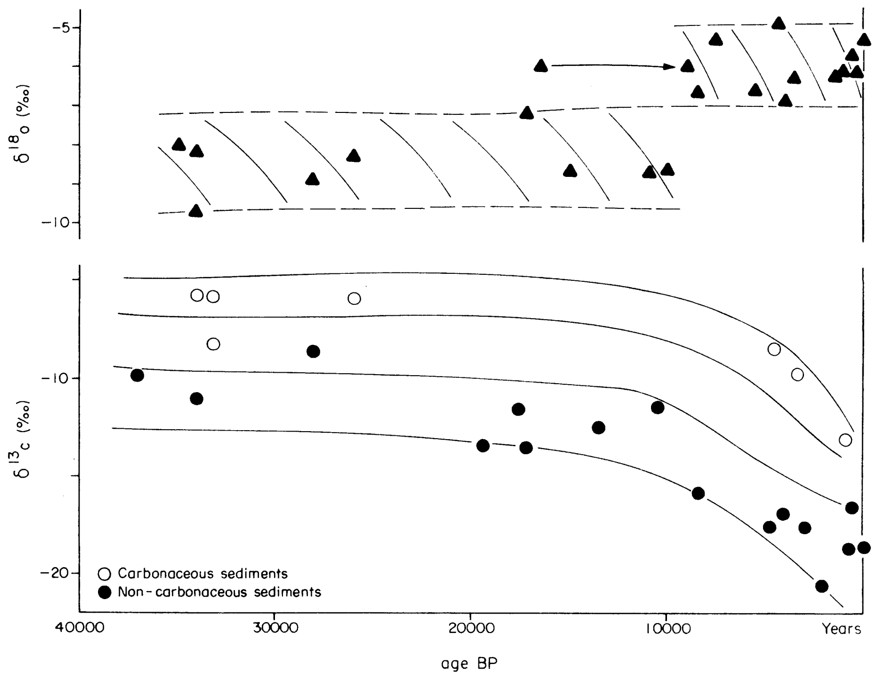

Fig 2. $^{18}O/^{14}C$ and $^{13}C/^{14}C$ age relationships

These few data do not solve the problem of whether a continuous groundwater recharge or a hiatus occurred since 40,000 years ago. For the latter, the groundwater age trend may not enable us to estimate groundwater velocities or even to recognize the direction of groundwater flow. Special interest for the hydrogeologist is related to the disturbing high fluoride content of some deep groundwaters. A correlation seems to exist between high ^{14}C ages (Kimmelmann e Silva *et al,* 1989) and very high fluoride values for some groundwater. This supports the hypothesis by Fraga (pers commun, 1988) that the origin of fluoride is also from the groundwater from the deepest part of the Pirambóia Formation and not, as believed from the basalts. Further isotope studies of the fluoride anomaly are planned to avoid expensive drilling without hope of success.

In spite of the apparently reasonable results, there are indications that the ^{14}C ages may not reflect the initial undisturbed conditions or may even be incorrect. These are our observations:

1) The two production wells 3-PR and 4-PR, both ca 1000m and only ca 500m away from each other, of the same geological position, yield with 13,000 and 37,000 yr, completely different ^{14}C ages. This may be due to an ill-fitting casing of well 4-PR, which allows an admixture of younger groundwater from the basalt aquifer. This may be the case for the samples from

TABLE 2

Stable isotope composition of the Botucatu Aquifer System groundwater in the Brazilian part of the Paraná Basin

No.	Code	Site	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	$\delta^{13}C$ (‰)
1	1–SP	Guariba	–9.6	–67	–11.1
2	2–SP	Monte Alto	–9.8	–65	–11.1
3	3–SP	Lins	–8.1	–56	–5.9
4	4–SP	Bauru	–8.7	–60	–11.8
5	5–SP	Jales	–8.3	–59	–6.0
6	6–SP	Araçatuba	–8.9	–63	–8.3
7	7–SP	Araçatuba	–8.6	–59	–8.5
8	8–SP	S J R Preto	–8.9	–61	–8.3
9	9–SP	Araraquara	–7.4	–49	–19.5
10	1–MS	Dois Irmãos	–6.3	–39	*
11	2–MS	Camapuã	–8.6	–58	–11.6
12	3–MS	Corguinho	–6.3	–37	–17.7
13	4–MS	Campo Grande	–6.3	–37	–18.6
14	5–MS	Sidrolândia	–6.2	–40	–13.1
15	6–MS	Maracaju	–5.7	–32	*
16	7–MS	Amambaí	–6.2	–36	–16.4
17	8–MS	Dourados	–6.8	–42	–12.1
18	9–MS	Cassilândia	–6.6	–45	–20.4
19	10–MS	Cassilândia	–6.9	–47	–20.6
20	1–GO	Itajá	–8.2	–56	–10.9
21	1–PR	Cambará	–6.7	–47	–15.9
22	2–PR	Rib do Pinhal	–6.7	–42	–23.7
23	3–PR	Corn Procopio	–8.0	–57	–9.3
24	4–PR	Corn Procopio	–8.7	–59	–12.5
25	5–PR	S Cec Pavão	–6.6	–45	–17.7
26	6–PR	Grandes Rios	–5.7	–41	–18.6
27	7–PR	Inácio Martins	–6.7	–43	–*
28	8–PR	Cruz Machado	–7.2	–46	–13.3
29	1–SC	P Alta Norte	–5.9	–40	*
30	2–SC	S Cristov Sul	–6.2	–38	*
31	1–RS	Encantado	–5.2	–33	–11.4
32	2–RS	Feliz	–4.9	–28	–17.0
33	3–RS	S Ant Patrulha	–4.8	–29	–12.2
34	4–RS	Alegrete	–5.3	–33	–12.4
35	5–RS	S Franc Assis	–5.3	–33	–9.9
36	6–RS	Uruguaiana	–6.0	–44	–13.6
37	7–RS	Itaqui	–5.5	–32	*
38	8–RS	S L Gonzaga	–5.4	–37	*

*Unavailable

the center of the basin, where older ages were expected. However, this explanation needs to be tested by special isotopic analyses.

2) Another observation is the remarkable change of ^{14}C ages over time, eg, for well 3-SP. Similar observations have been made in Germany (Geyh & Sonne, 1983). The time span, 2000–30,000 yr, is so great, that the reliability of the data may be suspect.

3) Final doubts arise from an interlaboratory experiment conducted by two laboratories on aliquots of the two samples from well 4-PR and 8-PR. The differences are too large to explain via the negative experiences gathered during the first international intercomparison project (International Study Group, 1982).

Further isotopic analyses are necessary to verify the reliability of the data.

CONCLUSIONS

The conclusions of the isotopic hydrological analyses of samples of ca 25 deep wells in the Botucatu Aquifer System in the Brazilian part of the Paraná Basin are as follows:

1) ^{14}C ages gradually increase from the outcrop area at the border towards the center of the basin, associated with progressive confinement conditions of the aquifer. ^{14}C ages exceed 30,000 yr in the center.

2) $\delta^{13}C$ values reflect the "isotope maturation" of the groundwater towards the center of the basin and enable us to distinguish two groundwater types. The more depleted the $\delta^{13}C$ values are, the younger is the groundwater.

3) $\delta^{18}0$ values change at 10,000 yr, reflecting climatic variations.

4) Fluoride anomalies may be correlated with ^{14}C ages exceeding 25,000 yr. More investigation on the origin of the fluoride is needed, however. Mineralized groundwater from deeper aquifers or from the basalts are the alternatives.

ACKNOWLEDGMENTS

The financial sponsors of this study were the International Atomic Energy Agency, Project no. 3648–BR and the Brazilian FINEP/PADCT, Project no. 53.84.01755.00. This project was initiated with Rosa Beatriz Gouvêa da Silva, who died during a political accident in Peru, in 1986. Mebus A Geyh, Hannover, made three ^{14}C analyses, read the paper very critically and made valuable suggestions. Eichii Matsui, Piracicaba, carried out the ^{18}O, ^{2}H and ^{13}C analyses.

REFERENCES

Geyh, M A and Michel, G, 1982, Isotopical differentiation of groundwater of different hydrogeologic origin: Jour Hydrol, v 59, p 161–171.

Geyh, M A and Sonne, V, 1983, Monitoring of groundwater-budget changes with isotope techniques in the NE Mainz Basin, *in* Groundwater resources planning, vol D, Proc: Internatl Groundwater conf, Koblenz, p 357–365.

International Study Group, 1982, An inter-laboratory comparison of radiocarbon measurements in tree rings: Nature, v 259, p 619–623.

Kimmelmann e Silva, A A, Rebouças, A C, Santiago, M M F and Silva, R B G (in memoriam), 1989, Isotopic study of the Botucatu Aquifer System in the Brazilian portion of the Paraná Basin, *in* Isotope hydrology investigations in Latin America, Proc of a regional seminar for Latin America on the use of isotope techniques in hydrology, Salaza: IAEA – TEC DOC – 502, p 51–71.

Rebouças, A C, (ms) 1976, Recursos hídricos subterrâneos da Bacia do Paraná. Análise de pré-viabilidade: Post-PhD dissert, Univ São Paulo, 143 p.