# STUDY OF THE EFFECT OF FOSSIL ORGANIC CARBON ON $^{14}$C IN GROUNDWATER FROM HVINNINGDAL, DENMARK

*E. BOARETTO,[1,2] L. THORLING,[3] Á. E. SVEINBJÖRNSDÓTTIR,[4] Y. YECHIELI[5] and J. HEINEMEIER[1]*

**ABSTRACT.** The carbonate hydrochemistry of groundwater from the Hvinningdal aquifer (Denmark) was studied by radiocarbon (accelerator mass spectrometry (AMS)) and $\delta^{13}$C measurements as a preliminary step towards $^{14}$C groundwater dating. The $^{14}$C concentrations varied between 30 and 100 percent modern carbon (pMC) in apparent contradiction with tritium ($^3$H) data, which in most cases indicate a post-bomb date. The dilution of $^{14}$C can be explained as being due to the combined effect of dissolution of old soil carbonate and oxidation of old organic carbon. The last effect proved to be essential. To calculate this correction the dissolved oxygen concentration was used together with the $\delta^{13}$C values. The combined corrections bring the $^{14}$C concentrations up to post-bomb levels in better agreement with the $^3$H data.

## INTRODUCTION

In Denmark the planning of future uses of water resources is becoming increasingly important due to the endangering impact of anthropogenic activities on groundwater resources. The planning depends critically on information on ages of groundwater reservoirs. Age data can be obtained from radiocarbon measurements, but since chemical processes (*e.g.*, dissolution of fossil carbonate) will influence the $^{14}$C concentration, it is important that the hydrochemical evolution of the groundwater carbonate system is fully understood (Mook 1980). Until recently, no $^{14}$C measurements had been performed on Danish groundwater. The present research was initiated to investigate the hydrochemistry of Danish groundwater of known (recent) age *via* carbon isotope measurements ($^{14}$C by accelerator mass spectrometry (AMS) and $\delta^{13}$C). Our goal is to apply the knowledge gained here to date older groundwaters. As a test case we have chosen the Hvinningdal aquifer in central Jutland, Denmark, which is known to contain young, bomb-produced tritium groundwater.

### The Aquifer

The Hvinningdal aquifer is part of one of the largest groundwater reservoirs in Denmark (Thorling *et al.* 1995). It is located in a raised plain (80 m above sea level (asl)) that descends towards the site of the waterworks (30 m asl). The average local precipitation is 800 mm a$^{-1}$ and the recharge is *ca.* 400 mm a$^{-1}$. The water abstraction is extensive, *ca.* 3 million m$^3$ a$^{-1}$. The matrix consists of tertiary quartz sand covered by quaternary meltwater sand/gravel with moraine deposits on top. The aquifer is hydraulically connected, but inhomogeneous, as evidenced by the different chemical composition of the water from different wells. The matrix is almost carbonate-free, but contains scattered deposits of lignite (brown coal) and reworked black organic material of tertiary origin. The water temperature is in the range 8–10°C. The groundwater is soft and acidic (pH typically *ca.* 6). Since there is good contact with the atmosphere throughout the unsaturated zone, the oxygen content in the first few meters below the groundwater table is close to the saturation value, *ca.* 12 mg L$^{-1}$ O$_2$. Due to intensive farming, the nitrate content is high (40 to 100 mg L$^{-1}$ NO$_3^-$) in some of the wells. Nitrate is the only component that shows strong time variation. Tritium ($^3$H) measurements are available for all the wells and indicate that most of the water is of recent, post-bomb origin.

[1] AMS $^{14}$C Dating Laboratory, Institute of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark
[2] Present address: Kimmel Center for Archaeological Sciences, ESER Dept., Weizmann Institute of Science IL-76100 Rehovot, Israel
[3] Aarhus Amtskommune, Miljøkontoret, Lyseng Allé, DK-8270 Højbjerg, Denmark
[4] Science Institute, Dunhaga 3, IS-107 Reykjavík, Iceland
[5] The Geological Survey of Israel, 30 Malkei Israel, IL-95501 Jerusalem, Israel

915

## SAMPLE PREPARATION AND MEASUREMENTS

Groundwater samples for chemical analysis and measurement of $^{14}C$ and $\delta^{13}C$ were recovered from wells through filters (1 m long) positioned in different depths below the groundwater table. The oxygen was measured in the field together with pH, temperature and conductivity. The samples were normally filtered through a 0.45 μm polycarbonate filter to stop suspended particles. To investigate whether the omission of such filter might influence the $^{14}C$ concentration of the sample, parallel samples were taken with and without a filter: the difference in $^{14}C$ concentration between parallel samples was at most 2.6 percent modern carbon (pMC), which is less than the scatter due to the sampling procedure. The water samples were collected in 0.5 L brown glass bottles. Since the $CO_2$ extraction was made within a few days after sample collection, it was not considered necessary to add poison ($HgCl_2$) to the samples. The $CO_2$ was extracted with $N_2$ gas after acidification with 4 mL 85% phosphoric acid. Part of the $CO_2$ was converted to graphite for AMS $^{14}C$ measurement with the EN tandem accelerator at the University of Aarhus, and a fraction was used for $\delta^{13}C$ measurement by conventional mass spectrometry at the Science Institute, Reykjavik, Iceland. The $^3H$ concentrations were measured by liquid scintillation counting (LSC) after enrichment (±0.5 TU). For normalization purposes the data were decay corrected to 1990 and not to the date of sampling. However, this is sufficiently precise for our purpose, since we only use the $^3H$ data to distinguish pre-bomb from post-bomb water.

TABLE 1. Chemical and Carbon Isotopic Composition of Groundwater from the Hvinningdal Aquifer

| Well no.* | Filter m b gt† | Filter m b s‡ | $^3H$ TU§ | $\Sigma CO_2$ mg $L^{-1}$# | $O_2$ mg $L^{-1}$ | $\delta^{13}C_m$ ‰ vs. PDB | $A_m$ pMC | $A_d$ pMC | $A_{corr}$ pMC |
|---|---|---|---|---|---|---|---|---|---|
| 3.1 | 2.41 | 35.4 | 34 | 86.7 | 0.3 | −23.5 | 23.9 | 25 | 32 |
| 8.1 | 2.49 | 35.4 | 17 | 40.6 | 9.2 | −22.5 | 89.2 | 99 | 111 |
| 4.2 | 3.51 | 25.1 | 34 | 38.9 | 10.6 | −20.8 | 91.4 | 110 | 117 |
| 10.1 | 4.12 | 35.9 | 17 | 39.4 | 11.8 | −18.7 | 87.6 | 117 | 118 |
| 7.1 | 4.13 | 38.4 | 18 | 62.1 | 11.9 | −16.8 | 65.7 | 98 | 98 |
| 1.1 | 4.30 | 14.1 | 36 | 52.8 | 0.1 | −19.8 | 52.1 | 66 | 109 |
| 2.1 | 4.38 | 37.8 | 41 | 50.8 | 8.1 | −21.6 | 71.1 | 82 | 94 |
| 13.1 | 4.78 | 41.8 | 20 | 89.4 | 8.1 | −16.0 | 46.8 | 73 | 81 |
| 9.1 | 4.80 | 36.6 | 18 | 30.5 | 11.8 | −19.9 | 93.8 | 118 | 120 |
| 12.1 | 5.28 | 31.0 | 19 | 56.1 | 7.8 | −20.6 | 107.5 | 131 | 149 |
| 5.1 | 5.63 | 24.7 | 15 | 31.6 | 11.0 | −20.0 | 103.3 | 129 | 137 |
| 14.2 | 10.88 | 45.1 | 38 | 76.0 | 3.2 | −19.0 | 59.4 | 78 | 99 |
| 4.1 | 15.22 | 37.1 | 27 | 49.1 | 0.5 | −21.4 | 47.0 | 55 | 88 |
| 15.1 | 15.42 | 51.8 | 62 | 62.4 | 0.1 | −18.7 | 39.7 | 53 | 82 |
| 14.1 | 24.53 | 60.5 | 18 | 53.9 | 0.1 | −19.9 | 50.1 | 63 | 102 |
| 16.2 | 55.10 | 94.0 | <1 | 38.5 | 0.0 | −22.5 | 45.8 | 51 | 96 |
| 18.1 | 59.40 | 85.0 | <1 | 67.0 | 0.0 | −16.6 | 45.7 | 69 | 109 |
| 17.1 | 76.80 | 99.0 | <1 | 134.0 | 0.0 | −12.3 | 45.4 | 93 | 125 |
| wworks | 50.00 | 58–88 | n.m. | 58.9 | 0.1 | −20.2 | 57.8 | 72 | 110 |

*Digit(s) before decimal point: well number; digit after decimal point: filter number counted from below.
†Filter position in meters below groundwater table
‡Filter position in meters below surface
§Tritium concentration is given in $^3H$ units (T.U.) and decay corrected to 1990
#$\Sigma CO_2$ is total inorganic carbon in groundwater (in mg $L^{-1}$ $CO_2$)

## RESULTS AND DISCUSSION

The results shown in Table 1 are ordered according to filter depth below groundwater table. Concentrations are given in mg $L^{-1}$ $CO_2$ and $O_2$, respectively. Figure 1 shows the oxygen concentration as a function of depth below groundwater table. Apart from two almost oxygen-free samples close to the water table (#1.1 and #3.1), the oxygen is constant in the first 5 m but then decreases sharply to zero between 5 and 7 m. The low oxygen of sample #3.1 could be explained by the fact that its content of dissolved organic carbon (*ca.* 3 mg $L^{-1}$) is very high compared to the average value of *ca.* 0.3 mg $L^{-1}$ in the rest of the wells. The low oxygen in sample #1.1 is not understood. We believe that this decrease is caused by oxidation of organic material. Pyrite as a reducing agent can be ruled out since the matrix only contains negligible amounts of pyrite. For detailed results of the chemical analysis, see Thorling *et al.* (1995).
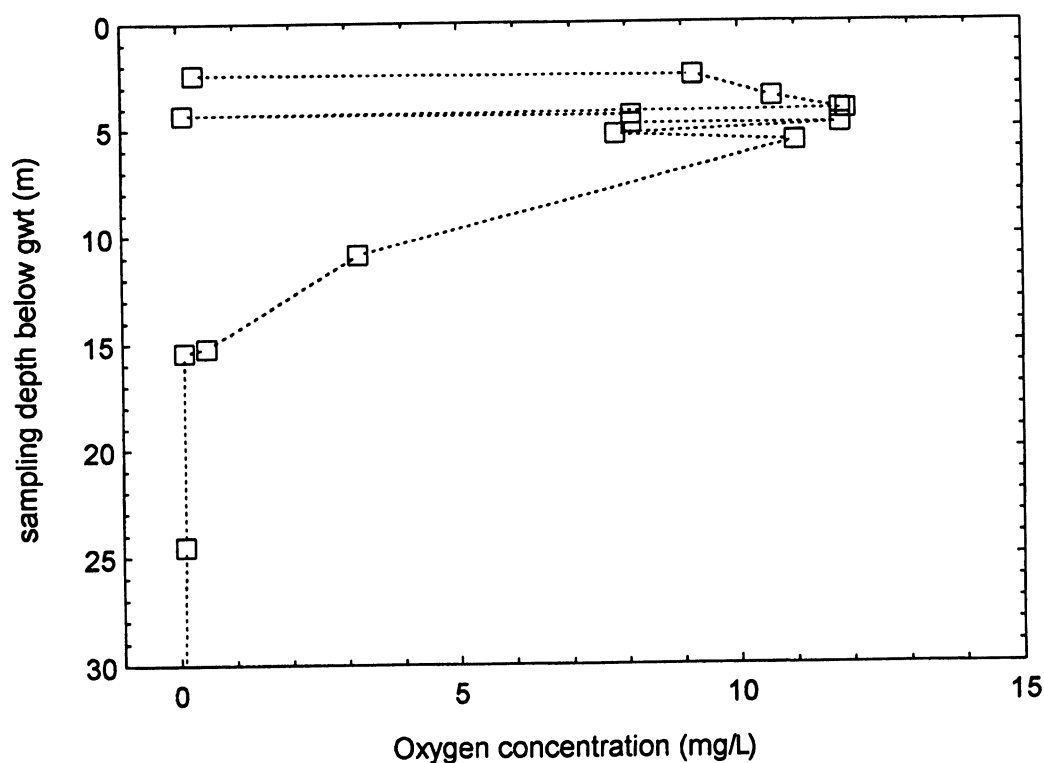


Fig. 1. Concentration of dissolved oxygen *vs.* depth below groundwater table for all wells from the Hvinningdal aquifer investigated in this work

The $^3H$ data show that the groundwater from wells #1–15 is post-bomb, *i.e.*, after *ca.* 1955; the uncertainty in the $^3H$ measurements does not allow for more precise dating. The water from wells #16–18 is older than 40 yr and has longer residence time compared to the rest of the samples.

The measured stable carbon isotope ratio is given as $\delta^{13}C_m$ in per mil (*‰*) relative to the PDB standard. The measured $^{14}C$ concentrations $A_m$ in pMC. Both values are compiled in Table 1. The measured $^{14}C$ activities $A_m$ fall in general far below the modern value, in strong disagreement with the $^3H$ data. Only two samples (5.1 and 12.1) show post-bomb $^{14}C$ concentrations. It is well known that

low $^{14}$C values may result from dilution with dissolved "dead" soil carbonate. The dilution process takes place when modern $CO_2$, formed in the root zone by root respiration and decay of plant material, dissolves fossil soil carbonate (Münnich 1968; Pearson and Hanshaw 1970; Mook 1980; Dörr *et al.* 1987). The measured $\delta^{13}C$ value of the groundwater carbonate can be used to quantify the effect. To do this, we adopt the model values $\delta^{13}C = 0\%o$ for soil carbonate (marine limestone) and $\delta^{13}C = -25\%o$ for the root-zone $CO_2$. Further, we assume that the dissolution is a closed-system process. The last assumption is justified to the extent that the $CO_2$ production in the root zone is separated from the carbonate dissolution zone. In such a case, the $^{14}$C concentrations $A_d$ corrected for fossil-carbonate dissolution are calculated from
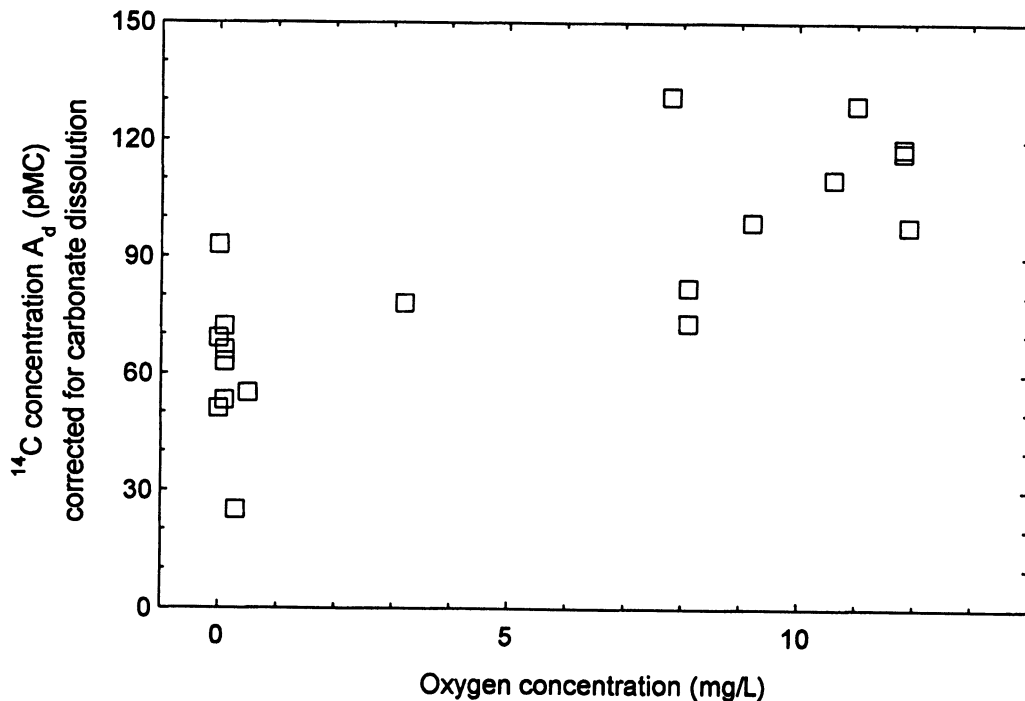
$$A_d = A_m(-25)/\delta^{13}C_m . \tag{1}$$



Fig. 2. Corrected $^{14}$C concentrations $A_d$ for dissolution of fossil soil carbonate *vs.* oxygen content. The data show a correlation between $A_d$ and oxygen.

The corrected values $A_d$ are listed in Table 1. Note that low values of $A_d$ are correlated with low oxygen concentrations (Fig. 2). The correlation leads us to propose that oxidation of fossil organic carbon in the aquifer matrix by dissolved oxygen might cause further dilution of $^{14}$C. After correcting for the effect of organic matter, the effect of fossil-carbonate was also evaluated. In order to quantify the effect of organic matter, we assume an original oxygen content of 12 mg L$^{-1}$ $O_2$ and that the "missing" oxygen in the actual water samples has been used to produce $CO_2$ in the reaction

$$C_{org} + O_2 = CO_2. \tag{2}$$

Thus, the fraction F of total inorganic carbon in the groundwater coming from oxidation of old organic carbon is

$$F = 1.38(12-[O_2])/[\Sigma CO_2], \tag{3}$$

where $[\Sigma CO_2]$ and $[O_2]$ are the measured concentrations in mg $L^{-1}$; the factor 1.38 is the ratio of molecular weights. If we furthermore assume $\delta^{13}C = -25‰$ for the old organic carbon, the $^{14}C$ activity corrected for both carbonate dissolution and organic carbon oxidation, $A_{corr}$, becomes

$$A_{corr} = A_m(-25)/(\delta^{13}C_m+25\cdot F). \qquad (4)$$

The corrected values are listed in Table 1. Figure 3 shows a plot of both $A_d$ and $A_{corr}$ *versus* the measured $A_m$. Note that most of the corrected $A_{corr}$ are above or close to 100 pMC, in better agreement with the $^3H$ measurements. The extremely low $A_{corr}$ of 32 pMC for sample #3.1, taken from a filter in a silt layer only 2.4 m below the groundwater table, can be explained by the combined effect of a high content of organic material and fluctuations of the groundwater table which exposes the organic material to fresh oxygen. Thus, we exclude this point from the discussion. The samples #12.1 and 5.1 with the highest $A_{corr}$ could belong to the peak of the bomb pulse. Some of the samples (4.1, 15.1) are low in nitrate (<1 mg $L^{-1}$; Thorling *et al.* 1995). If this reflects a nitrate loss caused by oxidation of old organic carbon, a further dilution of $^{14}C$ is expected. If this effect could be corrected for, it might be possible to improve the agreement with the $^3H$ data. For example, such correction might narrow down the difference in $A_{corr}$ value of 29 pMC between filters 1 and 2 of well #4. However, it is difficult to quantify this contribution in view of the time variation of the anthropogenic nitrate input.
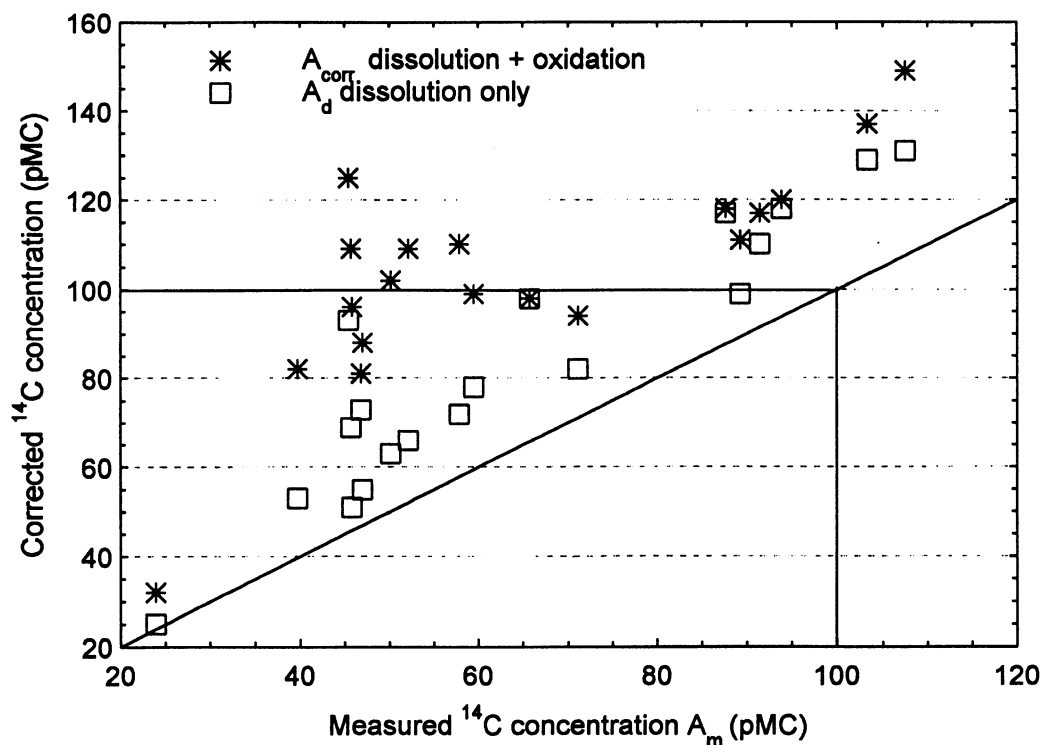


Fig. 3. Corrected $^{14}C$ concentrations *vs.* measured $^{14}C$ concentrations. $A_d$ is the $^{14}C$ concentration corrected for dissolution of fossil ($^{14}C$ dead) soil carbonate. The $^{14}C$ concentration $A_{corr}$ includes also the effect of oxidation of fossil organic carbon. Errors for the measured $^{14}C$ concentrations are of the order of ±0.5 pMC.

The $^3$H concentration of the samples from wells #16, 17 and 18 is below the detection limit showing that the water is pre-bomb. If we accept the above model leading to the corrected $^{14}$C activities $A_{corr}$ of 96, 109 and 125 pMC, respectively, we may conclude that the water is of recent origin. However, in view of the uncertainty of the assumptions underlying the model it can only be said that the ages of these waters are of the same order of magnitude as the rest of the samples. These waters are therefore not older than several hundred years.

## CONCLUSION

We have shown that it is possible to adjust the measured $^{14}$C concentrations of groundwater carbonate from the Hvinningdal aquifer for the dilution with $^{14}$C-free carbonate. Our model takes into account 1) dissolution of fossil soil carbonate by soil carbon dioxide, and 2) oxidation of fossil organic carbon by dissolved oxygen. We have shown that the effect of the latter can be significant for $^{14}$C groundwater dating and the fact that the corrected $^{14}$C ages agree with the presence of $^3$H indicates that the assumptions taken into account for the model are justified. The problem of the possible effect of nitrate on the model is discussed but should be the subject of further research.

## ACKNOWLEDGMENT

## REFERENCES

Dörr, H., Sonntag, C. and Regenberg, W. 1987 Field study on the initial $^{14}$C content as a limiting factor in $^{14}$C groundwater dating. In *Isotope Techniques in Water Resources Development*. Vienna, IAEA: 73–86.

Mook, W. G. 1980 Carbon-14 in hydrogeological studies. *In* Fritz, P. and Fontes J.-C., eds., *Handbook of Environmental Isotope Geochemistry*. Amsterdam, Elsevier: 49–74.

Münnich, K. O. 1968 Isotope-Datierung von Grundwasser. *Naturwissenschaften* 55: 158–163.

Pearson, F. J. and Hanshaw, B. B. 1970 Sources of dissolved carbonate species in groundwater and their ef-

fects on carbon-14 dating. *In* Isotope Hydrology, Proceedings of the Vienna Symposium. Vienna, IAEA: 271–286.

Thorling, L., Boutrup, S., Hundahl, M. and Søndergaard, V. 1993 *Statusrapport 1992 Vandmiljøovervågning af Grundvandet*. Århus Amt, Natur og Miljøe: 109 p. + appendix.

Thorling, L., Boutrup, S., Søndergaard, V., Reiter, C. and Thomsen R., 1995 *Statusrapport 1994 Vandmiljøovervågning af Grundvandet*. Århus Amt, Natur og Miljoe: 136 p. + appendix.