Pilot Project on Groundwater Dating in Confined Aquifers of the North Carolina Coastal Plain **Casey Kennedy**¹, **David Genereux**¹, and Niel Plummer² ¹Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh, NC 27695-8208 ²U.S. Geological Survey, National Center, MS 432, Reston, VA 22092

Introduction

Confined Cretaceous aquifers are a major water source for the North Carolina Coastal Plain but have been heavily overused. The Black Creek and Upper Cape Fear aquifers have been particularly heavily affected; total head losses in these aquifers from "pre-development" times (year 1900, Giese et al., 1997) to present (Lautier, 2001) have been well over 100 ft in some areas (apparently >200 ft near Kinston). Head losses of this magnitude have a range of problems for long term use of the aquifers including loss of a critical water resources, permanent decrease in porosity due to compaction effects, and salt water intrusion. Quantitative data on the hydrogeology of these aquifers is needed to adequately address these problems. Some estimates of hydraulic conductivity are available, but quantitative data are lacking on important aspects of flow (travel times, groundwater ages, vertical exchange between aquifers). In this poster we present results from groundwater dating in the Black Creek and Upper Cape Fear aquifers in which ¹⁴C groundwater ages were determined, the relationship between ⁴He concentration and groundwater age was evaluated, and the presence of very young water (<40 years) in the study aquifers was tested using measurements of ³H.



Z. Site Map

The 15 counties shaded in gray make up the Central Coastal Plain Capacity Use Area (NCDENR, 2000). The CCPCUA went into effect on August 1, 2001 and establishes new requirements for water conservation including major reductions in groundwater withdrawals from the Black Creek and Upper Caper aquifers over the next 16 years. The sampling transect is in red and runs from the North Carolina Dept. of Energy and Natural Resources (NCDENR) Saulston site (SL) to the Savannah site (SV) to the Cove City Site (CC). A hydrogeologic cross-section of transect A-A` is shown in black. The two lines in the inset map are the same sampling transect and hydrogeologic transect shown in the main map.



5. Hydrogeologic Cross-Section

East-west hydrogeologic cross-section through the Coastal Plain of North Carolina along line A-A' shown in the site map (Geise et al., 1997). Aquifers are shown in color and aquitards are in black. The sampling transect does not correspond exactly to the line of the hydrogeologic transect (see site map), but the sampling wells are shown here to illustrate their approximate relationship to the geology and to each other. Wells are grouped by site (SS = left, SV = middle, CC = right).

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4. Methods

- Groundwater samples were collected from 7 monitoring wells (operated by NCDENR) in July 2003. Each well was sampled once, and all samples were collected with a positive displacement Bennett pump (recommended by USGS) to avoid possible artifacts in trace gas concentrations.
- The principal tracers measured were ¹⁴C (for dating the groundwater), ⁴He (a tracer that can be used in future age dating projects if calibrated against ¹⁴C), and H (to test for the presence of young groundwater less than about 40 years old). ¹³C, DIC, DOC, He, Ne, Ar, N₂, O₂, CO₂, CH₄, H₂, ³H, S, Fe, Si, Al, Mn, Na, K, Ca, Mg, Cl, SO₄, and NO₃ were also measured, because they provide helpful information for interpretation of ¹⁴C and ⁴He in groundwater. Analyses were carried out at specialized laboratories with recognized expertise in the relevant analytes (at NCSU and elsewhere).

5. NETPATH Modeling

¹⁴C groundwater dating commonly requires corrections to account for geochemical reactions affecting ¹⁴C activity in groundwater. In our study aquifers, the most important geochemical reactions affecting ¹⁴C activity in groundwater are calcite (0 pmc) dissolution, lignite (0 pmc) oxidation, and Ca/Na exchange. Each of these reactions lowers ¹⁴C activity of groundwater by increasing DIC without adding ¹⁴C $(^{14}C \text{ activity} = \text{grams of } ^{14}C \text{ per gram of total carbon}).$

NETPATH, a rigorous and widely-accepted inverse mass balance model, was used to account for geochemical reactions affecting ¹⁴C activity in groundwater (Plummer et al., 1994). NETPATH deduces the mass transfers responsible for isotopic and chemical differences between two groundwater samples along a flow path. NETPATH calculates a corrected ¹⁴C groundwater age in two steps. First, NETPATH estimates A₀ for "initial water," a groundwater sample that is representative of recharge water, by accounting for reaction effects in the recharge area only. Then, a separate calculation is made that accounts for the reaction effects occurring between the upgradient "initial water" and the downgradient "final water" (the latter is the groundwater sample to be dated). The reaction effects occurring between "initial water" and "final water" are applied to A_0 . This value, denoted A_{nd} , represents the 14 C activity the final water would have in the absence of radioactive decay. NETPATH uses A and A_{nd} in the radioactive decay equation to calculate the groundwater age of the final water.

Diffusion Correction

¹⁴C in groundwater can be lost by natural radioactive decay, geochemical reactions affecting carbon chemistry, and diffusion into contiguous aquitards. The correction for diffusion is analogous to correcting for geochemical reactions with NETPATH, in the sense that loss of ¹⁴C by diffusion is another process that must be accounted for if ¹⁴C data are used to date groundwater. ¹⁴C is expected to be lower in aquitards because of the slower flow and diffusion would follow accordingly. The diffusioncorrection approach of Sanford (1997) was used in this study. The Sanford (1997) approach is based on the conceptual model of steady state diffusion and decay of ${}^{14}C$. Under steady state, the effects from diffusion depend on the ratio of fluid volume in aquitards to aquifers and the effective diffusion coefficient.

7. Results: ¹ C Groundwater Ages



8. Results: Determination of ⁴He_{terr}

⁴He in groundwater is expected to grow over time from radiogenic production ($^{4}\text{He}_{rad}$) and diffusion-in ($^{4}\text{He}_{di}$). The use of ^{4}He as an age-dating tracer requires that ⁴He from solubility with air (${}^{4}He_{sol}$) and "excess air" (${}^{4}He_{ea}$) be separated from ${}^{4}He$ measured in groundwater (⁴He_{meas})

 ${}^{4}\text{He}_{\text{terr}} = {}^{4}\text{He}_{\text{rad}} + {}^{4}\text{He}_{\text{di}}$

 ${}^{4}\text{He}_{\text{terr}} = {}^{4}\text{He}_{\text{meas}} - {}^{4}\text{He}_{\text{sol}} - {}^{4}\text{He}_{\text{ea}}$

 ${}^{4}\text{He}_{ea} = [\text{Ar}_{meas} - \text{Ar}_{sol}]\text{R}_{He-Ar}$

 X_{sol} = Henry Law constants, recharge temperature

 R_{He-Ar} = ratio of He-Ar in atmosphere

Recharge temperature was estimated using N₂ and Ar data (e.g., Stute and Schlosser, 1999).

9. Results: ⁴He Concentration and Groundwater Age

The relationship between ⁴He concentration and groundwater age was evaluated. Well J3 is the only well that directly overlies crystalline basement rocks, and its proximity to the basement rocks is believed to be the reason for its very high ⁴He concentration. Although, well X8 is deeper than wells U7 and U8, it is farther from the basement rocks and consequently affected less by diffusion-in from below. In most cases, ⁴He concentration increases with groundwater age, which suggests that ⁴He may be useful as a quantitative age-dating tracer in future studies. However, distance from basement rocks appears to be an important factor influencing ⁴He concentration and should be controlled in future studies.

• Groundwater ages increase in both the horizontal and vertical directions. The increase in age with depth would be expected if flowlines remained equally spaced from the land surface in the unconfined zone downward into the aquifer. • In both the Black Creek and Upper Cape Fear aquifers, groundwater age increases with distance from recharge area, which is consistent with the expected trend of groundwater flow toward the coast.



 ${}^{4}\text{He}_{\text{meas}} = {}^{4}\text{He}_{\text{rad}} + {}^{4}\text{He}_{\text{di}} + {}^{4}\text{He}_{\text{sol}} + {}^{4}\text{He}_{\text{ea}}$





Well	Aquifer	Year	³ H	Field/lab	In-situ	Drilling	Downward
ID			(TU)	error		fluid	leakage
U8	BC	1999	0.08	no	maybe	maybe	maybe
U5	UCF	1984	0.24	no	maybe	maybe	maybe
X9	UCF	2000	0.26	no	maybe	maybe	maybe
U7	BC	1999	0.45	no	no	maybe	maybe
J3	UCF	1982	0.67	no	no	maybe	maybe
X8	BC	2000	0.81	no	no	maybe	maybe
J1	BC	1982	5.71	no	no	maybe	likely

10. Results: Testing for Young Water with 'H

In general, there are four possible explanations for ³H in groundwater that is at least hundreds of years old: errors related to sampling or analytical techniques, natural in-situ production, relict drilling fluid, or downward leakage. Sampling of ³H went without error, and the experienced laboratory that performed the analysis is confident with their results. ³H produced from natural in-situ production should be about 0.2 TU or less (Andrews and Kay, 1982). Thus, it seems possible (though not likely) that in-situ production alone could explain most or even all of the ³H concentration in groundwater from wells U8, X9, and U5. Most likely the ³H found at depth is the result of downward leakage of relatively young ³H-bearing groundwater or relict drilling fluid left in the formations after well installation (and of these the former seems the more likely explanation).

11. Conclusions, Future Work

- ¹⁴C groundwater ages in the Black Creek and Upper Cape Fear aquifers are evidence that groundwater from these aquifers is likely only quasi-renewable over very long time scales. These groundwater ages, together with falling heads, suggest that groundwater withdrawals in these aquifers represent a sort of "mining."
- Further ¹⁴C dating on additional wells would be useful in developing a more detailed three-dimnersional picture of groundwater age (and thus long-term average flow rate) in these critical aquifers.
- ▶ ⁴He may be useful as a quantitative age-dating tracer in these aquifers. Necessary input to such an effort would be information on rates of radiogenic ⁴He emission by the aquifer solids and an improved analytical framework (i.e., model) for quantitatively interpreting the relationship between ⁴He_{terr} and groundwater age.
- ▶ ³H concentrations are consistent with the presence of young water in many of the wells, but it is uncertain whether the young water in these wells is from relict drilling fluid or downward leakage of young water. This issue could be addressed by dating the young groundwater (using for example ³H/³He method) in these mixed samples of old and young groundwater; if the young groundwater is younger than the age of the installation of the well sampled, then relict drilling fluid is not the source of ${}^{3}H$.

12. References

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