DISTRIBUTION OF RECHARGING AND VULNERABILITY OF THE TERTIARY LIMESTONE AQUIFER, SOUTH CAROLINA: REGIONAL GRADIENTS AND IMPORTANT OUTLIERS

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Abstract. The distribution of ground-water radiocarbon ages from the Tertiary limestone aquifer (includes the Floridan aquifer) in South Carolina shows both a typical trend for a regional sedimentary aquifer plus a less-commonly reported occurrence of disjunct outliers of recharging and thus high vulnerability to contamination located farther down the regional flow system. The main recharge area, and thus high vulnerability, is apparently in the updip Tertiary sand aquifers of the upper (inner) coastal plain that receive recharge directly and only later deliver this as ground water to the limestone formations by lateral coastward flow. In places, a considerable degree of isolation ("confinement") and protection is achieved by the time and location that this flow reaches the sand-to-limestone lateral transition near the outer (seaward) edge of the inner coastal plain. A substantial to high degree of isolation and protection is achieved or maintained in the limestone aquifer in a large part of the middle and lower coastal plain, basically where the Cooper marl and related confining layers occur. Notable exceptions exist though even within these downflow areas. Recharging and thus high vulnerability occurs in large or small-but-intense areas isolated within interior and coastal portions of the middle and lower coastal plain.

THE TERTIARY LIMESTONE AQUIFER

The major regional Tertiary limestone aquifer of southeastern United States extends into southern South Carolina where it is an important source of drinking water. Coastal plain aquifers have a generally seaward flow direction and thus both upflow and downflow boundaries of flowlines exist within the state. Upflow boundaries lie in recharge areas. Recharging is important not only in terms of ground-water replenishment but it is also the mechanism by which aquifers can most easily become contaminated by materials originating at the ground surface (e.g., accidentally spilled fuels or chemicals, disposed waste, leached fertilizer or pesticides). Recharge areas are the most vulnerable to such contamination and deserve special consideration in planning for protection of wells and in responding to existing contamination. The limestone aquifer is also widely confined and protected (effectively or partially) by younger sedimentary formations that overlie it and thus has areas of lower to low vulnerability. It is best protected where a thick sequence of low permeability (generally finer grained) materials overlie it.

A "textbook" regional coastal-plain sedimentary aquifer is recharged in its inland, highest elevation portion (often the geologic formation's outcrop area), becomes confined at some point downflow where younger formations with fine-grained strata bury and isolate it hydraulically, and remains highly confined until reaching some offshore location where water leaks out slowly or actively. Determining where the Tertiary limestone aquifer is highly vulnerable in this state is made more complex by several factors. The upflow boundaries of main regional flowlines lie not in limestone but in Tertiary sand formations and aquifers that connect with (interfinger or grade into) the limestone at its inland edge. A main question presents itself: is the limestone recharged principally by lateral flow into it across this boundary, or is vertical leakage from overlying sandy formations toward the limestone's inland boundary also important, i.e., where is the seaward boundary of principal recharging? Secondly, the ground surface drops more steeply in a seaward direction than the seaward dip of the buried top of the limestone: the limestone becomes more shallowly buried rather than more deeply buried in a downflow direction when one crosses the Orangeburg Scarp (roughly parallel to the coast and inland at the city of Orangeburg). In the large limestone subcrop area just seaward of the scarp the aquifer is more shallowly buried and very possibly less confined than in areas just above the scarp farther upflow. Thirdly, hydraulic modeling suggests that a broad area nearer the southern tip of the state is "leaky" and this implies the possibility of widespread slow natural or more rapid pumping-induced recharging, which if rapid enough can raise vulnerability appreciably. Finally, small areas of active or rapid recharging were suspected or known from potentiometric data from near the coast, these being outliers of recharging far away from the major recharge area. These last could easily be overlooked in any vulnerability assessment envisioning a typical regional aquifer. In this study we sought geochemical evidence of local or nearby recharging from an array of well sites that span the geographic extent of the limestone aquifer and encompass the several main stratigraphic settings.

TRACER METHOD

Investigation of innate aquifer vulnerability to contamination is basically the investigation of recharging. Testing for recharging has many available methods, which differ greatly in cost, time and effort, and strength of evidence (confidence). Tracer methods have high strength of evidence and environmental tracers (applied naturally and long in place) are generally less expensive and far less time consuming. For this regional scale, and given the aquifer depths that occur even in probable recharge areas (whereby ground-water ages very possibly exceed the ~40-year useful range of tritium), radiocarbon (^{14}C) was chosen as a useful tracer. ^{14}C methods are well investigated and are now routine in ground-water hydrology (Clark and Fritz, 1997). The carbon of interest is dissolved inorganic carbon (DIC, mostly bicarbonate in a limestone aquifer) and the ^{14}C tracer is naturally added as dissolved CO_2 in the soil zone at recharging. The principal complication is variable dilution of the ^{14}C by reaction of dissolved CO_2 with the ancient ^{14}C-free $CaCO_3$ of the limestone. The proportion of the bicarbonate carbon coming from the tracer, i.e., the degree of dilution, is determined from stable-isotope $\delta^{13}C$ measurement, where the two intermixed sources have well-known and very different initial values and an intermediate value measured from the sample is used to estimate the proportion of each present. Soil CO_2 and water in an acidic carbonate-free aquifer in typical vegetation will have a value of about –25 per mil (–25‰ vs. the PDB isotopic standard) and this value thus indicates undiluted ^{14}C. As the slowly flowing water reaches dispersed and then dominant carbonate in its long-distance flow, a reaction with $CaCO_3$ (~0‰) shifts the DIC toward this latter value. Where virtually all CO_2 has been reacted the proportions become equal (1 CO_2 reacting with 1 $CaCO_3$) and the sample value is ca. –12.5‰. Later, in some places, more complex reactions (e.g., hydrolysis, precipitation/dissolution) can increase the representation of the dilutant from the mineral source (>–12.5‰), but the correction method still holds. The corrected radioactivity is used to calculate the age of the soil-derived recharge tracer alone.

200+ liter (55-gal. drum) samples were collected mainly from production wells but also from one spring. DIC was extracted by one of two standard methods: 1) conversion of DIC to CO_2 by acidification, then closed-loop gas stripping and CO_2 trapping of the ultimate sample, or 2) conversion to carbonate by adding pure hydroxide and precipitating as barium carbonate, the ultimate sample (Yang, 1983; Clark and Fritz, 1997). ^{14}C and ^{13}C analyses were made at radiocarbon dating laboratories but ^{14}C was reported not as dates (ages) but rather as relative radioactivities (PMC, *P*ercentage of the radioactivity of the *M*odern *C*arbon dating standard). Ages were later calculated after accounting for the chemical dilution of ^{14}C by aquifer carbonates. Ages are in ^{14}C years, these being acceptable approximations of real years.

RESULTS AND SIGNIFICANCE

Distribution of Apparent Ground-Water Ages

The sampled sites can be considered to form two broad transects from updip/upflow locations to downdip/downflow. The middle area has an additional site representing it, located between the two broad transects. These subsets are separated by short dashed lines in the table: the top series roughly parallels the Santee River, the lower the Savannah River. The series however do not lie on single flowlines and are not strict transects. They are discussed here mainly in terms of their geographic positions and geologic settings. Samples from near the Orangeburg Scarp (OS), which divides the upper from the middle coastal plain lie near the inland edge of the limestone, near where it grades laterally into updip sand aquifers. The limestone subcrop (SC) area lies seaward of the scarp near the Santee River and is defined as where the limestone is not deeply buried and has no widespread and substantial tight clayey formation above it. The Cooper Marl is just such a formation and overlies part of the area seaward of the subcrop area (CM), though the subcrop area has a narrowed seaward extension (SC-Ext) north of the Cooper Marl area. The Cooper Marl extends part way southwest toward the second broad transect (the single CM sample, from Walterboro). For the broad transect nearer the Savannah River, there is data from Cretaceous sand aquifers of the upper coastal plain (UCP), which immediately underlie the Tertiary sand aquifers that connect with the limestone to the southeast. Seaward there is a dropoff of surface elevation but no subcrop area for the limestone and the confining unit is less pronounced in this middle coastal plain (MCP) area. Nearer the coast, in the outer or lower coastal plain (LCP) is the area with hints of having "leaky" confined conditions. On the immediate coast, Hilton Head Island (HHI) at its northern end has one of the outlier recharge areas (Back et al., 1970).

Results (Table 1) show a very wide distribution of ground water ages (the time elapsed since recharging), from modern or very young back to ancient, apparently to the last ice age (≥18,000 yr). Ages have been rounded off and should not be considered precise in any event (due in

Table 1. Radiocarbon Ages of Ground Water from the Tertiary System Aquifer, Except as Noted.

Site/Well See Text	^{14}C pmc	$\delta^{13}C$ per mil	Age ^{14}C years	Setting Or Area
OS-1	8.9	-10.1	12200	Orangeburg
OS-2	4.4	-10.3	18000	Scarp
SC-1	20.5	-11.9	6800	Limestone
SC-2	40.5	-8.9	-1000	Subcrop Area
CM-1	2.9	-13.3	23400	Cooper Marl
CM-2	3.9	-10.5	19100	Confinement
CM/SC-Ext	0.35	-6.6	34800	Boundary
SC-Ext Spr	59.6	-12	-1700	Subcrop Area Extension. Spring

CM-3	1.6	-2.2	13700	Cooper Marl Confinement

UCP-C2-A	93	-22.4	-300	Upper
UCP-C2-B	88.9	-23.2	350	Coastal
UCP-C2-C	80.8	-22.5	850	Plain Cretaceous
UCP-C3-A	78.4	-22.9	1250	Aquifers
UCP-C3-B	78.1	-23.0	1300	(Below Tertiary)
MCP-1	52.6	-13.1	0	Middle
MCP-2	30.2	-11.9	3700	Coastal
MCP-3	13.9	-12.9	10500	Plain
LCP-1	3.5	-11.4	20500	Lower CP
HHI-1	42.8	-12.4	1200	Barrier Is.

part to mixing over the depth range sampled by typical wells, but also by mixing in ground water flow). Negative ages result from the presence of nuclear-era ^{14}C contamination of atmospheric CO_2, or if of small magnitude perhaps merely the analytical uncertainty for modern water barely older than the nuclear age. A "textbook" one-way trend toward old age in a seaward direction does not hold in several areas and hydrogeologic complexity of the recharging system is demonstrated. Some younger to modern ages lie toward or at the coast. A decrease in groundwater age toward the coast, especially in the large area of the subcrop area, implies mixing of older ground water derived from the regional flow system with modern recharge from local vertical downward leakage. A mixed origin implies that the computed age is a weighted average and not close to the true age of either component.

Distribution of Recharging and Vulnerability

The broad transect near the Santee River is discussed first. Even near the inland boundary of the limestone aquifer, at sites close to the Orangeburg Scarp (OS) and close to where the aquifer is at its highest elevations and highest potentiometric-levels, the samples still do not evidence modern or very young ground water. This indicates that the limestone aquifer there is not primarily recharged directly (i.e., from above) but rather apparently is recharged laterally from the interconnecting (geologically correlated) sand aquifers that extend to recharge areas farther inland in the upper coastal plain, basically the sand-hills region. Ground water in limestone very near the Orangeburg Scarp is quite old, well over 10,000 years. This is where the aquifer shifts from being more deeply buried above the scarp to more shallowly buried in the limestone subcrop area.

In the subcrop area the aquifer was suspected to be hydrologically less isolated. Ages of ground water from the subcrop area (SC sites) range from substantial (but not as old as upflow) to young or modern. The substantial age (i.e., 6800 years) would, if taken solely, suggest that no local recharging is occurring. But when compared to much older ages of ground water being delivered by the regional flow system (ca. 12,000-18,000 years) it instead indicates an introduction and intermixture of young recharge water into the limestone subcrop area near or somewhere upflow of the sampled well. The shallow burial in the subcrop area apparently allows recharge to leak into the limestone, even where a considerable cover of younger sediments overlie. These must not offer tight confinement and isolation. Farther into the subcrop area there occurs much younger to modern ground water, indicating that local recharging is predominant there. This sample, with a substantial negative computed age (-1000 years) is assuredly modern but the negative value is possibly a curious artifact above and beyond modern atmospheric contamination by nuclear weapons. This well was at a dairy and the abundant organic matter there was possibly derived inordinately from corn (maize), a C4-metabolism semitropical grass whose $\delta^{13}C$ value is much higher than that assumed for recharge CO_2 in the correction equation (natural vegetation here is C3). (Note: artificial contamination by modern organic matter is not particularly a problem with this dating method, so long as it is delivered by recharging and no C4 source is involved.) It is concluded that in parts of the subcrop area, local recharging is a predominant source of the aquifer water and the aquifer is highly vulnerable.

Seaward of the main body of the limestone subcrop area (to the SE) and in a large area to the west and southwest—the broad middle zone of the flow system—thicker sediments overlie the limestone, including a large area of thick and distinctly lower-permeability material (Cooper Marl, CM sites, CM-3 lies west of the informal transect). Old to very old ground-water ages were obtained there, even from heavily pumped production wells where induced recharging would be most likely. CM-3 at Walterboro is heavily pumped and perhaps does evidence some slight admixture of younger water. But recharging cannot be appreciable in the Cooper Marl area judged by results from the several sites and substantial hydrologic isolation and protection is indicated.

An extension of the subcrop reaches to near the coast north of Charleston. A well penetrating through Cooper Marl but located close to the boundary of the subcrop area (CM/SC-Ext) showed very old ground water. Ground water there must move toward the subcrop area (and ultimately the Santee River). The farther reaches of the subcrop area itself is represented by a distinct spring (SC-Ext Spr: Blue Spring). Modern ground water (apparently nuclear-era) is being discharged, despite this being an area the generalized model might suggest having the oldest ground water. Recharging must take place near this spring (<~35-year flow time).

The second broad transect does not possess a limestone subcrop area, but otherwise is similar. Cretaceous sand aquifers at two monitoring-well clusters in the upper coastal plain (UCP sites) south of Aiken show young to modern ground water and it is assumed that water in overlying Tertiary sand formations would not be older.

Middle coastal plain sites (MCP) show a progression of ground-water ages from the landward edge thence toward the seaward edge. The "zero" age comes from a well of notably higher water-level elevation near the landward boundary. Local recharging must be facilitated there by some stratigraphic or topographic condition. It is a good example of an isolated recharge area whose vulnerability might easily be underestimated or unrecognized. Far less and possibly no recharging is indicated for the remaining middle coastal plain sites.

The lower coastal plain (LCP) here is suspected to have "leaky" artesian conditions, but a very old ground-water age was obtained (20,500 years), and this from a heavily pumped production well where induced recharging would be most likely. Recharging cannot be appreciable at or immediately upflow of this site and substantial hydrologic isolation and protection is indicated. (This condition applies as well to the southern and perhaps middle portions of Hilton Head Island on the coast: data not shown.) The hints for leaky conditions have inference to a wide area, not individual locales, so it is best not to use this single site to conclude a high level of protection for the entire area.

This lower coastal plain region also has areas of local recharging, though these are much smaller than the subcrop area. These form outliers or "islands" of vulnerability within a large area of overall substantial natural protection of the limestone aquifer. Several were discovered by others as local potentiometric "highs" and here the "age" evidence for recharging is merely supportive. One, on the northern end of Hilton Head Island at the coast, was shown to have local recharge mixing into old ground water in one of the earliest U.S. studies using ^{14}C (Back et al., 1970). At Hilton Head Island the recharging appears to be both natural and induced by regional heavy pumping. Vulnerability is raised in either case.

LESSONS

Assessing the subregional distribution of recharging as an indicator of vulnerability to contamination needs to encompass the "greater" aquifer, defined by flow system rather than simply main geologic formation: here it required considering the updip sand aquifers. The "textbook" model of one-way achievement and then maintenance of effective confinement and isolation downflow is too simple for assessing vulnerability and risk. There is also danger in assessing the vulnerability of a locality by a single age determination, that is without knowledge of the age of the water being delivered by the regional flow system: local recharging and high vulnerability may be masked by dilution with old ground water. A physiographic area (e.g., middle or lower coastal plain, limestone subcrop area) is too large to generalize across safely.

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