In situ removal of iron, manganese, and radium from groundwater. 1994

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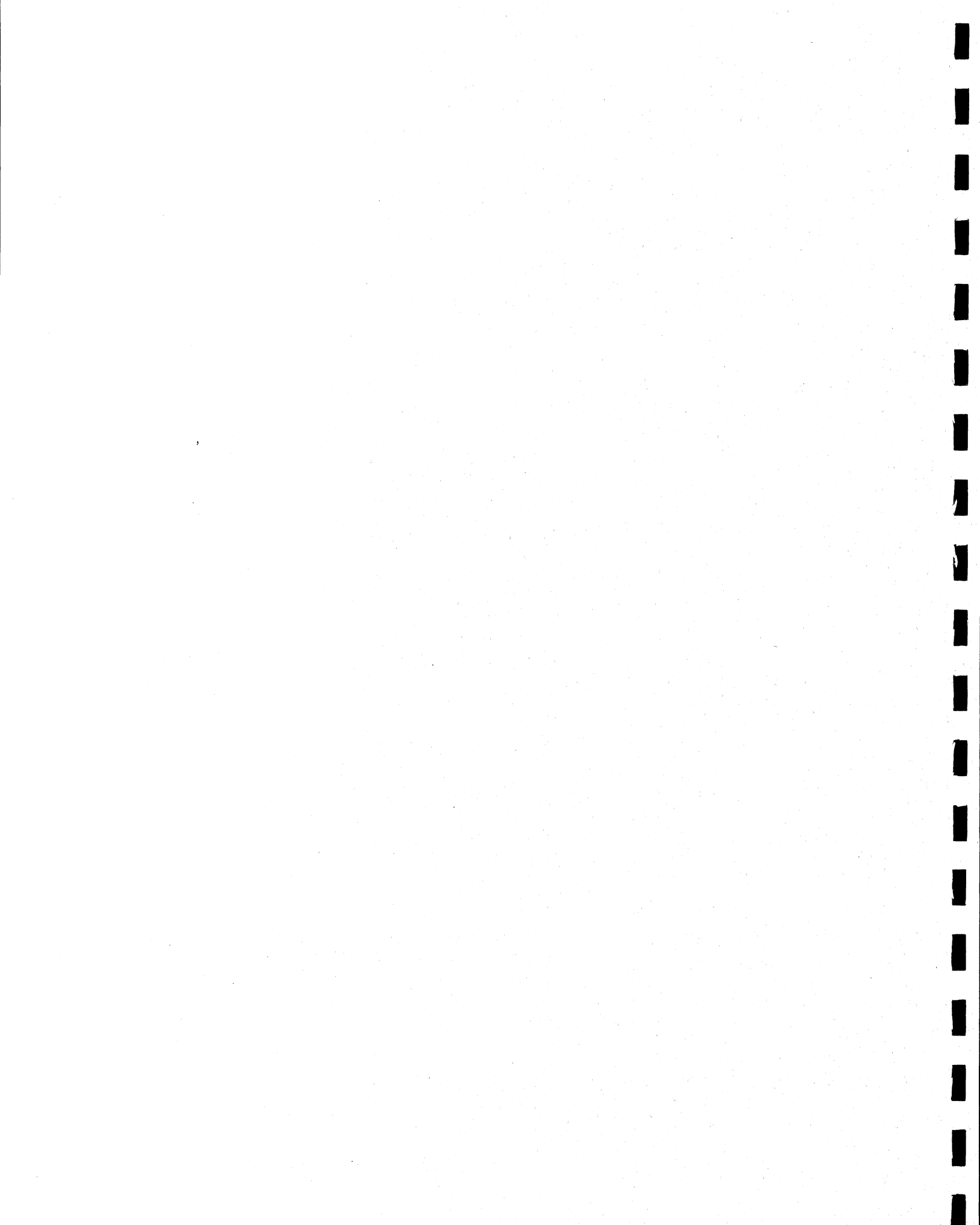https://digital.library.wisc.edu/1711.dl/OQ2NADXCFO3RC8K

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IN SITU REMOVAL OF IRON, MANGANESE, AND RADIUM FROM GROUNDWATER

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1994

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ABSTRACT

The project was undertaken to determine if Radium (Ra) coprecipitates with iron (Fe) and manganese (Mn) during *in situ* oxidation of groundwater and whether there are locations in Wisconsin where the coincidence of these elements in aquifers would make the process a viable treatment option. Concentration of Fe and Mn in public groundwater supplies are sufficiently high to be nuisances and warrant removal in many locations. However, *in situ* oxidation treatment is effective only in unconsolidated Quaternary deposits. Known occurrences of high Ra (>5 pci/liter) have been mapped, but are extremely spotty. The only area where high Fe and Mn coincides with known high levels of Ra is a region between Marathon and Adams Counties, although the Fe and Mn are highest in the glacial aquifer and the Ra is in the crystalline and sandstone aquifers. *In situ* oxidation could be effective in this region and is already in use at Rib Mountain. For the overall area defined, Ra-rich water would need to be drawn from the bedrock aquifers, aerated, and injected in the glacial aquifer. Other areas of the state might have suitable conditions for *in situ* treatment, but Ra data are too sparse to tell.

Determining the effectiveness of Ra coprecipitation was largely unsuccessful because of extremely low Ra recovery levels in laboratory experiments. Discussion in this report will emphasize development of radiochemical processes for the determination of low-level Ra activity in water samples along with the tracer (^{225}Ra). The associated problems or difficulties and the results of the recovery of Ra from the sample will be discussed.

FIGURES

TABLES

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INTRODUCTION

Radium (Ra) is a naturally occurring radioactive element found in some groundwaters in Wisconsin. It has been implicated in human health problems when ingested. Iron (Fe) and manganese (Mn) are two nuisance constituents of groundwaters which cause discoloration and taste problems.

Previous studies have shown that in aquifers of appropriately high permeability, Fe and Mn are removed *in situ* (directly in the aquifer) by injection of oxygenated water. The process -- Vyredox™ (Hallberg and Martinell, 1976) -- avoids expensive, above-ground water treatment to remove these two metals. Other studies have noted that in standard water treatment facilities, Ra often coprecipitates with oxides of Fe and Mn. It was the premise of this study, therefore, that if Fe, Mn and Ra occur together in an aquifer in undesirable concentrations then *in situ* oxidation might serve as a viable, cost-effective means to remove all three.

The purpose of the project was to examine that viability. Specifically, it was to determine whether there were groundwater systems in Wisconsin where the three elements occurred in elevated concentrations, and whether Ra coprecipitates with Fe and Mn in aquifers. The second objective required development of a procedure for determination of low-level Ra activity in samples.

The study has shown that existing data allow identification of only one area in the state where the *in situ* process might be effective. It ranges from Marathon to Adams Counties in central Wisconsin, where the glacial aquifer has high Fe and Mn and bedrock aquifers show high Ra. Because of low permeability and greater depth, bedrock aquifers generally are not efficient locations for injection, so in this area high-Ra water would need to be drawn from the deeper aquifer, aerated and injected in the glacial aquifer to produce *in situ* removal of the three metals. The viability of this two-step process was not investigated. There may be other parts of the state where elevated Ra coexists with high Fe and Mn, but too few Ra analyses have been published to identify them.

Investigation of Ra coprecipitation was not particularly successful. The findings from the experiments showed that chemical recovery of Ra was too low to produce reliable results. No in-depth investigation about why such poor quantitative recovery of Ra occurred and no definite conclusion could be drawn. However, a strong indication exists that primary loss of Ra was due to cation exchange. Attempts were made to overcome the cation exchange problem by coprecipitating Ra with barium sulfate ($BaSO_4$). Again, Ra recovery was inadequate due to incomplete removal of sulfate (SO_4) in the anion exchange process. Further adjustments produced no better than 6% chemical recovery. The trials indicate chemical recovery by the suggested procedure is qualitative but not quantitative. Losses of Ra activity ranged from 75 to 94%. However, a detailed analysis is needed to quantify and confirm losses of Ra during the processes. Because of the inability to develop an efficient means of detecting Ra, the project could not address the question of whether Ra coprecipitates with Fe and Mn in groundwater.

Regardless, we are unable to identify many areas in Wisconsin where *in situ* coprecipitation would be particularly promising. And in lieu of the U.S. Environmental Protection Agency's (EPA) recent proposal to raise the Ra standard for drinking water, it appears the issue is no longer as urgent as it was. Very few public water supplies exceed the new Ra standards and removal is unnecessary.

MATERIALS AND METHODS

The distribution of Fe and Mn in groundwater were determined from previously collected and published data (Syftestad, 1985). All public water supply wells in Wisconsin were subdivided on the basis of the aquifer from which they produce. Four interim aquifer maps, which appear later in this report, locating the wells were developed:

1. Quaternary unconsolidated deposits;
2. Silurian/Devonian dolomite;
3. Cambrian/Ordovician sandstone/dolomite; and
4. Pre-cambrian crystalline rocks.

Combined values of Fe and Mn concentrations were contoured to produce a map, appearing later in the report, which shows distribution of Fe and Mn concentrations in each aquifer.

The original plan was to produce a similar set of maps for Ra. Locations where high Ra coincides with elevated Fe and Mn would be targeted for *in situ* treatment. Unfortunately, Ra concentration data in Wisconsin groundwater are sparse and do not justify statewide contour maps. Instead we produced a single map showing all identified locations of high Ra concentrations in well water for comparison with the Fe-Mn maps.

Analyses for radon (Rn) are more common in groundwater than for Ra. For samples where Ra and Rn have been determined, statistical analyses have been used to determine whether areas of elevated Rn are indicative of high Ra.

The second objective -- determination of efficiency of Ra co-removal with Fe and Mn -- was approached by examining the response of Fe, Mn and Ra in aqueous solution to different, controlled conditions in the laboratory. The concentrations of Fe and Mn have been measured by atomic absorption spectroscopy using standard procedures. However, Ra concentration was measured through a surface barrier detector, with the counting source prepared from the sample by coprecipitation, ion exchange, and electrodeposition.

Conventionally, Rn emanation followed by scintillation counting or gamma (γ) spectrometry has been used to measure the activity of Ra. However, a surface barrier detector with an electroplated source may be preferable for the purpose of this study. Among the reasons are insensitivity of the Rn emanation detector, inability to incorporate a yield tracer, or the inordinate amount of time necessary for ingrowth of the daughter radionuclides. Using an alpha (α) detector, a much lower level of activity can be detected (0.01 dpm), and because it counts the isotope itself and not the daughters, a tracer can be incorporated.

A Ra source can be prepared in many ways and counted by α spectrometry. For example, after coprecipitating Ra in the sample solution with Ba as $BaSO_4$, a counting source can be prepared directly by laying down a thin layer of the precipitate on a planchet. However, because of the use of a carrier (Ba), the spectrum is degraded through self-absorption. Furthermore,

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particle recoil and loose precipitate contaminates the detector, resulting in poor resolution. In addition, losses of the Rn through gas diffusion can be significant resulting in poor spectral resolution. To prevent these problems, a counting source is prepared after taking additional steps to separate Ra from Ba. With the carrier-free Ra solution, a layer of thin, stable Ra which is resistant to abrasion and leaching can be deposited on a steel planchet, eliminating the problems.

The suggested process involved three steps (Figure 1). Ra in the sample is coprecipitated with Ba as $BaSO_4$ (American Public Health Association, 1989; Goldin, 1961). The SO_4 containing Ba and Ra is dissolved by heating with ethylenediaminetetraacetic acid (EDTA). The dissolved SO_4 is removed by an anion exchange column and the Ra is separated from Ba using cyclohexylenediaminetetraacetic acid, Aldrich (DcyTA) in a cation exchange column (Gleason, 1980). The carrier-free Ra is evaporated and dissolved in ammonium acetate, and is then ready for electrodeposition on a steel planchet (Benoit and Harmon, 1988; Garcia and Garcia, 1988; Gleason, 1990; Masayoshi et al., 1989; Ramon, 1984; Short, 1986). Since the present work was completed, an improved technique for the determination of ^{226}Ra had been published by Orlandini et al. (1991).

A tank 1.5 x 1.5 ft (approximately 95 liter) with a sealable cap was used as a reactor for simulating the groundwater environment. The groundwater material (clay or sand) was suspended. The control variables are Ra, Fe, and Mn concentrations, pH and oxygen.

Analytical reagents were used throughout the investigation. A 0.05 M DCyTA solution was prepared by diluting 0.1 M DCyTA solution with an equal volume of saturated boric acid (H_3BO_3) and adjusting to the designated pH (5.0 and 8.5). The 0.1 M DCyTA solution is prepared by dissolving 18.2 g of DCyTA with 4.0 g NaOH in 500 ml distilled water. ^{226}Ra solution is prepared as described in standard methods (American Public Health Association, 1989), and the thorium tracer (^{229}Th) was prepared in a 1 MHNO$_3$ solution.

Three steps are involved before Ra can be counted: Coprecipitation, ion exchange, and Ra electrodeposition. First, to a 1 liter sample solution (filtered through 0.45 μm filter paper) that has been acidified, 1 to 2 dpm of ^{229}Th (obtained from National Institute of Standards and Technology), 5 ml 1 M citric acid, 2.5 ml of concentrated NH_4OH, 200 mg of lead nitrate and 10 to 20 mg of $BaCl_2$ carrier were added. The solution was heated to boiling and 10 drops of methyl orange indicator (yellow at this point) was added. While stirring, 18 N H_2SO_4 was added slowly until a permanent pink color was reached and an additional 0.25 ml acid was added. The solution was boiled gently for 5 to 10 min and allowed to stand until the precipitate was settled (3 to 5 hr or more). The clear supernate was decanted and the precipitate transferred to a 50 ml centrifuge tube with distilled water. After centrifugation the supernate was decanted. The precipitate was washed with 10 ml of concentrated HNO_3, stirred and centrifuged again. The washing step was repeated twice to allow sufficient decontamination. After the final wash, 10 ml of distilled water and two drops of phenolphthalein indicator solution were added. The solution was stirred to loosen the precipitate and 5 N NH_4OH was added until the solution became red. Then 10 ml of 0.25 M EDTA and 3 ml of NH_4OH were added and the solution was stirred occasionally for 2 min to dissolve the precipitate. If necessary, the solution was warmed in a steam bath for 10 min to clear the solution. Concentrated acetic acid was added until the red color

B
Filter 1 L of
sample solution

Coprecepitate Ra
as $BaPb(SO_4)$

Remove Pb at pH 5
as Pb-EDTA complex

A

$BaRa(SO_4)$ precipitate

Solubilize BaRa
(SO_4) with EDTA
at pH 10-11

Convert $BaRa(SO_4)$ to
$BaRa(CO_3)$ by heating
with $NaCO_3$ and dissolve
in HCl

C

Reprecipitate $BaRaCO_3$
as $BaRaCrO_4$ with
$NaCrO_4$ at pH 7 and
dissolve in HCl

Remove SO_4 by
anion exchange
column in Cl form

Remove CO_3 by anion
exchange column in
Cl form

Remove CrO_4 by anion
exchange column in
Cl form

Adjust effluent
containing BaRAEDTA
$(Cl)_2$ to pH5

Evaporate and dissolve
in DCyTA/Boric acid
buffer to pH 5

Separate Ra from Ba in
cation exchange column
in sodium form

Elute Ba with DCyTA/Boric
acid buffer to pH 8.5
Elute complexung agent
(EDTA or DCyTA) with HBr

Elute Ra with HNO_3

Evaporate and dissolve
in ammonium acetate
buffer to pH 5

Electrodeposit Ra onto
a steel planchet at a
control voltage and
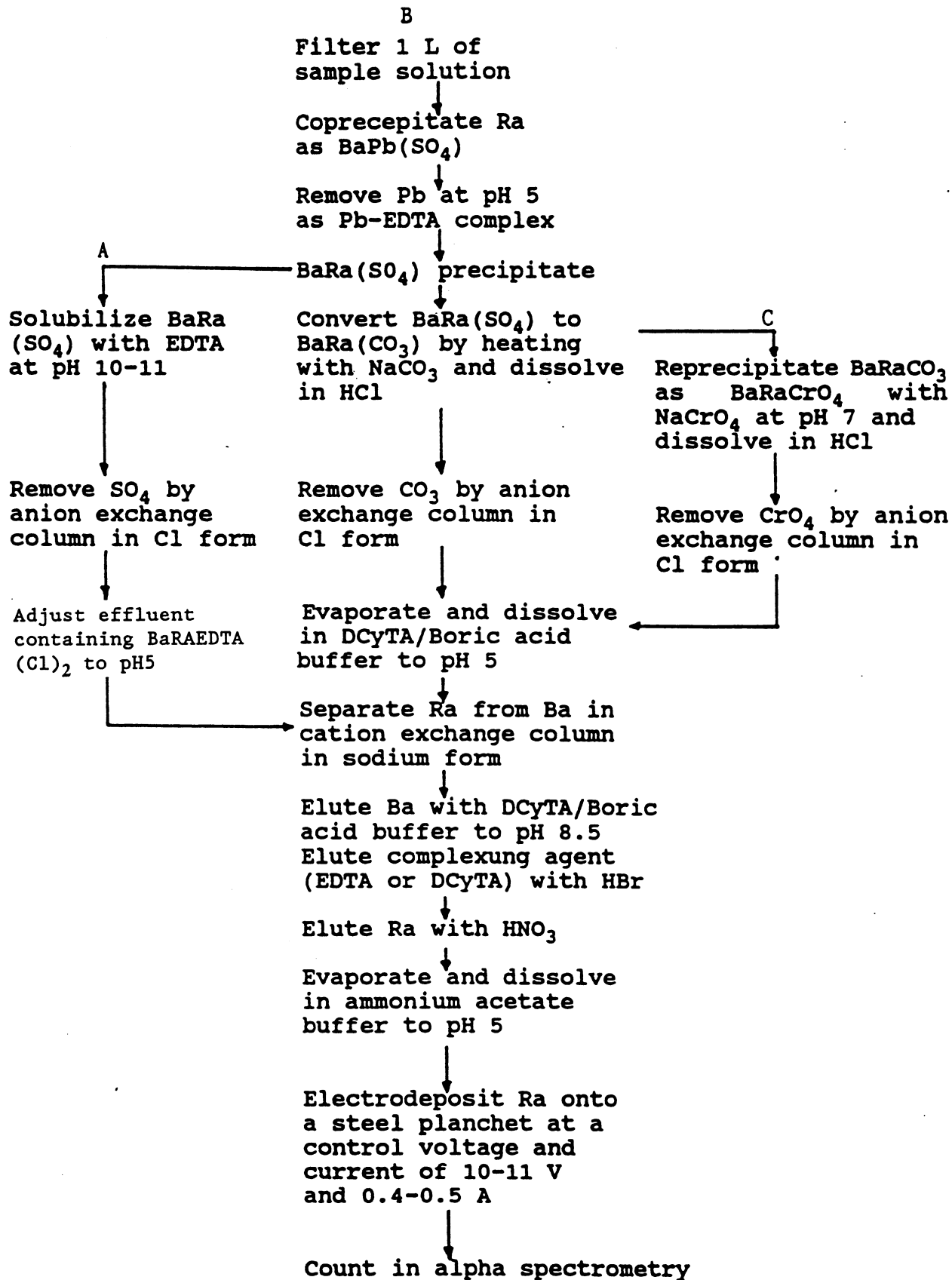current of 10-11 V
and 0.4-0.5 A

Count in alpha spectrometry

Figure 1. Flow chart of three radiochemical procedures.

disappeared, followed by 2 drops of bromcresol green indicator and acetic acid was added until the color turned aqueous green (pH 4.5). The solution was digested in a steam bath for 5 to 10 min. After cooling, the solution was centrifuged and the supernate decanted. The precipitate was redissolved with 10 ml of EDTA at a pH between 10 and 11 (adjusted with 10 N NaOH) while the solution was stirred and warmed in a steam bath. The solution was cooled to room temperature before proceeding to the next step.

Two ion exchangers are used in step 2. The clear solution was passed through an anion exchange resin column (50 mm x 8 mm) in Cl form at a flow rate of 0.2 ml/sec to remove SO_4. The column was previously developed by filling it with 2 g of resin bead (Bio=Rad AG 1-X8, 100 to 200 mesh, formate form) and sequentially passing through it 10 ml 6 M NaOH, 20 ml distilled water, 50 ml 4 M HCl and 20 ml distilled water. After the solution had drained through the anion exchange column, the effluent containing Ba, Ra and EDTA was collected and adjusted to pH 5 (at pH 5, Ba separates from the EDTA complex and is absorbed by the cation resin).

The solution was passed through the cation exchange column (100 mm x 4 mm) in Na form for separation of Ra from Ba. The cation exchange column was developed by filling it with 15 g of resin bead (Bio-Rad AG 1-X8, 100 to 200 mesh, hydrogen form) and sequentially passing 10 ml 6 M HCl, 30 ml saturated NaCl, 20 ml distilled water and 10 ml saturated H_3BO_3 adjusted to pH 5. The solution was drained through the column so that Ba, EDTA and Ra were adsorbed by the resin in order of increasing selectivity. The resin pH was adjusted to 8.5 by passing through it 10 ml of saturated H_3BO_3 adjusted to pH 8.5. Thymol blue indicator was useful in monitoring the pH. The Ba adsorbed by the column was removed by passing through it 20 ml of DCyTA/H_3BO_3 adjusted to pH 8.5. The resin was changed to the H form by passing 20 ml of 0.6 M hydrobromic acid or 0.5 M HCl. This washing flushes the complexing agent from the column (EDTA or CDyTA). Finally, Ra in the resin was eluted with 30 ml of 3 M HNO$_3$. In all cases flow rate was maintained at 0.2 ml/sec and it was important not to allow the resin to become dry or be stirred. This precaution improves analytical reproducibility.

In the third step, the isolated Ra solution collected from the cation exchange column was evaporated to dryness and dissolved in 10 ml of 0.35 M ammonium acetate. This electrolyte was prepared by adding 0.35 M ammonium acetate solution to 0.1 M HNO$_3$ with pH adjusted to 5. The Ra solution was readjusted to pH 5, if necessary.

A clean 20 ml polyethylene scintillation vial was assembled as shown in Figure 2. The bottom part of the vial was cut so that it could be fitted with a polyethylene cap, such that a 1 mm diameter platinum wire with spiral anode end can be suspended through the cap. The polyethylene cap is equipped with holes to allow escape of gas generated during the plating process. The cathode was made from a copper (Cu) plate soldered at the center with a 2 cm long (2 mm diameter) Cu wire and snug fitted into the plastic screw cap. The spiral anode end was adjusted to be 10 mm above the steel planchet. After checking for leaks, the electrolyte was poured into the cell and the plating process begun. The process was regulated by a power supply (Lambda model LH125 s) so that voltage ranged between 11 and 12 V and current ranged from 0.4 to 0.5 Amp. The pH must rise to 8 to 9 during the first 15 min and the temperature rises to about 60°C. After plating for at least 3 hr the plating cell was disassembled and the planchet

+

Platinum wire
(1.0 mm diam. 99.9%)

Polyethelene cap

Gas escape holes

Polyethelene
scintillation vial
(20 ml)

Stainless steel
planchet (19 mm diam.)

Platinum wire anode

Polyethelene screw cap

Copper conductor
cathode
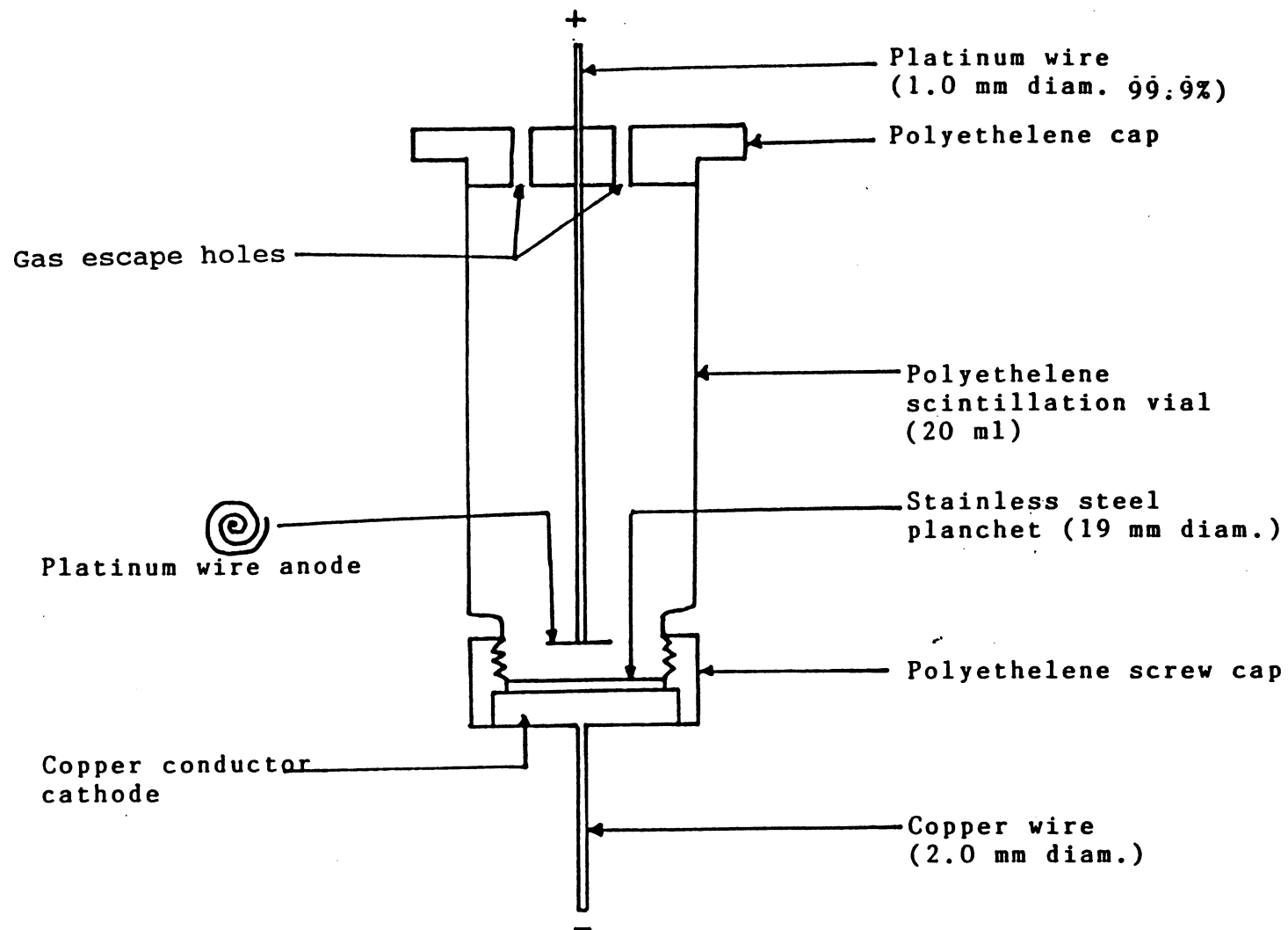
Copper wire
(2.0 mm diam.)

−

Figure 2. Schematic of electrodeposition cell.

washed with distilled water and allowed to air dry. The plated planchet was mounted and counted on an α spectrometer system consisting of an EG&G Ortec 576 surface barrier detector, an ADCAM multichannel analyzer buffer (model 918), a multiplexer-router (model 476), a vacuum pump, and an IMB-AT computer.

RESULTS AND DISCUSSION

IRON, MANGANESE AND RADIUM IN GROUNDWATER

Figures 3 to 6 show the distribution of Fe and Mn combined in the public water supply wells of Wisconsin. Whenever multiple samples were taken at a single location, the value of the average was plotted. Concentrations were separated into four categories and contoured: high (>1 mg/liter), moderately high (0.5 to 1.0 mg/liter), moderately low (0.1 to 0.5 mg/liter) and low (<0.1 mg/liter). Only the areas in the high category have sufficient Fe and Mn to be deemed undesirable and they are the only ones warranting further investigation for Ra removal by coprecipitation.

It should be added at this point that the *in situ* oxidation process requires injection of oxygenated water into the groundwater system. In Wisconsin, the only aquifer possessing high enough permeability and porosity to allow efficient injection is the Quaternary unconsolidated aquifer. So only the high Fe/Mn areas on Figure 3 would be readily amenable to Vyredox treatment.

For Ra, Figure 7 and Table 1 show all published occurrences of Ra in concentrations >5 pci/liter. The distribution is spotty because so few Ra analyses have been published. The absence of "hotspots" in any area on Figure 6 has little meaning; it could mean that Ra concentrations are low or no analyses have been published, or both. Only the presence of high Ra is meaningful and two basic trends are apparent. Many wells in eastern Wisconsin which are completed in multiple aquifers and some wells in north-central Wisconsin in the crystalline or sandstone aquifers have high Ra concentrations.

In eastern Wisconsin, the multiple aquifers are the Silurian/Devonian dolomite where present and the Cambrian/Ordovician dolomites and sandstones. These two aquifers are separated by the Maquoketa Shale, generally recognized as a Ra source. These wells are in aquifers that are too deep or too tight for *in situ* treatment to be effective, so this region probably does not warrant further investigation.

In central Wisconsin there are fewer incidences of high Ra reported in the area outlined on Figure 7, but conditions may be more appropriate for *in situ* treatment. Several wells in the crystalline aquifer exhibit high Ra. Wood County also happens to be a location where the aquifer has high Fe and Mn (Figure 6). The sandstone aquifer in Adams County has high Ra (Figure 7) and Fe and Mn (Figure 5). Again the hydraulic properties of the two aquifers probably preclude *in situ* treatment, but the high Ra wells tend to be in locations where the specific bedrock aquifer is directly overlain by glacial sediments. It is conceivable therefore, that treatment might be viable within the Quaternary material above the high-Ra aquifer. Some portions of the glacial aquifer in this area possess high enough Fe/Mn concentrations (Figure 3) to allow *in situ* removal if deeper aquifer water were injected in it. This possibility bears further investigation, but is beyond the scope of this study.
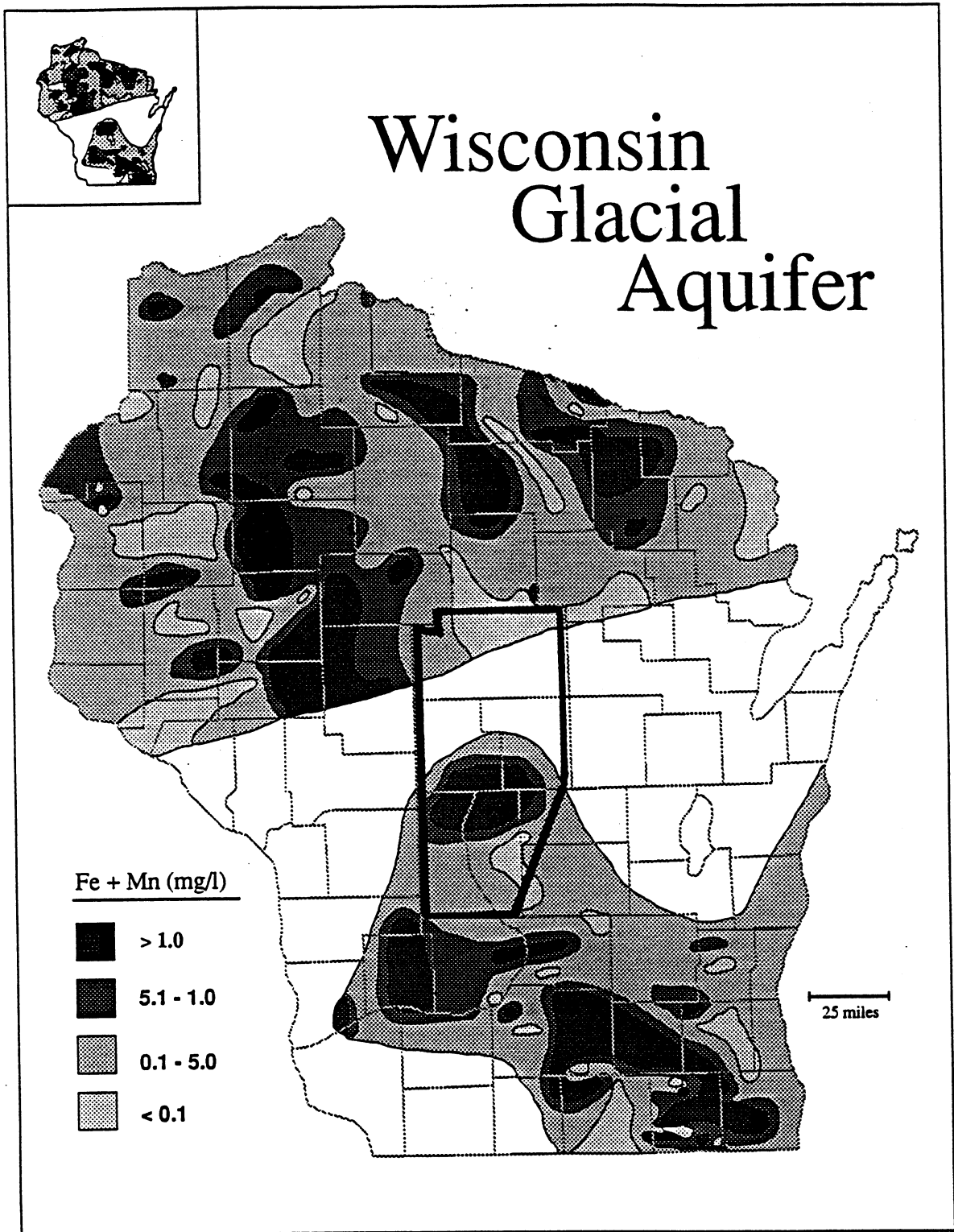
Figure 3.   Distribution of combined Fe and Mn in public water supply wells in the Quaternary deposits aquifer of Wisconsin. This aquifer is not continuous even in areas where the contours are. It is intended to show general trends in water quality, not point specific values. Box shows area discussed in text.

Wisconsin Dolomite Aquifer

Fe + Mn (mg/l)

- > 1.0
- 5.1 - 1.0
- 0.1 - 5.0
- < 0.1

25 miles
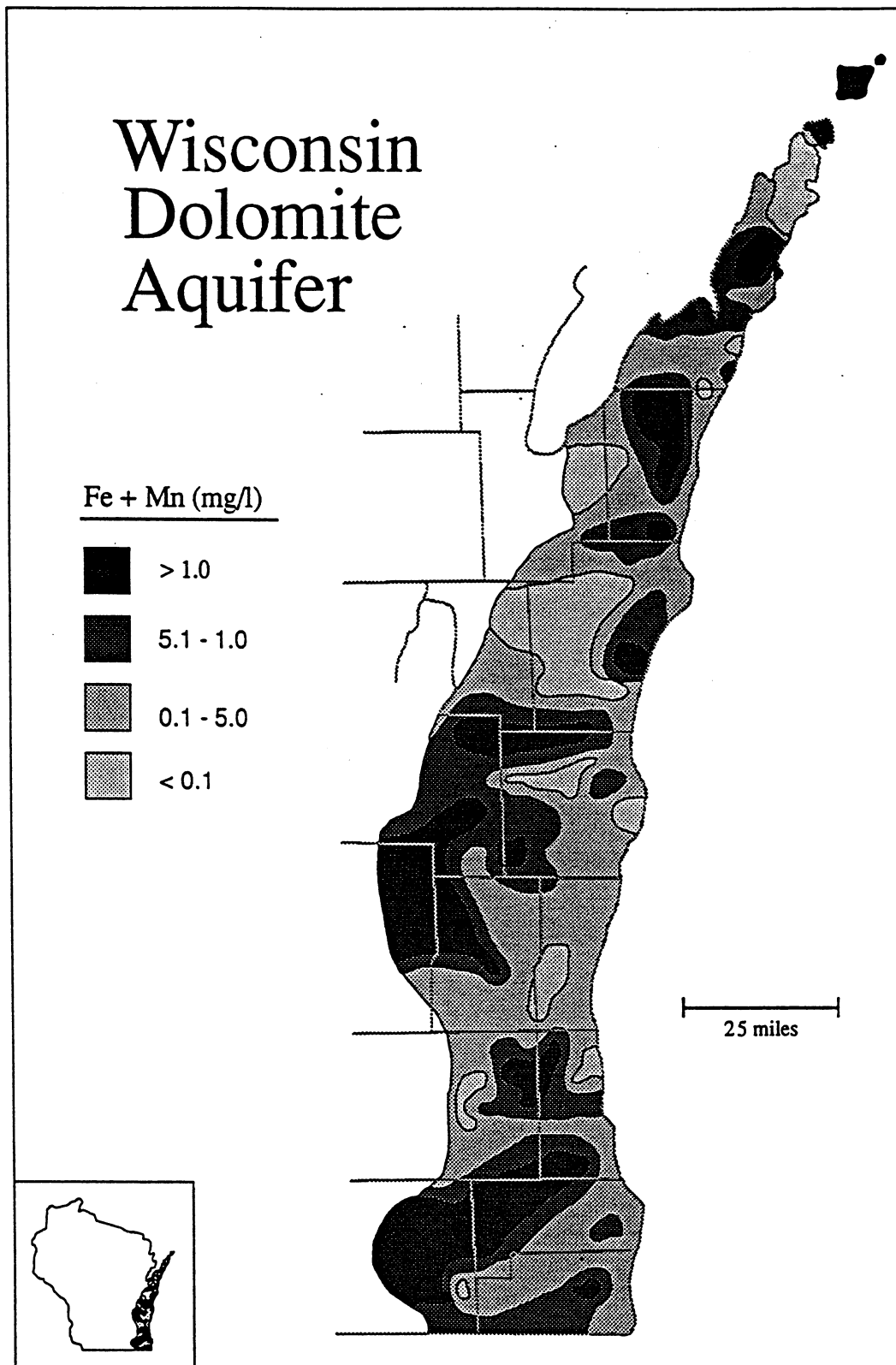
Figure 4.   Distribution of combined Fe and Mn in public water supply wells in the Silurian/Devonian dolomite aquifer of Wisconsin.
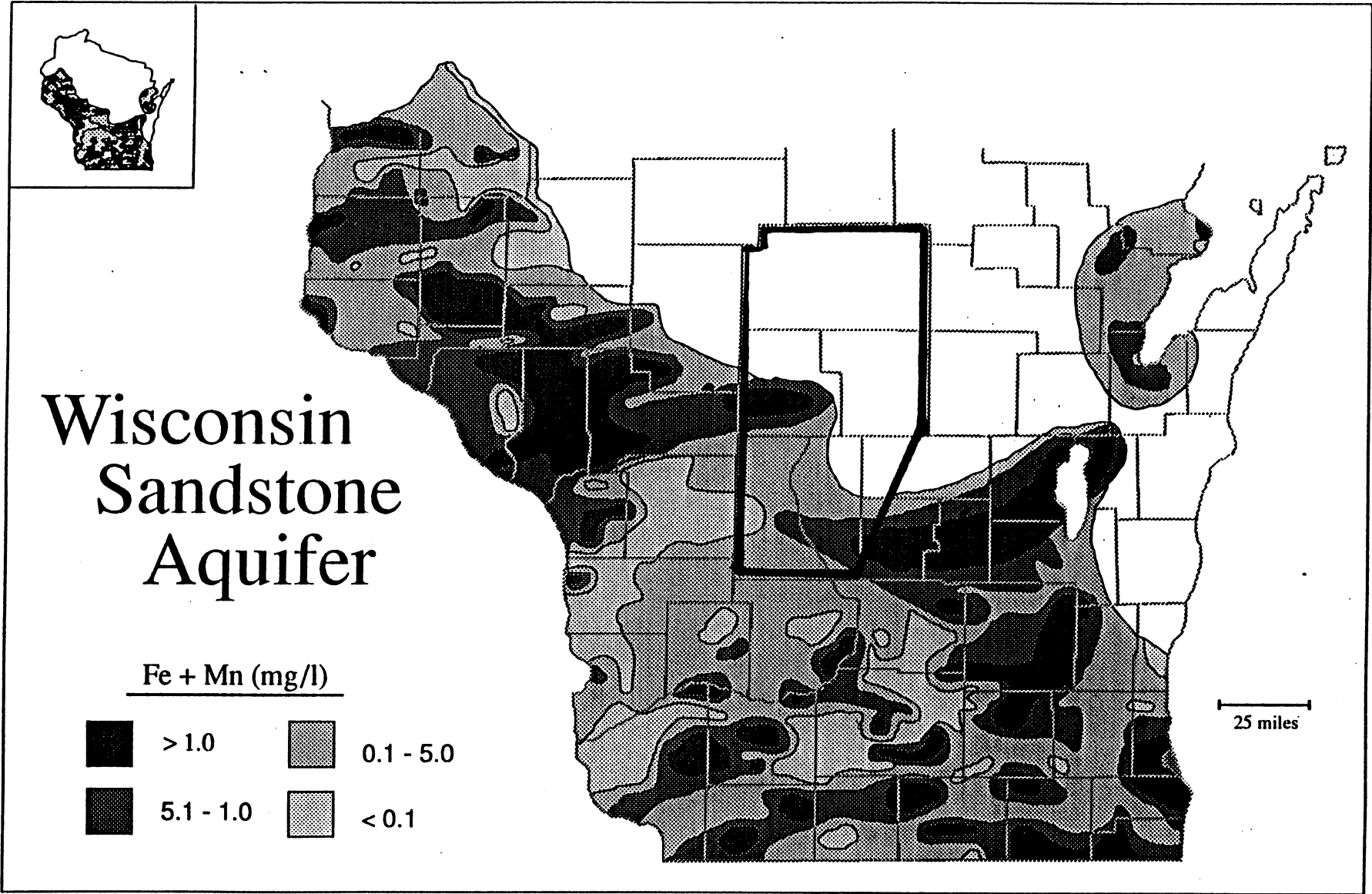
Figure 5. Distribution of combined Fe and Mn in public water supply wells in the Cambrian/Ordovician aquifer of Wisconsin. Box shows area discussed in text.

Wisconsin Precambrian Aquifer

Fe + Mn (mg/l)

■ (black)	> 1.0
■ (dark gray)	5.1 - 1.0
▨ (light gray)	0.1 - 5.0
▢ (white)	< 0.1

25 miles
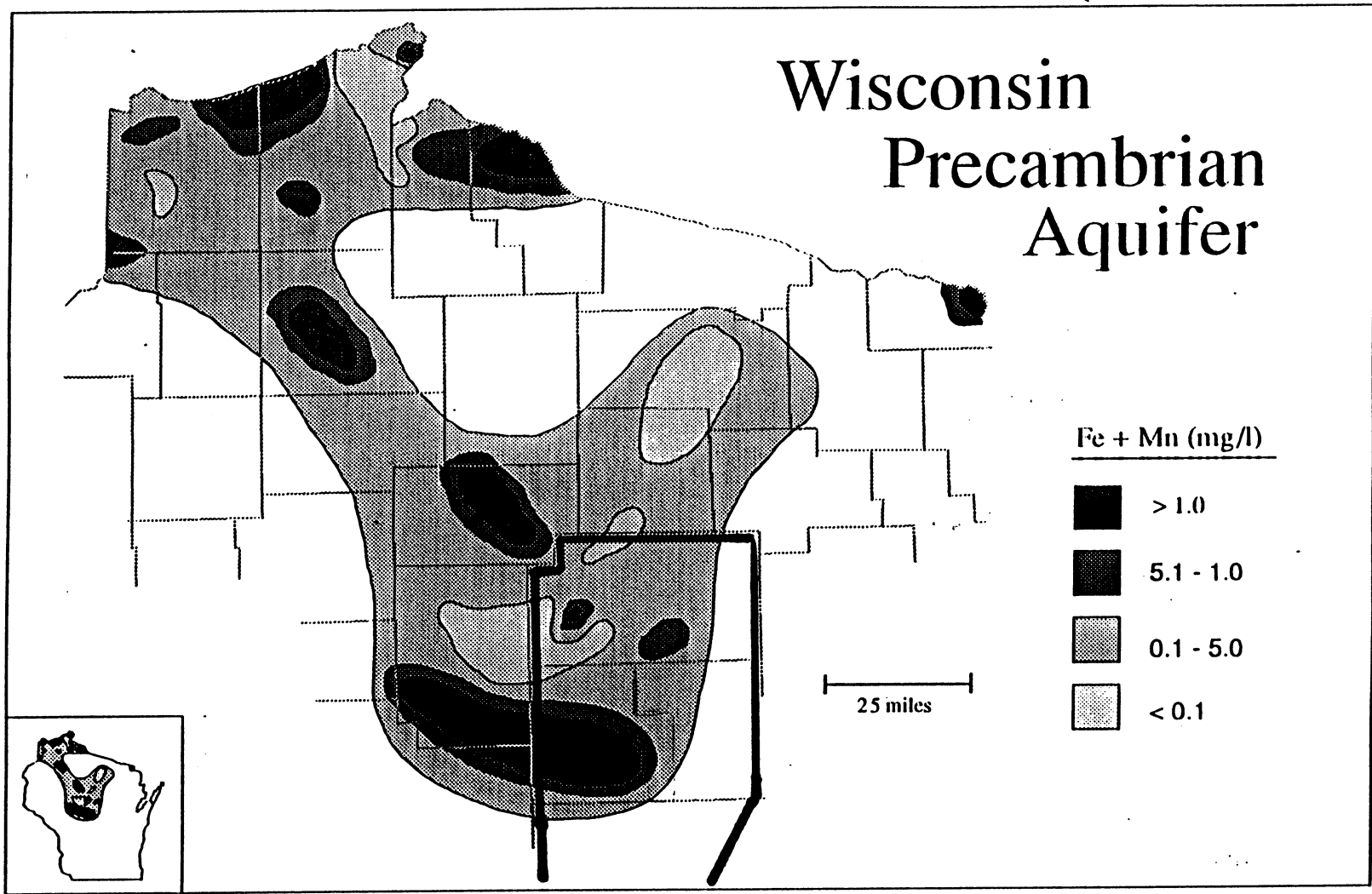
Figure 6. Distribution of combined Fe and Mn in public water supply wells in the crystalline rock aquifer of Wisconsin. Data for this unit are sparse; at best this map shows general water quality trends. Box shows area discussed in text.
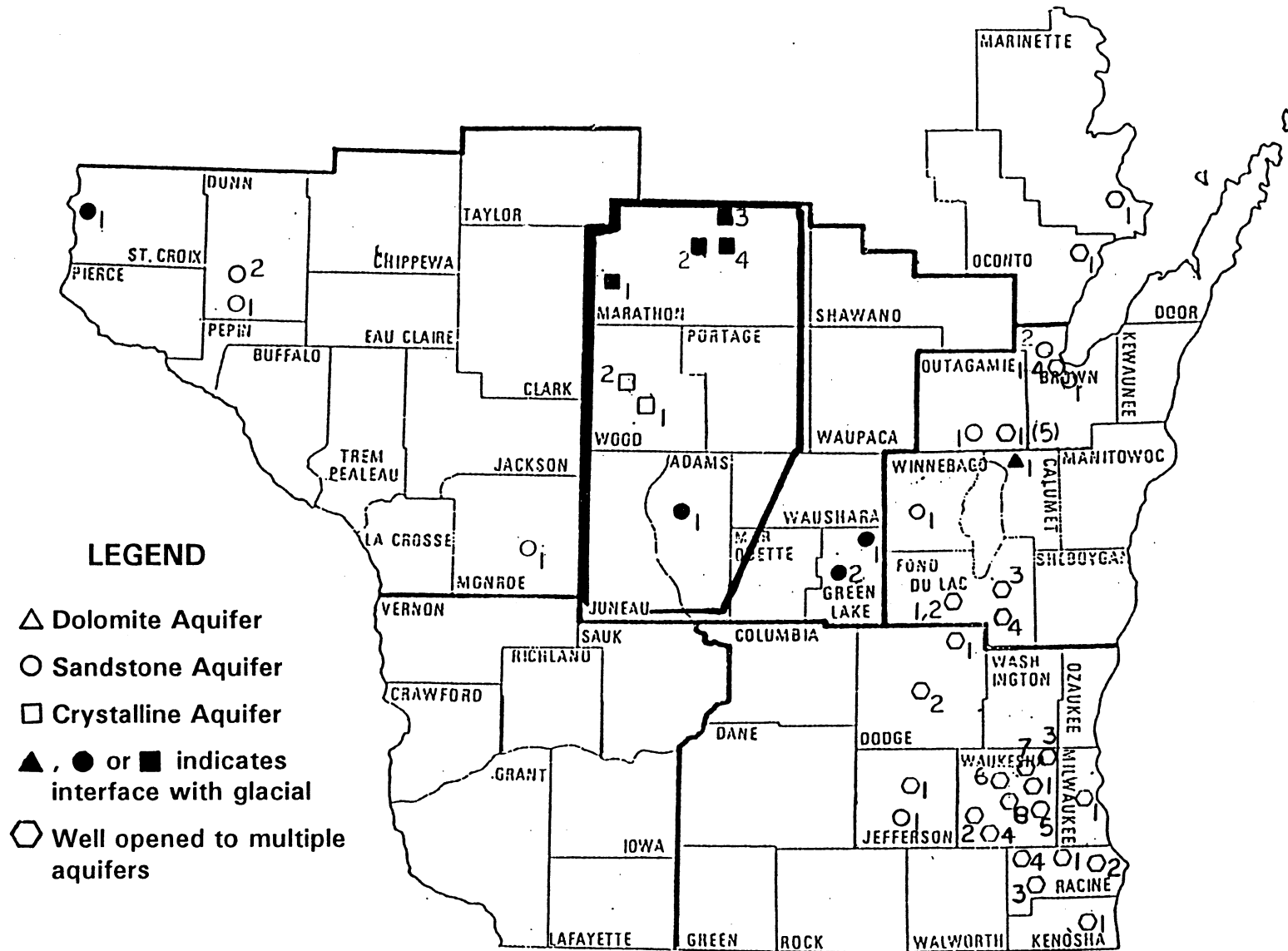
Figure 7. Locations of wells in Wisconsin with Ra concentrations >5 pci/liter. Wells are identified by the aquifer(s) from which they draw water. Solid symbols indicate a well in a bedrock aquifer which is in direct contact with Quaternary deposits. Well locations are given in Table 1. The zone of interest outlined on the map is discussed in the text and reproduced on Figures 3-6.

Table 1. Water supply wells in Wisconsin with total radium in excess of 5 pci/liter.†

| | | | Radium Hotspots | | | | |
| | | | Radioactivity (pci/liter) | | | | |
County	Number	City/Town	Rn	^{226}Ra	^{228}Ra	U	Aquifer‡
			Single Aquifers				
Adams	1	Preston		2.5	3		s
Brown	1	De Pere W.W.		~3.8	~3.0		s
	2	Howard		~3.5	~2.4		s
Calumet	1	Sherwood W.W.		~16	~16		1
Dunn	1	Downsville	~600	~8.0	~5.0		s
	2	Menominee W.W.	~928	~3.0	~4.0		s
Green Lake	1	Berlin W.W.		~3.0	~2.5		s
	2	Princeton	~300	~6.1	~3.8		s
Jefferson	1	Jefferson W.W.	~350	~3.1	~2.0		s
Marathon	1	Frankfort		6.4	2.3	19	c
	2	Maine	3400	2.3	3.3	<1.0	c
	3	Texas		4.6	5.9	129	c
	4	Wausau	6906	28.3	2.8	31	c
		Wausau	391394	46.5	10.6	24.7	c
		Wausau	31274	55.1	2.9	162	c
		Wausau	203455	31.3	2.5	88	c
		Wausau		35.5	2.4	105	c
Monroe	1	Tomah W.W.		~4.0	~1.8		s
Outagamie	1	Darboy (SD 1)	206	~3.2	~2.3		s
St. Croix	1	Hudson W.W.	~850	~3.5	~2.5		s
Winnebago	1	Winneconne W.W.		~3.5	~3.5		s
Wood	1	Grand Rapids		1.6	5.2		c
	2	Hansen		8.3	5.1		c
			Multiple Aquifers				
Brown	1	Allouez W.W.	~400	~5.0	~2.5		lss
	2	Ashwaubenon	~350	~4.0	~2.2		lss
	3	Bellevue	~350	~12.0	~6.0		lss
	4	Green Bay W.W.		~4.0	~2.0		lss
	5	Holland-Kaukana	~190	~16.0	~15.0		sls
Dodge	1	Brownsville	~600	~4.1	~2.5		ls
	2	Hustisford	~250	~6.0	~4.0		ls

Table 1. Continued

			Radium Hotspots				
			Radioactivity (pc/liter)				
County	Number	City/Town	Rn	^{226}Ra	^{228}Ra	U	Aquifer‡
Fond du Lac	1	Fond du Lac W.W.	~350	~5.5	~3.0		lsc
	2	Mary Hill Park S.D.	~220	~4.2	~3.0		ls
	3	N. Fond du Lac W.W.	~300	~6.0	~6.0		ls
	4	Taycheedah C.I.	~300	~12.0	~7.0		ls (?)
Jefferson	1	Johnson Creek W.W.	~500	~4.0	~3.0		sl
Kenosha	1	Pleasant Prairie I.P. Pleasant Prairie T.R.	103	~5.0	~6.0		lsls
Marinette	1	Peshtigo W.W.	~280	~3.9	~3.5		ls
Milwaukee	1	Franklin W.W.	~200	~4.5	~4.5		sl
Oconto	1	Oconto W.W.		~5.0	~1.1		ls
Outagamie	1	Kaukana (E&W)	~250	~2.9	~3.2		ls
Racine	1	Caledonia (Caddy Vista)	90	~4.6	~2.1		ls
	2	Racine (Crest View)	~160	~6.0	~3.0		ls
	3	Union Grove	~160	~25.0	~2.8		lssh
	4	Waterford W.W.		~4.5	~2.0		ls
Waukesha	1	Brookfield (Zone 1)		~3.5	~3.0		ls
	2	Eagle W.W.	~350	~5.0	~3.8		ls
	3	Menomonee Falls W.W.		~3.5	~2.5		lss
	4	Mukwanago W.W.	~300	~4.9	~3.5		ls
	5	New Berlin W.W.	~150	~4.2	~3.2		lss
	6	Pewaukee Village W.W.	~225	~2.8	~3.0		ls
	7	Sussex	~350	~3.9	~3.0		ls
	8	Waukesha	~250	~4.0	~7.0		ls

†Data are separated into two groups, one of wells in a single aquifer and the other of wells in more than one aquifer. Sources: Syftestad (1985), Fitzgerald (1991).

‡c: crystalline; l: limestone; sh: shale; s: sandstone (e.g., lssh: limestone, sandstone, shale aquifers used as sources).

Because Rn analyses have been done more commonly than Ra, an attempt was made to correlate the two. The attempt is confined to the north-central part of Wisconsin where Fitzgerald (1991) provides the best information and where Figure 6 shows a potential for Ra highs. A significant correlation is expected because ^{222}Rn is derived from ^{226}Ra. However, because the half-lives of the isotopes differ markedly and because Rn analysis are commonly done immediately while the sample is stored before Ra analysis, the relationship may be masked.

Fitzgerald's (1991) samples from Marathon County which were analyzed for Ra and Rn were correlated (Figure 8). A log-log relation exists with a correlation coefficient of 0.87 and a significance level of 99%. Using this relationship, samples with a Ra concentration 5 pci/liter should contain >27,000 pci/liter of Rn. Wells with Rn > 28,000 pci/liter could be added to the list of Ra "hotspots". However, this extrapolation is at best tenuous because no Ra analyses exist.

Fitzgerald (1991) lists the wells in the north central part of the state for which Rn analyses are available. Of these, five have high enough Rn for us to suspect that Ra may exceed 5 pci/liter. They are all in Marathon County and include: Eau Pleine, 33,000 pci/liter Rn; Rietbrock, 28,000 pci/liter Rn; Spencer, 38,000 pci/liter Rn; Texas, 32,000 pci/liter Rn; and Wausau, 130,000 pci/liter Rn. The latter two were already identified by Ra analyses directly, so the Rn data only allow inclusion of three more sites to Figure 7. All the high Rn wells are completed in the crystalline aquifer -- generally portions of the Wolf River group. This group of rocks, which extends northeastward from marathon County to northern Oconto County is potentially another area where high Ra concentrations might be found, but there is not much Fe or Mn in the overlying glacial aquifer.

The primary conclusion is that only one area in Wisconsin exists where high Fe, Mn, and Ra concentrations in groundwater have all been shown to occur. The area stretches from Marathon County in the north to Adams and Juneau County in the south. Within this area, the high Ra occurs in bedrock aquifers, while the Fe and Mn are in the glacial aquifer. Water would have to be drawn from the deeper aquifers, aerated, and injected in the glacial aquifer to achieve *in vitro* removal of the three metals. Whether such a system is feasible has not been addressed.

LABORATORY INVESTIGATION OF RADIUM REMOVAL

The first attempts were intended to check yields from electrodeposition of a standard ^{226}Ra solution. But since the standard solution of Ra had a Ba carrier which interfered with the electrodeposition of Ra, a separation of Ba from Ra by cation exchange was necessary. The separated Ra was electrodeposited and counted. The results are not favorable, showing 25% recovery for cation exchanger (Table 2). The α-spectra of Ra can be seen in Figures 9 and 10. Possible problems could be incomplete separation in the cation resin, absorption losses of Ra to the glassware and low chemical yield in the electrodeposition process.

The objective of the next attempt was to see how much ^{226}Ra is recovered by the total simulation, taking account of the low chemical yield in the cation exchange and electrodeposition processes. To meet this objective, groundwater was simulated in a reactor by adding distilled water along with aquifer material and ^{226}Ra standard solution, and the mixed solution was suspended in the reactor by a rotating blade. The final concentration of ^{226}Ra was 8 pci/liter and the pH of the solution was
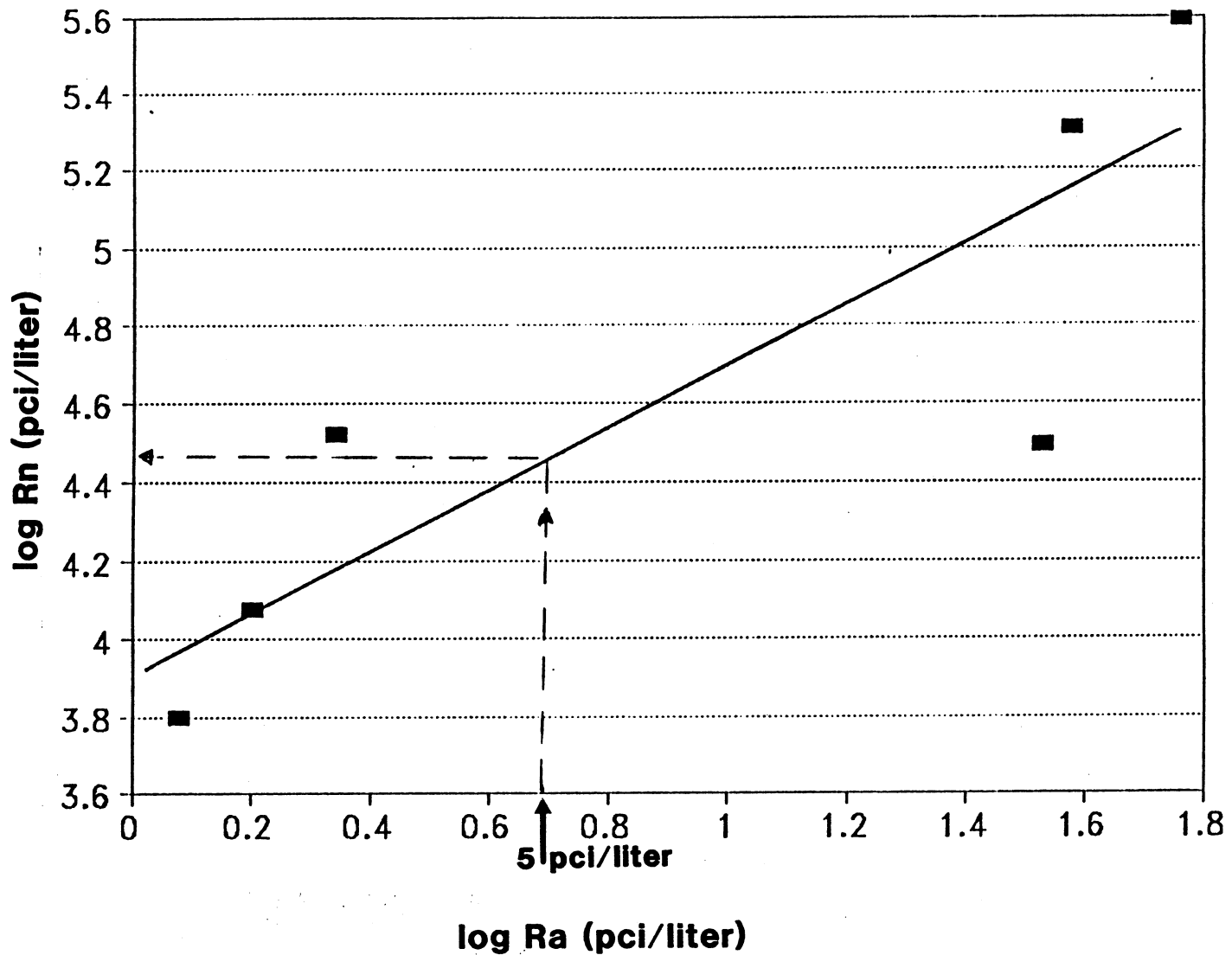
Figure 8.   Correlation of Ra and Rn activities for wells in Marathon County. Samples were analyzed for Ra and Rn, although not simultaneously. Data are from Fitzgerald (1991). Regression equation is log (Rn) = 0.78 log (Ra) + 3.9. Correlation coefficient is 0.87.
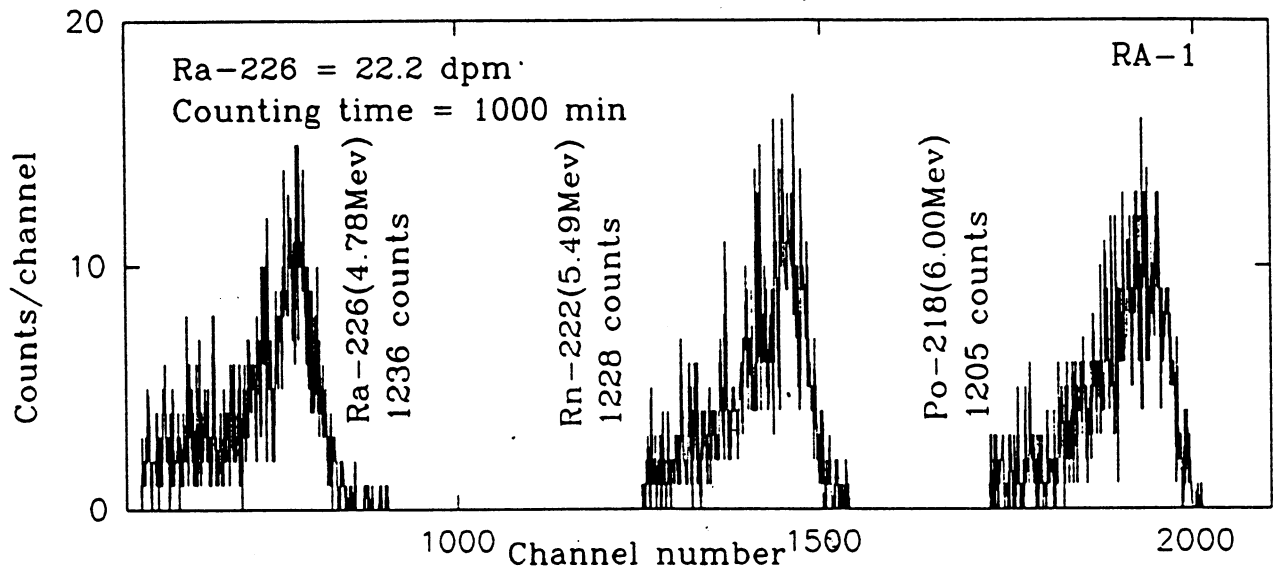
Figure 9. Alpha-ray spectra of ^{226}Ra, Run RA-1 (through cation resin only).
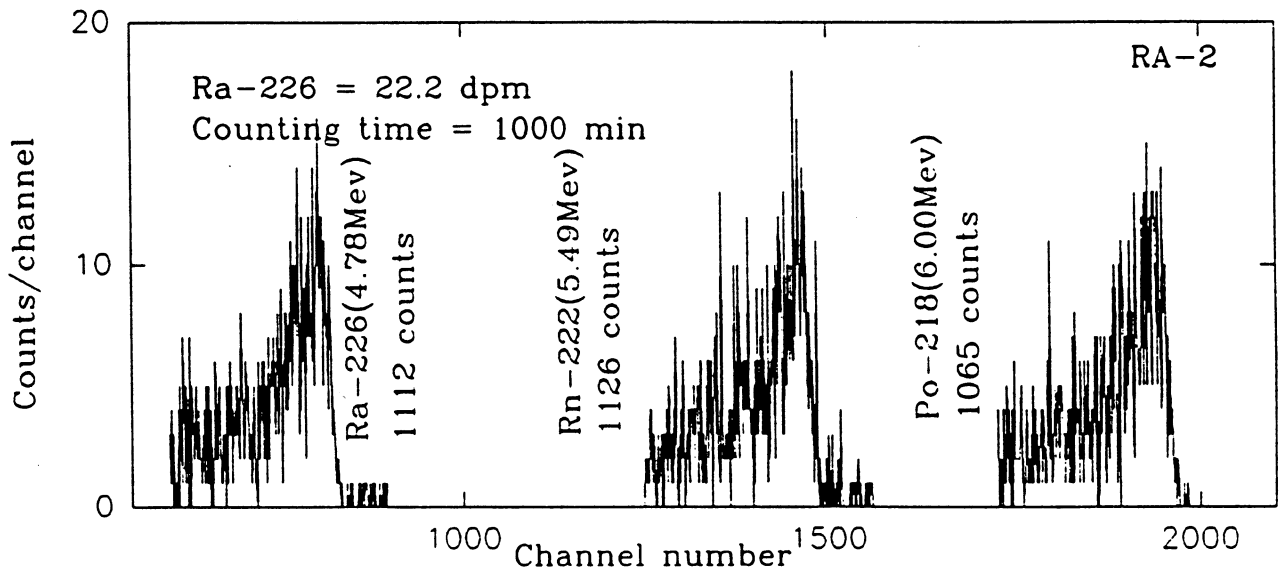

Figure 10. Alpha-ray spectra of ^{226}Ra, Run RA-2 (through cation resin only).

conditioned to pH 7. Sampling was conducted using a vacuum pump filter with 0.45-μm membrane filter paper. The sample solution was acidified, followed by coprecipitation and solubilization of $BaSO_4$.

Table 2. Recovery of ^{226}Ra from sample solution (1 liter).

Sample	^{226}Ra added (dpm)	Number of counts	Counting time (min)	Chemical recovery (%)	Overall recovery[†] (%)
RA-1[‡]	22.2	1236	1000	27.8	5.6
RA-2[‡]	22.2	1112	1000	25.0	5.0
RA-3[§]	21.5	503	5000	2.4	0.5
RA-4[#]	22.2	558	3225	3.9	0.8
RA-6[¶]	22.2	917	3224	6.4	1.3

[†]Detector efficiency about 20%.
[‡]^{226}Ra recovered from cation exchanger.
[§]^{226}Ra recovered from the chemical process through conversion from sulfate to carbonate form.
[#]^{226}Ra and ^{229}Th (^{225}Ra) recovered from cation exchanger.
[¶]^{226}Ra recovered from the chemical process through conversion from carbonate to chromate form.

However, a problem arose after the solubilized $BaSO_4$ solution was passed through the anion exchange column. Difficulties were found in trying to bring the pH of the effluent collected from the anion exchanger down to pH 5 as required for cation exchange. Theoretically, the effluent collected from the anion exchange column should be in the Cl form which should make H adjustment easy. In contrast, the effluent collected from the anion exchange column precipitated as pH was lowered to 5. After personal communication with Dr. Geoffrey Gleason -- a retired professor who developed the method for separation of Ra from Ba using DCyTA -- it was decided that SO_4 was not completely removed by the anion resin. A series of corrections were tried to achieve complete removal of SO_4 but none eliminated the problem. Possible solutions to the problem would be switching to NaCl instead of HCl for development of the anion resin in chloride form (to reduce the acidity of the resin), or lowering the pH of the solubilized $BaSO_4$ to pH 7, and passing through the anion resin two or three times. Another explanation for the discrepancy could be losses of Ra in the anion exchange.

Since there was only limited success in removing SO_4 in the anion exchange resin, a new attempt was made involving conversion of $BaSO_4$ to $BaCO_3$ by heating it in saturated Na_2CO_3 (Fig. 1). Without resorting to EDTA for solubilization of $BaSO_4$, the CO_3 is readily dissolved in 4 M HCL and passed through the anion exchanger, previously prepared in Cl form by a final wash with 4 M HCL, to remove CO_3. The effluent -- from the anion exchanger -- is evaporated and dissolved in 0.5 MDCyTA/H_3BO_3 solution buffered to pH 5. This solution was passed through the cation exchanger for separation of Ra from Ba. The final eluted Ra solution is evaporated and dissolved in 0.35 M

ammonium acetate buffered to pH 5, electrodeposited and counted. Overall recovery 0.5% (Table 2) was unacceptable. The α-spectrum is shown in Figure 11. Problems associated with this attempt might be due to the interference of carbonate ions in the cation exchange process, since CO_3 is not readily displaced by Cl.

Another alternative was to modify the conversion of $BaSO_4$ to $BaCO_3$ (Chart C, Figure 1). Converted CO_3 was dissolved in 1 M HCl, 5 ml of 4 M ammonium acetate and 10 ml 25% $NaCrO_4$. pH of the solution was adjusted to 7 to precipitate Ba as $BaCrO_4$ along with Ra. The $BaCrO_4$ was dissolved in 10 ml 4 M HCl and passed through the anion exchanger, previously prepared in Cl form by a final wash with 4 M HCl, to remove the CrO_4. The effluent was evaporated and dissolved in $DCyTA/H_3BO_3$ solution buffered to pH 5. The solution was passed through the cation exchange column for separation of Ra from Ba. The final eluted Ra was evaporated and dissolved in 0.35 M ammonium acetate buffered to 5 for electrodeposition. Chemical recovery was better (6.4%) than any other trials, as shown in Table 2, but still unsatisfactory. The α-ray spectrum is shown in Figure 12.

For checking chemical yield, ^{229}Th in equilibrium with ^{225}Ra was used as a tracer without milking ^{225}Ra from its parent ^{229}Th (National Institute of Standards and Technology). The ^{225}Ra was used because it does not occur naturally and does not produce Rn which may escape from the counting source. It cannot be measured directly by alpha spectrometry, but its daughters ^{225}Ac($T_{1/2}$ = 10 d), ^{221}Fr ($t_{1/2}$ = 4.9 m) and ^{217}At ($t_{1/2}$ = 3.2 x 10^{-2}s) can be detected after about 10 days. The spectrum of the ^{225}Ra series, using the same plating procedure is shown in Figure 13. None of these emitters interfered with the ^{226}Ra series.

A sample solution incorporating ^{226}Ra tracer was run through the chemical process, electrodeposited and counted (Figure 14). Apparently only the ^{226}Ra series was detected with 0.8% recovery of ^{226}Ra, while none of the ^{225}Ra series was detected. The possible reason for the absence of an α-ray spectrum from the ^{225}Ra series may be the extent of losses in the process and the small quantity of ^{229}Th used.
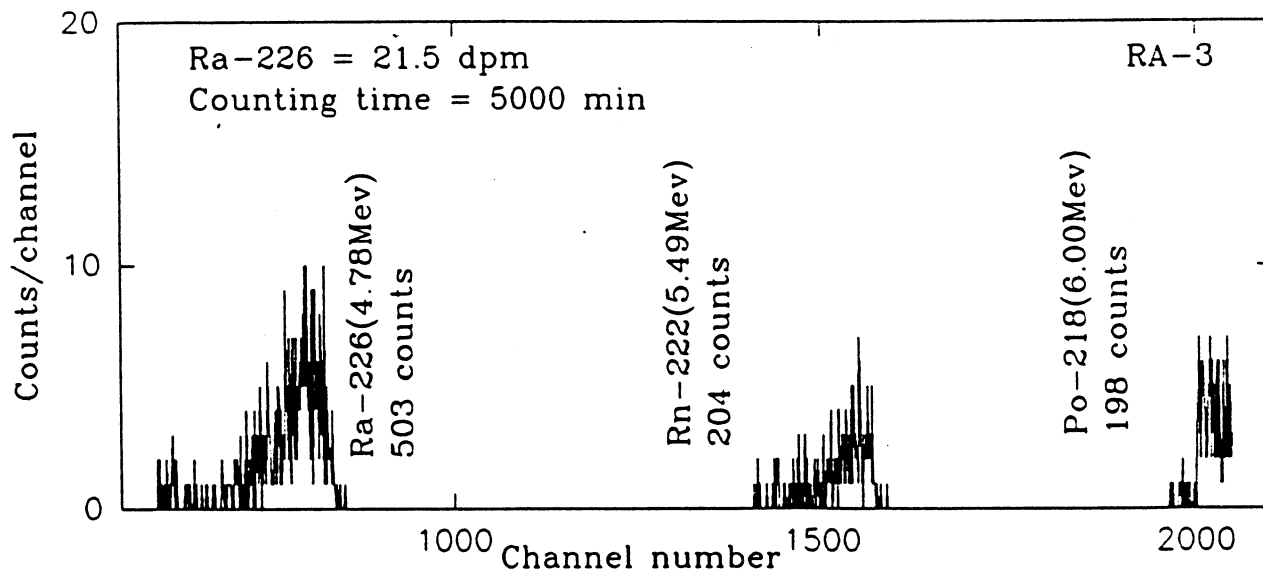
Figure 11.   Alpha-ray spectra of ^{226}Ra recovery from the whole chemical process (conversion of sulfate to carbonate).
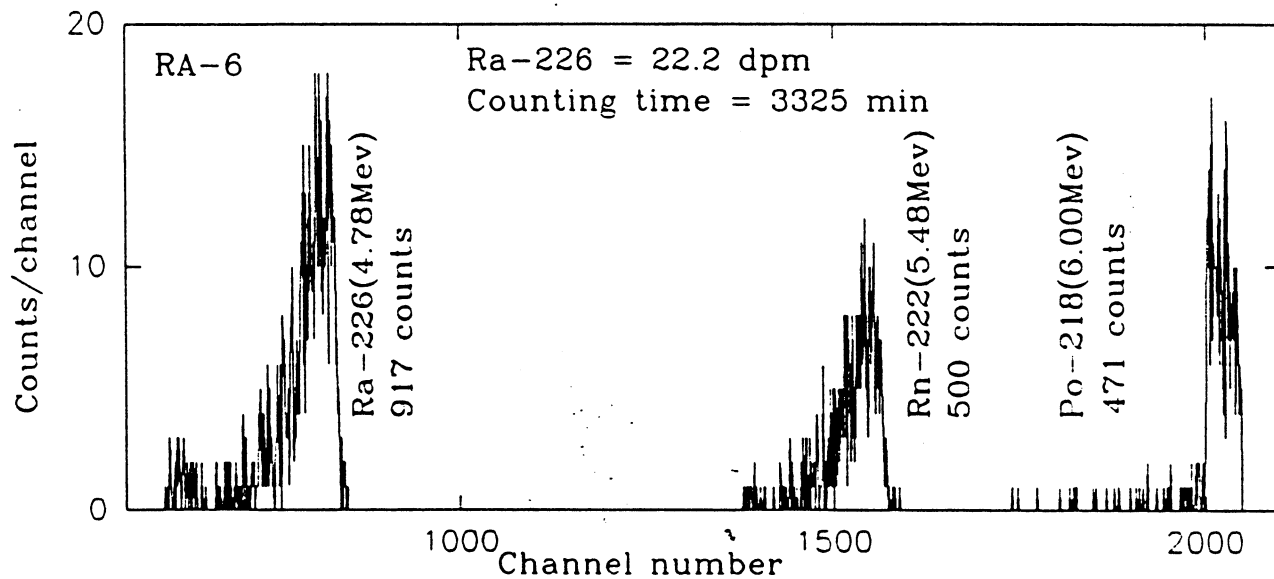

Figure 12.   Alpha-ray spectra of ^{226}Ra recovery from the whole chemical process (conversion of carbonate to chromate form).
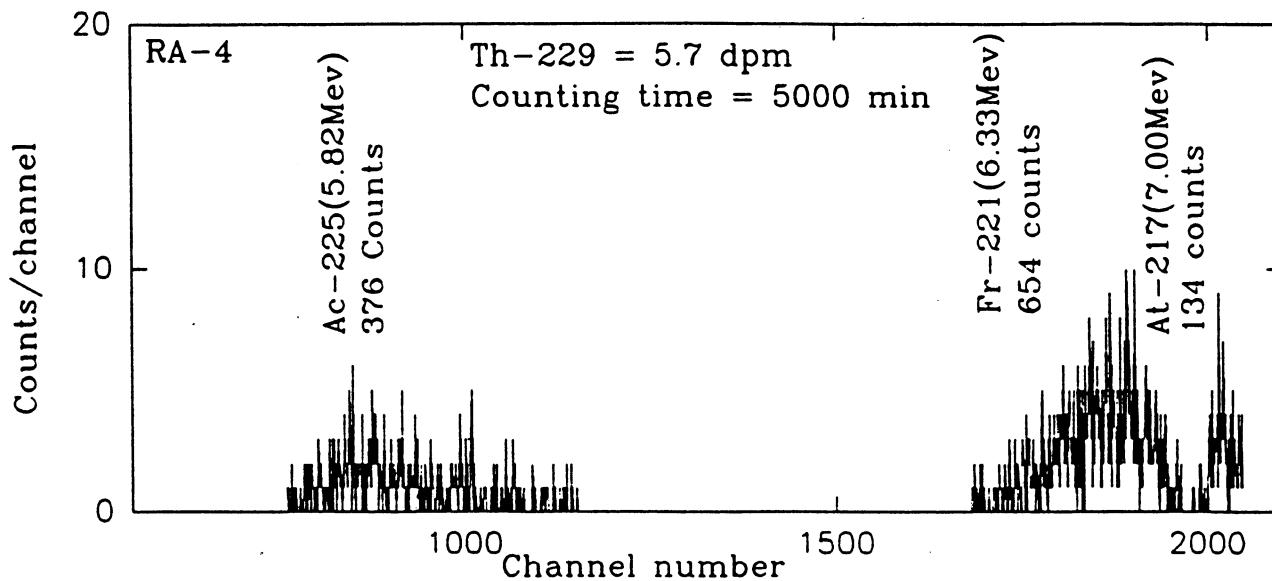
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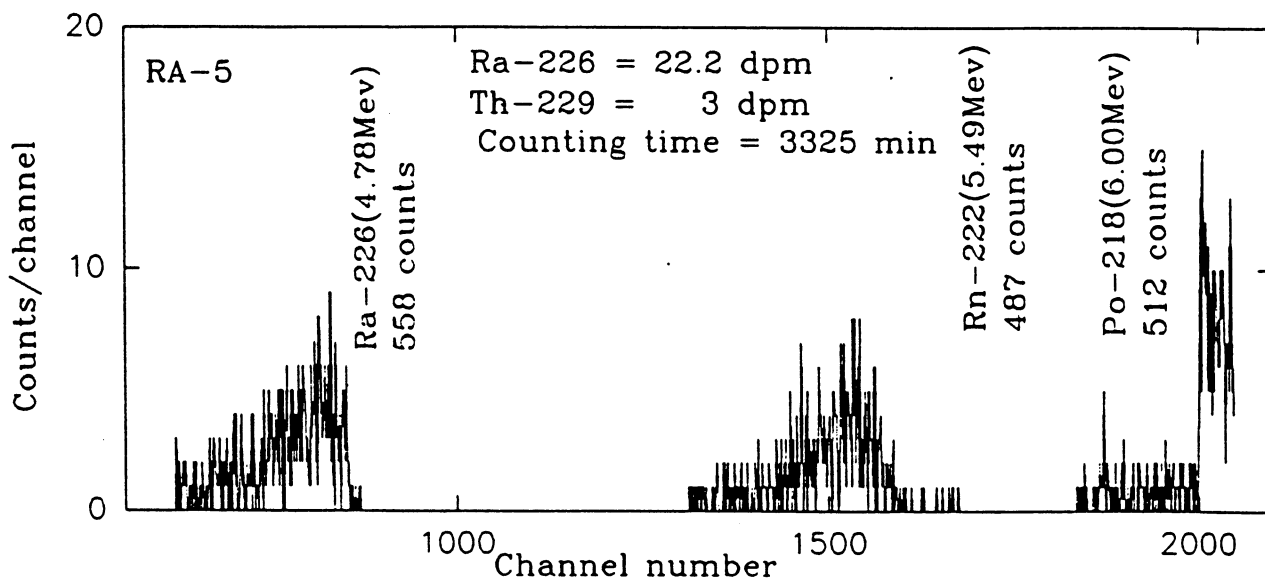Figure 13. Alpha-ray spectra of tracer ^{229}Th (^{225}Ra directly plated from the standard solution).

Figure 14. Alpha-ray spectra of ^{226}Ra with ^{229}Th (through cation resin only).

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CONCLUSIONS

Successful application of Vyredox™ to remove Ra from groundwater requires coincidence of four factors:

1. high concentrations of Fe and Mn,
2. in a shallow, high permeability aquifer,
3. which also has concentrations of Ra > 5 pci/liter, and
4. coprecipitation of the Ra on Fe and Mn oxides in groundwater.

The study has been able to identify extensive areas of Fe and Mn (combined) in concentrations > 1 mg/liter in all major aquifers. Condition 1 is extensively satisfied. Condition 2 restricts the application to permeable portions of the Quaternary glacial deposits, but extensive areas of high Fe and Mn occur in the deposits. However, identification of high Ra concentrations in Wisconsin groundwater was only marginally successful. High concentrations have been published for several dozen water supply wells in the eastern and north-central parts of the state, but no wells in the Quaternary aquifer are in this group. Several wells in central Wisconsin show high Ra in the crystalline or sandstone aquifer where it is directly in contact with glacial deposits, but water would probably need to be transferred from the bedrock to the unconsolidated aquifer for application of Vyredox. The main problem is the paucity of published Ra analyses. More sites may exist, but they cannot be identified with published data and it was beyond the scope of this project to run the statewide sampling that would be needed to overcome this deficit. Attempts to identify more hotspots using the more extensive Rn data base were unsuccessful. We conclude that only the area from Adams to Marathon Counties served by bedrock aquifers overlain by glacial deposits is a region where *in situ* oxidation might be applied to Ra removal.

The study did not demonstrate that the fourth condition can be met. The wide variety of methods tried to separate and quantify Ra attained a maximum -- but unsatisfactory -- chemical recovery of 25%. It is concluded that Ra in the sample is not effectively recovered by the procedures used. In addition, it is unclear as to where in the chemical process the Ra is lost. There is an indication that significant losses occur during the cation exchange process. Therefore, if recovery by the chemical process could be improved it might be used to determine low-level ^{226}Ra in environmental samples.

As an ancillary note, an attempt was made to measure Ra by gamma spectrometry (^{226}Ra, $t_{1/2}$ = 1,600 yrs, 186 kev). The precipitate of Ba/RaSO$_4$ prepared by the coprecipitation method was counted (Jacqueline et al., 1981; Jiang and Holtzman, 1989). Measurement of ^{226}Ra looked promising based on a 1 liter sample with 9.3 pci ^{226}Ra activity. The detection limit for a 1 liter sample is about 0.5 pci. Sufficient counts (about 800) were obtained in < 24 hr.

We cannot conclude that *in situ* oxidation will have any significant usefulness as a means of reducing Ra in Wisconsin groundwater to drinking water standards. Furthermore, in view of the proposed raising of that standard by the U.S. Environmental Protection Agency to a level above most water supplies in Wisconsin, the issue is probably moot.

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