

APPENDIX G

Geochemistry of the RA and Industrial Area

Introduction

As part of the RFI, Maine Yankee took groundwater samples in a period spanning late May 2002 to July 2002 from 16 locations within the RA and Industrial area of Bailey Point to characterize the geochemistry of the groundwater in that area. These data were collected to examine the cation and anion geochemistry and evaluate the potential impact from several historic, overlapping sources of contamination in that area. Some of the historic sources of contamination in the RA and Industrial Areas include: 1) seawater via intrusion and from both the storm water drain system and circulating cooling water pipes, 2) historic sodium chromate leaks associated with Secondary Component Cooling System, 3) leaching from subsurface concrete structures, and 4) historic release(s) of petroleum. **Table G-1** summarizes these data and compares them to earlier chemical analyses on the Knoll Well (the former plant drinking water supply), and later tests on the PAB Test Pit. There are a variety of ways to analyze and graphically portray the geochemistry of a groundwater. Maine Yankee utilized the Piper Diagram to evaluate the data, as this approach allows both cations and anions to be simultaneously evaluated. The Piper Diagram, **Figure G-1**, provides the most useful side-by-side comparison. **Table G-2** groups the various wells in standard categories that are defined by placement on the Piper Diagram.

Sodium was the dominant cation at seven of the monitoring well/sampling locations in the RA area (**Table G-2**). Even the Knoll Well, utilized for background comparison on Bailey Point, is dominated by sodium. The sources of sodium on the site are many, as discussed below. Despite the obvious effects of cement leaching in ground water near the massive underground concrete structures, only MW-401B, south of the “rad bunker,” had calcium as a dominant cation. The other eight locations tested had a mixture of sodium, calcium and magnesium (there is little potassium here), but no clear dominance (**Table G-2**).

Chloride is really only a dominant anion for three wells, two of which (B-201 and MW-401A) are clearly affected by saltwater intrusion, and the other (BK-1) most likely by winter deicing activities. The carbonate anion was dominant in MW-401B and the first PAB Test Pit sample, reflecting the influence of cement leaching. Carbonate is stabilized in groundwater relative to bicarbonate when pH is in excess of 9.0 (Hem, 1985). This is confirmed by the pH in MW-401B of 11.7 and in the PAB test pit of 9.8. Sulfate was only dominant in B-203B, although it occurred in relatively high concentrations in many other samples from the RA. The remaining locations (MW-306, MW-307, MW-403, B-202, and B-203B) were not dominated in the anion category by chloride, sulfate, carbonate or bicarbonate.

The PAB Test Pit was the only location sampled more than once for the full suite anions and cations. The first sampling, in July 2002, showed anomalously high concentrations of many constituents. This sample was taken during the early stages of PAB

decontamination and there was a concern that those activities may have contaminated the Test Pit water. The second sampling in February 2003 shows a marked decrease of one to two orders of magnitude in most cases in constituent concentration, indicating that the first PAB sample was impacted by the nearby decontamination activities.

Evaluation of Sodium and Chloride Distribution

High concentrations of both sodium and chloride have been found in the ground water at the site since 1989. In December 1988, an underground leak of a Secondary Component Cooling system (SCC) pipe containing sodium chromate as a corrosion inhibitor, released a large quantity of water. A fate and transport study (RGGI, 1990) was conducted to evaluate the spill. As a result of this study, monitoring wells and groundwater sampling took place in the RA area for sodium, chromate, and other parameters. High sodium concentrations observed at that time could not be explained by the SCC leak alone, so studies of other possible sources of sodium and chloride were initiated.

A review of design documents and a consideration of the construction and operation of the plant revealed several sources of sodium other than the sodium chromate leaks. In the stormwater system serving the south side of the RA and Industrial Area, the pipe outlet invert in the seal pit of the forebay was actually below the seal pit water level during very high tides (the seal pit was filled with seawater from the circulating water cooling system). Since storm drains and catch basins were not constructed to be water tight, when seawater backed up in the storm drain, the seawater leaked out into the ground around the storm drain system, dosing the groundwater intermittently with pure seawater. Furthermore, the circulating cooling water pipes, which were buried deeply in the RA and Industrial Area yard, continuously leaked seawater to the groundwater system during plant operations.

Figure G-2 shows the correlation of conductivity as a function of chloride in the 2002 sampling. Only B-201, which is clearly affected by seawater intrusion, now shows a high conductivity (greater than 1500 S/cm) whereas in 1989, B-202, B-205, and B-206 had extremely high conductivity at times (Fig. 22 of RGGI, 1990). B-201 remains in a similar range as in 1989. **Figure G-3** shows the weekly concentrations of sodium and chloride in wells B-201, B-202, B-205 and B-206 in 1989. The statistics of these data are shown to the right of each graph and compared with the 2002 measured concentrations. With the exception of B-201, there have been very large reductions in sodium and chloride concentrations from 1989 to 2002. Notice on **Figure G-3** that sodium generally tracked with chloride concentrations, although at lower concentrations, and sodium did not increase nor decrease so rapidly as chloride. Chloride is a very conservative tracer in groundwater. Sodium, on the other hand, is exchanged in complex ways with the geologic material (Hem, 1985). Therefore, the rate of change of the groundwater concentration of sodium is damped by the exchange process relative to chloride.

Since the plant ceased operation, the forebay level has dropped five feet, causing no further backup of seawater into the storm drain. Likewise, the continuous release of seawater from the circulating cooling water pipes has also ceased. The concentrations of

both sodium and chloride have decreased dramatically, although not proportionately from levels detected in 1989. Sodium previously exchanged with geologic materials is now releasing from those materials back into groundwater and keeping the ratio of sodium to chloride as shown in **Table G-3**, well above the normal seawater ratio at most test locations.

The summer 2002 distribution of chloride in the RA area is shown on **Figure G-4**. As indicated, the chloride concentrations are much lower than that observed in the 1989 results which were associated with plant operations. The concentrations in the wells range from 30 to 151 mg/l, with the exception of B-201 (639 mg/l), which is placed well below sea level near the shoreline and shows seawater intrusion effects. With the exception of those points probably affected by current saltwater intrusion (B-201, CS-1, and MW-401A), the other elevated 2002 chloride concentrations are probably due to deicing salts used liberally in the paved areas around the RA and industrial area for safety reasons.

Figure G-5 shows the 2002 sodium concentrations in the RA area. On the north and upgradient side of the industrial area MW-308 only had a sodium concentration of 15.4 mg/l, but on the south and downgradient side of the industrial area concentrations ranged from 36 to 91 mg/l, except B-201 at 305 mg/l. The elevated sodium concentrations in these downgradient monitoring wells are most likely related to the historic impacts of seawater from either storm sewers or circulating cooling water pipes. The PAB Test Pit sample from July 2002 had 254 mg/l sodium, but had decreased to 55 mg/l in February 2003. The source of this high sodium concentration in the PAB in July 2002 is not known but may be related to the cleaning and decontamination activities associated with the PAB. The somewhat elevated sodium concentration in the CFS of 119 mg/l may be sourced from the PAB Test Pit area.

Several other ways of showing the change in sodium and chloride on the site since 1989 are illustrated in **Figures G-6, G-7, and G-8**. Although the ratios of sodium and chloride may fluctuate somewhat with time in a groundwater regime affected by seawater intrusion, the magnitude of the decrease in all the wells that previously had high concentrations is shown clearly on the graphs. The decrease of sodium and chloride in these monitoring wells from values observed in 1989 clearly demonstrates the historic impact of seawater on shallow groundwater as a function of plant operations and the decrease of seawater impacts in the years following plant closure.

The history of the Knoll Well sodium concentration is shown on **Figure G-6**, but is not related to the same processes that affected the RA and Industrial Area. The Knoll Well, which was located just off the southeast corner of the ISFSI and well upgradient of the RA and Industrial areas, was a bedrock well of several hundred feet in depth that produced several gallons per minute of potable water. The chloride concentration in the well never exceeded 10 mg/l from 1987 to 1996, so saltwater intrusion was not the source of sodium, nor was deicing salt application on the nearby road or parking lot a likely source. The most probable explanation is that the sodium is a residual effect of the filling of the area north of the ISFSI with marine sediments dredged from the circulating water

intake channel. There is a suggestion from previous groundwater modeling (MY, 2001b, Fig. 5-23) that groundwater flowing through the Knoll Well area originates to the north under the area where dredge spoils were deposited. The chloride would have moved out fairly quickly through the soil groundwater flow system, but because of the exchange properties of the sodium, it would be released much more slowly with time. **Figure 4-11** shows that sodium concentrations in the area north of the Knoll Well are still elevated well above background. Sodium may have moved downward into the deep bedrock flow system.

In addition to the increasing sodium concentrations, arsenic in the knoll well is also observed to have increased with time (55 mg/l to 85 mg/l). The rising arsenic concentration in the Knoll Well may also be related to the filling of the marine sediments over the original marsh north of the ISFSI. The anaerobic conditions established at the base of the fill combined with the organic carbon source from the marsh may be responsible for release of arsenic from the natural, geologic materials and transport to the deep bedrock flow system (Ayotte, et. al., 2003).

Figure G-8 deals with the interesting geochemical history of the CFS. The sump at the bottom of the CFS goes to a maximum depth of 55 feet below MSL. The sump is emptied periodically by high- and low-level switches on a sump pump located in a deep manhole off to the west side of the containment. Therefore, the elevation of ground water under the containment fluctuated but was generally kept below about -45' MSL. It was clear from studies in 1988 and 1989 (RGGI, 1989a) that during plant operation the CFS contained a dilute 2% to 10% seawater mixture. When the plant was operating, the forebay was elevated 5 feet above normal sea level and this, combined with the depth and location of the CFS, permitted some upconing of seawater to the CFS. Since ceasing operation, the chloride concentration has significantly decreased. One can also see on **Figure G-8** that in 1989 the concentrations of sodium, nitrate, and potassium were very high and must have reflected various system leaks from tanks and buildings around the containment (the elevated sodium was probably due to the SCC leak). Hydrazine, a corrosion control agent used throughout the plant's history, would produce very high concentrations of nitrate in groundwater. Although the 2002 concentrations of calcium and magnesium were fairly low, the pH was fairly high (9.5) in the CFS, suggesting a cement leaching impact.

Carbonate, Bicarbonate and pH

To evaluate the effect of cement leaching, **Figure G-9** shows pH as a function of carbonate and bicarbonate. The concentration of bicarbonate and carbonate in groundwater represent a homogenous equilibrium that is a function of pH (Hem, 1985). For a fixed concentration of dissolved carbon, the carbonate/bicarbonate ratio will increase with increasing pH at pH in excess of 9.0 (Hem, 1985). When carbonate and pH are high, the source is likely cement leaching. The PAB Test Pit samples, MW-401B, CS-1, MW-312, and to a minor extent MW-307 placement on the graph suggest a cement leaching impact, particularly since they all have a pH over 9.

Sulfate

Figure G-10 shows the distribution of sulfate within the RA and Industrial Area. Sulfate is a common anion. It is present at fairly high concentrations in seawater with 2700 mg/l being typical. Therefore, those wells identified as being affected by saltwater intrusion such as B-201 would be expected to be high in sulfate. Sulfate may also be left over from dosing of the area through circulating water pipe or stormwater pipe leaks of seawater. Sulfate may also be derived from the use of sulfuric acid in the plant for pH control. Leaks did occur from the waste neutralization tank and could have created elevated sulfate concentrations. Sulfate is also naturally derived because of the presence of sulfide minerals like iron pyrite in the soil and rock.

B-203B had the highest concentration of sulfate at 124 mg/l. Most other wells within the RA and Industrial Area had sulfate concentrations elevated above what would be expected to be normal background. Only MW-401A and B had values in the normal range. MW-308 on the north side of the Industrial Area even had a relatively high concentration. Most of these elevated values can be ascribed to residual effects of seawater dosing associated with the storm water and circulating cooling water pipes.

Chromium

Since sodium chromate was used as a pipe corrosion inhibitor until the early 1990s at the plant, since there are documented underground pipe breaks that released chromated water, and since chromium is a moderately retarded metal in groundwater flow, it is reasonable to assume that some residual chromium might still be detected. **Figure G-11** shows a graph of chromium concentration as a function of sodium. The only elevated chromium appeared in the PAB Test Pit. Monitoring wells CS-1 and MW-312 (the PAB “alleyway”) have chromium concentrations slightly above the range detected in reference wells in the backlands (MY, 2003). Although other B-series wells south of the containment were originally affected by the sodium chromate underground pipe leaks, apparently all residual chromium has been flushed out of those areas. The concentration of chromium decreased significantly between July 2002 and February 2003 in the PAB Test Pit to concentrations consistent with the reference wells.

Nitrate

Another potential indicator of a historical plant system release to groundwater is high nitrate in groundwater. Hydrazine was used as a corrosion inhibitor throughout the plant’s operation. When it is released to the environment, nitrate is formed if oxygen is present. Nitrate is a conservative contaminant in groundwater flow unless there is a source of organic carbon present that may assist in denitrification. Otherwise, nitrate is not absorbed or retarded and is only reduced by dilution in mixing with other ground water low in nitrate. **Figure G-12** shows the distribution of nitrate in the RA and Industrial Area. Background levels of nitrate at the site would not be likely to exceed 0.5 mg/l and nitrate in seawater is very low, too.

MW-308 is low in nitrate (0.2 mg/l) and near background. MW-401A, MW-401B, B-201, MW-307, and CS-1 are all in the background range. However, a number of other wells still showed the residual effects of receding Hydrazine plumes on the site. MW-203B has the highest concentration, as it does for several other constituents. This seems to imply that the groundwater flushing rate through the area of B-203B is very slow. In fact, much of the distribution of residual nitrate probably reflects the flushing and dilution capacity of those areas of rock still elevated in nitrate.

Boron

Boron is a natural constituent of seawater, but was also used in some of the primary plant operating systems as a neutron moderator. Therefore, elevated boron concentrations could be an indicator of either diluted seawater or of a past leak in a primary system. **Figure G-13** shows the summer 2002 distribution of boron in the RA and Industrial Area. With the exception of B-201, a well with saltwater intrusion, the focus of high boron concentrations is in the containment area, south to MW-402. Given that the current chloride concentration of B-201 is six times higher than CS-1, but that the boron concentrations are comparable, it appears that the boron in CS-1 and MW-402 is most likely from a plant system leak or leaks, possibly from the RWST which was borated and did leak. Background concentrations of boron would be expected to be less than 0.05 mg/l.

DRO

There are areas of the RA and Industrial Area that have residual Diesel Range Organics (DRO) from historical petroleum releases. **Figure 4-17** shows the DRO in groundwater in the summer of 2002. Prominent elevated DRO results were found in MW-401B, B-205, B-206A, MW-312, B-202, MW-403, MW-307, and MW-318. MW-318 lies in the general area east of the main transformers that would have been affected by the release of oil during the transformer fire of May 1991. MW-307 is next to the former underground storage tanks of the emergency diesel generators (some leakage of diesel fuel was removed during the removal of the tanks; RGGI, 1994g). MW-312 was just below a construction-era spill that occurred in the gravel backfill in the PAB alleyway that was identified and cleaned up in late 2002. MW-403 lies along a fractured bedrock zone inferred to be connected to MW-312, and is hydraulically downgradient of MW-312 and the historic release of petroleum in the PAB alleyway.

Several documented accidental releases from construction equipment have occurred in the yard area south of containment that could account for the observed DRO concentrations at B-205, B-202, and B-206A. There was apparently a surface spill in the immediate vicinity of MW-401B based on the high concentration in that area. In general, the distribution of DRO in the RA and Industrial Area is consistent with the petroleum sources discussed above and the groundwater flow behavior in that area (**Figures 4-17 and 3-10B**)

Summary of Operational Influences on Groundwater Geochemistry

Table G-4 summarizes the probable effects that various operations have had on groundwater geochemistry in the RA and Industrial Area. We have subjectively assigned one of two different designations to each monitoring point if we interpreted a result to indicate an elevated concentration according to the appropriate column heading. If a measured groundwater concentration is roughly one order of magnitude greater than background, or over an MCL or MEG, than the designation of “some indication” is given. If a result is roughly two orders of magnitude or more over background, or an order of magnitude or more over an MCL or MEG, than the designation of “significant indication” is given.

Most of the wells in the RA and Industrial Area have had either an influence from previous dosing by seawater and/or an elevated sodium and chloride due to deicing compound application. The B-200 series wells formerly very high in sodium and chloride have shown significant concentration declines since 1992.

Effects of cement leaching, causing pH elevation (except at B-203B), are indicated in some wells in the immediate vicinity of massive concrete extending below groundwater level, or down-gradient of those points. Alkalinity, bicarbonate, and carbonate hardness is variable, but pH exceeds 8.5 at five sampling points. As the natural buffering capacity of the natural soils and rocks is used up over time, pH can be expected to increase to a steady-state distribution downgradient of the deep concrete foundations left in place at the site.

Petroleum contamination as measured by DRO concentrations is spread throughout much of the RA and Industrial Area. Many small spills have occurred and been remediated, but some residual contamination has reached the bedrock. One major remaining suspected source area that must be investigated is soil near MW-401B.

Although not exceeding MCLs, nitrate concentrations are still elevated in some wells in the RA and Industrial area on the site, probably due to the historical use of Hydrazine as a pipe corrosion inhibitor.

Elevated concentrations of sulfate in most of the RA and Industrial Area are most likely due to past seawater dosing. Some sulfate concentrations may be related to past use of sulfuric acid for pH control, but that effect would probably only be present south of the former waste neutralization tank. Some wells may have elevated sulfate due to local naturally-occurring pyrites, a sulfide-bearing mineral.

Small residual concentrations of chromium (not over the MCL except in the original PAB Test Pit sample) were found at CS-1, MW-312, and the PAB Test Pit. Sodium at those test points may also be elevated from the original releases of sodium chromate in those areas.

Molybdenum is present in elevated concentrations in some locations because it is a constituent of petroleum-based lubricants (such as at MW-401B). However, molybdenum may also be a naturally-occurring mineral in the granites and pegmatites at the site.

Concentrations of arsenic, iron, manganese, and aluminum are above background at numerous points in the RA and Industrial Area. All of these metals are probably naturally derived from the geologic materials present and have been released into soluble form due to some geochemical process related primarily to either seawater dosing or some release of plant-derived contaminants. The few occurrences of above-background mercury, nickel, zinc, and vanadium are more difficult to relate to natural causes.

Note that the concentrations of contaminants in the PAB Test Pit declined significantly between July 2002 and February 2003. We suspect that the decontamination activities within the PAB Test Pit affected the July 2002 results (this correlates with anomalous radioactive results in the July tests, too). Since the PAB Test Pit water flows to the CFS, this may also have affected some of the CS-1 results from summer 2002.

For the few sampling points with historical data from 1989 and 1992, there is an indication of significant decline in concentrations from sodium, chloride and chromium related to plant operations. The CMS study will use these results to estimate the length of time necessary for contaminants in groundwater to decline below MCLs and MEGs.