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**071519**

**AUG 0 4 1999**

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Acting Perimeter Areas Section Manager  
Nuclear Waste Program  
State of Washington  
Department of Ecology  
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Kennewick, Washington 99336-6018

**RECEIVED**

**AUG 0 5 1999  
BY DIS**

Mr. Douglas R. Sherwood  
Hanford Project Manager  
U.S. Environmental Protection Agency  
712 Swift Boulevard, Suite 5  
Richland, Washington 99352-0539



Dear Messrs. Leja and Sherwood:

**QUARTERLY RESOURCE CONSERVATION AND RECOVERY ACT (RCRA)  
GROUNDWATER (GW) MONITORING DATA FOR THE PERIOD JANUARY 1, 1999,  
THROUGH MARCH 31, 1999**

Please find enclosed the subject report. The RCRA groundwater chemistry and water level data for the subject period has been verified and evaluated. The information contained in the report is submitted to the State of Washington Department of Ecology in accordance with WAC 173-303-400 and WAC 173-303-645. The data are publicly available in electronic form in the Hanford Environmental Information System database. The electronic availability of the data and the summary provided fulfill the reporting requirements of WAC 173-303 (and by reference 40 CFR 265.94). Verification of data included a completion check (requested analyses were received), quality control checks (field blanks, field duplicates, and blind samples), and project scientist evaluation.

Seventeen RCRA sites were sampled during the reporting quarter (see enclosure, Attachment 1). Sampled sites include 10 monitored under indicator evaluation programs, six monitored under GW quality assessment programs, and one monitored under final-status corrective action. Detailed information on salient issues during this quarter are included in the enclosure.

Messrs. Leja and Sherwood

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AUG 04 1989

If you have questions about this quarterly data transmittal, please contact me at 373-9630.

Sincerely,



M. J. Furman, Project Manager  
Groundwater Project

GWP:MJF

Enclosure

cc w/encl:

B. M. Barnes, WMH  
J. V. Borghese, CHI  
R. C. Bowman, WMH  
V. R. Dronen, BHI  
D. L. Flyckt, WMH  
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QUARTERLY RESOURCE CONSERVATION AND RECOVERY ACT (RCRA)  
GROUNDWATER MONITORING DATA FOR THE PERIOD  
JANUARY 1, 1999, THROUGH MARCH 31, 1999.

- References:
- (1) M. J. Hartman, 1992, Results of Ground Water Quality Assessment Monitoring at the 1301-N Liquid Waste Disposal Facility and 1324-N/NA Facilities, WHC-SD-EN-EV-003, Rev. 1, Westinghouse Hanford Company, Richland, Washington.
  - (2) Ecology email to M. J. Furman from P. R. Staats "Ground water Monitoring Plan," dtd. June 22, 1998.
  - (3) RL ltr. to Stanislaw Leja from M. J. Furman "Notification of Specific Conductance Exceedance at 200 East Area Liquid Effluent Retention Facility (LERF)," dtd. March 4, 1999, (CCN 066939).
  - (4) RL ltr. to Douglas R. Sherwood, and E. R. Skinnarland from M. J. Furman "Exceedance of Critical Mean for Total Organic Halogen (TOX) at Waste Management Area (WMA)-U," dtd. August 25, 1998 (CCN 061067).

Comparison to Concentration Limits

Contamination indicator parameter data (pH, specific conductance, total organic halogen [TOX], and total organic carbon [TOC]) from downgradient wells were compared to background values at sites monitored under interim-status, indicator evaluation requirements, as described in 40 CFR 265.93.

**1324-N/NA Facilities:** Specific conductance at downgradient wells continued to exceed the critical mean. Previous groundwater quality assessment monitoring indicated that the high conductivity is caused by the nonhazardous constituents sulfate and sodium (Reference 1). Because an assessment has already been completed and the high conductivity is caused by nonhazardous constituents, verification sampling and additional assessment monitoring will not be conducted.

Groundwater in one downgradient well continued to exceed the critical mean for TOC, as it has since the fall of 1997. Ecology has agreed that the contamination is from another source so that assessment monitoring is not required. This agreement was sent via electronic mail (Reference 2) with the stipulation that a formal letter would follow. No letter has been received to date.

**Liquid Effluent Retention Facility:** Conductivity in two downgradient wells (299-E26-9 and 299-E26-10) exceeded the critical mean of 489.4  $\mu\text{S}/\text{cm}$ . Ecology was notified (reference 3) and a groundwater quality assessment plan and report is being transmitted separately. It is concluded that LERF is not the source of the elevation in conductivity and detection monitoring should be continued. Background conditions need to be re-established to reflect the most recent site conditions.

**Low-Level Waste Management Area 2:** It was reported last quarter that downgradient well 299-E34-9 exceeded the critical mean value for TOX in November 1998. Results of one of the quadruplicate samples were found to be in error and were re-reported this quarter. The new result does not exceed the critical mean value.

**Low-Level Waste Management Area 4:** Background concentrations were re-established because the influence of a nearby pump-and-treat system is causing a reversal in the groundwater flow direction. The critical mean for TOX (1,134.8 µg/L) was exceeded in downgradient well 299-W15-16 in January (average = 3,020 µg/L). This well used to be an upgradient well, and the exceedance is believed to originate at an upgradient source. No further action is necessary.

**Waste Management Area U:** The critical range for pH was exceeded in downgradient well 299-W19-12 in February (average = 9.28; upper end of critical range = 8.50). This well was a pre-RCRA well that has had higher pH historically. A new groundwater monitoring plan is being prepared, recommending that this well be replaced by a new RCRA standard well and this well be used for information only during the interim. No further action is necessary.

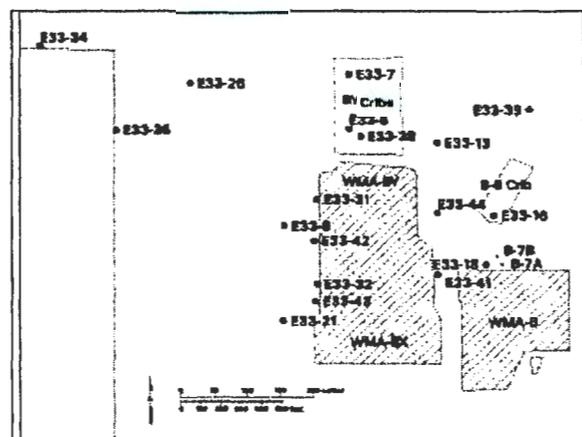
Two downgradient wells (299-W18-30 and 299-W19-42) exceeded the critical mean value for TOX. The exceedances are caused by an upgradient source and a letter of notification and assessment report was submitted to Ecology earlier (reference 4). Three downgradient wells had erroneous, high field conductivity values in February (see quality control discussion below). These high values are not indicative of groundwater contamination. No further action is necessary.

Contamination indicator parameters in downgradient wells were below the critical mean values for all other sites monitored under indicator evaluation requirements that were sampled during the quarter. Hence, there is no indication that these sites are impacting groundwater quality.

#### Status of Assessment Programs

##### **Single-Shell Tanks WMA B-BX-BY:**

Technetium-99 and nitrate continued to rise during the past quarter in most monitoring wells. Chemical ratios of nitrate to technetium-99 indicate that there are at least two distinct sources of contaminants, as discussed below. The area of investigation has been expanded because there is evidence of contaminants moving into the WMA from the north. The area now includes wells north of the BY Cribs, Low-Level Burial Grounds wells west of the WMA, and at least one well east of the WMA. Water levels continue to drop slowly. The gradient has flattened across the area, resulting in a slight decrease in the estimated groundwater flow rate.



**Technetium-99:** Technetium-99 and nitrate are increasing in wells 299-E33-34 and -26, west of the WMA. The nitrate technetium-99 ratio for both wells corresponds with that of well 299-E33-7, the current center for technetium-99 in the area. These data indicate that technetium-99 is moving into the area from sources to the north.

Technetium-99 in well 299-E33-13 rose to 2,500 pCi/L in January 1999 and 3,660 pCi/L in March, after declining to 800 pCi/L in August 1998. Analysis of the corresponding nitrate technetium-99 ratio would suggest that this technetium-99 is related to the technetium-99 seen at well 299-E33-7, which has a ratio of ~41 to 55.

Until this quarter, technetium-99 was distinctly rising in wells 299-E33-7, -5 and -38, all located in the BY Cribs. However, during the first quarter there was very little change in technetium-99 values along the west side of the WMA, although values are still above the 900-pCi/L drinking water standard in wells 299-E33-31 (1,780 pCi/L) and -42 (1,500 pCi/L). Values have fallen to 737 pCi/L in well 299-E33-32, further to the south, while well 299-E33-43 still shows slight increases in technetium-99 to 63.5 to 78.6 pCi/L over the quarter. Technetium-99 continued to rise in wells 299-E33-26 and E33-34, as stated above.

Technetium-99 concentrations remained low on the far east side of the assessment area, as reported last quarter. Three wells bracket the technetium-99 plume on the east and northeast, indicating that the elevated technetium-99 seen further to the north and west is not coming from the east or northeast. However, in well 299-E33-16, which has shown elevated technetium-99 since assessment monitoring began in 1997, technetium-99 values range from about 1,400 to 1,800 pCi/L with no distinct upward or downward trend. This well is associated with the B-8 Crib and tile field. It is the center of the second distinct nitrate technetium-99 ratio with values ranging from 274 to 251.

Technetium-99 concentrations have ranged between 3,470 and 4,480 pCi/L in well 299-E33-44, which was installed in September 1998. This wells appears to have a unique nitrate technetium-99 ratio along with a unique chemical suite, but with only a few months of data, it is too early to make definite conclusions.

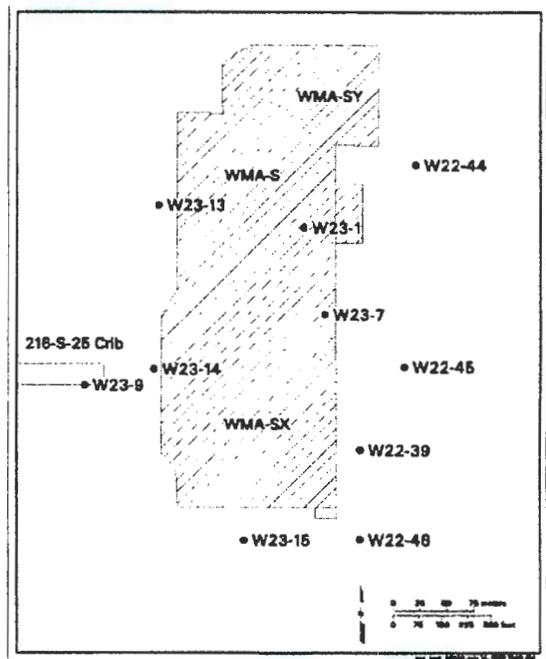
**Nitrate:** The 45-mg/L maximum contaminant level continued to be exceeded in all but the southern-most wells and well 299-E33-39 located northeast of the site. As explained above, the two local centers of nitrate contamination, seen in wells 299-E33-7 and -16, have distinctly different nitrate technetium-99 ratios.

Like technetium-99, nitrate rose in well 299-E33-13, from 228 mg/L in August 1998 to 293 mg/L in February 1999. The center at well 299-E33-7 increased from 319 mg /L in August 1998 to 346 mg /L in February 1999. Nitrate continued to increase in wells 299-E33-5 and -38. Nitrate in well 299-E33-35 increased from 19 mg/L in December 1995 to 34 mg/L in June 1997 to 46, mg/L in December 1998. This well has been placed on quarterly assessment monitoring to determine any corresponding increases in technetium-99 or uranium.

**Uranium:** This contaminant is found in the groundwater at WMA B-BX-BY east of 241-BY Tank Farm (north of 241-B Tank Farm) and in the southern part of the BY cribs. The uranium drinking water standard is 20 µg/L. Well 299-E33-44 had the highest concentration this quarter, at 282 µg/L for February. Well 299-E33-18 had the next highest value at 114 µg/L. Uranium has been generally decreasing in this well since November 1997 when it was 193 µg/L. Values in well 299-E33-13 peaked in April 1997 (197 µg/L), dropped to 18 µg/L in August 1998, and rose again in February 1999 (66 µg/L). Similar trends were seen in technetium-99 and nitrate. Currently it is not clear, whether the uranium forms a single plume or emanates from different sources. Although the uranium technetium-99 ratios suggest that the uranium found in the BY Cribs may be different from that at well 299-E33-18, the data are not as clear as the nitrate technetium-99 ratios. The changing contamination seen at well 299-E33-13 may help track distinct uranium plumes.

**Single-Shell Tanks WMA S-SX:** Groundwater beneath this WMA is contaminated with technetium-99, apparently from sources within the WMA. Other contaminants, including tritium and nitrate, originated at upgradient sites. The water has continued to drop across the site, but the gradient has changed little, therefore, the groundwater flow rate has not changed during this quarter.

Technetium-99 exceeded the 900-pCi/L drinking water standard in two downgradient RCRA wells (299-W22-45 and 299-W22-46). The technetium-99 concentration in well 299-W22-46 in March 1999 was 3,760 pCi/L and appears to be declining from the maximum of 5,020 pCi/L in May 1997. The concentration in well 299-W22-45 (1,410 pCi/L in February) indicates a continuing upward trend over the last five quarters.



Nitrate exceeded the 45-mg/L maximum contaminant level in upgradient well 299-W23-14. The concentration for this well was 67 mg/L in May 1999 as compared to 45 mg/L in February 1999. The upward trend in this well coincides with increasing concentrations of other major cations and anions. Nitrate in an alternative upgradient non-RCRA well (299-W23-9) was 97 mg/L in March 1999, indicating the continuing presence of residual groundwater contamination from past-practice upgradient sources (e.g., the 216-S-25 crib).

Tritium exceeded the drinking water standard of 20,000 pCi/L in three RCRA wells and in one non-RCRA well. The highest concentration occurred in upgradient well 299-W23-14. The concentration in this well was 325,000 pCi/L in February 1999 as compared to a concentration of 34,100 pCi/L in downgradient well 299-W22-46 in March. Concentrations in the downgradient well appear to be declining from a maximum of 65,200 pCi/L in May 1997. The tritium concentration was slightly above the drinking water standard in downgradient well 299-W22-39

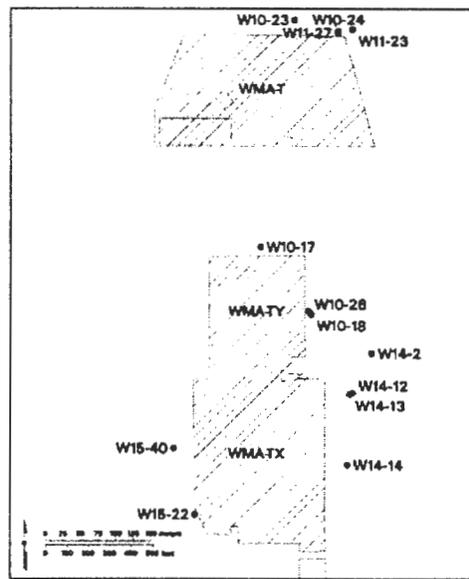
(21,100 pCi/L in February). The primary source of the tritium in these wells is attributed to residual contamination from past-practice crib disposal sites. For example, tritium concentrations in the non-RCRA well 299-W23-9, located immediately downgradient from 216-S-25 and upgradient from well 299-W23-14, was 262,000 pCi/L in March. There appears to be a gradual downward trend in well 299-W23-9.

Neither strontium-90 nor cesium-137 were detected in any RCRA monitoring wells in the network. The 2-sigma uncertainties were approximately 0.2 pCi/L and 2 pCi/L, respectively.

Anomalously high field specific conductance values occurred in five of the seven RCRA wells during this quarter. The erroneous readings were attributed to a bad batch of calibration solution (see quality control discussion below). A sample from well 299-W23-15 had high turbidity (149 NTU). Periodic turbidity problems have plagued this well since it was installed in 1992. Bentonite annular seal material in or near the screen is suspected as a possible source.

#### Single-Shell Tanks WMA T and TX-TY:

Technetium-99 and other contaminants, presumably from sources within the WMAs, decreased during the past quarter. Water levels near these waste management areas continued to decline this quarter. WMA T downgradient well 299-W11-27 and WMA TX-TY downgradient well 299-W14-12 will probably not be sampleable in the next quarter because of declining water levels. Replacement wells have been installed. While the water table has continued to drop, the gradient has changed little, therefore, the rate of groundwater flow has not changed during the quarter. As reported previously, groundwater flow directions have been affected by the 200-ZP-1 groundwater remediation. Groundwater flow beneath TY tank farm is to the east-southeast and to the south-southeast beneath the TX tank farm.



Technetium-99 activity in well 299-W11-27 declined to 6,000 pCi/L in March. The well was sampled with a Kabis sampler from the small quantity of water remaining within the screened interval. Replacement well 299-W10-24, drilled immediately adjacent to 299-W11-27, had a reported technetium-99 activity of 2,960 pCi/L, with the pump inlet set at ~5 m beneath the water table. Technetium-99 activity in well 299-W11-23, a non-RCRA well located ~30 m east of 299-W11-27, dropped to 2,755 pCi/L in March, down from a peak of 8,540 pCi/L in November 1998. This decrease in technetium-99 was accompanied by decreases in nitrate, chromium, and calcium.

Groundwater chemistry in WMA TX-TY well 299-W10-17 did not change significantly since the last sampling, i.e., nitrate continued to exceed the maximum contaminant level while chromium and technetium-99 were below applicable standards. Well 299-W10-17, one of the

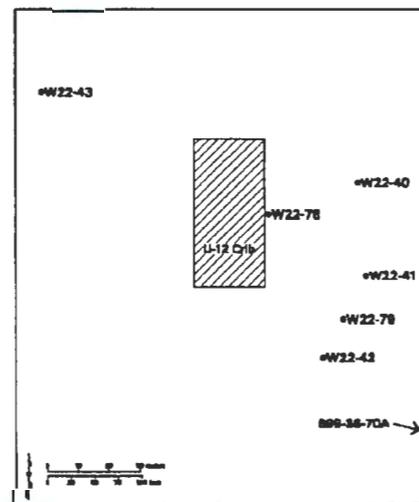
wells that initially placed WMA TX-TY in assessment, is no longer downgradient to the WMA, but is cross-gradient or marginally upgradient to the northeast corner of the WMA.

The high tritium groundwater plume first noted in well 299-W14-2 now includes well 299-W14-12 and its replacement 299-W14-13. In January, tritium activity in well 299-W14-12 was reported as 1,117,000 pCi/L. In March, tritium activities in wells 299-W14-2 and 299-W14-13 were 1,970,000 pCi/L and 1,160,000 pCi/L respectively. The iodine-129 activity in 299-W14-2 in the March sample was 47 pCi/L. Technetium-99 activity was 1,450 pCi/L in well 299-W14-13 and 1,450 pCi/L in well 299-W14-2. The source of the high tritium/iodine-129 component is unclear, but the most likely source is operational leaks from the nearby 242-T Evaporator that was closed in the early 1970s.

**216-U-12 Crib:** Nitrate, the most significant contaminant associated with this site, continued to exceed the maximum contaminant level in wells near the crib. Concentrations are gradually declining. The groundwater gradient has not changed during this quarter, therefore, the flow rate has not changed during this time.

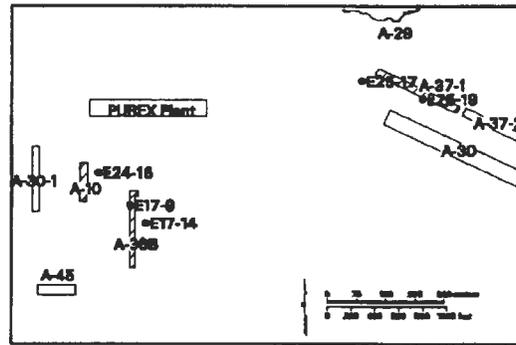
This past quarter two additional downgradient assessment wells, 299-W22-41 and 299-W22-42, have gone dry and will be removed from the groundwater assessment network. The revised downgradient network is composed of wells 299-W22-79 (a new well), and 699-36-70A. Upgradient well 299-W22-43 is expected to go dry within the year. The groundwater assessment plan is being updated to reflect these changes in the network. Ecology has approved Hanford Federal Facility Agreement and Consent Order interim milestone M-24-00J, thereby determining that these wells will not need to be replaced in FY 1999.

Technetium-99 (a constituent associated with the site) remained elevated above background in wells 699-36-70A, 299-W22-41, and 299-W22-79. An increasing concentration trend in technetium-99 in upgradient well 299-W22-43 indicates a possible upgradient source. Overall gross beta and technetium-99 concentrations in the downgradient wells appear to be declining near the U-12 Crib and increasing farther downgradient at 699-36-70A. Tritium and iodine-129, two regional contaminants, remained elevated above their drinking water standards in wells 699-36-70A and 299-W22-42, and tritium is near the drinking water standard in well 299-W22-79. Tritium values in 299-W22-41 (15,400 pCi/L) and 299-W22-42 (47,400 pCi/L) continued on trend with a slight increase. Tritium in 699-36-70A was 80,600 pCi/L, a slight decrease from last quarter. Tritium in new well 299-W22-79 was 19,600 pCi/L. The overall trend for the tritium plume indicates that the significant concentration increase may be changing, possibly due to the tritium plume moving farther east, away from the crib.



In upgradient well 299-W22-43, specific conductance and the associated nitrate (12 mg/L) decreased slightly compared to the last quarter. Technetium-99 and gross beta increased slightly this quarter. The technetium-99 activity for this quarter was 37.8 pCi/L.

**PUREX Cribs (216-A-10, 216-A-36B, and 216-A-37-1):** One well near each of the three cribs was sampled during the quarter. Maximum contaminant levels for manganese and nitrate and the interim drinking water standards for iodine-129, tritium, strontium-90, and gross beta continued to be exceeded. The water table gradient in the area has remained flat, therefore, the flow rate has not changed during the quarter.



- Iodine-129 (maximum contaminant level = 1.0 pCi/L) remained elevated at all three cribs. The well at 216-A-36B Crib (299-E17-14) had an iodine-129 activity level of 8.9 pCi/L, 216-A-10 Crib (well 299-E24-16) 10.4 pCi/L, and 216-A-37-1 Crib (well 299-E25-19) 1.8 pCi/L. There are no clear increasing or decreasing trends.
- Manganese concentrations have been increasing in concentration near the 216-A-37-1 Crib since late 1997. During the past quarter the manganese concentration at well 299-E25-19 was 57.3 µg/L, a slight decrease from the previous quarter's peak (64 µg/L). The maximum contaminant level is 50 µg/L.
- Nitrate concentrations remained above the drinking water standard (45 mg/L) near the 216-A-36B Crib. The concentration last quarter was 112 µg/L in well 299-E17-14. Nitrate in all three wells continued to exhibit an overall declining trend.
- Tritium activity remained above the drinking water standard (20,000 pCi/L) at all three of the PUREX Cribs. The results were 860,000 pCi/L (well 299-E17-14), 351,000 pCi/L (well 299-E24-16), and 165,000 pCi/L (well 299-E25-19) at the 216-A-36B, 216-A-10, and 216-A-37-1 cribs, respectively. Like nitrate, tritium is generally declining.
- Strontium-90 (drinking water standard = 8 pCi/L) remained elevated in concentration near the 216-A-36B Crib. The sample from well 299-E17-14 taken in January had an activity level of 16.5 pCi/L. Because strontium-90 is a beta emitter, the strontium-90 results are consistent with elevated gross beta (maximum contaminant level = 50 pCi/L) in the same well. In well 299-E17-14, the gross beta activity level was 63 pCi/L.

#### Other Monitoring Changes

The 100-D Ponds have recently been incorporated into the Hanford Site RCRA Permit. The ponds are considered "clean-closed," i.e. no waste left in place. No further groundwater

monitoring is required.

#### Quality Control

In February 1999, numerous measurements of field specific conductance were approximately twice as high as historical trends and lab measurements. The problem was traced to a bad batch of instrument calibration solution. The affected data were flagged in the database and were not used for statistical comparisons. Additional checks on calibration solutions will be made to avoid this type of problem in the future.

Results of blind standards for total organic halides (spiked with volatile organics) have been biased low for several consecutive quarters. These results indicate that some of the measured groundwater TOX concentrations could be biased low in areas where volatile organics are present. The groundwater project is continuing to investigate the problem. More details, and results of other quality control measures are included in the attachment.

Table 1. Status of RCRA Sites, January – March 1999.

Site	Routine sampling Jan-Mar 1999	Statistical exceedance
Indicator Evaluation Sites [40 CFR 265.93(b)] (sampled semiannually)		
100-D Ponds	Yes	No
1301-N Facility	Yes	No
1325-N Facility	Yes	No
1324-N/NA Site	Yes	Yes <sup>1</sup>
B-Pond	Yes	Yes <sup>2</sup>
A-29 Ditch	No	Not applicable
B-63 Trench	No	Not applicable
S-10 Pond and Crib	No	Not applicable
LERF	Yes	Yes
LLBG WMA 1	No	Not applicable
LLBG WMA 2	No	Not applicable
LLBG WMA 3	Yes	No
LLBG WMA 4	Yes	Yes <sup>1</sup>
SST WMA A-AX	No	Not applicable
SST WMA C	No	Not applicable
SST WMA U	Yes	Yes <sup>1,2</sup>
NRDWL	Yes	No
Groundwater Quality Assessment Sites [40 CFR 265.93(d)] (sampled quarterly)		
Six sites <sup>3</sup>	Yes	Not required
Final Status Sites (WAC 173-303-645)		
300 Area Process Trenches	Yes	Yes <sup>4</sup>
183-H Basins	No	Not applicable

LERF = Liquid Effluent Retention Facility

LLBG = Low-Level Burial Grounds

NRDWL = Nonradioactive Dangerous Waste Landfill

SST = Single-Shell Tanks

WMA = Waste Management Area

<sup>1</sup> No indication of hazardous waste contamination from facility; see text for explanation.

<sup>2</sup> Erroneous field conductivity value. No indication of hazardous waste contamination.

<sup>3</sup> U-12 Crib, PUREX Crib, SST WMA B-BX-BY, SST WMA S-SX, SST WMA T, SST WMA TX-TY.

<sup>4</sup> Site has entered corrective action because of previous exceedances.

## Attachment: Quality Control Results, January through March 1999.

**Completeness:** Completeness of data is determined by dividing the number of results that have not been rejected or flagged as suspect because of associated QC concerns by the total number of results received during the quarter. Greater than 90% completeness is considered acceptable. The suspect data may be useful for general interpretive use but should not be used to make regulatory decisions. Out of a total of 25,518 results, 92% of the results were considered valid for the 1<sup>st</sup> quarter of 1999. This percentage is slightly higher than the previous quarter (91%). Approximately 71% of the 1<sup>st</sup> quarter flags resulted from detection of conductivity, anions, and metals in field and method blanks. The majority of these results were at levels near the method detection limits; thus, the overall impact of laboratory contamination or false-detection on data quality is believed to be minor. Ninety-five 1<sup>st</sup> quarter results were flagged with an H to signify missed hold times. This value is significantly lower than the previous quarter's total of 250. Constituents affected for 1<sup>st</sup> quarter were anions (65), alkalinity (7), phenols (68), mercury (1), and TOX (5).

**Field Duplicates.** Field duplicates with at least one result greater than 5 times the detection limit must be within 20% of each other to be acceptable. Unacceptable results are flagged with a Q in the database. 820 pairs of results were generated from 17 duplicate samples. Sixteen pairs of qualifying duplicate results had relative percent differences greater than 20%. Sample reanalyses resulted in acceptable precision for 6 pairs of metals results. Most of the remaining out-of-limit results were for metals at low concentrations, where the variability of the measurements is expected to be high. Differences in suspended solids may account for poor precision in some metals. False detection or laboratory contamination is the suspected reason for the large difference for acetone. The discrepancies observed in 1,1,1-trichloroethane and gross alpha was  $\leq 25\%$ ; they appear to be isolated instances of poor sampling and/or analysis precision.

Field duplicates from last quarter exhibited poor agreement for alkalinity, cyanide, several metals and volatile organic compounds, and gross beta. Reanalyses of the affected samples for alkalinity, cyanide, lead, and gross beta produced results that were within QC limits. However, samples reanalyzed for chromium, iron, manganese and zinc appeared to confirm the original results, suggesting the samples were not identical.

**TOC and TOX Quadruplicates:** Samples for TOC and TOX analyses are normally collected in quadruplicate in accordance with RCRA requirements. While these samples are not intended as QC samples, quadruplicates may provide useful information about the overall sampling and analysis precision for organic indicator parameters. Beginning with 1<sup>st</sup> quarter 1999, TOC and TOX quadruplicate data were evaluated based on the relative standard deviation (RSD) for each set of quadruplicate results. For consistency with the field duplicates, each quadruplicate set having an RSD greater than 20% and at least one result greater than 5 times the method detection limit was considered to have poor precision. Twelve out of 130 TOC quadruplicates and 16 out of 105 TOX quadruplicates failed to meet the evaluation criteria. Table 4 lists the results for the quadruplicates having poor precision. In most cases, each set of quadruplicates appeared to include one outlier and removal of these anomalous results reduces the RPDs to less than 20%. The causes of the outliers are unknown, but many probably resulted from the low precision inherent with trace-level TOC and TOX measurements. In a few cases, the outliers probably resulted from inadvertent sample swaps in the field or at the laboratory. Since the quadruplicates are not QC samples, Q flags were not automatically applied to these data.

**Field blanks:** Full trip blanks, field transfer blanks, and equipment blanks are used to check for contamination in bottle preparation and/or field activities. Results from groundwater samples that are associated with an out-of-limit field blank are flagged with a Q in the database. A total of 1912 results were produced from the 1<sup>st</sup> quarter field blank samples. 185 of the results exceeded the QC limits for

field blanks (i.e., ~10%). Most of the flagged results were for conductivity (lab measurement), TOC, and ICP metals; however, results were also flagged for total carbon, total dissolved solids, total organic halides, anions, volatile organic compounds, gross beta, and tritium. The potential impacts on the data are minor in most cases. Several constituents had results that exceeded the QC limits in multiple field blanks (conductivity, total dissolved solids, chloride, nitrate, sulfate, calcium, magnesium, sodium, and elemental strontium), but the values were insignificant compared to the concentrations of these constituents in almost all 1<sup>st</sup> quarter groundwater samples. Some additional observations about the field blank results are briefly noted below.

Two full-trip blank results associated with different wells were unusually high. The first was a laboratory conductivity measurement of 713  $\mu\text{S}/\text{cm}$ . The second result was 710  $\mu\text{g}/\text{L}$  for TOX. Both results were probably caused by swapped samples in the field or at the laboratory. The laboratory has been asked to review the TOX data for errors and reanalyze the sample that had the high conductivity reading.

Twenty-one field-blank results for TOC were greater than 2 times the MDL, although none of the results exceeded the MDL by more than a factor of 4. Over the past several quarters, it was observed that the field blank results for TOC were slightly higher than had been observed previously. A possible explanation for the elevated results is that the water-purification system used to prepare reagent water for field blanks may not have been removing as much organic carbon from the source water as in the past. In order to test this hypothesis, 7 replicate samples of certified, organic-free water, along with 7 samples of water from the sampler's water-purification system, were collected throughout the quarter and submitted in blind fashion to the laboratory. Additional samples were also collected by filling sample bottles with the certified water at the site where full-trip blanks are normally prepared. The results from this study were somewhat inconclusive, because the TOC values for each sample type were highly variable, and the laboratory changed TOC analyzers approximately midway through the study. However, the data suggest that the water from the water-purification system was not significantly different from the certified, organic-free water. TOC results for the 2<sup>nd</sup> and 3<sup>rd</sup> quarter 1999 field blanks will be reviewed to determine whether the new analyzer is having any impact on data quality.

In general, the results from equipment blanks were similar to those from full trip blanks. Copper, nickel, and acetone exceeded the QC limits in equipment blanks only, but the small number of exceedances (3 or fewer for each constituent) do not appear to indicate a significant contamination problem. Thus, decontamination of nondedicated sampling equipment appears to have been effective overall.

Concentrations of carbon tetrachloride, chloroform, methylene chloride, and tetrahydrofuran were greater than the QC limits in several of the field-transfer blanks. Since these compounds did not exceed the QC limits in full-trip or equipment blanks, the results appear to suggest a field-contamination problem. However, 36 field-transfer blanks were analyzed for volatile organic compounds, while only 5 full-trip blanks and 2 equipment blanks were analyzed for VOCs. Most of the out-of-limit results were for methylene chloride, which was detected at similar concentrations in several laboratory method blanks. It is suspected that chloroform was present in the water used to prepare some of the field-transfer blanks due to incomplete removal by the water purification system.

Although 95% of the field blanks analyzed for metals exceeded one or more metal QC limits, the majority of the exceedances were within a factor of 3 of the QC limits. Many of these results are believed to be false detection's resulting from the use of the instrument detection limit as a reporting limit for metals.

**Blind Standards:** Double-blind standards containing known amounts of chromium and selected anions, organic compounds, and radionuclides were prepared and submitted to the primary and secondary labs in March. The samples were prepared as splits to ensure that both sets of laboratories received identical samples. Most of the standards were prepared in a groundwater matrix, although standards containing cyanide and organics were prepared using organic free, deionized water. Standards for indicator analyses were spiked using the following constituents: potassium hydrogen phthalate was used to prepare TOC standards, 2,4,6-trichlorophenol was used to prepare TOX-phenol standards, and TOX-VOA standards were prepared using a mixture of carbon tetrachloride, chloroform, and trichloroethene. Gross alpha and gross beta standards were spiked with plutonium-239 and strontium-90, respectively.

The acceptance limits for blind standard recoveries vary by constituent but are generally 75 – 125% except for chromium, which has limits of 80 – 120%, and specific radionuclides, which have a  $\pm 30\%$  acceptance range. The majority of the results for both labs were acceptable, indicating good analytical performance overall. However, the primary lab had low recoveries for TOX-VOA and one high result for plutonium-239. The secondary lab had high TOC recoveries and 2 low cyanide results. Moreover, both of the radiochemistry labs had low recoveries for 1-2 of the gross alpha standards and high biased results for all of gross beta standards. Most of the constituents with unacceptable results have been problematic in the past and are discussed in more detail below. With the exception of the TOC-VOA standards, all of the standards with unacceptable results have been reanalyzed or are currently being processed for reanalysis at the labs.

The secondary lab's high TOC values may be an indication that the lab cannot reliably quantify TOC at concentrations as low as 1000  $\mu\text{g/L}$ . However, this lab performed well on TOC blinds during the previous quarter. Based on the contradictory findings from the last two quarters, a decision was made to submit additional TOC blinds to the lab during the next 2 quarters.

The reasons for the low TOX-VOA recoveries obtained by the primary lab during the past several quarters are still unknown. Losses of volatile compounds due to volatilization or incomplete sorption on the carbon cartridges used in the analysis are suspected causes. A review of the raw TOX data for blind standards submitted during the past year suggested that sample breakthrough was not significant for most of the standards analyzed. However, breakthrough was observed in some samples. In-house analyses of the 1<sup>st</sup> quarter standards by gas chromatography confirmed that the standards were spiked correctly. The groundwater project will continue to investigate the low recoveries. Data users should recognize that TOX data on groundwater samples might be biased slightly low for volatile organic halides.

Both labs' cyanide results were low by ~20-30%. These data are consistent with the results from previous quarters. In-house analyses of the standards confirmed that the blinds were prepared correctly. In order to determine whether the samples might have been affected by shipping or storage, two of the 1<sup>st</sup> quarter standards were returned to PNNL after the lab had completed their analyses. Subsequent analyses indicated that the samples had not been affected by shipping or holding time. These findings have been discussed with the lab, and additional, joint analyses of split samples and calibration standards will be performed by PNNL and the two labs during the 3<sup>rd</sup> quarter of 1999.

The gross alpha and gross beta results for both labs were similar, with low recoveries for gross alpha and high recoveries for gross beta. The lab reanalyzed the gross beta standards, and the results appeared to confirm the originals. Thus, the standards may have been spiked incorrectly. Reanalyses have not yet been completed for the gross alpha standards.

**EPA Water Supply/Water Pollution Programs:** The primary analytical laboratory participates in the EPA Water Supply/Water Pollution (WS/WP) programs. In these programs, the EPA distributes standard water samples as blind samples to participating laboratories. These samples contain specific

organic and inorganic analytes at concentrations unknown to the participating laboratories. After analysis, the labs submit their results to the EPA. Regression equations are used to determine acceptance and warning limits. The results of these studies independently verify the level of laboratory performance and are expressed as a percentage of EPA-acceptable results.

The primary lab has responded to the unacceptable results from the WS study reported in February 1999. Alkalinity was incorrectly reported and was actually within control limits. Three regulated volatiles, three anions, boron, and hardness were within 5% of the control limits. The hardness result was probably outside the control limits because the sample was not freshly prepared. Three regulated herbicides were outside control limits, possibly because they were not fully resolved from other gas chromatographic peaks. The temperature program on the gas chromatograph will be adjusted to correct for this problem in the future. Because the three herbicides have not been observed in Hanford samples for the past six months, there should be no impact on groundwater project data. Orthophosphate is analyzed by a different technique for Hanford samples, and turbidity has not been measured in the lab in Hanford samples for the past six months; therefore, there is no impact from these data. Overall, it appears that the unacceptable results on the WS samples will not significantly impact groundwater project data because most of the problems are readily corrected, and most of the out-of-limit results do not pertain directly to project data.

Results were also received from Quanterra for the WP samples analyzed in May 1999. Nine of the 105 results (8.6%) were not acceptable: total suspended solids, total hardness, kjeldahl nitrogen, orthophosphate, mercury, 1,2-dichlorobenzene, 1,3-dichlorobenzene, tetrachloroethylene, and Aroclor 1016. Because these results were obtained recently, corrective actions have not yet been received.

**National Exposure Research Laboratory Performance Evaluation (NERL PE) Studies:** The National Exposure Research Laboratory sends out gamma, iodine-131, gross alpha, gross beta, tritium, radium, strontium, and uranium samples in a water matrix semi-annually to participating laboratories. Plutonium samples are sent out annually. Warning limits for laboratory results are at 2 normalized standard deviations above and below the known value. Control limits are at 3 normalized standard deviations above and below the known value.

The results from 3 studies were reported this quarter. All of the results except cesium-134 were within the control limits established by the EPA; Cs-134 was below the control limit for 43% of the laboratories participating in the gamma study.

**Laboratory QC Data:** Laboratory QC data includes the results from method blanks, laboratory control samples, matrix spikes, matrix spike duplicates, surrogates, and matrix duplicates. This information provides a means of assessing laboratory performance and the suitability of a method for a particular sample matrix. Laboratory QC data are not currently used for in-house validation of individual sample results unless the lab is experiencing unusual performance problems with an analytical method.

For the purposes of this evaluation, the types of constituents were divided into six general categories: (1) indicator parameters, (2) ammonia and anions, (3) volatile organic compounds, (4) semivolatile organic compounds, (5) metals, and (6) radiochemistry parameters. Laboratory control sample, matrix spike, and surrogate results were not evaluated for volatile and semivolatile organic compounds because the laboratory's QC limits for these parameters are not reported electronically. However, these QC limits should be available electronically in mid-1999.

Primary lab: results for method blanks were evaluated based on the frequency of detection above the blank QC limits. In general, these limits are 2 times the method detection limit (MDL) or instrument detection limit (IDL) for chemical constituents and 2 times the total propagated error for radiochemistry

components. For common laboratory contaminants such as acetone, methylene chloride, 2-butanone, toluene, and phthalate esters, the QC limit is 5 times the MDL. The indicator parameters and metals categories had the greatest percentage of method blank results exceeding the QC limits, with 16.8% and 15.4% exceeding twice the MDL or IDL, respectively. For metals, most of these results were for aluminum, calcium, iron, magnesium, manganese, sodium, vanadium, and zinc. For the indicator parameters, only conductivity showed high method blank results, with 100% above the MDL; however, these high method blanks for conductivity do not appear to be a significant problem because virtually all groundwater samples have conductivity values that are at least 100 times higher than the highest blank value. For all other categories, the QC limits were exceeded by fewer than 5% of the method blanks. Constituents in these categories with ten or more measurements that had greater than 10% of method blanks outside the QC limits included chloride (26%) and acetone (32%). The highest method blank for acetone was 8  $\mu\text{g/L}$  or 5 times the QC limit, and the highest result for chloride was 0.113  $\text{mg/L}$  or 1.6 times the QC limit. Laboratory control sample recoveries were excellent for all evaluated categories. The percentages of out-of-limit results were as follows: 0% for indicator parameters, 0% for ammonia and anions, 0% for metals, and 2.7% for radiochemistry parameters. For matrix spikes and matrix spike duplicates, the percentages of out-of-limit results were as follows: 4.4% for indicator parameters, 32% for ammonia and anions, 1.0% for metals, and 9.2% for radiochemistry parameters. Constituents with 10 or more measurements that had greater than 10% of matrix spikes outside QC limits included chloride, fluoride, nitrate, nitrite, sulfate, lead, and uranium. For matrix duplicates, with values five times greater than the MDL, out-of-limit results were as follows: 0.8% for indicator parameters, 0% for ammonia and anions, and 1.2% for radiochemistry parameters.

QC data from supporting labs are limited for 1<sup>st</sup> quarter due to the small number of samples submitted to those labs. For indicator parameters, ammonia and anions, and radiochemistry parameters, all the QC data were within limits. For VOAs, the matrix spike for trichloroethene was outside QC limits. For metals, five constituents exceeded the instrument detection limit by a factor of 2 or more in the method blanks: barium, calcium, magnesium, sodium, and silicon. Silicon also exceeded the QC limits in a matrix spike, and boron was out-of-limits for a matrix duplicate.