applied sciences

MDPI

Article

Interlaboratory Comparison of ^{226}Ra and ^{228}Ra Activity Concentrations in Groundwater and Surface Water

David B. Levy

Worthington Miller Environmental, LLC, 1027 W. Horsetooth Rd., Suite 200, Fort Collins, CO 80526, USA; david.levy@wm-env.com

Abstract: ^{226}Ra and ^{228}Ra are typically monitored for groundwater and surface water compliance at legacy U mining and milling sites. Groundwater monitoring results for combined Ra (^{226}Ra + ^{228}Ra) reported by the existing contract laboratory at a former U mine and mill Site (Converse County, WY, USA) have been highly variable and with increasing trends at the Site compliance and background wells since the method was changed in 2005. Sample reanalysis has indicated poor reproducibility and significant analytical error in ^{228}Ra measurements. An interlaboratory comparison was conducted to evaluate the potential causes of the high variability and analytical error. Two different methods were used for ^{226}Ra (M903.0 and M903.1) and ^{228}Ra (M904.0 and Ra-05). ^{226}Ra results were less variable compared to ^{228}Ra, and ^{228}Ra data from the existing laboratory were qualified as estimated with high bias due to detection of ^{228}Ra in the field blank. Compliance with the ^{226}Ra + ^{228}Ra groundwater standard was either met or not met, depending on which laboratory conducted the analyses. Specific laboratory techniques, rather than the analytical method, are contributing to elevated ^{228}Ra values being reported. It was recommended that samples whose ^{226}Ra + ^{228}Ra results exceed the Site standard in the future be reanalyzed by the existing laboratory with a sample split also being sent to an outside laboratory for confirmatory analysis.

Keywords: radium; uranium; groundwater; interlaboratory comparison

check for updates

Citation: Levy, D.B. Interlaboratory Comparison of ^{226}Ra and ^{228}Ra Activity Concentrations in Groundwater and Surface Water. *Appl. Sci.* **2022**, *12*, 12198. https://doi.org/10.3390/app122312198

Academic Editors: Claudia Stihi and Antoaneta Ene

Received: 10 November 2022
Accepted: 25 November 2022
Published: 29 November 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2022 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

An interlaboratory comparison (ILC) is an exercise carried out by a group of laboratories to compare their performance or to assess a measurement standard, and is typically used to (1) assess random variation in measurements across a population of laboratories, (2) determine the systematic differences in results among a fixed set of laboratories, or (3) determine the value of a physical property of an artifact or a population of artifacts [1]. An ILC was conducted to evaluate the variability of ^{226}Ra and ^{228}Ra activity concentrations (hereafter referred to as concentrations) in groundwater and an adjacent surface water impoundment (Impoundment) at a former U mine and mill (Site) located in Converse County, WY, USA. Assessment of ^{226}Ra + ^{228}Ra trends at the Site compliance well and selected groundwater monitoring wells has shown that ^{226}Ra + ^{228}Ra concentrations are highly variable, and there is some uncertainty regarding the quality of isotopic Ra data reported for the Site.

The most common isotopes of Ra are ^{226}Ra (produced by radioactive decay of ^{238}U) and ^{228}Ra (produced during radioactive decay of ^{232}Th) [2,3]. At the Site, ^{228}Ra is the dominate Ra isotope in groundwater, whereas ^{226}Ra is the dominant Ra isotope in the adjacent Impoundment. At the Site compliance well (Well 176), the historic concentrations of ^{226}Ra + ^{228}Ra have periodically exceeded the compliance standard (USEPA Maximum Contaminant Level, MCL) of 5 pCi/L; since approximately 2005, however, the concentrations have shown an increasing trend and with more frequent exceedances of the MCL. In addition to a downgradient well (Well 179), an unexpected increasing trend and high variability in ^{226}Ra + ^{228}Ra concentrations have also been measured in the unimpacted Site

background well (Well 182) since 2005 (Figure 1). The implication of ^{226}Ra + ^{228}Ra concentrations exceeding the MCL at the compliance location (Well 176) is that the Site boundary may potentially need to be expanded to demonstrate that downgradient groundwater ^{226}Ra + ^{228}Ra concentrations will remain protective of human health and the environment.

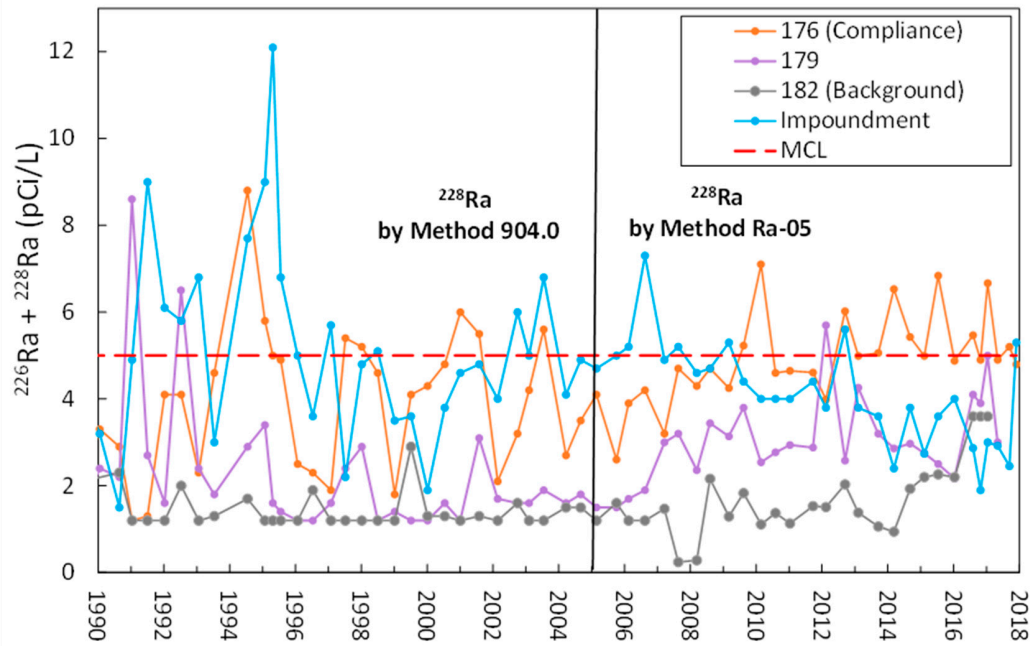

Figure 1. ^{226}Ra + ^{228}Ra concentrations in Site monitoring wells and the Impoundment.

A preliminary internal evaluation of ^{226}Ra + ^{228}Ra results for Site groundwater indicated that increasing trends and high variability could be the result of analytical error by the contract laboratory based on several key observations: (1) increases in both ^{226}Ra + ^{228}Ra and ^{228}Ra/^{226}Ra ratios occurred subsequent to a change in the ^{228}Ra analytical method from Method 904.0 (M904.0) to Method Ra-05 (Ra-05) in 2005 (Figures 1 and 2), (2) ratios of ^{228}Ra/^{226}Ra have been increasing in the non-impacted Site background Well 182 concurrently with several other monitoring wells and the Impoundment (Figure 2), and (3) re-analysis of samples with unusually elevated ^{228}Ra has demonstrated at least one occurrence of poor reproducibility and significant analytical error in ^{228}Ra measurements. For example, the reported ^{228}Ra value for Site Well 174 (3rd Quarter in 2016) was 8.6 pCi/L, while the field duplicate value was reported as <1.3 pCi/L. Re-analysis results for these two samples were reported as 2.8 pCi/L ^{228}Ra for the primary sample and 2.7 pCi/L ^{228}Ra for the duplicate sample. In addition to the poor reproducibility of the field duplicate, additional ^{228}Ra results appeared to be inaccurate. For instance, ^{228}Ra for the unimpacted background well (Well 182) was reported as 27 pCi/L which is not consistent with much lower historical results for the background location. Reanalysis of the sample from Well 182 produced a revised result of 2.0 pCi/L. Out of nine total samples which were reanalyzed, the initial results from five samples exceeded the MCL for ^{226}Ra + ^{228}Ra based on ^{228}Ra alone, but were reported as below the MCL after reanalysis. The contract laboratory was unable to provide an explanation as to why the reanalysis produced significantly different results from those initially reported.

Therefore, an ILC of ^{226}Ra and ^{228}Ra in selected groundwater wells and the adjacent Impoundment was conducted to evaluate the potential role of random variability and/or systematic error in producing the high variability in ^{226}Ra + ^{228}Ra concentrations and ^{228}Ra/^{226}Ra ratios observed during recent years. Four separate laboratories were evaluated which are designated as Lab A (Site contract laboratory), Lab B, Lab C, and Lab D. The specific objectives were to (1) evaluate potential differences between ^{226}Ra results when using a screening method (M903.0) and compare those results to a ^{226}Ra-specific method

(M903.1) and (2) evaluate potential differences between ^{228}Ra between laboratories using M904.0 and compare those results to ^{228}Ra when using Method Ra-05. Additional questions include the following: (1) Are there detectable levels of ^{232}Th in groundwater which could be migrating and influencing ratios of ^{228}Ra/^{226}Ra? (2) Are there differences between total (unfiltered) and dissolved (filtered, 0.45 µm) ^{226}Ra or ^{228}Ra, and if so, how do those fractions vary across laboratories? And (3) does M903.0 for ^{226}Ra (which measures all alpha-emitting isotopes) overestimate ^{226}Ra concentrations compared to M903.1 which is specific to ^{226}Ra? If the presence of additional alpha emitters were to produce higher apparent ^{226}Ra concentrations, it may be recommended to use M903.1, rather than M903.0, for future compliance monitoring at the Site.

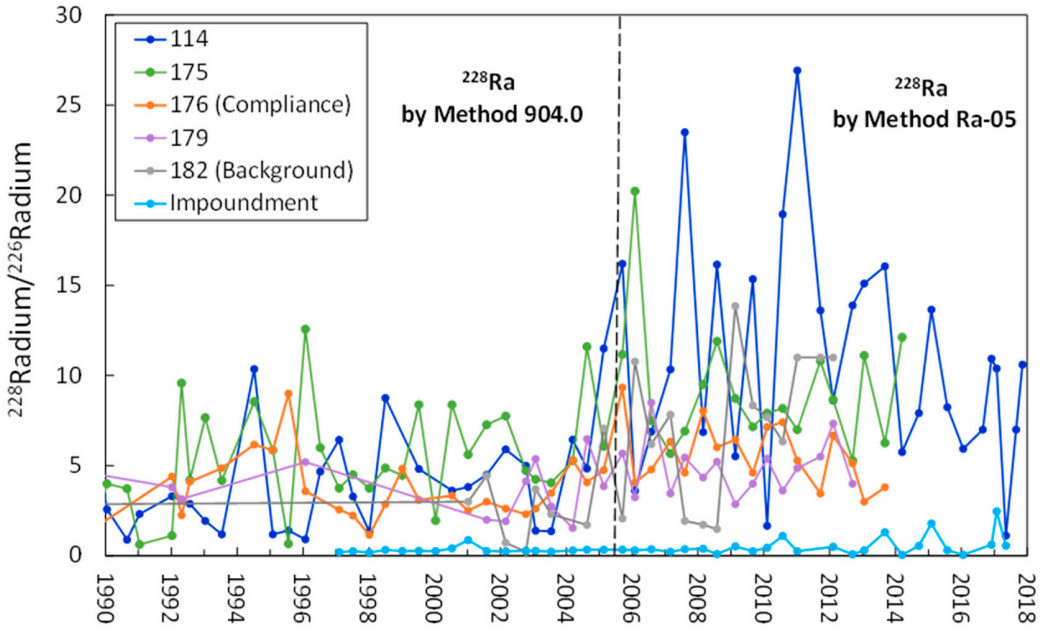

Figure 2. ^{228}Ra/^{226}Ra ratios in selected Site monitoring wells and the Impoundment.

2. Materials and Methods

The quality of ^{226}Ra and ^{228}Ra data reported by the existing contract laboratory (Lab A) was investigated using an ILC which included analysis of primary samples, a duplicate sample, and field blanks. Groundwater samples were collected from the Site compliance well (Well 176), the Site background well (Well 182), and from an intermediate well located outside of the Site boundary (Well 179). Surface water was collected from the adjacent Impoundment where the U ore was originally mined. Samples were collected for analysis of ^{226}Ra and ^{228}Ra, in addition to ^{232}Th to evaluate the potential role of ^{232}Th as a source of ^{228}Ra. Water samples were split and processed accordingly to evaluate their dissolved (filtered, 0.45 µm pore-size filter) and total (unfiltered) forms. A duplicate was collected from Well 176, and field blanks (filtered and unfiltered) were prepared using deionized H_2O supplied by each laboratory. All sample collection, preservation, and storage protocols followed standard methods for water sample collection [4]. At each location, the filtered and non-filtered samples were split into four groups and submitted to four laboratories designated as Lab A (existing contract laboratory), Lab B, Lab C, and Lab D. Each laboratory and their corresponding analytical methods are summarized in Table 1.

Table 1. List of laboratories and methods used in the ILC.

Lab	^{232}Th	^{226}Ra	^{228}Ra
A	M908.0	M903.0	Ra-05
B	ESM4506	M903.0	M904.0
C	ASTM D3972	M903.0	M904.0
D	DOE EML HASL-300 Th-01-RC Modified	M903.1	Ra-05

The methods used for ^{232}Th varied among laboratories but are all based on alpha spectroscopy; the methods used for ^{226}Ra and ^{228}Ra have been approved by the U.S. Environmental Protection Agency (USEPA) [5] and also varied among the laboratories (Table 2). For ^{226}Ra, three of the laboratories (Labs A, B, C) used Method 903.0 (M903.0). Although the results are reported as ^{226}Ra, M903.0 measures the total alpha emitting isotopes of Ra (^{223}Ra, ^{224}Ra, ^{226}Ra) and is therefore considered a screening method. Method 903.1 (M903.1), which is specific to ^{226}Ra, was used by Lab D and can be compared to results from M903.0 to determine if other alpha emitting isotopes contribute to the reported ^{226}Ra concentrations for the Site. For ^{228}Ra, two of the laboratories used Method 904.0 (M904.0) (Labs B, C), while Lab A and Lab D used Method Ra-05. Each Ra method in Table 2 has been approved for drinking water compliance analysis by the USEPA and therefore should not produce significantly different results [6].

Table 2. Comparison of USEPA-approved methods for Ra [5].

Analyte	Method/MDL [1]	Method Principle	Method Notes
^{226}Ra	903.0/0.5	Radiochemical precipitation; alpha counting by scintillation or gas-flow proportional counting.	Does not always provide an accurate measurement of ^{226}Ra with other alpha emitters present and often used for screening. Method states: "When the total radium alpha activity of a drinking water sample is greater than 5 pCi/L, then the ^{226}Ra analysis (Method 903.1) is required."
^{226}Ra	903.1/0.5	Radiochemical precipitation; radon emanation; alpha counting by scintillation.	No radioactive interferences. ^{226}Ra in solution is determined by co-precipitation with $BaSO_4$ and sample analyzed using de-emanation.
^{228}Ra	904.0/1.0	Radiochemical precipitation; counting by gas-flow proportional beta counter	Measures ^{228}Ra alone or in conjunction with ^{226}Ra. Ra in solution from ^{228}Ra determination is saved, and the Ra is reprecipitated for ^{226}Ra analysis. Ra is precipitated as Ra-$BaSO_4$, which is dissolved and purified from EDTA solution. After ingrowth of ^{228}Ac, the ^{228}Ac is precipitated with $Y(OH)_3$, reprecipitated with Y, and counted by beta counter.
^{228}Ra	Ra-05\NR [2]	Radiochemical precipitation; beta counting in a low-background proportional counter.	Ra is precipitated as Ra-$BaSO_4$ which is dissolved in a pentasodium diethylenetriamine pentacetate solution. After ingrowth of ^{228}Ac, ^{228}Ac is extracted with Di 2-ethylhexyl phosphoric acid and back-extracted with HNO_3.

[1] MDL = minimum detectable level (pCi/L). [2] NR = not reported.

3. Results

The analytical results for total and dissolved ^{226}Ra and ^{228}Ra at all locations reported by the four laboratories are provided in Table 3. All dissolved ^{232}Th results were below the detection limit (0.0131 to 1.11 pCi/L) and only two total ^{232}Th measurements were detectable at low concentrations (0.0074 and 0.017 pCi/L); therefore, the ^{232}Th results are not tabulated. This section provides (1) a summary of the quality assurance/quality control

(QA/QC) results (Section 3.1), (2) a general overview of the dissolved and total ^{226}Ra and ^{228}Ra results from the various laboratories, (3) a more detailed comparison of dissolved and total ^{226}Ra and ^{228}Ra, and (4) an evaluation of the combined ^{226}Ra + ^{228}Ra results between laboratories relative to the MCL.

3.1. Quality Assurance/Quality Control (QA/QC) Summary

Laboratory data quality was evaluated based on results from method blanks (MB), laboratory control samples (LCS), LCS duplicates (LCSD), matrix spikes (MS), and MS duplicates (MSD) using USEPA guidelines [7]. In the MBs, all ^{226}Ra and ^{228}Ra results were below their minimum detectable concentration (MDC). Data accuracy evaluation showed the percent recovery values for the LCS, LCSD, MS, and MSD were within recommended limits. Data precision evaluation showed that the relative percent differences (RPDs) for analytical duplicate samples and field duplicate samples were also within laboratory control limits for all analyses. Total ^{228}Ra was detected above the MDC in the field blank by Lab A and Lab B, and dissolved ^{226}Ra was detected above the MDC in the field blank by Lab C. Dissolved ^{228}Ra was also detected above the MDC in the field blank by Lab D. Sample results containing less than 10× the amount found in the field blanks were qualified as being estimated with high bias (Table 3) and were assigned a J+ qualifier.

Table 3. Comparison of ILC results (pCi/L) for ^{226}Ra and ^{228}Ra [1].

Location	Lab	^{226}Ra (Dissolved)	^{226}Ra (Total)	^{228}Ra (Dissolved)	^{228}Ra (Total)
Impoundment	A	1.8	1.5	1.7	3.7 J+
	B	2.2	1.5	<0.69	1 J+
	C	1.52 J+	1.56	<0.61	<0.69
	D	1.4	1.66	<0.7	<0.7
Well 176 (Compliance)	A	0.7	0.8	<1.9	4.1 J+
	B	0.97	0.74	3.2	3.2 J+
	C	1.37 J+	1.2	4.6	4.8
	D	0.965	<0.356	5.2 J+	5.9
Well 176 (Duplicate)	A	0.7	0.8	3	4.1 J+
	B	1.3	0.83	3.8	4.7 J+
	C	1.08 J+	0.96	3.9	5.1
	D	0.859	0.777	5.5 J+	7
Well 179	A	0.5	0.5	1.9	1.5 J+
	B	<0.66	0.58	1.7	4.8 J+
	C	0.77 J+	0.73	2.07	2.68
	D	0.334	0.639	3.7 J+	5.4
Well 182 (Background)	A	0.3	0.3	2.9	3.3 J+
	B	<1	<0.57	<0.75	<0.55
	C	0.4 J+	0.32	<0.62	<0.64
	D	<0.328	0.487	0.8 J+	1.8
Field Blank	A	<0.2	<0.2	<1.4	2
	B	<1.1	<0.55	<0.63	1.4
	C	0.28	<0.25	<0.51	<0.63
	D	<0.249	<0.234	0.8	<0.7

[1] Values with a J+ qualifier indicates the value is qualified as an estimate with high bias when detected in the field blank and the sample result is <10× the amount measured in the field blank.

Radiological data such as ^{226}Ra and ^{228}Ra are typically reported as the measured value ± the degree of precision. When a value is below the MDC, the actual value is still reported but the datum is flagged as non-detect and the MDC is provided. The sum of the ^{226}Ra and ^{228}Ra is subsequently calculated to determine the combined Ra (^{226}Ra + ^{228}Ra) that is typically used for compliance in the USA. If either of the ^{226}Ra or ^{228}Ra values are below detection, the value of the MDC for the non-detect value is summed with the

detectable value to calculate the ^{226}Ra + ^{228}Ra concentration. When both ^{226}Ra and^{228}Ra values are below detection, the respective MDC values are summed to obtain the MDC for the combined ^{226}Ra and^{228}Ra, which is then reported as below detection. The sum of individual precision values for ^{226}Ra and ^{228}Ra is used as the overall precision for ^{226}Ra + ^{228}Ra.

3.2. Summary of ^{226}Ra Results

The dissolved and total ^{226}Ra results for all samples are shown in Figure 3. The error bars represent the precision in the analyses. Any reported value which was below the MDC is indicated with the MDC shown in black, and any J+ qualified value (estimated with high bias) is shown in red. None of the dissolved ^{226}Ra results were significantly different based on their range in precision. The results from Lab C were J+ qualified and were the highest reported at each location, except for the Impoundment. The values reported by Lab D using M903.1, which is specific to ^{226}Ra, tended to be lower for all samples, with the exception of Well 176 where the Lab A value was slightly lower (Figure 3).

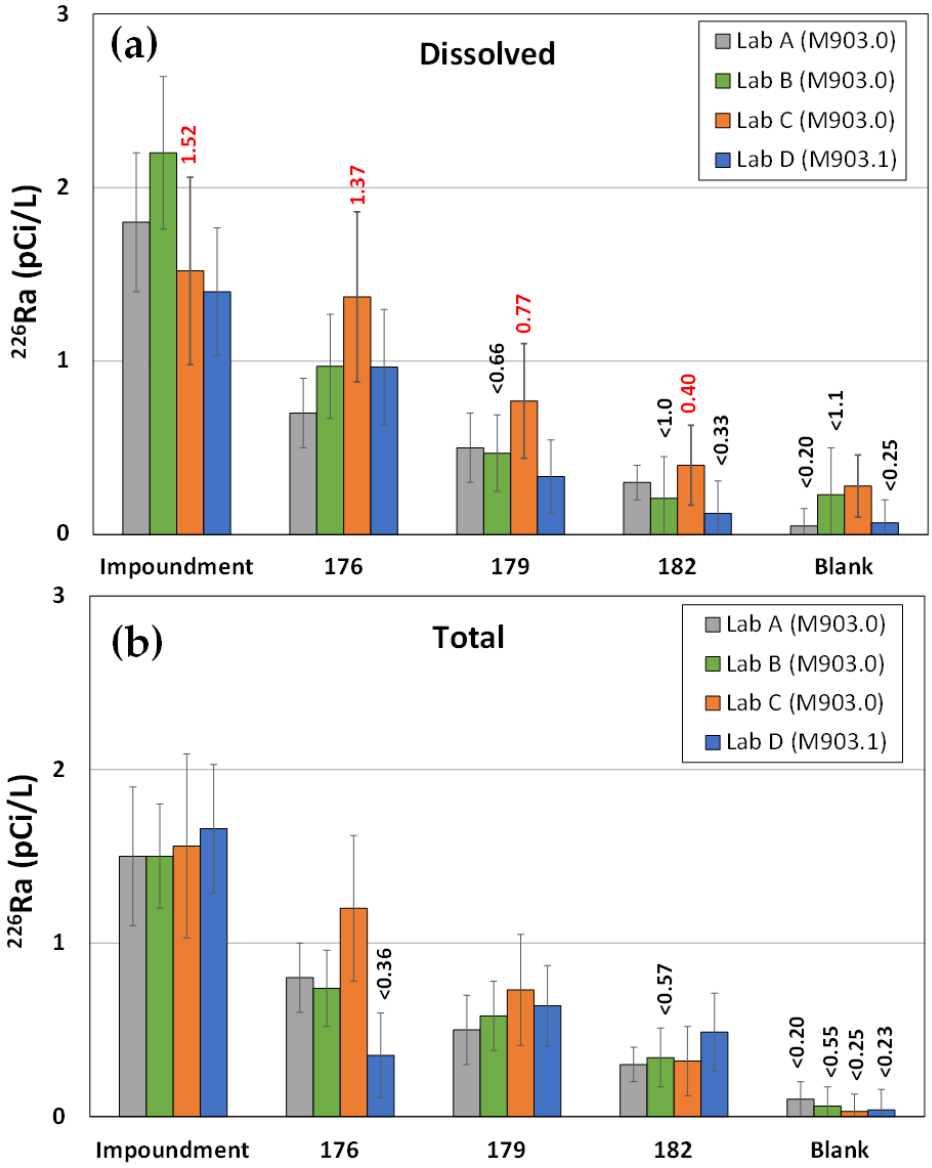

Figure 3. Comparison of (**a**) Dissolved ^{226}Ra; (**b**) Total ^{226}Ra. Values in red are qualified as estimated with high bias (J+) when sample result contained <10× the amount measured in the field blank. Values in black signify the MDC when the reported value is less than the MDC.

The trend in lower values using M903.1 was not observed for total ^{226}Ra (Figure 3), except in Well 176 where total ^{226}Ra was below detection. However, the value of <0.36 pCi/L for total ^{226}Ra in Well 176 should be equal to or greater than the dissolved value because the sample was not filtered; therefore, the value of <0.36 pCi/L is suspect. No ^{226}Ra was detected in the unfiltered field blanks, and therefore none of total ^{226}Ra values were qualified as estimated with high bias (Table 3, Figure 3).

3.3. Summary of ^{228}Ra Results

Overall, the ^{228}Ra results (Figure 4) tended to be more variable across locations and between laboratories compared to ^{226}Ra (Figure 3). A comparison of these results shows that ^{226}Ra tends to be higher in the Impoundment, whereas ^{228}Ra is higher in the groundwater, consistent with historical Site observations. However, no regular trends are apparent based on the method or laboratory used for dissolved ^{228}Ra. For example, although Lab A and Lab D use Ra-05, the Lab D results were notably higher than Lab A in samples where ^{228}Ra concentrations were overall higher ($\geq$2 pCi/L). The Lab D results were qualified as estimated with high bias due to detection of ^{228}Ra in the field blank. Although a higher concentration of ^{228}Ra was reported by Lab A for the field blank, the detection limit (<1.4 pCi/L) was higher compared to other laboratories and methods (Figure 4, Table 2). In samples containing overall lower ^{228}Ra concentrations ($\leq$2 pCi/L), the results from Lab A were notably higher compared to Lab D. The results from Lab B and Lab C using M904.0 tended to be intermediate between those from Lab A and Lab D, where Ra-05 was used (Figure 4).

Similar trends were observed for total ^{228}Ra compared to dissolved ^{228}Ra (Figure 4). However, for total ^{228}Ra, the results from Lab A, rather than Lab D, were qualified as estimated with high bias due to detection of ^{228}Ra in the field blank (Table 3, Figure 4). Lab A reported 2 pCi/L of ^{228}Ra in the field blank, and similar to ^{226}Ra values, results from Lab A were notably higher in samples containing overall low ^{228}Ra (Impoundment, Well 182).

3.4. Detailed Comparison of Total vs. Dissolved Ra

A comparison of total and dissolved ^{226}Ra from each laboratory is shown in Figure 5. The error bars represent the precision in the analyses, with non-detect values shown in black and all J+ qualified values shown in red. Theoretically, total concentrations should be equal to or greater than dissolved concentrations, with the extent of Ra partitioning to suspended particles depending on factors such as total suspended solids concentration and pH [2]. Total and dissolved ^{226}Ra were generally the same in all samples based on the range in precision of the analyses (Figure 5). However, the difference between the actual reported values in total vs. dissolved at a given location were not consistent between laboratories. For example, the reported total ^{226}Ra in the Impoundment was higher than dissolved for the Lab D data, lower than dissolved for Lab A and Lab B, and almost equal for Lab C. In the background Well 182, the reported total ^{226}Ra was greater than dissolved for Lab D and Lab B, less than dissolved for Lab C, and approximately equal for Lab A.

For the ^{228}Ra data shown in Figure 6, total ^{228}Ra was more consistently greater than or equal to the dissolved fraction when compared to ^{226}Ra in Figure 5. It is also apparent that both total and dissolved ^{228}Ra values from Lab A are elevated in the samples containing low Ra (Impoundment, Well 182, and field blank) compared to the other lab results, including those from Lab D where the same method (Ra-05) was used. In addition, the values reported for total ^{228}Ra in the field blank were higher compared to non-detectable dissolved ^{228}Ra from Lab A and Lab B. Differences between total and dissolved ^{228}Ra in the field blank suggests that processing of the sample for total analysis could have produced false positive results.

3.5. Combined ^{226}Ra + ^{228}Ra Results

The ^{226}Ra + ^{228}Ra values for the dissolved and total fractions are shown in comparison to the 5 pCi/L compliance value in Figure 7. The dissolved ^{226}Ra + ^{228}Ra values reported by

Lab C and Lab D exceeded the MCL at Well 176. Total ^{226}Ra + ^{228}Ra reported by Lab C and Lab D also exceeded the MCL at Well 176, in addition to total ^{226}Ra + ^{228}Ra reported by Lab A for the Impoundment and total ^{226}Ra + ^{228}Ra reported by Lab B and Lab D at Well 179. Overall, the trends are not entirely consistent between laboratories. For example, there was little difference between dissolved and total ^{226}Ra + ^{228}Ra for the Impoundment and Well 176 in the data reported by Lab B, Lab C, and Lab D, while the total ^{226}Ra + ^{228}Ra values reported by Lab A were higher than dissolved for the same two locations. Conversely, values were higher for total ^{226}Ra + ^{228}Ra compared to dissolved ^{226}Ra + ^{228}Ra at Well 179 for the data reported by Lab B add Lab D, while total vs. dissolved ^{226}Ra + ^{228}Ra concentrations reported by Lab A were similar. The dissolved ^{226}Ra + ^{228}Ra in the field blank was below detection as reported by Lab A and Lab B, while total ^{226}Ra + ^{228}Ra was detectable; the opposite trend was observed for the data reported by Lab C and Lab D (Figure 7).

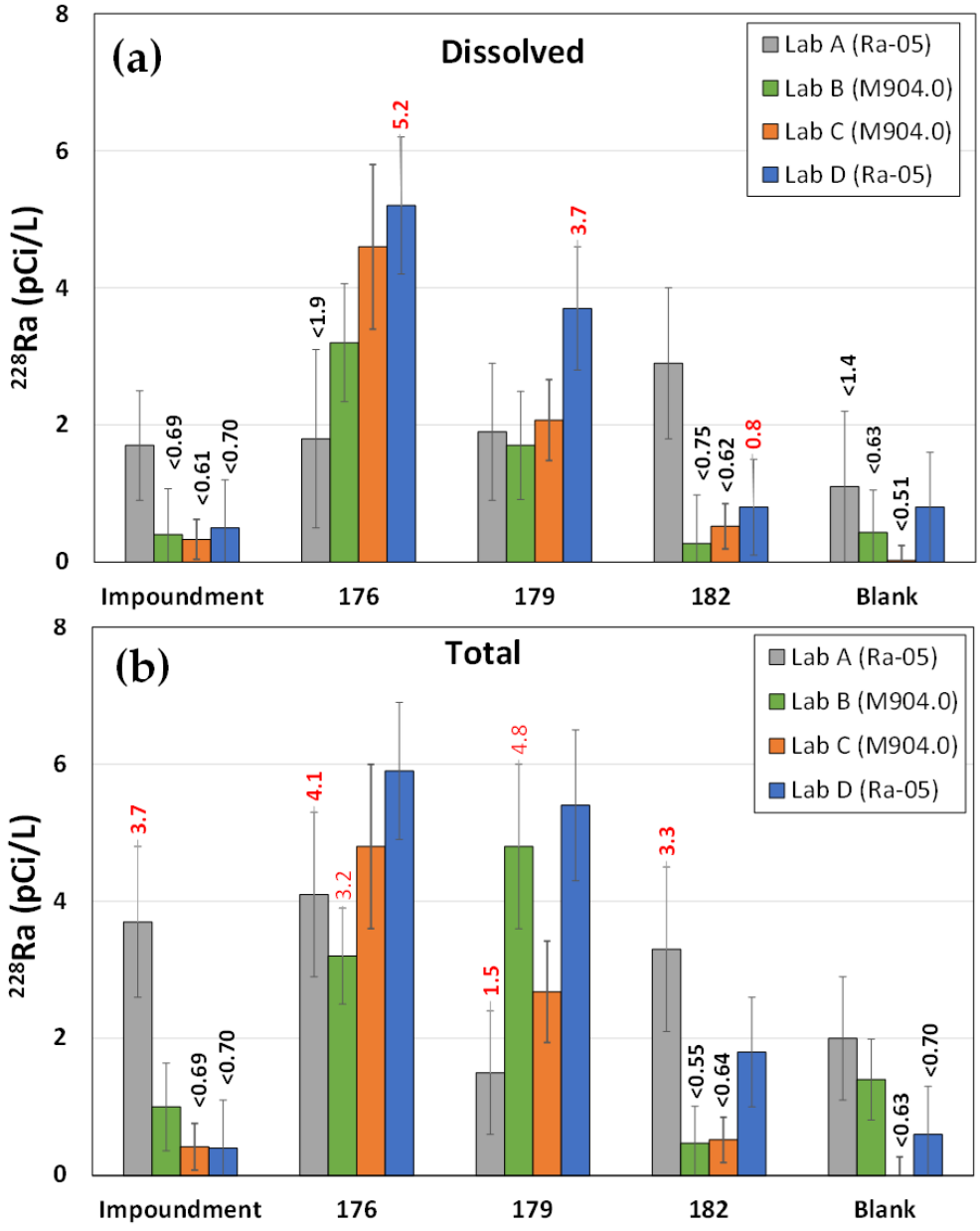

Figure 4. Comparison of (**a**) Dissolved ^{228}Ra; (**b**) Total ^{228}Ra. Values in red are qualified as estimated with high bias (J+) when sample result contained <10× the amount measured in the field blank. Values in black signify the MDC when the reported value is less than the MDC.

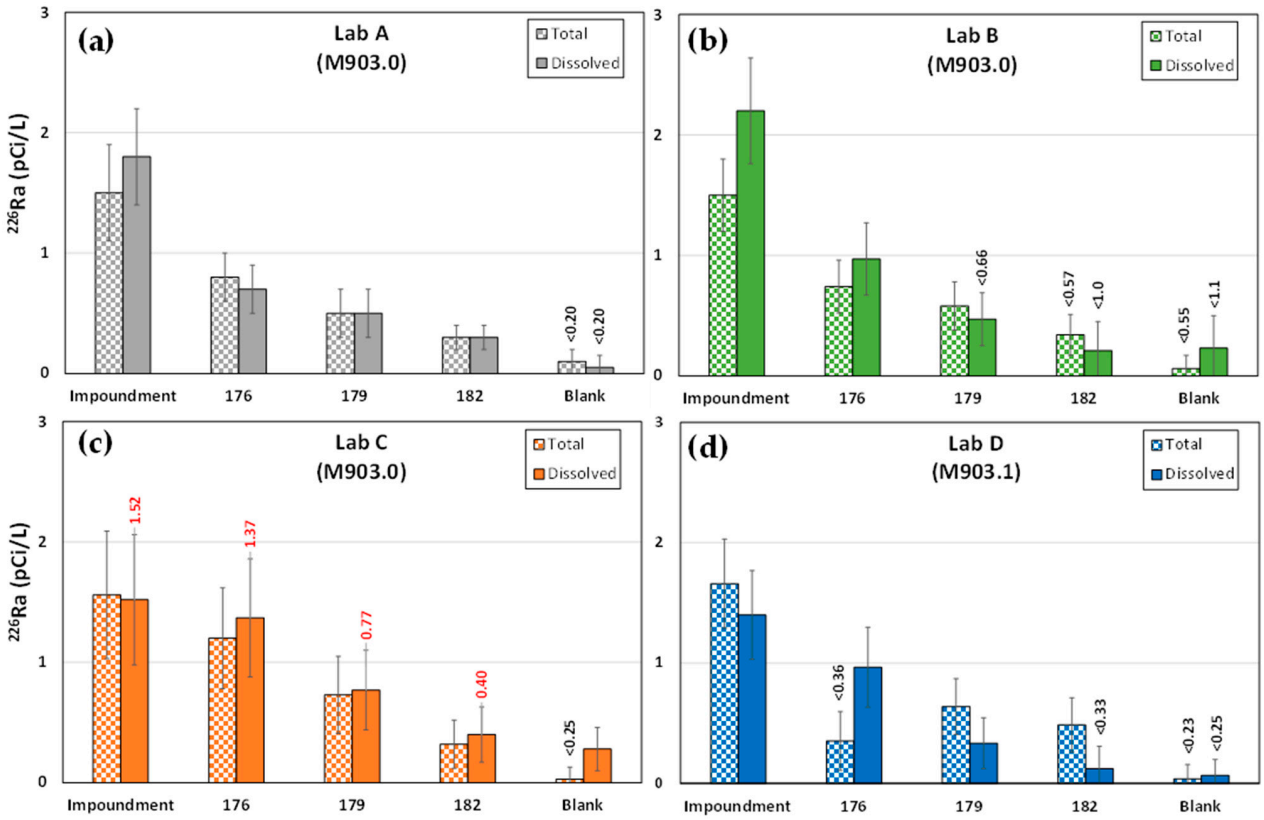

Figure 5. Comparison of total and dissolved ^{226}Ra concentrations: (**a**) Lab A; (**b**) Lab B; (**c**) Lab C; (**d**) Lab D.

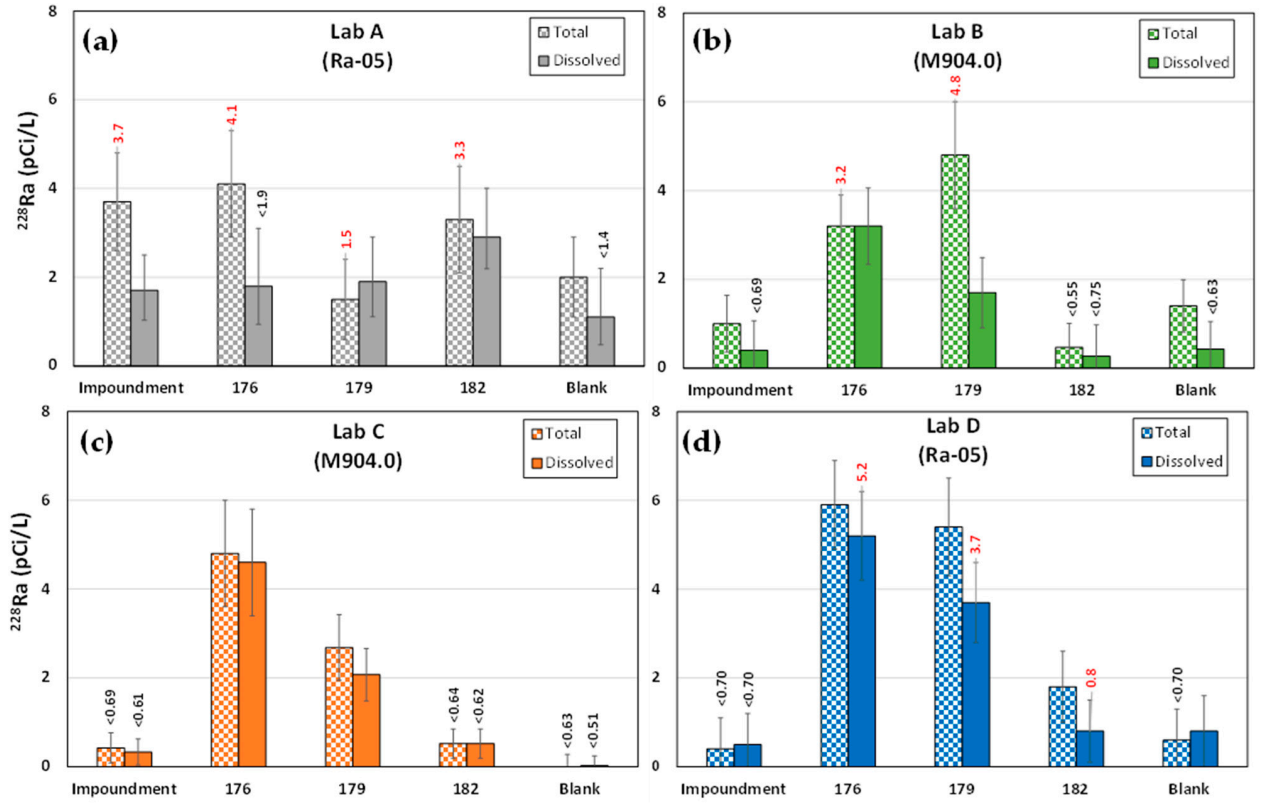

Figure 6. Comparison of total and dissolved ^{228}Ra concentrations: (**a**) Lab A; (**b**) Lab B; (**c**) Lab C; (**d**) Lab D.

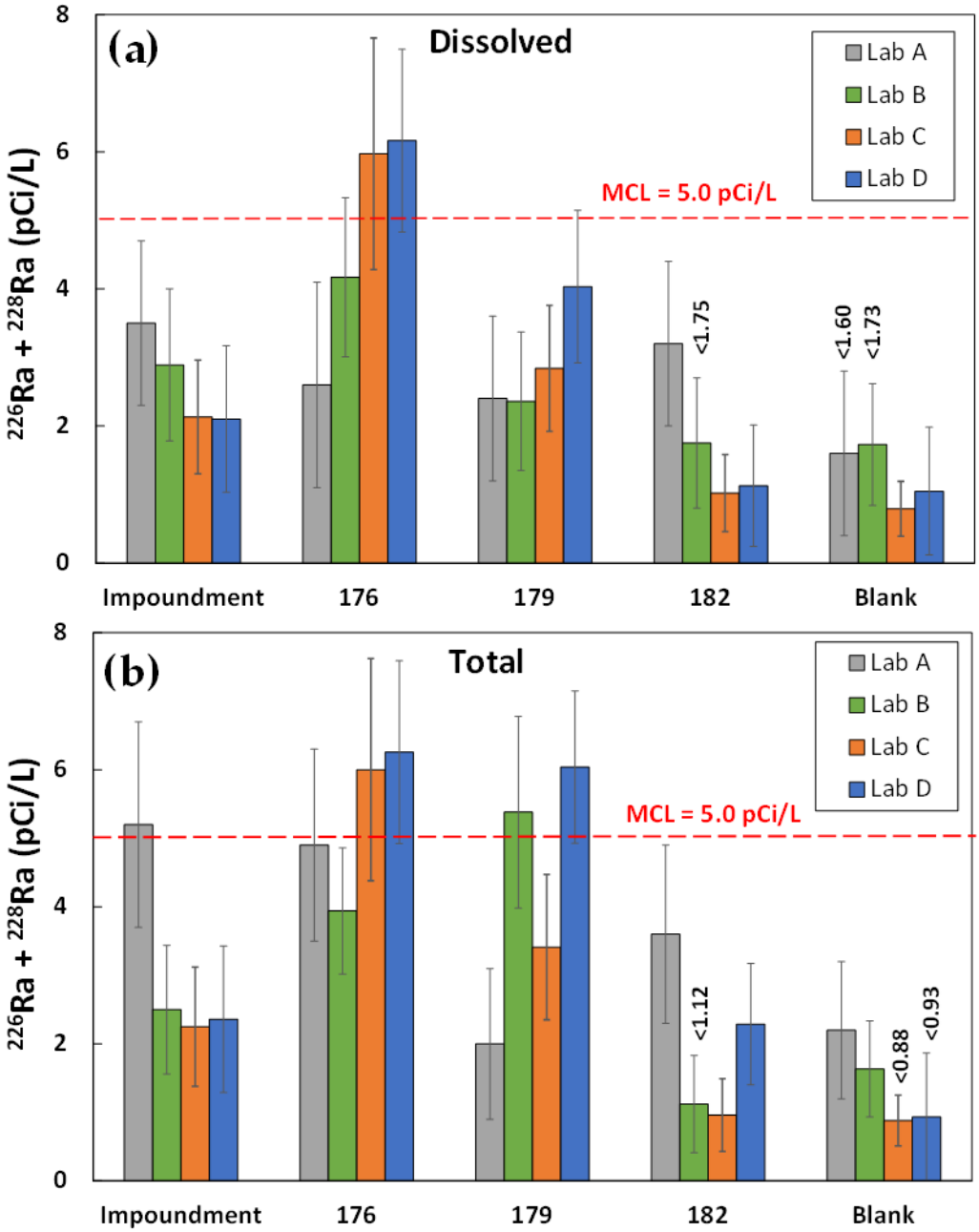

Figure 7. Interlaboratory comparison of (**a**) Dissolved ^{226}Ra + ^{228}Ra; (**b**) Total ^{226}Ra + ^{228}Ra. Values in black signify the MDC when the reported values were less than the MDC.

4. Summary and Discussion

This ILC of ^{226}Ra and ^{228}Ra was conducted to understand the potential reasons for high variability and increasing trends in ^{226}Ra + ^{228}Ra concentrations that have been observed in Site monitoring wells, including the compliance Well 176 and background Well 182. The results for ^{226}Ra were fairly consistent between laboratories, and with the exception of dissolved ^{226}Ra reported by Lab C, all ^{226}Ra concentrations were below detection in the field blanks. The concentrations of ^{228}Ra were more variable between laboratories and with a higher frequency of detection in the field blanks.

For both ^{226}Ra and ^{228}Ra, there were no consistent trends with respect to the total vs. dissolved concentrations across laboratories, which were essentially equal in most samples when the range in measured precision was considered. The largest differences between reported values for total vs. dissolved Ra were observed in the Lab A data for ^{228}Ra, where the total ^{228}Ra data were qualified as estimated with high bias. For both

dissolved and total ^{226}Ra + ^{228}Ra, the results from Lab C and Lab D for the compliance Well 176 exceeded the MCL, whereas the results from Lab A and Lab B were below the MCL. Therefore, compliance with the MCL was either achieved or not achieved, depending on which laboratory conducted the analyses.

Results for ^{226}Ra obtained using M903.1 (specific to ^{226}Ra) were usually equal to or slightly lower than those generated using M903.0; however, the differences are insignificant and may be due to analytical variability rather than method specificity. Results for ^{228}Ra reported by Lab D when using Method Ra-05 were more consistent with those from Lab B and Lab C when using M904.0. The ^{228}Ra results reported by Lab A when using Method Ra-05 tended to be higher in samples where the remaining laboratories reported low ^{228}Ra concentrations (<2 pCi/L), and tended to be lower in samples where the remaining laboratories reported higher ^{228}Ra concentrations (>2 pCi/L). Lab A also reported the highest measured ^{228}Ra concentration of all field blanks (2 pCi/L), and consequently those data for total ^{228}Ra were qualified as estimated with high bias.

A prior study relating to radionuclide variability in water samples [6] showed that radionuclide activity in groundwater can vary up to four-fold due to seasonal effects, but also noted that the variability could reflect issues related to method and laboratory variability. The greatest source of error for ^{226}Ra is counting uncertainty, but the overall accuracy and precision for ^{226}Ra results was acceptable among various laboratories. For ^{228}Ra, however, the methods are generally not as robust as those used for ^{226}Ra. No single laboratory was able to provide consistently accurate ^{228}Ra results, and due to the much greater relative standard deviation (RSD) values, it was concluded that the accuracy of ^{228}Ra results is dependent on laboratory technique and skill and "may also reflect less rugged analytical methods" [5].

5. Conclusions and Recommendations

The results obtained from this ILC of Site groundwater and surface water samples are generally consistent with the findings from the prior 2011 study [6] with respect to observed variability in ^{226}Ra compared to ^{228}Ra. The current ILC indicate that ^{228}Ra data reported by the existing contract laboratory (Lab A) are biased high relative to those reported by Lab B, Lab C, Lab D, and this may be due to differences in laboratory skill and technique among the various laboratory technicians [6]. However, the resulting upward trends in ^{228}Ra/^{226}Ra ratios (observed in both impacted wells and the background location) after the ^{228}Ra method was changed from 904.0 to Ra-05 are more difficult to explain.

Although the trends were not entirely consistent, the results from this study show a tendency for total Ra to be higher than dissolved Ra, especially for ^{228}Ra. For samples where the majority of the laboratories reported low ^{228}Ra concentrations (<2 pCi/L), it appears that the method and techniques used by Lab A for total ^{228}Ra is contributing to higher apparent ^{228}Ra concentrations. Therefore, it was recommended that ^{226}Ra and ^{228}Ra analyses (in additional to uranium and other radionuclides) be conducted on a filtered sample for Site compliance evaluations. Analysis for dissolved concentrations would also then be consistent with remaining metals analyses which are also analyzed as dissolved.

For ^{226}Ra, it was recommended that M903.0 be replaced with M903.1 which is specific to ^{226}Ra. Method 903.0 includes all alpha emitters and therefore can result in over-reporting of ^{226}Ra concentrations. The primary additional alpha emitter which could contribute to overestimation of ^{226}Ra is ^{224}Ra, which originates from ^{232}Th. Although ^{232}Th concentrations were very low to non-detect in the Site samples, the presence of ^{232}Th in the solid phase of aquifer materials could release ^{224}Ra into solution. Even though this study did not indicate that M903.0 results in consistent over-reporting of ^{226}Ra concentrations, use of M903.1 would better ensure that the appropriate analysis for ^{226}Ra is being conducted. Alternatively, it could be requested that the laboratory employ a 14-day waiting time which will effectively reduce the contribution of ^{224}Ra to the reported ^{226}Ra [6].

For ^{228}Ra, this study indicates that specific laboratory techniques, rather than the method (Ra-05) used by Lab A are potentially contributing to excessively elevated values

being reported for ^{228}Ra at the Site. It should be noted that even though standard methods [5] are being used, many laboratories have developed their own customized Standard Operating Procedures (SOPs) which are often proprietary and difficult to obtain. However, it is recommended that any location whose reported ^{226}Ra + ^{228}Ra concentrations exceed groundwater or surface water standards in the future be immediately re-sampled and re-analyzed by the existing laboratory, with a sample split also being collected and sent to an outside laboratory for additional confirmatory analysis.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data are contained within the article.

Acknowledgments: Thanks to Jill Richards (Worthington Miller Environmental, LLC) for her efforts with laboratory coordination and data validation.

Conflicts of Interest: The author declares no conflict of interest.

References

1. Guthrie, W.F. Interlaboratory Comparisons. In *Encyclopedia of Statistics in Quality and Reliability*; Ruggeria, F., Kenett, R.S., Faltin, F.W., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, USA, 2008. [CrossRef]
2. Langmuir, D.L. *Aqueous Environmental Chemistry*, 1st ed.; Prentice-Hall, Inc.: Upper Saddle River, NJ, USA, 1997; 600p.
3. International Atomic Energy Agency (IAEA). *The Environmental Behaviour of Radium: Revised Edition*; International Atomic Energy Agency: Vienna, Austria, 2014; 267p.
4. Baird, R.; Bridgewater, L. *Standard Methods for the Examination of Water and Wastewater*, 23rd ed.; American Public Health Association: Washington, DC, USA, 2017; 1545p.
5. U.S. Environmental Protection Agency (USEPA). *Compendium of EPA-Approved Analytical Methods for Measuring Radionuclides in Drinking Water*; U.S. Department of Energy, Office of Environmental Policy and Assistance, Air, Water, and Radiation Division: Washington, DC, USA, 1998; 62p.
6. Eaton, A.Y.; Cha, Y.; Morley, K.M. Evaluation of variability in radionuclide measurements in drinking water. *J. Am. Water Resour. Assoc.* **2011**, *103*, 119–130. [CrossRef]
7. U.S. Environmental Protection Agency (USEPA). *National Functional Guidelines for Inorganic Superfund Methods Data Review*; USEPA Office of Superfund Remediation and Technology Innovation: Washington, DC, USA, 2020; 158p.