COLORADO
Oil & Gas Conservation Commission
Department of Natural Resources

Sampling and Analysis of Naturally Occurring Radioactive Material in Oil and Gas Produced Water

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COGCC Special Project 10243

EXECUTIVE SUMMARY

In 2017, environmental staff members of the Colorado Oil and Gas Conservation Commission (COGCC) conducted a survey of naturally occurring radioactive materials (NORM) in aqueous fluids produced from 45 oil and gas facilities throughout the state. These aqueous fluids are typically referred to as produced water. Produced water is the largest volume waste stream produced by oil & gas exploration and production (E&P) operations in Colorado. Approximately 308 million barrels of produced water were reported to COGCC during the year of this study (2017). Special Project 10243 was undertaken to better understand the activities of NORM in this waste.

Both general water quality and NORM radiochemistry analytical parameters were determined as part of this study. All sampling and analyses were conducted as described in a project specific sampling and analysis plan. Sampling was performed by COGCC environmental protection staff and all analyses were conducted by independent laboratories. The analytical data gathered as part of this project has been uploaded in the COGCC environmental (COENV) database and the data and lab reports can be accessed through the COGCC web site.

Fifty-one samples of E&P fluids and 5 production gas samples were collected from fifteen separate producing formations in basins statewide. Characterization of NORM constituents in produced waters from basins with different geologic settings and different producing formations is necessary to understand what levels of NORM activities are present in the water co-extracted with hydrocarbons from producing basins across the state. Analysis for NORM constituents included screening level analyses (gross alpha and gross beta), analysis of concentrations of uranium (U) and thorium (Th), and determination of the activities of numerous U and Th progeny using alpha, beta and gamma radiochemistry analytical procedures. A subset of samples sites (5) were selected for water/gas sample couplets to evaluate radon isotopic (^{222}Rn) activities fractionation between water and gas phases. A small set of water samples were also analyzed for tritium (^{3}H) activities and for calculated ^{14}C ages of dissolved inorganic carbon (DIC).

Radiological activity levels from this study are at the low to middle end of ranges found in the literature from other states (New York, Pennsylvania and Texas) and in the literature from a worldwide compilation of NORM in produced water. When compared to data from three other states, produced water samples from this study shows activities of NORM radionuclides to be lower in Colorado produced water samples than in other states for which large published data sets are available, and in most cases, by more than one order of magnitude, as shown in Tables 23, 24, and 25 in Section 4.2. An international compilation of ranges of activities of NORM radionuclides in comparison to results from this study is shown in Table 31. As with the datasets discussed in Section 4.2, the maximum measured activities in Colorado samples are lower than the maximum of the ranges of activities compiled from the international data set (Jonkers et al., 1997, IAEA, 2003).
No relationship between water quality or radiological activities and the type of drilling technique or well stimulation/completion practices (hydraulic fracturing versus no hydraulic fracturing) was observed. The majority of the samples collected (10 of 16) with the highest activities of NORM analytes are from vertical wells that were not completed with hydraulic fracturing techniques. Only three of the highest activities of the NORM analytes were present in wells that had been completed by hydraulic fracturing, and none of the wells contributing to those sites were horizontal wells (Facilities 755501, 755657 and 755646).

General water quality parameters including major cations and anions, trace metals, pH, electrical conductivity, and suspended and dissolved solids, were determined for all of the study samples to better understand sources of solutes in produced water and relationship with NORM activities. Significant variations in the geochemistry of produced waters were observed within waters produced from the same formations in the same basin and even in formations in stratigraphic proximity to one another.

High concentrations of TDS has been observed in previous studies in other states to be related to elevated radiological activities and that relationship is observed in samples collected for this study. This demonstrates that the composition of the rocks in contact with the produced water is the dominant factor in both the overall water quality (TDS for example) and the radiological content of the produced waters. Facility **755645** (Lyons Fm.), had the highest gross beta activity and highest activities of ^{40}K, ^{228}Ra, ^{226}Ra, ^{222}Rn, ^{210}Pb and ^{210}Po and the highest TDS concentration of all of the samples collected. Two other sampling sites, Facility **755541** (gross alpha, Osage Limestone) and Facility **755523** (^{214}Pb and ^{214}Bi, Topeka Limestone) also had highest reported activities and have the second- and fifth-highest TDS concentrations reported in samples collected for this study.

Sodium and, to a lesser extent, potassium are the dominant cations in the samples collected and chloride the dominant anion with lesser occurrences of bicarbonate alkalinity and sulfate. In general, the overall concentrations of total dissolved solids concentrations limit the use of produced waters for beneficial reuse without treatment. Road spreading of produced water for dust control is not possible in most situations as 71% of the samples exceed the 3,500 mg/l threshold under COGCC rule. The high sodium content relative to calcium and magnesium in these waters contributes to a high sodium adsorption ratio (SAR) with most of the samples having SAR ratios exceeding 9 which would severely limit produced water reuse in irrigation because of possible reduction of infiltration due to reactions induced in soils by the sodic waters. These limitations on use reduce the likelihood of the public coming in contact with most produced waters in the state.

Mass ratios (Cl/Br) and molar ratios (Na/Cl) are used to better understand sources of solutes present in the produced water samples and in conjunction with water isotope ratios can be used to better understand sources and history of produced waters. Stable isotopes of water (δ^{18}O & δ deuterium (^{2}H)) in study samples do not in general reflect modern or recent meteoric water sources of produced water (except for the coal-bed methane samples and samples from a few other producing formations). Tritium and ^{14}C activities were determined for eight of the samples and the results indicate non-modern water in all but the frac source water sample (Facility **755461**). Percent modern carbon results (^{14}C) yielded ages from 60 years before present (BP) (the frac source water sample) to 43,600 years BP.

The analytical data collected under Special Project 10243 provide staff, operators, other agencies, and the public with summary and detailed NORM-related analytical data for produced water from across Colorado's oil and gas producing basins. In general, NORM activities in Colorado are significantly lower (in some cases lower by more than one order of magnitude) when compared to published NORM data from other states.

A very strong correlation between high TDS and elevated gross beta activities is observed in the study samples and is attributable to predominantly to ^{40}K and to a lesser extent ^{228}Ra and ^{210}Pb. ^{40}K is present in produced waters from dissolution of K bearing minerals in shales, sandstones and evaporite minerals in O&G reservoir rocks and may also be added as KCL in products used in drilling, in well control fluids or in completion fluids.

No risk assessment or exposure modeling related to NORM was done as part of this study, as both are outside the scope of the project and not within the expertise of COGCC staff. However, a guiding concept (as developed by the Health Physics Society) with respect to all exposure to or potential exposures to ionizing radiation, is to keep exposure to ionizing radiation as low as reasonably achievable (ALARA) in a workplace environment (or other places where people may come in contact with radiation). Oil and gas facilities are the workplace in which this concept is most appropriate with respect to NORM in E&P wastes.

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ACKNOWLEDGEMENTS

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1. INTRODUCTION, PURPOSE, AND APPROACH

The National Research Council (1999) Committee on Evaluation of EPA Guidelines for Exposure to Naturally Occurring Radioactive Materials states that “All natural media – earth, air, water and biota, including humans – are radioactive to some degree, and the concentrations of radionuclides in these media are highly variable, both between and within media.” For this study it is important to understand the ranges of activities present in groundwater co-produced with oil and natural gas (generally referred to as produced water). The Colorado Oil and Gas Conservation Commission (COGCC) (special project 10243) acquired data to better understand the activities of naturally occurring radioactive materials (NORM) in Colorado aqueous exploration and production (E&P) wastes (produced water).

Produced water was chosen for this study as it is the E&P waste produced in greatest volume in Colorado, and produced water is a waste stream for which the COGCC has primary regulatory authority. The COGCC production database shows that oil and gas operators reported producing 308,414,523 barrels of water in 2017 (Eisinger and Robertson, personal communication, 2018). Disposal mechanisms of produced water that may be more likely to result in NORM accumulations in soils include disposal in pits (lined and unlined) or discharge to surface waters under permit from the Colorado Department of Public Health and Environment (CDPHE). In 2017 approximately 12% of the produced water from Colorado oil and gas operations was disposed of in pits, mainly in Washington and Las Animas counties, or by surface discharge, mainly in Las Animas county. Approximately 85% (or greater) of the produced water is re-injected in Underground Injection Control (UIC) wells with less chance of impacts to soils or shallow groundwater.

A process to obtain representative, precise, and accurate data regarding NORM and other inorganic analytes in produced water was developed for this study and is described in the study-specific sampling and analysis plan (SAP) (COGCC, 2017a). COGCC staff collected 51 aqueous samples and 5 gas samples from 15 producing formations from across the state for this study. COGCC also collected one shallow groundwater sample (source water for drilling or completions collected prior to use downhole). Operator cooperation and assistance in accessing production facilities and production equipment was essential. After sample collection and analyses, COGCC staff conducted geological and geochemical evaluations to understand what geologic formations and what types of produced water geochemistry may be associated with relatively greater or lesser activities of NORM. Inorganic analytes such as metals and anions were also analyzed to aid understanding of geochemical associations with NORM constituents. Produced water samples were collected from vertical, directional, and horizontal wells to investigate if drilling techniques are a significant influence on produced water geochemistry. To examine if completion techniques are a significant influence on produced water geochemistry, produced water samples were collected from wells, some of which were completed using hydraulic fracture stimulation techniques, and some that were not.

No risk assessment or exposure modeling related to NORM was done as part of this study, as both are outside the scope of the project and not within the expertise of COGCC staff. As developed by the Health Physics Society with respect to all exposure to or potential exposures to ionizing radiation, a general guidance is to keep exposure to ionizing radiation as low as reasonably achievable (ALARA) in a workplace environment.

The data gathered in this study will provide staff, operators, other agencies, and the public with summary and detailed NORM-related analytical data from across Colorado's oil and gas producing basins. The ranges of NORM constituent activities are compared to published NORM data from other states and other nations in an effort to help understand the relative scale of potential impacts. The study was conducted in order to *"investigate, prevent, monitor or mitigate conditions that threaten to cause or that actually cause a significant adverse environmental impact on any air, water, soil, or biological resource"* and to *"gather background or baseline data on any air, water, soil, or biological resource that the commission determines may be so impacted by the conduct of oil and gas operations*" as described in the Oil and Gas Conservation Act (Colorado Revised Statutes Title 34, Article 60). Analysis of inorganic components of the produced water (other than NORM) was also performed so that staff, operators, other agencies, and the public have summary and detailed inorganic analytical data to better inform about possible impacts from produced water spills/releases.

This special project is responsive to concerns and questions raised in the October 2011 review of COGCC rules, policies, and practices by the State Review of Oil & Natural Gas Environmental Regulations (STRONGER). The STRONGER review noted that the COGCC did not have appreciable data concerning concentrations or activities of radioactive constituents in E&P waste streams in Colorado. The limited NORM data in COGCC records is because the COGCC has no statutory authority over use or disposal of radioactive materials. As assigned by the Colorado State Legislature, regulatory authority over radioactive materials in Colorado lies with the CDPHE in all processes and wastes, even though COGCC does regulate many other aspects of storage and disposal of E&P wastes along with requiring remediation of spills or releases of E&P wastes to ensure compliance with thresholds established by rule.

In 2014 COGCC staff addressed part of the STRONGER review concerns with Special Project 2136 which evaluated drill cuttings, soils into which cuttings had been mixed, and background soils by analysis of NORM constituents in these matrices (COGCC, 2014b). This project also used a project-specific SAP (COGCC, 2014a). The evaluation of NORM constituents in drilling cuttings was a priority because cuttings from drilling with water based muds have often been land-disposed under COGCC purview. Analyses of drill cuttings also presented opportunities to evaluate the activities of uranium (U) and thorium (Th) and their radioactive progeny in the rocks that are in contact with water, gas, and oil produced by a well. The rocks in which a well is completed are assumed to be a main source of NORM in E&P products and wastes that are brought to surface. Activities of NORM constituents in drill cuttings were found to be similar to or lower than activities of NORM analytes in background soils in the Wattenberg field.

Prior to this study, two other data sets contained the majority of the NORM constituent analyses from E&P wastes available to COGCC. Data on radioactivity in gas wells drilled near Project Rulison (Garfield County) and in wastes from those oil and gas wells is submitted to COGCC by operators in the area under policies first adopted in 2007 (URS, 2010a). One operator voluntarily provided a data set containing analyses of selected NORM constituents in produced water from just over 100 coal bed methane (CBM) wells in the Raton Basin. Before this current study, the Raton Basin dataset gathered in 1998 was a very high proportion of the Colorado produced water NORM analyses available to the COGCC.

A wide variety of uses for produced water range from options included in current rules such as reuse in drilling and production activities or dust control. Potential uses not currently listed in COGCC rules such as fire suppression, agricultural uses, sources of water for aquifer replenishment, or even as sources of drinking water have been proposed in Colorado or are active in other areas. As many suggestions about uses of produced water have been voiced to staff or are done in other oil and gas producing areas, it is useful to better understand the chemistry of water produced from oil and gas wells.

Treatment of produced water may be needed prior to any of these uses, and such treatment may produce residuals or wastes that would be regulated under authority of CDPHE and not under COGCC rules. Characterization of the general inorganic and NORM components of produced water done as part of this study provides useful information regarding what might end up in treatment residuals.

Produced water is a primary source of NORM that can be also found in sediments and scale in oil and gas storage or processing facilities. The NORM found in sediments and scale may be considered technologically enhanced NORM (TENORM) after treatment or processing. Radon (Rn), a gas that is produced in the decay chain of both Th and U, may be found in the aqueous (waste) as well as in oil and gas (product) phases brought up from well bores, as illustrated in Figures 1 and 2. When Rn migrates out of the mix of liquids and gases that are produced from oil and gas wells, as gases by design do in liquid/gas separators used in-line at or near wells, then the progeny of Rn (also NORM) might be more likely found in gas pipelines or further downstream in gas processing facilities. Rn may also be found dissolved in produced water or in natural gases produced from oil and gas wells. To better understand the fractionation of the ^{222}Rn isotope between the produced water phase and the natural gas phase, a subset of samples of natural gas and produced water from the same wells were analyzed for activities of ^{222}Rn. Radon carried in the gas stream could result in presence of its progeny in production facilities processing gas but not receiving produced water.

Characterization of NORM constituents in aqueous E&P wastes from basins around the state with different geologic settings, different producing lithologies, and different drilling and completions techniques was conducted to better understand what levels of NORM activities are present in water produced in basins other than the Raton and from geologic formations other than coals. Significant variations in the geochemistry of produced waters can be present even within waters produced from the same formations in the same basin. For example, some CBM produced waters from the Raton Basin have concentrations of total dissolved solids (TDS) as low as 500 milligrams per liter (mg/l) while a few produced waters in the same formation in the same basin have TDS >25,000 mg/l. Aqueous wastes from production of gas in tight sandstones of the Williams Fork Formation (Fm.) in the Piceance Basin of western Colorado will have different geochemical signature than produced water from wells completed in carbonate mineral bearing chalk and marl zones in the Niobrara Fm. of the Wattenberg field in northeastern Colorado. The produced water chemistry from each is expected to reflect those differences in chemistries of the rocks with which the waters are in contact as well as the source(s) of water in the formations. Analysis of stable isotopes of water together with major ion compositions of produced water can be used to better understand the sources of water in producing formations. A broad suite of inorganic water quality parameters other than NORM were also determined on all water samples collected as part of this study for two reasons. Determination of general water quality measurements such as pH, TDS, major anions such as chloride, and major cations such as sodium can be used to better understand sources of solutes in produced water and relationship with NORM activities. Also, the analysis of trace elements including arsenic (As) and selenium (Se) can provide relevant information about potential impacts to soils or water from spills and releases of E&P waste.

A project-specific SAP (COGCC, 2017a) was developed to provide COGCC staff procedures for the collection of representative aqueous E&P wastes (and one E&P product – natural gas) as well as for the accurate and precise determination of NORM activity levels in those aqueous wastes and gaseous products.

Naturally occurring Th and U isotopes, and one radioactive isotope of potassium (K), are present in many rocks and, together with the progeny produced by the decay of U and Th, are the primary sources of NORM in E&P wastes (IAEA, 2003). Potassium is estimated to be the eighth most abundant element (1.84%) in the earth's crust (Greenwood and Earnshaw, 1997), and its long-lived, naturally occurring radioactive isotope (^{40}K) is present as a fraction (0.0117%) of K present in the earth (Meija et al., 2016; CIAAW, 2017) or approximately 2 milligrams per kilogram (mg/kg) of ^{40}K present on average in rocks making up the earth's crust. Although Th and U are estimated to be the 39th (8.1 mg/kg) and 47th (2.3 mg/kg), respectively, most abundant elements in the earth's crust by Greenwood and Earnshaw (1997), it is helpful to keep in mind that even small concentrations of radionuclides may represent a significant amount of radioactivity.

^{232}Th (99.98%) and ^{238}U (99.2742%) are the most abundant isotopes of Th and U in the earth (Meija et al., 2016; CIAAW, 2017) and are ubiquitous in the earth's crust with activities dependent on rock type (IAEA, 2003). ^{40}K and the 23 radionuclides in the Th and U decay chains are the primary NORM components in E&P wastes. These are listed in Figure 1 (^{238}U) and Figure 2 (^{232}Th) as modified from an International Atomic Energy Agency (IAEA, 2003) guidance document concerning management of NORM in E&P wastes. Th and, to a lesser extent U, are thought to be relatively immobile under the geochemical conditions present in many oil-producing rocks (Langmuir, 1978; Langmuir and Herman, 1980; Hem, 1992; IAEA, 2003). Two elements found among the decay products of the U and Th decay chains, radium (Ra) and Rn, tend to be more soluble in water and gas phases, respectively. Thus, Ra and Rn are likely to be brought to the surface by production activities at oil and gas wells. Radium isotopes (^{224}Ra, ^{226}Ra and ^{228}Ra) may be found in significant concentrations in waters while isotopes of Rn gas (^{222}Rn, ^{220}Rn, and other Rn isotopes) are typically found in natural gas as discussed by Hem (1992) and IAEA (2003). These mobility concepts, illustrated in Figures 1 and 2, are explained in more detail in the IAEA publication cited (IAEA, 2003). Potassium is relatively soluble in water (Hem, 1992) and is another potential source of NORM in produced water. The decay of ^{40}K is directly to stable isotopes of calcium (Ca) by beta decay (89%) and to argon (Ar) through electron capture (11%) and subsequent gamma emission (National Research Council, 1999), so there are no radioactive progeny of ^{40}K of concern in this study.

In Colorado, E&P activities for oil and natural gas are conducted in many parts of the state. These activities include drilling through various subsurface layers of rock that contain U, Th, their decay products, and K, with the purpose of producing oil and natural gas from those geologic formations. Rock cuttings brought to the surface by drilling, and waters and gas co-produced when natural gas and crude oil are brought to surface, are expected to contain NORM. In addition to Special Project

2136, in which rock cuttings from drilling activities in the Greater Wattenberg field of Colorado were analyzed for NORM activities (COGCC, 2014b), a nationwide 1989 survey (Otto, 1989) was performed on behalf of the American Petroleum Institute (API) with screening type analyses reported from multiple sites in five counties in Colorado. Studies from other states were reviewed, and a brief summary is provided in Section 4.2 with comparisons to data from this study.

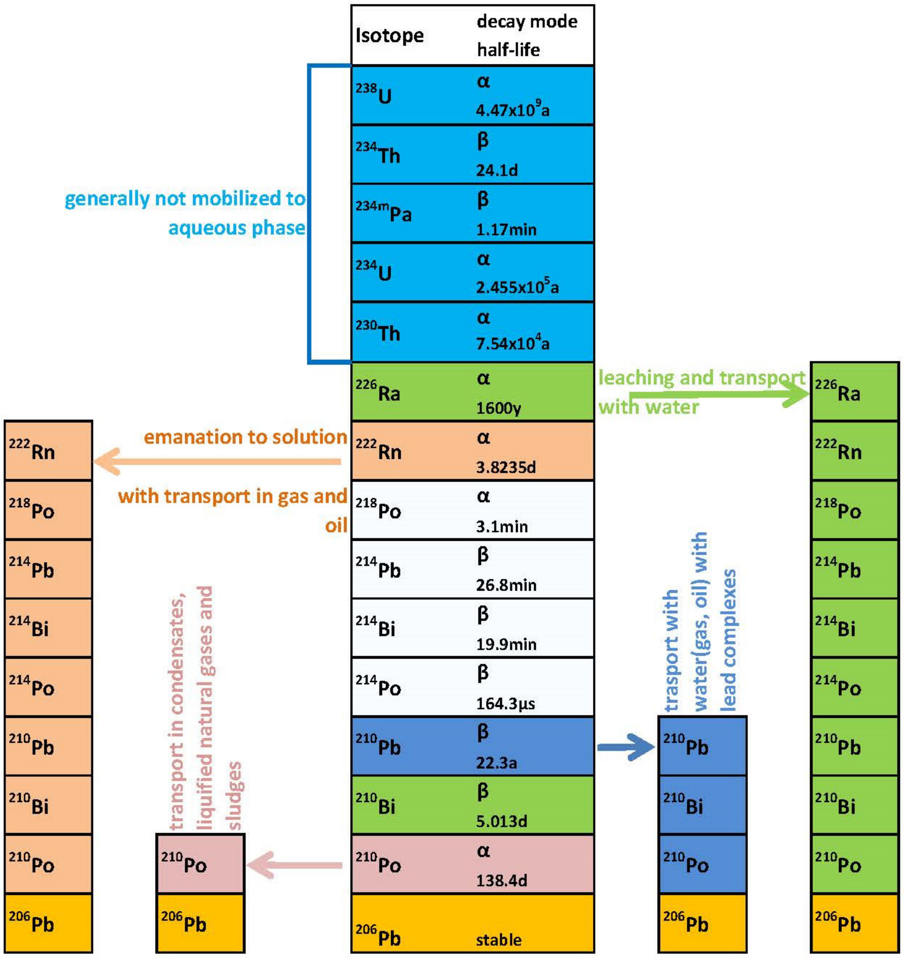

Figure 1. Decay Chain of ^{238}U

Decay modes are alpha = α and beta = β. Abbreviations for time units as follows: a=year, d=day, min=minute, µs=10-6 seconds. Modified from IAEA, 2003.

NORM in produced waters from E&P wastes in Pennsylvania (PESI, 2016) were sampled and analyzed, and the data were used for comparison to data from Colorado E&P wastes collected in the current study and also from Special Project 2136 (COGCC, 2014b). New sampling and analysis of Pennsylvania produced water to be used for road spreading was reported recently (Tasker et al., 2018). The United States Geological Survey (USGS) maintains a database containing produced water analyses from around the country, and recently they have incorporated gross alpha, gross beta, radon, and radium activity concentrations in their database (NASE&M, 2016, p.42). Inspection of the USGS data indicates that the Colorado data contained in the USGS files are from the Raton Basin and currently reside in the COGCC database. Samples of produced water from New York state oil and gas wells were analyzed for the presence of several radionuclides by gamma spectroscopy (NYDEC, 1999). Existing data were compiled and new sampling and analysis of produced water from Texas geothermal and oil and gas wells were summarized in a 1995 (Fisher, 1995) report of the Texas Bureau of Economic Geology. Existing data were compiled and new sampling and analysis of produced water from Pennsylvania and New York oil and gas wells was summarized in a 2011 USGS report (Rowan et al., 2011). The 2011 USGS compilation included the NYDEC (1999) data already summarized. The other sources of data included in the 2011 compilation include data hand-compiled from a manual search of Pennsylvania documents from 2009 and 2010 at Pennsylvania Department of Environmental Protection (PADEP) offices by USGS staff (Rowan et al., 2011) as well as data from a New York study (NYDEC, 2009) and a Pennsylvania study (PADEP, 1992).The data available from Pennsylvania, New York, and Texas are compared to data from this study in Section 4.2 of this report.

For purposes of this study, any water emerging from the well is considered produced water, even if was previously injected for hydraulic fracturing or is from aqueous liquids added to a wellbore such as potassium chloride (KCl) brines used to control pressure in wells or for other purposes. Although the primary focus of the study is the analysis of aqueous E&P wastes from oil and gas-producing formations in sedimentary basins across the state, a subset of the sample sites included source water for drilling and completion activities prior to use downhole, and included sampling and analysis of water produced soon after hydraulic fracture stimulation, referred to as frac flowback or flowback fluids.

The numbers of samples collected for this study include:

- produced water (50, including 6 duplicates)
- fresh source water prior to use downhole(1)
- frac flowback (1)
- natural gas (5)

Two of the produced water sampling facilities in the Piceance Basin were centralized facilities from which produced water was predominately reused in drilling or completion activities. Produced water from any oil and gas well may be recycled and re-used for enhanced recovery, drilling, or other approved uses following COGCC Rule 907.c.(3).

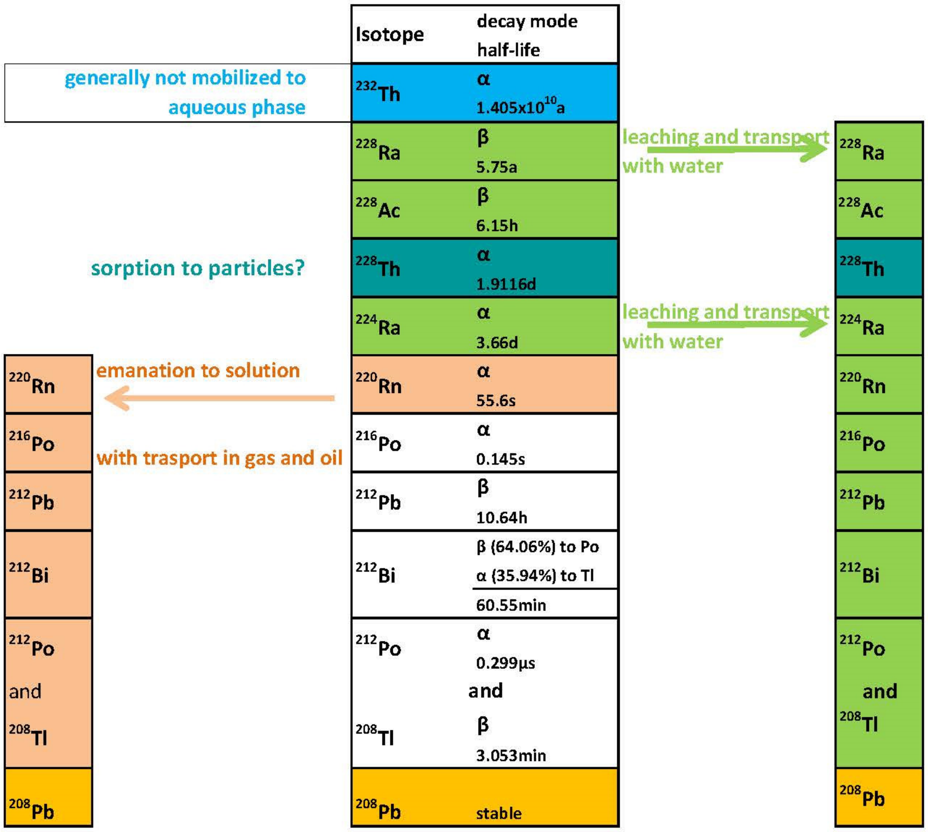

Figure 2. Decay Chain of ^{232}Th

Decay modes are alpha = α and beta = β. Abbreviations for time units as follows: a=year, d=day, h=hour, min=minute and µs=10^{-6} seconds. Modified from IAEA, 2003.

2. STUDY IMPLEMENTATION

All samples for this study were collected from existing oil and gas production wells or aqueous fluid handling facilities with an emphasis on basins and formations from which relatively large volumes of E&P waste are produced, as documented in COGCC production database since 1999. Figure 3 shows the locations of samples collected for this study. Source water and flowback samples were collected opportunistically in an area where wells were being drilled and completed at the time of sampling.

2.1 Sampling Methods

Grab samples were collected from wells or their production facilities from locations outlined below and based on criteria discussed previously:

- Produced water collected directly from well or from phase separators
- Produced water collected from storage vessels (such as produced water tanks)
- One sample collected from hydraulic fracturing “flow back” operations
- One fresh water drilling and hydraulic fracturing water sampled from a process piping sampling port
- Two produced water samples collected from process piping at centralized E&P waste management facilities

2.2 Sampling Activities

Sampling activities were performed in accordance with the SAP developed for this project (COGCC, 2017a). The project-specific SAP provides documentation of the analytes of interest as well as documentation of the laboratory methods used in the analysis of the specified target list, guidance for record-keeping in the field and laboratory, and general quality assurance (QA) practices and procedures used in the field and laboratory. The names of the facilities sampled as well as information about geographic locations (public land survey system known as PLSS) are listed in Appendix 1.

2.3 Analytes and Analytical Methods

Laboratory analyses of aqueous samples include the following parameters, as specified in Table 1:

- gross alpha and gross beta
- gamma spectroscopy to identify radionuclides present
- alpha spectroscopy for uranium (^{238}U, ^{235}U, and ^{234}U) and thorium (^{232}Th, ^{230}Th and ^{228}Th) following chemical separation, if total concentration of Th or U >3 micrograms per liter (µg/l)
- liquid scintillation for ^{222}Rn in water samples
- ^{224}Ra and ^{226}Ra by alpha spectroscopy following chemical separation
- ^{228}Ra by gas flow proportional counting (GFPC) beta analysis of its short-lived progeny (^{228}Ac) following chemical separation
- alpha spectroscopy following chemical separation of ^{210}Po
- liquid scintillation spectrometry following chemical separation of ^{210}Pb
- metals analysis (total) of U and Th by inductively couple plasma/mass spectrometry
- metals analysis of dissolved phase major cations
- analysis of major anions by ion chromatography
- analysis of alkalinity by titration

- analysis of general water quality parameters such as pH, specific conductance, dissolved and suspended solids
- stable isotopes of water by isotope ratio mass spectrometry
- determination of isotopic carbon ratio of dissolved inorganic carbon (DIC) by isotope ratio mass spectrometry
- accelerator mass spectrometry for determination of ^{14}C in DIC (selected samples)
- electrolytic enrichment and GFPC of ^{3}H in H_2O (selected samples)

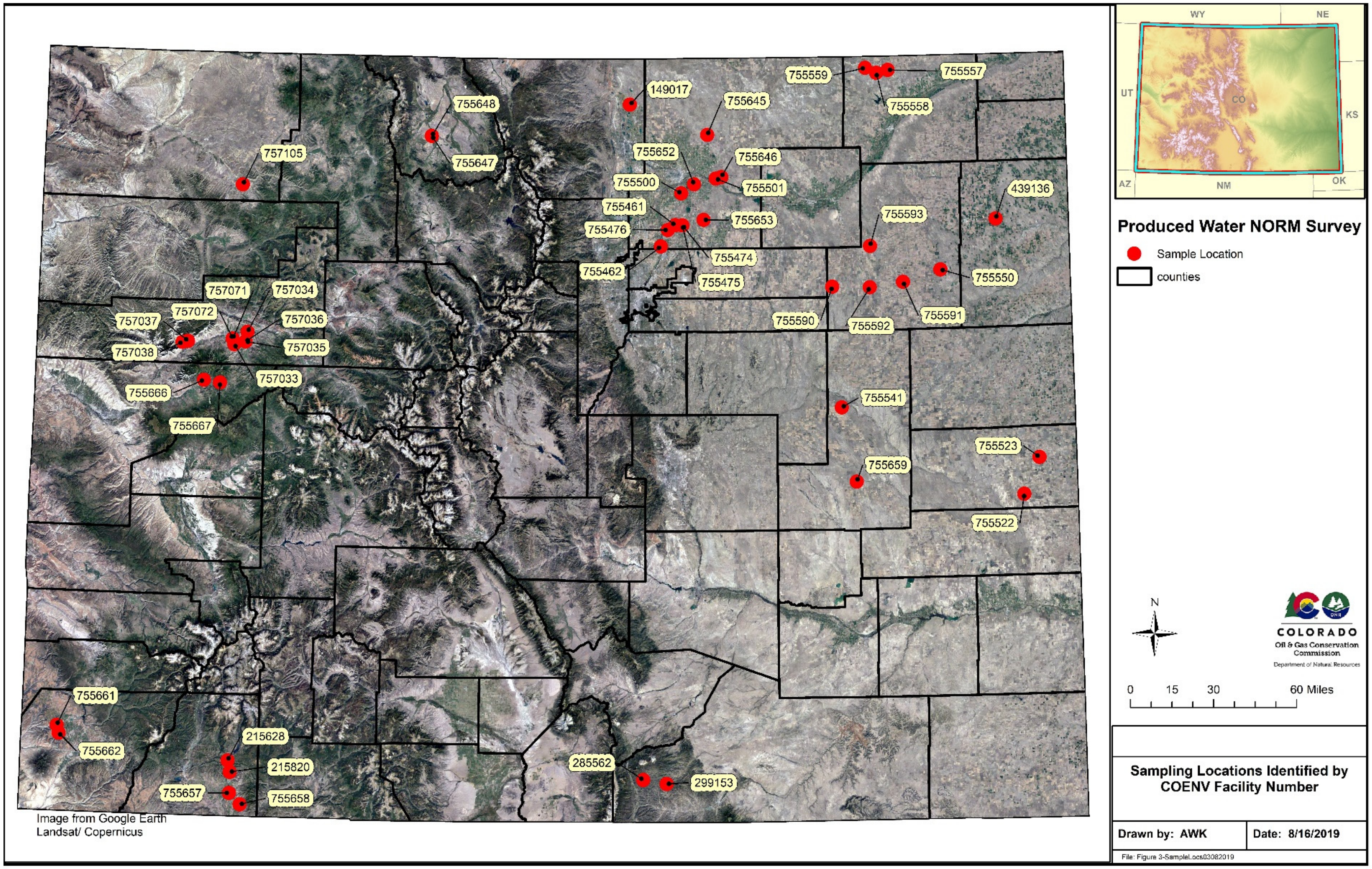

Figure 3. Sampling Locations Identified by COENV Facility Number

A list of facility names and corresponding facility number can be found in Appendix 1.

Table 1. Analytes, Matrices, Methods and Number of Samples Collected

Analyte(s)	Sample Matrices	Analytical Methods	Number of Samples Collected
gross alpha	PW/FSW/FFB	E900.0 as modified in ALS SOP 702r20, ALS SOP 786r7 (coprecipitation preparation) and 724r12	52*
gross beta	PW/FSW/FFB	E900.0 as modified in ALS SOP 702r20 and 724r12	
^{234}U, ^{235}U, ^{238}U	PW/FSW/FFB	DOE-U-02 as modified in ALS SOP 776r14, 778r14 and 714r13 (if total U>3µg/l)	3 analyzed of 52 collected
^{228}Th, ^{230}Th, ^{232}Th	PW/FSW/FFB	ASTM D3972 as modified in ALS SOP 776r14, 777r12 and 714r13 (if total Th >3µg/l)	0 analyzed of 52 collected[1]
^{210}Pb	PW/FSW/FFB	ALS SOP 704	52*
^{210}Po	PW/FSW/FFB	ASTM D3972 as modified in ALS SOP 711r10 and 714r13	52*
^{222}Rn	PW/FSW/FFB	SM 7500-Rn B as modified in ALS SOP 799r5 and 704r11	52*
^{222}Rn	natural gas	E903.1 as modified in ALS SOP 783r12	5**
^{224}Ra and ^{226}Ra	PW/FSW/FFB	E903.0 as modified in ALS SOP 701	52*
^{228}Ra	PW/FSW/FFB	E904.0 as modified in ALS SOP 749r3 and 724r12	52*
gamma emitters ^{40}K,-^{137}Cs, ^{208}Tl, ^{212}Pb, ^{212}Bi, ^{214}Pb, ^{214}Bi, ^{226}Ra/^{235}U, ^{228}Ac/^{228}Ra, ^{234m}Pa ^{234}Th	PW/FSW/FFB	E901.1 as modified in ALS SOP 739r12 and 713r14	52*
^{3}H	PW/FSW/FFB	SOP -electrolytic enrichment and GPC of H_2 gas	8**
^{14}C of DIC	PW/FSW/FFB	SOP –accelerator mass spectrometry (AMS)	8**
total metals B, Be, Ca, Cr, Fe, K, Li, Mg, Na, Ni, P, S, Si, V	PW/FSW/FFB	SW3010A/SW6010B	52*
total metals Al, Ag, As, Ba, Cd, Co, Cu, Mo, Mn, Na, Pb, Se, Sr, Th, Tl, U, Zn	PW/FSW/FFB	SW3010A/SW6020A	52*
dissolved metals Ba, Ca, Fe, K, Mg, Na, Si, Sr	PW/FSW/FFB	SW3005A/SW6010B	52*
pH	PW/FSW/FFB	SW9040	52*
specific conductance	PW/FSW/FFB	SM2510 B	52*
alkalinity (total, bicarbonate and carbonate) as $CaCO_3$)	PW/FSW/FFB	SM2320B	52*
total suspended solids	PW/FSW/FFB	SM2540 D	52*
total dissolved solids	PW/FSW/FFB	SM2540 C	52*
Anions Br, Cl, F, SO^4	PW/FSW/FFB	SW9056	52*
$\delta^{18}O$ & δD of H_2O	PW/FSW/FFB	laboratory SOP	51***
δ13C of DIC	PW/FSW/FFB	laboratory SOP	51***

Note: PW - produced water, FSW - frac source water and FFB - frac flowback fluid, * - 46 primary and 6 field duplicate samples
** - No duplicate samples collected, *** - 46 primary and 5 field duplicate samples. [1]Th was not detected ≥3µg/l in any samples so isotopic Th analyses were not triggered

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3. ANALYTICAL DATA

The analytical data presented and discussed in Section 3 is solely from the samples collected as part of this study. In Sections 4 and 5, data from other sources is compared and contrasted to the analytical data gathered as part of this study. The results discussed in this section and all analytical data gathered as part of this study can be accessed in tabular form through the COGCC environmental database using the Sample Site search tool under the Data tab on the COGCC website by querying the database facility number for each sampling site listed in Appendix 1. Lab reports can also be accessed as images using the sample site query tool to get to the scout card for each sample site sampled as during this study (http://cogcc.state.co.us/data.html#/cogis). Using the sample site query under the data tab search by facility number provided in Appendix 1 and then by clicking on the docs tab of the scout card for that facility. Hyperlinks to the scout card for each sample site are also present in Appendix 1 in the column containing the facility numbers which lead to sample data that can be downloaded from the scout card as well as laboratory reports that can be downloaded (under the Docs tab). An example of the hyperlink to the scout card from one facility sampled as part of this study is **299153** . Data from 2017 sampling event is part of this study. Other sampling of produced water from this CBM well was performed as parts of other investigations.

3.1 Radiochemistry Results

All water samples were analyzed for radionuclides as shown in Table 1. Gross alpha and gross beta analyses are not isotope-specific but provide alpha and beta activity screening data. Uranium isotopic data for three samples was triggered, and specific isotope data from all water samples for ^{238}U progeny are discussed below in descending order along the decay scheme from ^{226}Ra, then ^{222}Rn, followed by ^{210}Pb and ^{210}Bi. At five sites, gas samples were collected for ^{222}Rn analysis so that comparison to ^{222}Rn activities in water and gas samples from the same sites could be done. Two progeny of ^{232}Th were analyzed by specific isotope methods as discussed below in descending order in the decay chain with discussion of ^{228}Ra analyses followed by discussion of ^{224}Ra analyses. Gamma spectroscopy analyses of all water samples were also completed. Discussion of gamma results are presented in three parts with ^{40}K and man-made isotopes presented first, followed by gamma analysis of U progeny, and finally discussion of gamma analysis of thorium progeny.

3.1.1 Gross Alpha and Gross Beta

Analysis of gross alpha and gross beta activities of each water sample was performed using GFPC techniques. Samples for gross alpha analysis were prepared using a co-precipitation step in order to improve the sensitivity of samples with high concentrations of dissolved solids. All samples were prepared and counted within four days of collection in an effort to minimize changes in samples due to in-growth of isotopes or loss of short-lived gas phase derived alpha or beta emitters. The preparation of samples for both analyses involves evaporation to dryness. Any volatile components such as ^{222}Rn and ^{220}Rn would be lost in the preparation. Thus, both gross alpha and gross beta activities are from non-volatile radionuclides only and are reported in units of picoCuries/liter (pCi/l).

Table 2. Summary Statistics for Gross Alpha & Gross Beta

	gross α		gross β	
Statistic	**all samples**	**samples >MDC**	**all samples**	**samples >MDC**
Minimum pCi/l	0.1	1.73	0.3	1.98
Median pCi/l	34.1	40.3	62.5	81.5
Mean pCi/l	118.5	130.9	268.8	316.8
Maximum pCi/l	730	730	5,710	5,710
Std. Deviation pCi/l	183.3	188.8	845.0	911.9
n=	52	47	52	44
# U flag included in calculation	5	0	8	0
range of & median MDC of U flag results pCi/l (number of U flag results)	2.6-3.7, 3.4 (n=5)		1.9-10.6, 3.7 (n=8)	

Table 2 summarizes the ranges of gross alpha and gross beta activities reported by the laboratory for water samples collected as part of this study. The maximum gross alpha activity detected was 730pCi/l (facility 755523). The minimum activity was <0.1 pCi/l (facility 755658) among samples with reported activities greater than minimum detectable concentration (MDC). The median gross alpha activity was 40.3 pCi/l among samples with reported activities >MDC. The gross alpha activity detected is related to naturally occurring alpha-emitting radionuclides such as ^{226}Ra, ^{224}Ra, and ^{210}Po and other alpha emitters (Figures 1 and 2) found in the water samples. Appendix 2 lists the results of the gross alpha and gross beta analytical procedures for each sample. The appendix also includes two sigma (Ϭ) total propagated uncertainties (TPU), MDCs, and qualifiers (data flags), if any, that the lab applied to these results.

The x-axis of Figure 4 is gross alpha activity in pCi/l. The y-axis is number of samples with activities in the given ranges (20pCi/l ranges). The histogram of gross alpha activities (Figure 4) is skewed to the lower concentrations (to the left of the histogram). The majority of the samples (71%) had reported gross alpha activities of <100 pCi/l. The clustering of results towards lower gross alpha activities with a few scattered higher activities indicate that the data in not normally distributed but is likely representative of the broader population of gross alpha activities in Colorado produced waters.

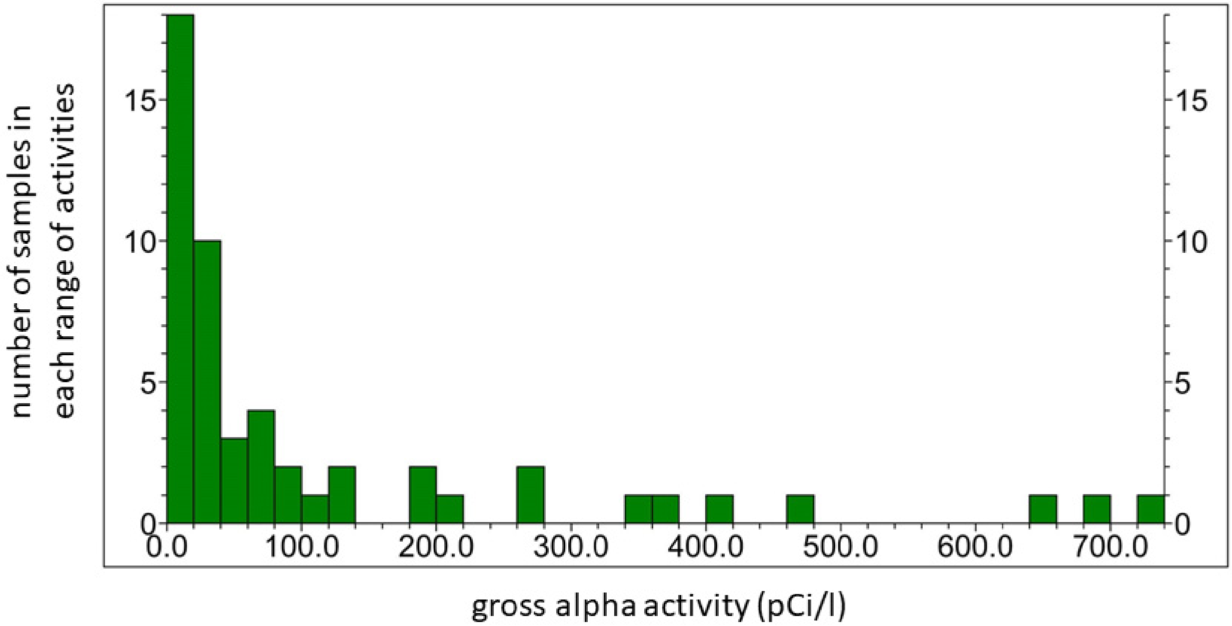

Figure 4. Histogram of Gross Alpha activities

y-axis = number of sample results in each range of 20pCi/l. x-axis = reported gross alpha activity in units of pCi/l.

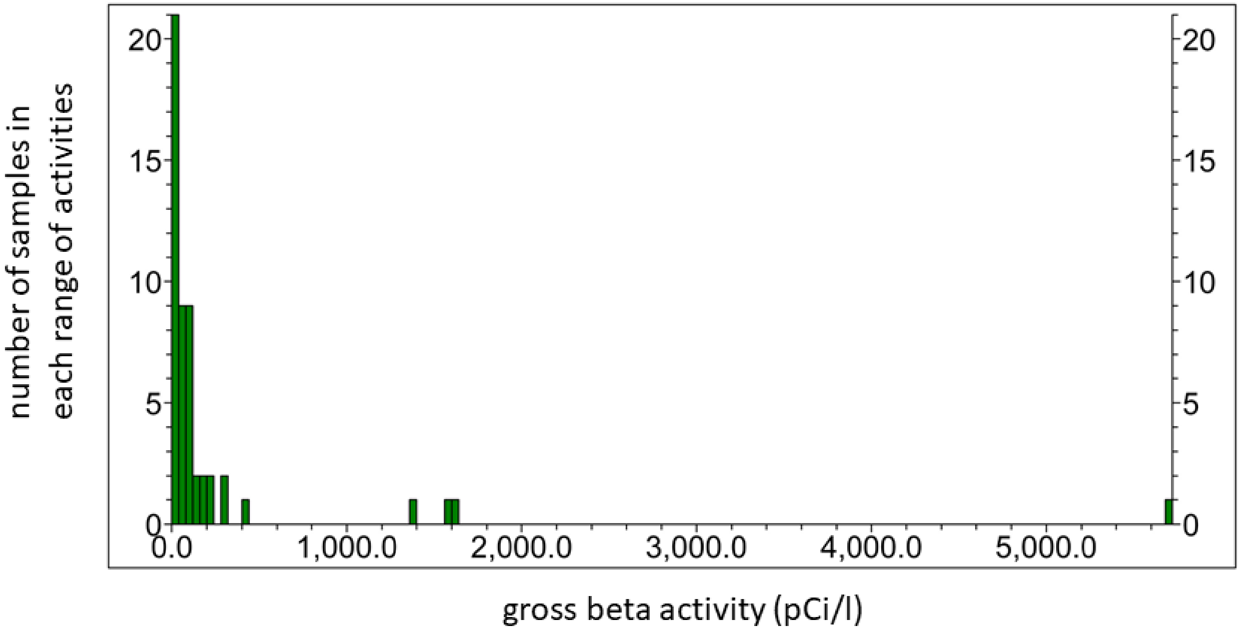

Figure 5. Histogram of Gross Beta Activities

y-axis = number of sample results in each range of 40pCi/l. x-axis = reported gross beta activity in units of pCi/l.

The maximum gross beta activity detected was 5,710pCi/l (facility 755645). The minimum activity was <0.3pCi/l (U flag, facility 215628) among all samples. The median gross beta activity was 81.5 pCi/l among samples with reported activities >MDC. The x-axis of Figure 5 is gross beta activity in pCi/l. The y-axis is number of samples with activities in the given ranges (40pCi/l ranges). The histogram of gross beta activities detected (Figure 5) is skewed to the lower concentrations (to the left of Figure 5). The majority of the samples (67%) had reported gross beta activities of <100pCi/l. The clustering of results towards lower gross beta activities with a few scattered higher activities indicate that the data in not normally distributed but is likely representative of the broader population of gross alpha activities in Colorado produced waters.

The reported gross beta activities are partly related to naturally occurring ^{228}Ra and ^{40}K in the formation fluids or naturally occurring ^{40}K in waters used for drilling or completion. ^{40}K is one of the most abundant naturally occurring radionuclides and occurs in clay minerals and other K-bearing minerals in shales and in K mineral-bearing sandstones that make up the bulk of non-carbonate oil and gas reservoirs. Potassium may also be present in rocks containing evaporitic minerals such as sylvite, halite and anhydrite. Other beta emitters that may be present include ^{210}Pb and other beta emitting radionuclides as shown in Figures 1 and 2. The four samples with gross beta activity >1000pCi/l all contain elevated levels of potassium which likely comes from dissolution of minerals in proximity to or in the producing formations itself.

Gross alpha analyses are not isotope-specific but provide alpha activity screening data. Figure 6 illustrates the ranges of gross alpha activity for each sample collected and provides a broad overview of gross alpha activities in produced water from across the state. The geologic basins of the state are labeled on the map, and producing formation(s) from which each sample was collected is included in abbreviated form along with the facility number of the sampling location. The smallest marker on the Figure 6 map indicates measured gross alpha activities <15pCi/l, which is the current Colorado groundwater standard (excluding activities of U and Rn) and is the same as the drinking water standard for gross alpha activity. The laboratory-reported gross alpha activities of 16 of the samples were <15pCi/l.

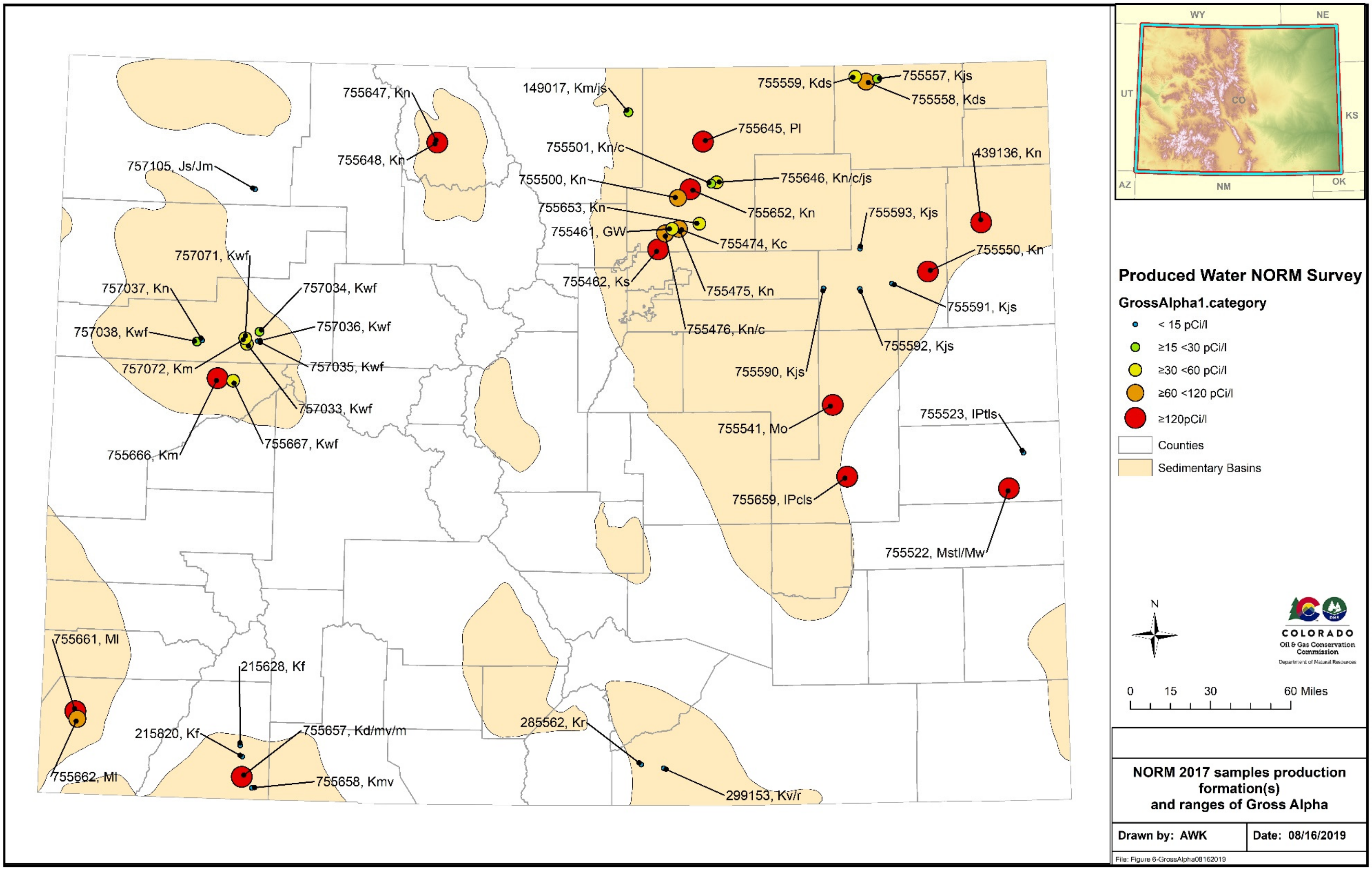

Figure 6. Ranges of Gross Alpha Activities

Each facility sampled is captioned with facility number and an abbreviated identification of the formation(s) from which oil and/or gas and water samples were produced. A legend explaining the abbreviated formations names can be found at the end of Appendix 1.

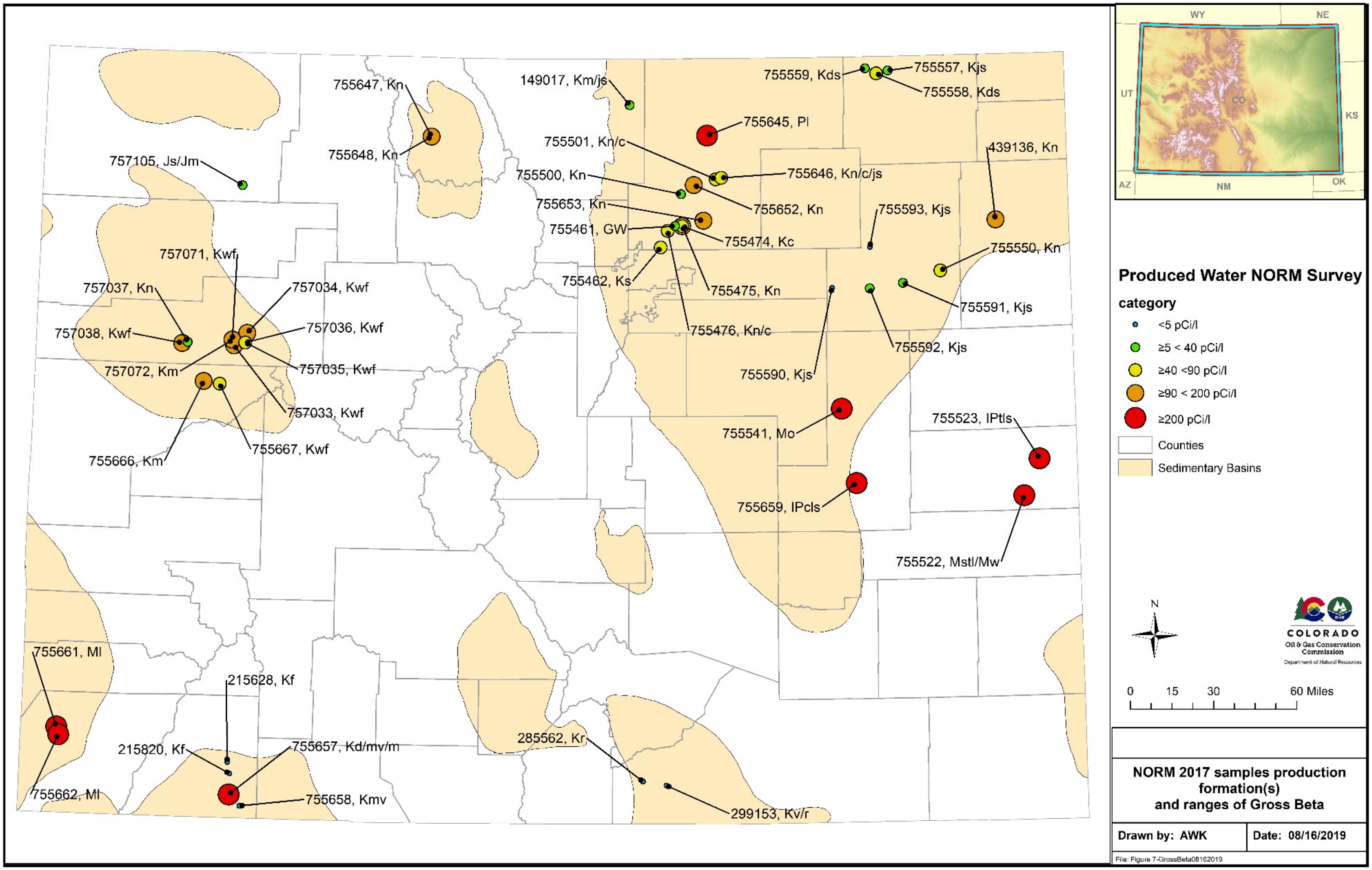

Figure 7. Ranges of Gross Beta Activities

Each facility sampled is captioned with facility number and an abbreviated identification of the formation(s) from which oil and/or gas and water samples were produced. A legend explaining the abbreviated formations names can be found at the end of Appendix 1.

Gross beta analyses are not isotope-specific but provide beta activity screening data. Figure 7 illustrates the ranges of gross beta activity for each sample collected and provides a broad overview of gross beta activities in produced water from across the state. The geologic basins of the state are labeled on the map, and producing formation(s) from which each sample was collected is included in abbreviated form along with the facility number of the sampling location. The smallest marker on the Figure 7 map indicates measured gross beta activities <5 pCi/l, which is the current Colorado groundwater standard for the sum of ^{226}Ra and ^{228}Ra and is the same as the drinking water standard for combined ^{226}Ra and ^{228}Ra activities. ^{226}Ra is an alpha emitter while ^{228}Ra is a beta emitter and together with ^{40}K, the two radionuclides are likely the primary beta emitters in many of these samples. The laboratory-reported gross beta activities of eight samples were <5 pCi/l. Isotope-specific analyses of ^{226}Ra and ^{228}Ra will be presented and discussed in a later section of this report.

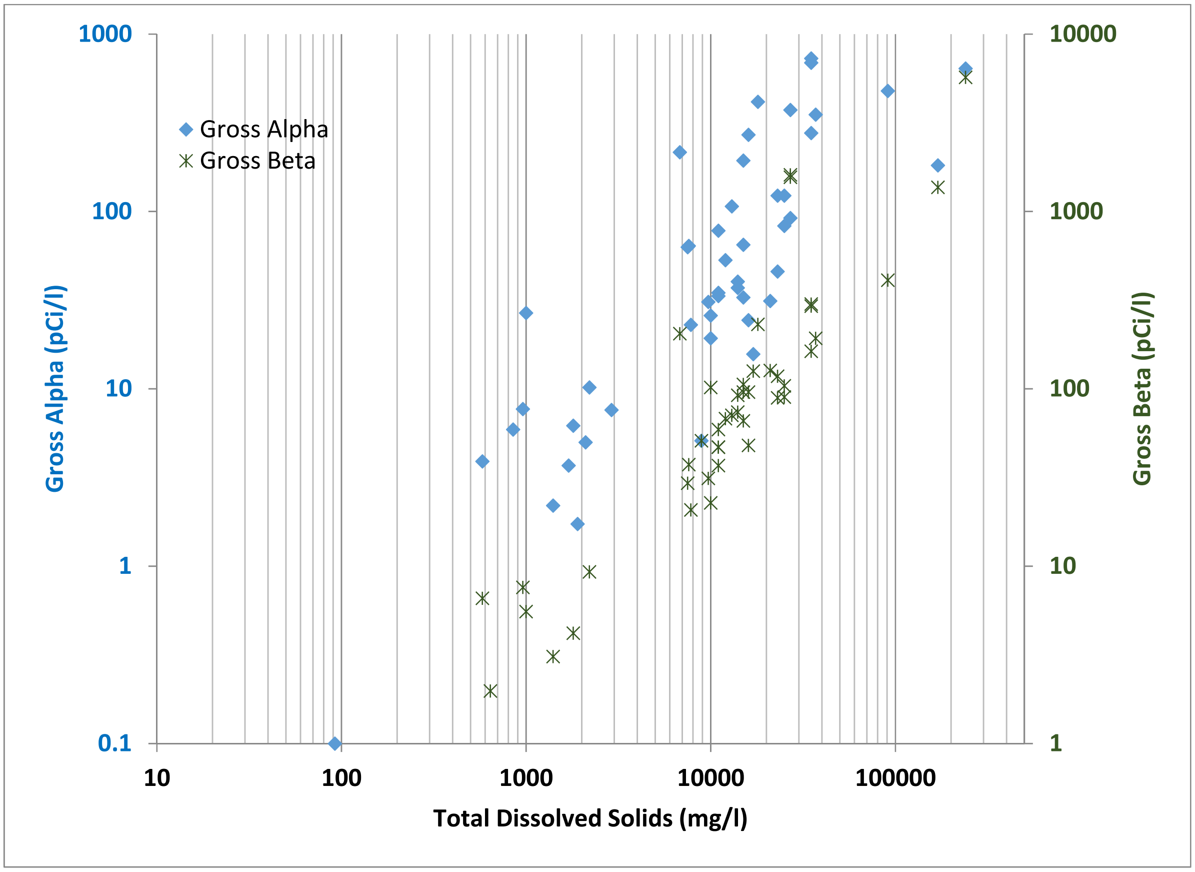

Figure 8. Gross Alpha and Gross Beta Activities Plotted versus TDS Concentration

x-axis at bottom is the concentration of TDS of each sample in mg/l and the axis is in a logarithmic scale between 10-500,000mg/l. Left y-axis = gross alpha activity of each sample (**blue diamonds**) and is a logarithmic scale between 0.1-1,000pCi/l. Right y-axis = gross beta activity of each sample (**green asterisk**) and is a logarithmic scale between 1-10,000pCi/l.

As shown on Figure 8, both gross beta and alpha activities show a general trend of increasing activity with increasing total dissolved solids concentrations. The scale of the x-axis for TDS is a logarithmic scale. Also note that that gross alpha is plotted against the left side y-axis and that gross beta is plotted against the right side y-axis. The left and right side y-axes have different scales due to differences in the ranges of measured gross alpha and gross beta activities, and both y-axes have logarithmic scales.

3.1.2 Isotopic Analyses of U and ^{238}U Progeny

Uranium isotopic analyses of three water samples were triggered by the presence of total U >3 µg/l. All water samples were analyzed for four specific isotope analyses (^{226}Ra, ^{222}Rn[aq], ^{210}Pb, and ^{210}Po). Gas samples were collected at five sites for analysis of ^{222}Rn(g). Specific isotopic analyses of U and ^{238}U progeny for the gas and water samples are discussed in the next sections.

3.1.2.1 ^{234}U, ^{235}U, and ^{238}U

The reported U concentration (total by SW6020) of three samples was >3 µg/l, which triggered isotopic analysis for ^{234}U, ^{235}U, and ^{238}U. Table 3 provides a brief summary of the total U analyses (SW6020).

Uranium was isolated from the three samples by chemical separation techniques. An isotopic tracer (^{232}U) was added in a known activity level to each of the samples prior to the chemical separation process. The use of the tracer allows the lab to determine the efficiency of the separation procedure. Appendix 3 lists the results of the U isotopic analyses procedures for each sample with total U >3 µg/l. The appendix also includes two б TPUs, MDCs, and qualifiers (data flags), if any, that the lab applied to these results.

Table 3. Total U Summary

Statistic	Total Uranium >MDL
Minimum µg/l	0.03
Median µg/l	0.9
Mean µg/l	4.35
Maximum µg/l	23
Std. Deviation µg/l	8.33
n=	7
n of U flag not included in statistics =	45
range of & median MDL of the 45 U flag results µg/l	0.023-0.75, 0.075

The maximum activity observed of ^{234}U in the three samples for which U isotopic analysis was triggered is 10 pCi/l (facility 755461) and the minimum activity for ^{234}U was 0.46 pCi/l (facility 439136). The maximum activity reported for ^{235}U was 0.4 pCi/l (facility 755461). The measured activity of ^{235}U was below the MDC in the two other samples for which U isotope analysis was conducted. The maximum activity observed for ^{238}U was 8 pCi/l (facility 755461), and the minimum activity of ^{238}U was 0.038 pCi/l (facility 439136). The sample with the highest total U concentration and highest activities of the U isotopes analyzed by alpha spectroscopy is a sample from a near surface aquifer used as drilling and completion source water and is not E&P produced water.

The concentration of total U in the other 49 samples were less than the concentration in the three samples for which isotopic U analysis was triggered by a factor of 3 or greater. It can be assumed that the activities of U isotopes in the other 49 samples collected as part of the study are less than the ranges of activities discussed above. For example, the highest MDL of a U flagged result was 0.75 µg/l, which would equate to a ^{238}U activity of 0.25 pCi/l.

3.1.2.2 ^{226}Ra

All water samples were analyzed for ^{226}Ra by alpha spectroscopy. Radium was isolated from the sample by chemical separation techniques. An isotopic tracer (^{217}At) was added in known activity level to each of the samples prior to the chemical separation process. The use of the isotopic tracer allows the lab to determine the efficiency of the separation procedure. Table 4 provides a summary of ^{226}Ra activities reported by the lab from water samples collected as part of this study. Appendix 4 lists the results of the ^{226}Ra isotopic analysis procedures for each water sample. The appendix also includes two σ TPUs, MDCs, and qualifiers (data flags), if any, that the lab applied to these results.

Table 4. Summary Statistics for ^{226}Ra

	^{226}Ra	
Statistic	**all samples**	**samples >MDC**
Minimum pCi/l	-0.0580675	0.14902
Median pCi/l	15.1013	20.80225
Mean pCi/l	52.4	61.8
Maximum pCi/l	376.858	376.858
Std. Deviation pCi/l	83.7	87.9
n=	52	44
n <MDC =	8	0
range of & median MDC of the eight U flag results pCi/l	0.0719-16.66, 0.351	

The maximum activity for ^{226}Ra was reported as 376.8 pCi/l in the Lyons Fm. produced water sample collected from facility 755645. The minimum ^{226}Ra activity was measured at 0.149 pCi/l in sample 755658 among samples with reported activities >MDC. The median activity observed for all samples was 20.8 pCi/l among samples with reported activities >MDC. The activity of ^{226}Ra was reported as <MDC in eight samples.

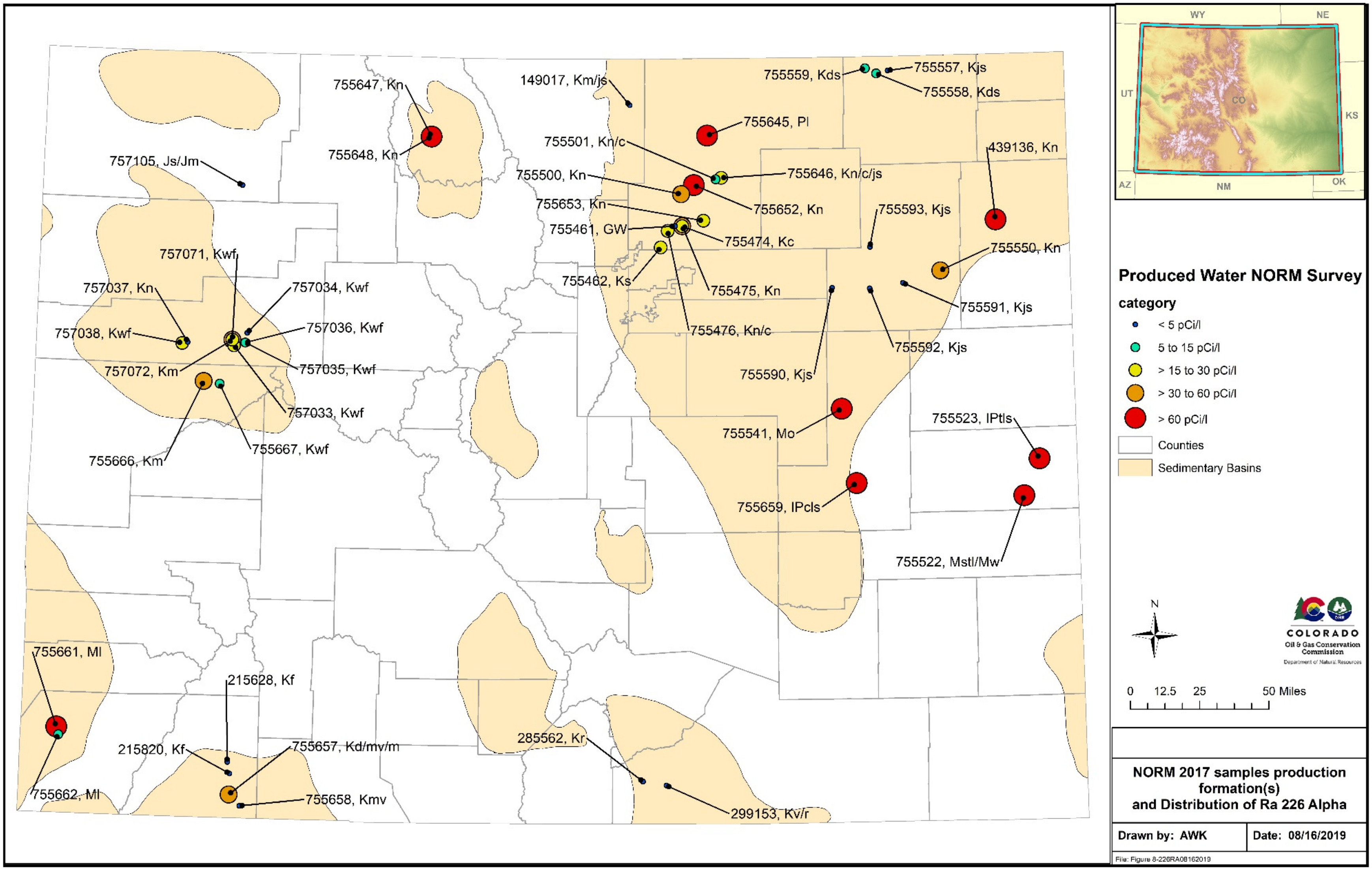

Figure 9. Ranges of ^{226}Ra Activities

Each facility sampled is captioned with facility number and an abbreviated identification of the formation(s) from which oil and/or gas and water samples were produced. A legend explaining the abbreviated formations names can be found at the end of Appendix 1. Size of circle at a site is larger with increasing ^{226}Ra activity of sample collected at the facility.

Figure 9 illustrates the ranges of ^{226}Ra activity for each sample collected and provides a broad overview of ^{226}Ra activities in produced water from across the state. The ^{226}Ra activities shown here are from the specific isotope analysis by alpha spectroscopy following chemical separation described in this section. The geologic basins and producing formation(s) from which each sample was collected is included in abbreviated form along with the facility number of the sampling location. The smallest marker on the Figure 9 map indicates measured ^{226}Ra activities <5 pCi/l, which is the current Colorado groundwater standard for the sum of ^{226}Ra and ^{228}Ra and is the same as the drinking water standard for combined ^{226}Ra and ^{228}Ra activities. The laboratory reported ^{226}Ra activities of 16 samples (31%) were <5 pCi/l.

All five of the produced water samples from CBM wells had reported ^{226}Ra activities <5 pCi/l. Two of the CBM-produced water samples were collected from Raton Basin wells, and the other three were collected from San Juan Basin wells (includes one well sampled in duplicate). Six produced water samples were collected from Cretaceous J Sand Fm. wells in eastern Colorado. All of the produced water samples from eastern Colorado J Sand Fm. wells had reported ^{226}Ra activities <5 pCi/l. ^{226}Ra is a radionuclide that is progeny of ^{238}U, as shown in Figure 1. In each of the CBM and J Sand Fm. produced water samples, total U concentrations were reported as not detected with detection limits of 0.075 µg/l. Uranium concentrations were anticipated to be low in produced water samples due to assumed reducing geochemical conditions (Hem, 1992; IAEA, 2003). The rocks in contact with the produced water could contain U even if geochemical conditions limit the solubility in water. As shown in Figure 1, U atoms present in rocks are assumed to be the source of ^{226}Ra in produced water. In one analysis found in the literature (Levinthal, 2016), total U in Niobrara Fm. rock samples was 27.9 µg/g or approximately 19 pCi/g of ^{238}U. In the five CBM and six J Sand Fm. produced water samples with ^{226}Ra activities <5 pCi/l, the rocks in contact with the produced water may be assumed to have relatively low content of total U and by assumption also have low concentrations of the most naturally abundant isotope (^{238}U) because of the low activities of the Ra progeny of ^{238}U. A second factor limiting ^{226}Ra activities in these 11 samples may be the major ion composition of the produced waters.

The water sample with the highest total U concentration was the shallow groundwater source water sample collected at facility **755461**, which had the second lowest activity of ^{226}Ra of samples with activities greater than sample-specific MDC. The same sample had the second highest ^{222}Rn activity of all water samples collected in this study. ^{222}Rn is the progeny of ^{226}Ra, and both are progeny of ^{238}U. The high ^{222}Rn activity simultaneous with very low ^{226}Ra activity indicates the presence of Ra in the aquifer solids, even if very low in the water sample collected perhaps due to the geochemistry of the water sample itself, which has dominant anions of sulfate and bicarbonate alkalinity unlike many of the produced waters, which are more frequently dominated by chloride anions.

3.1.2.3 ^{222}Rn (in H_2O)

All water samples were analyzed for ^{222}Rn by liquid scintillation counting. An aliquot of each water sample was mixed with scintillation cocktail and then counted. Table 5 provides a summary of ^{222}Rn activities reported by the lab from water samples collected as part of this study. Appendix 4 lists the results of the ^{222}Rn analyses for each water sample. The appendix also includes two Ϭ TPUs, MDCs, and qualifiers (data flags), if any, that the lab applied to these results.

Table 5. Summary Statistics for ^{222}Rn in H_2O

Statistic	^{222}Rn in H_2O	
	all samples	samples >MDC
Minimum pCi/l	-22	32
Median pCi/l	24	74.5
Mean pCi/l	58.3	136.6
Maximum pCi/l	681	681
Std. Deviation pCi/l	117.1	161.1
n=	52	20
n <MDC =	32	0
range of & median MDC of the 32 U flag results pCi/l	26-44, 34	

The maximum activity for ^{222}Rn was reported as 681 pCi/l in facility 755645. ^{222}Rn is the direct progeny of ^{226}Ra, and the reported activity of ^{226}Ra in the same sample was also the highest among all samples collected as part of this study. The minimum activity was reported as 32 pCi/l in facility 215628 for samples with activities >MDC. The median activity observed for samples with activities >MDC was 74.5 pCi/l. The reported activities of 32 water samples were <MDC.

3.1.2.4 ^{222}Rn (in Gas Samples)

Five natural gas samples were collected as part of this study. Each of the gas samples was analyzed for ^{222}Rn by direct counting in an alpha scintillation cell. Table 6 provides a summary of ^{222}Rn activities reported by the lab from gas samples. Appendix 5 lists the results of the ^{222}Rn analyses for each natural gas sample. The appendix also includes two σ TPUs, MDCs, and qualifiers (data flags), if any, that the lab applied to these results.

Table 6. Summary Statistics for ^{222}Rn in Gas

Statistic	^{222}Rn in Gas
Minimum (pCi/l)	17.5
Median (pCi/l)	46
Mean (pCi/l)	61.2
Maximum (pCi/l)	150
Std. Deviation (pCi/l)	53.9
n=	5

The maximum activity for ^{222}Rn in gas was reported as 150 pCi/l in facility 755501. The minimum activity was reported as 17.5 pCi/l in facility 755474. The median activity reported for all gas samples was 46 pCi/l.

3.1.2.5 ^{210}Pb

All water samples were analyzed for ^{210}Pb by liquid scintillation counting. ^{210}Pb was isolated from the sample by chemical separation techniques. Lead (Pb) was added in a known concentration level to each of the samples prior to the chemical separation process. The use of the chemical tracer allows the lab to determine the efficiency of the separation procedure. Table 7 provides a summary of ^{210}Pb activities reported by the lab from water samples collected as part of this study. Appendix 4 lists the results of the ^{210}Pb isotopic analysis procedures for each water sample. The appendix also includes two Ϭ TPUs, MDCs, and qualifiers (data flags), if any, that the lab applied to these results.

Table 7. Summary Statistics for ^{210}Pb

	^{210}Pb	
Statistic	**all samples**	**samples >MDC**
Minimum pCi/l	-3.7	0.71
Median pCi/l	0.265	
Mean pCi/l	5.90	
Maximum pCi/l	253	253
Std. Deviation pCi/l	35.3	
n=	52	4
n <MDC =	48	0
range of & median MDC of the 48 U flag results pCi/l	0.56-8.1, 0.81	

The maximum activity reported for ^{210}Pb was reported as 253 pCi/l in Lyons Fm. produced water sampled at facility 755645. The minimum activity was reported as 0.71 pCi/l in facility 755657. The activities reported by the lab for 48 samples were <MDC. No mean or median calculation are included for the four samples in which the ^{210}Pb activity exceeded the MDC due to the small population of activities reported as >MDC.

3.1.2.6 ^{210}Po

All water samples were analyzed for ^{210}Po by alpha spectroscopy. Polonium was isolated from the sample by chemical separation techniques. An isotopic tracer (^{209}Po) was added in a known activity level to each of the samples prior to the chemical separation process. The use of the isotopic tracer allows the lab to determine the efficiency of the separation procedure. Table 8 provides a summary of ^{210}Po activities reported by the lab from water samples collected as part of this study. Appendix 4 lists the results of the ^{210}Po isotopic analysis procedures for each water sample. The appendix also includes two Ϭ TPUs, MDCs, and qualifiers (data flags), if any, that the lab applied to these results.

Table 8. Summary Statistics for ^{210}Po

Statistic	^{210}Po	
	All Samples	samples >MDC
Minimum pCi/l	-0.2	0.2
Median pCi/l	0.29	0.88
Mean pCi/l	1.79	8.30
Maximum pCi/l	72	72
Std. Deviation pCi/l	9.96	22.4
n=	52	10
n <MDC =	42	0
range of & median MDC of the 42 U flag results pCi/l	0.3-56, 0.76	

The maximum activity for ^{210}Po was reported as 72 pCi/l in Lyons Fm. produced water collected at facility 755645. The minimum activity was reported as 0.2 pCi/l in facility 755590 in samples with activities >MDC. The median activity observed for samples with activities >MDC was 0.8 pCi/l. The reported activities of 42 water samples were <MDC.

3.1.3 Isotopic Analyses of Th and ^{232}Th Progeny

No thorium isotopic analyses of three water samples were triggered by the presence of total Th >3 µg/l. Two specific isotope analyses of ^{232}Th progeny were performed on all water samples (^{228}Ra and ^{224}Ra), and the results are presented in sections 3.1.3.2 and 3.1.3.3.

3.1.3.1 ^{228}Th, ^{230}Th, and ^{232}Th

The reported concentration of Th (total by SW6020) in all samples was <3 µg/l. No analyses of the isotopic composition of Th were triggered because of the relatively low reported concentrations of Th in water samples collected as part of this study. The presence of Th (total) was reported as greater than the lab's sample-specific method detection limit in only three water samples. The maximum reported sample-specific detection limit was 0.96 µg/l total Th as illustrated in Table 17.

Table 9 provides a brief summary of the total U analyses (SW6020). The maximum reported total Th concentration of 0.31 µg/l would result in a ^{232}Th activity of 0.034 pCi/l. The ^{232}Th activity of all samples would be <0.11 pCi/l from the highest not detected concentration of 0.96 µg/l.

Table 9. Summary Statistics for Th

Statistic	Total Thorium >MDL
Minimum µg/l	0.04
Median µg/l	
Mean µg/l	
Maximum µg/l	0.31
Std. Deviation µg/l	
n=	3
n of U flag not included in statistics =	49
range of & median MDL of the 49 U flag results µg/l	0.025-0.96, 0.091

3.1.3.2 ^{228}Ra

All water samples were analyzed for ^{228}Ra by GFPC of the ^{228}Ac progeny of ^{228}Ra. Radium was isolated from the sample by chemical separation techniques. Barium was added in a known concentration level to each of the samples prior to the chemical separation process. The use of the chemical tracer allows the lab to determine the efficiency of the separation procedure. Table 10 provides a summary of ^{228}Ra activities reported by the lab. Appendix 6 lists the results of the ^{228}Ra isotopic analysis procedures for each water sample. The appendix also includes two Ϭ TPUs, MDCs, and qualifiers (data flags), if any, that the lab applied to these results.

Table 10. Summary Statistics for ^{228}Ra

	^{228}Ra	
Statistic	**all results**	**>MDC**
Minimum pCi/l	-0.18	0.94
Median pCi/l	6.1	9.65
Mean pCi/l	14.20	18.29
Maximum pCi/l	221	221
Std. Deviation	31.84	35.37
n=	52	40
n <MDC included in statistics above=	12	0
range of & median MDC of the 12 U flag results pCi/l	0.63-1.79, 0.705	

The maximum activity for ^{228}Ra was reported as 221 pCi/l in facility 755645. The minimum activity was reported as 0.94 pCi/l in facility 755593 in samples with activities >MDC. The median activity observed for samples with activities >MDC was 9.65 pCi/l. The reported activities of 12 water samples were <MDC.

Figure 10 illustrates the ranges of ^{228}Ra activity for each sample collected and provides a broad overview of ^{228}Ra activities in produced water from across the state. The ^{228}Ra activities shown here are from the specific isotope analysis by GFPC following chemical separation previously described in this section. The geologic basins and producing formation(s) from which each sample was collected is included in abbreviated form along with the facility number of the sampling location. The smallest marker on the Figure 10 map indicates measured ^{228}Ra activities <5 pCi/l, which is the current Colorado groundwater standard for the sum of ^{226}Ra and ^{228}Ra, and is the same as the drinking water standard for combined ^{226}Ra and ^{228}Ra activities. The laboratory reported ^{228}Ra activities of 23 samples (44%) were <5 pCi/l.

All five of the produced water samples from CBM wells had reported ^{228}Ra activities <5 pCi/l. Two of the CBM produced water samples were collected from Raton Basin wells, and the other three CBM produced water samples were collected from San Juan Basin wells (includes one well sampled in duplicate). Six produced water samples were collected from Cretaceous J sand wells in eastern Colorado. Five of the six produced water samples from eastern Colorado J sand wells had reported ^{228}Ra activities <5 pCi/l. ^{228}Ra is a radionuclide that is progeny of ^{232}Th as shown previously in Figure 2. In each of the CBM and J sand produced water samples, total Th concentrations were reported as not detected with detection limits of 0.091 µg/l. Thorium concentrations were anticipated to be low in produced water samples due to the very low solubility of thorium in most aqueous systems (Langmuir and Herman, 1980).

The rocks in contact with the produced water may have significant concentrations of Th even if solubility limits the concentration of Th in produced water. One analysis found in the literature (Levinthal, 2016) of total Th in Niobrara Fm. rock samples was 5.2 µg/g or approximately 0.6 pCi/g of ^{232}Th. As shown in Figure 2, Th atoms present in rocks are presumed to be the source of ^{228}Ra in produced water, in that ^{232}Th in minerals undergoes alpha decay to ^{228}Ra, which is considered to be more soluble in water than the Th parent nuclide. In the cases of the five CBM and five J sand produced water samples with ^{228}Ra activities <5 pCi/l, the rocks in contact with the produced water may be assumed to have relatively low content of total Th and by assumption also have low concentrations of the most naturally abundant isotope (^{232}Th) because of the low activities of the Ra progeny of ^{232}Th. A second factor limiting ^{228}Ra activities in these ten samples may be the major ion composition of the produced waters, which are of relatively low dissolved solids concentration. The TDS concentration of nine of the ten samples is <5,000 mg/l. In all ten of the samples with ^{228}Ra activities <5 pCi/l, the TDS concentration is <10,000 mg/l and less than the median TDS concentration of samples (11,000 mg/l).

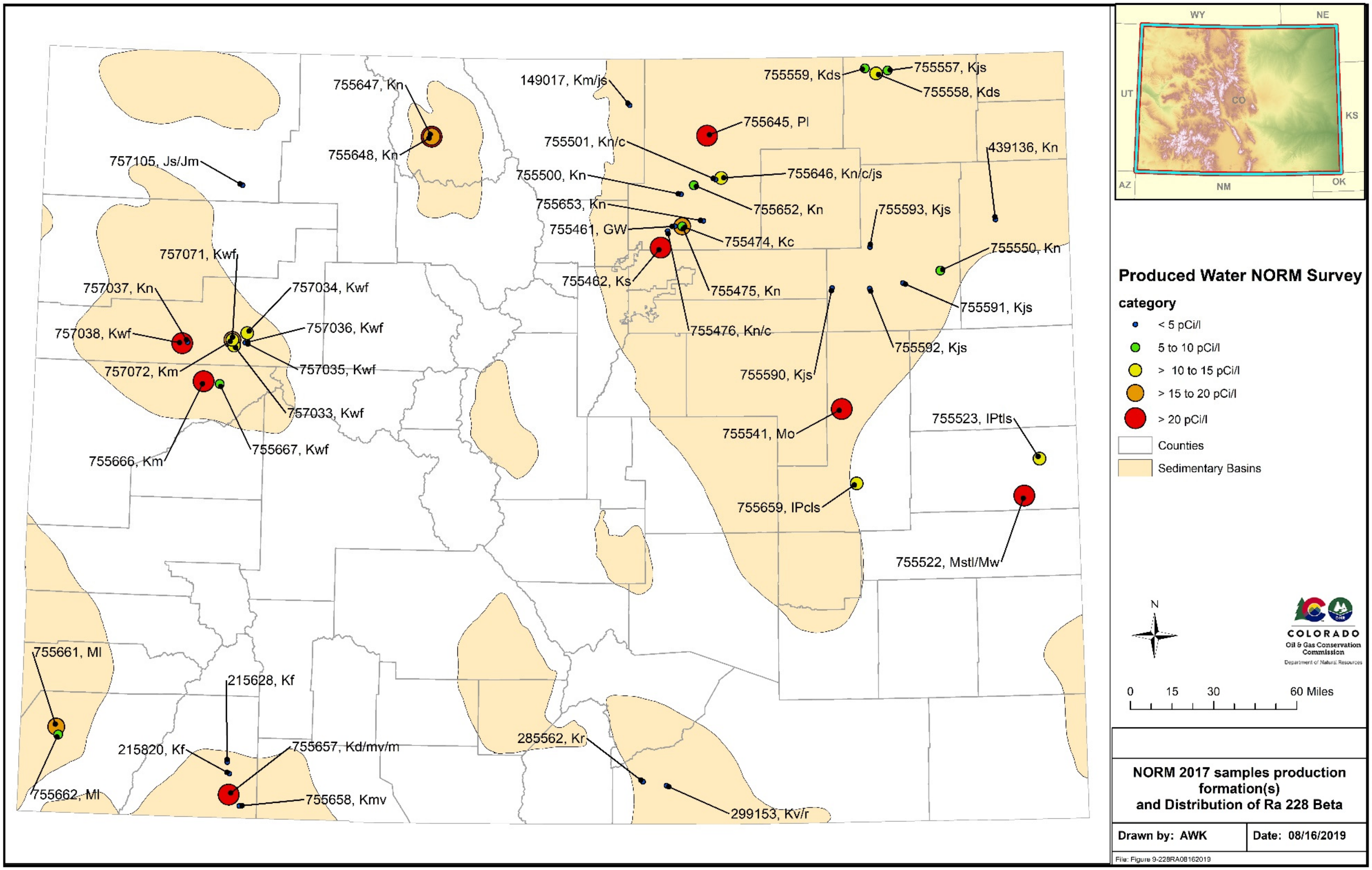

Figure 10. Ranges of ^{228}Ra Activities

Each facility sampled is captioned with facility number and an abbreviated identification of the formation(s) from which oil and/or gas and water samples were produced. A legend explaining the abbreviated formations names can be found at the end of Appendix 1. Size of circle at a site is larger with increasing ^{228}Ra activity of sample collected at the facility.

3.1.3.3 ^{224}Ra

All water samples collected as part of this study were analyzed for ^{224}Ra by alpha spectroscopy. Radium was isolated from the sample by chemical separation techniques. An isotopic tracer (^{217}At) was added in a known activity level to each of the samples prior to the chemical separation process. The use of the isotopic tracer allows the lab to determine the efficiency of the separation procedure. Table 11 provides a summary of ^{224}Ra activities reported by the lab. Appendix 6 lists the results of the ^{224}Ra isotopic analyses procedures for each sample. The appendix also includes two Ϭ TPUs, MDCs, and qualifiers (data flags), if any, that the lab applied to these results.

Table 11. Summary Statistics for ^{224}Ra

	^{224}Ra	
Statistic	**all results**	**>MDC**
Minimum pCi/l	-4.89899	0.51125
Median pCi/l	3.95378	16.1393
Mean pCi/l	10.45	19.90
Maximum pCi/l	78.0933	78.0933
Std. Deviation	16.08	18.51
n=	52	20
n <MDC included in statistics above=	32	0
range of & median MDC of the 32 U flag results pCi/l	0.759-102.7, 13.76	

The maximum activity of ^{224}Ra was reported as 78.0933 pCi/l in sample 755657. The minimum activity in samples with activities >MDC was reported as 0.51125 pCi/l in sample 755461. The median activity observed for samples with activities >MDC was 9.65 pCi/l. The reported activities of 32 water samples were <MDC.

3.1.4 Analysis by Gamma Spectrometry

Gamma spectroscopic analyses of water samples were performed to identify and quantify gamma-emitting radionuclides using specific libraries that include members of ^{232}Th and ^{238}U decay chains, as well as ^{235}U, ^{137}Cs, and ^{40}K. The thorium decay chain radionuclides include ^{208}Tl, ^{212}Pb, ^{212}Bi, and ^{228}Ra/Ac. Uranium decay chain radionuclides include ^{214}Bi, ^{214}Pb, ^{234m}Pa, ^{234Th}, and ^{226}Ra. Although it contributes only modestly to the overall activity of NORM mixtures, ^{235}U, the head of the third natural decay chain, the actinium chain, emits an intense gamma ray. Note that ^{137}Cs is not expected in samples but rather it is included as a reference nuclide against which relative detection capability is assessed. The presence of ^{235}U in samples can interfere with the analysis of ^{226}Ra by gamma spectroscopy due to the near coincidence in their gamma ray energies.

Several gamma spectrometry analytes in aqueous matrices that are routinely requested of and performed by laboratories may produce unreliable results. The analyses of the potentially unreliable results are being requested here as screening for ^{214}Pb and ^{214}Bi and to allow assessment of data quality relative to definitive isotope-specific tests for Ra and U isotopes. They include:

- ^{226}Ra, ^{228}Ra, and ^{235}U – Due to relatively low sensitivity by gamma spectrometry, results for these radionuclides may show very high uncertainty until they are present in high concentration. Isotopic determinations of ^{226}Ra, ^{228}Ra and ^{235}U (when performed) are considered to be the definitive results and the gamma spectrometry measurements as supporting data.
- ^{226}Ra – Determinations for ^{226}Ra by gamma spectroscopy are not specific for this radionuclide and may exhibit high errors in precision and accuracy due to spectral interferences. Results are used in this study only as qualitative indicators of the possible presence of ^{226}Ra in samples, and a more definitive isotope-specific testing for ^{226}Ra was performed on all samples.
- ^{214}Pb and ^{214}Bi – These two isotopes are frequently used as indicators of ^{222}Rn in samples. These results are unreliable since water samples for gamma analysis are generally not managed to protect against loss of radon during sampling, transport, storage, preparation, and analysis.

3.1.4.1 ^{40}K and Man-Made Nuclides

Each of the water samples collected in this study was analyzed for ^{40}K, ^{60}Co, ^{137}Cs and, ^{241}Am by gamma spectroscopy with direct counting. Table 12 provides a summary of reported activities for 40 and man-made radionuclides. Appendix 7 lists the results of the gamma analysis for these analytes for each water sample. The appendix also includes two σ TPUs, MDCs, and qualifiers (data flags), if any, that the lab applied to these results.

Table 12. Summary Statistics for Gamma Analytes (^{40}K and Man-Made Nuclides)

Statistic	^{40}K all samples	^{40}K samples >MDC	^{60}Co	^{137}Cs	^{241}Am
Minimum pCi/l	-74	338			
Median pCi/l	14				
Mean pCi/l	138.7				
Maximum pCi/l	2,840	2,840			
Std. Deviation pCi/l	448.1				
n=	52	5			
n <MDC or NQ =	47		52	52	52
range of & median MDC of the U flag results pCi/l	71-230, 62		5.2-13.7, 8.8	4.9-10, 7.55	6.4-360, 56

Only 5 of the 52 samples collected for ^{40}K analysis had activities above the MDC. The maximum activity reported was in facility 755645 at 2,840 pCi/l, and the minimum reported ^{40}K activity in samples with activities >MDC was 338 pCi/l in facility 755659. No activities greater than the sample-specific MDC were reported for man-made radionuclides in samples collected as part of this project. Thus, no statistics except for those related to sample-specific MDC are included in Table 12 for ^{60}Co, ^{137}Cs, and ^{241}Am.

As discussed earlier, the major source of ^{40}K in the produced water samples is from K-bearing minerals of rocks the water has been in contact with (such as clays, feldspars, and evaporite minerals) and with other possible contributions when KCl brines have been used in drilling, completions and workover operations. Figure 11 shows the strong correlation of ^{40}K activities with K total metals analytical concentrations for the five samples with ^{40}K activities >MDC by gamma analysis. Two of the five samples are from CO_2 wells in Montezuma County completed in Mississippian Leadville Limestone. Two of the five were from oil and gas wells in southeastern Colorado (Lincoln County) with one completed in the Mississippian Osage Limestone and one completed in the Pennsylvanian Cherokee Fm. The last of the five was from an oil well in Weld County completed in the Permian Lyons Fm. COGCC records indicated that none of the five wells with the highest ^{40}K activities in produced water were completed using hydraulic fracturing techniques. The five facilities with detectable ^{40}K activities in produced water samples from this study also were reported by the lab to have the highest five concentrations of total K determined by SW6010 analysis.

Produced water from facility 755645 had the highest reported gross beta activity as well as the highest activity of ^{40}K. Other beta emitters for which analyses were performed include progeny of ^{238}U (^{234}Th, ^{234m}Pa, ^{214}Pb, ^{214}Bi, ^{214}Po, ^{210}Pb, and ^{210}Bi) and progeny of ^{232}Th (^{228}Ra, ^{228}Ac, ^{212}Pb, ^{212}Bi, and ^{208}Tl) as shown in Table 1. Other beta emitters reported above the sample-specific MDCs in produced water samples from facility 755645 included ^{214}Pb, ^{214}Bi, ^{210}Pb, ^{228}Ra, ^{228}Ac, and ^{212}Pb.

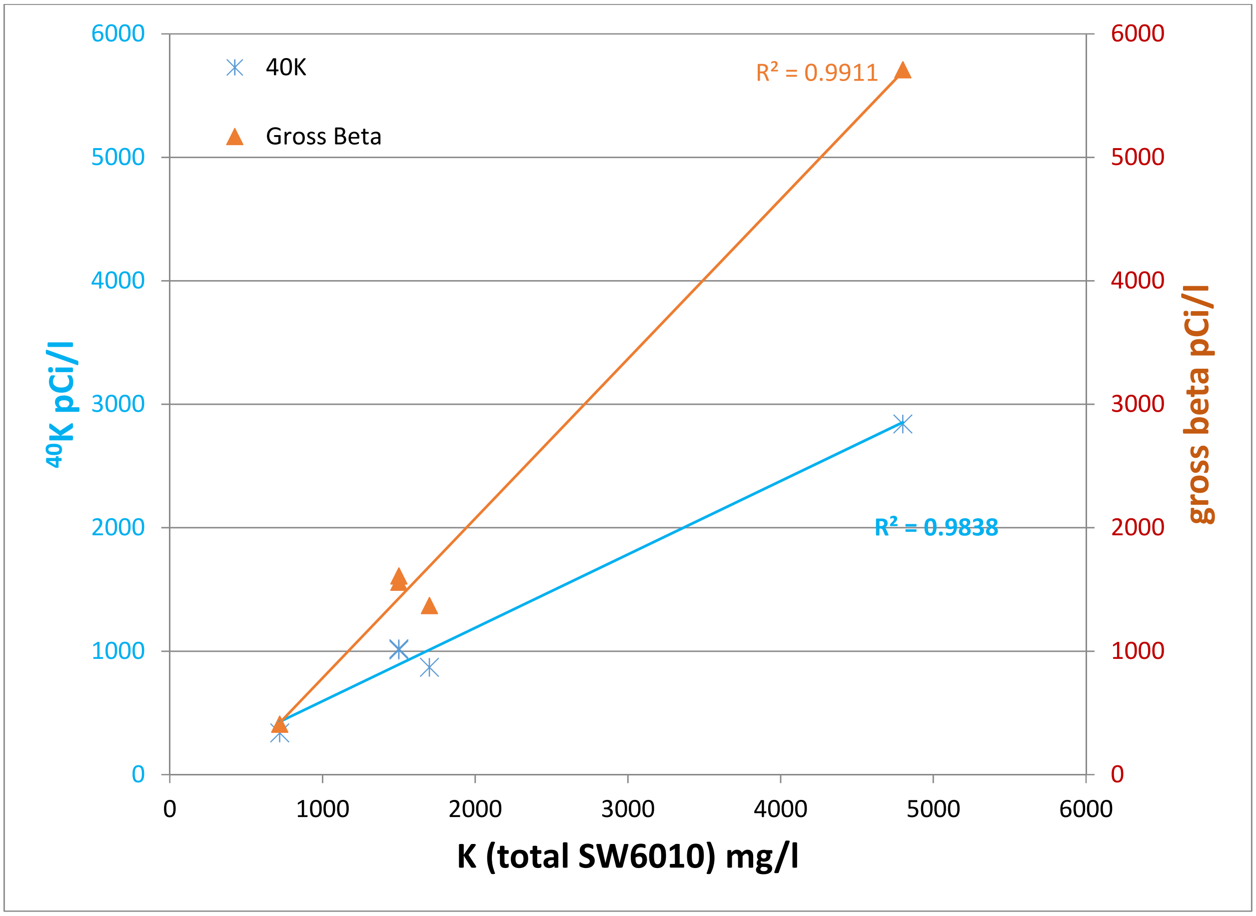

Figure 11. ^{40}K and Gross Beta Activities in Comparison to K Concentration

x-axis at bottom is the concentration of potassium of each sample in mg/l. Left y-axis = activity ^{40}K in each sample (**blue asterisk**). Right y-axis = gross beta activity of each sample (orange diamond). Each axis is plotted in arithmetic scales.

3.1.4.2 ^{238}U Progeny and ^{235}U

Each of the water samples collected in this study was analyzed for ^{235}U as well as for ^{234}Th, ^{234m}Pa, ^{226}Ra, ^{214}Pb, and ^{214}Bi by gamma spectroscopy with direct counting. ^{234}Th, ^{234m}Pa, ^{226}Ra, ^{214}Pb, and ^{214}Bi are progeny of the most abundant U isotope (^{238}U). A summary of uranium-related gamma analytes is in Table 13. Appendix 8 lists the results of the gamma analysis for these analytes for each water sample. The appendix also includes two σ TPUs, MDCs, and qualifiers (data flags), if any, that the lab applied to these results.

The gamma spectroscopy determined activities of ^{235}U, $^{234\mathrm{Th}}$, and ^{234m}Pa in water samples collected as part of this study were reported as less than the sample-specific MDC for all water samples. The sample-specific MDCs can be found in Appendix 8. No summary statistics for these three analytes except for those related to sample-specific MDCs are included in Table 13. Three water samples were analyzed for activities of ^{235}U by chemical separation followed by alpha spectroscopy, and this analysis was discussed previously with data presented in Appendix 11. The highest reported alpha spectroscopy activity of ^{235}U was 0.4 pCi/l which is far less than any of the sample-specific MDCs for ^{235}U by gamma spectroscopy.

Table 13. Summary Statistics for Uranium-Related Gamma Analytes

	^{235}U	^{234}Th	^{234m}Pa	^{226}Ra		^{214}Pb		^{214}Bi	
Statistic				all samples	samples >MDC	all samples	samples >MDC	all samples	samples >MDC
Minimum pCi/l				-400	156	-10	26	-9	25
Median pCi/l				30	280	8	49	11	54
Mean pCi/l				57.2	267.7	21.1	63.5	20.9	66.1
Maximum pCi/l				400	390	121	121	119	119
Std. Deviation pCi/l				125.4	81.9	32.3	36.3	30.8	35.7
n=	52	52	52	52	7	52	14	52	12
n<MDC or flagged NQ	52	52	52	45		38		40	
range of & median MDC of the U flag results pCi/l	18-76, 39	44-300, 156	830-2000, 1350	116-2000, 190		7.3-32, 20		13.7-40, 25	

The maximum activity for ^{226}Ra by gamma spectroscopy was reported as 390 pCi/l in facility 755645. The minimum ^{226}Ra activity in the seven samples in which activities were >MDC was reported as 156 pCi/l in facility 755661. The median activity reported for all samples with activities >MDC was 280 pCi/l. All of the ^{226}Ra results by gamma spectroscopy were flagged a qualifier of SI indicating possible spectral interference. The SI flag indicates the gamma spectroscopy results for ^{226}Ra may have a high bias when analyzed at the 186.21 kiloelectron volts (keV) utilized in these analyses. The positive interference could be present from the 185.72 keV photopeak of ^{235}U if that isotope is present in the samples at significant activities. The median MDC reported by the lab for the gamma analysis of ^{226}Ra in samples from this project was 232 pCi/l. The mean MDC reported by the lab for the chemical separation followed by alpha spectroscopy analysis of ^{226}Ra was 2.9 pCi/l. The gamma spectroscopy ^{226}Ra activities were greater than the sample-specific MDC in 7 of the 52 samples. The alpha spectroscopy ^{226}Ra activities were greater than the sample-specific MDC in 44 of the 52 samples.

Due to the relatively low sensitivity by gamma spectrometry, results for ^{226}Ra may show very high uncertainty until they are present in high concentration. Isotopic determinations of ^{226}Ra by alpha spectroscopy following chemical separation are considered to be the definitive results with 40 out of 52 alpha spectroscopy ^{226}Ra activities reported as greater than the sample-specific MDC (Appendix 8). The less sensitive gamma spectrometry measurements with 7 of 52 gamma spectroscopy ^{226}Ra activities greater than sample-specific MDCs are considered as supporting data in this study.

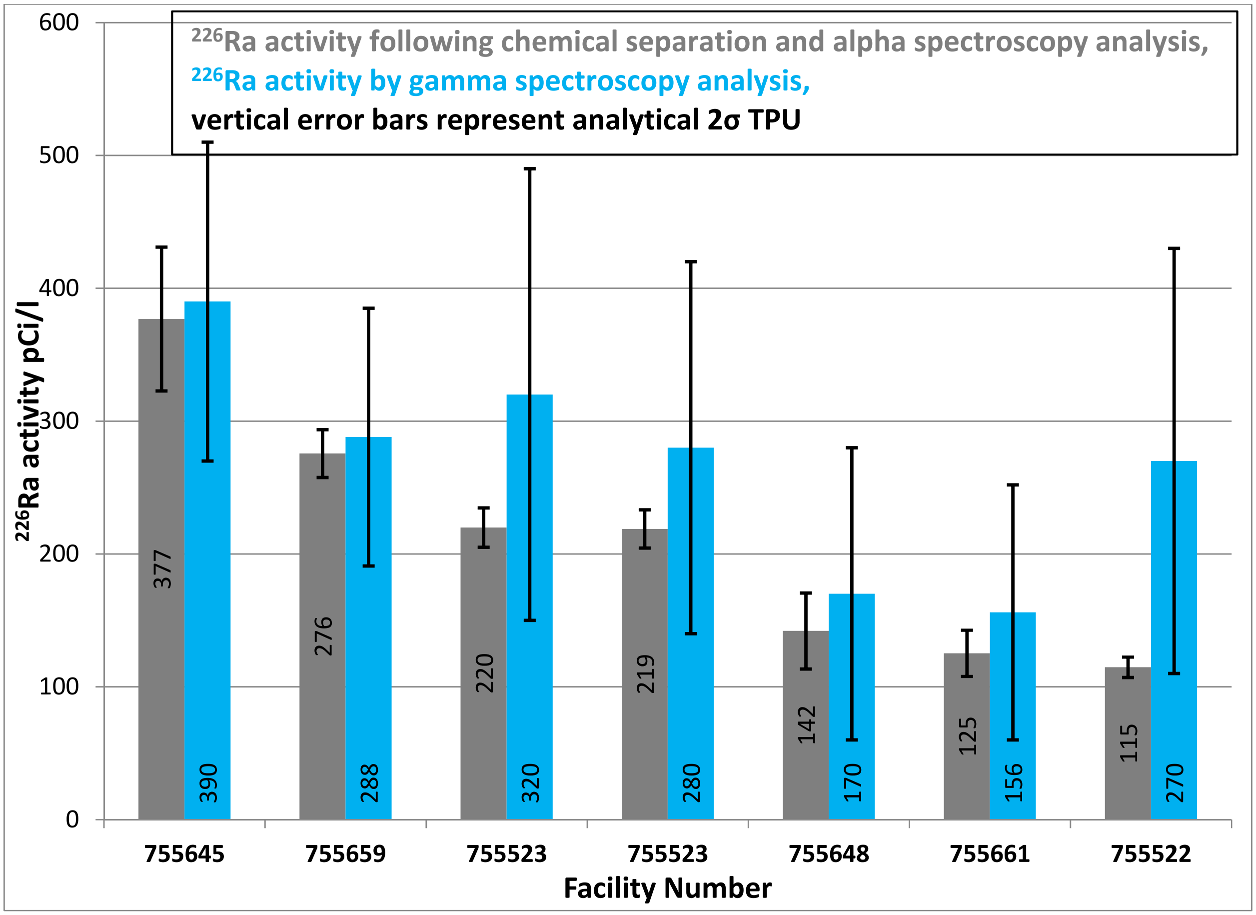

Figure 12. Comparison of ^{226}Ra Activities by Two Analytical Methods

The isotope-specific analyses utilizing chemical separation and alpha spectroscopy analysis of ^{226}Ra activities were discussed in a previous section of this report. Figure 12 includes measured activities for ^{226}Ra utilizing the two analytical approaches described previously for all seven samples in which ^{226}Ra was reported as greater than sample-specific MDCs by the less sensitive gamma spectroscopy method. Error bars representing the laboratory-reported 2σ TPU associated with each result are plotted. Pairs of reported activities from each of the seven samples are similar when including the associated analytical uncertainty. Facility 755523 was sampled in duplicate in the field.

The maximum activity reported for ^{214}Pb as determined by gamma spectroscopy is 121 pCi/l in facility 755541. The minimum reported activity in samples with activities >MDC is 26 pCi/l in facility 755500.

The median activity of samples with reported activities >MDC is 49 pCi/l. ^{214}Pb activities were reported as greater than the sample-specific MDC in 14 of the 52 samples.

The maximum activity for ^{214}Bi reported is 119 pCi/l in facility 755541. The minimum reported activity from samples with reported activities >MDC is 25 pCi/l in facility 755657. The median activity observed for all samples with reported activities >MDC is 56 pCi/l.

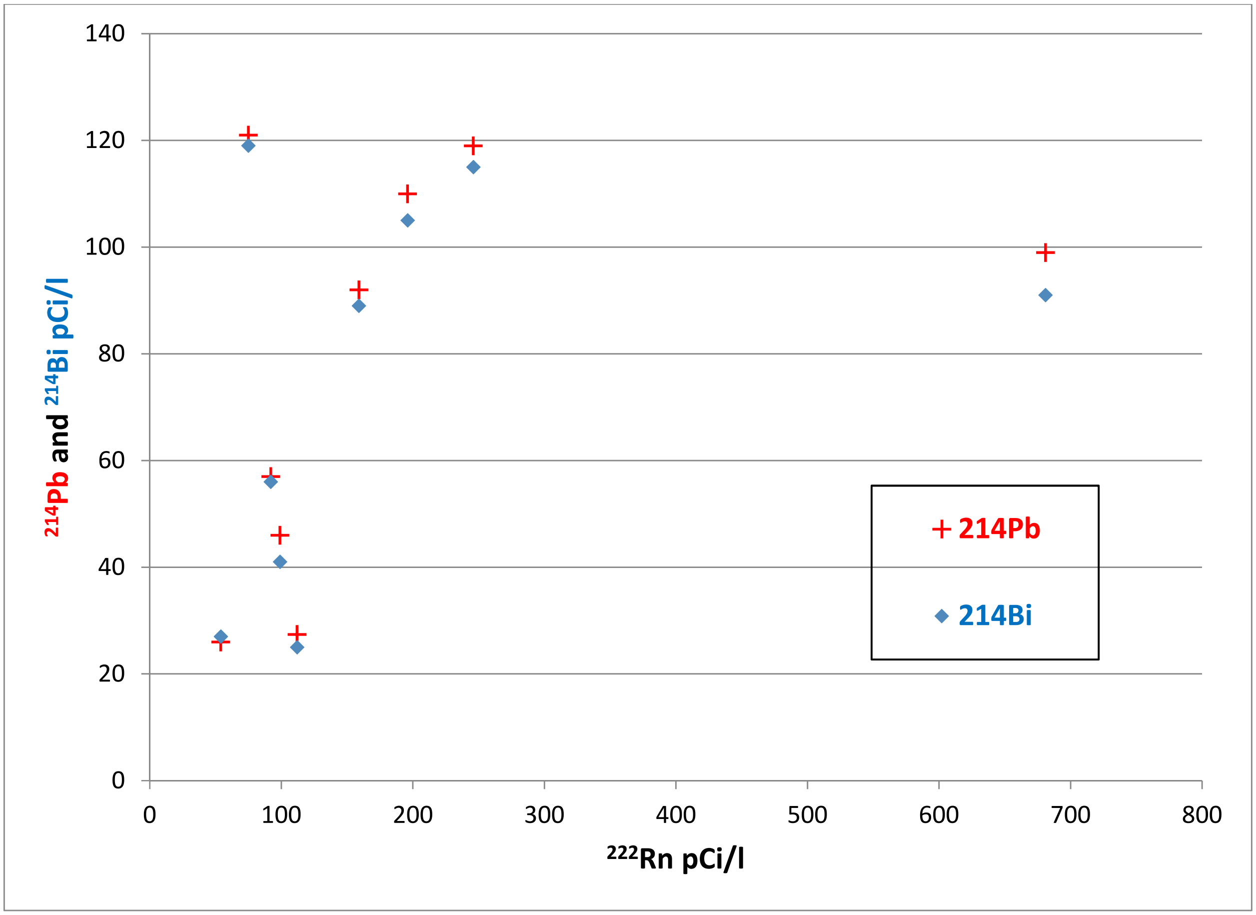

Figure 13. Comparison of ^{222}Rn Activities versus Gamma Spectroscopy ^{214}Pb and ^{214}Bi Activities

As discussed above the presence of ^{214}Pb and ^{214}Bi are frequently used as indicators of the presence of ^{222}Rn in samples. Direct measurements of ^{222}Rn were performed in all water samples collected as part of this study. The liquid scintillation results for ^{222}Rn are considered to be more definitive indicators of the activity of ^{222}Rn than are the gamma analysis for the radon progeny since water samples for gamma analysis are generally not managed to protect against loss of radon during sampling, transport, storage, preparation, and analysis. The gamma-based activities for ^{214}Pb and ^{214}Bi are decay-corrected based on the assumption that these progeny of ^{226}Ra are in secular equilibrium with the parent radium nuclide. Loss of the gaseous intermediate radionuclide ^{222}Rn during gas phase separation from produced water near the wellhead or during sampling and sample handling invalidates the assumption of secular equilibrium, which likely causes the decay corrected gamma spectroscopy-based ^{214}Pb and ^{214}Bi activities to be erroneous.

Figure 13 includes data from all nine samples for which activities of ^{222}Rn (by liquid scintillation) and ^{214}Pb and ^{214}Bi (both by gamma spectroscopy) were simultaneously greater than sample-specific

MDCs. The sample with the highest ^{222}Rn activity, which plots to the right of the chart, arguably should also have the highest activities of ^{214}Pb and ^{214}Bi under ideal sampling, storage, and analytical conditions. If samples are homogenous and no loss of radon gas occurs from the sample analyzed by gamma spectroscopy, then one would expect the ^{214}Pb and ^{214}Bi activities to be several times greater than were reported by the lab for this sample.

3.1.4.3 Th Progeny

Each of the water samples collected in this study was analyzed for ^{228}Ra, ^{228}Ac, ^{212}Pb, and ^{212}Bi by gamma spectroscopy with direct counting. Each of these radionuclides is the progeny of the most abundant Th isotope (^{232}Th). A summary of reported activities of thorium-related gamma analytes is in Table 14. Appendix 9 lists the results of the gamma analysis for these analytes for each water sample. The appendix also includes two σ TPUs, MDCs, and qualifiers (data flags), if any, that the lab applied to these results. Summary statistics for these thorium-derived gamma analytes are in Table 14.

Table 14. Summary Statistics for ^{232}Th-Related Gamma Analytes

	^{228}Ra		^{228}Ac		^{212}Pb		^{212}Bi
Statistic	**all samples**	**samples >MDC**	**all samples**	**Samples >MDC**	**all samples**	**samples >MDC**	**all samples**
Minimum	-11	35	-11	35	-5	18	
Median	19	39.5	19	39.5	4		
Mean	22.1	71	22.1	71	5.2		
Maximum	229	229	229	229	29	29	
Std. Deviation	32.4	77.5	32.4	77.5	6.6		
n=	52	6	52	6	52	3	0
n<MDC or NQ flag included in statistics	46	0	46	0	49	0	52
range of & median MDC of the U flag results pCi/l	22-58, 35.5				9.2-20, 14.3		67-153, 106

The gamma spectroscopy ^{228}Ra activities are derived from emissions of the short-lived ^{228}Ac progeny of ^{228}Ra (Figure 2) based on an assumption that these two nuclides are in secular equilibrium. The reported activities for these two radionuclides are identical for each sample as seen in Appendix 9. The maximum gamma spectroscopy activity for ^{228}Ra was reported as 229 pCi/l in facility 755645. The minimum reported activity from samples with reported activities >MDC is 35 pCi/l in facility 755462. The median activity observed for all samples with reported activities >MDC is 39.5 pCi/l. No separate discussion of ^{228}Ac gamma results is presented since the data is identical to the ^{228}Ra data discussed.

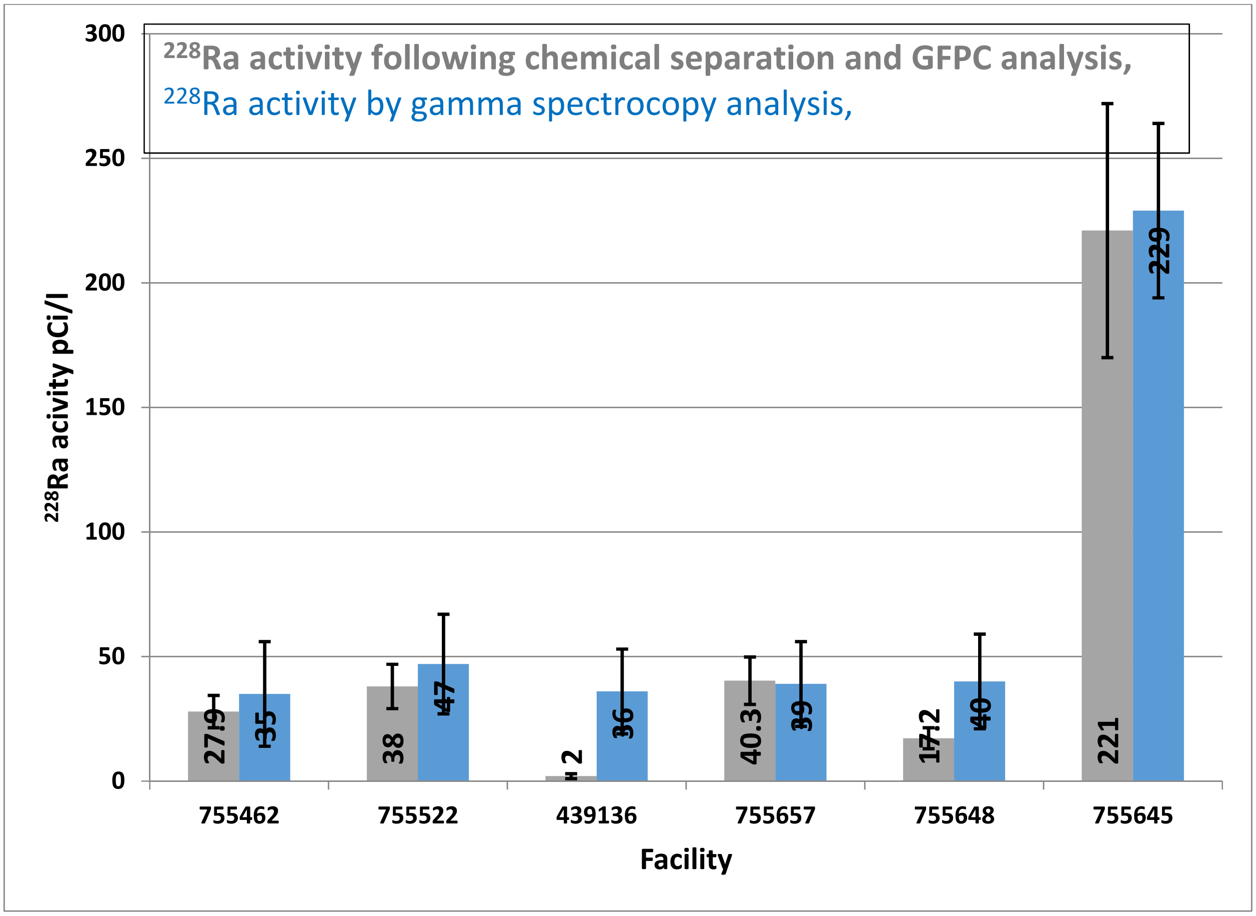

Figure 14. Comparison of ^{228}Ra Activities by Two Analytical Methods

Due to relatively low sensitivity by gamma spectrometry, results for ^{228}Ra may show very high uncertainty until they are present in high concentration. Isotopic determinations of ^{228}Ra by GFPC following chemical separation are considered to be the definitive results and the gamma spectrometry measurements as supporting data. The isotope-specific analyses utilizing chemical separation and GFPC analysis of ^{228}Ra activities were discussed in a previous section of this report with data in Appendix 9. Figure 14 includes measured activities for ^{228}Ra utilizing the two analytical approaches described previously for the six samples in which ^{228}Ra was reported as greater than sample-specific MDCs by gamma spectroscopy. Error bars representing the laboratory reported 2σ TPU associated with each result are plotted.

Pairs of reported activities from four of the six samples (755462, 755522, 755657, and 755645) are similar when associated analytical uncertainties are included. The sample results of the two analytical methods including lab estimated analytical uncertainty for two of the samples (439136 and 755468) are not similar. Samples from facility 439136 and 755648 have the lowest isotope-specific ^{228}Ra activity of the six, and relatively low sensitivity and high uncertainty of the second analytical technique (gamma spectroscopy) discussed previously may be a cause of the discrepancy between ^{228}Ra activities seen in these two samples. The gamma ^{228}Ra activity for sample 755648 was flagged as TI (tentative identification) due to a poor spectral match to reference spectra which may indicate the gamma ^{228}Ra activity for this sample may be biased high.

The maximum gamma spectroscopy activity for ^{212}Pb was reported as 29 pCi/l in facility 755646. The minimum reported activity from samples with reported activities >MDC is 18 pCi/l in facility 755647. Activities of ^{212}Pb >MDC were reported in three samples and no median, mean of standard deviation are presented due to the small number of results greater than sample-specific MDC.

The activities of ^{212}Bi were reported as less than the sample-specific MDC for all water samples. The sample-specific MDCs can be found in Appendix 9. No summary statistics for ^{212}Bi except for those related to sample-specific MDC are included in Table 14.

The lab calculates activities for ^{212}Pb and ^{212}Bi based on an assumption that these two radionuclides are in secular equilibrium with the long-lived parent isotope of ^{232}Th. Because of potential losses of gaseous intermediate nuclide (^{220}Rn) during separation of water and hydrocarbons in production equipment as well as possible losses of radon in sampling, storage, and analysis of water samples, the assumption that the samples are in secular equilibrium is not supported by the analytical date available in this study.

3.2 General Water Quality Parameters

All water samples collected were analyzed for metals and general water quality parameters. Gathering overall water chemistry information is important to understanding the sources of water and the solutes, such as the NORM constituents contained in the water samples.

3.2.1 Metals Including U and Th

All water samples were analyzed for major and trace elements composition. Major elements were analyzed as dissolved (filtered <0.45 µm) and total fractions. Trace elements such as As, Cd, Pb, Se, Th, and U were analyzed as total fractions to better understand potential impacts from produced water.

3.2.1.1 Dissolved Metals (SW6010)

Dissolved metals were analyzed in all water samples collected for the study, and the results of these analyses are summarized in Table 15. The samples were filtered at the lab using a 0.45 µm filter before acidification and sample preparation. The laboratory analyzed the sample by inductively coupled plasma emission spectroscopy (ICP) using procedures outlined in SW846 method 6010. Four cation metals are generally present at greatest concentrations in most groundwater samples (Hem, 1992) and those four (Ca, Mg, K, and Na) are the dissolved cations present at highest concentrations in samples collected as part of this study. The maximum concentrations observed were 74,000 mg/l for Na, 18,000 mg/l for Ca, 4,700 mg/l for K, and 1,800 mg/l for Mg. The median Na, Ca, K, and Mg concentrations (mg/l) are 4,000; 135; 39.5; and 15, respectively. The remaining dissolved metals Ba, Fe, Si, Sr were observed at varying concentrations as summarized in Table 15. Appendix 10 has dissolved fraction SW6010 results for all water samples collected as part of this study. The appendix also includes detection limits and qualifiers (data flags), if any, that the lab applied to results.

Table 15. Summary Statistics for Dissolved Metals (SW6010)

Statistic	Ba	Ca	Fe	K	Mg	Na	Si	Sr
Minimum mg/l	0.008	1	0.045	2.3	0.32	0.11	0.2	0.14
Median mg/l	4.3	135	8	39.5	15	4,000	18	14.5
Mean mg/l	15	613	21.3	250	99.7	6,507	23.0	36.0
Maximum mg/l	73	18,000	130	4,700	1,800	74,000	78	650
Std. Deviation mg/l	21.4	2,557	32.3	744	295	11,388	15.3	94.0
n=	44	50	49	50	47	51	52	50
# U flag and not included in calculations	8	2	3	2	5	1	0	2

3.2.1.2 Total Metals (SW6010)

Total metals were analyzed in all water samples collected for the study, and the results of these SW6010 analyses are summarized in Table 16. The samples were acidified in the field and then prepared at the lab using SW846 method 3010. The laboratory analyzed the sample by ICP using procedures outlined in SW846 method 6010. As with the dissolved metals, the four major cations were reported at the highest concentrations among the analytes shown in Table 16. The maximum concentration observed were Na (72,000 mg/l), Ca (16,000 mg/l), K (4,800 mg/l), and Mg (2,300 mg/l). The median Na, Ca, K, and Mg concentrations (mg/l) are 3,650; 140; 50; and 15, respectively. The ranges of total metal concentrations of the major cations are similar to the concentration ranges of the same cations in the dissolved phase, which indicates the major cations are present largely in the dissolved phase in these samples.

Among the other total metals analyzed by ICP, B, Fe, Li, Si were detected at varying concentrations as summarized in Table 16. The lab reported that Be, Cr, Ni, V were not detected above the laboratory's method detection limits in the majority of the samples. Appendix 11 has total metals by SW6010 results for all water samples collected as part of this study. The appendix also includes detection limits and qualifiers (data flags), if any, that the lab applied to results.

Table 16. Summary Statistics for Total Metals (SW6010)

Statistic	Be mg/l	B mg/l	Ca mg/l	Cr mg/l	Fe mg/l	Li mg/l	Mg mg/l	Ni mg/l	K mg/l	Si mg/l	Na mg/l	V mg/l
Minimum mg/l	0.076	0.019	1	0.0042	0.029	0.03	0.35	0.0031	2.1	0.26	0.32	0.042
Median mg/l		13.5	140	0.017	6.85	3.5	15	0.140	50	20.5	3650	
Mean mg/l		16.3	562	0.080	23.7	6.6	109	0.218	253	23.4	6329	
Maximum mg/l	0.09	83	16,000	0.38	140	48	2,300	0.950	4,800	75	72,000	0.042
Std. Deviation mg/l		17.0	2,256	0.125	36.2	10.6	358	0.285	748	14.3	11,067	
n=	2	52	51	9	50	51	48	10	51	52	52	1
# U flag and not included in calculations	50	0	1	43	2	1	4	42	1	0	0	51

3.2.1.3 Total Metals (SW6020)

Total metals were analyzed in all water samples collected for the study, and the results of these SW6020 total metals analyses are summarized in Table 17. The samples were acidified in the field and then prepared at the lab using SW846 method 3010. The laboratory analyzed each sample by inductively coupled plasma mass spectrometry (ICP/MS) using procedures outlined in SW846 method 6020. Of the four major cations, only Na was analyzed by this method, and of the 17 analytes reported by the lab using ICP/MS instrumentation, Na was again present at the highest concentrations. The maximum concentration reported for Na was 86,000 mg/l with a median concentration of 4,150 mg/l. Four of the SW6020 analytes were detected in more than 50% of the samples collected (Al, Ba, Mn, and Sr). Median concentrations for Al, Ba, Mn, and Sr (mg/l) in samples with those elements detected are 0.14, 1.55, 0.145 and 16, respectively. Maximum concentrations for Al, Ba, Mn, and Sr (mg/l) in samples collected for this study are 120, 73, 3.3, and 690. As, Cd, Co, Cu, Pb, Mo, Se, Ag, Tl, Th, U, and Zn were detected in fewer than half of the samples collected as part of this study. Appendix 12 lists the total metals results by SW6020 for each water sample. The appendix also includes detection limits and qualifiers (data flags), if any, that the lab applied to these results.

Table 17. Summary Statistics for Total Metals (SW6020)

Statistic	Al	As	Ba	Cd	Co	Cu	Pb	Mn
Minimum mg/l	0.023	0.00017	0.0085	0.0001	0.00008	0.0047	0.00036	0.0069
Median mg/l	0.14	0.0016	1.55		0.00093	0.038	0.0043	0.145
Mean mg/l	4.22	0.66	13.65		0.00566	0.435	0.0347	0.473
Maximum mg/l	120	8.4	73	0.0042	0.025	2.2	0.33	3.3
Std. Deviation mg/l	21.9	2.2	20.5		0.00949	0.709	0.0828	0.742
n=	30	25	52	4	8	13	16	52
# U flag not included in statistics	22	27	0	48	44	39	36	0

Statistic	Mo	Se	Ag	Na	Sr	Tl	Th	U	Zn
Minimum mg/l	0.0011	0.00078	0.00039	0.34	0.002	0.00002	0.00004	0.00003	0.012
Median mg/l	0.0036			4,150	16	0.00022		0.0009	0.145
Mean mg/l	0.00838			7,278	37.5	0.016		0.00435	0.616
Maximum mg/l	0.072	0.0054	0.012	86,000	690	0.11	0.00031	0.023	3.5
Std. Deviation mg/l	0.0147			13,247	98.5	0.0324		0.00833	0.98
n=	24	4	2	52	51	19	3	7	24
# U flag not included in statistics	28	48	50	0	1	32	49	45	28

3.2.2 Anions

Major anions were analyzed in all of the aqueous samples for the study, and the results are summarized on Table 18. Water samples were analyzed for Br, Cl, F, and SO_4 by ion chromatography using procedures from SW 846 method 9056. Alkalinity was determined by titrimetric methods following procedures outlined in SM 2320. The anions reported at highest concentrations in samples analyzed by SW9056 are Cl and SO_4, with median concentrations (mg/l) of 12,725 and 549, respectively, though SO_4 was not detected by the lab in 25% of the samples collected as part of this study. Alkalinity in the samples is assumed to be from carbonate species (HCO_3^- and CO_3^{2-}) and reported as mg/l of $CaCO_3$. Oil and gas produced waters may also contain short chain organic acid anions as documented in produced waters from the Alberta Basin (Connolly et al., 1990a). When present, short chain organic acid anions also contribute to the total alkalinity of water samples (Lozovik, 2005). The presence of short chain organic acid anions in the produced water samples would result in a partial overestimate of the concentrations of carbonate species in the samples when interpreted from the alkalinity titration process followed by the lab. The median alkalinity (as bicarbonate) concentration in sample from this study is 585 mg/l as $CaCO_3$. The maximum alkalinity (as bicarbonate) concentration in these samples is 5,400 mg/l as $CaCO_3$. Fluoride was detected in fewer than half of the samples in this study and Br was detected in the majority of the samples and at much lower concentrations than Cl in the same samples.

Table 18. Summary Statistics for Major Anions

Statistic	Bromide	chloride	fluoride	sulfate	bicarbonate alkalinity as $CaCO_3$	carbonate alkalinity as $CaCO_3$	total alkalinity as $CaCO_3$
Minimum mg/l	0.34	0.064	0.85	0.17	30	not detected in all samples	30
Median mg/l	42	6,700	2.3	25	585		585
Mean mg/l	61.4	12,725	2.4	549	998		998
Maximum mg/l	300	170,000	6	3,800	5,400		5,400
Std. Deviation mg/l	71.3	27,335	1.3	1,057	1,091		1,091
n=	43	52	23	39	52	0	52
# U flag and not included in statistics above	9	0	29	13	0	52	0

Chloride, alkalinity, and SO_4 are the three major anions in most groundwater (Hem, 1992). Chloride and alkalinity are the dominant anions with lesser SO_4 in the majority of the samples collected for this study. Appendix 13 lists the results of the anions analytical procedures for each water sample. The appendix also includes detection limits and qualifiers (data flags), if any, that the lab applied to these results.

3.2.3 pH, Specific Conductance, TDS and TSS

Table 19. Summary Statistics for General Water Quality Parameters

Statistics	pH SU	specific conductivity µmhos/cm	total dissolved solids mg/l	total suspended solids mg/l
Minimum	5.7	105	92	22
Median	7.50	17,850	11,000	75.5
Mean		28,547	21,400	151
Maximum	8.63	237,000	240,000	720
Std. Deviation		42,370	40,546	176
n=	52	52	52	32
# U flag results (not included in statistics above)	0	0	0	20

The pH of water samples was determined using specific ion electrode methods as described in SW 846 method 9040. The conductance of the water samples was determined using conductivity cell as described in SM 2510. Gravimetric determination of dissolved (TDS) and suspended solids (TSS) in the water samples was done using procedures described in SM 2540. The pH of most of the samples was basic with the median pH equal to 7.5 as shown in Table 19 with a range from 5.7 to 8.63 (SU).

Total suspended solids are gravimetrically determined filterable solids present in water samples. Both TDS and TSS are operationally derived parameters based on filtering and drying using method-defined pore size filters and method-defined drying temperatures and times. Appendix 14 lists the results of the general water quality analytical procedures for each water sample. The appendix also includes detection limits and qualifiers (data flags), if any, that the lab applied to these results.

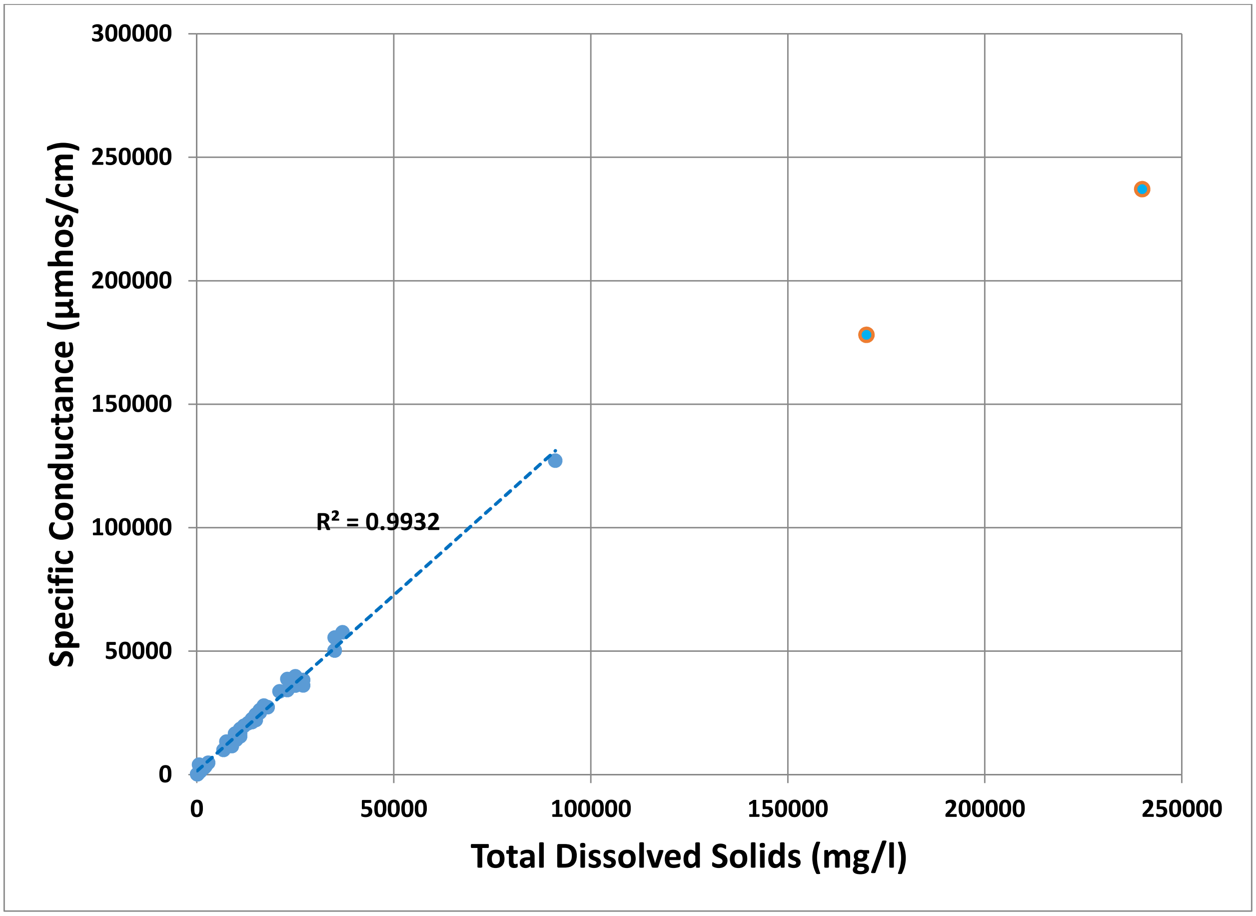

Figure 15. Total Dissolved Solids (TDS) versus Specific Conductance
y-axis = measured conductivity of samples (electrometric data) in µmhos/cm, x-axis = concentration of TDS of each sample (gravimetric determination) in mg/l.

Electrical conductivity of water is a function of the concentration and types of cations and anions present in a water sample and can be related to the measured TDS. Figure 15 shows a linear relationship between TDS and specific conductance in 50 of the 52 samples. In the two samples with >150,000 mg/l TDS, the relationship between the two measured parameters is different because of interactions between the ions which are thought to occur when the dissolved solids are present at very high concentrations.

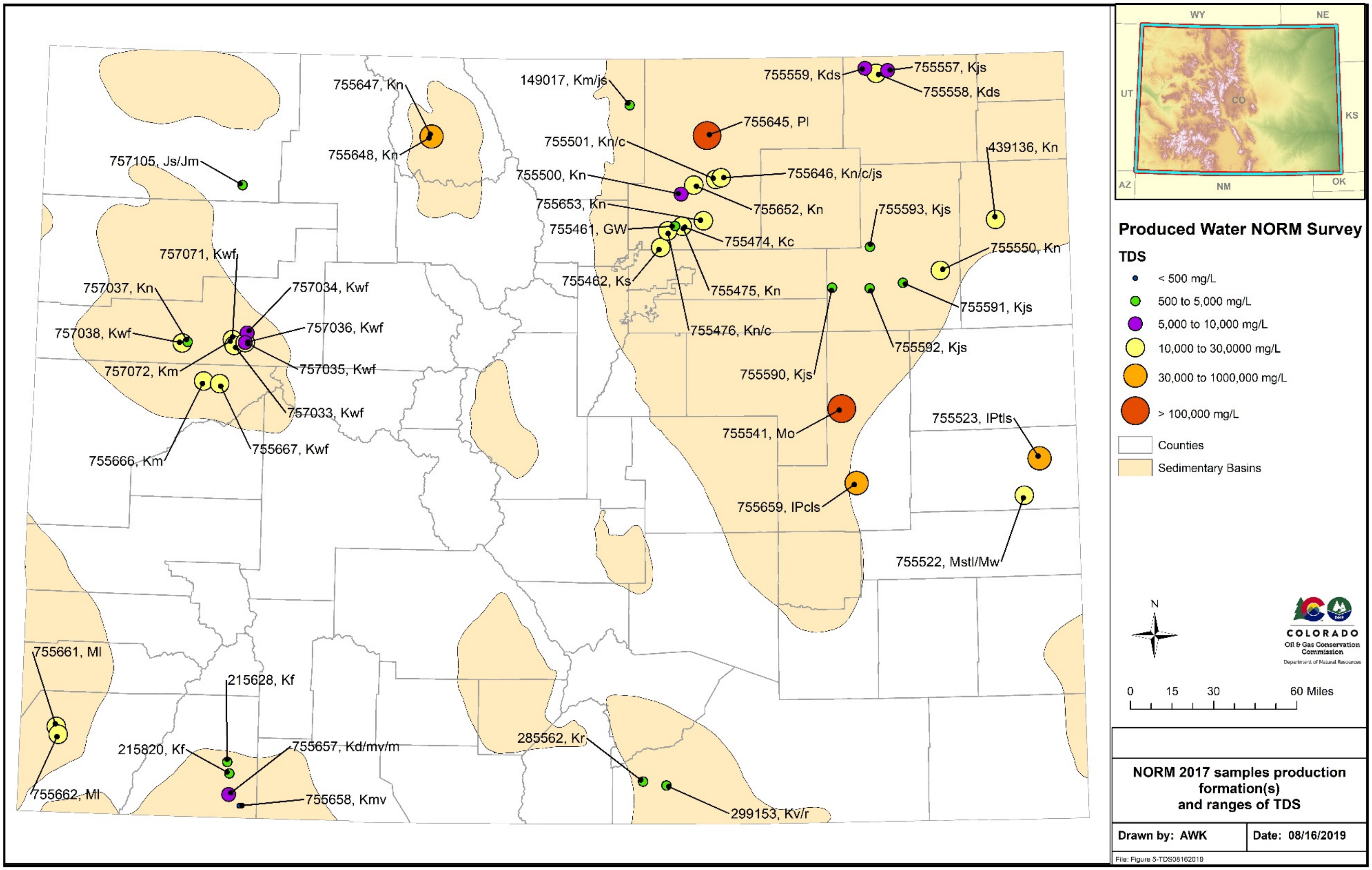

Figure 16. NORM 2017 Samples Production Formation(s) and Ranges of TDS

Each facility sampled is captioned with facility number and an abbreviated identification of the formation(s) from which oil and/or gas and water samples were produced. A legend explaining the abbreviated formations names can be found at the end of Appendix 1. Size of circle at a site is larger with increasing concentration of TDS in sample collected at the facility.

The reported TDS concentration of 31 of the 52 water samples collected as part of this study are >10,000 mg/l, and thus would not be considered underground sources of drinking water (USDW) as defined by U.S. EPA. All of the samples with one exception were also collected from hydrocarbon producing wells, and thus only the source water sample (facility **755461**) would be considered a USDW under the current definition.

Figure 16 shows the range of TDS measurements for each sample collected and provides a broad overview of concentrations of dissolved solids across the state. The geologic basins and producing formation(s) from which each sample was collected is included in abbreviated form with the facility number of the sampling location. TDS concentrations are a general indicator of water quality. As can be seen in Figure 16, most of the samples collected from wells producing from the eastern slope Niobrara formation are broadly of similar TDS concentration with most between 10,000 to 30,000 mg/l TDS.

3.2.4 Major Ion Chemistry and General Water Chemistry Discussion

The major ion and general chemistry of the water samples can be used to evaluate potential for re-use of these water in agricultural or industrial uses outside of oil and gas exploration and production recycling. The non-radiochemistry data gathered as part of this study provides useful data for potential users of produced water outside the oil and gas industry as to if treatment is needed or what types of treatment systems might be needed to make the water suitable for an intended use. Potential beneficial uses of produced water in Colorado may involve other agencies such as the Division of Water Resources, water courts, and CDPHE. Solid wastes are likely to be produced if E&P wastes waters are treated for other uses. In Colorado, such solid wastes would need to be characterized and disposed of in accordance with applicable solid waste regulations.

Several types of general evaluation of the major ion and general water chemistry data are present in this section including general evaluation by use of Piper diagrams, evaluation of potential problems if produced water reuse in irrigation of crops is to be considered, and use of Cl/Br mass ratios and Na/Cl molar ratios as indicators of possible water-rock interactions and sources of solutes in the produced water samples. Stable isotope ratios of the hydrogen and oxygen present in the water samples also provide useful indicators of sources of water including potential mixing of two sources of water.

Piper diagrams are a means of categorizing similarities and differences in sources of water using major ion compositions of the waters (Piper, 1944). Piper diagrams can also be used to evaluate the possibility of mixing two water sources (Hem, 1992). Figure 17 below is a Piper diagram of the sample set discussed above and shown on the map (Figure 16) above. Piper diagrams are in three parts. The two triangles at the bottom of the Piper plot illustrate cation composition (left triangle) and anion composition (right triangle). The scales of both the triangles are in percent of milliequivalents of the sum of cations and sum of anions in each sample.

Sodium and, to a lesser extent, K are the dominant cations in the majority of the samples collected for this study. Chloride is the dominant anion observed in the majority of the sample results with lesser occurrences of bicarbonate alkalinity and SO_4.

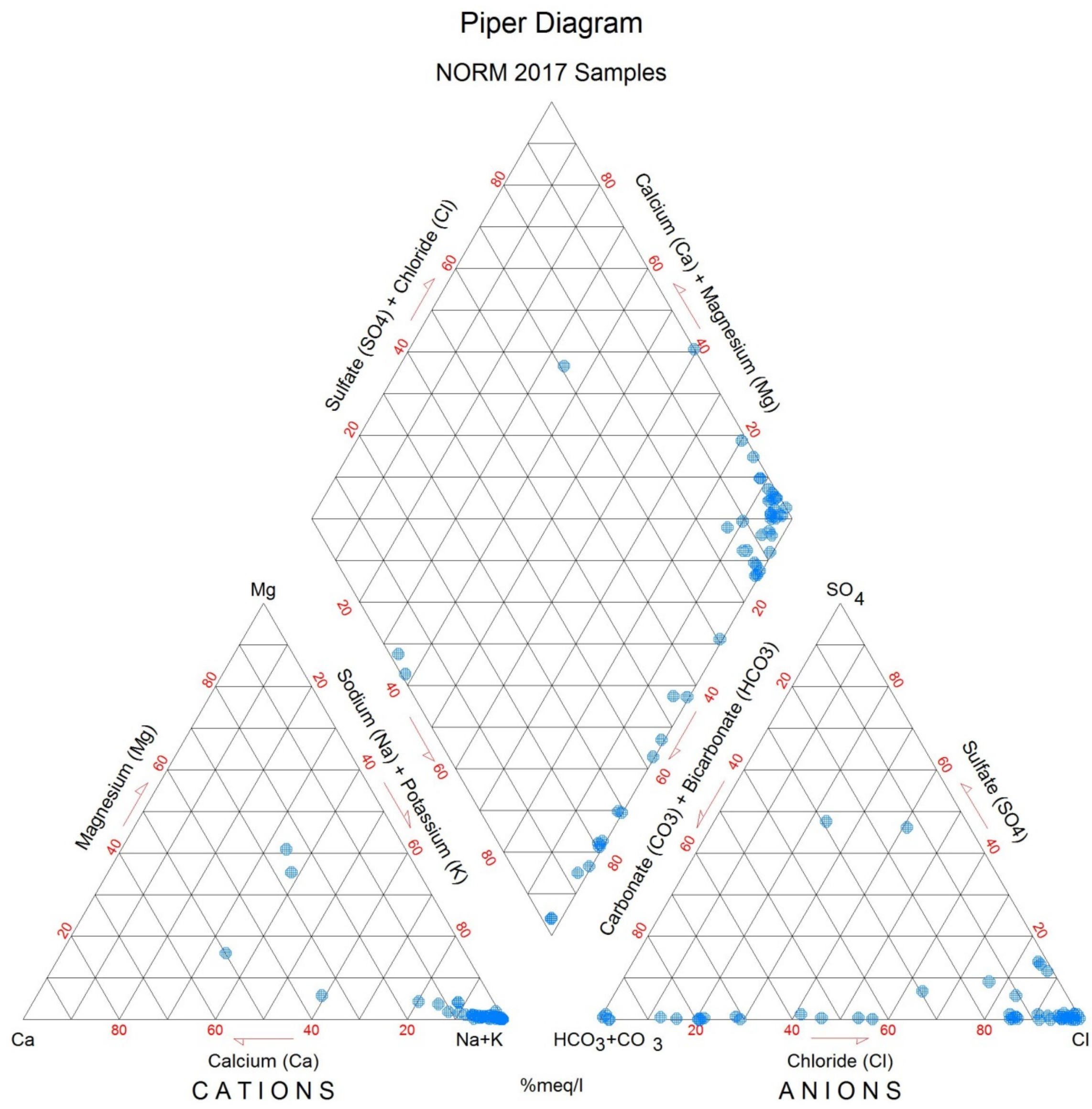

Figure 17. Piper Diagram Showing Major Ion Composition of 2017 NORM Produced Water Samples

All but four samples which are from three facilities (755461, 755541 and 755658) analyzed have Na (and K) as 80% or more of the major cations as seen in the cation triangle at lower left of Figure 17. The triangle of cation composition at the lower left of Figure 17 indicates that the four samples with <80% of the cations as Na have 40 to 70% of the cations as Ca and 5 to 40% of the cations as Mg. Facility 755461 is a source water sample from shallow aquifers in eastern Colorado and would be expected to contain more calcium than water from deeper sources. Facility 755541 is a produced water sample from a well producing from the Osage Limestone. Higher proportion of Ca relative to Na is likely because of the interaction with calcium bearing minerals in the producing formation. The overall composition of water sampled at facility 755658 is likely not indicative of contact with the producing formation as discussed later in this section.

In only two of the samples collected as part of the study are Cl and carbonate <85% of the major anions, as seen in the anion triangle at the lower right of Figure 17. Those two samples (755461 and 755658) with <85% of the anions being chloride and bicarbonate have sulfate as 40 to 50% of the major anions. Facility 755461 is a source water sample from shallow aquifers in eastern Colorado and would be expected to contain more calcium than water from deeper sources. The overall composition of water sampled at facility 755658 is likely not indicative of contact with the producing formation as discussed later in this section.

Sodium is the primary cation in many of the produced water samples collected as part of this study, as discussed in previous sections of this report. High concentrations of Na in produced water samples can pose problems if beneficial use of produced water in agriculture is desired, an enquiry the agency fields regularly. Sodic soils can hinder reclamation of sites where spills or releases of produced water with elevated sodium adsorption ratio (SAR) have occurred. Soil thresholds for sodicity are present in COGCC rules for this reason. Calculation of a ratio of Na to Ca plus Mg is a useful tool in understanding the potential to use water whose primary cation is Na in irrigation of crops.

The SAR is calculated from water analyses, as shown in this equation from the Agriculture Handbook No. 60 (USDA, 1954):

$$\mathbf{SAR} = \frac{\mathbf{Na}}{\sqrt{\left(\frac{\mathbf{Ca} + \mathbf{Mg}}{\mathbf{2}}\right)}}$$

where, Na, Ca, and Mg concentrations are expressed in milliequivalents per liter (meq/l). The calculated value of SAR provides a means of estimating potential sodicity impacts to soils from spills or releases of produced water. The SAR of each water sample is shown in Figure 18.

General tolerances of crops with respect to the salinity and sodicity of irrigation waters as well as tolerances to individual ions in irrigation water can be found in the compilation of Ayers and Westcot (1985) for crops grown around the globe. Salinity tolerances are generally expressed with respect to the loading of TDS, or more commonly in terms of the specific conductance (EC) of the potential source of irrigation water while SAR as described above is the measure of sodicity used to evaluate potential sources of irrigation water. Elevated SAR in irrigation water can be a causal factor in reduced crop yield due to reduced ability of water to infiltrate some soils (Ayers and Westcot, 1985; Bauder et al., 2014). Sodicity-induced reduction of water infiltration is most pronounced in soils containing expandable clays, which are common in agricultural soils in Colorado (Bauder et al., 2014). Information about irrigation water quality with respect to crops, soils, and climatic conditions in Colorado can be found in Bauder et al. (2014). Figure 18 includes a dashed red, horizontal line drawn at SAR of 9. Irrigation waters with SAR of 9 or greater are considered to be of severely limited use (Table 1, Ayers and Westcot, 1985) due to possible deleterious impacts on infiltration and also because of potential specific ion toxicity of Na to sensitive crops.

Corn is a crop frequently raised in parts of Colorado and generally requires irrigation in addition to rain and snowfall-supplied water. Corn crop yields of 50% at 3,900 micromhos per centimeter (µmhos/cm) and 0% at 6,700 µmhos/cm in comparison to 1,100 µmhos/cm irrigation water (100%

corn yield) are shown in Ayers and Westcot (Table 4, 1985). Over 70% of the water samples had >6,700 µmhos/cm specific conductance, and those high TDS waters would in general not be suitable for use in irrigation of corn crops without treatment. For many crops, the higher the specific conductance of the irrigation water, the more plants struggle to bring water into the organism (Bauder et al., 2014). Soil types such as sandy or clay rich, irrigation practices such as flood or overhead, climatic conditions, and other water quality factors will also be factors in crop yields.

Crops may also exhibit specific ion toxicity to elevated concentrations of Cl, Na, and boron (B). Corn is considered moderately tolerant of B with the maximum tolerated B concentration in the range of 2 to 4 mg/l (Table 16, Ayers and Westcot, 1985). A majority of samples collected in this study (67%) contained B >4 mg/l. Wheat is more sensitive to B in irrigation waters than is corn with the maximum tolerance for wheat at 0.75 to 1 mg/l (Table 16, Ayers and Westcot, 1985), and 86% of the samples collected in this study contained B >1 mg/l. The concentrations of B present in many of the produced waters indicates that they might not be suitable for use in irrigation of corn or wheat crops without treatment.

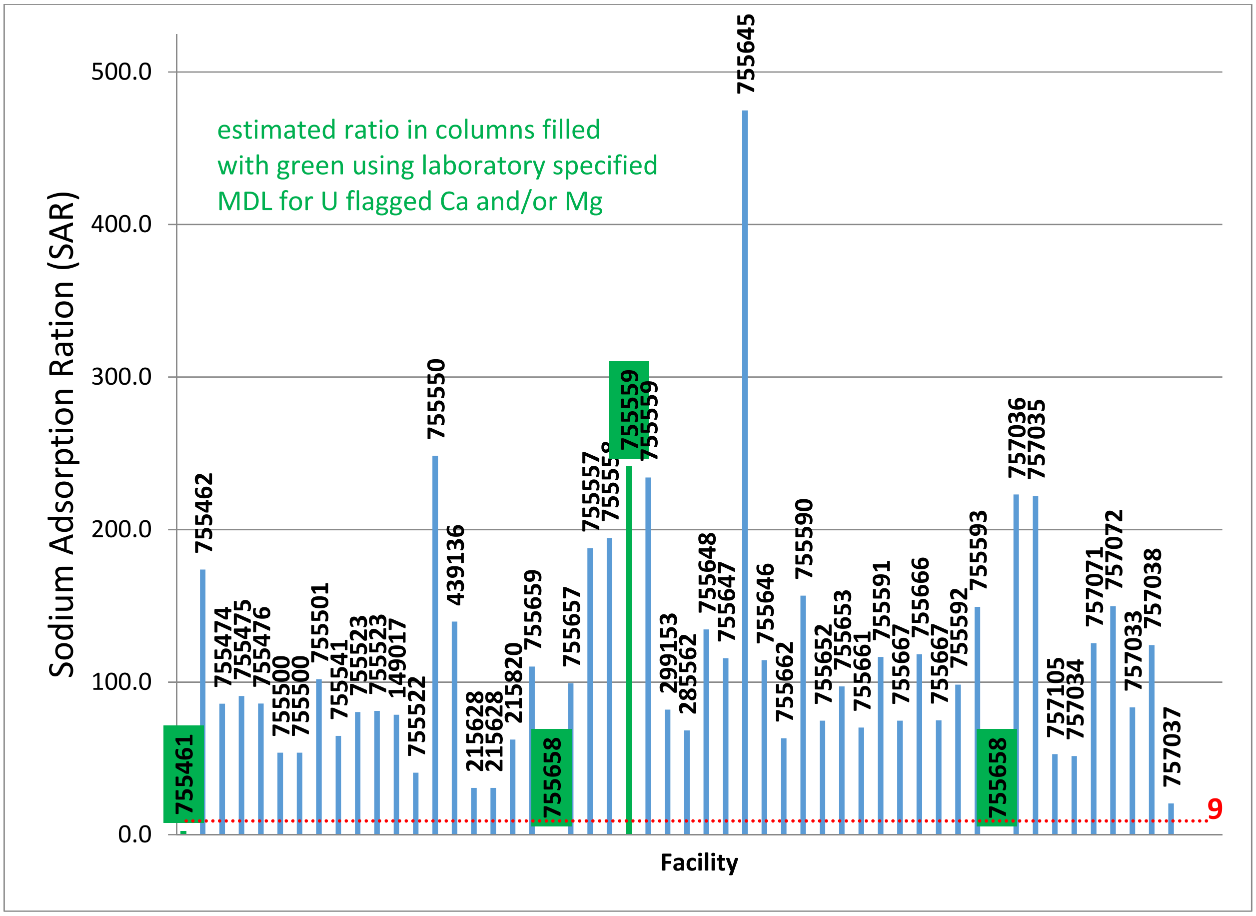

Figure 18. Sodium Adsorption Ratio (SAR) of Samples Collected as Part of this Study
SAR calculated from dissolved concentrations of Na, Ca and Mg for each water sample collected during this study. Each bar indicates ratio of one sample and each is labeled with COGCC facility number.

Chloride and bromide (Br) ions are ubiquitous solutes in all natural waters. Chloride is generally a major component, and Br is generally a minor one. Both Cl and Br are generally viewed as conservative tracers in groundwater systems (Whittemore, 1995; Davis et al., 1998; Davis et al., 2004; Freeman, 2007). Cl/Br mass ratios can be used to help determine the origin and evolution of water including water produced from oil and gas reservoirs and surface waters (Davis et al., 1998). Seawater has a relatively uniform Cl/Br mass ratio around 290±4 (Katz et al., 2011). Groundwater Cl/Br mass ratios close to that of seawater may in some instances reflect water trapped when marine sediments were originally deposited. Shallow potable groundwater derived from meteoric water in Colorado as shown in Table 4 of Davis et al., (2004) is expected to have Cl/Br mass ratios of about 50 if no anthropogenic inputs are present.

Groundwater Cl/Br ratios greater than the seawater ratio generally indicate increased contributions of solutes from water-rock interactions, and ratios >1,000 may be from dissolution of the evaporite mineral halite (Davis et al., 1998; Freeman, 2007). Groundwater Cl/Br mass ratios less than the seawater ratio would indicate fluid sources from a fresher source (such as more recent fresh water recharge) or less water-rock interaction (residence time). Atmospheric precipitation generally has Cl/Br mass ratios between 50 and 150 and typically after even short residence times, shallow groundwaters have ratios between 100 and 200; ratios between 1,000 and 10,000 reflect solutes derived from halite dissolution (Davis, et al., 1998).

Results of the Cl/Br mass ratios determined from analytical data of this study are presented on Figure 19. Note the y-axis (Cl/Br ratio) is plotted on a logarithmic scale. The bulk of the fluid samples collected have Cl/Br mass ratios between 100 and 200 (29 samples) with 10 samples having Cl/Br ratios exceeding 290; one has a ratio at 11,333 (facility 755645). The Cl/Br mass ratio of nine samples was <100. Five of the samples with Cl/Br mass ratios <100 were from wells which had been hydraulically fractured in the 12 months prior to sampling (**facility # in gold**) and in which 90% or more of the frac fluid was reported as fresh water on form 5A submissions to COGCC for these wells. The sources of fresh water are not identified on COGCC Form 5A Completed Interval Report so it is not known if the source water was from groundwater or surface water. The Cl/Br mass ratios of the five samples from wells hydraulically fracture stimulated in the 12 months prior to sampling likely indicate much of the water being produced at these sites may be from the fresh water used in the fracs. Rosenblum et al., (2017) observed a Cl/Br mass ratio of 69.1 in produced water about eight months after the completion of one well producing from the Niobrara Fm. in northeastern Colorado. In general, the bulk of the samples from this study reflect fluids that have Cl/Br mass ratios that would be expected to be present in waters that have evolved geochemically during contact with rocks over geological time frames.

Analysis of stable isotopes of water, which can aid in interpretation of water sources, was also performed on all samples and are presented in general in Section 3.3 and discussed in more detail in Section 4.3.7. Three of the samples with fracs in the 12 months prior to sampling were among the subset of samples on which analysis of tritium activities and ^{14}C of DIC ages were performed. The tritium analyses are summarized in Section 3.4 and the ^{14}C of DIC analyses are summarized in Section 3.5. Tritium and ^{14}C of DIC analyses are discussed in Section 4.3.8.

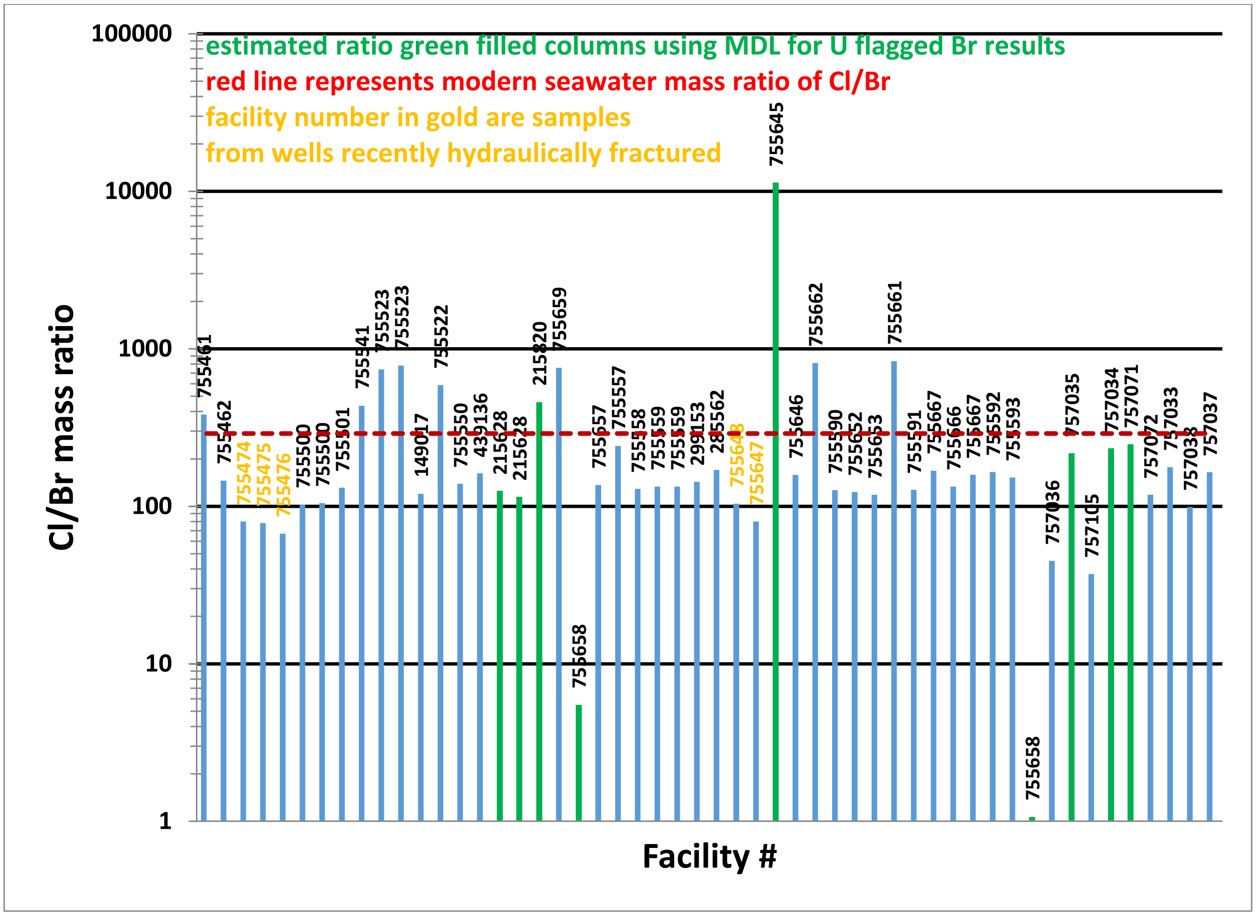

Figure 19. Chloride/Bromide Mass Ratio of Samples Collected as Part of this Study
Ratio of Cl concentrations (mg/l) to Br concentrations (mg/l) present in each water sample collected during this study. The red dotted horizontal line represent the Cl/Br mass ratio in modern seawater. Each bar indicates ratio of one sample and each is labeled with COGCC facility number.

Two sample sites are anomalous as having the highest and lowest mass Cl/Br ratios, facilities 755645 and 755658. Facility 755645 is produced water from the Permian Lyons Fm., and has a Cl/BR ratio of over 10,000. The presence of evaporite minerals within the Lyons Fm. is apparent in review of geophysical logs from producing wells in the same area as facility 755645 and has been reported as a formation cement (anhydrite) in the Lyons Sandstone (Lee and Bethke, 1994). Halite and gypsum beds are present throughout the Permian age rocks (late Desmoinesian/Wolfcampian time) in the northern Denver Basin (Garfield, et al., 1988). The presence of evaporate minerals likely contributes to the high Cl/Br present in the Facility 755645 sample.

Facility 755658 was sampled once in May 2017 and again in October 2017. Both samples were collected from the water/gas separator that receives production from well 05-067-08097. Gas production from this well (and associated separator) has been reported at approximately 4,000 to 5,000 thousand cubic feet (MCF)/month during 2017 from the Cretaceous Mesaverde Group. No water production has been reported subsequent to April 2017 (before sampling events) until after the sampling events. The water may not be formation-related as the concentration of TDS was reported as 92 mg/l from the May sample and 160 mg/l in the October sample. The Cl/Br mass ratios of two samples from facility **755658** are <10. These low Cl/Br ratios may be indicative that the water is not produced groundwater but may be condensation or rainwater.

Na and Cl are dominant cation and anion in the majority of samples collected as part of this study. The ratio of the concentrations of these two ions has been used in studies of seawater intrusion into fresh water aquifers (Anders et al., 2013). The Na/Cl ratio can also be used to help understand sources of solutes in the samples. The mole ratio of Na/Cl in seawater is 0.859 using composition data compiled by Pilson (2013).

The Na/Cl molar ratios of the majority of samples (65%) are within ±50% of the seawater ratio shown as a red horizontal line on Figure 20. Note the y-axis (Na/Cl ratio) is plotted on a logarithmic scale. The samples more than 50% different than the seawater ratio all have Na/Cl ratios >1.5 times the seawater ratio (18 samples or 35% of all samples). The TDS concentrations of the 18 samples with Na/Cl ratio >1.29 are all lower than the median TDS concentration (11,000 mg/l) of samples collected as part of this study. The 18 samples with Na/Cl ratio >1.29 contain relatively lower concentrations of chloride. The samples with Na/Cl molar ratio >1.29 are 18 of the 20 samples with the lowest chloride concentrations. The 18 samples with Na/Cl molar ratio >1.29 also all have Na concentrations ≤ the median Na concentration (4,000 mg/l) of samples collected as part of this study. Chloride is generally considered to be a conservative tracer in groundwater systems. The relatively low concentrations of chloride in these 18 samples indicate the source(s) of the water were also relatively low in chloride and that the rocks these 18 samples have been in contact with do not contain seawater or solids such as halite in appreciable amounts. Weathering of silicate minerals as groundwater migrates through alluvium and near surface rock layers is a possible source of waters with relatively low chloride in relation to Na concentrations.

The Na/Cl molar ratios of the majority of samples (65%) are within ±50% (0.43 to 1.29) of the seawater ratio (0.859) shown as a red horizontal line on Figure 20. Note the y-axis (Na/Cl ratio) is plotted on a logarithmic scale. The samples more than 50% different than the seawater ratio all have Na/Cl ratios >1.5 times the seawater ratio (18 samples or 35% of all samples with ratio > 1.29). The TDS concentrations of the 18 samples with Na/Cl ratio >1.29 are all lower than the median TDS concentration (11,000 mg/l) of samples collected as part of this study and contain relatively lower concentrations of chloride. This group of samples comprise 18 of the 20 lowest chloride concentration samples. The 18 samples with Na/Cl molar ratio >1.29 also all have Na concentrations ≤ the median Na concentration (4,000 mg/l) of samples collected as part of this study. Chloride is generally considered to be a conservative tracer in groundwater systems. The relatively low concentrations of chloride in these 18 samples indicate the source(s) of the water were also relatively low in chloride and that the rocks these 18 samples have been in contact with do not contain seawater or solids such as halite in appreciable amounts. Weathering of silicate minerals as groundwater migrates through alluvium and near surface rock layers is a possible source of waters with relatively low chloride in relation to Na concentrations.

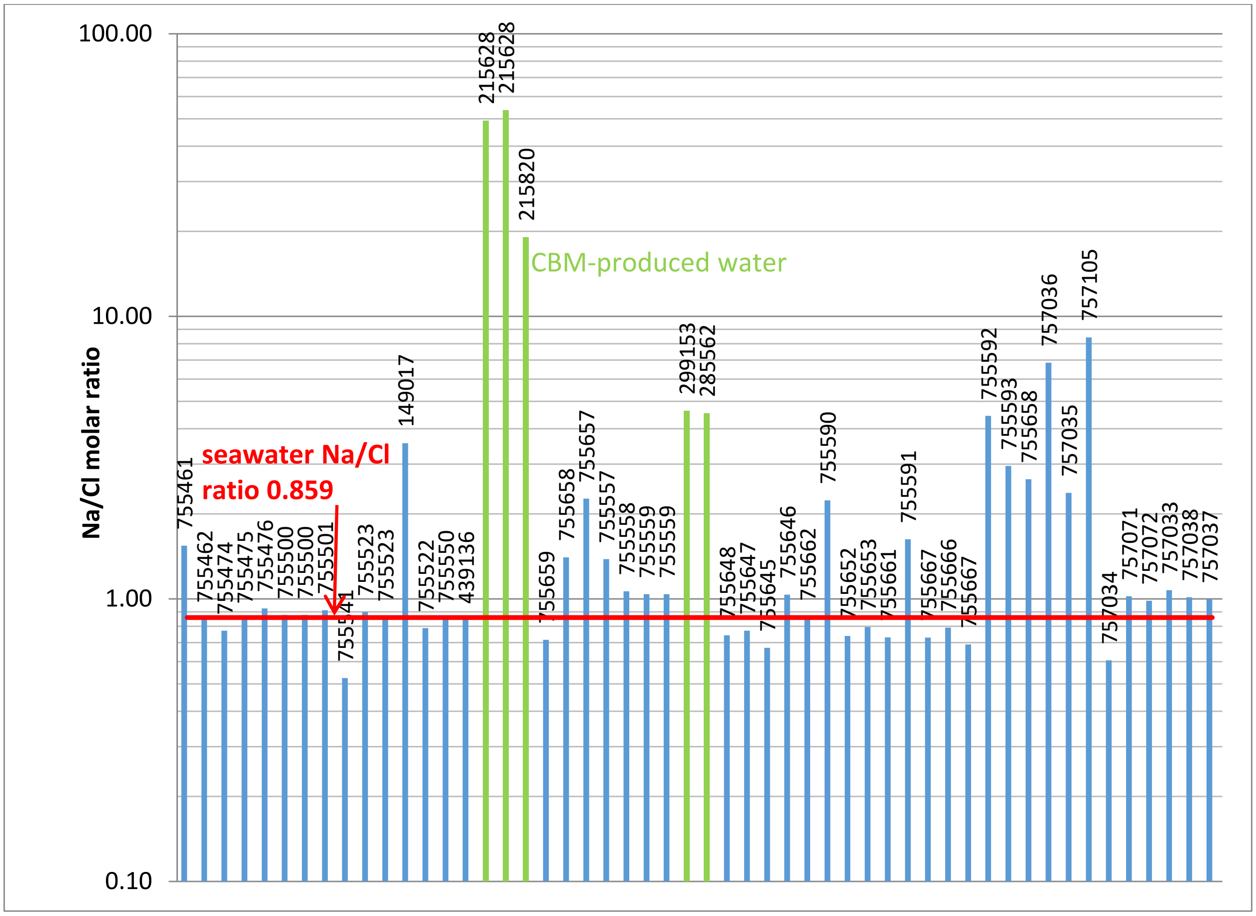

Figure 20. Na/Cl molar ratios of NORM 2017 Samples

Ratio of Na concentrations (moles/l) to Cl concentrations (moles/l) present in each water sample collected during this study. The red horizontal line represents the Na/Cl molar ratio in modern seawater. Each bar indicates ratio of one sample and each is labeled with COGCC facility number.

Figure 21 is a comparison of the Na/Cl molar ratio (x-axis) and the Cl/Br mass ratios (y-axis) just presented and discussed. Note that both axes are plotted using a logarithmic scale. The seawater Na/Cl molar ratio of 0.859 is shown as a labeled dark blue dashed vertical line and the seawater Cl/Br mass ratio of 290 is shown as the green dashed horizontal line on Figure 21. In addition a vertical line representing a Na/Cl molar ratio of 1.29, which is 50% greater than the seawater ratio, is drawn on the plot as a gray dashed vertical line.

The Na/Cl molar ratio of 18 of the samples collected as part of this study are >1.29 (Groups A 1, A 2 and A 3 on Figure 21) The Cl/Br mass ratio of 16 of the 18 with >1.29 Na/Cl ratios are also <290 (seawater ratio). The two samples shown as purple circle symbols (Group A 2) with >1.29 Na/Cl ratios and Cl/Br ratios >290 are the source water sample (755461) and produced water from a San Juan Basin CBM well (215820). The greater than seawater Cl/Br ratio in samples 755461 and 215820 may be the result of anthropogenic inputs of Cl such as from road salt (755461) or from input of dissolved solids from other anthropogenic inputs (215820). The two samples shown as red triangles in Figure 21 (Group A 3) with >1.29 Na/Cl ratios and Cl/Br ratios <290 represent analyses of water from facility 755658. Bromide was not detected in samples from 755658 so the Cl/Br ratio was calculated using the detection limit for bromide. The use of the detection limit would likely result in an underestimation of the Cl/Br mass ratio for the two samples collected from 755658. As discussed previously the source of these water samples is thought to be rain or perhaps water vapor carried in the gas stream from the well served by the separator from which the samples were collected. Blue circle symbols (Group A 1) mark the other 14 samples (of 18) with >1.29 Na/Cl ratios and Cl/Br ratios <290. The relatively high Na/Cl ratio of the 14 samples in Group A 1 is indicative that the waters have not been mixed with seawater. Seawater could possibly have been present in producing formations deposited in marine settings or which were subsequently overlain by sea water. Thirteen of the 14 samples in Group A 1 come from formations which in part were deposited in fluvial or deltaic terrestrial environments and the lack of sea water characteristics may be expected. Many of the samples with Na/Cl ratios >1.29 may be the product of weathering of silicate minerals by meteoric water as it migrates through the earth. Many silicate minerals frequently contain sodium but contain little or no chloride. One means of further examining that concept is to utilize the stable isotopes of water data collected as part of this study. Section 4.3.7 presents an analysis of the stable isotopes of water from the subset of samples with >1.29 Na/Cl ratios and Cl/Br ratios <290.

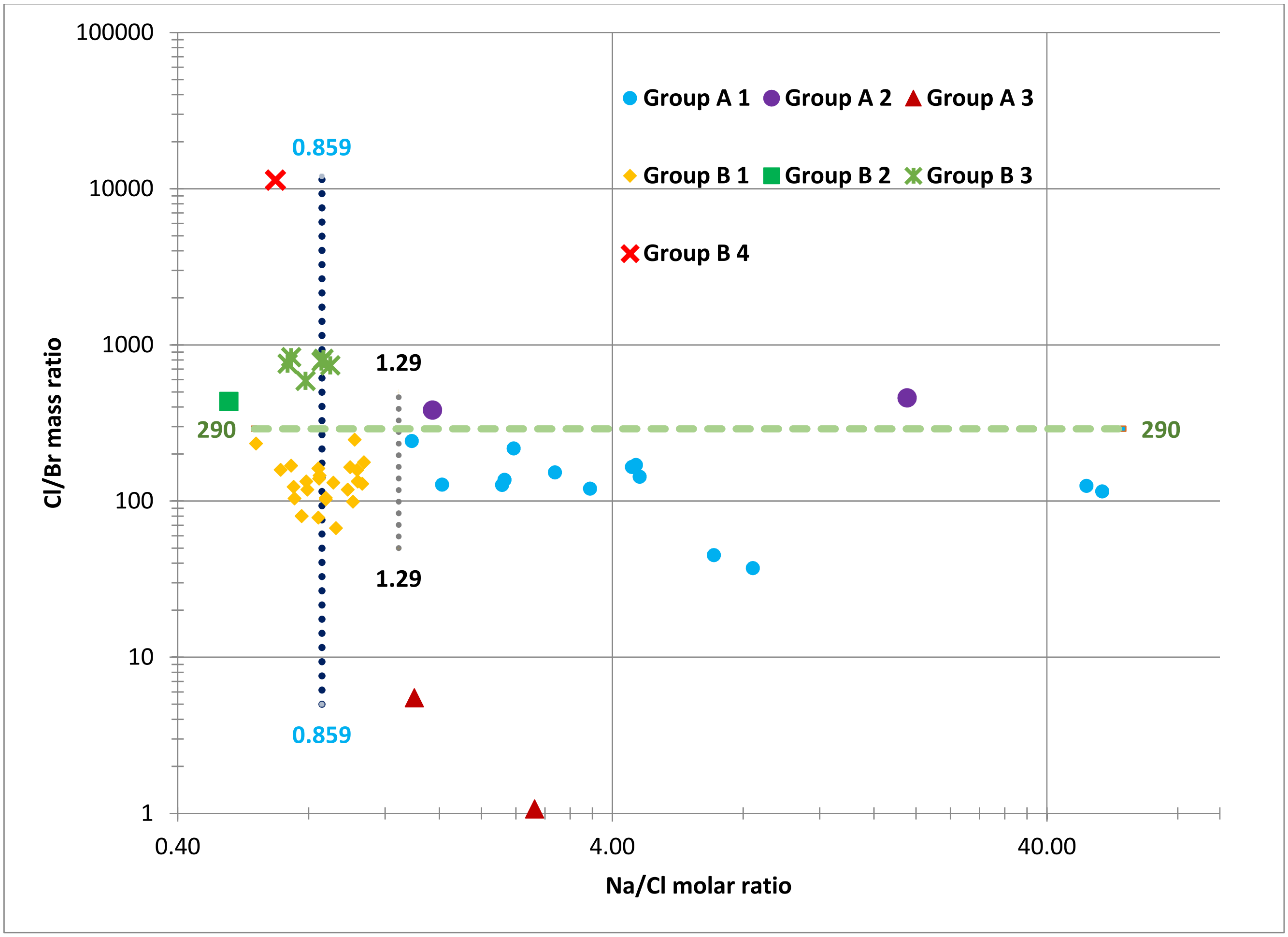

Figure 21. Na/Cl ratio Plotted versus Cl/Br Ratio of 2017 NORM Samples

Vertical reference line at Na/Cl molar ratio (0.859) is plotted to highlight the Na/Cl molar ratio of modern seawater. Horizontal reference line at Cl/Br mass ratio (290) is plotted to highlight Cl/Br mass ratio of modern seawater. Both x- and y-axes are plotted as logarithmic scales.

Six samples are indicated with green asterisks (Group B 3) and have Cl/Br mass ratios between approximately 400 and 800 with Na/Cl ratios near that of seawater. These samples may represent groundwaters derived from connate or later incursions of sea water and which have also been in contact with halite as a source of the elevated chloride in comparison to bromide present in these samples. One sample labeled as Group B 4 has a Cl/Br ratio >10,000 (755645) and is shown in Figure 21 with a red X. The elevated Cl/Br ratio in this produced water sample is thought to be from contributions from halite present in formations in contact with the Lyons Fm., which is of terrestrial origin. One sample 755541 (Group B 2) has the lowest Na/Cl molar ratio likely due to interactions with calcium bearing minerals in the producing formation. Dissolution of calcium from the formation has resulted in elevated calcium ratio of total cations in this sample compared to most other samples collected as part of this study as illustrated in Figure 17 and discussed previously in this section. Seven of the eight samples with Cl/Br >400 have Na/Cl ratios similar in a general sense to modern seawater, even though the Cl/Br ratios are more than 35% greater than that of modern seawater.

The eight samples (from seven facilities with one duplicate) with Cl/Br >400 are produced water from oil and gas wells developed in Paleozoic era formations (Appendix 1). All other samples in this study are from wells developed in Mesozoic era formations (Appendix 1) with the exception of the source water sample and one sample partially from Raton Fm. coals, which were deposited in part in the Cenozoic era. The Paleozoic producing formations are of marine origin with the exception of the Lyons Fm., which is of terrestrial origin (Maughan and Wilson, 1960; Thompson, 1949; Weimer and Lund, 1972). All the reported concentrations of TDS in these eight samples are among the 15 highest concentrations in samples collected as part of this study and include the first, second, third and fifth highest TDS concentrations. One means of further examining the sources of water in these eight samples from seven facilities is to utilize the stable isotopes of water data collected as part of this study. None of the wells producing to the seven facilities with Cl/Br ratios >400 were completed by hydraulic fracturing techniques. Section 4.3.2 presents an analysis of the stable isotopes of water from the subset of eight samples with Cl/Br ratios >400.

The samples plotted with gold diamonds (Group B 1) in Figure 21 are those with Na/Cl and Cl/Br ratios similar to that of modern seawater. One can hypothesize that connate (remnant) formation water from marine sediments is present in the produced water at these sites even if mixed with more recent fresh water, which in some cases has been introduced to the system by hydraulic fracturing.

3.3 Stable Isotopes of H_2O and of Carbon in Dissolved Inorganic Carbon

Isotopic composition of the oxygen and hydrogen that make up water (H_2O) can be used as a tool in understanding differences in sources of groundwater. Appendix 15 lists the results of the stable isotope of water and DIC analytical procedures for each water sample. Water isotopic data available from this study are plotted below with water oxygen isotope ratios plotted as the x-axis and water hydrogen isotope ratios plotted as the y-axis (Figure 22). The hydrogen isotope (^2H) ratio plotted is also referred to as deuterium and the label on the plot of δD refers to the ratio of deuterium (^2H) to the more abundant ^1H isotope. The carbon isotopic composition of DIC in waters (Figure 23) can also be used in interpretation of interactions between groundwater and the rocks they are in contact with and used in interpretation of biological processes in the groundwater.

One line drawn diagonally across the water isotope plot (Figure 22) is known as the global meteoric water line (GMWL) and represents a regression line to unevaporated precipitation data from across the world (Craig, 1961; Rozanski et al., 1993). A nearly parallel line to the GMWL represents the local meteoric water line from precipitation samples collected in the Pawnee Grasslands in northeastern Colorado (Harvey, 2005). The isotopic composition of precipitation (meteoric water) is a function of source of the atmospheric moisture which gives rise to the precipitation with isotopically depleted waters associated with cold regions and enriched waters in warm regions as noted by Craig (1961). Variability of δD and $\delta^{18}O$ in precipitation reflects the source and seasonal transport patterns of the atmospheric moisture, the amount of precipitation that has previously fallen, and orographic effects on isotopic composition (Bowen and Revenaugh, 1993).

Figure 22 illustrates that there is a large degree of variability of water isotope ratio between the sources of produced water sampled in this study. However there is some overlap between the dataset gathered as part of this study and with the meteoric water lines and data from local aquifers. This is illustrated by including data from a recent study of upper Pierre aquifer water wells (Allison, 2017).

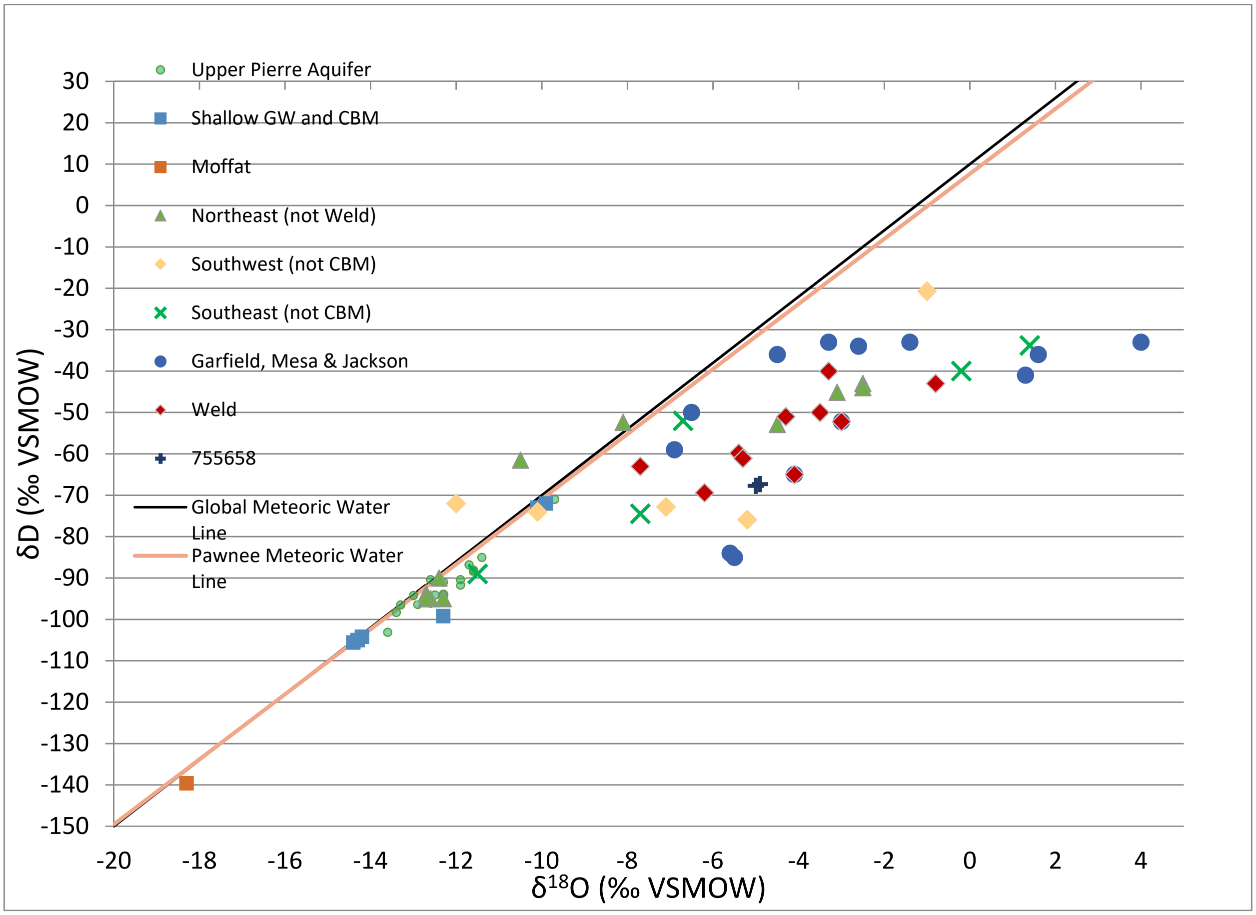

Figure 22. Water Stable Isotopes of NORM 2017 Samples

Global Meteoric Water Line from Craig, 1961, Rozanski et al., 1993, Pawnee Meteoric Water Line from Harvey, 2005. The isotopic ratio of deuterium (^2H) in water from samples collected as part of this study relative to Vienna standard mean ocean water reference is plotted against the y-axis. The isotopic ratio of ^{18}O (oxygen) in water from samples collected as part of this study relative to Vienna standard mean ocean water reference is plotted against the x-axis.

The focus of this study is on aqueous fluids co-produced with oil and gas production. Those produced waters, from reservoir rocks, are generally considered to have been isolated from surface precipitation and groundwater recharge for some time due to the depth of the oil and gas producing formations. Significant differences in the stable O and H isotopes of older isolated water and present-day meteoric water would be expected. The bulk of stable O and H isotope results shows that most produced fluids analyzed have stable isotopic signatures of ^{18}O that plot well below the global and local meteoric water lines. A few results will be highlighted and discussed here. More interpretation and discussion of the water isotope data will be presented in Section 4 of this report.

Many factors other than the near surface recharge of meteoric water to the subsurface may affect the isotopic composition of aqueous fluids in petroleum reservoirs. Mixing with older water sources in reservoir rocks, which may include ancient seawater or water that has undergone evaporation, are possible mechanisms that may cause produced water to plot off the meteoric water line.

The CBM produced fluids sampled as part of this study have water stable isotope values similar to meteoric waters, which suggests a geologically recent recharge from meteoric waters. The frac source water sample (**755461**)has water stable isotope ratios similar to Upper Pierre aquifer groundwater and falls near the meteoric water lines. The water isotope ratios for water samples from facility **755658** plots well below the global and local MWL. Water samples collected from the separator at this well also have very low concentrations of TDS. The water isotope data may indicate these samples are not rainwater but more likely water vapor condensed from the gas produced in that well.

The carbon isotopic ratios of the DIC species (bicarbonate and carbonate ions and $CO_{2(g)}$) present in groundwater systems is influenced by numerous processes. The simplest case is near surface interaction of meteoric water infiltrating through soils reacting with gaseous soil carbon dioxide (Geyh, 2000). Carbon dioxide is produced in soil through biological processes such as organic matter decomposition and root respiration (Amundson et al., 1998). Dissolution or precipitation reactions with carbonate minerals may also be factors in the ^{13}C ratio of DIC in the groundwater when carbonate minerals are present in soils or in rocks. As groundwater infiltrates and oxygen in the groundwater is depleted, biological processes such as sulfate reduction (Londry and Des Marais, 2003), methanogenesis and methanotrophy (Whiticar, 1999) may occur and may alter the isotopic composition of carbon in DIC. Carbon stable isotopic data for nine samples from the Dawson aquifer has a median ^{13}C ratio in DIC of -13.4 per mil (VPDB) from data found in Musgrove, et al., 2014. The median ^{13}C ratio in DIC of 21 samples from the deeper and older upper Pierre aquifer is -2.7 per mil (VPDB) using data from Allison (2017). The more positive (heavier) composition of the upper Pierre aquifer DIC in comparison to the shallower Dawson aquifer likely reflects longer residence time as well as biogenic processes including sulfate reduction and methanogenesis.

The five most positive isotopic ratios of ^{13}C in DIC are from CBM wells (Figure 23). The isotopic composition of carbon in DIC from produced water at Colorado CBM wells typically is a positive (heavier) ratio, reflecting longer residence times of water than in shallow domestic water sources and processes such as sulfate reduction and methanogenesis. The water stable isotopes for the CBM samples all fall on or near the meteoric water lines, as shown in Figure 22.

The two most negative isotopic ratios of ^{13}C in DIC are from duplicate samples collected at facility **755523** (Figure 23). The well is completed in and produces from upper Pennsylvanian Topeka Limestone. Topeka Limestone produced water and the isotopic ratio of the DIC likely reflect interactions with the carbonate minerals in the limestone rocks more than biological processes. The water stable isotopes fall below the meteoric water lines (Figure 22).

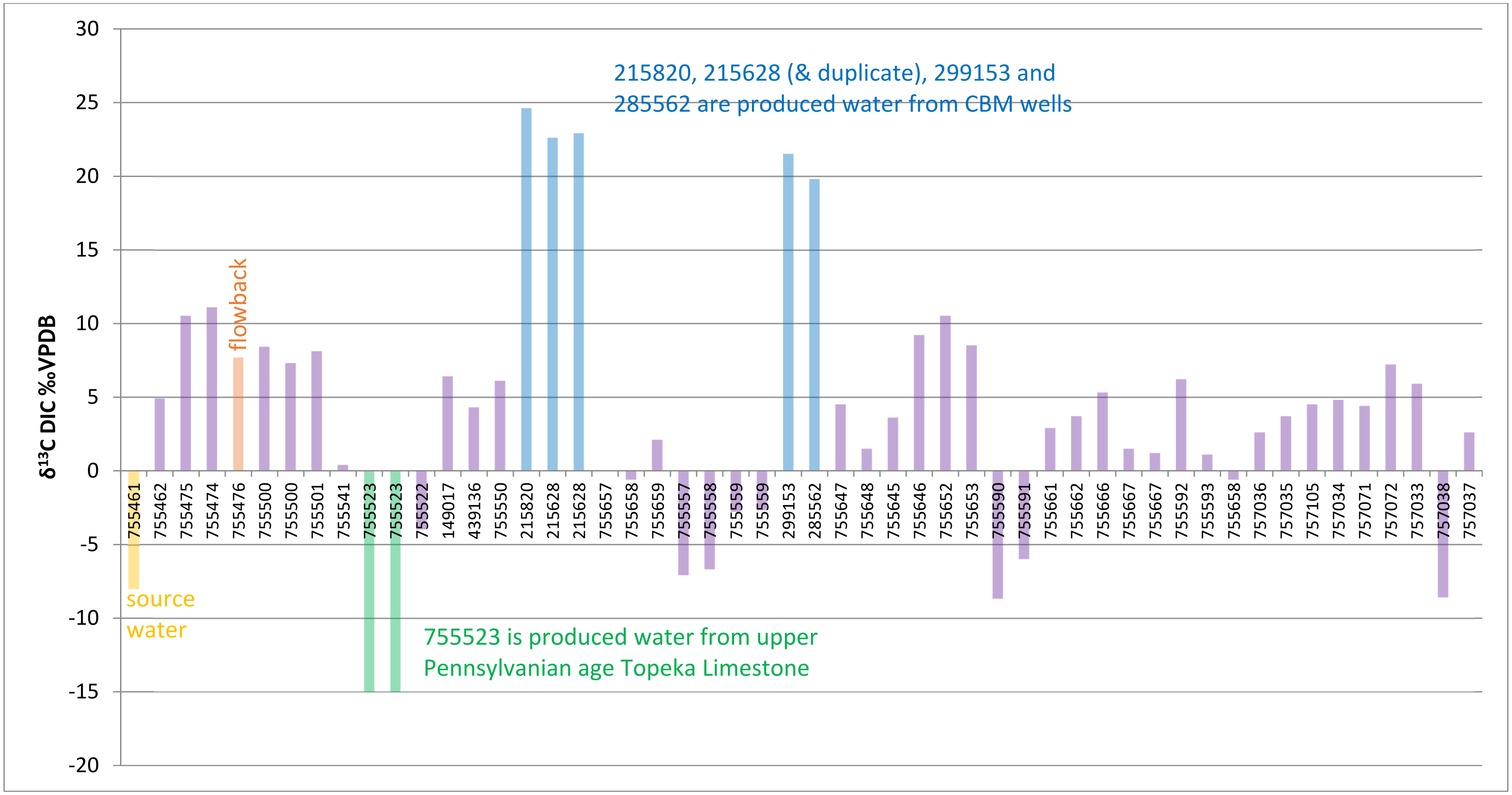

Figure 23. Carbon Isotope Ratios of Dissolved Inorganic Carbon in NORM 2017 samples
The isotopic ratio of ^{13}C (carbon) present as inorganic carbon species dissolved in water from samples collected as part of this study relative to Vienna Pee Dee belemnite reference standard is plotted against the y-axis for each water sample collected as part of this study.

The isotopic ratios of ^{13}C in DIC in 755658 and duplicate, 755657 and **755541** are approximately 0 per mil (Figure 23). Sample 755658 was collected at two sampling events from a separator and may represent condensation present in the separator and not produced water as previously discussed. The DIC present in samples from 755658 may be from the atmosphere or may reflect carbon isotopic ratio of carbon dioxide present in the produced gas (Mesa Verde Fm. production) which the water has been in contact. The sample from 755657 has similar carbon isotopic composition of DIC as 755658 and the water and gas produced from this well is in part from completions in the Mesa Verde Fm. which may point to carbon dioxide in the natural gas produced as a possible source of DIC in water samples from these two sites. Sample **755541** is produced water from a well completed in the Osage Limestone and the isotopic composition of DIC may be representative of carbonate mineral solids in the formation. Gas sales have not been reported from the three wells served by the production facility where sample **755541** was collected so carbon dioxide present in gas phases in the production are a less likely source of the DIC than carbonate mineral dissolution.

3.4 Tritium (^3H) in H_2O

Tritium (^3H) is a radioactive isotope of hydrogen that is naturally produced at small amounts in the upper atmosphere through the interaction of cosmic rays with nitrogen, oxygen, or deuterium (^2H). Tritium also is produced industrially in nuclear reactors or in other fission processes related to nuclear weapons tests. Electrolytic enrichment of the tritium in water samples can be used to enable detection of low levels of tritium in water samples.

Tritium in the atmosphere falls to the earth as part of water molecules in precipitation. Tritium undergoes beta (β) decay with a half-life of 12.3 years. Prior to atmospheric nuclear weapons testing during the 1950s and 1960s, ^3H concentrations in meteoric waters were low (≈5 tritium units [TU]) and went up a thousand fold or more in the early 1960s (Mook, 2000). Concentrations in meteoric water peaked in 1963 and have since been decreasing rapidly as it has rained out of the atmosphere (Mook, 2000; Musgrove, et al. 2014). Groundwater with a ^3H concentration >20 to 30 TU (1 TU equals 3.24 pCi/l) likely contains bomb-pulse water, and groundwater with activities of $^3H<5$TU likely have mean residence time older than the bomb pulse of the early 1960s (Musgrove, et al. 2014; Mook, 2000).

Eight of the study samples were analyzed for ^3H activity levels by gas proportional counting of hydrogen gas produced from the water samples. The sample results are presented in Appendix 16. With the exception of facility **755461** (shallow groundwater source), all of the remaining samples show lower TU activities, which would be expected of fluids that have not been in recent contact with meteoric waters or the atmosphere or are mixtures of some modern water and waters older than the bomb pulse. Further discussion and interpretation of tritium results from this study will be presented in Section 4.

3.5 ^{14}C in Dissolved Inorganic Carbon

^{14}C is a radioactive isotope of carbon, and like tritium, is also created cosmogenically at small amounts in the atmosphere through the interaction of cosmic rays with nitrogen. ^{14}C was also produced as a result of above ground nuclear explosions between 1945 and 1963, which increased the quantity of ^{14}C in the atmosphere. ^{14}C falls to the earth incorporated in precipitation as carbon dioxide. ^{14}C undergoes β decay with a half-life of 5,715 years (Bechtel 2010). ^{14}C (in waters) is measured in the DIC and expressed as a percent modern carbon (PMC). The age of the DIC present in the water samples can also be calculated and expressed as BP or years before present (Musgrove, et al. 2014). The sample results are presented in Appendix 17.

The analytically indicated ^{14}C DIC age of the inorganic carbon in the shallow groundwater source water sample (facility 755461) is 60 years BP (102.63 PMC). This indicates the inorganic carbon in the source water may have in part been from the bomb pulse years. The tritium activity of the water from this source water is likely indicative of younger water than from the bomb pulse years. The source of the inorganic carbon dissolved in the source water is likely from decay of organic sources of carbon in soils the shallow groundwater passed through. The organic matter source of the DIC is assumed to be older than the infiltrating groundwater itself.

The ^{14}C DIC ages of calculated for all of the produced water samples are older than the source water sample age by more than two orders of magnitude. The calculated ages of the DIC in the produced waters samples range from 17,115 to 43,600 years BP. Further discussion and interpretation of ^{14}C DIC ages from this study is presented in section 4.3.8.

4. DISCUSSION

Data from this study and other surface water and groundwater radiochemistry data in the COGCC database and records will be summarized and compared in this section. Radionuclide activities of produced water from three other states (NY, PA and TX) were found in the literature, and those data will also be summarized and compared to data from this study. The last portion of this section will present more detailed interpretations of data collected as part of this study.

4.1 Other Colorado Data

The COGCC environmental database contains surface water and groundwater radionuclide or U and Th data from several hundred sampling events. Project Rulison related data with its primary focus on fission related radionuclides and not on NORM has not been brought into the database at this time. Some of the Rulison data includes analytical data comparable to data collected as part of this study and that data has been reviewed as part of this project and is discussed and summarized in the next sections. Temporal changes in total U, ^{234}U, ^{226}Ra, ^{210}Pb, and ^{210}Po were analyzed and reported (Rosenblum et al., 2017) in produced water from one oil and gas well and collected over a nine month period following well completion. Rosenblum et al. (2017) did not disclose the well from which the produced water came but did state the well was in northeastern Colorado and was completed in the Cretaceous Niobrara Fm. As the specific well sampled is not disclosed by the authors, the Rosenblum data cannot be incorporated in the COGCC database but will be summarized and compared to data from data from Niobrara wells gathered as part of this study in Section 5 of this report.

4.1.1 Project Rulison

Project Rulison was part of a program, generally called Project Plowshare, conducted by the Atomic Energy Commission (AEC) to pursue peaceful uses of nuclear explosives. One proposed use was the idea of detonating nuclear blasts in the subsurface to stimulate natural gas production from low-permeability sandstone reservoirs in sedimentary basins throughout the Rocky Mountain states. The creation of an effectively large wellbore together with the creation of related connecting fractures in the adjacent formation using a nuclear explosive device was proposed as possibly more efficient than using chemical explosives or hydraulic fracturing techniques (Rubin et al., 1972).

Project Rulison was conducted in 1969. Gas production rates were found to be high initially; however, pressure recovery measurements during shut-in periods indicated limited effectiveness of the blast stimulation to exploit the low-permeability reservoir. Extensive environmental radiological monitoring at and around the project site before and after the tests by the AEC and later by DOE, USGS, and EPA has shown that no radioactive fission products attributable to the tests have been found in these near surface environmental samples collected to present, with the exception of radioactive natural gases vented from the site in the first year following the test. A summary of the Project Rulison related sampling and analysis scheme is found in the most recent version of the Rulison Sampling and Analysis Plan (COGCC 2017b).

Renewed interest in natural gas production from the Williams Fork Fm. near Project Rulison in the mid 2000s prompted the COGCC to establish specific radiological sampling of drilling and production fluids and gasses from oil and gas wells drilled within a 3-mile radius centered on the Project Rulison blast well (also known as Lot 11 [40-acre lot]) (COGCC Cause Number 139-43). Subsurface drilling below 6,000 feet is restricted under Lot 11 by the federal government and Garfield County deed restriction (COGCC, 2017b).

Exploration and production sample media including produced water and both frac source water and flow back fluid have been collected from 2008 through 2018, with the bulk of the sampling in 2008 through 2010. Table 20 presents a summary of results extracted from the 4th Quarter 2009 summary that was provided to COGCC by operators in the Rulison area (URS, 2010b) which is available in the Project Rulison section under the Piceance Basin area of the Library link on the COGCC webpage (http://cogcc.state.co.us/library.html#/areareports).

The database for the Project Rulison E&P radiological sampling is not yet incorporated into the COGCC environmental database, as the current COGCC environmental database did not exist at the time when the initial Rulison sampling and analysis plan went into effect. The Rulison data presented below in Table 20 and 21 (URS 2010b) are from subsets of the entire project and were compiled manually as part of this project. The main focus of the Rulison sampling is on fission products such as ^{14}C and ^{3}H that may have migrated from the blast cavity and not on NORM related radionuclides.

Table 20. Comparison of Rulison and This Study Produced Water Screening and Isotopic Data

Analyte	Rulison Area Produced Water		This Study Produced Water	
	Minimum Activity (>MDC) (pCi/l)	Maximum Activity (pCi/l)	Minimum Activity (>MDC) (pCi/l)	Maximum Activity (pCi/l)
gross α	19.1	37.5	0.1	730
gross β	14.6	43.2	1.98	5,710
^{214}Bi	5.76	8.38	25	119
^{40}K	39.1	60.6	189	2,840
^{210}Pb	3.73	5.27	0.71	253
^{214}Pb	6.2	7.32	26	78.09
^{228}Ra	8.25	13.4	0.94	221

Analytical results show higher maximum activities for produced water samples from this study (Table 20) than for those measured for the Rulison Project. Minimum activities were lower for all analytes for this study than for the Rulison results (with the exception of ^{40}K). The Rulison samples are all from a single producing formation (Cretaceous Williams Fork), whereas the data from this study are a compilation of results from 15 different formations across the state.

Table 21. Rulison Source Water and Frac Flowback and COGCC 2017 Comparison

Analyte	Rulison Area Source Water and Flowback		This Study Source Water and Flowback	
	Minimum Activity >MDC'	Maximum Activity	Minimum Activity >MDC	Maximum Activity
gross α (pCi/l)	142.8 (**U**) (s)	266 (f)	26.8 (s)	53.2 (f)
gross β (pCi/l)	2,300 (f)	5,420 (f)	5.56 (s)	68 (f)
tritium (TU)	10 (s)	12.1 (s)	1.3 (f)	6.71 (s)
^{214}Bi (pCi/l)	11.2 (f)	39.4 (s)	U	U<29
^{40}K (pCi/l)	2,860 (f)[1]	4,390 (s) [1]	U	U<200
^{210}Pb (pCi/l)	908 (**U**) (s)	387 (s)	U	U<1.19
^{214}Pb (pCi/l)	15.2 (s)	30.7 (s)	U	U<24
^{228}Ra (pCi/l)	32.3 (f)	36.5 (f)	U	1.47 (f)

f -frac flowback, s – frac source water ([1] **2% KCL added for Rulison samples**) **U - not detected**

Activities of the analytes included in Table 21 indicate higher maximum and minimum activities for both the Rulison frac source and flowback water samples than for activities determined for this study (Table 21). It is worth noting that the Rulison frac source water was conditioned with the addition of 2% KCl as an additive, whereas no KCl was added chemical modifier in the frac source water sampled from the DJ Basin. Records available on FracFocus website indicate that KCl was not added as a primary component to any of the eight wells from which a comingled flowback sample was collected as part of this study. The addition of KCl to the Rulison source waters is presumably responsible for much if not all of the higher activities for gross beta and ^{40}K in Rulison source waters and in Rulison flowback waters than in the one 2017 source water and one 2017 flowback sample.

4.1.2 Surface Water, Domestic Groundwater, and Raton Basin and NORM 2017 Produced Water Data

Some NORM-related analyses of surface water and groundwater, including produced water, are found in the COGCC environmental database. The NORM-related analyses of produced water that predate this study are primarily from CBM produced water in the Raton Basin. Many of the groundwater and surface water samples with NORM-related analytes have been collected as part of voluntary baseline sampling conducted for oil and gas operators. The data discussed below incorporates data from this study and data from other sources that were found in a query of the COGCC environmental database. Enough results for metals analysis of Th and U concentrations in water, activities of two ^{238}U progeny (^{226}Ra and ^{222}Rn) in water, and activities of one ^{232}Th progeny (^{228}Ra) in water samples were found in the database and will be summarized and discussed below. The data for domestic groundwater and surface water samples are being used in aggregate and for comparison. Much of the data in the COGCC database has not received thorough review and validation and has been received from many sources and many labs. In this report the large data set will be used for comparison of broad trends and not be used in detailed evaluation of individual groundwater sources.

Metals analyses of water samples for U and Th are found in the COGCC database as summarized below. A total of 775 results for U reported as concentration (not activity) in water samples were found in the 23February2018 query. Figure 24 illustrates the minimum, median, mean, and maximum concentrations for the surface and domestic groundwater samples (detected in 336 out of 658 results), with the same set of statistics shown from the produced water samples (detected in 24 samples out of 117 results). Note that the y-axis (U concentration) is plotted on a logarithmic scale. The minimum, median, mean, and maximum concentrations of U are lower in Colorado produced water samples than the minimum, median, mean, and maximum U concentrations in Colorado surface water and domestic groundwater sources for which data are available. Overall the concentration of U in deeper sources such as produced water are lower than the U concentrations in shallower water sources, including surface water and domestic well groundwater (Figure 24).

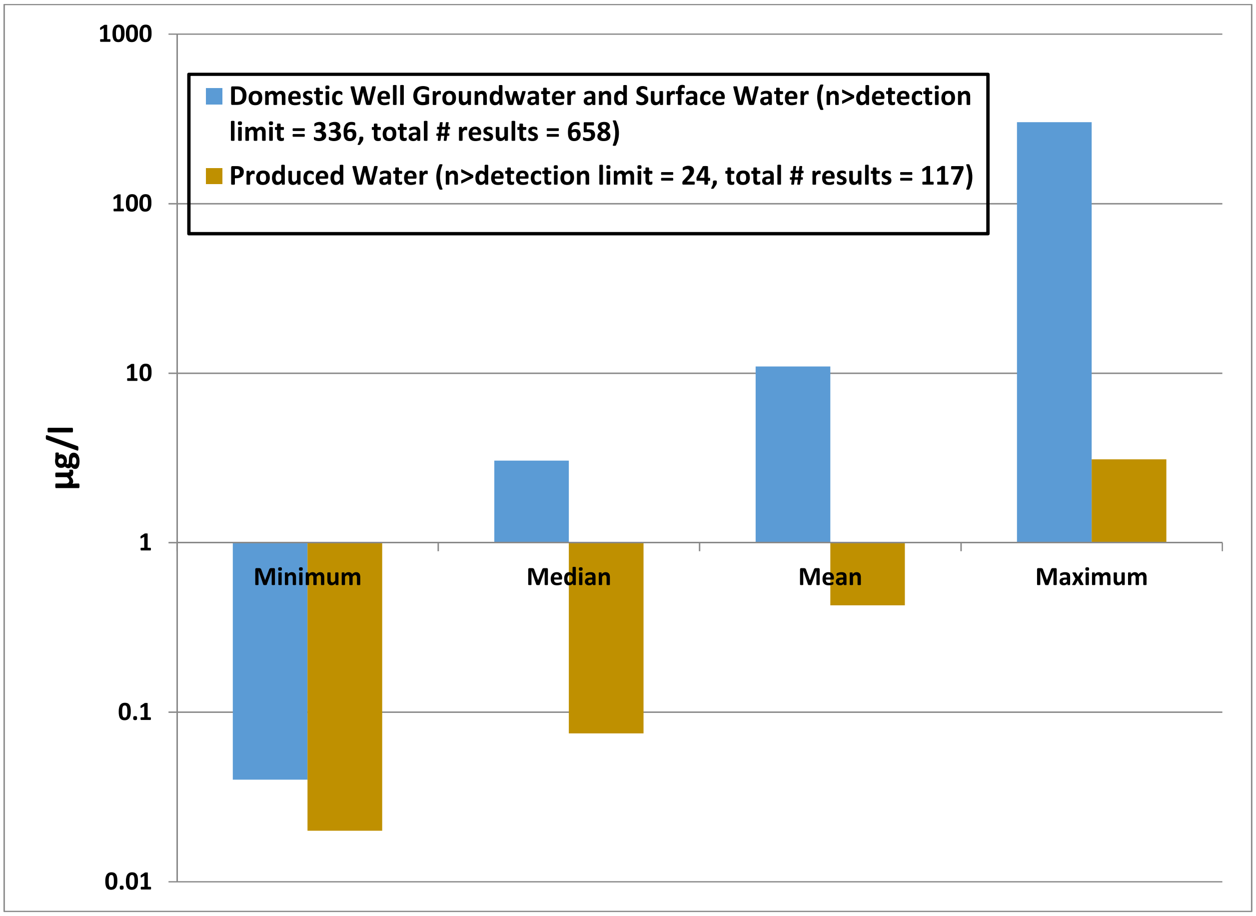

Figure 24. Comparison of Domestic Groundwater and Produced Water Uranium Concentrations

Relatively low concentrations of U in groundwater from deeper water sources, such as produced water in which oxygen has been depleted and in which strongly reducing conditions prevail, was expected and assumed based on available scientific literature referenced in the Introduction to this report such as Langmuir (1978), Hem (1992), and IAEA (2003).

Many of the domestic groundwater samples for which data are available were collected in areas of Weld County. A number of the shallow sandstones known to contain U and that have been considered as potential sites for in-situ extraction of U are present in northern Weld County (Reade, 1978). It is likely that many of the shallow groundwaters are not as depleted in oxygen as produced water samples. The presence of oxygen or in general of oxidizing conditions favors the dissolution of U present in the shallow aquifer rocks and sediments (Hem, 1992; IAEA, 2003).

Thorium is generally considered to be relatively insoluble in water but can be present as complexes with sulfate, phosphate, fluoride, and organic anions (Langmuir and Herman, 1980). A total of 323 results for Th reported as concentration (not activity) in water samples were found in the 23February2018 query, and Table 22 presents the minimum, median, mean, and maximum concentrations for the surface and domestic groundwater samples (detected in 84 out of 239 results), with the same set of statistics shown from the produced water samples (detected in 12 samples out of 84 results).

The median, mean, and maximum concentrations of Th are lower in Colorado produced water samples than the median, mean, and maximum Th concentrations in Colorado surface water and domestic groundwater sources for which data are available. Dissolved Th concentrations in surface waters are thought in general to be between 0.01 to 1μg/l (Langmuir and Herman, 1980). The Th concentrations in shallow groundwater and surface water samples from Colorado mostly fall in the range reported by Langmuir and Herman (1980).

Table 22. Comparison of Domestic Well Groundwater and Produced Water Thorium Concentrations

Thorium			
Domestic Well Groundwater and Surface Water Samples (n>detection limit = 84, total # Th results = 239)		**Produced Water Samples (n>detection limit = 12, total # Th results = 84)**	
Minimum μg/l	0.030	**Minimum μg/l**	0.040
Median μg/l	0.715	**Median μg/l**	0.085
Mean μg/l	0.949	**Mean μg/l**	0.145
Maximum μg/l	4.5	**Maximum μg/l**	0.57
range of & median MDL of 239 results μg/l	0.03-10, 0.55	**range of & median MDL of 84 results μg/l**	0.2-2, 0.2

Gross alpha and gross beta analyses of Colorado water samples are found in the COGCC database as summarized below. A total of 573 results for gross alpha activities and 450 results for gross beta activities in water samples were found in the 23February2018 query, and Figure 25 illustrates the minimum, median, mean, and maximum concentrations for the surface and domestic groundwater samples. Note that the y-axis (pCi/l) is in a logarithmic scale. Gross alpha activities present above sample-specific MDC in 202 out of 415 results and gross beta activities were present above sample-specific MDC in 184 out of 293 results found from surface water and domestic well groundwater sample data. The same set of statistics shown from the produced water samples indicate gross alpha activities present above sample-specific MDC in 81 out of 158 results and gross beta activities present above sample-specific MDC in 93 out of 157 results available from produced water samples. Gross alpha and gross beta activities are a general screening analysis for the presence of many radionuclides but do not provide information regarding the activity of individual radionuclides.

The medians, means, and maximums of gross alpha and gross beta activities of produced water samples are higher than the same statistics for surface and domestic groundwater samples for which data is present in the COGCC database. The median, mean, and maximum concentrations of U and Th are both greater in the COGCC database set of surface water and domestic groundwater sample results than in the COGCC database's produced water sample results, but as discussed above the opposite is found for gross alpha and gross beta activities. Analyses of samples for gross alpha and gross beta activities do not indicate specific isotopes responsible for the measured radioactivity. In addition, the preparation step for the analysis does not retain gaseous radon isotopes. From the U and Th metals analytical data, one can infer that the greater range of gross alpha activity present in produced waters (Figure 25) is not primarily from alpha decay of Th and U isotopes, but from alpha decay of progeny of U and Th such as ^{226}Ra and ^{224}Ra. As discussed in this report, it has been inferred that the primary beta emitters responsible for the gross beta activity are ^{40}K (Figure 11) and, as will be discussed later in this section, ^{228}Ra (Figure 27). The surface water and domestic groundwater samples may have greater concentrations of U and Th on average than Colorado produced water samples for which data is available, but presumably the concentrations (inferred from gross beta as well as from specific Ra isotope activities data to be discussed below) of K and alpha and beta emitting Ra isotopes are on average greater in produced water samples.

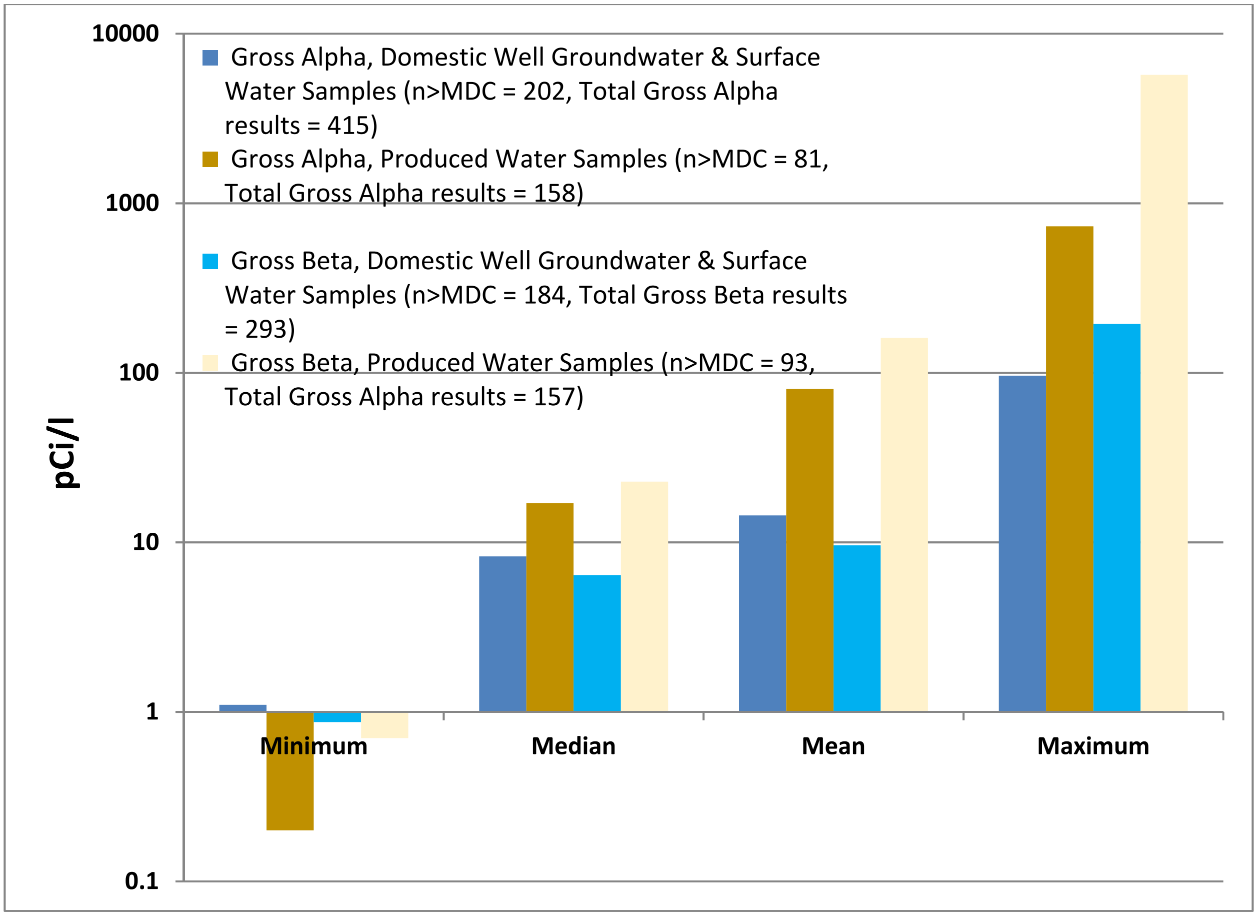

Figure 25. Comparison of Gross Alpha and Gross Beta in Colorado H_2O Samples

The COGCC environmental database contains 344 results of ^{226}Ra and 213 analyses of its ^{222}Rn progeny (22 Feb 2018 query). Both of these radionuclides are progeny of ^{238}U. Radium is thought to be more soluble in produced water than either U or Th (parent nuclides) as shown in Figures 1 and 2 (Hem, 1992; IAEA, 2003). Figure 26 is a comparison of the ranges of ^{226}Ra and ^{222}Rn activity data in the COGCC database from surface water and domestic groundwater sources to data from produced water sources. Note that the y-axis (pCi/l) is plotted in a logarithmic scale.

The ^{226}Ra activity of 15 water samples was reported as >MDC out of 136 samples from surface and domestic well sources. The ^{222}Rn activity of 39 water samples was reported as >MDC out of 44 samples from surface and domestic sources. The ^{226}Ra activity of 138 produced water samples was reported as >MDC out of 208 samples from produced water sources. The ^{222}Rn activity of 104 water samples was reported as >MDC out of 169 samples from produced water sources.

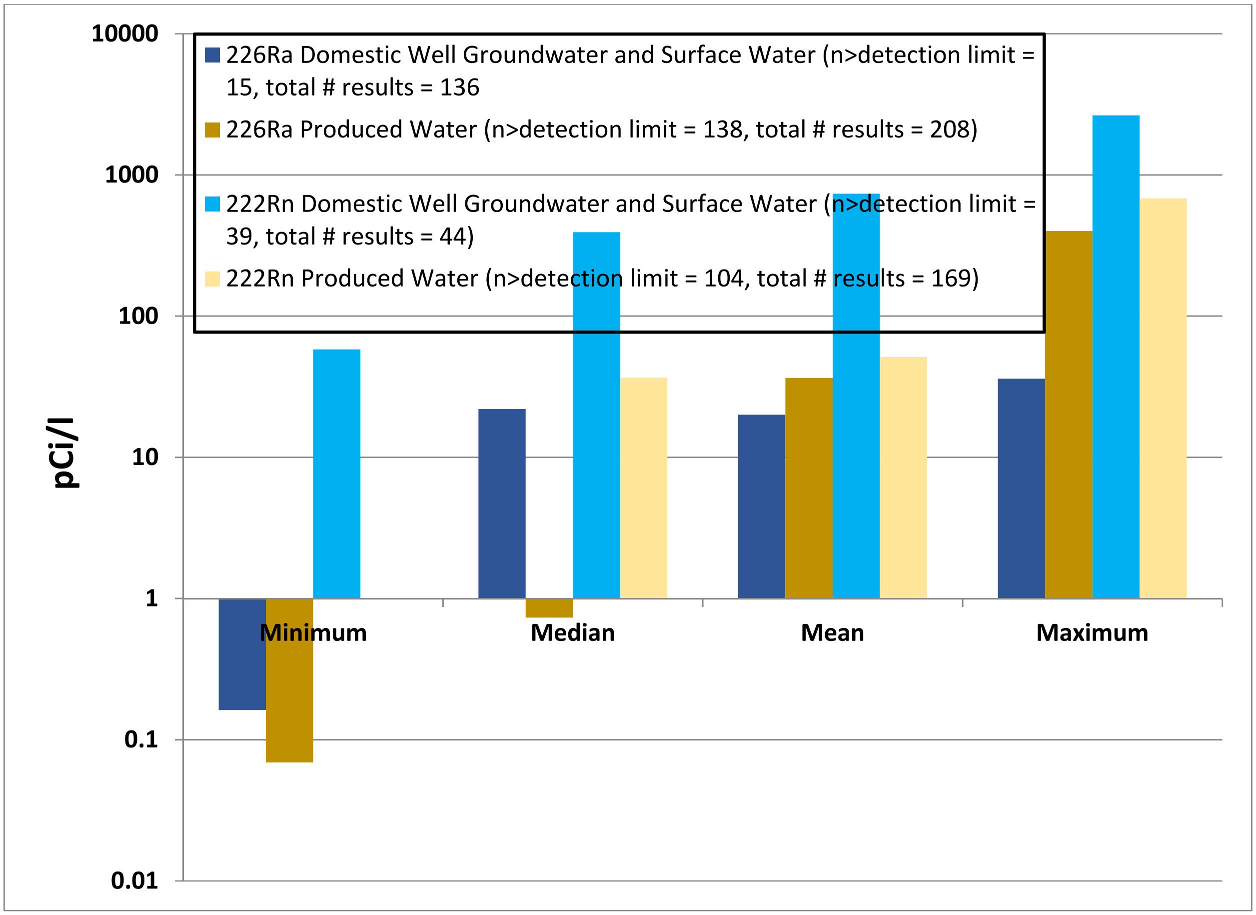

Figure 26. Comparison of Domestic Groundwater and Produced Water ^{226}Ra and ^{222}Rn Activities

The median, mean, and maximum activities of ^{226}Ra and of its progeny ^{222}Rn of produced water samples are lower than the same statistics for surface and domestic groundwater samples for which data is present in the COGCC database. A hydrocarbon gas phase is present in produced water and some or much of the radon present in the water in the subsurface may be portioned into natural gas during the production process and this may be responsible for relatively lower radon activities in produced water samples in comparison to shallow groundwater samples for which data is available in the COGCC database. Domestic groundwater samples may be interacting with rocks and sediments that contain greater concentrations of U and its progeny such as ^{226}Ra and ^{222}Rn which may in part be responsible for the results shown in Figure 26. As discussed elsewhere in this report with repsect to produced water samples, the chemistry of domestic groundwater is in many cases dependent on the rocks or sediments it has flowed through or in which is now present instead of the manner or style of drilling or completion processes done to develop the well.

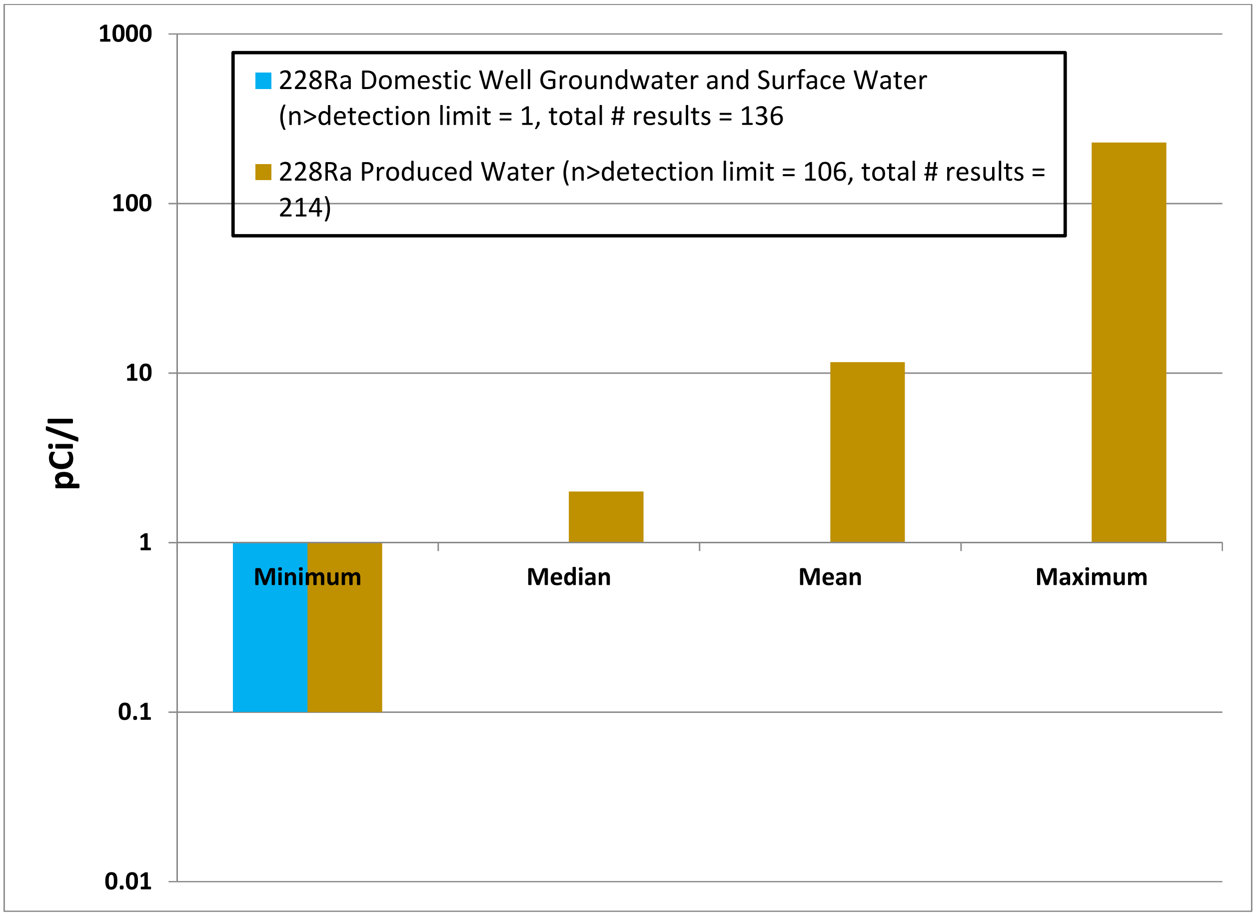

Figure 27. Comparison of Domestic Groundwater and Produced Water ^{228}Ra Activities

The COGCC environmental database contains 350 results of ^{228}Ra analyses (22 Feb 2018 query). Many of the results from domestic groundwater sources are from less sensitive gamma spectroscopy analysis with elevated MDC in the range of 20 to 50 pCi/l. Most produced water analyses in the COGCC database of ^{228}Ra are from GFPC analysis following chemical separation with much lower MDC (typical range of 1 to 2 pCi/l or less). Figure 27 is a comparison of the ^{228}Ra data in the COGCC database. Note that the y-axis (pCi/l) is plotted on a logarithmic scale. Only one domestic groundwater sample was reported as >MDC out of 136 samples from domestic sources, so no median, mean, or maximum are plotted. The median and mean of the produced water ^{228}Ra activities are 2 and 11.6 pCi/l respectively. Both the median and mean activities of the produced water ^{228}Ra analyses are less than the typical MDCs for the domestic groundwater analyses. ^{228}Ra is the progeny of ^{232}Th. The presence of ^{228}Ra in samples even when total Th concentrations are very low is indicative of the assumed greater solubility of Ra than Th in produced waters (Hem, 1992; IAEA, 2003).

^{224}Ra and ^{220}Rn are radionuclides in the ^{232}Th decay chain illustrated in Figure 2. ^{224}Ra was analyzed in all water samples collected as part of this study. The COGCC database does not contain other analyses for this Ra isotope or for the ^{220}Rn isotope. The ^{220}Rn isotope has a half-life of <1 minute (IAEA, 2003) and would need to be analyzed in the field immediately upon collection.

4.2 Data from Other States

Samples of produced water from Pennsylvania oil and gas wells were analyzed for gross alpha and gross beta activity as part of a study conducted by contractors to the Pennsylvania Department of Environmental Protection in 2014 with a revised report released in 2016 (PESI, 2016) and those samples are listed under the columns labeled **PA** in Table 23. A 2011 USGS study (Rowan et al., 2011) gathered new and existing data analyses of produced water from oil and gas wells in Pennsylvania and New York and summaries of that data are under the columns labeled **PA & NY** in Table 23. Data included in the Table 23 statistical summary of PA and NY produced water analyses include data hand-compiled from a manual search of Pennsylvania documents from 2009 and 2010 at PADEP offices by USGS staff (Rowan et al., 2011) as well as data from a New York study (NYDEC, 2009). A comparison of the ranges of Pennsylvania and New York gross alpha and gross beta activities in comparison to the ranges of alpha and beta activities of Colorado samples from this study is presented below in Table 23.

The range of gross alpha activities reported in Table 23 are lower by one to two orders of magnitude in the Colorado produced water samples than in the Pennsylvania and New York sample data from the sources listed above. The ranges of produced water gross beta activities in Colorado and Pennsylvania are more similar than the ranges of gross alpha activities, but the median gross beta of the Colorado samples collected in this study is lower by more than one order of magnitude than the PA or PA & NY median gross beta activities.

Table 23. Comparison of CO (this study), PA and PA &NY Ranges of Gross Alpha and Gross Beta Activities in Produced Water Samples

	gross α			gross β		
Statistic	**CO**	**PA**	**PA & NY**	**CO**	**PA**	**PA & NY**
Minimum pCi/l	1.73	**233**	**14**	1.98	**113**	**7**
Median pCi/l	40.3	**9,760**	**6,845**	81.5	**2,300**	**1,170**
Mean pCi/l	130.9	**11,500**	**12,064**	316.8	**2,660**	**2,287**
Maximum pCi/l	730	**41,700**	**123,000**	5,710	**7,600**	**12,000**
Std. Deviation pCi/l	188.8	**12,800**	**22,228**	911.9	**2,460**	**3,181**
n=	47	**13**	**33**	44	**13**	**32**

PA data from PESI, 2016. ***PA & NY*** data from Rowan et al., 2011, NYDEC, 2009 and PADEP, 1992.

Table 24 summarizes reported activities of ^{226}Ra, ^{228}Ra, and ^{40}K in produced water from this study and from studies conducted in Pennsylvania, New York, and Texas. The columns labeled **PA** have summary statistics from the PADEP (PESI, 2016) study and the columns labeled **PA (2018)** come from the more recent study by Tasker et al. (2018). Analyses from this data set include ^{226}Ra and ^{228}Ra activities by gamma spectroscopy. The data in the columns labeled **NY** come from the NYDEC (1999) study. Analyses from the 1999 New York dataset include ^{238}U progeny activities, ^{232}Th progeny activities, and ^{40}K activities, all determined from gamma spectroscopy.

Existing data were compiled and new sampling and analysis of produced water from Pennsylvania and New York oil and gas wells were summarized in a 2011 USGS report (Rowan et al., 2011). The 2011 compilation included the NYDEC (1999) data already summarized. The Table 24 columns labeled **PA & NY** have summary statistics for analyses from Pennsylvania and New York but do not include the NYDEC (1999) data. The other sources of data included in the 2011 compilation include data hand-compiled from a manual search of Pennsylvania documents from 2009 and 2010 at PADEP offices by USGS staff (Rowan et al., 2011) as well as data from a New York study (NYDEC, 2009) and a Pennsylvania study (PADEP, 1992). Existing data were compiled and new sampling and analysis of produced water from Texas geothermal and oil and gas wells was summarized in a 1995 report (Fisher, 1995) by the Texas Bureau of Economic Geology. Analyses from the Texas dataset include ^{226}Ra and ^{228}Ra activities by gamma spectroscopy, and summary statistics from this Texas study are shown in the columns labeled **TX**.

Ranges of ^{226}Ra (^{238}U decay chain) are available from this study and the five studies listed above. The median, mean, and maximum of ^{226}Ra activities from this study are lower than the same statistical parameters from the four studies in PA, NY, and TX. For example the ^{226}Ra median, mean, and maximum activities are from the 2016 PA study and are one to two orders of magnitude greater than ^{226}Ra activities in samples collected in Colorado as part of this study. One can surmise that the rocks in contact with the PA, NY, and TX produced waters contain higher activities of ^{226}Ra, and presumably also the ^{238}U isotope from which it has decayed, than the ^{226}Ra and ^{238}U activities of rocks in contact with the produced waters collected as part of the study in Colorado. An alternative hypothesis is that the geochemistry of the produced water limits solubility of Ra in the formation waters. The alternate hypothesis and the supposition regarding higher presence of Ra are not mutually exclusive in that the U content of the producing formation's rocks and minerals and the geochemistry of the waters in contact with the producing formation's rocks and minerals both matter.

Ranges of ^{228}Ra (^{232}Th decay chain) are available from this study and the five studies listed above. The median, mean, and maximum of ^{228}Ra activities from this study are lower than the same statistical parameters from the five studies in PA, NY, and TX. For example the ^{228}Ra median, mean, and maximum activities from each of the other five studies are roughly one to two orders of magnitude greater than the median, mean, and maximum ^{228}Ra activities in samples collected in Colorado as part of this study. As with ^{226}Ra, one can surmise that the rocks in contact with the PA, NY and TX produced waters contain higher activities of ^{228}Ra, and presumably also the ^{232}Th isotope from which it has decayed, than the ^{228}Ra and ^{232}Th activities of rocks in contact with the produced waters collected as part of this study in Colorado. An alternative hypothesis is that the geochemistry of the produced water limits solubility of Ra in the formation waters. The alternate hypothesis and the supposition regarding higher presence of Ra are not mutually exclusive as discussed above.

Activities of ^{40}K were reported in two of the studies (**PA** and **NY**) as shown in Table 24. ^{40}K activities were greater than the sample-specific MDC in 5 of 52 samples collected as part of this study, and summary statistics except for minimum and maximum were not calculated. The ranges of concentration of K in produced water as well as the activities of its radioactive ^{40}K isotope are more similar between CO, **PA** and **NY** samples than the activities of U and Th-derived radium isotopes discussed previously.

Table 24. Comparison of CO, PA, NY and TX Ranges of ^{226}Ra, ^{228}Ra and ^{40}K Activities in Produced Water Samples

	^{226}Ra					
	alpha spectroscopy at 4781keV following chemical separation	gamma emission 186keV direct	gamma emission (inferred from ^{214}Pb or ^{214}Bi)	gamma emission (inferred from higher of ^{214}Pb or ^{214}Bi	various methods	various methods
Statistic	**CO**	**PA**	**PA (2018)**	**NY**	**PA & NY**	**TX**
Minimum pCi/l	0.149	40.5	51	64	0.16	0.1
Median pCi/l	20.45	4,490	506	445	1,040	138
Mean pCi/l	62.6	5,880	439	614	2,427	356
Maximum pCi/l	377	26,600	1,220	3,800	16,920	5,150
Std. Deviation pCi/l	88.8	7,450	315	617	3,607	625
n=	43	13	14	50	93	153
	^{228}Ra					
	beta emission of ^{228}Ra progeny (^{228}Ac) using GFPC following chemical separation	gamma emission 911keV inferred	gamma emission 911keV inferred from ^{228}Ac	gamma emission inferred from highest of ^{228}Ac, ^{212}Pb or ^{208}Tl	various methods	various methods
Statistic	**CO**	**PA**	**PA (2018)**	**NY**	**PA & NY**	**TX**
Minimum pCi/l	0.94	26	8	19	0.03	8.2
Median pCi/l	9.65	636	464	565	515	226
Mean pCi/l	18.29	773	719	1,352	607	541
Maximum pCi/l	221	1,900	1,760	24,000	2,589	5,490
Std. Deviation pCi/l	35.4	604	652	3,682	604	1,143
n=	40	13	14	44	88	22
	^{40}K					
	gamma emission 1460.75keV direct	gamma emission 1460keV direct		gamma emission direct		
Statistic	**CO**	**PA**		**NY**		
Minimum pCi/l	338	15.5		120		
Median pCi/l		220		2,000		
Mean pCi/l		335		2,259		
Maximum pCi/l	2,840	852		6,800		
Std. Deviation pCi/l		260		1,502		
n=	5	13		50		

PA data from PESI, 2016.*PA (2018)* data from Tasker et al., 2018. ***NY*** data from NYDEC, 1999. ***PA & NY*** data from Rowan et al., 2011, NYDEC, 2009 and PADEP, 1992. ***TX*** data from Fisher, 1995.

A limited number of gas samples were collected as part of this study for analysis of ^{222}Rn activity. Data from the **PA** study (PESI, 2016) is compared to the limited set of ^{222}Rn activities of Colorado gas samples in Table 25. The ranges of the two sets of ^{222}Rn activities of gas samples are similar despite the much higher activities of the radon parent nuclide (^{226}Ra) reported in Pennsylvania produced water samples. Alpha decay of ^{226}Ra (^{238}U decay chain) is the immediate precursor of ^{222}Rn. As discussed previously the activities of ^{226}Ra were one to two orders of magnitude greater in the PA produced water samples. Higher activities of ^{226}Ra should result in higher activities of ^{222}Rn in the PA samples if collected in the same manner and assuming minimal losses of radon gas during and after sample collection. We view the PA ^{222}Rn activities as anomalous but do not know enough about the systems from which the PA gases were collected or the processes of collection, storage, and analysis of the PA gas samples to hypothesize an explanation of the anomaly.

Table 25. Comparison of CO and PA Ranges of ^{222}Rn Activities in Natural Gas Samples

	^{222}Rn in natural gas samples	
Statistic	**CO**	**PA (2016)**
Minimum pCi/l	17.5	3
Median pCi/l	46	41.8
Mean pCi/l	61.2	47.9
Maximum pCi/l	150	148
Std. Deviation pCi/l	53.9	34.5
n=	5	22

PA data from PESI, 2016.

4.3 Data from this Study

Analytical data obtained as part of this study have been described and summarized in Section 3 and presented in tabular form in the appendices to this report. Discussion of specific and general results from this study will be found in the next sections under this heading.

4.3.1 Gross Alpha and Gross Beta

Gross alpha and gross beta analyses of all water samples collected as part of this study were performed. Analyses of individual alpha and beta emitting isotopes were also performed on all water samples collected as part of this study. Gross alpha and gross beta analyses are not isotope-specific analyses but do provide alpha activity and beta activity screening data from non-volatile radionuclides present in the samples as discussed in Section 3.1.1. of this study.

Figure 1 and Figure 2 show that 14 isotopes in the decay chains of ^{238}U and ^{232}Th decay by alpha emission, and 12 of the 14 are non-volatile. Specific isotope analyses of three of the non-volatile alpha emitters were performed on all water samples (^{226}Ra, ^{224}Ra and, ^{210}Po). The sum of the reported activities of ^{226}Ra, ^{224}Ra, and ^{210}Po (if >MDC) are plotted versus the reported gross alpha activity of the same sample (if >MDC) in Figure 28. Activities of three U isotopes are included in the sum for the three samples in which uranium isotopic analyses were triggered (Appendix 4). Reported activities of ^{238}U, ^{235}U, and ^{234}U were minimal in comparison to gross alpha activity in samples from two produced water samples (439136 – 0.3%, 755653 – 4%). Reported activities of the three uranium isotopes were approximately 69% of the gross alpha activity of the source water sample (755461). Uranium concentrations observed by Rosenblum et al. (2017) in frac source water were also much higher than in produced water samples from the Niobrara Fm. well in which the source water had been utilized in a hydraulic fracture completion.

The equation to the linear best fit line shown in Figure 28 indicates that approximately 48% of the gross alpha activity of the samples is accounted for by the sum of the activities of the three isotope-specific analyses of alpha emitters. Alpha emitting radon isotopes (^{222}Rn and ^{220}Rn) present would be lost during the preparation process for the gross alpha analysis. Nine of the non-volatile alpha emitters listed in Figures 1 and 2 were not subject to specific chemical separation and analysis and would be expected to be present in these samples at varying levels. Low levels of naturally occurring alpha emitters other than in the ^{238}U and ^{232}Th decay chains may also be present including other uranium and thorium isotopes.

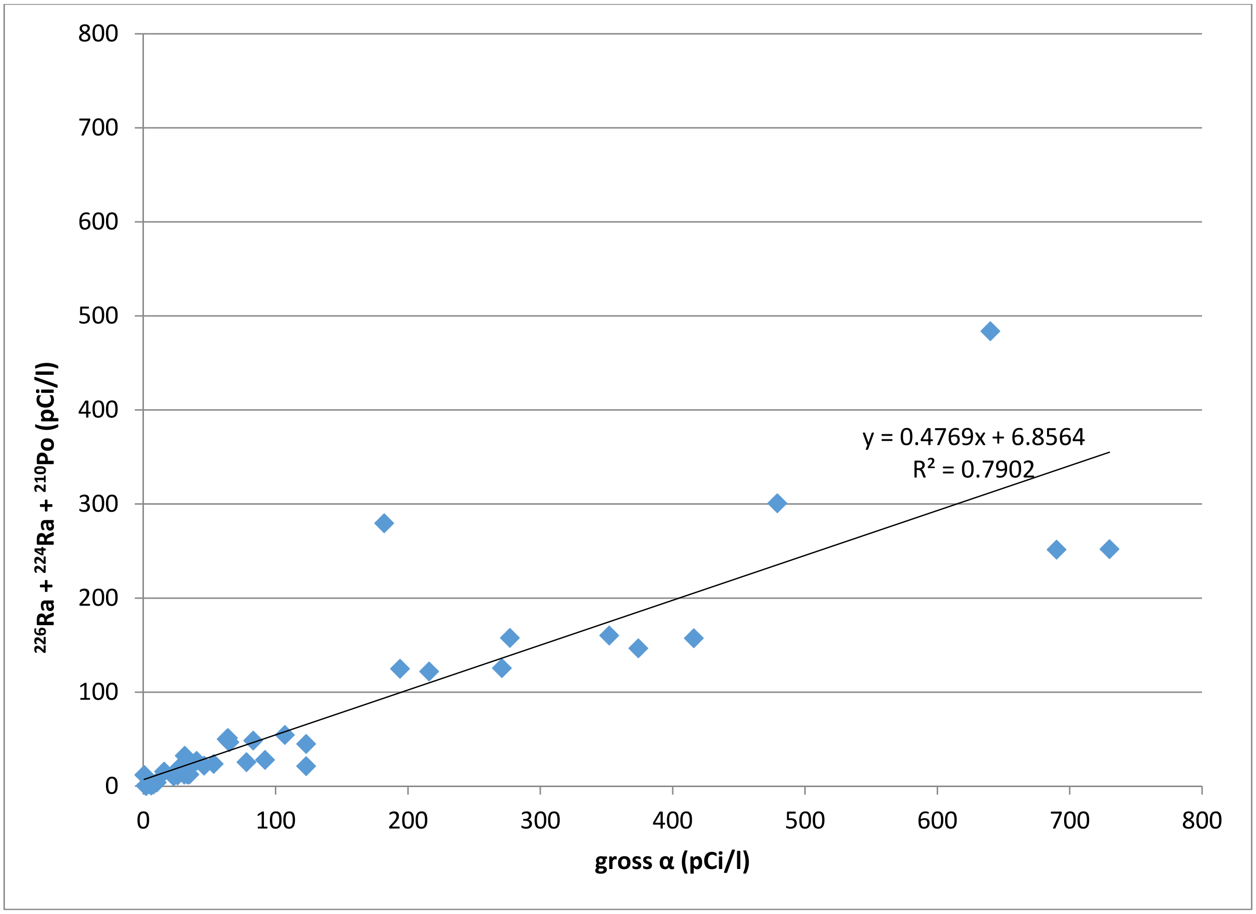

Figure 28. Gross Alpha Activities Versus Sum of ^{226}Ra, ^{224}Ra and ^{210}Po Activities from Samples Collected as Part of this Study

Figure 1 and Figure 2 show that 12 isotopes in the decay chains of ^{238}U and ^{232}Th decay by beta emission, and each of the 12 are non-volatile. Specific isotope analyses of two of the non-volatile beta emitters were performed on all water samples (^{228}Ra and ^{210}Pb). ^{40}K also decays by beta emission but is not part of uranium or thorium decay chains. Analysis of ^{40}K was done by gamma spectrometry with limited sensitivity and as was discussed in section 3.5.4.1 the activity of ^{40}K was above the MDC in only five of the samples collected as part of this study, which are also the samples with the five highest concentrations of K.

The sum of the reported activities of ^{228}Ra and ^{210}Pb (if >MDC) from specific isotope separations and analysis are plotted versus the reported gross beta activity of the same sample (if >MDC) in Figure 29. The concentration of K in each sample collected as part of this study is also plotted (if >MDL) versus the gross beta activity of the same sample (if >MDC) in Figure 29. The concentration of K is used as an analog for the concentration of ^{40}K in naturally occurring K, since 0.0117% of the atoms in naturally occurring K (CIAAW, 2017) are the radioactive isotope (^{40}K).

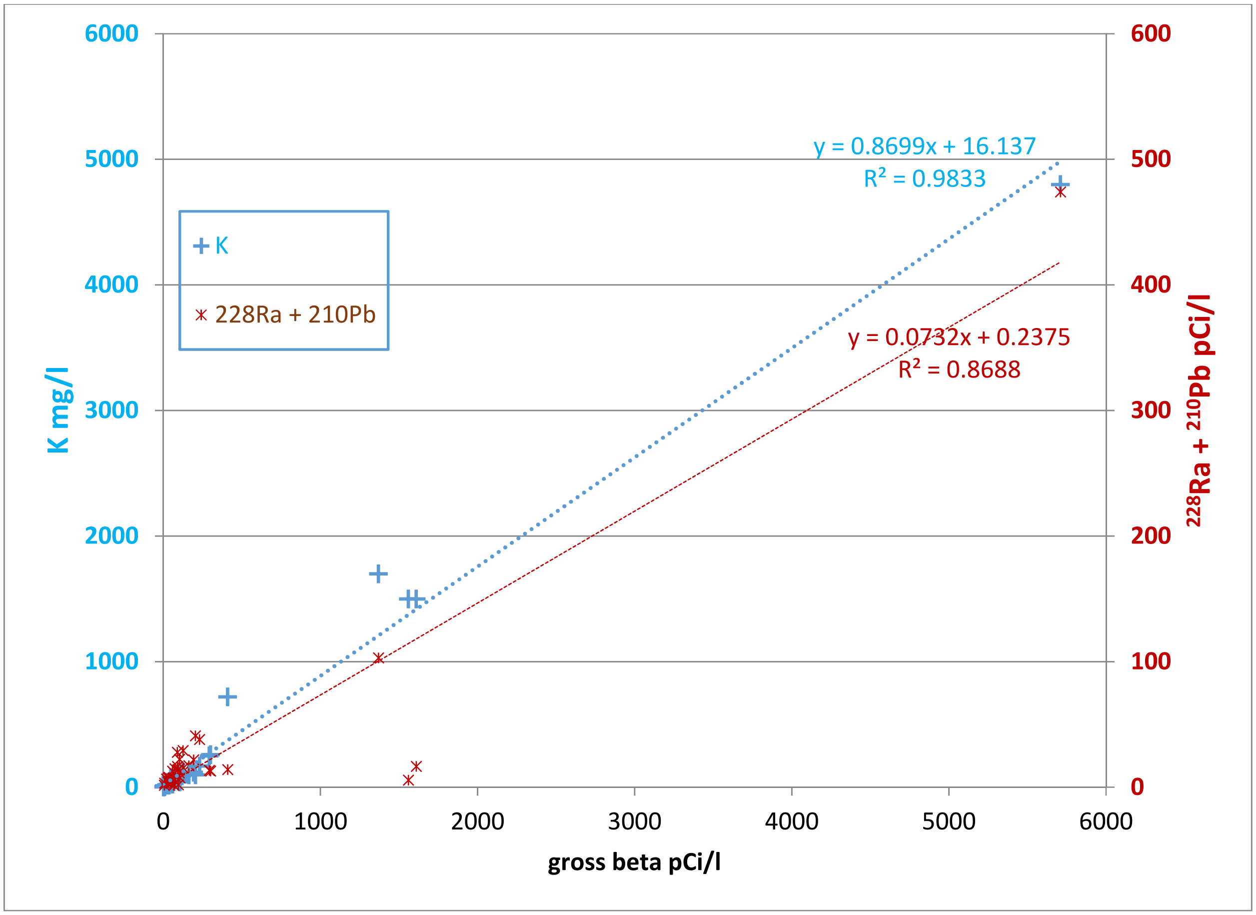

Figure 29. Gross Beta and Major Beta Emitters from Samples Collected as Part of this Study

The sum of activities of ^{228}Ra and ^{210}Pb account for about 10% of the gross beta activity in samples collected as part of this study. The activity of ^{40}K accounted for between 40 to 100% of the gross beta activity for the five samples with highest metals analysis K concentrations (Figure 11).

The gross alpha and gross beta activities in samples collected as part of this study both increase as the concentration of dissolved solids increase, as illustrated in Figure 8, and the gross beta activity is strongly correlated to ^{40}K activities, which proportionally increase as a function of K concentration in samples collected as part of this study.

4.3.2 ^{238}U and Progeny

The highest reported activities of four ^{238}U progeny analyzed by isotope-specific chemical separation followed by alpha or beta analysis were from one sample facility (755645). The concentration of U reported from total metals analysis (Appendix 12) was 0.9 µg/l, which was the fourth highest concentration of U in the seven samples in which U was reported as >MDL. Uranium was reported above the sample-specific MDL in six of the produced water samples and in the one source water sample, and U was reported as <MDL in the other 45 samples collected as part of this study (Table 3). A recent study (Rosenblum et al., 2017) observed the highest concentrations of U in the Colorado groundwater source used in hydraulic fracture completion of one Niobrara Fm. well in comparison to produced water samples collected from one oil and gas well over more than seven months following completion. As discussed in the Introduction to this report, the geochemical conditions present in producing formations are likely to control and minimize uranium concentrations in solution (Langmuir, 1978; IAEA, 2003; Hem, 1992). Uranium concentration data from this study support that hypothesis in that the highest concentration of U was reported in the shallow source groundwater sample with much lower concentrations (if detected at all) in produced water samples.

Rosenblum et al. (2017) noted their analyses indicated that parent ^{210}Pb and progeny ^{210}Po were not in secular equilibrium in water samples collected in the first seven months following hydraulic fracture completion of a Niobrara Fm. well in Colorado. Figure 30 shows the ratio of ^{210}Pb to ^{210}Po activities of the only four produced water samples with ^{210}Pb activities >MDC. As discussed in Rosenblum et al. (2017), the activities of the longer lived parent (^{210}Pb – 23.3 years) and the shorter lived progeny (^{210}Po – 138.4 days) should be equal if the isotopes present in the water are in secular equilibrium (Nelson et al., 2015). Figure 30 has a dashed line plotted at equal activities (ratio of 1) of the two radionuclides. The water-rock system before drilling and completion would be expected to be at secular equilibrium due to the length of time (typically tens of million years or more) the Colorado oil and gas producing formations have been in place in the subsurface and not disturbed.

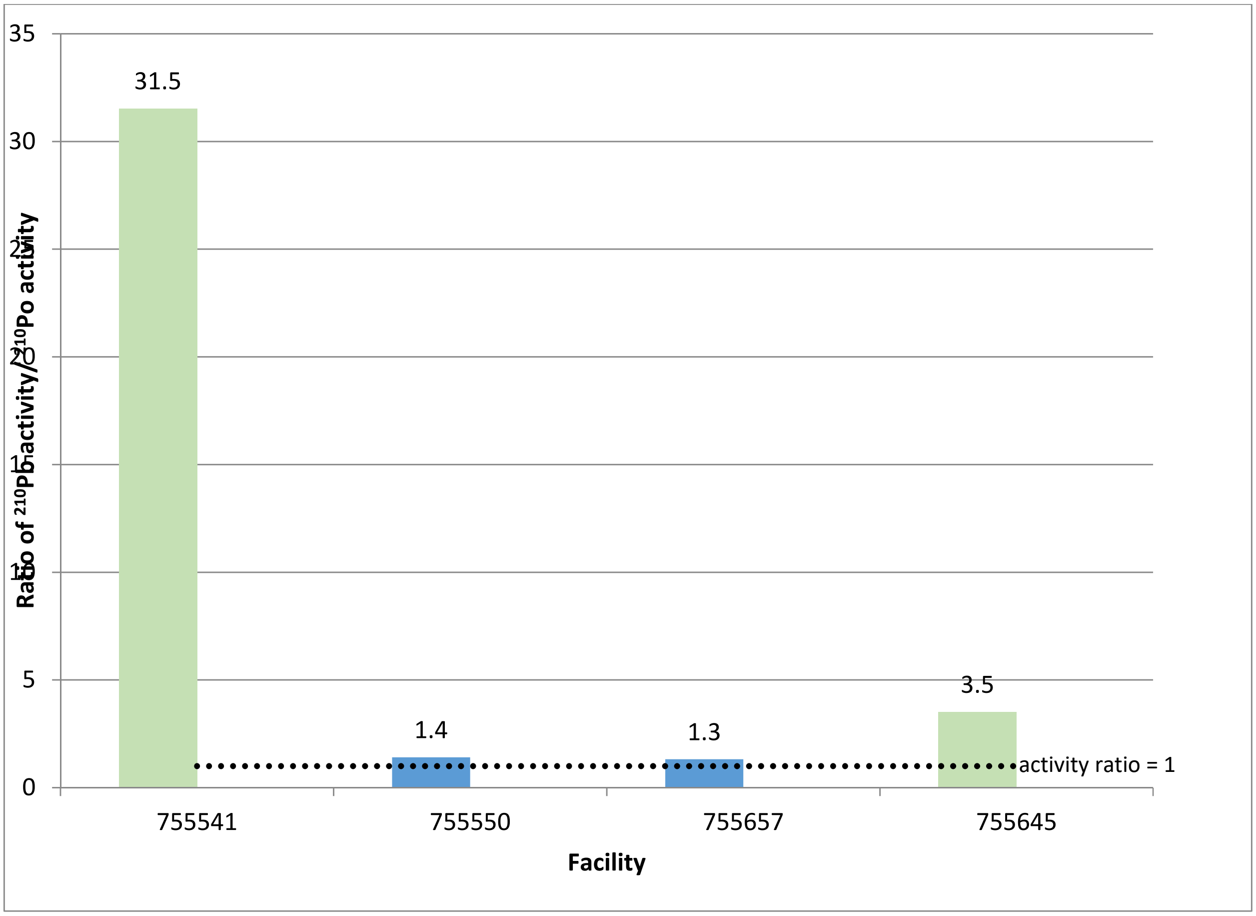

Figure 30. . Ratio of ^{210}Pb Activity to ^{210}Po Activity in Samples with >MDC Activities of ^{210}Pb (this study)

Activity ratio of ^{210}Pb to ^{210}Po in samples with reported ^{210}Pb activities >MDC. Dotted line plotted at ratio of 1 as indicator of secular equilibrium. Columns in **blue** at or near secular equilibrium. Columns in **green** not in secular equilibrium.

Two of the samples in Figure 30 with both parent and progeny activity ratios near 1 are likely at or near secular equilibrium and are plotted in blue. The two samples in Figure 30 with much higher activity ratios of the parent and progeny nuclide (plotted in green), approximately 31 for the sample from **755541** and 3 for the sample from **755645**, indicate a lack of secular equilibrium even if the rock-water system in the producing formation may be at secular equilibrium. Rosenblum et al. (2017) suggested that differences in solubility in water of Pb and Po may be responsible for the apparent lack of secular equilibrium observed in water analyses. The wells producing the two samples not in secular equilibrium were not completed by hydraulic fracturing techniques, so the water-rock system has not been perturbed as much as in the well sampled by Rosenblum et al. (2017). The two samples from this study which appear to be in secular equilibrium between parent Pb and progeny Po (**755550** and **755657**) were completed using hydraulic fracturing techniques, but the completions were performed 32 years prior to sampling **755550** and 19 and 6 years prior to sampling **755657**. Operators of the wells at the two sampling sites (facilities **755541** and **755645**) which are not at secular equilibrium indicated that scale inhibitor chemical products were used downhole at wells producing water to **755541** and **755645**. The operators of the wells at facilities **755550** and **755657**, both of which are at or near secular equilibrium with respect to the parent Pb and progeny Po isotopes, indicated they were not using scale inhibitor products downhole at the time of sampling. The presence of some scale inhibitor chemical products in a well and the water it produces may enhance the solubility of the Pb relative to Po, and this may be a cause of the lack of secular equilibrium observed in those two samples with respect to activities of ^{210}Pb and ^{210}Po. Rosenblum et al. (2017) did not discuss if any chemical products such as scale inhibitors were used at the well they sampled.

4.3.3 Radon Fractionation Between Gas and Aqueous Phases

Radon is a gas that is produced in the decay chain of both ^{238}U (^{222}Rn) and ^{232}Th (^{220}Rn)and may be found in the water as well as the oil and gas produced in oil and gas wells, as illustrated in Figures 1 and 2. When radon migrates out of the mix of liquids and gases produced from oil and gas wells, as gases by design do in liquid/gas separators used in-line at or near wells, then the progeny of radon isotopes (also NORM) may more likely be found in gas pipelines or further downstream in gas processing facilities. Preferential fractionation of radon from natural gas into ethane and propane streams at gas processing plants has been well documented (Gesell, 1973; Gesell, 1975). To better understand the fractionation of the ^{222}Rn isotope between the produced water phase and the natural gas phase, a subset of samples of natural gas and produced water from the same wells was analyzed for activities of ^{222}Rn. Radon carried in the gas stream could result in presence of its progeny in production facilities processing gas but not receiving produced water, as discussed by Hem (1992) and IAEA (2003). ^{232}Th derived ^{220}Rn, ^{235}U derived ^{219}Rn, and ^{238}U derived ^{218}Rn may also be present in these samples. The relatively short half-lives (<60s) of these three radon isotopes hinder or preclude accurate and representative laboratory analysis, and thus activities of ^{222}Rn were used to test fractionation between gas and water at five sites.

The reported ^{222}Rn activities of the limited sampling of production gases at five sites are shown in Table 26 with reported aqueous ^{222}Rn activities of produced water samples at the same sites. The limited data set indicates a slight fractionation preference to the gas phase in sample 755462. No preference can be determined for the other four samples. There may also be fractionation of radon into the hydrocarbon liquids at these wells or at gas processing plants. For example, laboratory studies indicate a strong fractionation of Rn into hexane from nitrogen gas phase as summarized in a review by Clever (1979). No liquid hydrocarbon samples were analyzed for presence of NORM in this study.

Table 26. Comparison of ^{222}Rn activities in Gas and Water Samples (this study)

Facility ID COENV DB	Natural Gas Samples			Water Samples		
	^{222}Rn +/- TPU pCi/l	MDC pCi/l	Data Flags	^{222}Rn +/- TPU pCi/l	MDC pCi/l	Data Flags
755462	70+/-18	1		22+/-21	35	U
755475	22.5+/-6.8	2.6	M3	37+/-26	41	U
755474	17.5+/-5.5	2	M3	36+/-25	39	U
755500	46+/-12	1	M3	36+/-22	34	LT
755500	NA			54+/-23	33	
755501	15-+/-38	2	M3	26+/-21	34	U

4.3.4 ^{232}Th and Progeny

Thorium was reported as >MDL in 3 of the 52 samples collected as part of this study. The ^{232}Th activity of all samples would be <0.11 pCi/l from the highest not detected concentration of 0.96 µg/l. The progeny of ^{232}Th were shown in Table 2 of this report.

The highest reported activities of two ^{232}Th progeny analyzed by isotope-specific chemical separation followed by beta or alpha analysis were from two sample facilities (755645 – ^{228}Ra and 755657 – ^{224}Ra). A third progeny of ^{232}Th (^{212}Pb) was analyzed directly in water samples by gamma spectrometry. The highest ^{212}Pb activity reported as >MDC was in samples from facility 755646. Thorium was not detected in any of the three samples with the highest reported activities of Th progeny. The relative lack of solubility of Th under geochemical conditions present in oil and gas producing formations was discussed in Sections 1 and 3.1.3.2, in references including Hem, 1992; IAEA, 2003; and Langmuir and Herman, 1980, and as seen in the data from this study.

The relatively greater solubility of Ra in comparison to Th in water present in oil and gas producing formations was discussed in Sections 1 and 3.1.3.2, in references such as Hem, 1992; IAEA, 2003; and Langmuir and Riese, 1985, and as seen in data from this study. For example ^{228}Ra was reported as >MDC in 40 of the samples (beta decay) collected as part of this study, and ^{224}Ra was reported as >MDC in 20 of the samples (alpha decay) collected as part of this study, even though total Th was detected in only 3 of the samples.

4.3.5 ^{40}K

^{40}K is a naturally occurring radioactive isotope of K, as discussed in Section 1 of this report. Potassium is relatively abundant in the earth's crust (1.84% of the crust) (Greenwood and Earnshaw, 1997), and the natural abundance of the long-lived radioactive ^{40}K isotope is 0.0117% of the total K concentration (Meija et al., 2016; CIAAW, 2017). ^{40}K decays primarily by beta decay with lesser percentage of decay by electron capture, which then produces gamma emission. The amount of ^{40}K activity present in produced water is directly proportional to the total concentration of K present in produced water at approximately 0.8 pCi/mg of total K present (National Research Council, 1999). Figure 11 showed a correlation between activity of the radioactive K isotope and total concentration of K in produced water samples with ^{40}K activities >MDC by gamma analysis.

4.3.6 General Inorganic Chemistry

A brief overview of the major ion chemistry of the samples collected as part of this study is found in section 3.2.4 and illustrated in the Piper diagram (Figure 17). Geographic and geologic subsets of the major ion composition data will be presented and discussed in this section using tools such as the Piper plot and the Stiff diagram to illustrate compositional differences or possible mixing of fresh water and formation water (Hem, 1992). Stiff diagrams (Stiff, 1951) provide a means of categorizing similarities and differences in major ion composition and sources of waters (Hem, 1992). The width of each component of the Stiff plots is a measure of the concentration of and the charges of (in meq/l), the major cations (plotted to the left) and the major anions (plotted to the right) in each water.

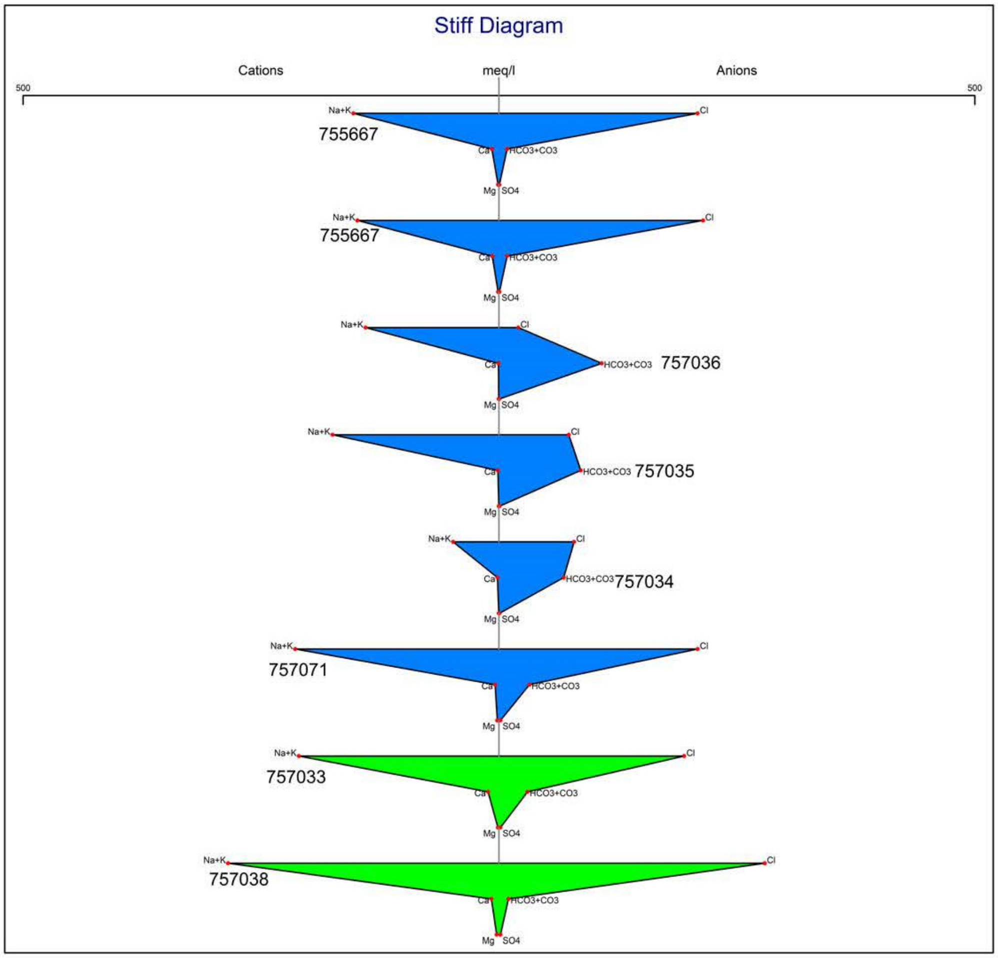

Figure 31. Major Ion Differences Shown on a Stiff Diagram – Williams Fork Fm. Samples (this study)
Samples shown in blue in Figure 31 are from wells producing from Williams Fork Fm. Samples show in green in Figure 31 are from centralized E&P waste management facilities which receive water from many wells. Produced water at the two centralized E&P facilities primarily comes from Williams Fork Fm. production. Each polygon is labeled with facility number where the water sample was collected.

Six samples were collected as part of this study from wells reported to be completed in the Williams Fork Fm. Cole and Cumella (2003), Lorenz (1983), and Hemborg (2000) all classify the producing sandstones in the Williams Fork Fm. as terrestrial fluvial or fluvial-deltaic in origin. Completion records for the wells producing to each of the six of the Williams Fork Fm. sampling facilities indicate all wells were completed using hydraulic fracture stimulation. Two other samples were collected from centralized water handling facilities which primarily receive water from oil and gas wells completed in the Williams Fork Fm. The Stiff diagram (Figure 31) illustrates similarities and differences in the major ion composition of these eight samples. The sample compositions shown in green are from the two centralized water handling facilities and are predominantly of Na-Cl character. Three of the Williams Fork Fm. samples are also predominantly of Na-Cl major ion character (755667 and field duplicate as well as 757071). Three of the Williams Fork Fm. samples have bicarbonate as a significant anion component other than chloride (757034, 757035, and 757036).

The well associated with 755667 is reported to produce from the Cameo coals section of the Williams Fork Fm., and the well was hydraulically fractured in 2012. Records of production volumes available on the COGCC website indicate that water equivalent to 42% of the volume used in the stimulation have been produced to surface. Water volume produced during flowback was not separately reported but would be expected to increase the percentage returned to surface. The dominant cation and anion in the samples from this facility are Na and Cl, and not Na and bicarbonate, as might be expected in water produced from a formation containing coals.

Completion records for the well associated with 755667 do not indicate if the source of the water used in the frac was fresh water or recycled water. The Frac Focus report for this well indicates that the frac solution included 2% KCl. At the time of sampling and analysis, the produced water was reported to contain 28 mg/l K (Appendix 10) or <0.3% of the approximate 10,000 mg/l that would be expected in a 2% KCL solution used in the well completion. The produced water samples from 2017 are likely formation water, or the K has been removed by sorption to or reaction with minerals in the Williams Fork Fm.

As shown in Figure 31, the produced water from facility 757036 has Na and bicarbonate as the dominant ions, which is a major ion composition typical of water produced from coals. Production records for the well served by this facility indicate that the volume of water pumped from this well is approximately 3.6 times greater than the volume of water used in the hydraulic fracture stimulation of the well, indicating the water and associated chemistry are likely that of all or of some rock units in the completed interval. The completed interval in the Williams Fork Fm. is over 2,000 feet in length at this site and may include sections with coals.

The major ion compositions of 10 samples collected at facilities associated with production of oil and gas from the Niobrara Fm. are shown in Figure 32. Five of the samples (including one duplicate) are from wells producing from the Niobrara in the GWA and are shown as orange dots (755475, 755500 in duplicate, 755652 and 755653). Two of the samples are from wells producing what is reported to be biogenic gas (Rice, 1984) from carbonate horizons in the Niobrara Fm. in eastern Colorado and are shown as red triangles in Figure 32. Three samples shown as blue circles are produced water samples from western Colorado wells producing from the Niobrara Fm. The 10 samples of Niobrara Fm. produced water are all of dominantly Na-Cl major ion composition.

While the major ion composition of the 10 Niobrara samples is similar, the range of dissolved solids (TDS in Appendix 14) varies considerably. For example the TDS of water at facility 757037 (Garfield County) was reported by the lab as 960 mg/l, and the circle around the composition circle for this sample is so small as to be indistinguishable from the symbol. The TDS of the other two western slope Niobrara produced water samples (Jackson County) was more the 35 times greater (755648 – 35,000 mg/l and 755647 – 37,000 mg/l) than that reported for the Garfield County Niobrara Fm. produced water sample.

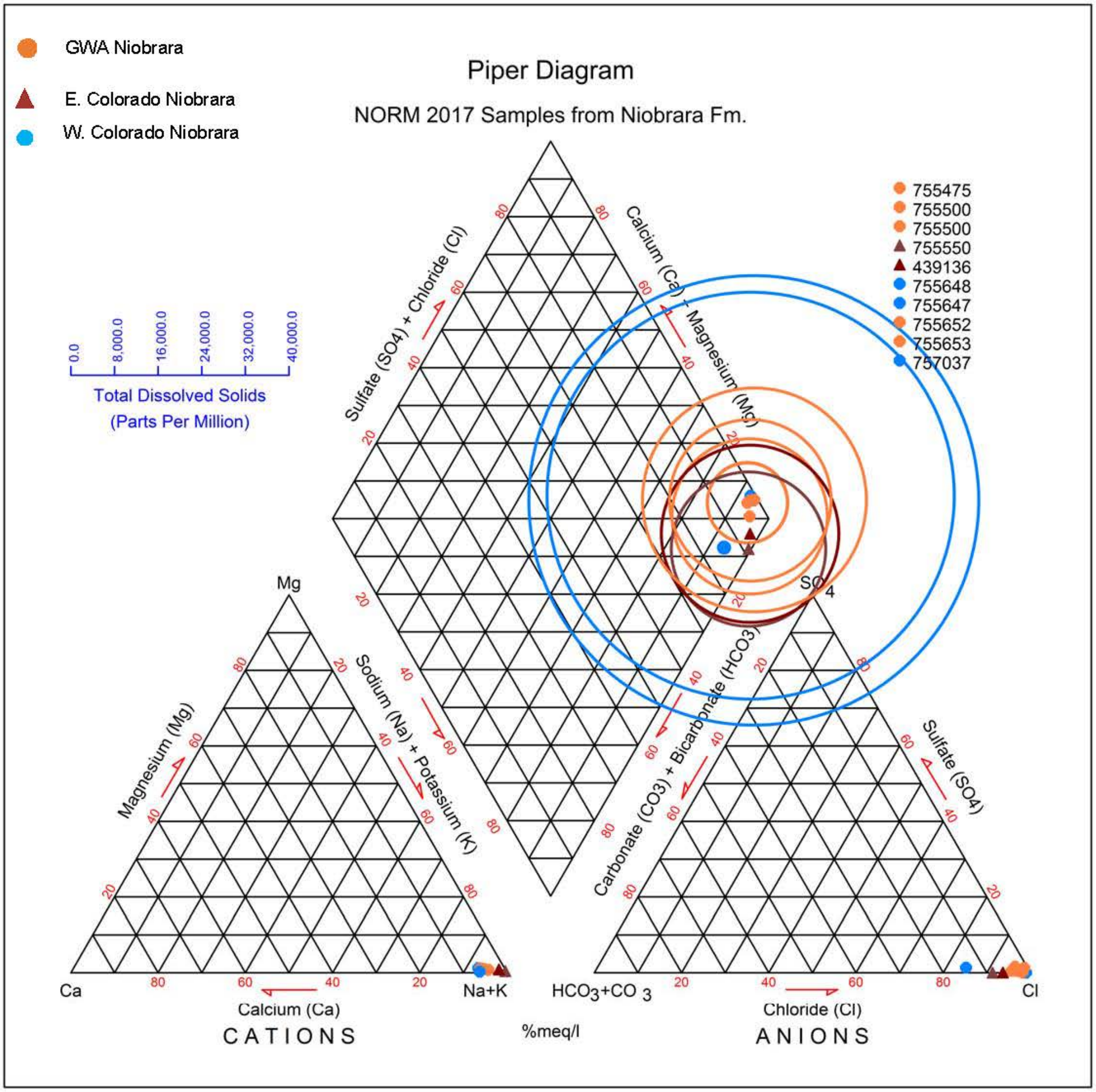

Figure 32. Major Ion Composition of Niobrara Fm. Produced Waters (this study) Shown on Piper Diagram.

Samples collected statewide as part of this study. Two samples were collected from eastern Colorado Niobrara wells producing what has been described as biogenic methane and are shown as red triangles. Five samples from wells producing from Niobrara Fm. in the GWA are shown as orange dots. Three samples from wells producing from Niobrara Fm. in western Colorado are shown as blue dots.

A Piper diagram illustrating major ion composition of the subset of eight water samples in which analyses of ^{3}H activities and ^{14}C (of DIC) ages were performed is shown in Figure 32. The analyses for tritium in water and ^{14}C of DIC were discussed in sections 3.3 and 3.4 with data in Appendices 8 and 9. Interpretation of the tritium activity data together with the calculated ^{14}C in DIC ages are discussed in more detail in section 4.3.3.

Facility **755461** was a sample of source water to be later used in drilling and completions by one operator in northeastern Colorado. As shown in Figure 33, the major ions in the source water are Ca and sulfate with lesser Na, Mg, bicarbonate alkalinity, and Cl, and the source water sample has the lowest TDS concentration among these eight samples. The circle around the green star symbol for this sample is so small as to be indistinguishable from the symbol itself. Major ion chemistry of each sample is shown with a different symbol and color.

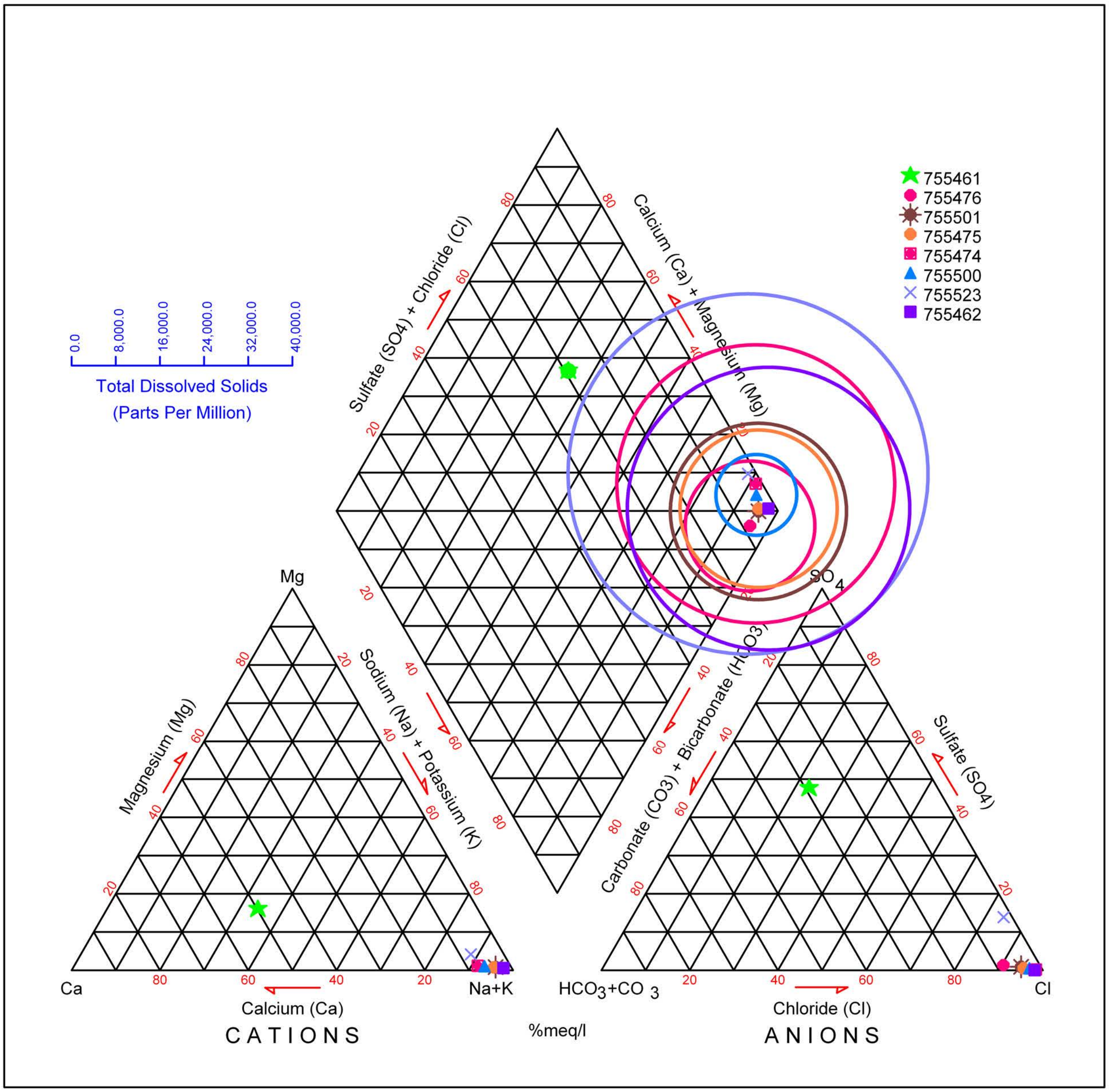

Figure 33. Piper Diagram Showing Major Ion Composition of Water Samples with ^3H and ^{14}C DIC Analyses (this study).

Open circles are scaled to the concentrations of TDS for each sample shown. Colors of the TDS circles match the symbol colors for each sample. A different symbol and color are used to illustrate the anion, cation and overall major ion composition of each sample.

The dominant cation and anion in the other seven samples are Na and Cl, respectively. The seven other samples include one flowback sample (755476) and six produced water samples. The flowback sample was collected from a facility that was receiving flowback from several wells recently completed in the Niobrara and Codell Fms. Analytical data for a produced water sample (facility 755523) from eastern Colorado which produces from the Pennsylvanian Topeka Limestone, have minor amounts of Ca and sulfate present. The presence of more than trace amounts of Ca and sulfate in this sample may indicate the presence of evaporite minerals such as gypsum or anhydrite in the formation or in nearby formations in contact with the groundwater produced at this oil well. The oil well producing to 755523 was not completed by hydraulic fracturing techniques so the water chemistry can be assumed to be that of the formation. The reported TDS concentration of sample 755523 was the highest among this subset of eight samples. The five other samples shown on Figure 33 come from wells that produce from the Sussex Fm., the Niobrara Fm. and the Codell Fm.

4.3.7 Stable Isotopes of Water and DIC

Isotopic composition of the oxygen and hydrogen that make up water (H_2O) can be used as a tool in understanding differences in sources of groundwater. Water isotopic data available from this study were shown previously in Section 3.3 with water oxygen isotope ratios plotted as the x-axis and water hydrogen isotope ratios plotted as the y-axis (Figure 22). The hydrogen isotope (^2H) ratio plotted is also referred to as deuterium, and the label on the plot of δD refers to the ratio of deuterium (^2H) to the more abundant ^1H isotope. A general description of stable isotopes of water plots was presented previously in Section 3.3. Plots of several subsets of samples are presented below to facilitate discussion and interpretation of the data.

Stable isotopes of water from samples collected in northeastern Colorado as part of this study are plotted in Figure 34. The data is plotted as groupings by production formation(s) from which the samples were collected and also by geographic area for water produced from the Niobrara Fm. Two samples from eastern Colorado Niobrara gas wells plot just above the GWML, and five of the six J Sand samples plot just below the GMWL as does the source water sample. Ratios of the stable isotopes of water for the remainder of the samples from several formations listed in the legend for Figure 34 plot below or well below the GMWL including one flowback sample. The stable isotopes of water for one GWA Niobrara sample plot intermediate between the GMWL and the bulk of the GWA samples (755500) and may represent a mix of some formation water with mainly fresh water used in the frac at this well. At the time of sampling the reported produced water volume was less than 11% (Table 27) of the fluid volume used in the hydraulic fracture completion (755500). Our one source water sample may not be representative of all fresh waters used in hydraulic fracture stimulations in the GWA.

Water isotopic data from aquifers present in the Denver Basin obtained from the literature (>70 samples) and are summarized in Figure 34 as a cigar-shaped outline of data points with individual points not shown. The cigar shape is labeled Denver Basin aquifers. Samples from surface to depth are from water table, Dawson, Denver, Arapahoe, Laramie-Fox Hills and upper Pierre aquifers with data from Musgrove et al., 2014 and Allison, 2017.

The flowback sample (755476) was collected within 30 days of the frac completion, and the completion reports indicate that 95% of the water used in the frac was fresh water. The shallow aquifers (source water **755461** green triangle) sample water isotope ratio shown in Figure 34 can be considered as an analog for the fresh water used in the completions in the wells producing to facility 755476 (blue asterisk). The water isotope ratios of comingled Niobrara-Codell produced water samples (orange squares) in Figure 34 can be considered as the other end of a mixing line between the fresh water used in the completion and the formation water. The stable isotope ratios of the produced water from recently completed Niobrara and Codell wells sampled at 755476 indicate mixing between the fresh water component of the frac fluid and the native formation waters. The stable isotopes of water from the flowback sample 755476 indicate a relatively rapid mixing with or exchange of formation water, as at the time of sampling no more than 1.4% of the frac volume had been returned to surface (Table 27). The blue dotted line on Figure 34 is to illustrate possible mixing of fresh and formation waters following the completions of the wells at 755476. Tritium activities of the source water 755461, the flowback water sample 755476 and of GWA Niobrara sample 755500 were measured as part of this study and will be discussed in terms of percentage of fresh water present in the flowback in Section 4.3.8.

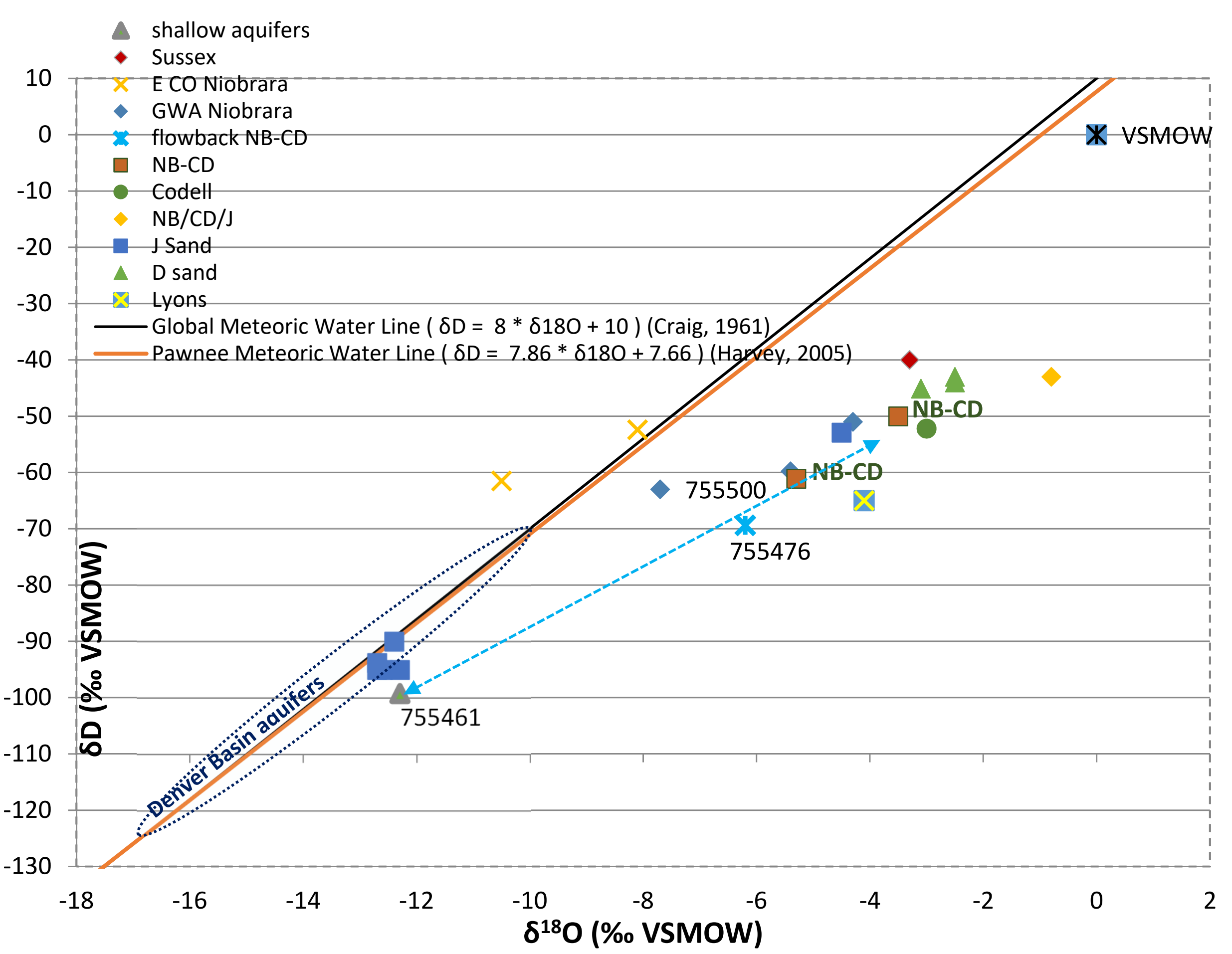

Figure 34. Stable Isotopes of Water Plot of Northeastern Colorado 2017 NORM Study Samples

Global Meteoric Water Line from Craig, 1961, Rozanski et al., 1993, Pawnee Meteoric Water Line from Harvey, 2005. The isotopic ratio of deuterium (^{2}H) in water from samples collected as part of this study relative to Vienna standard mean ocean water reference is plotted against the y-axis. The isotopic ratio of ^{18}O (oxygen) in water from samples collected as part of this study relative to Vienna standard mean ocean water reference is plotted against the x-axis. The composition of the reference standard mean ocean water is plotted as VSMOW. The cigar shaped outlined in blue dots and labeled Denver Basin aquifers encompasses water isotopic data from shallow water table aquifers down to the upper Pierre aquifer and also includes data from Dawson, Denver, Arapahoe, Laramie-Fox Hills aquifers. Data for Denver Basin aquifers is from Musgrove et al., 2014 and Allison, 2017.

The stable isotopes of water data from samples collected in northwestern Colorado as part of this study are plotted in Figure 35. The data is plotted as groupings by production formation(s) from which the samples were collected. Two samples from water collections systems in the Parachute and Hunter Mesa areas (yellow asterisk), two samples from the Mancos Fm. (blue asterisk), and three samples from the western Colorado portion of the Niobrara Fm. (blue crosses) plot well to the right of the GMWL. Sample 757072 plots furthest to the right of the GWML. The well completed in the Mancos Fm. that produces to facility 757072 was completed using hydraulic fracturing in 2011 using 100% recycled produced water and had produced approximately 220% of the frac volume as produced water at the time of sampling. The second sample collected from a Mancos Fm. well sampled as part of this study was completed in 2014 by hydraulic fracture techniques using 31.9% recycled produced water and 67.8% fresh water and had produced approximately 104% of the frac volume as flowback and produced water at the time of sampling. The results of the stable isotopes of water from the two Mancos Fm. samples likely are representative of formation waters as is the major ion chemistry.

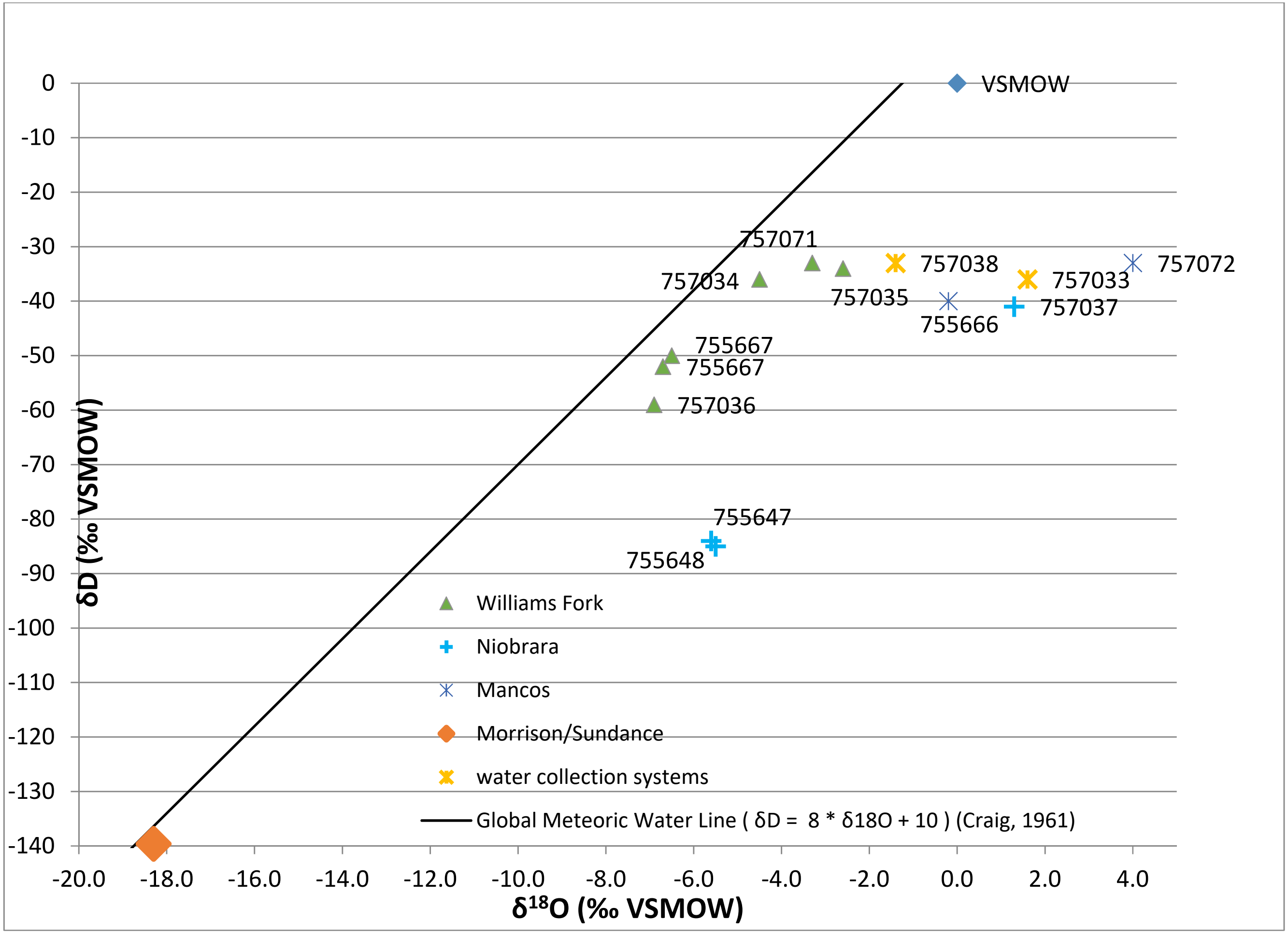

Figure 35. Stable Isotopes of Water Plot of NORM 2017 Northwest CO samples (this study)

Global Meteoric Water Line from Craig, 1961, Rozanski et al., 1993. The isotopic ratio of deuterium (^{2}H) in water from samples collected as part of this study relative to Vienna standard mean ocean water reference is plotted against the y-axis. The isotopic ratio of ^{18}O (oxygen) in water from samples collected as part of this study relative to Vienna standard mean ocean water reference is plotted against the x-axis. The composition of the reference standard mean ocean water is plotted as VSMOW.

The stable isotope ratios of six water samples from five Williams Fork Fm. wells (one duplicate) are plotted in Figure 35. The stable isotope ratios from Williams Fork Fm. samples plot near the GWML. The major ion chemistry of the same six samples was previously plotted in Figure 31 on Stiff diagrams with three of the six having Na and Cl as the dominant major cation and anion, respectively, and the other three having Na-bicarbonate along with chloride as dominant major ions. The stable isotope ratios do not vary greatly even though the solutes in the water do vary significantly. Production records for the well served by facility 757036 indicate that the volume of water pumped from this well is approximately 3.6 times greater than the volume of water used in the hydraulic fracture stimulation of the well. The stable isotopes of water for this sample plot close to the meteoric water line, and together with the greater produced water volume relative to frac volume, indicate the water and associated major ion chemistry (Na-bicarbonate) are likely representative of some rock units in the completed interval of this Garfield County well completed in the Williams Fork Fm.

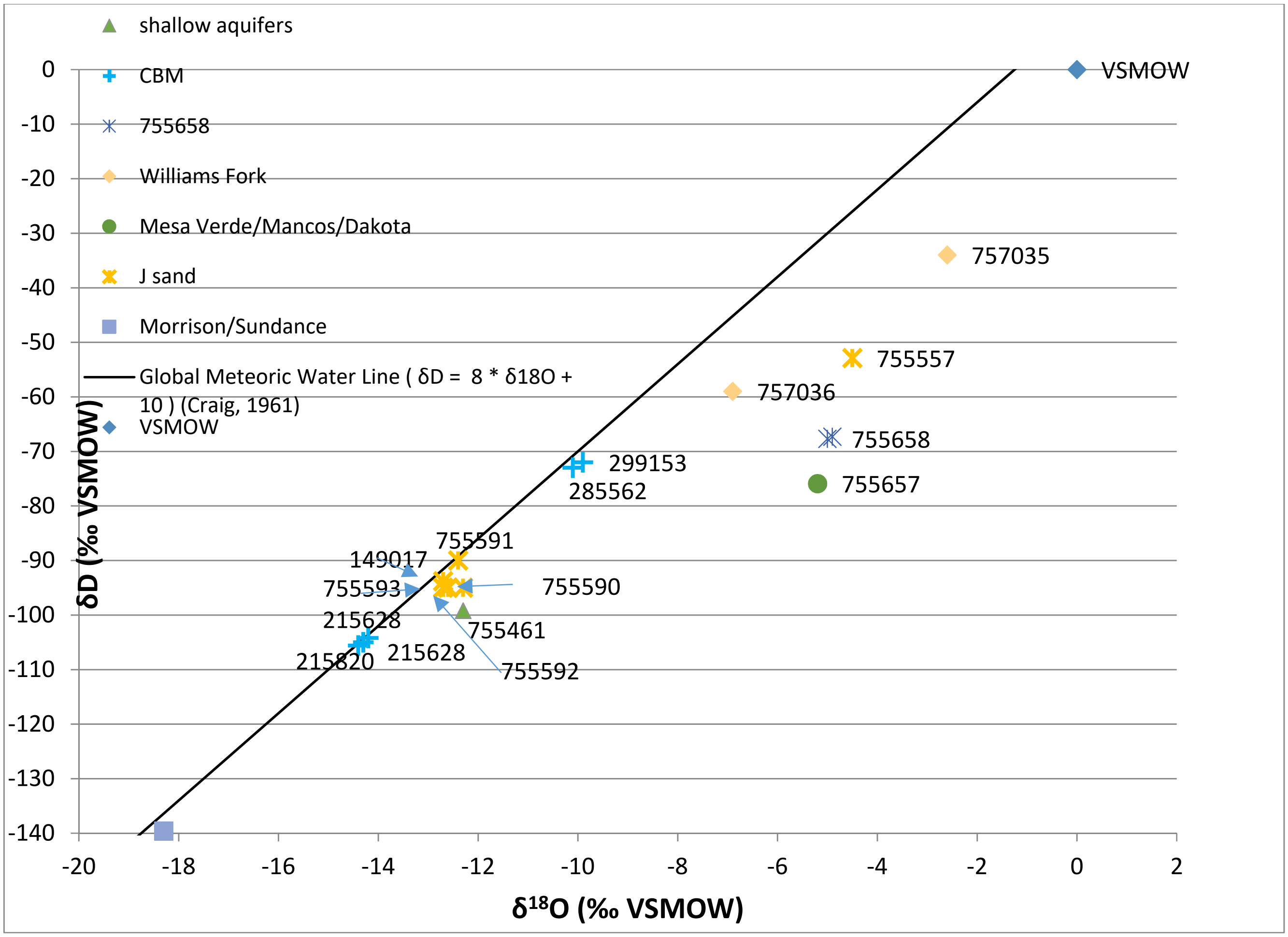

Figure 36. Stable Isotopes of Water Plot of NORM 2017 Samples with Na/Cl Molar Ratio >1.29

Global Meteoric Water Line from Craig, 1961, Rozanski et al., 1993. The isotopic ratio of deuterium (^{2}H) in water from samples collected as part of this study relative to Vienna standard mean ocean water reference is plotted against the y-axis. The isotopic ratio of ^{18}O (oxygen) in water from samples collected as part of this study relative to Vienna standard mean ocean water reference is plotted against the x-axis. The composition of the reference standard mean ocean water is plotted as VSMOW.

Facility 755667 (Mesa County) was sampled in duplicate after approximately 42% of the frac volume had been returned to the surface as produced water, but the records do not indicate the source of the frac water at this well. The stable isotopes of water for the sample and duplicate plot very close to the GWML (Figure 35), but the major ion chemistry is dominantly Na-Cl unlike the Garfield County Williams Fork Fm. sample from 757036, discussed above and illustrated in the Stiff diagram (Figure 31). The major ion chemistry differences in 755667 may be due to the presence of relict water from the hydraulic fracture stimulation fluids to which KCl and HCl had been added. The major ion and stable isotope of water data from the 757036 indicate that relict seawater was not present in the Williams Fork Fm. accessed by the well that produces to 757036. The Cl/Br mass ratio data (Figure 19) and the Na/Cl molar ratio data (Figure 20) for sample 757036 support this conclusion. The variability in major ion composition of Williams Fork Fm. produced waters cannot be explained with the data we have at present. The producing sandstones of the Williams Fork have been classified as terrestrial origin by Cumella (2003), Lorenz (1983), and Hemborg (2000) and in which originally there was connate fresh water but there may have been recharge events in in parts of the Piceance Basin which contained water derived from marine sources or rocks deposited in marine systems with connate sea water.

The stable isotopes of water for the subset of samples collected as part of this study with Na/Cl molar ratios >1.29 are plotted in Figure 36. The present day seawater Na/Cl molar ratio is 0.859 using composition data compiled by Pilson (2013) as discussed in section 3.1.4 and the entire set of Na/Cl ratios from this study is shown in Figure 20. The data is plotted as groupings by production formation(s) or type of production formation (CBM) from which the samples were collected. A general interpretation of the source of solutes in water samples with Na/Cl ratios significantly greater than that of seawater is that those waters have no major contributions from relict seawater. The stable isotopes of water from 13 of the 18 samples with Na/Cl ratios >1.29 plot on or very close to the GWML, indicating that the sources of water in the 13 are likely of meteoric origin with little contribution of water from relict seawater. The 13 include 5 samples from CBM production, 5 samples from J Sand Fm. production, 1 sample from Morrison Fm. production, 1 from Williams Fork Fm. production, and the source water sample. Replicate samples from sample 755658 plot well below the line, and likely sources of this water which may not be produced water were discussed in Section 3.1.4. The three remaining samples plotted in Figure 36 are from the Williams Fork Fm., J Sand Fm., and a well completed in the Dakota, Mancos, and Mesa Verde Fms., and may have some component of relict seawater based on the water isotope data.

Stable isotopes of water for eight samples (one duplicate) with Cl/Br ratios >400 and with Na/Cl ratios similar to that of seawater collected at seven facilities as part of this study are plotted in Figure 37. The major ion chemistry of these samples was discussed in section 3.1.4. Each of the samples with Cl/Br ratios >400 are produced water from Paleozoic era formations and have relatively high concentrations of TDS, as discussed in Section 3.1.4. None of these wells were completed using hydraulic fracture techniques, so there is no need to consider mixing of frac water with formation waters in the discussion of the origin of the water or the solutes present in the water from these wells.

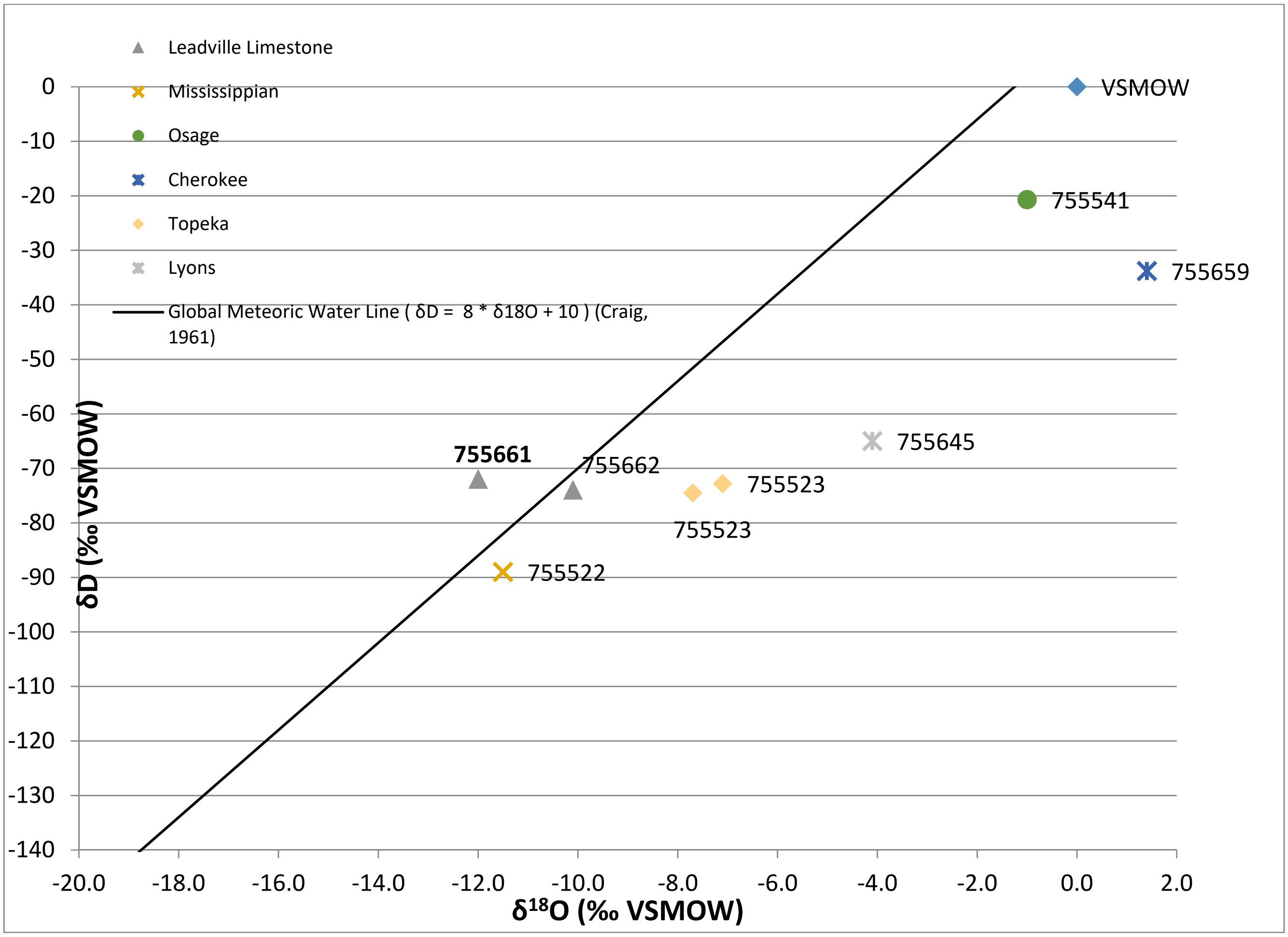

Figure 37. Stable Isotopes of Water NORM 2017 Samples with Cl/Br Mass Ratio >400 and Na/Cl Molar Ratio Similar to Seawater

Global Meteoric Water Line from Craig, 1961, Rozanski et al., 1993. The isotopic ratio of deuterium (^{2}H) in water from samples collected as part of this study relative to Vienna standard mean ocean water reference is plotted against the y-axis. The isotopic ratio of ^{18}O (oxygen) in water from samples collected as part of this study relative to Vienna standard mean ocean water reference is plotted against the x-axis. The composition of the reference standard mean ocean water is plotted as VSMOW.

While the solutes in each of these groundwater samples appear to be related to evaporite minerals or relict seawater or both, the stable isotopes of water in three of the samples plot near the GMWL. The stable isotopes of water from two samples produced from Mississippian Leadville Limestone carbon dioxide wells and from one eastern Colorado Mississippian limestone oil well are similar to modern meteoric waters. Water samples with stable isotopes similar to meteoric water but with solutes similar to seawater (Na/Cl) ratio and evaporite dissolution (Cl/Br) could result from relatively geologically recent recharge of meteoric water followed by interactions with and dissolution of minerals in the recharge path towards the wells. The cap rocks of the McElmo Dome field are salt-bearing units in the overlying Paradox Fm. (Gilfillan et al., 2008), which is the likely source of the solutes in the water samples collected from the Leadville Limestone. Cappa and Rice (1995) suggested the source of the carbon dioxide in McElmo Dome was contact metamorphic degradation of carbonate minerals in the Leadville Limestone. Carbon dioxide derived from deeper magmatic (mantle) sources based on rare gas geochemistry was later suggested as the carbon dioxide source by Gilfillan et al. (2008), who also concluded that the produced water in the field had been in contact with atmospheric gases indicating a likely meteoric origin of the produced water. The stable isotopes of water data gathered as part of this study supports this conclusion.

Analysis of tritium activities and of ^{14}C of DIC ages was performed on a subset of eight samples from this study, as discussed in Sections 3.4 and 3.5, as part of an effort to understand if these tests might be useful in understanding the sources of produced water from formations in the state as shown in Figure 22. Specifically, analyses of water stable isotopes have been effectively used to differentiate water sources in recently completed wells in the Permian Basin (Laughland et al., 2014) and in Saudi Arabia (Birkle, 2016a; 2016b) and was seen in this study and discussed previously in this section (Figure 34). The stable isotopes of water (D and H) of this subset are plotted on Figure 38.

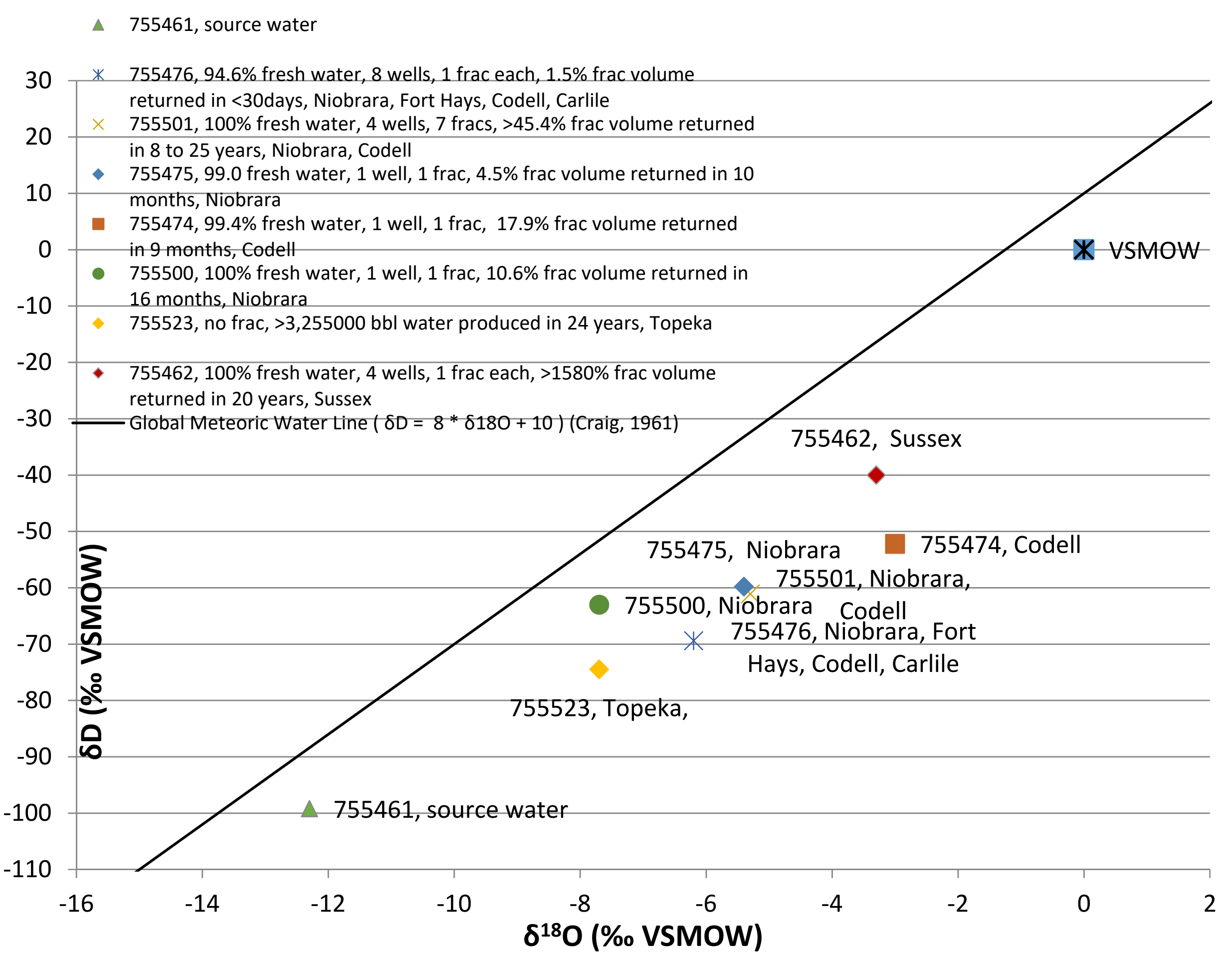

Figure 38. Stable Isotopes of Water Plot of NORM 2017 Samples with ^{3}H of Water and ^{14}C in DIC Analyses

Global Meteoric Water Line from Craig, 1961, Rozanski et al., 1993. The isotopic ratio of deuterium (^{2}H) in water from samples collected as part of this study relative to Vienna standard mean ocean water reference is plotted against the y-axis. The isotopic ratio of ^{18}O (oxygen) in water from samples collected as part of this study relative to Vienna standard mean ocean water reference is plotted against the x-axis. The composition of the reference standard mean ocean water is plotted as VSMOW.

The example source water sample (**755461**) plots as distinctly different stable isotopes of water ratios than any of the produced water sample plotted in Figure 38. The water stable isotope ratios of the example source water are similar to those of near surface and shallow aquifer groundwater in the Denver basin (Musgrove et al., 2014; Allison, 2017) as shown in Figure 34. The flowback sample (**755476**) was sampled from a site that comingled produced water from eight wells. All of the wells flowing to **755476** were hydraulically fractured fewer than 30 days prior to sampling. In total <1.4% of the volume of fluids used in the fracs had been returned to surface at the time of sampling (Figure 38 and Table 27). About 95% of the frac fluids used at this site were fresh water with about 5% recycled produced water and with minor amounts of hydrochloric acid. No discrete sample of the water used in the fracs at facility **755476** is available to compare with the flowback. The example source water sample will be used as a basis for comparisons because it is believed to be typical of fresh waters used at present in the Wattenberg field and by the operator of **755476** wells. For example, the ratios of the stable isotopes of water for the flowback sample (Figure 38) are much different than those of the example source water (facility **755461**), indicating a rapid mixing with free formation water or with water held in formation pores or sorbed to clay minerals is likely to have occurred. The stable carbon isotope ratios of the DIC in the example source water sample also show a rapid change from negative to positive delta ^{13}C DIC of flowback samples from facility **755476**, as shown in Figure 23 in Section 3.3, in comparison to the example source water. A further discussion of tritium activities and ^{14}C of DIC ages of the samples included in the subset of Figure 38 is presented in Section 4.3.8.

The water stable isotope ratios of samples **755462** and **755523** are assumed to be representative of the formations that are produced by the well at each facility. The well at **755523** (Topeka Limestone) was not hydraulically fractured so no large amounts of water from another source were introduced into that well (Figure 38 and Table 27). Sample **755462** was completed by hydraulic fracturing techniques, but since completion, the wells producing to this facility have produced water volumes equivalent to more than 15 times the volumes of fresh water fluid introduced to the Sussex Fm. in and around the four wells producing to this facility.

The other four facilities sampled and plotted on Figure 38 all produce from Niobrara or Codell completions. Sample **755500** has stable isotopes of water ratios that plot closer to the GMWL than any of the samples in Figure 38 other than the source water sample. Both oxygen and hydrogen isotope ratios of water in the produced water sample from **755500** are more positive (heavier) than shallow groundwater samples from the Denver Basin (Musgrove et al., 2014; Allison, 2017), which indicates in this and all other samples in Figure 38 that there has been significant interaction with formation water in each of the wells in which fresh water was used in hydraulic fracture well completions.

4.3.8 Tritium in H_2O and ^{14}C of DIC

Tritium in H_2O and ^{14}C of DIC are geologically relatively short lived radioactive (non-NORM) analytes. The levels of activities of these analytes in conjunction with stable isotopes of water and major ion chemistry are used to help evaluate the hypothesis stated in the SAP for this project (COGCC, 2017a) that much of the water produced to the surface from wells drilled and completed in the Niobrara and Codell Fms. is not native formation water but comes from the source water used in hydraulic fracture well completions. The presence of, as well as the activity levels of, tritium in produced water can be used as a transient tracer of water sources that have been at the earth's surface in the last 50 to 60 years. This study treats tritium like a conservative tracer (in the short term) even though it is radioactive and continually undergoing decay, as chloride and bromide are treated as conservative tracers in earlier discussions of sources of solutes present in produced water (Section 3.1.4).

The activities of tritium and ^{14}C in DIC were determined in an eight sample subset of the 52 samples collected along with the NORM and major ion chemical analyses. The eight sample subset consisted of one source water sample (755461), one flowback sample (755476), produced water from one eastern Colorado well that records indicated had not been hydraulically fractured (755523), and produced water from one Sussex Fm. well (755462) and four Niobrara, Codell or comingled Niobrara-Codell Fm. wells completed over the last 25 years (755501, 755475, 755474, and 755500). As it is not possible to have tritium measurements of each source water used in completing any of the seven wells with data in Table 27, the fraction of tritium relative to the example source water is considered to be an approximate fraction of fresh water in the produced water samples. The fraction of tritium activity in each of the seven produced water sample compared to the tritium activity of the example source water is shown in Table 27.

The ^{3}H and ^{14}C in DIC results are summarized in Table 27 in order of descending activity of tritium. Tritium was not detected in produced water from the eastern Colorado well that had been treated with 12 barrels (bbl) of acid in the perforated zone but not been completed by hydraulic fracture stimulation. The well producing to 755523 has produced more than 3,250,000 bbl of produced water since completion. Tritium was not detected in the comingled water produced from four Sussex Fm. wells that were stimulated 20 years prior to sampling(755462), indicating the 100% fresh water frac volume has been completely returned to the surface or some fraction could still be trapped in the formation. The cumulative produced water volume at the time of sampling from the four Sussex wells is >16 times the total volume of fluids used in the well stimulations, and the low activity of tritium in this sample is not unexpected, as the water appears to be water from the formation. The two produced water samples in which tritium was not detected also had the sixth and seventh oldest ^{14}C of DIC apparent ages, which supports the conclusion that little or no fresh water from fracs or the surface is being produced from these sites, based primarily on the low tritium activities reported by the lab. The stable isotopes of oxygen and hydrogen of H_2O in the two produced water samples in which ^{3}H was not detected also fall well below the local and global meteoric water lines (Figure 38), which also supports the conclusion that both are primarily formation water.

Table 27. ^{3}H and ^{14}C in DIC, Water Source of Frac, Time after Frac and % of Frac Returned to Surface as Produced Water (this study)

Facility # COENV DB	^{3}H H_2O TU (tritium units)	fraction of ^{3}H in PW compared to example source H_2O	^{14}C DIC (pmc - % modern carbon)	^{14}C DIC Age (years BP)	% of fresh water, % acid and volume of water in frac	time since frac(s) at sampling	Primary rock type()s in production zones	Sum of produced water at time of sampling as % of frac fluid used
755461	6.71		102.63	60	source water	-	near surface aquifer	-
755476	4.13	0.62	1.31	34,840	94.6% fresh water, 0.4% acid, 8 wells, 1 frac each, 117,0347 bbl total	<30 days	carbonate, shale and sandstone	1.4
755501	2.81	0.42	11.88	17,115	100% fresh water, 4 wells, 7 fracs, 25,563 bbl total	25, 10 and 8 years	carbonate, shale and sandstone	45.4
755475	2.74	0.41	0.44	43,600	99.0 fresh water, 0.3%acid, 1 well, 1 frac, 147,455 bbl	10 months	carbonate and shale	4.5
755474	1.91	0.29	1.13	36,030	99.4 fresh water,).2% acid, 1 well, 1 frac, 95,479 bbl	9 months	sandstone and carbonate	17.9
755500	1.66	0.25	6.85	21,540	100% fresh water, 0% acid, 1 well, 1 frac, 78,659 bbl	16 months	carbonate and shale	10.6
755523	*U (-0.01)*		0.64	40,500		no frac	carbonate	-
755462	U (-1)		0.69	39,900	100% fresh water, 4 wells, 4 fracs, 88, 126 bbl total	20 years	sandstone	1580

Tritium activities were above detection limits in six of the eight samples collected, as discussed in section 3.3. The source water sample (755461) had the highest ^{3}H activity and the youngest ^{14}C of DIC age. The source water sample was collected to illustrate an example for near surface, modern groundwater that one operator uses in completion operations, but water from this site was not necessarily used in completions at any of the sites sampled in this project. The frac flowback sample (755476) had the second highest ^{3}H activity of about 62% of the example source water, which is to be expected from the reported use of 95% fresh water in the fracs completed fewer than 30 days prior to sampling. The frac flowback sample (755476) has the fourth youngest ^{14}C of DIC apparent age despite the reported use of nearly 95% fresh water in the fracs completed fewer than 30 days prior to the sampling event. The inorganic carbon dissolved in the produced water samples can be from sources other than the predominantly fresh water used in the frac for several reasons which are discussed below.

Carbon dioxide is present in gas samples from most producing zones in the state and can readily and rapidly dissolve in the produced water. That carbon dioxide intrinsically present in the hydrocarbon gases can be assumed to be geologically “old.” Data available from the COGCC environmental database for production gas samples from Weld County have a median carbon dioxide concentration of 2 mole percent (mol%) (1,028 samples on 28September2018) with a median $\delta^{13}C$ CO_2 of 2.79 per mil VPDB (318 samples on 28September2018). The gaseous carbon dioxide can be assumed to be geologically “old” and also to interact with, dissolve into, and exchange with fresh water introduced into the producing formations. Carbonate minerals and organic material in producing formations are also likely sources of geologically “old” carbon in flowback or produced water. Water present in the pore space of the producing formation is also expected to have geologically “old” DIC, which may exchange or dissolve into the frac fluid before returning to the surface. Carbonate minerals are approximately 70% or more of the productive chalk zones with in the Niobrara Fm. (Pollastro, 1992; Sonnenberg, 2016) in portions of the Denver basin. Interactions between aqueous fluids, carbon dioxide gas, and carbonate minerals are likely to alter the ^{13}C isotopic ratio of DIC of produced waters as well as increase the apparent ^{14}C age of the DIC in produced waters when fresh waters are used to make hydraulic fracture fluids. Hefton (2015) measured carbon isotope ratios of 718 Niobrara carbonate mineral samples and described a $\delta^{13}C$ range between 0 and 2.5 per mil VPDB of carbon in the carbonate minerals in the Niobrara. Nakamura (2015) analyzed Niobrara Fm. core samples and also compiled carbon and oxygen isotope data of Niobrara carbonate rocks from the literature, which showed a slightly greater range of $\delta^{13}C$ between -2 to 3.5 per mil VPDB of carbon in the carbonate minerals in the Niobrara. The reported range of Niobrara Fm. $\delta^{18}O$ in carbonate minerals (Nakamura, 2015) was between 0 to -20 per mil VPDB (not VSMOW as for water samples in this report).

The stable carbon isotope ratios of the DIC flowback samples also indicate a rapid change from negative to positive delta ^{13}C of DIC in comparison to the example source water. As shown in Figure 23 and Section 3.3, this indicates the DIC in the flowback is in part from sources other than the reference (example) source fresh water. Completion reports for the eight wells contributing flowback to sample 755476 indicate that 0.4% of the fluids used were acids, with a greater relative percentage used in Niobrara Fm. horizontals than in Codell Sandstone Fm. horizontals at the location. Acid-induced dissolution of carbonate minerals in the chalk horizons of the Niobrara Fm. would release to solution geologically “old” inorganic carbon. Interactions of the frac fluid with water, gas, and rocks in the formation would alter the apparent ^{14}C of DIC age towards older than recent. The apparent ^{14}C of DIC age for sample of flowback is much older than what would be calculated simply based on the relative activity of tritium in the flowback sample (≈62%) in comparison to the tritium activity of the source water sample. As discussed in Section 3.2.4 and illustrated in Figure 19, relatively low Cl/Br mass ratio of the flowback water and other recently completed wells also supports the explanation of the presence of significant amounts of fresh water in the frac fluid. In agreement with these observations, the recent study of Rosenblum et al. (2017) observed a Cl/Br mass ratio of 69.1 in produced water about eight months after the hydraulic fracture completion of one well producing from the Niobrara Fm. in northeastern Colorado in which fresh water was used as base of the frac fluid.

Sample 755501 had the third highest tritium activity and the second youngest ^{14}C of DIC apparent age. The set of four wells whose produced water is comingled in the production facility where the sample was collected vary in time of completion between 25 and 8 years prior to sampling, with two of the four wells having been fracture stimulated more than once.

The cumulative produced water volume as a fraction of the sum of fluids used in the multiple frac jobs at the time of sampling was 45%. The four wells were shut in for several months in early 2016 while nearby horizontal wells were completed. The reported produced water volumes were much greater following the return to production of three of the four wells that the facility serves, as shown in Figure 39. Produced water volumes from 05-123-25209 remained relatively constant between 2015 reports and late 2016 to early 2017 reports. The sudden increase in monthly produced water volumes at the other three wells that produce water to facility 755501 is hypothesized to be the result of hydraulic fracture stimulations of nearby horizontal Niobrara Fm. wells. The horizontal wells closest to the three older wells in Figure 39 that show increased water production in late 2016 and early 2017 were reported on Frac Focus as using 100% fresh water in the completions which were done in January 2016.

Fresh water used in the completions on nearby horizontal Niobrara Fm. wells may have introduced water with higher tritium activities than one would expect in wells isolated from near surface recharge and which were completed more than 8 years prior to sampling with recovery as produced water of 45% or more of introduced fluid volume. The ^{14}C of DIC age calculated for this sample is the youngest of the six produced water samples ^{14}C analysis.

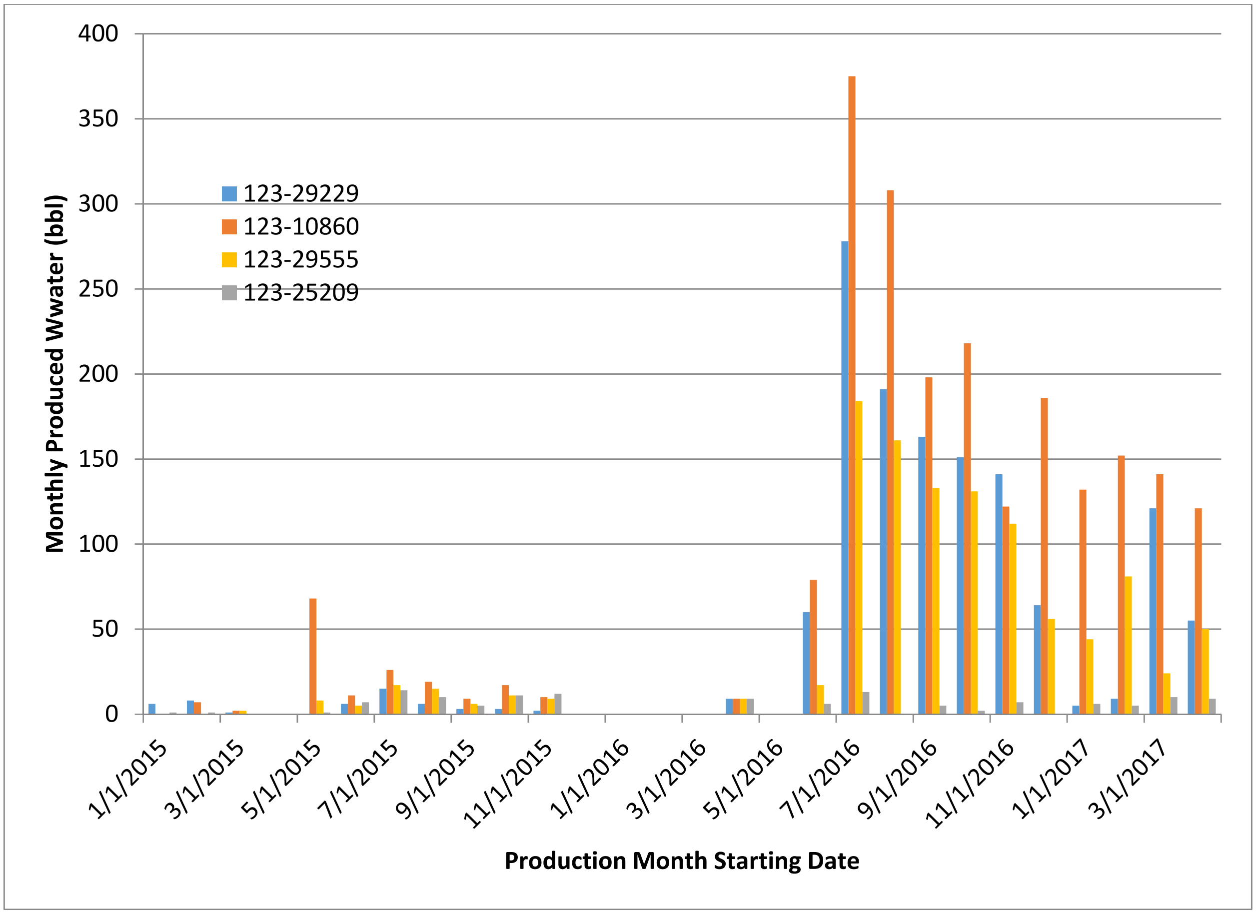

Figure 39. Reported Water Production from the Four Wells which Produced to Facility 755501 in the 28 Months Prior to and Including the Sampling Event

The produced water sample from the separator at 755475 is of water produced from the Niobrara Fm. and has the oldest reported apparent ^{14}C of DIC age among the produced water samples. The activity of ^{3}H in this sample is the third highest of the six produced water samples or approximately 40% of the activity of tritium measured in the source water sample. The frac fluid used at the well served by the separator was indicated as >99% fresh water on the completion report. The ^{3}H levels of the produced water from 755475 (Niobrara Fm.) and the nearby Codell Fm. sample (755474) are approximately 41% and 29%, respectively, of the example source water activity of ^{3}H. The wells producing to 755475 and 755474 had been completed using hydraulic fracture techniques using 99% fresh water fewer than 10 months prior to sampling, but both have relatively old ^{14}C of DIC ages, and the stable isotopes of water are not similar to the example source water. The waters from both 755475 and 755474 have positive stable carbon isotope ratios of the DIC like the flowback sample and unlike the source water sample. A relatively rapid change from negative to positive delta ^{13}C of DIC as shown in Figure 23 in Section 3.3 indicates the DIC in the samples at 755475 and 755474 are in part from sources other than example source fresh water.

Tritium activities of produced water, together with stable isotope ratios of water, are useful tools in aiding the understanding of mixing of frac waters and formation waters in the subsurface as well as in understanding what water is being returned to the surface at least for a period of several years after use of fresh water in hydraulic fracturing processes. The ^{14}C of DIC ages of samples from wells completed with fresh water fracs are not indicative of the ages of the water due to rapid exchange of carbon dioxide between gases in the producing formation and the injected water and also due to exchange of carbon dioxide between the injected water and carbonate minerals in producing formation. Hydraulic fracture stimulation of four wells listed in Table 27 utilized acids as a small fraction of the liquids injected (**755476**, **755475**, **755474**, and **755500**). Carbonate minerals are approximately 70% or more of the productive chalk zones with in the Niobrara Fm. (Pollastro, 1992; Sonnenberg, 2016) in portions of the Denver basin, and the four wells listed above are all completed in the Niobrara Fm. Dissolution of carbonate minerals present in producing zones of the Niobrara Fm. is expected to be induced by the presence of acids in the fracture fluid. The dissolution of geologically old carbonates would also increase the apparent age of DIC in any produced water samples from those wells in which acid was a portion of the frac fluid.

5. SUMMARY

The COGCC conducted Special Project 10243 to gain a better understanding of the activities of NORM in aqueous E&P wastes statewide. Produced fluids (mainly water with occasionally minor quantities of organic liquids present) were chosen as the subject of this study as those fluids are the E&P waste produced in greatest volumes. Produced water is a primary source of NORM found as sediments and scale present in storage tanks, in pipes and in gas and produced water processing facilities. For this study, any water emerging from the well is considered to be produced water, even if was previously introduced into the producing formation for hydraulic fracturing, or if it is derived in part from produced water used in secondary recovery operations or if the water is derived from aqueous liquids added to a wellbore such as dense KCl brines used to control downhole pressure in wells or when KCl brines are used for other purposes downhole in oil and gas wells such as clay control.

Regulatory authority over radioactive materials in Colorado lies with the CDPHE, in general and also specific to TENORM. The Radiation Program of the Hazardous Material Division of CDPHE provides regulatory oversight and guidance for handling and disposal of TENORM materials.

There are currently no regulatory rules specifically related to handling or disposal of NORM materials in COGCC rules as the state legislature has not specifically delegated such authority to the Commission. However, in some cases, the level of NORM activity in E&P wastes may be equal to activities of materials governed under TENORM regulatory programs in Colorado or other states. In some instances the handling and disposal of produced water and associated E&P wastes may create situations with potential for increased radiation exposures particularly to workers who may come in close contact with produced water or sediments from produced water or with scale formed from produced water and found in storage tanks or in pipe used for transport of oil and gas produced fluids.

Sampling for this project was conducted by COGCC staff with analysis conducted by commercial or research laboratories. The sampling and the analyses were conducted following the SAP developed for this study (COGCC, 2017a). Fifty-one samples of E&P fluids and five natural gas samples (for ^{222}Rn analysis only) were collected for this study. Fluids were collected and analyzed from 45 sites that produce from 15 separate geologic formations in basins statewide (Denver-Julesburg, Piceance, Raton, North Park, San Juan and Sand Wash Basins). One sample of drilling and hydraulic fracturing source water from shallow aquifer water wells in the Denver-Julesburg Basin was also collected. A summary of sampling sites and associated formations from which the water is produced is provided in Appendix 1. The map included as Figure 3 shows that samples of produced water were collected from geologic basins with oil and gas production throughout the state. All analyses performed on samples collected as part of this study were conducted by independent commercial or research laboratories.

All aqueous samples collected as part of this study were analyzed for the NORM analytes by analytical methods as described in Table 1. Analysis of gross alpha and gross beta activities were performed on all aqueous samples to provide generalized information regarding the activities of non-volatile NORM in the water samples. Chemical separation and isotope-specific analysis of ^{238}U, ^{235}U and ^{234}U were performed on the one source water and the two produced water samples with total U concentrations

>3µg/l. Chemical separation and isotope-specific analyses of ^{238}U progeny including ^{226}Ra, ^{222}Rn, ^{210}Pb and ^{210}Po were performed on all aqueous samples. Isotope-specific analyses of ^{222}Rn were performed for the five natural gas samples collected. Chemical separation and isotope-specific analyses of ^{232}Th progeny including ^{228}Ra and ^{224}Ra were performed on all aqueous samples. Summaries of the laboratory data acquired regarding NORM activities in produced water samples collected as part of this study were presented in more detail in section 3.1 of this report and discussed in section 4.3.

The ranges of NORM analytes present in the samples collected as part of this study were presented in Tables 3 to 14 in section 3 of this report. These summary tables can be used broadly to better understand the ranges of NORM activities present in groundwater present in oil and gas producing formations throughout Colorado. All of the analytical data obtained from samples collected as part of this study are accessible to the public, other agencies, operators or any interested party through the COGCC web site and summarized in the appendices to this report.

A set of NORM data available from the Raton Basin CBM produced water was compiled and compared to data from this study. NORM analytical data from the area surrounding Project Rulison were compiled and compared to data gathered as part of this study. The ranges of NORM activities in produced water from three other states were compiled from the available literature and compared and contrasted to data gathered as part of this study. The summaries of NORM activities from the Raton Basin, the dataset of samples from near project Rulison and datasets from Texas, Pennsylvania and New York are presented in tables in section 4.2. Discussion of differences and similarities between ranges of NORM activities in produced water from Colorado, Texas, Pennsylvania and New York are also presented in the text and in the tables in section 4.2.

All liquid samples collected for this study were analyzed for gross alpha and gross beta activity. Of the 52 samples analyzed, 47 samples were above sample-specific MDC for gross alpha and 42 samples were above sample-specific MDC for gross beta (Table 2). The maximum gross alpha activity (730 pCi/l) was sample facility **755523**, and the minimum activity (0.1 pCi/l) from sample facility **755658**. The median gross alpha activity was 40.3 pCi/l. The gross alpha activities are skewed to lower concentrations (Figure 4) with the majority (71%) of the samples from this study reporting gross alpha activities <100 pCi/l. The maximum gross beta activity detected in the samples was 5,710 pCi/l from sample facility **755645**, and the minimum gross beta activity was <0.3 pCi/l from sample facility 215628. The median gross beta activity was 81.5 pCi/l. As with the gross alpha, the gross beta activities are skewed to lower concentrations (Figure 5) with the majority of the samples (67%) reporting gross beta activities <100 pCi/l.

All aqueous samples were analyzed for general water quality parameters including major cations and anions, metals (dissolved and total), pH, electrical conductivity, and both total and dissolved solids. Table 1 includes more details of what analytical methods were used in this to determine inorganic water quality parameters for this study. Summaries of the laboratory data acquired for general water quality parameters in produced water samples collected as part of this study were presented in more detail in section 3.2 of this report and discussed in section 4.3.

The ranges of general inorganic analytes present in the samples collected as part of this study were presented in Tables 3 to 14 in section 3.2 of this report. These summary tables can be used broadly to better understand the ranges of such general water quality parameters as pH or TDS, the ranges of concentration of major anions and cations such as Na and Cl and the ranges of concentration of trace elements such as Pb and As present in water brought to surface from oil and gas producing formations throughout Colorado.

Section 3.2.4 includes discussion of general inorganic chemistry of the produced waters sampled as part of this study with a particular emphasis on overall water quality and suggested possible uses of produced water in agriculture. Discussion of the ratios of Cl/Br and Na/Cl in produced waters sampled as part of this study was presented in section 3.2.4 as these ratios are useful in understanding possible sources of the produced water and also in understanding if the waters are mainly fresh water or are partly derived from water from sediments deposited in saline waters including seawater and/or evaporite brines.

Section 3.3 includes summary plots of the stable isotope ratios of hydrogen ($\delta^{2}H$ and also called δD) and oxygen ($\delta^{18}O$) and discussion of general use in each water sample collected as part of this study.

Analysis of the carbon stable isotope composition of DIC in each water sample collected was performed. Summary discussion and plot of $\delta^{13}C$ of DIC is in section 3.3.

A small set of water samples were analyzed for ^{3}H activities and the ^{14}C ages of DIC in the same water samples were also determined. The data for the ^{3}H analyses is discussed in section 3.4 of the report and the ^{14}C analyses are discussed in section 3.5. Analysis of both ^{3}H activities and ^{14}C ages may be useful in understanding ages of produced water and also in aiding interpretation of sources of produced water at the facilities sampled.

6. CONCLUSIONS

The analytical data from this study provides staff and others with NORM radionuclide activities and general inorganic water quality parameters for produced water from across the state. Analytical data for all samples and all analyses have been uploaded to the COGCC environmental database, which enables any and all interested parties to view and obtain the analytical data.

The laboratory measured activity levels from NORM radionuclides in produced water samples from this study are generally at the low to middle end of activity ranges found in this country from New York, Pennsylvania and Texas studies and in the literature from a worldwide compilation. Even in instances with very low NORM radionuclide activity in any setting, it is important to understand that even low levels of ionizing radiation might be harmful. In keeping with the ALARA principle, it is always advisable to limit exposure to ionizing radiation by minimizing possible exposures.

The gross alpha and the gross beta activities of the samples are not specific for individual isotopes. Both gross alpha and gross beta activities provide informative and useful screening level results for naturally occurring radionuclides. Gross alpha results typically are from ^{226}Ra, ^{224}Ra, ^{210}Po, and other alpha emitters. Gross beta results provide informative and useful screening level data to the presence of naturally occurring beta-emitting radionuclides ^{228}Ra and ^{40}K, and other beta-emitters such as ^{210}Pb. Review of the gross alpha and beta activities statewide do show some specific geologic controls by formation or groundwater type (Figures 6 and 7). In general there is a trend of increasing gross alpha and gross beta activity with increasing TDS concentration. A state map view of general TDS concentration ranges is shown in Figure 16. For example, produced waters from CBM production in the Raton Basin have relatively low concentrations of dissolved solids and low activities of NORM radionuclides from both gross alpha and beta analyses and also from isotope-specific analyses. Conversely, produced waters from geologic formations with evaporite minerals in the oil and gas producing formation or in adjacent formations with which the produced water has been in contact have high concentrations of dissolved solids and relatively high activities of alpha and beta emitters. Produced water from the Lyons Fm. in north central Weld County is one example of the coincident high levels of dissolved solids (highest in the study) and high levels (for this study) of specific radionuclides and gross alpha and gross beta activities. Produced waters from Topeka Limestone and Osage Limestone also have elevated concentrations of dissolved solids (fifth and second highest respectively) and generally elevated activities of individual radionuclides and elevated gross alpha and gross beta activities. One sample each from Lyons Fm., Topeka Limestone, and Osage Limestone production wells were collected, as this was a general survey with more samples collected from geologic formations with relatively greater oil, gas, and produced water volumes. Even if the single samples from each of these three formations are not representative of produced water from every well drilled into and producing from these three formations, they provide useful data when taken in the context of all samples collected as part of this study.

Table 28. Facilities with Highest Reported Activities by Analyte

Analyte	Facility with Maximum Activity	Facility Name	Producing Formation(s)	Comments	TDS rank
Gross α	755523	UPRC 1-35 produced water tank	Penn. Topeka Limestone	Vertical & no frac	5
Gross β	755645	McKay Federal AB02-15 FWKO	Permian Lyons Sandstone	Vertical & no frac	1
^{238}U	755461	Gobbler Water Handling Facility	Shallow aquifer	Frac source water	45
^{235}U	755461	Gobbler Water Handling Facility	Shallow aquifer	Frac source water	45
^{234}U	755461	Gobbler Water Handling Facility	Shallow aquifer	Frac source water	45
^{226}Ra & ^{226}Ra (γ)	755645	McKay Federal AB02-15 FWKO	Permian Lyons Sandstone	Vertical & no frac	1
^{222}Rn (in water)	755645	McKay Federal AB02-15 FWKO	Permian Lyons Sandstone	Vertical & no frac	1
^{222}Rn (in gas)	755501	West Harden 1 Battery Prod. Water Tank	Cretaceous Niobrara Fm. & Codell SS.	3 Vert. & 1 Dir. 1 vert. & fracs 1982 & 2007, other 3 2009 fracs	17
^{214}Pb (γ)	755541	Ma-State Battery PW Tank	Miss. Osage Limestone	3 Vert. & no fracs	2
^{214}Bi (γ)	755541	Ma-State Battery PW Tank	Miss. Osage Limestone	3 Vert. & no fracs	2
^{210}Pb	755645	McKay Federal AB02-15 FWKO	Permian Lyons Sandstone	Vertical & no frac	1
^{210}Po	755645	McKay Federal AB02-15 FWKO	Permian Lyons Sandstone	Vertical & no frac	1
^{228}Ra & ^{228}Ra (γ)	755645	McKay Federal AB02-15 FWKO	Permian Lyons Sandstone	Vertical & no frac	1
^{224}Ra	755657	Ignacio 33-8 001C Separator	Cretaceous Mancos Shale, Mesa Verde Group and Dakota SS	Vertical, fracs in 1998 & 2011	37
^{212}Pb (γ)	755646	70 Ranch USX BB 27-02, -08 & -17 PW tank	Cretaceous Niobrara Fm., Codell SS. & J SS	3 vert. , fracs in 2010	22
^{40}K (γ)	755645	McKay Federal AB02-15 FWKO	Permian Lyons Sandstone	Vertical & no frac	1

Table 28 shows each NORM analyte from this study along with the facility number and name in which the highest reported activity of all samples collected as part of this study was present. Producing formations at the facilities along with the relative rank of total dissolved solids concentration of water samples from that facility are listed in Table 28. Comments regarding the drilling style of oil and gas well(s) at the facility and if the well(s) were completed using hydraulic fracture techniques are also included in Table 28.

Only 7 facilities out of 46 had samples with maximum radiological activities for the 18 NORM analytes listed in Table 28. Two-thirds of the maximum reported activities were reported from only two of the facilities. Facility **755645** (McKay Federal AB02-15 Free Water Knock Out) and facility **755461** (shallow groundwater source), respectively, account for 50% and 16.7% of the total maximum activities reported for samples collected as part of this study. The remaining five sample sites listed in Table 28 had either one or two maximum activities. The elevated activities present in **755461** and **755645** are discussed below.

Facility **755461** is not produced water but is a source water supply for drilling and completions activities obtained from shallow groundwater wells. Facility 755461had the highest total U concentration of samples collected as part of this study, which results in the highest isotopic U activities. Due to the geochemical controls on uranium solubility (Langmuir, 1978; Hem, 1992; IAEA, 2003), it is expected to find elevated U concentration in shallow oxidized source groundwater in comparison to deeper oxygen-depleted produced water. Higher concentrations of U in source water than in produced water from the well in which the shallow groundwater was used as a base of the frac fluid have previously been reported in Colorado (Rosenblum et al., 2017). The data from facility **755461** collected as part of this study together with domestic groundwater U analyses present in the COGCC database (Figure 24) also indicate geochemical controls enhance solubility of U in shallow oxidized groundwater compared to organic-rich produced water as discussed in Section 4.1.2 previously.

The geochemistry of most oil-producing formations and the groundwater produced from those formations is expected to limit the solubility of U and Th in those produced waters (Langmuir, 1978; Langmuir and Herman, 1980; Hem, 1992; IAEA, 2003). The reported concentrations of U and Th in produced water samples from this study are relatively low as expected. Thus the contributions from alpha emitting isotopes of U (^{238}U, ^{235}U and ^{234}U) and Th (^{232}Th, ^{230}Th and ^{228}Th) to NORM gross alpha of produced water samples from this study is low.

Twelve of the maximum activity samples (66.7%) were from three sampling sites related to vertical oil and gas wells, with one of the three completed in the Lyons Fm. (**755645**), one completed in the Osage Limestone (**755541**), and one completed in the Topeka Limestone (**755523**). The wells producing to these three facilities are vertical wells that had not been stimulated using hydraulic fracturing techniques and have the first, second, and fifth highest TDS concentrations reported in samples collected as part of this study. One sample each was collected from Lyons, Osage, and Topeka production wells, so the produced water chemistries measured in these three formations/wells to production can only be extrapolated with some confidence to the same or similar age or similar lithology units elsewhere in the state.

Geology of the formations the samples were produced from and the geochemistry of the water samples in general can be used to better understand the elevated levels of radioactivity in these samples. The project's radiochemistry data and geochemistry results demonstrate that the composition of the rocks in contact with the produced water is the dominant factor in the overall water quality (TDS for example) and radiological content of the produced fluids. As seen in Table 28, there is no connection between overall water quality or elevated radioactive isotope activities to the type of drilling technique (i.e., horizontal versus vertical well) or to well stimulation practices (frac versus no frac). The majority of samples (10 of 16) with the highest activities of NORM analytes reported from this study are from vertical oil and gas wells that were not completed by hydraulic fracture techniques. The highest activities of uranium isotopes were observed in shallow groundwater used as source water for drilling and completions and not in produced water. Only three of the highest activities of the NORM analytes were present in wells that had been completed by hydraulic fracturing, and none of the wells contributing to those sites were horizontal wells (Table 28).

Variability in water chemistry between formations based on varying lithologic composition and variability within a formation is expected and was observed in this study. Eight samples were collected from wells developed in the Niobrara and/or Codell formations in the Greater Wattenberg Area of the Denver-Julesburg basin of eastern Colorado and producing to seven facilities. A brief summary of general water quality results and the activities of two Ra isotopes is presented in Table 29 to illustrate the variability of the selected analytical parameters within one geographic area and between two producing formations. Wells producing to six of the seven sampling sites in Table 29 are horizontal wells. Wells producing to one of the sampling sites (755501) are vertical or directionally drilled wells. All of the wells producing to the seven facilities were completed using hydraulic fracture completion techniques.

The concentrations of Na and Cl when added together compose the majority of the total dissolved solids present in these samples (Table 29), which vary from 7,500 to 23,000 mg/l in the five Niobrara Fm. samples and a slightly higher TDS concentration in the one Codell sandstone. The reported concentrations of dissolved solids in the samples listed in Table 29 are less than that of modern day seawater, which is approximately 35,000 mg/l (Pilson, 2013). That the TDS of all samples in Table 29 are lower than TDS of seawater likely indicates mixing of fresher water with formation waters and possible reaction of formation water with rocks and elements in rocks more reactive than chloride or bromide.

Table 29. Activities and Concentrations of Selected Analytes in GWA Niobrara and Codell Produced Water (this study)

Facility	**^{226}Ra pC/l**	**^{228}Ra pCi/l**	**^{226}Ra/^{228}Ra activity ratio**	**TDS mg/l**	**Na mg/l**	**Cl mg/l**	**Na/Cl molar ratio**	**Cl/Br mass ratio**
GWA Niobrara								
755475	46.7	5.8	**8.1**	15,000	4,900	8,600	0.84	78
755500	50.0	4.2	**11.9**	7,500	2,600	4,400	0.88	102
755500 **(dup.)**	51.1	4.9	**10.4**	7,600	2,700	4,400	0.88	105
755652	124.8	7.6	**16.4**	15,000	4,700	13,000	0.71	123
755653	19.96	U<1.19	**>16.8**	23,000	7,100	13,000	0.79	118
GWA Niobrara/Codell comingled								
755501	14.9	4.6	**3.2**	16,000	5,500	9,300	0.91	131
755476 **flowback**	23.5	1.5	**15.7**	12,000	4,100	6,500	0.93	67
GWA Codell								
755474	28.4	16.5	**1.7**	25,000	7,800	16,000	0.84	80

The Na/Cl ratios of each of the eight samples are within approximately 15% of the seawater Na/Cl ratio discussed in Section 3.2.4, indicating that relict seawater is likely a main source of the solutes in the produced waters at each of these facilities. The Cl/Br mass ratios of the produced water samples highlighted in Table 29 are lower than the seawater ratio, which can be interpreted that the waters also have significant fresh water mixed in, presumably from use of fresh water in hydraulic fracture stimulation of each of the wells producing to these facilities. As shown in Figure 34 and discussed in section 4.3.7, the stable isotopes of water from each produced water sample listed in Table 29 lies below the meteoric water line by varied amounts. The stable isotopes of water results for the samples listed in Table 29 are likely from mixing of fresh water with formation waters.

The calculated ratios of ^{226}Ra/^{228}Ra from the sample sites shown in Table 29 vary from 1.7 to >16.8. ^{226}Ra is progeny of ^{238}U, and ^{228}Ra is progeny of ^{232}Th. The ^{226}Ra/^{228}Ra is likely to reflect the relative activities of the parent uranium and thorium isotopes in rocks that have been in contact with the water from wells developed in that geologic formation or aquifer (Stackelburg et al., 2018). There are limited numbers of U and Th analyses from the Niobrara Fm. and Codell sandstones in the literature for comparison to the isotopic Ra analyses of produced water from the same formations conducted as part of this study. Nakamura (2015) and Levinthal (2016) are recent studies with ICP/MS analyses of the U and Th concentrations present in the Niobrara and Codell (Nakamura, 2015) and in the Niobrara (Levinthal, 2016). The ^{238}U/^{232}Th activity ratios shown in Table 30 are calculated from specific activities for the two isotopes (Peterson et al., 2007) and the concentrations of the elements in rocks reported by Nakamura (2015) and Levinthal (2016). Dellenbach (2016) suggested that interpretation of U/Th ratios in rocks from spectral gamma well logs from the Niobrara in the Sand Wash Basin could be used to aid identification of carbonate mineral rich zones from higher U/Th ratios of carbonate zones than observed in clay rich shale zones. The differences in relative U/Th ratio between the carbonate dominated formation (Niobrara) with higher U/Th ratio and the sandstone formation (Codell) can be seen in Table 30 for eastern Colorado from the analytical data of Nakamura, 2015 and Levinthal, 2016.

Table 30. Uranium and Thorium Concentrations in Niobrara and Codell Rocks

	Niobrara				Codell			
Source of Data	**U mg/kg**	**Th mg/kg**	**U/Th mass ratio**	**$^{238}U/^{232}Th$ activity ratio (calc.)**	**U mg/kg**	**Th mg/kg**	**U/Th mass ratio**	**$^{238}U/^{232}Th$ activity ratio (calc.)**
Nakamura (2015) medians	9.5	3.25	2.9	**9.1**	2.9	8.1	0.4	**1.1**
Levinthal (2016)	26.2	5.4	4.9	**15.0**				

This study did not find any analyses of Ra isotope activities in Niobrara or Codell rocks in the literature. Assuming the ^{238}U and ^{232}Th isotopes and their respective ^{226}Ra and ^{228}Ra progeny in the rocks of the two formations are in secular equilibrium, then the activity ratio $^{226}Ra/^{228}Ra$ in the rocks should be the same as the activity ratio of the parent isotopes in the rocks. The secular equilibrium assumed Ra isotope ratios of the Niobrara (9.1-15) are in the ranges of the same ratio calculated from measured activities of ^{226}Ra and ^{228}Ra in produced water samples from wells completed in Niobrara Fm. as shown in Table 29 (8.1 to >16.8). The Table 30 secular equilibrium assumed ratio (one rock analysis) of the Codell (1.1) and the same ratio calculated from measured activities of ^{226}Ra and ^{228}Ra in produced water samples from wells completed in the Codell, as shown in Table 29, is 1.7. The differences between formations in the measured and in the secular equilibrium assumed $^{226}Ra/^{228}Ra$ activity ratios supports the general conclusion that differences in the chemistry of the rocks in contact with produced water is a major influence on the composition of the produced water. The measured $^{226}Ra/^{228}Ra$ activity ratios in the two Niobrara-Codell comingled produced water samples (Table 29, facilities 755501 and 755476) are intermediate and may be considered as indicators of the relative contributions of each formation to the produced water sample.

Table 31. Ranges of NORM Radionuclides from IAEA International Compilation and from this Study

	IAEA, 2003 from Jonkers et al., 1997		This study	
radionuclide	**Natural gas pCi/l**	**Produced water pCi/l**	**Natural Gas pCi/l**	**Produced Water pCi/l**
^{238}U		0.008-2.7		0.38-0.67
^{226}Ra		0.002-1,200		0.14-376
^{222}Rn	135-5,400,000		17.5-150	32-681
^{210}Pb		13.5-5,140		0.71-253
^{210}Po				0.2-72
^{232}Th		0.008-0.027		<0.11
^{228}Ra		8.1-4,860		0.94-221
^{224}Ra		13.5-1,080		0.5-78

When compared to data from three other states, produced water samples from this study shows activities of NORM radionuclides to be lower in Colorado produced water samples than in other states for which large published data sets are available, and in most cases, by more than one order of magnitude, as shown in Tables 23, 24, and 25 in Section 4.2. An international compilation of ranges of activities of NORM radionuclides in comparison to results from this study is shown in Table 31. The IAEA (2003) data set was originally compiled by Jonkers et al. (1997). As with the datasets discussed in Section 4.2, the maximum measured activities in Colorado samples are lower than the maximum of the ranges of activities compiled from the international data set (Jonkers et al., 1997, IAEA, 2003).

Facility 755545 (McKay Federal) produces oil, gas, and produced water from the Permian Lyons Fm. As noted previously, this sample is the highest in both K (total and dissolved) and TDS of all of the samples collected for this study in addition to highest activities for gross beta, ^{226}Ra, ^{222}Rn (in water), ^{210}Pb, ^{228}Ra, and ^{40}K. As can be seen in Figure 8 there is a general increase in gross beta and gross alpha activities with increasing TDS of samples collected as part of this study. Fisher (1995) noted no broad correlation between TDS concentration and Ra activities of the same samples. Fisher (1995) however did note a general correlation of higher ^{226}Ra and ^{228}Ra activities with increasing chloride concentrations (when >20,000 mg/l Cl present) of produced water in some samples from Texas. As chloride is the dominant anion in many produced water samples, increase in chloride concentration would imply a more general correlation between greater activities of Ra isotopes and higher TDS concentrations.

Figure 40 shows all activities >MDC of three Ra isotopes plotted against the Cl concentration of the same produced water samples. Linear best fit lines are plotted for activities of each Ra isotope in samples for which the reported concentration of chloride was 20,000 mg/l or greater. Only 5 of the 52 samples contained 20,000 mg/l Cl or greater, but there is a general increase in activities of ^{226}Ra and ^{228}Ra with increasing Cl concentration when Cl>20,000mg/l is present in produced water as observed and discussed by Fisher (1995) for produced water from Texas. The correlations between increased TDS (or Cl) concentrations and increasing activities or Ra isotopes may be from increased desorption of Ra from mineral surfaces as the relative concentrations of ions other than Cl (such as Ca and Na) increase as part of increasing TDS levels (Sturchio et al., 2001). Figure 8 in section 3.1.1 showed a general trend of increasing gross alpha and gross beta activities with increasing concentrations of TDS is samples collected as part of this study. Figure 11 in section 3.1.4 showed good correlation between gross beta activities, ^{40}K activities and the concentration of K (^{40}K activity) in samples collected as part of this study.

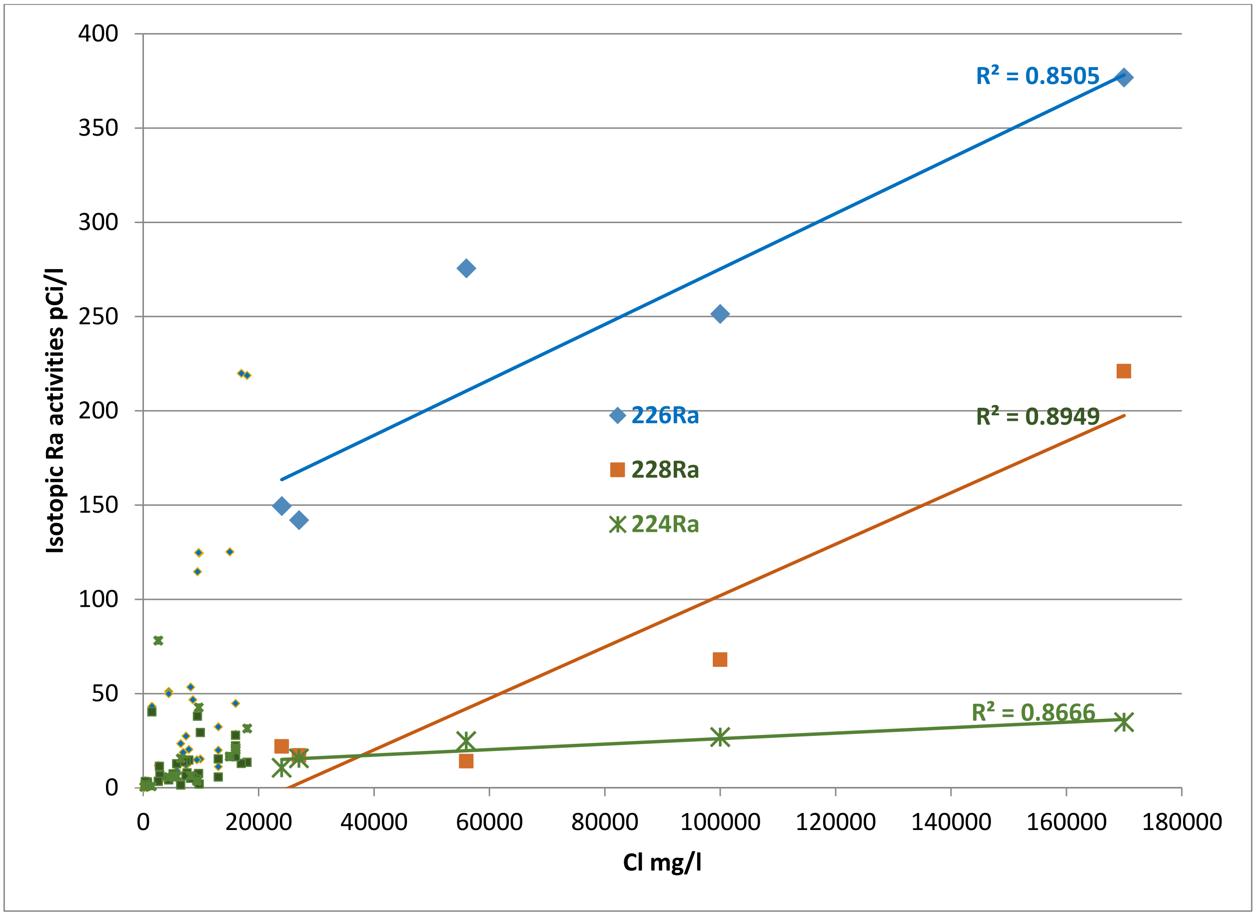

Figure 40. Activities of Ra isotopes in Comparison to Chloride Concentration (this study)
Linear regressions shown are based solely on activities from the five samples with Cl concentration >20,000mg/l. Ra activities from samples with Cl <20,000mg/l are also plotted but no meaningful correlation between Ra activities and Cl concentration for those samples is observed in this dataset.

The ratios of the reported activities of ^{226}Ra/^{228}Ra have been used as indicators of the relative contributions of their parent radionuclides (^{238}U and ^{232}Th) to NORM radionuclides in the formation(s) from which water is produced (Fisher, 1995; Sturchio et al., 2001; Stackelburg et al., 2018; this study). Fisher (1995) reported a near 1:1 correspondence of the ^{226}Ra and ^{228}Ra activities in 20 samples with analyses of both isotopes as interpreted from a slope of 1.03 for the regression line with a correlation coefficient r^2 of 0.96. Fisher (1995) suggested that the activity of ^{228}Ra in Texas produced waters could be predicted based on measured activity of ^{226}Ra even though they are progeny of different parent isotopes. Overall, the data from this study do not show a 1:1 relationship between produced water ^{226}Ra and ^{228}Ra activities. Only 2 out of 38 samples for which the both isotopes were reported as >MDC had ratios between 0.9 and 1.1.

Figure 41 illustrates that there is considerable variability in the ratios of activity of the ^{238}U-derived ^{226}Ra and the activity of the ^{232}Th-derived ^{228}Ra in the produced water samples collected as part of this study, and there is not a 1:1 correlation between the activities of the ^{238}U-derived ^{226}Ra and the activity of the ^{232}Th-derived ^{228}Ra in the produced water samples collected as part of this study, unlike the Texas produced water dataset reported by Fisher (1995). There are 19 Ra activity ratios between 3 and 62 for samples in which the reported activity was >MDC. There are also 19 Ra activity ratios between 0.5 and 2. The data from this study indicate there is no statistical correlation between activities of the U-derived ^{226}Ra and the Th-derived ^{228}Ra. Since these two Ra isotopes are progeny of different parent radionuclides, one would expect that the activities of the parent radionuclides present in the rocks from which the produced water has been in contact would be the primary determinant of the ^{226}Ra/^{228}Ra activity ratio with no reason to expect a direct correspondence between the two unrelated progeny (Sturchio et al., 2001; Stackelburg et al., 2018). Variations in U and Th concentrations in the producing formations are likely responsible for the varying ratios of activities of Ra isotopes. Different lithologies or formations contain different amounts of U and Th because of their varying mineralogy, differences in depositional history, and varying diagenetic histories. A summary of worldwide average U and Th concentrations of three types of sedimentary rocks in which oil and gas accumulations are frequently present are shown in Table 32 (National Research Council, 1999 ; National Council on Radiation Protection and Measurements, 1987). In Table 32 the activities of ^{40}K, ^{232}Th, and ^{238}U are expressed in units of Becquerels per kilogram (Bq/kg) which can be converted to picoCuries per unit as used in this report. The table shows the relative ratio of the specific activities of Th and U in the carbonate rocks data. The specific activity per unit weight of ^{238}U is approximately 3 times greater than the specific activity of ^{232}Th as reflected in the 3 times greater activity per 2 mg/kg U in carbonate rocks than for 2 mg/kg Th average in carbonate rocks. The half-life of ^{238}U (Figure 1) is roughly 3 times shorter than the half-life of ^{232}Th (Figure 2), which accounts for the lower activities per unit weight of ^{232}Th than for ^{238}U. Carbonate aquifers in the midcontinent area of the United States were reported to have mean ^{226}Ra/^{228}Ra activity ratios of 3 with a range upwards to >16 (Sturchio et al., 2001) and good correlation to high U/Th ratios in the rocks of the carbonate aquifers. Available U and Th analytical data for two oil and gas producing formations in Colorado were presented in Table 30 and discussed in this section of the report. The available local data are better suited for use in this study than the worldwide averages presented in Table 32.

Table 32. Average Concentrations and Activities of K, Th, and U in Three Types of Sedimentary Rocks

	K		^{232}Th		^{238}U	
Rock Type	**% total K**	**Bq/kg**	**mg/kg**	**Bq/kg**	**mg/kg**	**Bq/kg**
shale	2.7	800	12	50	3.7	40
sandstone	<1	<2	<2	<8	<1	<10
carbonate rocks	0.3	70	2	8	2	25

Adapted from National Research Council, 1999 and National Council on Radiation Protection and Measurements, 1987

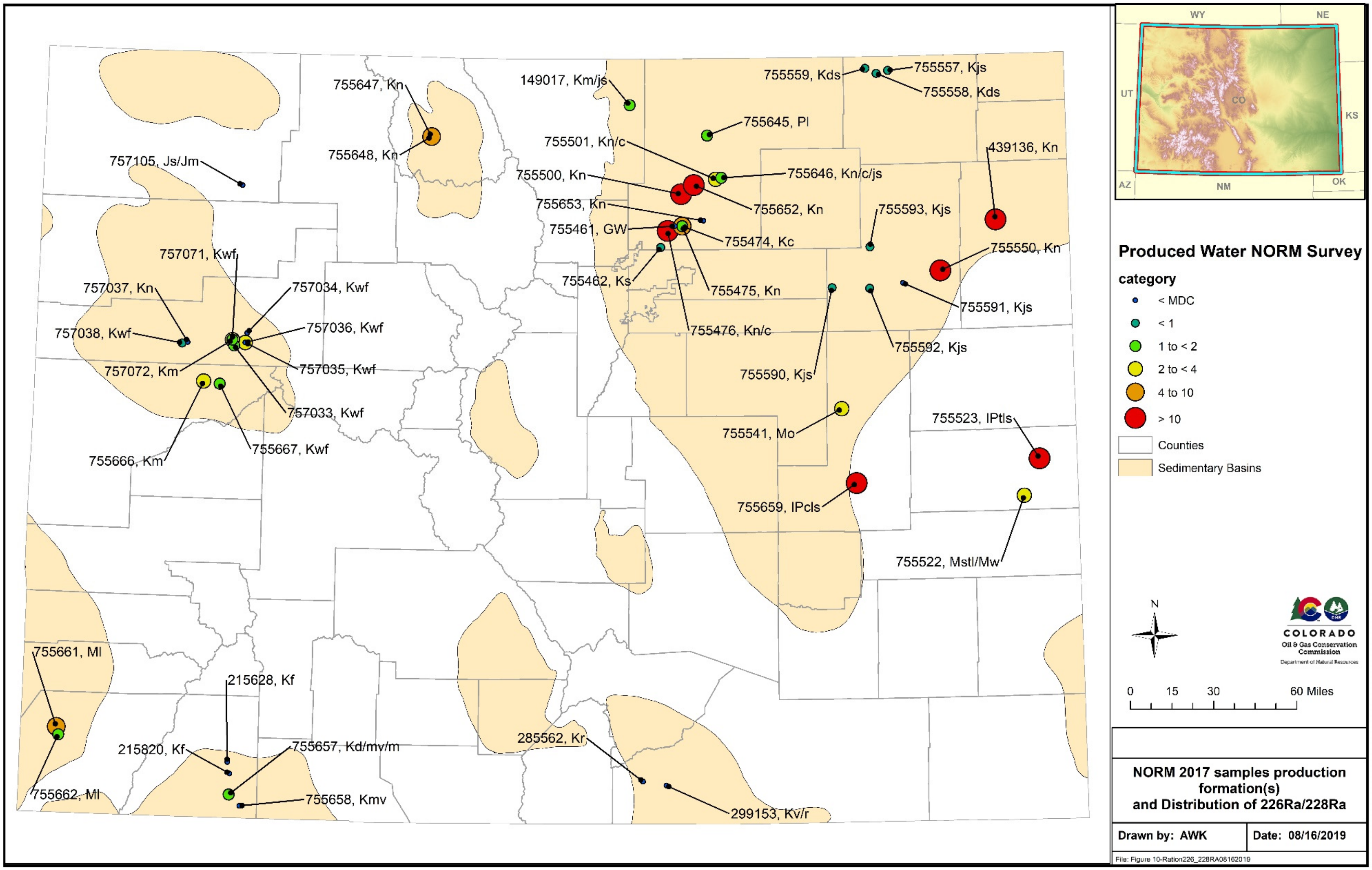

Figure 41. Production Formation(s) for Each Sampling Facility and Ranges of ^{226}Ra/^{228}Ra Ratio for NORM 2017 Samples

Each facility sampled is captioned with facility number and an abbreviated identification of the formation(s) from which oil and/or gas and water samples were produced. A legend explaining the abbreviated formations names can be found at the end of Appendix 1.

At seven of the sites shown in Figure 41, the ^{226}Ra/^{228}Ra activity ratios are >10. Each of the seven produced waters with >10 activity ratios came from formations dominated by carbonate minerals (Cherokee, Topeka, and Niobrara Fms.) as shown in Table 33. Seven of the eastern Colorado produced water samples had ^{226}Ra/^{228}Ra activity ratios of <1. Each of the seven produced water samples in Table 33 with activity ratios <1 are produced from predominantly sandstone formations (D sand, J sand, and Sussex units). One can assume that the relative ratios of uranium and thorium activities in the producing formations are similar to the produced water activities of their progeny Ra isotopes. In this study we compared Niobrara (carbonate) and Codell (sandstone) ^{226}Ra/^{228}Ra activity ratios to U/Th concentration and activity ratios in the same formations, and could show based on limited data from the literature and data from this study that the activity ratios of the parent isotopes in the rocks were similar to the activity ratio of the progeny isotopes in produced water.

Table 33. Produced Water Samples with Lowest and Highest ^{226}Ra/^{228}Ra Activity Ratios (this study)

Facility ID	Formation, Vertical or Horizontal, Completion
^{226}Ra/^{228}Ra activity ratios <1	
755557	J sand, vertical, frac
755590	J sand, vertical, no frac
755593	J sand, vertical, no frac
755558	D sand, vertical, no frac
755462	Sussex, vertical, frac
755592	J sand, vertical, no frac
755559	D sand, vertical, frac
^{226}Ra/^{228}Ra activity ratios >10	
755550	Niobrara, vertical, frac
755500	Niobrara, horizontal, frac
755476	Niobrara (7 of 8 wells), horizontal, frac
755652	Niobrara, horizontal, frac
755523	Topeka, vertical, no frac
755659	Cherokee, vertical, no frac
439136	Niobrara, vertical, frac

The data in Table 30 and Table 33 and in the summary just presented and seen in Figure 41 indicate that differences in NORM composition are based on differences in U/Th ratios resulting from differences in lithology of the production formation and not based on drilling style or completions practices. The samples with ^{226}Ra/^{228}Ra activity ratios <1 (Table 33) are all from vertical wells producing from sandstone units, with three of the seven having been completed by hydraulic fracture techniques and four of the seven not having undergone hydraulic fracture completions. The samples with ^{226}Ra/^{228}Ra activity ratios >10 (Table 33) are all from wells producing from carbonate mineral bearing formations, and four of those seven are produced water from vertical wells completed in carbonates, and three from horizontal wells completed in carbonates. Each of the five Niobrara produced water samples in Table 33 are from wells that had been completed by hydraulic fracture techniques. The samples from the Cherokee and Topeka Limestone (Table 33) are from vertical wells that were not completed by hydraulic fracture techniques.

TDS concentrations of the majority (71%) of samples collected as part of this study were in excess of 3,500 mg/l, and thus road spreading as a means of waste disposal of produced water is restricted by COGCC rules in most areas of the state. A limited amount of produced water with TDS <3,500mg/l is discharged to surface water in Colorado under Colorado Discharge Permitting System (CDPS) permits. Figure 42 shows that in 2017 the reported percentage of produced water discharged under CPDHE permits to waters of the state was 5.9% (≈18,000,000 bbls) of the total volume (3.08 x 10^8 bbls) of water produced. Discharges to waters of the state (COGCC database disposal code S) were reported as a disposal mechanism in only two counties (Las Animas and Moffat), and more than 99% of the produced water reported as discharged in 2017 was in Las Animas County. For example, in Las Animas County (2017 production reports) approximately 47% of the produced water was discharged under CDPS permit as reported by operators. Disposal of produced water by discharge to waters of the state are potential sources of release of NORM radionuclides into the near surface environment. However, as only produced waters with TDS <3,500 mg/l can be discharged under CDPS permits, and given the general correlation between lower NORM activities and lower TDS waters, there is less likelihood of impacts from NORM radionuclides present in the produced water than if high TDS waters could be discharged to surface under CPDS permits.

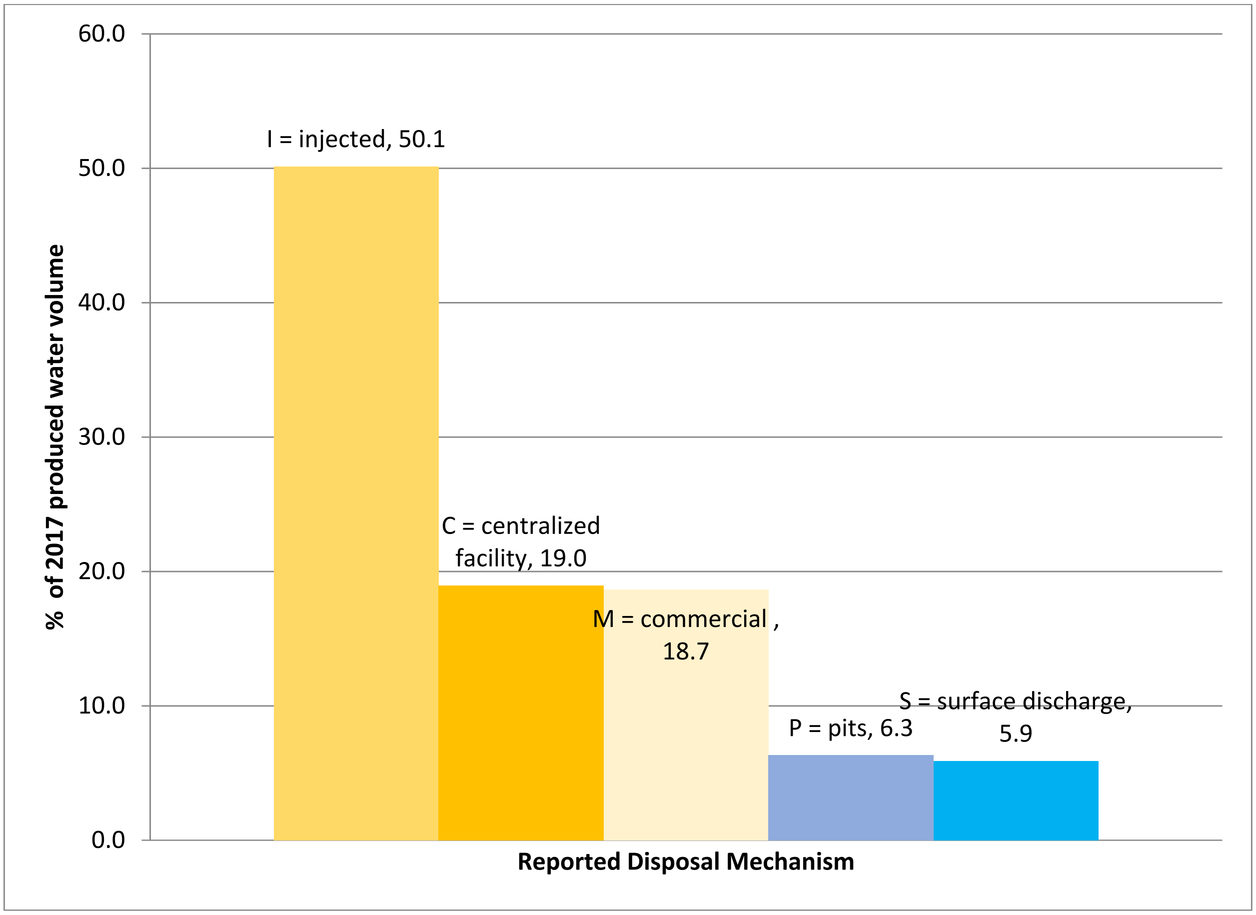

Figure 42. Reported Percentages of Produced Water Disposal by Mechanism in Colorado for 2017

Produced water disposal in lined and unlined pits (COGCC database disposal code P) was reported as 6.3% of the 2017 total produced water volume. More than half of the produced water disposal (10,739,324bbls≈59%) reported as going to pits in 2017 occurred in Washington County. Disposal of produced water in pits (particularly unlined pits) is another potential route by which produced water NORM radionuclides may be introduced into the near surface environment including soils and shallow groundwater. Unlike waters discharged to surface under CDPS permit, the COGCC does not have TDS threshold above which produced waters cannot be disposed of into permitted pits. Establishing a TDS threshold might serve to lessen the potential for NORM accumulations in pits or shallow groundwater near pits.

Approximately 88% of the water produced in Colorado during 2017 as part of oil and gas production was reported to be injected, sent to a centralized waste management facility, or disposed of at commercial facilities (COGCC database codes I, C, and M respectively). This study assumes that most of the water at centralized facilities is re-used in oil and gas operations or injected in UIC wells and that most of the produced water reported as commercially disposed was also injected in UIC wells. Careful storage, handling, and transport practices for produced water at the surface and before injection can minimize the potential for release of NORM radionuclides into the near surface environment.

Sodium and lesser concentrations of K are the dominant cations in the majority of the samples collected for this study. Chloride is the dominant anion in the majority of the sample results with lesser concentrations of bicarbonate alkalinity and SO_4. Crops may also exhibit specific ion toxicity to elevated concentrations of Cl and B (Ayers and Westcot, 1985) that are present in many of the produced water samples collected as part of this study. High concentrations of Na in produced water samples in comparison to Ca and Mg concentrations can pose problems if it is desired to use produced water beneficially in agriculture (Ayers and Westcot, 1985). Sodic soils that result from direct release/application of Na-dominated waters can hinder reclamation of sites where spills or releases of produced water with elevated SAR have occurred. Elevated SAR in irrigation water can be a causal factor in reduced crop yield due to reductions of the water infiltration ability of some soils (Bauder et al., 2014). In general, produced waters are unsuitable for irrigation due to sodicity and salinity concerns (see section 3.2.4) without treatment. Regulatory issues from varied agencies such as COGCC, CDPHE or Division of Water Resources (DWR limit reuse in irrigation). Cost of produced water treatment together with the regulatory issues have limited use of produced water in agriculture. Cost and regulatory issues have to date limited the possibility of release of NORM radionuclides into the near surface environment from beneficial reuse of produced water for irrigation.

Mass ratios of Cl/Br for the bulk of the samples had ratios between 100 and 200, which are characteristic of many shallow groundwaters (Davis et al., 1998). Nine samples had Cl/Br ratios exceeding 290; one with a ratio at 11,333 (Facility 755645). Cl/Br ratios in deeper groundwater such as produced water that are 200 to 400 have been described as representative of connate water (Davis et al., 1998). Connate water is water trapped in the sediments (typically marine) when originally deposited (Whitten and Brooks, 1972). Five of the samples collected as part of this study have Cl/Br mass ratios of 200 to 400. When ratios of Cl/Br are >1,000, it is typically thought that much of the solutes in those groundwaters are derived from evaporite minerals (Davis et al., 1998) that have come into contact with the produced water. Overall, Cl/Br mass ratios observed in this study were consistent with ratios expected for geologically isolated fluids and in some cases with mixing of fresh water into the existing groundwater.

Ratios of stable isotopes of O and H can be used to help understand differences in water sources and were evaluated in all the water samples collected as part this study. Water isotope data are typically compared to present day global precipitation as represented by the GMWL, which is a regression line to unevaporated precipitation data from across the world (Craig, 1961). A large degree of water isotope composition variability and differences was observed in this study's results when compared to present-day meteoric water, and similar to the interpretations of the Cl/Br mass ratio previously discussed, the water stable isotope ratios observed are generally indicative of geologically isolated waters in some cases mixed with near surface water. A small subset of samples collected from coal-bed methane wells have isotopic values at or near the GMWL, reflecting the more recent groundwater recharge. Effective use of stable isotopes as an aid in determining sources of produced water have recently been documented in the Permian Basin (Laughland et al., 2014) and in Saudi Arabia (Birkle, 2016a; 2016b). In conjunction with water well water stable isotope data in the COGCC database, the produced water stable isotope dataset gathered as part of this study can be used effectively to aid in understanding if produced water spills/release are present in water wells.

Water samples from eight sites were analyzed for tritium (^{3}H) and ^{14}C activity levels. With the exception of the source sample from Facility **755461**, the remaining seven samples (all produced water) show low tritium activities, which would be expected for fluids that have not been in recent contact with meteoric water or the atmosphere, or are mixtures of some modern water and waters older than bomb pulse water. Analyses of tritium in produced water can be useful in understanding the mixing of fresh water based hydraulic fracture stimulations with the water present in producing formations at the time of the hydraulic fracture process.

The shallow groundwater sample from Facility **755461** has a ^{14}C of DIC age of 60 years BP (102.63 PMC). The remaining samples had ^{14}C DIC ages older than the water from the **755461** site by more than two orders of magnitude, with calculated ages ranging from 17,115 to 43,600 years BP. The presence of geologically "old" carbon in producing formations may cause ^{14}C ages of DIC in produced water to not be meaningful in understanding age of the water being produced. In particular, carbon dioxide in different concentrations in many natural gases together with DIC already present in formation water are two likely sources of geologically "old" carbon that would interact rapidly with any water introduced into the formations that produce oil and gas. The ^{14}C ages of DIC in the seven produced water samples with ages between 17,115 to 43,600 years BP are likely reflective of interactions between the rocks, gases, and organic matter in the producing formations and any fresh water introduced into the formation, and are not realistic ages of the water.

Regulatory authority over radioactive materials and TENORM in Colorado lies with the CDPHE. The Radiation Program of the Hazardous Material Division provides regulatory oversight and guidance for handling and proper disposal of TENORM materials in Colorado. There are currently no regulatory rules over NORM materials; however, in some cases, the level of NORM may be equal to materials governed under TENORM regulatory programs, or the handling of NORM materials can create issues which may increase potential for health exposures whether those NORM containing materials are from E&P waste or from other sources. The National Research Council (1999) Committee on Evaluation of EPA Guidelines for Exposure to Naturally Occurring Radioactive Materials states that "All natural media – earth, air, water and biota, including humans – are radioactive to some degree, and the concentrations of radionuclides in these media are highly variable, both between and within media," and for this study it is important to understand the ranges of activities present in water co-produced with oil and natural gas. The COGCC (special project 10243) study acquired representative samples from across the state in order to gain a better understanding of the activities of NORM in Colorado aqueous E&P wastes than existed before the study was conducted.

The data gathered in this study will be used to provide staff, operators, other agencies, and the public with summary and detailed NORM-related analytical data for produced water from across Colorado's oil and gas producing basins. The ranges of NORM constituent activities is also compared to published NORM data from other states and from other nations in an effort to help understand relative scale of potential impacts. The study was conducted using funds allocated in the Oil and Gas Conservation Act in order to investigate conditions that threaten to cause or that actually cause a significant adverse environmental impact and to gather background or baseline data related to oil and gas operations (Colorado Revised Statutes Title 34, Article 60). The Act also requires that the Commission shall promulgate rules and regulations to protect the health, safety, and welfare of any person at an oil or gas well, and the data gathered in this study can help inform worker safety concerns at oil and gas operational facilities.

7. RECOMMENDATIONS

The E&P waste produced in largest volume in Colorado is produced water. The majority of produced water in Colorado is disposed of by injection in permitted UIC wells. Colorado produced water is also disposed of by surface discharge to waters of the state under permit from CDPHE and in pits permitted by COGCC. The latter two disposal mechanisms may result in impacts to soils, groundwater and surface water from NORM present in E&P wastes. COGCC should further assess the data in this report and determine if current practices of disposal are protective of water and soil quality. One recommendation related to COGCC permitted pits is to gather more data on the chemistry of produced water being disposed in unlined pits.

This study collected representative samples from many areas of the state and attempted to gather samples from all areas of the state with significant oil and gas operations in proportion to produced water production. That goal was not completely met as no produced water samples were collected from Rio Blanco County from which approximately 33% of the total produced water volume in Colorado (2017) was reported. Most of the produced water from Rio Blanco County is disposed of or reused in injection wells which may limit possible surface impacts from use of pits or surface discharge as disposal mechanisms. There are spills and releases of produced water in this county as in others so a survey type sampling of NORM and general water quality parameters in produced water from Rio Blanco County is recommended.

A limited study of the fractionation of Rn gas between produced water and natural gas phases was conducted as part of this study in an attempt to better define which progeny of U and Th may be present at which parts of the production, processing or distribution facilities. No analogous attempt to determine if Rn gas partitions into liquid hydrocarbon phases was performed as part of this study but may need to be considered. Any significant partitioning of Rn gas into liquid hydrocarbon phases would imply that significant activities for radiogenic progeny of Rn such as ^{212}Pb, ^{210}Pb, ^{212}Po and ^{210}Pb might be found at liquid hydrocarbon transport, processing and storage.

Water from each producing formation in the state were not sampled and analyzed as part of the study as the goal was to develop a general overview of NORM activities across the state. If large scale oil and gas operations are developed in formations and basins not sampled as part of this study then additional sampling and analysis may be needed.

REFERENCES

Allison, R., 2017. Water Quality and the Presence and Origin of Methane in the Upper Pierre Aquifer in Northeastern Weld County, Morgan County and Logan County, Colorado, COGCC Special Project 2141, 36 p. Accessed on 4 November, 2019 at: Upper Pierre Aquifer study

Amundson, R., Stern, L., Baisden, T. and Wang, Y., 1998. The isotopic composition of soil and soil respired CO_2, Geoderma, V. 82, p. 83-114.

Anders, R., Mendez, G.O., Futa, K. and Danskin, W.R., 2013. A Geochemical Approach to Determine Sources and Movement of Saline Groundwater in a Coastal Aquifer, Groundwater, v. 52, p. 756-768.

APHA, 2012. American Public Health Association, American Water Works Association, and Water Environment Federation. August 2012. Standard Methods for the Examination of Water and Wastewater, 22nd Edition.

ANSI HPS N13.53-2009, August 31, 2009. American National Standards Institute. "Control and Release of Technologically Enhanced Naturally Occurring Radioactive Material (TENORM)."

Ayers, R.S. and Westcot, D.W., 1985. Water Quality for Agriculture, FAO Irrigation and Drainage Paper 29 Rev. 1.

Bauder, T.A., Waskom, R.M., Sutherland, P.L. and Davis, J.G., 2014. Irrigation Water Quality Criteria, Colorado State University Extension Fact Sheet 0.506.

Bechtel Marine Propulsion Corporation, 2009. Nuclides and Isotopes. Chart of the Nuclides, Seventeenth Edition, 95 p.

Birkle, P., 2016a. Geochemical fingerprinting of hydraulic fracturing fluids from Qusaiba Hot Shale and formation water from Paleozoic petroleum systems, Saudi Arabia, Geofluids, v. 16, p. 565-584.

Birkle, P., 2016b. Recovery rates of fracturing fluids and provenance of produced water from fracturing of Silurian Qusaiba hot shale, northern Saudi Arabia, with implications on fracture network, AAPG Bulletin, v. 100, p. 917-941.

Bowen, G. and Revenaugh, J., 1993. Interpolating the isotopic composition of modern meteoric precipitation. Water Resources Research, Vol. 39, 1299.

Cappa J. and Rice D., 1995. Carbon dioxide in Mississippian rocks of the Paradox Basin and adjacent areas, Colorado, Utah, New Mexico and Arizona, U.S. Geological Survey Bulletin No. 2000-H.

CIAAW, 2017. Int. Union of Pure and Applied Chemistry Commission of Isotopic Abundances and Atomic Weights Current Isotopic Abundances.

Clever, H.L. (ed.) , 1979. Krytpon, Xenon and Radon – Gas Solubilities, in Solubility Data Series Volume 2, IUPAC Solubility Data Series, Pergamon, p. 227-322.

COGCC, 2014a. Sampling and Analysis Plan for Naturally Occurring Radioactive Material in Oil and Gas Well Drill Cuttings, COGCC Special Project 2136. Accessed on 4 November, 2019 at: NORM SAP for Cuttings 2014

COGCC, 2014b. Analysis of Radioactive Materials in Drill Cuttings, Greater Wattenberg Field, Weld County, COGCC Special Project 2136. Accessed on 4 November, 2019 at: NORM in Oil and Gas Drill Cuttings 2014

COGCC, 2017a. Sampling and Analysis Plan for Naturally Occurring Radioactive Material in Oil and Gas Produced Water, COGCC Special Project 10243. Document # 2496349 accessed on 4 November, 2019 as: document 2496349 in project 10243.

COGCC, 2017b. Rulison Sampling and Analysis Plan, July 2017 Rev. 4. Accessed on 4 November, 2019 at: Rulison Area SAP 2017

Cole, R. and Cumella, S., 2003. Stratigraphic Architecture and Reservoir Characteristics of the Mesa Verde Group, Southern Piceance Basin, Colorado, Ch. 18 in Field Trip Guidebook October 4 and 6, 2003. Rocky Mountain Association of Geologists and the American Institute of Professional Geologists.

Connolly, C.A., Walter, L.M., Baadsgard, H. and Longstaffe, F.J., 1990a. Origin and evolution of formation waters, Alberta Basin, Western Canada Sedimentary Basin. I. Chemistry, Applied Geochemistry, v. 5, p. 375-395.

Craig, H., 1961. Isotopic Variation in Meteoric Waters, Science, v. 133, p. 1702-1703.

Davis, S.N., Whittemore, D.O., and Fabryka-Martin, J., 1998. Uses of Chloride/Bromide Ratios in Studies of Potable Water: Groundwater, v. 36, p.338-350. Accessed on 4 November, 2019 at: https://onlinelibrary.wiley.com/doi/abs/10.1111/j.1745-6584.1998.tb01099.x

Davis, S.N., Fabryka-Martin, J. and Wolfsberg, L.E., 2004. Variations in Bromide in Potable water in the United States, Groundwater, v. 42, p. 902=909.

Dellenbach, B.A., 2016. An outcrop to subsurface stratigraphic analysis of the Niobrara Fm, Sand Wash Basin, Colorado, Colorado School of Mines M.S. thesis, 119p.

Eisinger, C. and Robertson, K, personal communication, 2018- COGCC database query as of 31August 2018).

ElGhonimy, R.S., 2015. Petrophysics, Geochemistry, Mineralogy and Storage Capacity of the Niobrara Formation in the Aristocrat PC H11-07 Core, Wattenberg Field, Denver Basin, Colorado, M.S. thesis, Colorado School of Mines, 142p.

Fisher, S., 1995. Naturally Occurring Radioactive Materials (NORM) in Produced Water and Scale from Texas Oil, Gas and Geothermal Wells: Geographic, Geologic and Geochemical Controls. Bureau of Economic Geology Geological Circular 95-3.

Freeman, J.T., 2007. The use of bromide and chloride mass ratios to differentiate salt-dissolution and formation brines in shallow groundwaters of the Western Canadian Sedimentary Basin. Hydrogeology Journal, v. 15, p. 1377-1385.

Garfield, T.R, Scott, A.J., and Walker, A.L., 1998. Overview: Late Paleozoic Geologic History of the Northern Denver Basin, in, Occurrence and Petrophysical Properties of Carbonate Reservoirs in the Rocky Mountain Region, S.M. Goolsby and M.W. Longman (eds), Rocky Mountain Association of Geologists., p. 1-18.

Gesell, T.F., 1973. Some radiological health aspects of radon-222 in liquefied petroleum gas, In Symposium on noble gases: Las Vegas 1973, eds. Stanley, R.E. and Moghissi, A.A.,

Gesell, T.F., 1975. Occupational Radiation Exposure Due to ^{222}Rn in Natural Gas and Natural Gas Products, Health Physics, v. 29, p. 681-687.

Geyh, M., editor, 2000. Environmental Isotopes in the Hydrological Cycle – Volume 4, Groundwater, Saturated and Unsaturated Zone, IAEA.

Gilfillan, S.M.V., Ballentine, C.J., Holland, G.D., Blagburn, D., Sherwood Lollar, B., Stevens, S., Schoell, M. and Cassidy, M., 2008. The noble gas geochemistry of natural CO_2 gas reservoirs from the Colorado Plateau and Rocky Mountain provinces, USA, Geochimica et Cosmochimica Acta, v. 72, p. 1174-1198.

Greenwood, N.N. and Earnshaw, A., 1997. Appendix 4 in Chemistry of the Elements 2nd ed. Elsevier, Amsterdam, 1294 p.

Harvey, F.E., 2005. Stable Hydrogen and Oxygen Isotope Composition of Precipitation in Northeastern Colorado. Journal of the American Water Resources Association, v. 41, p. 447-459.

Hefton, L., 2015. Diagenesis of the B Chalk, B Marl and Fort Hays Member of the Niobrara Formation, Denver Basin, Colorado, M.S. thesis, Colorado School of Mines, 224p.

Hem, J.D., 1992. Study and Interpretation of the Chemical Characteristics of Natural Water, USGS Water-Supply Paper 2254, Third Edition, 263p.

Hemborg, H.T., 2000. Gas Production Characteristics of the Rulison, Grand Valley, Mamm Creek and Parachute Fields, Garfield County, Colorado, Resource Series 39, Colorado Geological Survey.

IAEA, 2003. Radiation Protection and the Management of Radioactive Waste in the Oil and Gas Industry, Vienna, 130p.

Jonkers, G., Hartog, E.D., Knaepen, A.A.I. and Lancee, P.F.J., 1997. Characterization of NORM in the oil and gas production (E&P) industry, In Radiological Problems with Natural Radioactivity in the Non-Nuclear Industry, Proceedings International Symposium Amsterdam.

Katz, B.G., Eberts, S.M. and Kauffman, L.J., 2011. Using Cl/Br ratios and other indicators to assess potential impacts on groundwater quality from septic systems: A review and examples from principal aquifers in the United States, Journal of Hydrology, v.397, p. 151-166.

Langmuir, D., 1978. Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits, Geochimica et Cosmochimica Acta, v. 42, p. 547-569.

Langmuir, D. and Herman, J., 1980. The mobility of thorium in natural waters at low temperatures, Geochimica et Cosmochimica Acta, v. 44, p. 1753-1766.

Langmuir, D. and Melchior, D., 1985. The geochemistry of Ca, Sr, Ba and Ra sulfates in some deep brines from the Palo Duro Basin, Texas, Geochimica et Cosmochimica Acta, v.49, p. 2423-2432.

Langmuir, D. and Riese, A.C., 1985. The thermodynamic properties of radium, Geochimica et Cosmochimica Acta, v. 49, p. 1593-1601.

Laughland, M.M., Nelson, D.E., Wilson, P. and Eastridge, E., 2014. Uncharted waters: What we can learn from waters produced from horizontal wells in the Permian Basin, Unconventional Resources Technology Conference Denver CO. Accessed on 4 November, 2019 at: https://library.seg.org/doi/abs/10.15530/urtec-2014-1926712.

Lee, M.K. and Bethke, C.M., 1993. Groundwater flow, late cementation, and petroleum accumulation in the Permian Lyon Sandstone, Denver basin, AAPG Bulletin, v. 78, p. 217-237.

Levinthal, J.D., 2016. Mineralogical and Chemical Composition of Shale at Multiple Scales. M.S. thesis, University of Utah, 60p.

Londry, K.L. and Des Marais, D.J., 2003. Stable Carbon Isotope Fractionation by Sulfate-Reducing Bacteria. Applied and Environmental Microbiology, v. 69, p. 2942-2949.

Lozovic, P.A., 2005. Contribution of Organic Acid Anions to the Alkalinity of Natural Humic Water, Journal of Analytical Chemistry, v. 60, p. 1000-1004.

Maughan, E.K. and Wilson, R.F, 1960. Pennsylvanian and Permian Strata in Southern Wyoming and Northern Colorado, *in*, Guide to the Geology of Colorado, Geological Society of America, Rocky Mountain Association of Geologists, and Colorado Scientific Society, R.J. Weimer and J.D. Haun, eds., p. 34– 42.

Meija, J., Coplen, T.B., Berglund, M., Brand, W.A., De Bievre, P., Groning, M., Holden, N.E., Irrgeher, J., Loss, R.D., Walczyk, T. and Prohaska, T., 2016. Atomic Weights of the Elements 2013 (IUPAC Technical Report), Pure and Applied Chemistry, 88, 365-291.

Mook, W.G., editor, 2000. Environmental Isotopes in the Hydrological Cycle – Volume 1, Introduction, Theory, Methods and Review, IAEA.

Musgrove, M., Beck, J.A., Paschke, S.S., Bauch, N.J., and Mashcurn, S.L., 2014. Quality of Groundwater in the Denver Basin aquifer system, Colorado 2003-5: U.S. Geological Survey Scientific Investigations Report 2014-5051, 107p. Accessed on 4 November, 2019 at: http://dx.doi.org/10.3133/sir20145051.

Nakamura, KKK. 2015. Chemostratigraphy of the late Cretaceous Western Interior (Greenhorn, Carlile and Niobrara Formations), Denver Basin, CO, USA, Ph.D. Thesis, Colorado School of Mines, 93p.

NASE&M, 2016. National Academies of Sciences, Engineering and Medicine, Flowback and Produced Waters: Opportunities and Challenges for Innovation: Proceedings of a Workshop, Washington, DC., The National Academies Press. Accessed on 4 November, 2019 at: https://doi.org/10.17226/24620.

National Council on Radiation Protection and Measurements, 1987. Report No. 094 – Exposure of the population in the United States and Canada from Natural Background Radiation.

National Research Council, 1999. Evaluation of Guidelines for Exposures to Technologically Enhanced Naturally Occurring Radioactive Materials, The National Academies Press. Accessed on 4 November, 2019 at: http://nap.edu/6360.

Nelson, A.W., Knight, A.W., May, D., Eitrtheim, E.S. and Schultz, M.K., Naturally occurring radioactive materials (NORM) associated with unconventional drilling for shale gas. Ch. 4 in Hydraulic Fracturing Environmental Issues, ACS Symposium Series, p. 89-128.

NYDEC, 1999. An Investigation of Naturally Occurring Radioactive Materials (NORM) in Oil and Gas Wells in New York State, New York State Department of Environmental Conservation Division of Solid and Hazardous Materials.

NYDEC, 2009. Draft Supplemental Generic Environmental Impact Statement (SGEIS) on the oil, gas, and solution mining regulatory program (September 2009) Appendix 13, Department of Environmental Conservation, Division of Mineral Resources, Bureau of Oil and Gas Regulation.

Osselin, F., Nightingale, M., Hearn, G., Kloppmann, W., Gaucher, E., Clarkson, C.R. and Mayer, B., 2018. Quantifying the extent of flowback of hydraulic fracturing fluids using chemical and isotopic tracer approaches, Applied Geochemistry, v. 93, p. 20-29.

Otto, G.H., 1989. A National Survey on Naturally Occurring Radioactive Materials (NORM) in Petroleum Producing and Gas Processing Facilities, American Petroleum Institute, Dallas, 265p.

PADEP, 1992. Pennsylvania Department of Environmental Protection NORM Summary Survey September 1, 1992. Available (July 11, 2018) at: files.dep.state.pa.us/OilGas/BOGM/BOGMPortalFiles/RadiationProtection/NORM.pdf

PESI, 2013a. Sampling and Analysis Plan, Part I – Field Sampling Plan, Pennsylvania Department of Environmental Protection, April 3, 2013. Perma-Fix Environmental Services, Inc. Available (March 7, 2017) at: http://files.dep.state.pa.us/OilGas/BOGM/BOGMPortalFiles/RadiationProtection/Sampling_and_Analysis_Plan-Part-I-Field_Sampling_Plan.pdf

PESI, 2013b. Sampling and Analysis Plan, Part II – Quality Assurance Project Plan, Pennsylvania Department of Environmental Protection, April 3, 2013. Perma-Fix Environmental Services, Inc. Available (March 7, 2017) at: http://files.dep.state.pa.us/OilGas/BOGM/BOGMPortalFiles/RadiationProtection/Sampling_and_Analysis_Plan-Part-II-Quality_Assurance_Project_Plan.pdf

PESI, 2016. Technologically Enhanced Naturally Occurring Radioactive Materials (TENORM) Study Report Revision 1 May 2016, Pennsylvania Department of Environmental Protection. Perma-Fix Environmental Solutions, Inc. Available (4November, 2019) at http://files.dep.state.pa.us/OilGas/BOGM/BOGMPortalFiles/RadiationProtection/PA-DEP-TENORM-Study_Report_(Section_Text)_May_2016_track_change.pdf

Peterson, J., MacDonell, M., Haroun, L. and Monette, F., 2007. Radiological and Chemical Fact Sheets to Support Health Risk Analyses for Contaminated Areas, Argonne National Laboratory Environmental Science Division. Accessed on 4 November, 2019 at: https://www.remm.nlm.gov/ANL_ContaminantFactSheets_All_070418.pdf

Pilson, M.E.Q, 2013. An Introduction to the Chemistry of the Sea. Cambridge University Press, p. 67.

Piper, A.M., 1944. A graphic procedure in the geochemical interpretation of water-analyses, Transactions, American Geophysical Union, v. 25, p. 914-928.

Pollastro, R.M., 1992. Natural fractures, composition, cyclicity, and diagenesis of the Upper Cretaceous Niobrara Formation, Berthoud Field, Colorado, in Geological studies relevant to horizontal drilling – Examples from western North America, eds. Schmoker, J.W., Coalson, E.B. and Brown, C.A., Rocky Mountain Association of Geologists Guidebook, p. 243-255.

Reade, H. L., 1978. Uranium deposits: Northern Denver Julesburg Basin, Colorado in Energy Resources of the Denver Basin, Denver. Rocky Mountain Association of Geologists: pp. 161–171.

Rice, D.D., 1984. Relation of Hydrocarbon Occurrence to Thermal Maturity of Organic Matter in the Upper Cretaceous Niobrara Formation, Eastern Denver Basin: Evidence of Biogenic versus Thermogenic Origin of Hydrocarbons, in Hydrocarbon Source Rocks of the Greater Rocky Mountain Region, Rocky Mountain Association of Geologists, p. 365-367.

Rosenblum, J., Nelson, A.W., Ruyle, B., Schultz, M.K., Ryan, J.N. and Linden, K., 2017. Temporal characterization of flowback and produced water quality from a hydraulically fractured oil and gas well, Science of the Total Environment,

Rowan, E.L., Engle, M.A., Kirby, C.S. and Kraemer, T.F., 2011. Radium Content of Oil- and Gas-Field Produced Waters in the Northern Appalachian Basin (USA): Summary and Discussion of Data, USGS Scientific Investigations Report 2011-5135.

Rozanski, K., Araguas-Araguas, L. and Gonfiantini, R., 1993. Isotopic Patterns in Modern Global Precipitation. In Climate Change in Continental Isotopic Records, American Geophysical Union Geophysical Monograph Series 78, 1-36.

Rubin, B., Schwartz, L. and Montan, D., 1972. An Analysis of Gas Stimulation Using Nuclear Explosives, Lawrence Livermore Laboratory Report UCRL-51226.

Sonnenberg, S., 2016. Insights into Niobrara Stratigraphic Architecture and Diagenesis, Wattenberg Field, Denver Basin, Colorado, AAPG Search and Discovery Article 20373.

Stackelburg, P.E., Szabo, Z. and Jurgens, B.C., 2018. Radium mobility and the age of groundwater in public-drinking-water supplies from the Cambro-Ordovician aquifer system, north-central USA, Applied Geochemistry, v. 89, p. 34-48.

Stiff, H.A., 1951. The Interpretation of Chemical Water Analysis by Means of Patterns, J. of Petroleum Technology, v. 3, p. 15-17.

Sturchio, N.C., Banner, J.L., Binz, C.M., Heraty, L.B. and Musgrove, M., 2001. Radium geochemistry of groundwaters in Paleozoic carbonate aquifers, midcontinent, USA, Applied Geochemistry, v. 16, p 109-122.

Tasker, T.L., Burgos, W.D., Piotrowski, P., Castillo-Meza, L., Blewett, T.A., Ganow, K.B., Stallworth, A., Delompre, P.L.M., Goss, G.G., Fowler, L.B., Vanden Heuvel, J.P., Dorman, F. and Warner, N.R., 2018. Environmental Human Health Impacts of Spreading Oil and Gas Wastewater on Roads. Environmental Science and Technology v. 52, p. 7081-7091.

Thompson, W.O., 1949. Lyons Sandstone of Colorado Front Range: American Association of Petroleum Geologists Bulletin, V. 38, p. 52-72.

URS Corporation, 2008. First Quarter 2008 Report, Operational and Environmental Monitoring Within a Three-Mile Radius of Project Rulison, Prepared for Noble Energy Production, Inc. Accessed on 27April, 2018 at http://cogcc.state.co.us/library.html#/AreaReports/PiceanceBasin/Rulison/Rulison1qtr2008.zip

URS Corporation, 2010a. Final Rulison Sampling and Analysis Plan for Operational and Environmental Monitoring within a Three-Mile Radius of Project Rulison. Accessed on 27April, 2018 at http://cogcc.state.co.us/library.html#/AreaReports/PiceanceBasin/Rulison/ sampling and analysis plans for wells near the Rulison site

URS Corporation, 2010b. Fourth Quarter 2009 Report, Operational and Environmental Monitoring Within a Three-Mile Radius of Project Rulison, April 2010. Accessed on 27 April, 2018 at http://cogcc.stat.co.us/library.html#/AreaReports/PiceanceBasin/Rulison/Rulison4qtr2009.zip

USDA, 1954. Saline and Alkaline Soils, Agriculture Handbook 60.

USDOT Title 49 Code of Federal Regulations 173, Subpart I. 1996. US Department of Transportation. "Class 7 (Radioactive) Materials."

USEPA, January 2008. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846, Third Edition).

USEPA, June 1972. Handbook for Analytical Quality Control Water and Wastewater Laboratories (EPA 600/4-79-019).

USEPA, January 2010. Contract Laboratory Program National Functional Guidelines for Inorganic SUPERFUND Data Review (OSWER 9240.1-51, EPA 540-R-10-011).

USNRC, Title 10 Code of Federal Regulations 20. 1995. U.S. Nuclear Regulatory Commission. "Standards for Protection Against Radiation."

Weimer, R.J. and Lund Jr., C.B., 1972. Lyons Formation (Permian), Jefferson County, Colorado: A Fluvial Deposit, Mountain Geologist (Rocky Mountain Association of Geologists), V.9, pp. 289-297.

Whiticar, M.J., 1999. Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane, Chemical Geology, v.161, p. 291-314.

Whittemore, D.O., 1995. Geochemical Differentiation of Oil and Gas Brine from Other Saltwater Sources Contaminating Water Resources: Case Studies from Kansas and Oklahoma, AAPG Division of Environmental Geosciences Journal, v.2, p 15-31.

Whitten, D.G.A and Brooks, J.R.V., 1972. A Dictionary of Geology, Penguin Books.

LIST OF ABBREVIATIONS, ACRONYMS AND TECHNICAL JARGON

α – alpha decay mechanism

a – year, annum

^{228}Ac – actinium-228 isotope

AEC – Atomic Energy Commission

Ag - silver

Al – aluminum

ALARA – as low as reasonably achievable

ALS – ALS Laboratories

AMS – accelerator mass spectrometry

ANSI – American National Standards Institute

API – American Petroleum Institute

As – arsenic

ASTM – American Society for Testing and Materials

Ar – argon

β - beta decay mechanism

B - boron

Ba – barium

bbl – barrel of water or oil equal to 42 gallons

Be – beryllium

^{212}Bi – bismuth-212 isotope

^{214}Bi – bismuth-214 isotope

BP – before present as in years BP

Br – bromide anion or elemental bromine

Bq/kg – Becquerels per kilogram

^{14}C – carbon-14 isotope

^{o}C – degree Celsius

Ca – calcium

CBM – coal bed methane

Cd – cadmium

Cl – chloride anion or elemental chlorine

LIST OF ABBREVIATIONS, ACRONYMS AND TECHNICAL JARGON

Co – cobalt

CO - Colorado

^{137}Cs – cesium-137 isotope

Cu – copper

CDPHE - Colorado Department of Public Health and Environment

CDPS – Colorado Discharge Permitting System

CFR – Code of Federal Regulations

CLP – Contract Laboratory Program

COC – chain-of-custody

COGCC – Colorado Oil and Gas Conservation Commission

Cr – chromium

d – day

δ – delta

D – deuterium isotope of hydrogen, ^{2}H isotope

DER – duplicate error ratio

DIC – dissolved inorganic carbon

DOE – Department of Energy

DOT – Department of Transportation

DQL – data quality levels

DQO – data quality objectives

DUP – duplicate

DWR – Colorado Division of Water Rersources

E### - analytical method from EPA 900 series of methods of analysis of radioactivity

E&P – exploration and production

Fe – iron

F – elemental fluorine or in some instances shorthand for fluoride anion

Fm. - Formation

γ - gamma radiation (electromagnetic energy emitted by radionuclides)

GMWL – global meteoric water line

GFPC – gas-flow proportional counting system

LIST OF ABBREVIATIONS, ACRONYMS AND TECHNICAL JARGON

GPS – global positioning system

GWA – Greater Wattenberg Area

H - hydrogen

^{3}H – tritium isotope of hydrogen

HCl – hydrochloric acid

HDPE – high-density polyethylene

HNO_3 – nitric acid

IAEA – International Atomic Energy Agency

ICP – inductively coupled plasma emission spectroscopy

ICP/MS – inductively coupled plasma mass spectrometry

K – potassium

KCl – potassium choride

^{40}K – potassium-40 isotope

keV – kiloelectron volt

Li – lithium

LCS – laboratory control sample

LQAP – laboratory quality assurance plan

MB – method blank

MCF – thousand cubic feet

MDC – minimum detectable concentration

mg/kg – milligrams per kilogram

mg/l – milligrams per liter

Mg – magnesium

min - minute

Mn – manganese

Mo – molybdenum

mol% - mole percent

MS/MSD – matrix spike/matrix spike duplicate

NA – not applicable

N - nitrogen

LIST OF ABBREVIATIONS, ACRONYMS AND TECHNICAL JARGON

Na – sodium

NIST – National Institute of Standards and Technology

NORM - naturally occurring radioactive material

Ni – nickel

NRC – Nuclear Regulatory Commission

NY – New York

O- oxygen

^{18}O – oxygen-18 isotope

pCi/l – picoCuries/liter, 10^{-12} Curies per liter or approximately 2.2 disintegrations/minute

P- phosphorus

PA - Pennsylvania

^{234m}Pa – metastable protactnium-234 isotope

Pb – lead

^{210}Pb – lead-210 isotope

^{212}Pb – lead-212 isotope

^{214}Pb – lead-214 isotope

PESI – Perma-Fix Environmental Services, Inc.

pH – measure of acidity

PMC – percent modern carbon

^{210}Po - polonium-210 isotope

PTFE – polytetrafluoroethylene

PLSS – public land survey system

QA – quality assurance

QAP – quality assurance plan

QC – quality control

Ra – radium

^{224}Ra – radium-224 isotope

^{226}Ra – radium-226 isotope

^{228}Ra – radium-228 isotope

Rn – radon

LIST OF ABBREVIATIONS, ACRONYMS AND TECHNICAL JARGON

^{222}Rn – radon-222 isotope

RPD – relative percent difference

S- sulfur

SAP – sampling and analysis plan

Se – selenium

Si – silicon

SM####- analytical method from Standard Methods for the Examination of Water and Wastewater

SO$_4$ – sulfate anion

SOP – standard operating procedure

Sr – strontium

STRONGER - State Review of Oil & Natural Gas Environmental Regulations

SU – standard unit (for pH)

SW#### - analytical method from SW-846

TDS – total dissolved solids

TSS – total suspended solids

TENORM – technologically enhanced naturally occurring radioactive material

Th – the element thorium

^{228}Th – thorium-288 isotope

^{230}Th – thorium-230 isotope

^{232}Th – thorium-232 isotope

Tl – thallium

^{208}Tl – thalium-208 isotope

TPU – total propagated uncertainty

TX – Texas

UIC – underground injection control program

USDW – U.S. EPA acronym for underground source of drinking water (40CFR section 144.3)

U.S. EPA – United States Environmental Protection Agency

USGS – United States Geological Survey

U – the element uranium

LIST OF ABBREVIATIONS, ACRONYMS AND TECHNICAL JARGON

^{234}U – uranium-234 isotope

^{238}U – uranium-238 isotope

^{235}U – uranium-235 isotope

V – vanadium

VOA – volatile organic analysis

VPDB – Vienna Peedee belemnite reference for carbon isotopic composition

VSMOW – Vienna standard mean ocean water reference for hydrogen and oxygen isotope composition

Zn- zinc

% - percentage

‰ – per mil

< - less than

>- greater than

µg/l - micrograms per liter

µmhos/cm – micromhos per centimeter

µs – microsecond, 10^{-6} seconds

APPENDICES

Appendix 1. List of Samples Collected

COENV Facility #	Facility Name	Section	Township	T Dir.	Range	R Dir.	QuarterQuarter	Meridian	Producing Formation
149017	Wellington Production Water Treatment Facility	7	9	N	68	W	SWSW	6	Kjs
215628	WILBOURN FEDERAL GAS UNIT 1 and duplicate	19	35	N	7	W	NENW	N	Kf
215820	GEARHART C 1	8	34	N	7	W	SENW	N	Kf
285562	SANCHINATOR 11-36 TR	36	32	S	68	W	NWNW	6	Kr
299153	Panther 33-5	5	33	S	66	W	NWSE	6	Kv/r
439136	Gardner Trust 44-18 2N46W	18	2	N	46	W	SESE	6	Kn
755461	Gobbler Water Handling Facility	23	2	N	66	w	SENE	6	GW
755462	Baurer 41-36, Eiberger 32-36 & 42-36 PW tank	36	1	N	67	W	NENE	6	Ks
755474	Sarchet 38C-20Hz separator	20	2	N	65	W	SWNE	6	Kc
755475	Sarchet 16N-20Hz separator	20	2	N	65	W	SWNE	6	Kn
755476	Carter 33Hz temp. separator (frac flowback)	33	2	N	66	W	NENW	6	Kn/c
755500	Peschel 20H-232 separator and duplicate	20	4	N	65	W	SWSW	6	Kn
755501	West Hardin 1 Battery produced water tank	29	5	N	63	W	NWSE	6	Kn/c
755522	UPRR 1-1 free water knock out separator	1	16	S	45	W	SWSE	6	Mstl/Mw
755523	UPRC 1-35 produced water tank and duplicate	35	13	S	44	W	SENE	6	IPtls
755541	Ma-State battery PW tank	24	10	S	56	W	NWSW	6	Mo
755550	Mathies 1-13 separator	13	2	S	50	W	SWSW	6	Kn
755557	Michaels 1 PW discharge to pit	14	11	N	53	W	NWSW	6	Kjs
755558	H Smith location 312252 after sep. & filters	24	11	N	54	W	NESE	6	Kds
755559	Doud separator on location 312325 and duplicate	8	11	N	54	W	NESE	6	Kds
755590	Blomenkamp 1 outfall to PW pit	17	3	S	56	W	NENE	6	Kjs
755591	Marick State 1 skim tank outfall to PW pit	3	3	S	52	W	SWSE	6	Kjs
755592	Peterson 1 outfall to pit	15	3	S	54	W	NESW	6	Kjs
755593	Horn, Ruth B #1 outfall to pit	34	1	N	54	W	SESW	6	Kjs
755645	McKay Federal AB02-15 FWKO	2	7	N	64	W	SWSE	6	Pl
755646	70 Ranch USX BB 27-02, -08 & -17 PW tank	27	5	N	63	W	NWNE	6	Kn/c/js

COENV Facility #	Facility Name	Section	Township	T Dir.	Range	R Dir.	QuarterQuarter	Meridian	Producing Formation
755647	Castle 0780 1-17H_2O separator	17	7	N	80	W	NWNW	6	Kn
755648	Hebron 4-18H separator	17	7	N	80	W	NWNW	6	Kn
755652	Coalview G01 location 420148 PW tank	1	4	N	65	W	NESE	6	Kn
755653	Oscar Y 10-78HN separator	10	2	N	64	W	NESW	6	Kn
755657	Ignacio 33-8 001C separator	12	33	N	8	W	NWNE	N	Kd/mv/m
755658	Ignacio 33-7 3A separator and duplicate	34	33	N	7	W	NWNE	N	Kmv[2]
755659	James 1-2 separator	2	15	S	55	W	SENW	6	IPcls
755661	YB-5 separator @YB cluster facility	23	37	N	18	W	NWSW	N	Ml
755662	Goodman Point 9 @ GP central proc. fac. separator	2	36	N	18	W	NESE	N	Ml
755666	Hawxhurst 17-05B separator	17	9	S	94	W	NWNW	6	Km
755667	Jensen 17-13B separator and duplicate	19	9	S	93	W	NENE	6	Kwf
757033	Hunter Mesa Water Handling Facility	1	7	S	93	W	SESE	6	Kwf
757034	Valley Farms L pad	11	6	S	92	W	SESE	6	Kwf
757035	Circle B Land 11D-35-692 separator	35	6	S	92	W	SWNW	6	Kwf
757036	Circle B Land 13D-35-692 separator	35	6	S	92	W	SWNW	6	Kwf
757037	PA 701-32-HN1 PW tank	32	6	S	95	W	NWSW	6	Kn
757038	Parachute water handling facility	36	6	S	96	W	SWSW	6	Kwf
757071	Benzel 24-15B (F25NWB) separator	25	6	S	93	W	SENW	6	Kwf
757072	Benzel 35-2HM (F25NWB) separator	25	6	S	93	W	SENW	6	Km
757105	Iles Dome pit 116589 outfall	23	4	N	92	W	NWNW	6	Js/Jm

Jm – Morrison Formation
Js – Sundance Formation
Kc- Codell Formation
Kf – Fruitland Formation
IPcls – Cherokee Limestone
Kd – Dakota Formation
Kds – D Sand Formation
Kjs – J Sand Formation
Km – Mancos Formation
Kmv – Mesa Verde Formation
Kn – Niobrara Formation
Kr – Raton Formation
Kv – Vermejo Formation
Ml – Leadville Limestone
Mo – Osage Limestone
Pl – Lyons Formation
GW – groundwater
IPtls – Topeka Limestone
Mstl – St. Louis Limestone
Mw – Warsaw Limestone

Facility # in this appendix include hyperlink to COGCC website for sample sites (accessed 08/13/2019)

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[2] Overall water quality information for samples for this facility are not indicative of contact with the producing formation.

Appendix 2. Gross Alpha and Gross Beta Analyses

Facility COENV DB	Gross α pCi/l +/- TPU	MDC pCi/l	Lab Qualifiers	Gross β pCi/l +/- TPU	MDC pCi/l	Lab Qualifiers
755461	26.8+/-2.9	2		5.56+/-0.82	2.34	
755462	123+/-10	1		89+/-13	34	M3
755474	83+/-14	2		90+/-24	29	M3
755475	65+/-11	3		66+/-20	27	M3
755476	53.2+/-9.6	2.5		68+/-20	26	M3
755500	64+/-11	2		37.4+/-9.3	10.9	M3
755500	63+/-11	2		29.4+/-9.1	12.4	M3
755501	24.4+/-4.7	2		48+/-16	21	M3
755541	182+/-30	5	M3	1370+/-280	250	M3
755523	690+/-110	0	M3	301+/-61	56	M3
755523	730+/-120	0	M3	293+/-60	55	M3
149017	10.2+/-2.9	3		9.3+/-3.2	4.5	M3
755522	416+/-67	3	M3	231+/-42	29	M3
755550	107+/-18	3	M3	71+/-19	24	M3
439136	271+/-44	3	M3	96+/-23	25	M3
215628	3.1+/-2.2	3.4	U,M	0.3+/-1.1	1.9	U
215628	3+/-2.2	3.3	U,M	1.98+/-0.9	1.34	LT
215820	6.2+/-2.4	3.3	M3	4.2+/-2.3	3.5	
755659	479+/-78	6	M3	410+/-110	130	M3
755658	2.6+/-2.2	3.5	U,M	1.3+/-1.3	2.7	U
755657	216+/-35	3	M3	205+/-34	10	M3
755557	23+/-4.7	3.2	M3	20.8+/-6.9	9.4	M3
755558	78+/-13	3	M3	59+/-13	14	M3
755559	30.9+/-5.9	3		31.3+/-9	11.5	M3
755559	25.9+/-5.2	3.3	M3	22.8+/-7.4	10.1	M3
299153	1.73+/-0.75	1.02	LT	0.8+/-1.5	2.5	U
285562	2.2+/-0.94	1.39	LT	3.1+/-1.5	2.2	LT

Facility COENV DB	Gross α pCi/l +/- TPU	MDC pCi/l	Lab Qualifiers	Gross β pCi/l +/- TPU	MDC pCi/l	Lab Qualifiers
755648	277+/-46	8	M3	163+/-49	64	M3
755647	352+/-58	8	M3	193+/-53	68	M3
755645	640+/-100	10	M3	5710+/-960	350	M3
755646	40.3+/-6.7	0.9		74+/-22	29	M3
755662	92+/-16	4	M3	1560+/-250	30	M3
755590	7.6+/-1.4	0.7		4+/-14	23	U,M
755652	194+/-32	4	M3	106+/-25	27	M3
755653	45.9+/-8.5	3.9	M3	118+/-27	29	M3
755661	374+/-61	5	M3	1610+/-260	40	M3
755591	5+/-1.1	0.7		7+/-14	24	U,M
755666	123+/-21	4	M3	104+/-27	32	M3
755667	33.4+/-6.5	3.5	M3	47+/-18	26	M3
755667	34.8+/-6.6	3.2	M3	37+/-18	27	M3
755592	3.9+/-1.3	1.7		6.6+/-2.9	4.2	M3
755593	5.9+/-1.6	1.7		3.8+/-2.8	4.4	U,M
755658	0.1+/-1	2.6	U	1.7+/-1.5	3	U
757036	5.1+/-2.6	3.8	M3	51+/-13	15	M3
757035	0.7+/-3.3	5.6	U,M	47+/-19	27	M3
757105	3.7+/-2	2.9		17+/-14	23	U,M
757034	19.3+/-4.2	3.3	M3	102+/-24	26	M3
757071	32.8+/-6.3	3.3	M3	96+/-24	27	M3
757072	31.3+/-5.9	3		127+/-29	30	M3
757033	37.1+/-6.9	3	M3	92+/-23	28	M3
757038	15.7+/-3.7	3.5	M3	126+/-28	30	M3
757037	7.7+/-2.4	2.8		7.6+/-2.2	2.8	

U flag indicates result is less than the sample specific MDC, LT indicates result is less than Requested MDC and greater than the sample specific MDC, M indicates the requested MDC was not met, M3 indicates the requested MDC was not met but the reported activity is greater than the samples specific MDC.

Appendix 3. Isotopic Analyses of U

Facility #	**Total U**	**^{238}U**			**^{235}U**			**^{234}U**		
COENV DB	**µg/l**	**pCi/l +/-TPU**	**MDC pCi/l**	**Data Flags**	**pCi/l +/-TPU**	**MDC pCi/l**	**Data Flags**	**pCi/l +/-TPU**	**MDC pCi/l**	**Data Flags**
755461	23	8+/-1.5	0.1		0.4+/-0.18	0.11		10+/-1.8	0.1	
439136	3.1	0.38+/-0.15	0.07		0.009+/-0.052	0.077	U	0.46+/-0.17	0.07	
755653	3.1	0.67+/-0.34	0.21	M3	0.07+/-0.16	0.25	U,M	1.16+/-0.48	0.31	M3

U flag indicates result is less than the sample specific MDC, M indicates the requested MDC was not met, M3 indicates the requested MDC was not met but the reported activity is greater than the samples specific MDC.

Appendix 4. Isotopic Analyses of ^{238}U Progeny

Facility # COENV DB	Total Uranium µg/l	Data Flags	^{226}Ra pCi/l +/- TPU	MDC pCi/l	Data Flags	^{222}Rn in H_2O pCi/l +/- TPU	MDC pCi/l	Data Flags	^{210}Pb pCi/l +/- TPU	MDC pCi/l	Data Flags	^{210}Po pCi/l +/- TPU	MDC pCi/l	Data Flags
755461	23		0.1618584+/-4.280819E-02	0.087		449+/-58	26		0.34+/-0.39	0.63	U	0+/-0.19	0.45	U
755462	0.03	J	21.15603+/-5.472691	12.272	M3	22+/-21	35	U	0.5+/-1.8	3	U,M	0.2+/-0.22	0.36	U
755474	0.75	U	28.38854+/-3.037032	1.898	M3	36+/-25	39	U	1.2+/-3.6	6	U,M	0.16+/-0.38	0.73	U,M
755475	0.025	U	46.7602+/-3.779083	0.757	M3	37+/-26	41	U	1.1+/-1.5	2.4	U,M	0.14+/-0.35	0.52	U,M
755476	0.75	U	23.50775+/-2.006147	0.868	M3	23+/-24	39	U	0.45+/-0.73	1.19	U,M	0.13+/-0.18	0.3	U
755500	0.075	U	51.13597+/-4.49688	1.721	M3	36+/-22	34	LT	-0.08+/-0.37	0.62	U	0.08+/-0.42	0.79	U,M
755500	0.075	U	49.9565+/-4.433913	2.824	M3	54+/-23	33		-0.01+/-0.39	0.67	U	-0.08+/-0.62	1.26	U,M
755501	0.12		14.8575+/-1.434077	0.584		26+/-21	34	U	-0.25+/-0.38	0.65	U	0.7+/-0.52	0.57	M3
755541	0.075	U	251.411+/-17.70893	1.319	M3	75+/-23	31		35+/-10	8	M3	1.11+/-0.56	0.18	
755523	0.075	U	219.8841+/-14.83976	0.046		159+/-36	43		0.27+/-0.37	0.59	U	0.14+/-0.4	0.75	U,M
755523	0.075	U	218.8159+/-14.41345	0.057		196+/-39	44		-0.13+/-0.38	0.64	U	0+/-0.51	1.03	U,M
149017	0.075	U	3.882098+/-1.029634	2.263	M3	-11+/-25	42	U	0.39+/-0.39	0.62	U	0.34+/-0.42	0.64	U,M
755522	0.075	U	114.6859+/-7.703536	0.035		92+/-31	44		0.11+/-0.38	0.64	U	0.49+/-0.55	0.84	U,M
755550	0.075	U	53.46792+/-4.331821	1.224	M3	108+/-30	39		1.38+/-0.56	0.7		0.98+/-0.63	0.6	M3
439136	3.1		124.553+/-10.16901	2.995	M3	99+/-28	38		-0.04+/-0.51	0.87	U	0.5+/-1	1.9	U,M
215628	0.075	U	5.439881E-02+/-0.02825953	0.078	U	-2+/-22	37	U	-0.14+/-0.35	0.59	U	0.26+/-0.41	0.69	U,M
215628	0.075	U	4.485815E-02+/-0.02397427	0.072	U	-22+/-21	36	U	0.17+/-0.34	0.57	U	0.33+/-0.35	0.48	U
215820	0.075	U	0.318901+/-0.1465001	0.432	U	-15+/-21	37	U	0.02+/-0.35	0.59	U	-0.15+/-0.48	1.08	U,M
755659	0.075	U	275.6035+/-18.047	0.210		246+/-40	36		1.7+/-3.2	5.3	U,M	0.44+/-0.36	0.2	LT
755658	0.075	U	2.575443E-02+/-0.05161835	0.087	U	70+/-23	32		0.63+/-0.46	0.7	U	0.65+/-0.56	0.68	U,M
755657	0.075	U	43.24572+/-6.7019	0.195	Y2	112+/-26	32		0.71+/-0.41	0.59	LT	0.54+/-0.39	0.18	
755557	0.075	U	3.671774+/-0.6062813	0.134		20+/-17	28	U	0.33+/-0.38	0.62	U	0.97+/-0.6	0.64	M3
755558	0.075	U	9.098517+/-1.418087	0.138		10+/-17	28	U	0.22+/-0.37	0.62	U	0.79+/-0.56	0.66	M3
755559	0.075	U	5.951859+/-0.9108306	0.127		21+/-18	29	U	-0.13+/-0.38	0.65	U	0.47+/-0.5	0.73	U,M

Facility # COENV DB	Total Uranium µg/l	Data Flags	^{226}Ra			^{222}Rn in H_2O			^{210}Pb			^{210}Po		
			pCi/l +/- TPU	MDC pCi/l	Data Flags	pCi/l +/- TPU	MDC pCi/l	Data Flags	pCi/l +/- TPU	MDC pCi/l	Data Flags	pCi/l +/- TPU	MDC pCi/l	Data Flags
755559	0.075	U	5.751862+/-0.8900439	0.095		13+/-18	29	U	0.09+/-0.38	0.63	U	0.35+/-0.55	0.93	U,M
299153	0.075	U	0.4823406+/-0.1751	0.122		-5+/-23	39	U	0.05+/-0.33	0.56	U	0.2+/-0.33	0.49	U
285562	0.075	U	0.1490201+/-0.1016	0.123		8+/-24	40	U	-0.15+/-0.34	0.59	U	0.13+/-0.32	0.6	U,M
755648	0.075	U	142.0197+/-28.62898	8.436	M3	55+/-25	37		3.8+/-4.3	6.9	U,M	0.49+/-0.7	1.15	U,M
755647	0.075	U	149.4837+/-29.95405	8.625	M3	39+/-23	36	LT	2.3+/-4.2	7	U,M	0.72+/-0.69	0.89	U,M
755645	0.9	J	376.858+/-51.14682	0.203		681+/-87	40		253+/-61	6	M3	72+/-12	1	M3
755646	0.075	U	20.4485+/-3.049145	0.297		64+/-27	40		0.62+/-0.49	0.75	U	0.33+/-0.52	0.88	U,M
755662	0.075	U	11.20623+/-1.745818	0.107	Y2	-6+/-21	35	U	0.49+/-0.89	1.46	U,M	0.12+/-0.29	0.54	Y1,U,M
755590	0.075	U	1.04884+/-0.2401808	0.124		74+/-20	27		-0.04+/-0.38	0.65	U	0.2+/-0.33	0.18	LT
755652	0.075	U	124.7878+/-20.86287	4.233	M3	-3+/-15	26	U	0.2+/-0.9	1.51	U,M	0+/-0.35	0.66	U,M
755653	3.1		19.96004+/-3.844406	1.065	M3	10+/-16	26	U	0.93+/-0.92	1.46	U,M	0+/-30	56	Y2,U,M
755661	0.22		125.2102+/-17.47679	0.120		7+/-20	34	U	0.58+/-0.88	1.44	U,M	0.14+/-0.33	0.5	U
755591	0.075	U	0.8877606+/-0.3102073	0.281		4+/-16	27	U	0.02+/-0.38	0.64	U	0.36+/-0.38	0.53	U,M
755666	0.075	U	44.76707+/-13.02172	7.852	M3	25+/-20	33	U	0.01+/-0.88	1.49	U,M	0.07+/-0.35	0.53	U,M
755667	0.075	U	12.12199+/-6.715656	5.826	M3	39+/-21	32	LT	0.11+/-0.81	1.37	U,M	0.26+/-0.42	0.63	U,M
755667	0.075	U	12.42826+/-7.762828	8.367	M3	30+/-21	33	U	0.26+/-0.77	1.29	U,M	0.08+/-0.4	0.77	U,M
755592	0.075	U	1.298991+/-0.2858126	0.079		-1+/-17	29	U	-0.12+/-0.37	0.64	U	0.16+/-0.38	0.57	U,M
755593	0.075	U	0.5906044+/-0.1939299	0.164		-2+/-17	29	U	-0.12+/-0.4	0.68	U	0.2+/-0.33	0.5	U
755658	0.023	U	-5.806753E-02+/-0.1163932	0.269	U	51+/-18	26		0.05+/-0.39	0.66	U	0+/-0.84	1.58	U,M
757036	0.23	U	6.872674+/-7.061105	10.631	U,M	10+/-26	43	U	0.9+/-4.1	6.9	U,M	0.32+/-0.79	1.49	U,M
757035	0.23	U	11.82568+/-6.280188	6.893	M3	21+/-26	42	U	-2.2+/-4.7	8.1	U,M	0.33+/-0.81	1.21	U,M
757105	0.023	U	0.7556123+/-0.6070987	0.795	U,M	-2+/-26	44	U	0.61+/-0.92	1.49	U,M	0.49+/-0.8	1.19	U,M
757034	0.23	U	0.9986518+/-8.707063	16.655	U,M	-20+/-21	36	U	1.6+/-1.5	2.4	U,M	0+/-0.85	1.88	U,M
757071	0.23	U	27.44029+/-12.84951	12.218	M3	11+/-20	33	U	0.7+/-1.4	2.3	U,M	0.5+/-1.1	2	U,M
757072	0.23	U	32.34278+/-8.218379	2.969	M3	32+/-20	32	LT	2.4+/-1.7	2.6	U,M	0.7+/-1.1	1.8	U,M

Facility # COENV DB	Total Uranium µg/l	Data Flags	^{226}Ra			^{222}Rn in H_2O			^{210}Pb			^{210}Po		
			pCi/l +/- TPU	MDC pCi/l	Data Flags	pCi/l +/- TPU	MDC pCi/l	Data Flags	pCi/l +/- TPU	MDC pCi/l	Data Flags	pCi/l +/- TPU	MDC pCi/l	Data Flags
757033	0.23	U	18.8308+/-10.2282	10.008	M3	15+/-20	33	U	0.5+/-1.4	2.3	U,M	5.3+/-2.2	2	M3
757038	0.23	U	15.3451+/-11.61727	14.804	M3	10+/-20	34	U	-3.7+/-4.8	8.1	U,M	-0.2+/-1.1	2.3	U,M
757037	0.023	U	1.708694+/-0.3557627	0.134		30+/-21	33	U	0.1+/-4	6.7	U,M	0.5+/-1.4	2.6	U,M

Total Uranium flags

U flag indicates analyte not detected at concentration greater the MDL (method detection limit) specified by the laboratory

J flag indicates analyte detected at concentration greater the MDL (method detection limit) but less the RL (report limit) specified by the laboratory and considered as estimated

Radiochemistry flags for this appendix

U flag indicates result is less than the sample specific MDC, LT indicates result is less than Requested MDC and greater than the sample specific MDC, M indicates the requested MDC was not met, M3 indicates the requested MDC was not met but the reported activity is greater than the samples specific MDC. Y1 flag indicates chemical yield is in control at 100-110% and quantitative yield is assumed. Y2 flag indicates chemical yield is outside default limits.

Appendix 5. ^{222}Rn Analyses of Gas Samples

Facility ID COENV DB	^{222}Rn +/- TPU pCi/l	MDC pCi/l	Data
755461	70+/-18	1	
755475	22.5+/-6.8	2.6	M3
755474	17.5+/-5.5	2	M3
755500	46+/-12	1	M3
755501	15-+/-38	2	M3

M3 flag indicates the requested MDC was not met but the reported activity is greater than the sample specific MDC.

Appendix 6. Isotopic Analyses of ^{232}Th Progeny

Facility # COENV DB	Thorium (total)			^{228}Ra +/-TPU			^{224}Ra +/-TPU		
	µg/l	MDL	Data Flags	pCi/l	MDC	Data Flags	pCi/l	MDC	Data Flags
755461	0.04	0.025	J	0.4+/-0.33	0.67	U	0.5112497+/-0.152081	0.5552228	
755462	0.04	0.025	J	27.9+/-6.5	0.7		-3.04146+/-17.12824	79.61439	U,M
755474	0.91	0.91	U	16.5+/-4	1.2	M3	20.05298+/-4.670219	16.04583	M3
755475	0.025	0.025	U	5.8+/-1.6	1.4	M3	3.549666+/-2.053318	8.588546	U
755476	0.91	0.91	U	1.47+/-0.66	1.08	M3	0.6287665+/-1.367482	5.900128	U,M
755500	0.091	0.091	U	4.9+/-1.3	1.1	M3	-1.157423+/-5.079942	19.86004	U,M
755500	0.091	0.091	U	4.2+/-1.2	1.2	M3	-4.022472+/-4.028916	16.14057	U,M
755501	0.091	0.091	U	4.6+/-1.3	1.1	M3	1.827033+/-1.512547	6.100078	U,M
755541	0.091	0.091	U	68+/-20	19	M3	26.94463+/-4.587819	13.72625	M3
755523	0.091	0.091	U	12.9+/-3.2	1.2	Y1,M3	31.51903+/-2.228289	1.660681	M3
755523	0.091	0.091	U	13.5+/-3.3	1.3	M3	33.17127+/-2.267054	1.386986	M3
149017	0.091	0.091	U	3.3+/-1.2	1.8	M3	-2.463487+/-4.689348	21.01032	U,M
755522	0.091	0.091	U	38+/-8.9	1.5	M3	42.60556+/-2.933442	1.077992	M3
755550	0.091	0.091	U	5+/-1.6	1.9	M3	4.357892+/-2.825114	11.38827	U,M
439136	0.31	0.091		2+/-1	1.8	M3	5.142788+/-6.655595	28.1487	U,M
215628	0.091	0.091	U	-0.18+/-0.28	0.68	U	-0.1372491+/-0.2582475	1.129662	U,M
215628	0.091	0.091	U	0.32+/-0.33	0.69	U	1.381773E-02+/-0.2140328	0.9266994	U
215820	0.091	0.091	U	0.13+/-0.29	0.65	U	0.1638293+/-1.039711	4.63034	U,M
755659	0.091	0.091	U	14.1+/-4.5	5.3	M3	24.78524+/-1.901995	2.146535	M3
755658	0.091	0.091	U	1+/-0.87	1.79	U,M	-0.3116394+/-0.4066214	0.9022288	U
755657	0.091	0.091	U	40.3+/-9.5	1.7	M3	78.09334+/-12.06835	1.684091	Y2,M3
755557	0.091	0.091	U	6.6+/-2	2.1	M3	5.686288+/-0.9588314	0.6446335	
755558	0.091	0.091	U	12.8+/-3.3	1.8	M3	15.62343+/-2.400047	1.137106	M3
755559	0.091	0.091	U	7.4+/-2.2	2	M3	6.19665+/-1.016727	0.5903229	

Facility # COENV DB	Thorium (total)			^{228}Ra +/-TPU			^{224}Ra +/-TPU		
	µg/l	MDL	Data Flags	pCi/l	MDC	Data Flags	pCi/l	MDC	Data Flags
755559	0.091	0.091	U	6.4+/-1.9	1.9	M3	5.668857+/-0.9669993	0.6734044	
299153	0.091	0.091	U	0.35+/-0.34	0.72	U	0.1538308+/-0.45591	1.001346	U,M
285562	0.091	0.091	U	0.53+/-0.35	0.67	U	-0.1128863+/-0.39108	0.9273175	U
755648	0.091	0.091	U	17.2+/-4.2	1.4	M3	15.62313+/-31.33009	70.42085	M
755647	0.091	0.091	U	21.9+/-5.3	1.4	M3	10.59295+/-32.01507	72.71352	M
755645	0.91	0.91	U	221+/-51	2	M3	34.77879+/-5.315527	2.040596	M3
755646	0.091	0.091	U	14.7+/-3.6	1.2	M3	6.358658+/-1.739662	2.429833	M3
755662	0.091	0.091	U	5.7+/-1.5	1.2	M3	16.65525+/-2.628186	0.7287717	Y2
755590	0.091	0.091	U	1.69+/-0.74	1.2	M3	0.8474239+/-0.3691023	0.6322129	
755652	0.091	0.091	U	7.6+/-2	1.3	M3	11.63643+/-12.09997	25.52998	U,M
755653	0.091	0.091	U	0.63+/-0.57	1.19	U,M	2.481953+/-3.189251	6.635294	U,M
755661	0.091	0.091	U	16.6+/-4	1.2	M3	21.23936+/-3.566055	1.929901	M3
755591	0.091	0.091	U	1.33+/-0.73	1.33	U,M	1.008226+/-0.7392638	1.448751	U,M
755666	0.091	0.091	U	22.3+/-5.3	1.2	M3	28.79808+/-33.81166	74.44302	U,M
755667	0.091	0.091	U	6.4+/-1.7	1.2	M3	-4.339589+/-36.09553	84.26396	U,M
755667	0.091	0.091	U	7.9+/-2	1.2	M3	49.83281+/-37.60357	76.93273	U,M
755592	0.091	0.091	U	1.65+/-0.59	0.8		1.06917+/-0.4482507	0.7618658	
755593	0.091	0.091	U	0.94+/-0.43	0.74	LT	0.6518728+/-0.3990588	0.758777	U
755658	0.096	0.096	U	0.16+/-0.28	0.63	U	0.5930673+/-0.8108366	1.706472	U,M
757036	0.96	0.96	U	3.11+/-0.97	1.07	M3	-4.89899+/-29.13784	67.44949	U,M
757035	0.96	0.96	U	3.4+/-1	1.1	M3	11.6042+/-23.77834	50.7135	U,M
757105	0.096	0.096	U	0.62+/-0.51	1.04	U,M	1.316164+/-3.14534	6.926093	U,M
757034	0.96	0.96	U	11.4+/-3	1.9	M3	1.825642+/-34.10899	76.34924	U,M
757071	0.96	0.96	U	14.1+/-3.6	1.9	M3	15.63189+/-37.97866	82.50881	U,M
757072	0.96	0.96	U	15.3+/-3.8	1.8	M3	17.29358+/-12.73865	24.6576	U,M
757033	0.96	0.96	U	13.8+/-3.4	1.7	M3	-4.580721+/-27.12456	62.89407	U,M

Facility # COENV DB	Thorium (total)			^{228}Ra +/-TPU			^{224}Ra +/-TPU		
	µg/l	MDL	Data Flags	pCi/l	MDC	Data Flags	pCi/l	MDC	Data Flags
757038	0.96	0.96	**U**	29.3+/-7.1	2.2	M3	11.52535+/-47.67434	102.7375	**U,M**
757037	0.096	0.096	**U**	1.23+/-0.77	1.48	**U,M**	0.3118909+/-0.4419052	0.9622439	**U**

Total thorium flags

U flag indicates analyte not detected at concentration greater the MDL (method detection limit) specified by the laboratory

J flag indicates analyte detected at concentration greater the MDL (method detection limit) but less the RL (report limit) specified by the laboratory and considered as estimated

Radiochemistry flags for this appendix

U flag indicates result is less than the sample specific MDC, LT indicates result is less than Requested MDC and greater than the sample specific MDC, M indicates the requested MDC was not met, M3 indicates the requested MDC was not met but the reported activity is greater than the samples specific MDC. Y1 flag indicates chemical yield is in control at 100-110% and quantitative yield is assumed. Y2 flag indicates chemical yield is outside default limits.

Appendix 7. Gamma Spectroscopy Results for ^{40}K, ^{60}Co, ^{137}Cs and ^{241}Am

Facility # COENV DB	^{40}K			^{60}Co			^{137}Cs			^{241}Am		
	pCi/l +/- TPU	MDC pCi/l	Lab Qualifiers	pCi/l +/- TPU	MDC pCi/l	Lab Qualifiers	pCi/l +/- TPU	MDC pCi/l	Lab Qualifiers	pCi/l +/- TPU	MDC pCi/l	Lab Qualifiers
755461	-20+/-120	200	U	-3+/-5.4	9.8	U	1.2+/-4.8	8.1	U	-31+/-39	67	U
755462	-20+/-84	142	U	0+/-3.7	6.3	U	2.8+/-3.5	5.7	U	-60+/-160	270	U
755474	-60+/-110	180	U	-0.9+/-6.4	11.2	U	3.7+/-4.6	7.5	U	-15+/-30	52	U
755475	-38+/-90	156	U	2.9+/-4.9	8.2	U	-5.1+/-4.4	8	U	-40+/-210	360	U
755476	34+/-91	152	U	-1.9+/-5.2	9.3	U	2+/-4.5	7.6	U	-11+/-27	46	U
755500	-66+/-80	138	U	-3+/-4.2	7.6	U	0.3+/-3.4	5.8	U	20+/-20	33	U
755500	10+/-100	170	U	0+/-4.8	8.2	U	-1.5+/-3.6	6.2	U	-16+/-25	42	U
755501	21+/-73	123	U	2.3+/-3.1	5.2	U	-0.2+/-2.8	4.9	U	0.7+/-3.8	6.4	U
755541	870+/-190	210		-0.6+/-6.3	11.3	U	-0.6+/-5.6	9.8	U	14+/-58	97	U
755523	100+/-110	190	U	-3.1+/-6.8	12.4	U	1.6+/-5.2	8.8	U	-28+/-49	84	U
755523	50+/-140	230	U	2.4+/-4.6	7.7	U	-1.9+/-3.9	6.7	U	16+/-23	38	U
149017	-20+/-90	155	U	-0.6+/-5.2	9.2	U	-4.5+/-4.5	8.2	U	-20+/-120	200	U
755522	80+/-110	180	U	-3.7+/-5.4	10	U	0.7+/-4.8	8.3	U	-10+/-180	310	U
755550	40+/-110	180	U	-3+/-6.6	12.1	U	-3.7+/-5.4	9.8	U	4+/-30	52	U
439136	189+/-59	71	NQ	0.7+/-4.5	7.8	U	-1.2+/-4.2	7.2	U	2.3+/-4.7	7.8	U
215628	110+/-100	170	U	0.4+/-5.8	10.4	U	0.2+/-5.5	9.6	U	3.2+/-6.4	10.6	U
215628	20+/-100	170	U	1.1+/-5.1	9	U	-1.3+/-4.8	8.6	U	-2.7+/-5.8	10.1	U
215820	-20+/-100	180	U	-1+/-6.1	10.9	U	4.4+/-5.1	8.3	U	90+/-190	320	U
755659	338+/-95	128		-1.2+/-3.7	6.5	U	-0.4+/-3.2	5.6	U	4.5+/-4.8	7.9	U
755658	-16+/-90	154	U	-1.5+/-4.7	8.4	U	3.1+/-3.9	6.3	U	-13+/-32	54	U
755657	1+/-82	138	U	-1.5+/-4	7.1	U	-2+/-3.6	6.3	U	-21+/-91	154	U
755557	-20+/-120	200	U	-0.8+/-6.1	10.7	U	0.4+/-5.2	8.9	U	18+/-29	47	U
755558	22+/-91	152	U	1.3+/-3.8	6.5	U	0.8+/-3.5	5.9	U	-60+/-130	230	U
755559	-20+/-100	170	U	0.2+/-4.9	8.5	U	0.1+/-3.9	6.6	U	0+/-26	44	U
755559	2+/-77	132	U	-3.6+/-4.2	7.8	U	-0.7+/-3.9	6.8	U	1.9+/-4.2	7	U
299153	150+/-120	190	U	2.7+/-4.6	7.6	U	1.2+/-4.1	6.9	U	-10+/-40	68	U

Facility # COENV DB	^{40}K			^{60}Co			^{137}Cs			^{241}Am		
	pCi/l +/- TPU	MDC pCi/l	Lab Qualifiers	pCi/l +/- TPU	MDC pCi/l	Lab Qualifiers	pCi/l +/- TPU	MDC pCi/l	Lab Qualifiers	pCi/l +/- TPU	MDC pCi/l	Lab Qualifiers
285562	47+/-82	135	U	1.9+/-4.1	7	U	-2.6+/-3.4	6	U	32+/-91	152	U
755648	10+/-110	180	U	4.1+/-4.9	8.1	U	0.8+/-3.9	6.5	U	16+/-27	44	U
755647	249+/-83	107	NQ	-4.9+/-6.7	12.1	U	2.9+/-5.3	8.9	U	-21+/-31	53	U
755645	2840+/-370	150		-4.1+/-5.8	10.3	U	-0.9+/-4.6	7.8	U	2+/-28	47	U
755646	-8+/-70	119	U	0.3+/-3.5	6.1	U	-0.4+/-3.1	5.4	U	1.8+/-4.1	6.9	U
755662	1010+/-170	160		-5.1+/-5.1	9.3	U	-0.4+/-4	6.9	U	4+/-34	56	U
755590	-58+/-97	165	U	-0.2+/-3.8	6.6	U	0.4+/-3.5	6	U	-20+/-130	220	U
755652	9+/-92	156	U	-1.9+/-5	9	U	-2.6+/-4	7.1	U	-3+/-34	58	U
755653	186+/-86	126	NQ	-4.1+/-6.4	11.5	U	1.3+/-5.2	8.7	U	4+/-42	69	U
755661	1020+/-170	150		-0.4+/-4.6	8.2	U	1.1+/-4	6.7	U	3.9+/-4.7	7.7	U
755591	40+/-110	180	U	-4.6+/-5.4	9.7	U	0.9+/-3.7	6.3	U	-42+/-27	47	U
755666	-1+/-99	169	U	1.1+/-5.3	9.1	U	-3.8+/-4.5	8.1	U	-27+/-37	65	U
755667	-36+/-85	147	U	1.1+/-4.9	8.4	U	-2.3+/-4.2	7.4	U	-27+/-24	43	U
755667	-74+/-89	155	U	-3.5+/-4.6	8.4	U	-1.1+/-3.7	6.6	U	-90+/-140	250	U
755592	-60+/-120	200	U	-0.5+/-4.8	8.6	U	-1.9+/-4.4	7.9	U	7+/-44	75	U
755593	-3+/-82	139	U	1.5+/-4.6	7.9	U	2.1+/-3.9	6.5	U	4+/-97	164	U
755658	16+/-96	164	U	2.4+/-5.3	9.1	U	1.1+/-5.4	9.2	U	-70+/-150	250	U
757036	62+/-87	143	U	0.5+/-3.7	6.4	U	-3+/-3.8	6.7	U	30+/-100	170	U
757035	0+/-110	190	U	-2.4+/-4.2	7.8	U	-1.6+/-4.3	7.6	U	-17+/-40	69	U
757105	50+/-110	180	U	-0.3+/-4.9	8.6	U	-2.4+/-4.4	7.7	U	33+/-30	48	U
757034	9+/-85	146	U	-0.5+/-4.9	9	U	-3.1+/-4.7	8.6	U	1.3+/-5.8	9.8	U
757071	12+/-78	134	U	-0.6+/-5	9.1	U	-2.2+/-4.6	8.4	U	0.3+/-5.8	9.9	U
757072	40+/-100	170	U	-4+/-7.5	13.7	U	1.1+/-5.6	9.6	U	-16+/-32	56	U
757033	70+/-130	220	U	-0.3+/-6.2	11.1	U	-2.1+/-5.6	10	U	13+/-52	88	U
757038	110+/-140	220	U	-5.4+/-7.3	13.3	U	-4.1+/-5.5	9.8	U	1+/-33	56	U
757037	-60+/-100	180	U	1.3+/-6.4	11.2	U	6+/-5.5	8.9	U	-7+/-39	67	U

U flag indicates result is less than the sample specific MDC, NQ flag indicates analyst determined criteria for identification and quantification was not met and analyte is not present at any level above the sample specific MDC

Appendix 8. Gamma Spectroscopy Results for U Related Isotopes

Facility # COENV DB	^{235}U			^{234}Th			^{234m}Pa			^{226}Ra			^{214}Pb			^{214}Bi		
	pCi/l +/- TPU	MDC pCi/l	Data Flags	pCi/l +/- TPU	MDC pCi/l	Data Flags	pCi/l +/- TPU	MDC pCi/l	Data Flags	pCi/l +/- TPU	MDC pCi/l	Data Flags	pCi/l +/- TPU	MDC pCi/l	Data Flags	pCi/l +/- TPU	MDC pCi/l	Data Flags
755461	17+/-20	33	U	20+/-100	170	U	-10+/-810	1410	U	60+/-140	240	U,SI	6+/-15	24	U	14+/-16	29	U
755462	24+/-16	31	U	20+/-150	250	U	500+/-580	950	U	10+/-110	190	U,SI	-3+/-12	20	U	13+/-12	25	U
755474	0+/-27	45	U	11+/-91	153	U	550+/-910	1510	U	120+/-130	210	U,SI	5+/-14	24	U	6+/-17	28	U
755475	22+/-24	40	U	140+/-98	155	U	50+/-710	1240	U	90+/-130	210	U,SI	2+/-13	22	U	11+/-14	22	U
755476	7+/-20	33	U	8+/-89	149	U	-290+/-780	1390	U	-10+/-100	170	U,SI	6+/-13	22	U	13+/-15	25	U
755500	10+/-15	25	U	25+/-80	133	U	140+/-590	1000	U	14+/-87	145	U,SI	17+/-14	22	U	16+/-13	21	U
755500	-10+/-16	28	U	-46+/-82	137	U	-130+/-660	1140	U	80+/-100	160	U,SI	26+/-13	21	TI	27+/-13	25	
755501	15+/-10	18	U	-11+/-48	79	U	580+/-520	830	U	14+/-83	137	U,SI	3+/-9	15	U	3+/-14	23	U
755541	6+/-24	46	U	10+/-110	180	U	500+/-1000	1700	U	-400+/-1600	2600	U,SI	121+/-20	22		119+/-23	26	
755523	-5+/-26	44	U	-20+/-110	190	U	510+/-970	1620	U	320+/-170	260	SI	92+/-18	25		89+/-24	35	
755523	25+/-18	29	U	28+/-91	151	U	-500+/-1100	1900	U	280+/-140	220	SI	110+/-18	25		105+/-20	26	
149017	5+/-34	57	U	30+/-140	230	U	150+/-700	1200	U	60+/-140	240	U,SI	-1+/-13	23	U	-2+/-13	22	U
755522	-18+/-38	64	U	170+/-120	180	U	-310+/-850	1520	U	270+/-160	250	SI	57+/-15	25		56+/-17	25	
755550	-4+/-36	61	U	-25+/-88	156	U	590+/-920	1540	U	-20+/-120	200	U,SI	31+/-12	21		28+/-18	29	U
439136	9+/-16	26	U	161+/-36	44	NQ	610+/-730	1190	U	70+/-97	158	U,SI	46+/-12	20		41+/-15	25	
215628	-2+/-27	46	U	-34+/-62	106	U	1500+/-1100	1800	U	16+/-93	158	U,SI	6.5+/-9.4	15.5	U	-5+/-17	30	U
215628	9+/-20	33	U	30+/-47	96	U	-530+/-800	1500	U	-10+/-100	170	U,SI	5+/-14	23	U	6+/-14	24	U
215820	8+/-29	49	U	60+/-180	300	U	-150+/-870	1560	U	30+/-150	240	U,SI	13+/-10	16	U	4+/-16	27	U
755659	-2+/-18	30	U	-11+/-41	82	U	150+/-600	1020	U	288+/-97	142	SI	119+/-17	17		115+/-19	20	
755658	18+/-18	40	U	-44+/-95	161	U	670+/-660	1060	U	-30+/-100	170	U,SI	11+/-11	18	U	18+/-12	24	U
755657	16+/-22	37	U	70+/-140	220	U	350+/-580	970	U	30+/-130	220	U,SI	27.4+/-9.9	18.5		25+/-12	21	
755557	1+/-31	51	U	-20+/-100	170	U	250+/-850	1450	U	80+/-130	210	U,SI	3+/-15	25	U	18+/-20	33	U
755558	-5+/-38	64	U	60+/-170	280	U	370+/-610	1010	U	40+/-110	190	U,SI	5+/-12	20	U	5+/-15	26	U
755559	8+/-25	41	U	-10+/-80	134	U	-100+/-1100	1900	U	15+/-98	163	U,SI	8+/-11	18	U	25+/-12	18	
755559	22+/-20	37	U	-16+/-52	87	U	580+/-700	1150	U	29+/-85	140	U,SI	4.7+/-6.9	11.4	U	6+/-14	23	U

	^{235}U			^{234}Th			^{234m}Pa			^{226}Ra			^{214}Pb			^{214}Bi		
Facility # COENV DB	**pCi/l +/- TPU**	**MDC pCi/l**	**Data Flags**	**pCi/l +/- TPU**	**MDC pCi/l**	**Data Flags**	**pCi/l +/- TPU**	**MDC pCi/l**	**Data Flags**	**pCi/l +/- TPU**	**MDC pCi/l**	**Data Flags**	**pCi/l +/- TPU**	**MDC pCi/l**	**Data Flags**	**pCi/l +/- TPU**	**MDC pCi/l**	**Data Flags**
299153	-9+/-18	31	U	40+/-55	91	U	200+/-1200	2000	U	61+/-71	116	U,SI	10.1+/-8	12.8	U	7+/-8.9	14.6	U
285562	12+/-34	56	U	-20+/-140	240	U	600+/-1100	1900	U	-40+/-120	200	U,SI	12.7+/-7.7	12	NQ	7+/-8.4	13.7	U
755648	5+/-18	30	U	0+/-97	162	U	200+/-760	1280	U	170+/-110	170	SI	30+/-11	21		20+/-12	22	U
755647	28+/-23	37	U	222+/-67	93	NQ	1050+/-940	1500	U	400+/-150	220	NQ,SI	37+/-13	24		24+/-19	31	U
755645	-14+/-31	53	U	130+/-110	180	U	-170+/-830	1440	U	390+/-120	180	SI	99+/-17	21		91+/-19	24	
755646	11+/-12	20	U	18+/-49	81	U	480+/-540	870	U	55+/-84	138	U,SI	-1+/-11	18	U	-1+/-14	24	U
755662	-10+/-46	76	U	-5+/-97	162	U	280+/-720	1220	U	-30+/-100	170	U,SI	3.5+/-4.4	7.3	U	7+/-13	22	U
755590	-11+/-27	46	U	30+/-150	250	U	280+/-620	1050	U	40+/-130	220	U,SI	6+/-14	23	U	5+/-16	27	U
755652	12+/-26	51	U	8+/-91	152	U	290+/-690	1160	U	60+/-110	190	U,SI	42+/-13	25		48+/-14	21	
755653	9+/-30	50	U	-80+/-110	180	U	780+/-870	1420	U	20+/-120	210	U,SI	6+/-12	21	U	15+/-11	17	U
755661	9+/-17	27	U	-10+/-55	91	U	320+/-790	1320	U	156+/-96	152	SI	52+/-12	16		52+/-14	20	
755591	12+/-17	28	U	26+/-87	144	U	240+/-740	1260	U	20+/-110	180	U,SI	10.3+/-7.4	11.8	U	3+/-13	22	U
755666	0+/-24	41	U	-29+/-89	151	U	20+/-800	1380	U	60+/-100	170	U,SI	15+/-15	25	U	12+/-15	25	U
755667	11+/-23	38	U	24+/-91	152	U	220+/-740	1260	U	19+/-88	147	U,SI	8+/-14	24	U	15+/-15	25	U
755667	2+/-36	61	U	10+/-160	270	U	250+/-680	1140	U	-40+/-120	200	U,SI	7.2+/-8	13.1	U	6+/-14	23	U
755592	-9+/-19	33	U	37+/-60	100	U	490+/-780	1300	U	89+/-72	116	U,SI	-9+/-12	20	U	2+/-14	23	U
755593	23+/-20	39	U	30+/-150	250	U	450+/-690	1140	U	-20+/-120	200	U,SI	3+/-10	17	U	2+/-15	26	U
755658	-5+/-40	68	U	50+/-150	260	U	350+/-900	1540	U	0+/-140	240	U,SI	15+/-10	16	U	0+/-18	31	U
757036	10+/-21	35	U	90+/-150	240	U	30+/-590	1020	U	20+/-120	190	U,SI	-10+/-13	23	U	-9+/-15	26	U
757035	7+/-18	31	U	65+/-55	88	U	400+/-660	1100	U	40+/-110	180	U,SI	14.9+/-8.3	12.7	NQ	-2+/-15	25	U
757105	1+/-21	40	U	10+/-110	180	U	240+/-710	1200	U	-10+/-120	200	U,SI	10.5+/-7.8	12.3	U	-1+/-15	25	U
757034	9+/-17	28	U	-26+/-60	102	U	350+/-820	1400	U	28+/-98	165	U,SI	-3+/-13	22	U	1+/-16	28	U
757071	7+/-22	37	U	-13+/-56	95	U	570+/-840	1390	U	-19+/-89	152	U,SI	-4+/-12	20	U	11+/-13	24	U
757072	7+/-23	39	U	20+/-100	170	U	-800+/-1000	1800	U	50+/-130	210	U,SI	-1+/-14	23	U	0+/-16	28	U
757033	21+/-23	38	U	51+/-74	122	U	290+/-870	1500	U	121+/-91	144	U,SI	13+/-12	19	U	1+/-19	32	U
757038	31+/-25	40	U	20+/-120	200	U	470+/-920	1550	U	-40+/-140	240	U,SI	4+/-19	32	U	12+/-24	40	U

Facility # COENV DB	**^{235}U**			**^{234}Th**			**^{234m}Pa**			**^{226}Ra**			**^{214}Pb**			**^{214}Bi**		
	pCi/l +/- TPU	**MDC pCi/l**	**Data Flags**	**pCi/l +/- TPU**	**MDC pCi/l**	**Data Flags**	**pCi/l +/- TPU**	**MDC pCi/l**	**Data Flags**	**pCi/l +/- TPU**	**MDC pCi/l**	**Data Flags**	**pCi/l +/- TPU**	**MDC pCi/l**	**Data Flags**	**pCi/l +/- TPU**	**MDC pCi/l**	**Data Flags**
757037	8+/-24	40	U	-30+/-110	190	U	690+/-940	1550	U	-70+/-120	210	U,SI	3+/-19	31	U	4+/-18	30	U

U flag indicates result is less than the sample specific MDC, NQ flag indicates analyst determined criteria for identification and quantification was not met and analyte is not present at any level above the sample specific MDC, SI flag indicates nuclide identification and/or quantification is tentative, TI flag indicates nuclide identification is tentative

Appendix 9, Gamma Spectroscopy Results for Th Related Isotopes

	^{228}Ra			^{228}Ac			^{212}Pb			^{212}Bi		
Facility # COENV DB	**pCi/l +/- TPU**	**MDC pC/l**	**Data Flags**	**pCi/l +/- TPU**	**MDC pC/l**	**Data Flags**	**pCi/l +/- TPU**	**MDC pC/l**	**Data Flags**	**pCi/l +/- TPU**	**MDC pC/l**	**Data Flags**
755461	39+/-20	29	NQ	39+/-20	29	NQ	6.9+/-9.5	15.6	U	-35+/-61	107	U
755462	35+/-21	33	TI	35+/-21	33	TI	9.2+/-8.6	14	U	23+/-45	75	U
755474	20+/-30	49	U	20+/-30	49	U	6.9+/-9.2	15	U	25+/-67	114	U
755475	9+/-17	28	U	9+/-17	28	U	9+/-7.8	12.6	U	-6+/-57	100	U
755476	2+/-25	42	U	2+/-25	42	U	-2.9+/-9.7	16.5	U	29+/-66	110	U
755500	3+/-25	42	U	3+/-25	42	U	6.6+/-7.9	12.9	U	101+/-50	74	NQ
755500	24+/-15	24	NQ	24+/-15	24	NQ	6.9+/-8.6	14.1	U	41+/-51	84	U
755501	4+/-17	28	U	4+/-17	28	U	-3.3+/-6.7	11.2	U	-2+/-44	75	U
755541	43+/-21	55	U	43+/-21	55	U	5+/-12	20	U	-35+/-84	149	U
755523	25+/-22	35	U	25+/-22	35	U	4+/-10	17	U	20+/-80	136	U
755523	21+/-17	32	U	21+/-17	32	U	4+/-8.3	13.8	U	33+/-49	82	U
149017	33+/-19	28	NQ	33+/-19	28	NQ	4+/-11	19	U	45+/-71	118	U
755522	47+/-20	46		47+/-20	46		19+/-12	19	U	7+/-69	120	U
755550	20+/-21	45	U	20+/-21	45	U	4.5+/-8	13.4	U	66+/-71	115	U
439136	36+/-17	24		36+/-17	24		8.7+/-7.9	12.5	U	33+/-54	89	U
215628	14+/-29	49	U	14+/-29	49	U	-2+/-11	18	U	-12+/-67	122	U
215628	-7+/-24	42	U	-7+/-24	42	U	2.2+/-8.6	14.5	U	30+/-84	141	U
215820	15+/-29	49	U	15+/-29	49	U	4+/-12	19	U	11+/-71	122	U
755659	7+/-21	35	U	7+/-21	35	U	6.7+/-8.3	13.6	U	-11+/-70	119	U
755658	13+/-14	27	U	13+/-14	27	U	1.3+/-9.3	15.5	U	-55+/-87	153	U
755657	39+/-17	39		39+/-17	39		25+/-10	15		54+/-43	67	U
755557	25+/-22	35	U	25+/-22	35	U	1.1+/-9.7	16.3	U	-31+/-66	117	U
755558	19+/-17	37	U	19+/-17	37	U	8.2+/-8.7	14.2	U	60+/-50	79	U
755559	12+/-21	35	U	12+/-21	35	U	4.3+/-9.1	15.1	U	36+/-56	92	U
755559	17+/-13	24	U	17+/-13	24	U	1.5+/-8.2	13.7	U	9+/-54	91	U

Facility # COENV DB	^{228}Ra			^{228}Ac			^{212}Pb			^{212}Bi		
	pCi/l +/- TPU	MDC pC/l	Data Flags	pCi/l +/- TPU	MDC pC/l	Data Flags	pCi/l +/- TPU	MDC pC/l	Data Flags	pCi/l +/- TPU	MDC pC/l	Data Flags
299153	13+/-17	28	U	13+/-17	28	U	10.9+/-5.9	9.2	NQ	8+/-62	105	U
285562	-11+/-24	41	U	U -11+/-24	41	U	2+/-10	17	U	38+/-51	85	U
755648	40+/-19	39	TI	40+/-19	39	TI	-0.9+/-8.5	14.3	U	39+/-57	93	U
755647	42+/-16	32	NQ	42+/-16	32	NQ	18+/-11	17		67+/-70	113	U
755645	229+/-35	42		229+/-35	42		29+/-11	16		45+/-69	113	U
755646	21+/-15	23	U	21+/-15	23	U	1.5+/-6.4	10.7	U	25+/-47	78	U
755662	8+/-32	54	U	8+/-32	54	U	4.7+/-7.6	12.6	U	59+/-58	93	U
755590	14+/-13	25	U	14+/-13	25	U	0+/-9.6	16	U	23+/-50	84	U
755652	2+/-27	46	U	2+/-27	46	U	-1.4+/-7.7	12.9	U	7+/-60	102	U
755653	-6+/-34	58	U	-6+/-34	58	U	2.4+/-8.7	14.4	U	76+/-69	110	U
755661	26+/-30	49	U	26+/-30	49	U	11.3+/-8	12.7	U	-17+/-55	96	U
755591	15+/-16	34	U	15+/-16	34	U	-0.1+/-8.7	14.6	U	34+/-57	95	U
755666	23+/-18	36	U	23+/-18	36	U	6+/-8.7	14.3	U	1+/-62	108	U
755667	21+/-22	43	U	21+/-22	43	U	1.2+/-8.5	14.2	U	62+/-62	100	U
755667	14+/-15	29	U	14+/-15	29	U	-5+/-11	18	U	10+/-55	94	U
755592	-7+/-34	58	U	-7+/-34	58	U	4+/-6.3	10.4	U	12+/-79	135	U
755593	19+/-16	25	U	19+/-16	25	U	3+/-10	17	U	36+/-57	94	U
755658	5+/-33	57	U	5+/-33	57	U	-0.7+/-9.4	16	U	68+/-70	112	U
757036	24+/-15	22	NQ	24+/-15	22	NQ	2.2+/-9.5	15.9	U	28+/-48	80	U
757035	19+/-17	27	U	19+/-17	27	U	9.5+/-6	9.4	NQ	1+/-58	100	U
757105	16+/-16	26	U	16+/-16	26	U	-3+/-10	17	U	64+/-60	97	U
757034	25+/-16	33	U	25+/-16	33	U	0.8+/-8.1	13.7	U	58+/-71	116	U
757071	21+/-26	43	U	21+/-26	43	U	9+/-8.1	13.1	U	-27+/-81	143	U
757072	12+/-30	51	U	12+/-30	51	U	12.8+/-8.2	12.8	NQ	-33+/-79	141	U
757033	-1+/-32	55	U	-1+/-32	55	U	4+/-11	18	U	47+/-79	132	U
757038	41+/-22	56	U	41+/-22	56	U	6.5+/-8.3	13.6	U	43+/-76	127	U

Facility # COENV DB	^{228}Ra			^{228}Ac			^{212}Pb			^{212}Bi		
	pCi/l +/- TPU	MDC pC/l	Data Flags	pCi/l +/- TPU	MDC pC/l	Data Flags	pCi/l +/- TPU	MDC pC/l	Data Flags	pCi/l +/- TPU	MDC pC/l	Data Flags
757037	10+/-27	46	U	10+/-27	46	U	2+/-12	20	U	60+/-77	126	U

U flag indicates result is less than the sample specific MDC, NQ flag indicates analyst determined criteria for identification and quantification was not met and analyte is not present at any level above the sample specific MDC, SI flag indicates nuclide identification and/or quantification is tentative, TI flag indicates nuclide identification is tentative

Appendix 10. Dissolved Metals

Facility # COENV DB	Ba			Ca			Fe			K			Mg			Na			Si			Sr		
	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag
755461	0.051	0.00099	J	170	0.023		0.046	0.016	J	6.6	0.17		33	1		130	0.026		9.8	0.05		1.3	0.01	
755462	55	0.0099		150	0.23		21	0.16		93	1.7		27	10		8800	2.6		17	0.5		34	0.1	
755474	10	0.3		570	3		8	0.3		95	3		54	10		8000	30		51	0.5		71	0.1	
755475	4.5	300		170	3000		4.7	300		55	3000		20	10		4700	30		49	0.5		23	0.1	
755476	4.1	0.3		130	3		28	0.3		43	3		16	10		3900	30		46	0.5		14	0.1	
755500	9.1	0.3		140	3		17	0.3		18	3		15	10		2500	30		15	0.5		20	0.1	
755500	9.1	0.3		140	3		17	0.3		18	3		15	10		2500	30		15	0.5		20	0.1	
755501	4.1	0.3		180	3		25	0.3		78	3		25	10		5500	30		35	0.5		23	0.1	
755541	6.2	0.3		18000	300		41	0.3		1700	3		1800	10		34000	300		15	0.5		650	10	
755523	0.3	0.3	U	740	3		0.3	0.3	U	250	3		250	10		9900	30		14	0.5		21	0.1	
755523	0.3	0.3	U	740	3		0.3	0.3	U	250	3		250	10		10000	30		14	0.5		21	0.1	
149017	8.8	0.03		6	0.3		0.096	0.03	J	10	0.3		1.5	1		830	3		15	0.05		0.93	0.01	
755522	0.3	0.3	U	830	3		1	0.3		170	3		140	10		4800	30		17	0.5		24	0.1	
755550	6.2	0.3		8.4	3	J	12	0.3		100	3		10	10		4500	30		8.7	0.5		4.5	0.1	
439136	14	0.3		68	3		25	0.3		48	3		25	10		5300	30		10	0.5		9.5	0.1	
215628	0.34	0.03		3.6	0.3		2.9	0.03		2.7	0.3		0.65	1	J	240	3		8.8	0.05		0.42	0.01	
215628	0.34	0.03		3.6	0.3		2.7	0.03		2.3	0.3		0.65	1	J	240	3		8.9	0.05		0.43	0.01	
215820	1.6	0.03		6.9	0.3		0.82	0.03		4.9	0.3		1.3	1		680	3		11	0.05		1.3	0.01	
755659	0.32	0.3	J	3200	3		2.9	0.3		730	3		620	10		26000	150		14	0.5		140	5	
755658	0.03	0.03	U	0.3	0.3	U	53	0.03		0.3	0.3	U	0.3	1	U	0.3	0.3	U	0.21	0.05		0.003	0.01	U
755657	0.3	0.3	U	32	3		12	0.3		110	3		3.2	10	J	2200	30		36	0.5		3.5	0.1	
755557	0.3	0.3	U	9.6	3	J	0.3	0.3	U	17	3		3	10	U	2600	30		24	0.5		0.88	0.1	
755558	0.89	0.3	J	24	3		0.33	0.3	J	28	3		4.9	10	J	4000	30		24	0.5		2.2	0.1	
755559	0.34	0.3	J	11	3		1.3	0.3		22	3		3	10	U	3500	30		26	0.5		1.2	0.1	
755559	0.33	0.3	J	12	3		1.4	0.3		21	3		3	10	U	3500	30		26	0.5		1.2	0.1	
299153	0.62	0.03		2.7	0.3		0.37	0.03		4.9	0.3		0.83	1	J	600	3		9.4	0.05		0.75	0.01	

Facility # COENV DB	Ba			Ca			Fe			K			Mg			Na			Si			Sr		
	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag
285562	0.74	0.03		2.6	0.3		0.32	0.03		4.7	0.3		0.89	1	J	500	3		7	0.05		0.44	0.01	
755648	58	0.3		590	3		86	0.3		110	3		72	10		13000	150		35	0.5		90	0.1	
755647	58	0.3		680	3		130	0.3		110	3		83	10		12000	150		37	0.5		120	5	
755645	0.84	0.3	J	490	3		15	0.3		4700	150		820	10		74000	150		26	0.5		18	0.1	
755646	1.3	0.3		120	3		14	0.3		120	3		26	10		5300	150		41	0.5		13	0.1	
755662	0.3	0.3	U	860	3		1.5	0.3		1500	3		93	10		7300	150		24	0.5		23	0.1	
755590	0.4	0.03		2.9	0.3		0.083	0.03	J	8.5	0.3		0.51	1	J	1100	3		17	0.05		0.33	0.01	
755652	16	0.3		240	3		45	0.3		40	3		29	10		4600	150		21	0.5		39	0.1	
755653	1.2	0.3		300	3		120	0.3		84	3		37	10		6700	150		34	0.5		43	0.1	
755661	0.3	0.3	U	650	3		2.5	0.3		1500	3		77	10		7100	150		17	0.5		15	0.1	
755591	1	0.03		2.6	0.3		0.87	0.03		8	0.3		0.54	1	J	790	3		16	0.05		0.21	0.01	
755666	42	0.3		320	3		8.7	0.3		60	3		27	10		8200	15		57	0.5		74	0.1	
755667	41	0.3		150	3		96	0.3		28	3		10	10		3500	3		29	0.5		17	0.1	
755667	39	0.3		140	3		99	0.3		28	3		10	10		3400	3		28	0.5		17	0.1	
755592	0.33	0.03		5.1	0.3		0.085	0.03	J	7.3	0.3		1.2	1		950	1.5		19	0.05		0.37	0.01	
755593	0.47	0.03		1	0.3		0.31	0.03		5.4	0.3		0.32	1	J	670	1.5		22	0.05		0.14	0.01	
755658	0.008	0.0048	J	0.12	0.12	U	36	0.017		0.15	0.15	U	0.097	1	U	0.11	0.11	J	0.2	0.05		0.0026	0.01	U
757036	35	0.048		11	1.2		40	0.17		36	1.5		2.8	10	J	3200	1.1		25	0.5		4.1	0.1	
757035	26	0.0048		21	0.12		4.8	0.017		33	0.15		2.2	1		4000	1.1		29	0.05		7.7	0.01	
757105	3.9	0.0048		9.6	0.12		0.045	0.017	J	13	0.15		2.5	1		710	0.54		15	0.05		0.96	0.01	
757034	12	0.0048		31	0.12		4	0.017		13	0.15		2.2	1		1100	0.54		8.7	0.05		5.2	0.01	
757071	62	0.048		81	1.2		3.7	0.17		39	1.5		21	10		4900	1.1		37	0.5		44	0.1	
757072	17	0.0048		210	0.12		19	0.017		59	0.15		14	1		8300	5.4		78	0.5		76	0.1	
757033	55	0.048		230	1.2		24	0.17		55	1.5		13	10		4800	1.1		38	0.5		46	0.1	
757038	73	0.048		160	0.12		4.3	0.017		72	0.15		29	1		6500	5.4		16	0.05		49	0.1	
757037	0.54	0.0048		19	0.12		9.3	0.017		3.3	0.15		0.53	1	J	330	0.11		0.49	0.05		5.2	0.01	

U flag indicates analyte not detected at concentration greater the MDL (method detection limit) specified by the laboratory

J flag indicates analyte detected at concentration greater the MDL (method detection limit) but less the RL (report limit) specified by the laboratory and considered as estimated

Appendix 11. Total ICP Metals (SW6010)

	Be			B			Ca			Cr			Fe			Li		
Facility # COENV DB	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag
755461	0.00049	0.00049	U	0.24	0.007		160	0.021		0.00069	0.00069	U	0.059	0.1	J	0.03	0.0024	
755462	0.0049	0.0049	U	7.3	0.07		150	0.21		0.0069	0.0069	U	22	1		2.4	0.024	
755474	0.015	0.015	U	34	0.3		560	3		0.03	0.03	U	8.3	1		14	0.03	
755475	0.015	0.015	U	25	0.3		180	3		0.03	0.03	U	5.2	1		7.4	0.03	
755476	0.015	0.015	U	20	0.3		140	3		0.03	0.03	U	32	1		5.1	0.03	
755500	0.015	0.015	U	9.4	0.3		140	3		0.03	0.03	U	17	1		3	0.03	
755500	0.015	0.015	U	9.5	0.3		140	3		0.03	0.03	U	17	1		3	0.03	
755501	0.015	0.015	U	23	0.3		180	3		0.03	0.03	U	25	1		6.2	0.03	
755541	0.015	0.015	U	18	0.3		16000	300		0.03	0.03	U	51	1		35	0.03	
755523	0.015	0.015	U	14	0.3		740	3		0.03	0.03	U	0.3	1	U	4.7	0.03	
755523	0.015	0.015	U	14	0.3		740	3		0.03	0.03	U	0.3	1	U	4.7	0.03	
149017	0.0015	0.0015	U	2.4	0.03		7.1	0.3		0.003	0.003	U	0.096	0.1	J	0.39	0.003	
755522	0.015	0.015	U	5	0.3		850	3		0.03	0.03	U	3.1	1		11	0.03	
755550	0.015	0.015	U	13	0.3		8.7	3	J	0.03	0.03	U	13	1		0.81	0.03	
439136	0.015	0.015	U	14	0.3		120	3		0.38	0.03		79	1		1.1	0.03	
215628	0.0015	0.0015	U	0.092	0.03	J	3.6	0.3		0.0083	0.003	J	3.2	0.1		0.085	0.003	
215628	0.0015	0.0015	U	0.092	0.03	J	3.5	0.3		0.0042	0.003	J	2.8	0.1		0.082	0.003	
215820	0.0015	0.0015	U	0.62	0.03		7	0.3		0.0064	0.003	J	1.5	0.1		0.73	0.003	
755659	0.015	0.015	U	17	0.3		3100	3		0.03	0.03	U	4.6	1		3.7	0.03	
755658	0.015	0.015	U	22	0.3		21	3		0.03	0.03	U	76	1		1.3	0.03	
755657	0.015	0.015	U	7.6	0.3		30	3		0.03	0.03	U	13	1		8.8	0.03	
755557	0.015	0.015	U	30	0.3		9.3	3	J	0.03	0.03	U	0.69	1	J	0.86	0.03	
755558	0.0015	0.0015	U	29	1.5		7.8	0.3		0.003	0.003	U	0.24	0.1		0.92	0.003	
755559	0.015	0.015	U	23	0.3		11	3		0.03	0.03	U	1.4	1		1.1	0.03	
755559	0.015	0.015	U	23	0.3		11	3		0.03	0.03	U	1.7	1		1.1	0.03	

Facility # COENV DB	Be			B			Ca			Cr			Fe			Li		
	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag
299153	0.0015	0.0015	U	0.4	0.03		2.7	0.3		0.003	0.003	U	0.48	0.1		0.27	0.003	
285562	0.0015	0.0015	U	0.036	0.03	J	2.6	0.3		0.003	0.003	U	0.42	0.1		0.045	0.003	
755648	0.015	0.015	U	49	0.3		570	3		0.16	0.03		87	1		5.2	0.03	
755647	0.015	0.015	U	47	0.3		700	3		0.11	0.03		130	1		6.3	0.03	
755645	0.015	0.015	U	55	0.3		520	3		0.03	0.03	U	12	1		18	0.03	
755646	0.015	0.015	U	32	0.3		120	3		0.03	0.03	U	13	1		3.5	0.03	
755662	0.076	0.015		37	0.3		630	3		0.03	0.03	U	2.1	1		45	1.5	
755590	0.0015	0.0015	U	3	0.03		2.7	0.3		0.003	0.003	U	0.11	0.1		0.29	0.003	
755652	0.015	0.015	U	15	0.3		260	3		0.03	0.03	U	47	1		5.8	0.03	
755653	0.015	0.015	U	25	0.3		320	3		0.03	0.03	U	140	1		8.1	0.03	
755661	0.09	0.015		38	0.3		830	3		0.03	0.03	U	1.6	1		48	1.5	
755591	0.0015	0.0015	U	1.5	0.03		2.4	0.3		0.003	0.003	U	0.93	0.1		0.19	0.003	
755667	0.015	0.015	U	3.1	0.3		140	3		0.03	0.03	U	96	1		2.3	0.03	
755666	0.015	0.015	U	30	0.3		300	3		0.03	0.03	U	10	1		15	0.03	
755667	0.015	0.015	U	3	0.3		140	3		0.03	0.03	U	88	1		2.3	0.03	
755592	0.0015	0.0015	U	2.4	0.03		4.7	0.3		0.003	0.003	U	0.21	0.1		0.31	0.003	
755593	0.0015	0.0015	U	1.9	0.03		1	0.3		0.003	0.003	U	0.44	0.1		0.18	0.003	
755658	0.00056	0.00056	U	0.019	0.011	J	0.12	0.12	U	0.017	0.0019		97	0.1		0.0057	0.0057	U
757036	0.0056	0.0056	U	3.5	0.11		11	1.2		0.019	0.019	U	6.5	1		4.9	0.057	
757035	0.0056	0.0056	U	6.2	0.11		23	1.2		0.019	0.019	U	4.1	1		4.3	0.057	
757105	0.00056	0.00056	U	1.1	0.011		8.8	0.12		0.0019	0.0019	U	0.029	0.1	J	0.39	0.0057	
757034	0.0056	0.0056	U	2.5	0.11		95	1.2		0.034	0.019	J	7.2	1		4.2	0.057	
757071	0.0056	0.0056	U	7.7	0.11		74	1.2		0.019	0.019	U	3.1	1		4.2	0.057	
757072	0.0056	0.0056	U	83	0.11		220	1.2		0.019	0.019	U	25	1		28	0.057	
757033	0.0056	0.0056	U	15	0.11		200	1.2		0.019	0.019	U	21	1		7	0.057	
757038	0.0056	0.0056	U	7.3	0.11		150	1.2		0.019	0.019	U	4.2	1		4.9	0.057	
757037	0.00056	0.00056	U	17	0.11		17	0.12		0.0043	0.0019	J	7.4	0.1		1.2	0.0057	

Facility # COENV DB	Mg			Ni			K			Si			Na			V		
	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag
755461	32	1		0.0019	0.02	U	6.4	1		9.3	0.05		120	1		0.0011	0.01	U
755462	26	10		0.019	0.2	U	88	10		16	0.5		8100	500		0.011	0.1	U
755474	53	10		0.06	0.2	U	93	10		51	0.5		7800	100		0.03	0.1	U
755475	21	10		0.06	0.2	U	58	10		49	0.5		4900	100		0.03	0.1	U
755476	16	10		0.06	0.2	U	44	10		48	0.5		4100	100		0.03	0.1	U
755500	15	10		0.06	0.2	U	18	10		14	0.5		2500	100		0.03	0.1	U
755500	15	10		0.06	0.2	U	19	10		15	0.5		2600	100		0.03	0.1	U
755501	24	10		0.06	0.2	U	79	10		34	0.5		5500	100		0.03	0.1	U
755541	2300	10		0.06	0.2	U	1700	10		18	0.5		36000	1000		0.03	0.1	U
755523	250	10		0.1	0.2	J	260	10		14	0.5		10000	100		0.03	0.1	U
755523	250	10		0.06	0.2	U	250	10		14	0.5		10000	100		0.03	0.1	U
149017	1.5	1		0.006	0.02	U	10	1		14	0.05		800	10		0.003	0.01	U
755522	140	10		0.06	0.2	U	170	10		18	0.5		4900	100		0.03	0.1	U
755550	11	10		0.06	0.2	U	100	10		9.4	0.5		4300	100		0.03	0.1	U
439136	26	10		0.95	0.2		50	10		13	0.5		5200	100		0.042	0.1	J
215628	0.66	1	J	0.4	0.02		2.9	1		8.8	0.05		220	10		0.003	0.01	U
215628	0.64	1	J	0.18	0.02		2.1	1		8.6	0.05		220	10		0.003	0.01	U
215820	1.3	1		0.049	0.02		4.9	1		11	0.05		680	10		0.003	0.01	U
755659	610	10		0.06	0.2	U	720	10		14	0.5		24000	500		0.03	0.1	U
755658	4.6	10	J	0.06	0.2	U	25	10		22	0.5		3500	100		0.03	0.1	U
755657	3.1	10	J	0.06	0.2	U	100	10		36	0.5		2100	100		0.03	0.1	U
755557	3	10	U	0.06	0.2	U	18	10		25	0.5		2600	100		0.03	0.1	U
755558	1.7	1		0.006	0.02	U	25	1		22	0.05		2600	50		0.003	0.01	U
755559	3	10	U	0.06	0.2	U	22	10		26	0.5		3100	100		0.03	0.1	U
755559	3	10	U	0.06	0.2	U	21	10		26	0.5		3200	100		0.03	0.1	U
299153	0.79	1	J	0.006	0.02	U	4.9	1		9	0.05		600	10		0.003	0.01	U
285562	0.88	1	J	0.006	0.02	U	4.7	1		6.6	0.05		490	10		0.003	0.01	U
755648	69	10		0.06	0.2	U	100	10		35	0.5		12000	500		0.03	0.1	U

Facility # COENV DB	Mg			Ni			K			Si			Na			V		
	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag	result mg/l	MDL mg/l	flag
755647	82	10		0.06	0.2	U	120	10		38	0.5		12000	500		0.03	0.1	U
755645	870	10		0.22	0.2		4800	500		26	0.5		72000	500		0.03	0.1	U
755646	21	10		0.06	0.2	U	89	10		40	0.5		5000	500		0.03	0.1	U
755662	75	10		0.06	0.2	U	1500	10		17	0.5		6900	500		0.03	0.1	U
755590	0.48	1	J	0.006	0.02	U	8.2	1		17	0.05		1000	10		0.003	0.01	U
755652	30	10		0.06	0.2	U	43	10		23	0.5		4700	500		0.03	0.1	U
755653	39	10		0.22	0.2		91	10		37	0.5		7100	500		0.03	0.1	U
755661	90	10		0.06	0.2	U	1500	10		24	0.5		7300	500		0.03	0.1	U
755591	0.52	1	J	0.006	0.02	U	7.8	1		16	0.05		740	10		0.003	0.01	U
755667	10	10		0.06	0.2	U	39	10		26	0.5		3500	500		0.03	0.1	U
755666	27	10		0.06	0.2	U	98	10		51	0.5		7900	500		0.03	0.1	U
755667	10	10		0.06	0.2	U	39	10		27	0.5		3600	500		0.03	0.1	U
755592	0.92	1	J	0.006	0.02	U	12	1		17	0.05		970	50		0.003	0.01	U
755593	0.35	1	J	0.006	0.02	U	8.6	1		19	0.05		670	50		0.003	0.01	U
755658	0.079	1	U	0.027	0.02		0.2	1	U	0.26	0.05		0.32	1	J	0.0018	0.01	U
757036	1.6	10	J	0.027	0.2	U	51	10		24	0.5		3000	100		0.018	0.1	U
757035	2.4	10	J	0.027	0.2	U	50	10		28	0.5		3700	100		0.018	0.1	U
757105	2.4	1		0.0027	0.02	U	22	1		14	0.05		660	10		0.0018	0.01	U
757034	6.9	10	J	0.029	0.2	J	58	10		27	0.5		3500	100		0.018	0.1	U
757071	18	10		0.027	0.2	U	65	10		34	0.5		4800	100		0.018	0.1	U
757072	15	10		0.027	0.2	U	110	10		75	0.5		7100	100		0.018	0.1	U
757033	12	10		0.027	0.2	U	85	10		35	0.5		4600	100		0.018	0.1	U
757038	31	10		0.027	0.2	U	120	10		14	0.5		5900	100		0.018	0.1	U
757037	0.56	1	J	0.0031	0.02	J	4	1		0.46	0.05		360	10		0.0018	0.01	U

U flag indicates analyte not detected at concentration greater the MDL (method detection limit) specified by the laboratory

J flag indicates analyte detected at concentration greater the MDL (method detection limit) but less the RL (report limit) specified by the laboratory and considered as estimated

Appendix 12. Total ICP/MS Metals (SW6020)

Facility # COENV DB	Al			As			Ba			Cd			Co			Cu		
	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag
755461	0.052	0.011	J	0.00041	0.00016	J	0.051	0.00024		7.90E-05	7.90E-05	U	0.00022	7.90E-05	J	0.0061	0.0009	J
755462	0.23	0.011		0.00094	0.00016	J	57	0.024		0.00024	7.90E-05	J	0.00055	7.90E-05	J	0.0055	0.0009	J
755474	0.5	0.5	U	0.0091	0.0091	U	11	0.036		0.0095	0.0095	U	0.022	0.022	U	0.12	0.12	U
755475	0.052	0.011	J	0.001	0.00016	J	4.5	0.00024		7.90E-05	7.90E-05	U	8.00E-05	7.90E-05	J	0.0009	0.0009	U
755476	0.5	0.5	U	0.0091	0.0091	U	1.5	0.036		0.0095	0.0095	U	0.022	0.022	U	0.12	0.12	U
755500	0.21	0.05		0.00091	0.00091	U	9.5	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
755500	0.15	0.05		0.00091	0.00091	U	9.6	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
755501	0.14	0.05		0.0016	0.00091	J	4.7	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
755541	0.37	0.05		0.014	0.00091		8.9	0.0036		0.0042	0.00095		0.0022	0.0022	U	0.057	0.012	
755523	0.14	0.05		0.001	0.00091	J	0.016	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	1.6	0.012	
755523	0.055	0.05	J	0.00091	0.00091	U	0.015	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.35	0.012	
149017	0.067	0.05	J	0.00091	0.00091	U	9.4	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
755522	0.05	0.05	U	0.00091	0.00091	U	0.11	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
755550	0.05	0.05	U	0.00091	0.00091	U	6.5	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
439136	0.65	0.05		0.018	0.00091		14	0.036		0.0014	0.00095	J	0.016	0.0022		0.52	0.012	
215628	0.069	0.05	J	0.00091	0.00091	U	0.33	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.015	0.012	J
215628	0.05	0.05	U	0.00091	0.00091	U	0.31	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
215820	0.05	0.05	U	0.00091	0.00091	U	1.6	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.038	0.012	
755659	0.054	0.05	J	0.00091	0.00091	U	0.39	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
755658	0.05	0.05	U	0.00091	0.00091	U	0.0085	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
755657	0.05	0.05	U	0.00091	0.00091	U	0.045	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
755557	0.05	0.05	U	0.00091	0.00091	U	0.092	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
755558	0.05	0.05	U	0.00091	0.00091	U	0.89	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
755559	0.067	0.05	J	0.00091	0.00091	U	0.34	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U

Facility # COENV DB	Al			As			Ba			Cd			Co			Cu		
	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag
755559	0.05	0.05	U	0.00091	0.00091	U	0.32	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
299153	0.05	0.05	U	0.00091	0.00091	U	0.65	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
285562	0.05	0.05	U	0.00091	0.00091	U	0.74	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
755648	0.076	0.05	J	0.0011	0.00091	J	63	0.036		0.00095	0.00095	U	0.0022	0.0022	U	0.017	0.012	J
755647	0.05	0.05	U	0.00091	0.00091	U	59	0.036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
755645	0.5	0.5	U	0.34	0.0091		1.3	0.036		0.0095	0.0095	U	0.022	0.022	U	0.83	0.12	
755646	0.059	0.05	J	0.00091	0.00091	J	1.4	0.036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
755662	0.22	0.05		8.4	0.00091		0.096	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
755590	0.05	0.05	U	0.00091	0.00091	U	0.42	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
755652	0.05	0.05	U	0.0015	0.00091	J	18	0.036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
755653	0.07	0.05	J	0.11	0.00091		4.5	0.036		0.00095	0.00095	U	0.025	0.0022		2.2	0.012	
755661	0.19	0.05		7.7	0.00091		0.15	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
755591	0.05	0.05	U	0.00091	0.00091	U	1.1	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
755666	0.05	0.05	U	0.0099	0.00091		42	0.036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
755667	0.16	0.05		0.0029	0.00091		38	0.036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
755667	0.05	0.05	U	0.0018	0.00091	J	37	0.036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
755592	0.05	0.05	U	0.0011	0.00091	J	0.32	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
755593	0.05	0.05	U	0.0012	0.00091	J	0.44	0.0036		0.00095	0.00095	U	0.0022	0.0022	U	0.012	0.012	U
755658	0.23	0.0075		0.00059	0.00017	J	0.0094	0.00012		0.0001	5.10E-05	J	0.0013	0.00015	J	0.014	0.0016	J
757036	0.3	0.075	J	0.0017	0.0017	U	30	0.0012		0.00051	0.00051	U	0.0015	0.0015	U	0.016	0.016	U
757035	0.63	0.075	J	0.0017	0.0017	U	28	0.0012		0.00051	0.00051	U	0.0015	0.0015	U	0.016	0.016	U
757105	0.023	0.0075	J	0.00017	0.00017	J	3.9	0.00012		5.10E-05	5.10E-05	U	0.00015	0.00015	U	0.0016	0.0016	U
757034	0.094	0.075	J	0.0018	0.0017	J	37	0.0012		0.00051	0.00051	U	0.0015	0.0015	U	0.016	0.016	U
757071	0.09	0.075	J	0.0017	0.0017	U	60	0.0012		0.00051	0.00051	U	0.0015	0.0015	U	0.016	0.016	U
757072	1.9	0.075		0.0017	0.0017	U	19	0.0012		0.00051	0.00051	U	0.0015	0.0015	U	0.016	0.016	U
757033	120	0.075		0.0022	0.0017	J	49	0.0012		0.00051	0.00051	U	0.0015	0.0015	U	0.016	0.016	U

Facility # COENV DB	Al			As			Ba			Cd			Co			Cu		
	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag
757038	0.36	0.075	J	0.0026	0.0017	J	73	0.0012		0.00051	0.00051	U	0.0019	0.0015	J	0.016	0.016	U
757037	0.036	0.0075	J	0.00042	0.00017	J	0.51	0.00012		5.10E-05	5.10E-05	U	0.00024	0.00015	J	0.0047	0.0016	J

U flag indicates analyte not detected at concentration greater the MDL (method detection limit) specified by the laboratory

J flag indicates analyte detected at concentration greater the MDL (method detection limit) but less the RL (report limit) specified by the laboratory and considered as estimated

Facility # COENV DB	Pb			Mn			Mo			Se			Ag			Na		
	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag
755461	0.00074	0.00017	J	0.023	0.0003		0.0023	0.00038		0.0054	0.00066	J	3.30E-05	3.30E-05	U	130	0.16	
755462	0.00069	0.00017	J	0.34	0.0003		0.0046	0.00038		0.00078	0.00066	J	3.30E-05	3.30E-05	U	9500	0.16	
755474	0.014	0.014	U	0.33	0.023		0.0098	0.0098	U	0.049	0.049	U	0.0022	0.0022	U	9200	4.6	
755475	0.00017	0.00017	U	0.12	0.0003		0.0029	0.00038		0.00082	0.00066	J	3.30E-05	3.30E-05	U	5200	0.16	
755476	0.014	0.014	U	0.54	0.023		0.022	0.0098		0.049	0.049	U	0.0022	0.0022	U	4600	4.6	
755500	0.0014	0.0014	U	0.29	0.0023		0.00098	0.00098	U	0.0049	0.0049	U	0.00022	0.00022	U	2700	0.46	
755500	0.0014	0.0014	U	0.29	0.0023		0.00098	0.00098	U	0.0049	0.0049	U	0.00022	0.00022	U	2600	0.46	
755501	0.0078	0.0014		0.47	0.0023		0.02	0.00098		0.0049	0.0049	U	0.00022	0.00022	U	6300	0.46	
755541	0.092	0.0014		2.9	0.0023		0.00098	0.00098	U	0.0049	0.0049	U	0.00022	0.00022	U	40000	46	
755523	0.062	0.0014		0.017	0.0023		0.00098	0.00098	U	0.0049	0.0049	U	0.00039	0.00022	J	13000	46	
755523	0.016	0.0014		0.012	0.0023		0.00098	0.00098	U	0.0049	0.0049	U	0.00022	0.00022	U	17000	46	
149017	0.0014	0.0014	U	0.032	0.0023		0.00098	0.00098	U	0.0049	0.0049	U	0.00022	0.00022	U	910	0.46	
755522	0.0014	0.0014	J	0.1	0.0023		0.00098	0.00098	U	0.0049	0.0049	U	0.00022	0.00022	U	9000	46	
755550	0.0014	0.0014	U	0.33	0.0023		0.00098	0.00098	U	0.0049	0.0049	U	0.00022	0.00022	U	4900	0.46	
439136	0.018	0.0014		1.1	0.0023		0.072	0.00098		0.0049	0.0049	U	0.00022	0.00022	U	5100	4.6	
215628	0.0014	0.0014	U	0.063	0.0023		0.002	0.00098	J	0.0049	0.0049	U	0.00022	0.00022	U	250	0.46	
215628	0.0014	0.0014	U	0.043	0.0023		0.0014	0.00098	J	0.0049	0.0049	U	0.00022	0.00022	U	230	0.46	
215820	0.0014	0.0014	U	0.026	0.0023		0.0012	0.00098	J	0.0049	0.0049	U	0.00022	0.00022	U	760	0.46	
755659	0.0014	0.0014	U	0.11	0.0023		0.00098	0.00098	U	0.0049	0.0049	U	0.00022	0.00022	U	31000	46	
755658	0.0014	0.0014	U	0.9	0.0023		0.00098	0.00098	U	0.0049	0.0049	U	0.00022	0.00022	U	1.3	0.46	
755657	0.0014	0.0014	U	0.17	0.0023		0.003	0.00098		0.0049	0.0049	U	0.00022	0.00022	U	2300	0.46	
755557	0.0014	0.0014	U	0.016	0.0023		0.00098	0.00098	U	0.0049	0.0049	U	0.00022	0.00022	U	3000	0.46	
755558	0.0014	0.0014	U	0.034	0.0023		0.00098	0.00098	U	0.0049	0.0049	U	0.00022	0.00022	U	4400	0.46	
755559	0.0014	0.0014	U	0.056	0.0023		0.00098	0.00098	U	0.0049	0.0049	U	0.00022	0.00022	U	3700	0.46	
755559	0.0014	0.0014	U	0.061	0.0023		0.00098	0.00098	U	0.0049	0.0049	U	0.00022	0.00022	U	3900	0.46	
299153	0.0014	0.0014	U	0.0072	0.0023		0.00098	0.00098	U	0.0049	0.0049	U	0.00022	0.00022	U	670	0.46	

Facility # COENV DB	Pb			Mn			Mo			Se			Ag			Na		
	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag
285562	0.0014	0.0014	U	0.0081	0.0023		0.0011	0.00098	J	0.0049	0.0049	U	0.00022	0.00022	U	560	0.46	
755648	0.0031	0.0014		1.2	0.023		0.013	0.00098		0.0049	0.0049	U	0.00022	0.00022	U	13000	4.6	
755647	0.0014	0.0014	U	1.6	0.023		0.0062	0.00098		0.0049	0.0049	U	0.00022	0.00022	U	12000	4.6	
755645	0.33	0.014		3.3	0.023		0.0098	0.0098	U	0.049	0.049	U	0.012	0.0022		86000	4.6	
755646	0.0032	0.0014		0.25	0.023		0.00098	0.00098	U	0.0049	0.0049	U	0.00022	0.00022	U	5000	4.6	
755662	0.0054	0.0014		0.06	0.0023		0.0048	0.00098		0.0049	0.0049	U	0.00022	0.00022	U	7900	4.6	
755590	0.0014	0.0014	U	0.021	0.0023		0.00098	0.00098	U	0.0049	0.0049	U	0.00022	0.00022	U	1200	0.46	
755652	0.0014	0.0014	U	0.64	0.023		0.0024	0.00098		0.0049	0.0049	U	0.00022	0.00022	U	5100	4.6	
755653	0.0014	0.0014	U	2.6	0.023		0.012	0.00098		0.0049	0.0049	U	0.00022	0.00022	U	7500	4.6	
755661	0.0097	0.0014		0.027	0.0023		0.0042	0.00098		0.0049	0.0049	U	0.00022	0.00022	U	7800	4.6	
755591	0.0014	0.0014	U	0.046	0.0023		0.00098	0.00098	U	0.0049	0.0049	U	0.00022	0.00022	U	860	0.46	
755666	0.0014	0.0014	U	0.2	0.0023		0.0013	0.00098	J	0.0049	0.0049	U	0.00022	0.00022	U	8700	4.6	
755667	0.003	0.0014		1.3	0.0023		0.0011	0.00098	J	0.0049	0.0049	U	0.00022	0.00022	U	3700	4.6	
755667	0.0014	0.0014	U	1.2	0.0023		0.00098	0.00098	U	0.0049	0.0049	U	0.00022	0.00022	U	3700	4.6	
755592	0.0014	0.0014	U	0.03	0.0023		0.00098	0.00098	U	0.0049	0.0049	U	0.00022	0.00022	U	1000	0.46	
755593	0.0014	0.0014	U	0.0069	0.0023		0.00098	0.00098	U	0.0049	0.0049	U	0.00022	0.00022	U	730	0.46	
755658	0.0015	0.00018	J	0.97	0.00042		0.0022	0.00016		0.00017	0.00017	U	8.10E-05	8.10E-05	U	0.34	0.17	J
757036	0.0018	0.0018	U	0.069	0.0042		0.0016	0.0016	U	0.0017	0.0017	U	0.00081	0.00081	U	2900	1.7	
757035	0.0018	0.0018	U	0.088	0.0042		0.0017	0.0016	J	0.0017	0.0017	U	0.00081	0.00081	U	3600	1.7	
757105	0.00018	0.00018	U	0.025	0.00042		0.00016	0.00016	U	0.00017	0.00017	U	8.10E-05	8.10E-05	U	660	0.17	
757034	0.0018	0.0018	U	0.23	0.0042		0.0016	0.0016	U	0.0017	0.0017	U	0.00081	0.00081	U	3300	1.7	
757071	0.0018	0.0018	U	0.075	0.0042		0.0016	0.0016	U	0.0017	0.0017	U	0.00081	0.00081	U	4900	1.7	
757072	0.0018	0.0018	U	0.35	0.0042		0.0016	0.0016	U	0.0017	0.0017	U	0.00081	0.00081	U	7300	1.7	
757033	0.0018	0.0018	U	0.49	0.0042		0.0054	0.0016	J	0.0017	0.0017	U	0.00081	0.00081	U	4400	1.7	
757038	0.0018	0.0018	U	0.21	0.0042		0.0087	0.0016	J	0.0017	0.0017	J	0.00081	0.00081	U	6000	1.7	
757037	0.00036	0.00018	J	1.2	0.00042		0.0055	0.00016		0.00017	0.00017	U	8.10E-05	8.10E-05	U	290	0.17	

Facility # COENV DB	Sr			Tl			Th			U			Zn		
	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag
755461	1.4	0.0003		1.40E-05	1.40E-05	U	4.00E-05	2.50E-05	J	0.023	2.50E-05		0.012	0.0081	J
755462	41	0.03		2.00E-05	1.40E-05	J	4.00E-05	2.50E-05	J	3.00E-05	2.50E-05	J	0.033	0.0081	J
755474	81	0.03		0.0007	0.00062	J	0.00091	0.00091	U	0.00075	0.00075	U	2.4	0.48	
755475	23	0.003		0.00022	1.40E-05		2.50E-05	2.50E-05	U	2.50E-05	2.50E-05	U	0.0081	0.0081	U
755476	15	0.03		0.00062	0.00062	U	0.00091	0.00091	U	0.00075	0.00075	U	0.48	0.48	U
755500	21	0.03		0.00022	6.20E-05		9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.048	0.048	U
755500	20	0.03		0.00021	6.20E-05		9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.048	0.048	U
755501	24	0.03		6.20E-05	6.20E-05	U	9.10E-05	9.10E-05	U	0.00012	7.50E-05		0.048	0.048	U
755541	690	0.3		0.11	6.20E-05		9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	1.6	0.048	
755523	25	0.3		6.20E-05	6.20E-05	U	9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	2.9	0.048	
755523	33	0.3		6.20E-05	6.20E-05	U	9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.89	0.048	
149017	0.96	0.003		0.00019	6.20E-05		9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.048	0.048	U
755522	41	0.3		0.00011	6.20E-05		9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.31	0.048	
755550	4.7	0.003		6.20E-05	6.20E-05	U	9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.048	0.048	U
439136	9.8	0.003		0.00034	6.20E-05		0.00031	9.10E-05		0.0031	7.50E-05		0.29	0.048	
215628	0.4	0.003		6.20E-05	6.20E-05	U	9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.054	0.048	J
215628	0.37	0.003		6.20E-05	6.20E-05	U	9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.048	0.048	U
215820	1.3	0.003		6.20E-05	6.20E-05	U	9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.05	0.048	J
755659	150	0.3		7.00E-05	6.20E-05	J	9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.048	0.048	U
755658	0.003	0.003	U	6.20E-05	6.20E-05	U	9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.048	0.048	U
755657	3.4	0.003		0.00014	6.20E-05		9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.048	0.048	U
755557	0.88	0.003		6.20E-05	6.20E-05	U	9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.048	0.048	U
755558	2.2	0.003		6.20E-05	6.20E-05	U	9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.048	0.048	U
755559	1.2	0.003		6.20E-05	6.20E-05	U	9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.048	0.048	U

Facility # COENV DB	Sr			Tl			Th			U			Zn		
	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag
755559	1.2	0.003		6.20E-05	6.20E-05	U	9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.048	0.048	U
299153	0.76	0.003		6.20E-05	6.20E-05	U	9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.048	0.048	U
285562	0.43	0.003		6.20E-05	6.20E-05	U	9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.048	0.048	U
755648	95	0.03		0.00062	0.00062	U	9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.059	0.048	J
755647	110	0.3		0.00062	0.00062	U	9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.41	0.048	
755645	26	0.03		0.069	0.00062		0.00091	0.00091	U	0.0009	0.00075	J	3.5	0.48	
755646	13	0.03		0.00062	0.00062	U	9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.048	0.048	U
755662	17	0.03		0.049	6.20E-05		9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.086	0.048	J
755590	0.36	0.003		6.20E-05	6.20E-05	U	9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.048	0.048	U
755652	43	0.03		0.00062	0.00062	U	9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.048	0.048	U
755653	49	0.03		0.00062	0.00062	U	9.10E-05	9.10E-05	U	0.0031	7.50E-05		0.58	0.048	
755661	26	0.03		0.067	6.20E-05		9.10E-05	9.10E-05	U	0.00022	7.50E-05		0.17	0.048	
755591	0.22	0.003		6.20E-05	6.20E-05	U	9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.048	0.048	U
755666	73	0.03		0.0009	6.20E-05		9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.12	0.048	
755667	16	0.03		0.00017	6.20E-05		9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.1	0.048	J
755667	16	0.03		0.00011	6.20E-05		9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.048	0.048	U
755592	0.34	0.003		6.20E-05	6.20E-05	U	9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.048	0.048	U
755593	0.12	0.003		6.20E-05	6.20E-05	U	9.10E-05	9.10E-05	U	7.50E-05	7.50E-05	U	0.048	0.048	U
755658	0.002	0.00019	J	1.50E-05	1.50E-05	U	9.60E-05	9.60E-05	U	2.30E-05	2.30E-05	U	0.17	0.0038	
757036	3.7	0.0019		0.00015	0.00015	U	0.00096	0.00096	U	0.00023	0.00023	U	0.76	0.038	J
757035	7.6	0.0019		0.00015	0.00015	U	0.00096	0.00096	U	0.00023	0.00023	U	0.061	0.038	J
757105	0.89	0.00019		1.50E-05	1.50E-05	U	9.60E-05	9.60E-05	U	2.30E-05	2.30E-05	U	0.079	0.0038	J
757034	16	0.0019		0.00015	0.00015	U	0.00096	0.00096	U	0.00023	0.00023	U	0.038	0.038	U
757071	42	0.0019		0.00015	0.00015	U	0.00096	0.00096	U	0.00023	0.00023	U	0.038	0.038	U
757072	71	0.0019		0.0016	0.00015		0.00096	0.00096	U	0.00023	0.00023	U	0.038	0.038	U
757033	40	0.0019		0.00015	0.00015	U	0.00096	0.00096	U	0.00023	0.00023	U	0.11	0.038	J

Facility # COENV DB	Sr			Tl			Th			U			Zn		
	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag	mg/l	MDL mg/l	data flag
757038	48	0.0019		0.00015	0.00015	U	0.00096	0.00096	U	0.00023	0.00023	U	0.038	0.038	U
757037	4.9	0.00019		0.0046	1.50E-05		9.60E-05	9.60E-05	U	2.30E-05	2.30E-05	U	0.036	0.0038	J

U flag indicates analyte not detected at concentration greater the MDL (method detection limit) specified by the laboratory

J flag indicates analyte detected at concentration greater the MDL (method detection limit) but less the RL (report limit) specified by the laboratory and considered as estimated

Appendix 13. Anions

	bromide			chloride			fluoride			sulfate			bicarbonate alkalinity			carbonate alk.			total alkalinity		
Facility COENV DB	**result mg/l**	**MDL mg/l**	**flag**	**result mg/l**	**MDL mg/l**	**flag**	**result mg/l**	**MDL mg/l**	**flag**	**result mg/l**	**MDL mg/l**	**flag**	**result mg/l (as $CaCO_3$)**	**RL mg/l**	**flag**	**result mg/l (as $CaCO_3$)**	**RL mg/l**	**flag**	**result mg/l (as $CaCO_3$)**	**RL mg/l**	**flag**
755461	0.34	0.06		130	0.6		0.85	0.03		360	1.5		230	20		20	20	U	230	20	
755462	110	2.4		16000	60		1.2	1.2	U	6	6	U	420	20		20	20	U	420	20	
755474	200	2.4		16000	60		1.2	1.2	U	45	6		340	20		20	20	U	340	20	
755475	110	1.5		8600	30		1.3	0.75	J	64	3.8		520	20		20	20	U	520	20	
755476	97	1.2		6500	30		1.8	0.6	J	130	3		840	20		20	20	U	840	20	
755500	43	12		4400	30		6	6	U	30	30	U	180	20		20	20	U	180	20	
755500	42	12		4400	30		6	6	U	98	30	J	180	20		20	20	U	180	20	
755501	71	15		9300	30		7.5	7.5	U	120	38	J	620	20		20	20	U	620	20	
755541	230	12		100000	600		6	6	U	400	30		150	20		20	20	U	150	20	
755523	23	3		17000	60		3.3	1.5	J	3800	7.5		550	100		100	100	U	550	100	
755523	23	3		18000	60		2.3	1.5	J	3800	7.5		540	100		100	100	U	540	100	
149017	3	0.3		360	1.5		3.8	0.15		13	0.75		1300	100		100	100	U	1300	100	
755522	16	1.5		9400	60		2.5	0.75		1700	3.8		180	50		50	50	U	180	50	
755550	59	1.5		8200	30		1.8	0.75	J	3.8	3.8	U	1100	100		100	100	U	1100	100	
439136	60	1.5		9700	60		1.7	0.75	J	7.1	3.8	J	920	100		100	100	U	920	100	
215628	0.06	0.06	U	7.5	0.06		1.3	0.03		0.15	0.15	U	530	20		20	20	U	530	20	
215628	0.06	0.06	U	6.9	0.06		1.3	0.03		0.29	0.15	J	540	50		50	50	U	540	50	
215820	0.12	0.12	U	55	1.2		2.3	0.06		0.6	0.3	J	300	20		20	20	U	300	20	
755659	74	7.5		56000	300		3.8	3.8	U	1100	19		570	100		100	100	U	570	100	
755658	0.06	0.06	U	0.33	0.06		0.03	0.03	U	1	0.15		81	20		20	20	U	81	20	
755657	11	0.6		1500	6		2.6	0.3		2300	15		680	50		50	50	U	680	50	
755557	12	0.6		2900	30		0.86	0.3	J	420	1.5		1900	100		100	100	U	1900	100	
755558	45	1.2		5800	30		0.3	0.3	U	16	3	J	1400	100		100	100	U	1400	100	
755559	39	1.2		5200	30		0.99	0.6	J	23	3		1100	100		100	100	U	1100	100	

	bromide			chloride			fluoride			sulfate			bicarbonate alkalinity			carbonate alk.			total alkalinity		
Facility COENV DB	**result mg/l**	**MDL mg/l**	**flag**	**result mg/l**	**MDL mg/l**	**flag**	**result mg/l**	**MDL mg/l**	**flag**	**result mg/l**	**MDL mg/l**	**flag**	**result mg/l (as $CaCO_3$)**	**RL mg/l**	**flag**	**result mg/l (as $CaCO_3$)**	**RL mg/l**	**flag**	**result mg/l (as $CaCO_3$)**	**RL mg/l**	**flag**
755461	0.34	0.06		130	0.6		0.85	0.03		360	1.5		230	20		20	20	U	230	20	
755559	39	1.2		5200	30		1	0.6	J	25	3		1200	100		100	100	U	1200	100	
299153	1.4	0.12		200	1.5		3.4	0.06		0.74	0.3	J	1100	100		100	100	U	1100	100	
285562	1	0.12		170	1.2		3.3	0.06		0.63	0.3	J	910	20		20	20	U	930	20	
755648	260	3		27000	150		1.5	1.5	U	7.5	7.5	U	390	20		20	20	U	390	20	
755647	300	3		24000	120		1.5	1.5	U	7.5	7.5	U	380	20		20	20	U	380	20	
755645	15	15	U	170000	600		7.5	7.5	U	3000	38		140	20		20	20	U	140	20	
755646	50	1.5		7900	120		0.75	0.75	U	110	3.8		770	20		20	20	U	770	20	
755662	16	3		13000	150		1.5	1.5	U	2100	7.5		3500	100		100	100	U	3500	100	
755590	6	0.3		760	3		3.1	0.15		32	0.75		1500	100		100	100	U	1500	100	
755652	78	1.5		9600	30		0.75	0.75	U	9.5	3.8	J	250	20		20	20	U	250	20	
755653	110	2.4		13000	60		1.2	1.2	U	230	6		150	20		20	20	U	150	20	
755661	18	3		15000	150		1.5	1.5	U	1400	7.5		2700	100		100	100	U	2700	100	
755591	5.9	0.3		750	3		3.6	0.15		2.8	0.75	J	810	100		100	100	U	810	100	
755667	44	3		7400	30		1.5	1.5	U	19	7.5	J	430	50		50	50	U	430	50	
755666	120	3		16000	150		1.5	1.5	U	23	7.5	J	600	100		100	100	U	600	100	
755667	48	3		7600	30		1.5	1.5	U	18	7.5	J	430	50		50	50	U	430	50	
755592	2	0.06		330	3		3.9	0.03		8.3	0.15		1700	500		500	500	U	1700	500	
755593	2.3	0.06		350	3		6	0.03		1.5	0.15		1200	500		500	500	U	1200	500	
755658	0.06	0.06	U	0.064	0.06	J	0.03	0.03	U	0.17	0.15	J	30	20		20	20	U	30	20	
757036	16	6	J	720	6		3	3	U	15	15	U	5400	100		100	100	U	5400	100	
757035	12	12	U	2600	12		6	6	U	30	30	U	4300	50		50	50	U	4300	50	
757105	3.5	0.6		130	0.6		1.4	0.03		8.1	0.15		1300	20		20	20	U	1300		
757034	12	12	U	2800	12		6	6	U	30	30	U	3400	100		100	100	U	3400	100	
757071	30	30	U	7400	30		15	15	U	75	75	U	1600	100		100	100	U	1600	100	
757072	110	30		13000	60		30	30	U	150	150	U	400	100		100	100	U	400	100	

	bromide			chloride			fluoride			sulfate			bicarbonate alkalinity			carbonate alk.			total alkalinity		
Facility COENV DB	**result mg/l**	**MDL mg/l**	**flag**	**result mg/l**	**MDL mg/l**	**flag**	**result mg/l**	**MDL mg/l**	**flag**	**result mg/l**	**MDL mg/l**	**flag**	**result mg/l (as $CaCO_3$)**	**RL mg/l**	**flag**	**result mg/l (as $CaCO_3$)**	**RL mg/l**	**flag**	**result mg/l (as $CaCO_3$)**	**RL mg/l**	**flag**
755461	0.34	0.06		130	0.6		0.85	0.03		360	1.5		230	20		20	20	U	230	20	
757033	39	30	J	6900	30		15	15	U	75	75	U	1500	100		100	100	U	1500	100	
757038	100	30		9900	30		15	15	U	75	75	U	500	100		100	100	U	500	100	
757037	3.1	3	J	510	3		1.5	1.5	U	11	7.5	J	120	20		20	20	U	120	20	

U flag indicates analyte not detected at concentration greater the MDL (method detection limit) specified by the laboratory

J flag indicates analyte detected at concentration greater the MDL (method detection limit) but less the RL (report limit) specified by the laboratory and considered as estimated

Appendix 14. pH, Specific Conductance, TDS and TSS

Facility COENV DB	pH Result SU	qualifier	specific conductivity result µmhos/cm	qualifier	total dissolved solids result mg/l	qualifier	total suspended solids result mg/l	RL mg/l	qualifier
755461	7.44		1458		1000		20	20	U
755462	7.09		38700		23000		33	4	
755474	6.67		39800		25000		43	20	
755475	7.21		24300		15000		27	20	
755476	7.10		19720		12000		95	20	
755500	6.96		13270		7600		24	20	
755500	7.09		13330		7500		130	20	
755501	7.23		26100		16000		78	20	
755541	5.92		178000		170000		75	20	
755523	7.55		50200		35000		100	20	
755523	7.58		50300		35000		180	20	
149017	8.45		3410		2200		20	20	U
755522	7.10		27300		18000		20	20	U
755550	7.75		20790		13000		32	20	
439136	7.75		25100		16000		620	20	
215628	7.84		1026		660		20	20	U
215628	7.83		997		640		20	20	U
215820	8.36		2910		1800		20	20	U
755659	7.39		127100		91000		55	20	
755658	6.24		105		160		54	20	
755657	8.01		9960		6800		20	20	U
755557	7.95		11880		7800		20	20	U
755558	8.19		18440		11000		20	20	U
755559	8.21		16560		9700		20	20	U
755559	7.83		16340		10000		20	20	U
299153	8.53		2880		1900		20	20	U
285562	8.63		2440		1400		20	20	U

Facility COENV DB	pH Result SU	qualifier	specific conductivity result µmhos/cm	qualifier	total dissolved solids result mg/l	qualifier	total suspended solids result mg/l	RL mg/l	qualifier
755648	5.70		55500		35000		250	20	
755647	6.00		57600		37000		720	80	
755645	6.12		237000		240000		70	20	
755646	6.82		22500		14000		180	20	
755662	7.02		36100		27000		20	20	U
755590	7.97		4770		2900		20	20	U
755652	6.54		24200		15000		160	20	
755653	6.22		34200		23000		110	20	
755661	6.65		38300		27000		20	20	U
755591	7.99		3700		2100		20	20	U
755667	6.10		16930		11000		61	20	
755666	6.37		36000		25000		22	20	
755667	7.42		17260		11000		58	20	
755592	8.10		3990		2300		20	20	U
755593	7.73		2920		1700		20	20	U
755658	5.76		188.6		92		76	20	
757036	8.29		11520		8900		230	40	
757035	7.95		15490		11000		350	49	
757105	8.34		2680		1700		20	20	U
757034	8.56		14090		10000		410	40	
757071	7.98		22100		15000		29	20	
757072	7.05		33700		21000		26	20	
757033	7.78		21260		14000		440	71	
757038	8.43		27900		17000		47	20	
757037	6.67		2105		960		31	20	

U flag indicates analyte not detected at concentration greater the RL (report limit) specified by the laboratory

Appendix 15. Stable Isotopes of H_2O and Carbon Isotopes of Dissolved Inorganic Carbon

Facility # COENV DB	$\delta^{18}O$ H_2O per mil VSMOW	δD H_2O per mil VSMOW	$\delta^{13}C$ DIC per mil VPDB
755461	-12.3	-99.2	-8
755462	-3.3	-40	4.9
755474	-3	-52.2	*11.1*
755475	-5.4	-59.8	10.5
755476	-6.2	-69.4	7.7
755500	-7.7	-63	8.4
755501	-5.3	-61.1	8.1
755541	*-1*	*-20.7*	*0.4*
755523	-7.7	-74.5	-15
755523	-7.1	-72.8	-15
149017	-12.7	-93.8	6.4
755522	-11.5	-89	-4
755550	-10.5	-61.5	6.1
439136	-8.1	-52.4	4.3
215628	-14.3	-105	22.6
215628	-14.2	-104.2	22.9
215820	-14.4	-105.6	24.6
755659	1.4	-33.8	2.1
755658	-5	-67.7	-0.6
755657	-5.2	-75.9	0
755557	-4.5	-52.9	-7.1
755558	-3.1	-45.1	-6.7
755559	-2.5	-43.1	-2.8
755559	-2.5	-44	-2.7
299153	-9.9	-72.1	21.5
285562	-10.1	-73.3	19.8
755648	-5.6	-84	1.5
755647	-5.5	-85	4.5
755645	-4.1	-65	3.6
755646	-0.8	-43	9.2
755662	-10.1	-74	3.7
755590	-12.3	-95	-8.7
755653	-3.5	-50	8.5
755652	-4.3	-51	10.5
755661	-12.0	-72	2.9
755591	-12.4	-90	-6.0
755667	-6.5	-50	1.2
755666	-0.2	-40	5.3

Facility # COENV DB	**$\delta^{18}O$ H_2O per mil VSMOW**	**δD H_2O per mil VSMOW**	**$\delta^{13}C$ DIC per mil VPDB**
755667	-6.7	-52	1.5
755592	-12.6	-95	6.2
755593	-12.7	-95	1.1
755658	-4.9	-67	-0.6
757036	-6.9	-59	2.6
757035	-2.6	-34	3.7
757105	-18.3	-140	4.5
757034	-4.5	-36	4.8
757071	-3.3	-33	4.4
757072	4.0	-33	7.2
757033	-2.4	-36	5.9
757038	-1.4	-33	-8.6
757037	1.3	-41	2.6

Appendix 16. Tritium (^{3}H) in Water (U of Miami)

Facility # COENV DB	^{3}H H_2O TU (tritium units)	one σ uncertainty (TU)	Data Flags
755461	6.71	0.22	
755462	-1	2	**U**
755474	1.91	0.09	
755475	2.74	0.09	
755476	4.13	0.14	
755500	1.66	0.09	
755501	2.81	0.09	
755523	*-0.01*	*0.09*	**U**

U flag indicates analyte not detected by the laboratory

Appendix 17. ^{14}C in Dissolved Inorganic Carbon (DIC) University of Arizona

Facility # COENV DB	δ^{13}C DIC per mil VPDB	^{14}C DIC	^{14}C DIC Units	^{14}C DIC Age	Units
755461	-9.9	102.63	pMC	60	years BP
755462	2.8	0.69	pMC	39900	years BP
755474	12.9	1.13	pMC	36030	years BP
755475	12	0.44	pMC	43600	years BP
755476	6.9	1.31	pMC	34840	years BP
755500	7.3	6.85	pMC	21540	years BP
755501	-2.7	11.88	pMC	17115	years BP
755523	*-17.2*	*0.64*	*pMC*	*40500*	*years BP*