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Accuracy of methods for reporting inorganic element concentrations and radioactivity in oil and gas wastewaters from the Appalachian Basin, U.S. based on an inter-laboratory comparison†

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Accurate and precise analyses of oil and gas (O&G) wastewaters and solids (*e.g.*, sediments and sludge) are important for the regulatory monitoring of O&G development and tracing potential O&G contamination in the environment. In this study, 15 laboratories participated in an inter-laboratory comparison on the chemical characterization of three O&G wastewaters from the Appalachian Basin and four solids impacted by O&G development, with the goal of evaluating the quality of data and the accuracy of measurements for various analytes of concern. Using a variety of different methods, analytes in the wastewaters with high concentrations (*i.e.*, >5 mg L^{-1}) were easily detectable with relatively high accuracy, often within ±10% of the most probable value (MPV). In contrast, often less than 7 of the 15 labs were able to report detectable trace metal(loid) concentrations (*i.e.*, Cr, Ni, Cu, Zn, As, and Pb) with accuracies of approximately ±40%. Despite most labs using inductively coupled plasma mass spectrometry (ICP-MS) with low instrument detection capabilities for trace metal analyses, large dilution factors during sample preparation and low trace metal concentrations in the wastewaters limited the number of quantifiable determinations and likely influenced analytical accuracy. In contrast, all the labs measuring Ra in the wastewaters were able to report detectable concentrations using a variety of methods including gamma spectroscopy and wet chemical approaches following Environmental Protection Agency (EPA) standard methods. However, the reported radium activities were often greater than ±30% different to the MPV possibly due to calibration inconsistencies among labs, radon leakage, or failing to correct for self-attenuation. Reported radium activities in solid materials had less variability (±20% from MPV) but accuracy could likely be improved by using certified radium standards and accounting for self-attenuation that results from matrix interferences or a density difference between the calibration standard and the unknown sample. This inter-laboratory comparison illustrates that numerous methods can be used to measure major cation, minor cation, and anion concentrations in O&G wastewaters with relatively high accuracy while trace metal(loid) and radioactivity analyses in liquids may often be over ±20% different from the MPV.

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Environmental significance

Accurate analyses are important for regulating oil and gas (O&G) development and tracing potential contamination events. In this work, an inter-laboratory comparison among commercial and academic labs revealed that reported radioactivity and trace metal concentrations (*i.e.*, Ra, Cr, Ni, Cu, Zn, As, Cd, and Pb) in O&G wastewaters can be ±40% different from the most probable value (MPV). Out of all the analytes measured in this study, reported ^{226}Ra activities—a known carcinogen—were the most inconsistent and ranged by approximately 200% for a single sample. This variability in reported Ra activities could influence how the wastewaters are managed or identified in the environment, warranting further attention and research. We propose that the variable Ra activities could be due to calibration inconsistencies among labs, radon leakage, or failure to account for self-attenuation. Future work is necessary to develop standard methods and reference materials for Ra analyses of O&G wastewaters.

Introduction

Horizontal drilling and hydraulic fracturing has increased oil and gas (O&G) production from low permeability shale formations throughout the United States (U.S.). In 2017, the U.S. Energy Information Administration (EIA) estimated that nearly 60% (0.48 trillion cubic meters) of the U.S. natural gas production was produced from shale resources throughout the U.S., including the Marcellus, Utica, Permian, Haynesville, Eagle Ford, Barnett, Woodford, and Bakken Shales.[1] This shale development has aided in lowered national carbon dioxide (CO_2), nitrogen oxide (NO_x), and sulfur dioxide (SO_2) emissions by shifting energy production from coal to natural gas.[2] However, the increased production has also resulted in concerns with respect to seismic activity,[3] methane emissions,[4] ground water and surface water contamination,[5,6] and the disposal of solid and liquid wastes that can lead to substantial increases in seismic activity and concentrations of some contaminants in surface waters.[7,8]

O&G production creates large quantities of high salinity (>100 000 mg L^{-1} total dissolved solids [TDS]) liquid wastes that cause challenges for wastewater management and disposal. Wastewater production volumes from U.S. shale plays have been estimated at 27–130 liters of produced water per billion cubic meters of gas (L Bm^{-3}) in the Eagle Ford and Haynesville shales, more than 130 L Bm^{-3} from the Barnett Shale, and approximately 3.3–94 L Bm^{-3} from the Marcellus Shale, which generated approximately 0.67 billion cubic meters of natural gas per day (Bm^3 per day) in 2017.[9,10] Depending on the shale play, these fluids typically contain high concentrations of salts, metals, naturally occurring radioactive materials (NORMs), and organic compounds that make proper management *via* treatment and/or disposal particularly important in limiting potential human and environmental health concerns.[11,12] O&G wastewater disposal options include injection into subsurface formations, reuse to develop other wells, treatment at wastewater treatment facilities with surface water discharge permits, storage in evaporation ponds, or beneficial reuse for other practices such as irrigation, dust suppression and de-icing of roads, or livestock watering.[13–16] Particular concerns with these practices are related to the salinization of freshwater resources,[17] accumulation of radium or trace metals in roads treated with O&G wastewaters[15,18] or in sediments downstream of O&G wastewater treatment facilities,[19] and human health impacts (*e.g.*, mutagenesis, endocrine disruption, neurotoxicity, or cytotoxicity) by exposure to organic compounds in the wastewaters.[20,21] One way that State and Federal regulators monitor O&G wastewater disposal is by requiring chemical analyses of surface water discharges from facilities treating O&G wastewaters (40 CFR part 122) or analyses of O&G wastewaters being permitted for other beneficial uses (*e.g.*, irrigation, dust suppression, de-icing, or livestock).[13,15] States such as Pennsylvania also require O&G operators who generate more than 1000 kilograms of waste per well in a calendar year to report the chemistry of their wastewater to the Pennsylvania Department of Environmental Protection (PADEP) along with a description of disposal facilities that have received the waste.[22] The accuracy of these chemical analyses are important for regulatory purposes, proper treatment, as well as fingerprinting applications for identifying O&G wastewaters after potential contamination events.[23–25]

Accurate analyses of metal and radioactivity concentrations in O&G wastewaters are challenging due to the complex fluid matrix.[26] Common analytical methods for detecting metals in O&G wastewaters, such as inductively coupled plasma optical emission spectrometry (ICP-OES) or mass spectrometry (ICP-MS), can be hampered by non-spectral and spectral interferences in high salinity fluids. Non-spectral interferences include signal suppression from easily ionized elements (*e.g.*, Na and K) as well as the accumulation of salts or oxide minerals on cones in ICP-MS systems.[26] Other spectral interferences such as superimposing element emission lines in ICP-OES or the presence of polyatomic species (*e.g.*, as $^{40}Ar^{23}Na^{+}$ on $^{63}Cu^{+}$) in ICP-MS can also influence analytical results.[27,28] Several techniques are available to correct for these differences, including sample dilution, wet chemical separation, alternative sample introduction, mathematical calculations, and calibration and internal standard modifications.[29,30] Sample dilution is the most common way of reducing potential matrix effects, but often results in decreased sensitivity and elevated method detection limits for trace metal(loids) of concern (*e.g.*, As, Pb) in O&G wastewaters.[26]

Numerous techniques exist for measuring radium in O&G wastewaters including methods by alpha particle spectrometry (EPA method 903.0),[31] ^{222}Rn emanation counting in a scintillation cell (EPA method 903.1),[32] gamma ray spectrometry (EPA method 901.1),[33] beta particle spectroscopy (EPA method 904.0),[34] or ICP-MS.[35] Some of these methods measure Ra activities directly by ICP-MS or alpha, beta, and gamma emissions while other methods measure Ra indirectly based on emissions by daughter products. Among these, the ^{222}Rn emanation technique involves the collection and indirect

counting of alpha particles emitted by ^{222}Rn, a daughter product of ^{226}Ra.[32] In some cases, this method may also require the pre-concentration of ^{226}Ra from samples using co-precipitation techniques with barium sulfate (EPA method 903.1).[32,36,37] There are some undesirable aspects of this method including long waiting periods required for radon ingrowth (>21 days ingrowth) and potential loss of Ra during sample pre-concentration.[32,36,37] Co-precipitation techniques are also required to remove ^{228}Ra from solutions prior to indirect measurements of its ^{228}Ac daughter using beta particle spectroscopy.[34] Methods by alpha particle spectrometry can measure ^{226}Ra directly based on α emissions at 4.78 MeV but also often require pre-concentration, chemical separation, and purification techniques to remove other alpha emitters.[38] High-salinity O&G samples can reduce Ra yields during chemical separation and purification but can likely be accounted for using tracers.[37,38] Because of the high-salinity of O&G wastewaters and potential difficulty in recovering Ra from these solutions, standard EPA methods that require Ra separation prior to analyses have been discouraged for analyses of O&G wastewaters.[37]

One method that has been encouraged for radioactivity analyses of O&G waste is gamma ray spectrometry.[37] This method requires no sample preparation or pre-concentration techniques and potentially reduces the risk of low Ra yields from co-precipitation or chemical separation methods; yet, it is still common to concentrate Ra in co-precipitates or evaporites and analyze the solids using gamma ray spectrometry.[39] ^{226}Ra can be measured directly using the gamma emission energy at 186.2 keV. However, gamma emissions from ^{235}U at 185.7 keV can also interfere with direct ^{226}Ra measurements. This interference is more likely an issue in O&G drill cuttings or sediment materials than O&G wastewaters due to their relative activities of ^{235}U.[37] An alternative method for ^{226}Ra is to measure the indirect gamma emission of ^{214}Pb at 295.2 keV and 351.9 keV and ^{214}Bi at 609.3 keV following equilibrium between ^{226}Ra and ^{222}Rn. Similarly, the indirect method for determining ^{228}Ra is based on the gamma emission of its ^{228}Ac daughter at 911.2 keV. There are several factors that could lead to inaccurate Ra measurements of O&G wastes using gamma spectrometry. Rn leakage in sample containers can influence indirect measurements of ^{222}Rn progeny (*i.e.*, ^{214}Pb and ^{214}Bi). Leakage could occur *via* improperly sealed containers or by diffusion through polyethylene plastics which commonly make up Marinelli beakers and other containers used for gamma ray spectroscopy measurements.[40] O&G solid and liquid wastes may also have different chemical compositions (*e.g.*, high-salinity, radio-barite co-precipitates) and densities (*e.g.*, often greater than 1.2 g mL^{-1} densities in O&G wastewaters) in comparison to standards. This can result in differences in attenuation of gamma photons between samples and standards, and lead to analytical inaccuracies.[41] Attenuation may be accounted for using a variety of techniques although standard EPA methods do not require these corrections.[33,41,42]

An inter-laboratory comparison was organized among commercial, academic, and government labs throughout the U.S., Canada, and Germany to determine how these potential sources of error affect the accuracy of O&G waste characterizations. Several of the commercial labs had previously analyzed O&G wastes for certificate of analyses in regulatory applications. The main goals of the comparison were to (1) evaluate the overall quality of data from laboratories analyzing O&G wastes, (2) identify methods that produce acceptable quality data for the analytes of concern in O&G wastes, and (3) evaluate the analytical accuracy for various analytes of concern in O&G wastes, including Na, K, Mg, Ca, Sr, Ba, Li, B, Al, Fe, Mn, Cr, Ni, Cu, Zn, As, Pb, Cl^-, Br^-, SO_4^{2-}, ^{226}Ra, and ^{228}Ra.

Methods

Sample preparation and shipment

Three O&G wastewaters chosen for the study were collected from oil and gas wells throughout the Appalachian Basin, located in the Northeastern United States, and stored in 20 liter high density polyethylene (HDPE) containers. One liter of each of the wastewaters was filtered with a 0.45 μm cellulose acetate filter and then stored at 4 °C for anion analyses (*i.e.*, Cl^-, Br^-, SO_4^{2-}). The remaining portion of the wastewater samples were acidified with 5% nitric acid and filtered for elemental and radioactivity analyses (*i.e.*, Na, K, Mg, Ca, Sr, Ba, Li, B, Al, Fe, Mn, Cr, Ni, Cu, Zn, As, Pb, ^{226}Ra, ^{228}Ra). Thereafter, sub-aliquots of each of the samples were stored in HDPE bottles for sample shipment.

In addition to the three oil and gas wastewaters, four solid samples were pulverized and sieved (<1.18 mm) for interlab comparisons. Each solid sample was selected to have a matrix similar to solids commonly analyzed in environmental studies accessing O&G impacts (*i.e.*, river sediments impacted by O&G wastewater, barite sludge from treatment facilities, and shale core or cuttings). These solid samples were as follows: solid sample 1 (SS1) was a stream sediment collected from Blacklick Creek, Pennsylvania; solid sample 2 (SS2) was from a Marcellus Shale outcrop; and solid samples 3 (SS3) and 4 (SS4) were both Blacklick Creek stream sediments mixed with radio-barite sludge at different ratios. All solid samples were homogenized with a mixing paddle before packaging and shipment.

A parcel from each sample was sent to 15 labs; delivery was made within 1–4 days after shipment. The labs included eight academic, six commercial, and one government lab. Each lab was instructed to use their own preparation and analytical methods to analyze the liquid samples for a suite of cations and anions including Cl^-, Br^{2-}, SO_4^-, Li, B, Na, K, Mg, Ca, Sr, Ba, Al, Fe, Mn, S, Cr, Ni, Cu, Zn, As, Cd, Pb, ^{226}Ra, and ^{228}Ra. Due to the analytical capabilities of participating labs and the interest in technologically enhanced naturally occurring radioactive material (TENORM) in oil and gas wastes, only ^{226}Ra and ^{228}Ra were measured for solid samples. Many labs did not have the analytical equipment to measure all the cations or anions and were therefore asked to only report analytes and values within their capabilities. An anonymous online portal was created for data submission and reporting of sample preparation procedures (*i.e.*, dilution factors, precipitation or pre-concentration methods), analytical equipment and methods used for analyses, uncertainties, and calibration standards.

Data processing and statistical analysis

All submitted data were evaluated according to nonparametric statistical methods in Hoaglin *et al.* (1983)[43] that are commonly used in inter-laboratory comparisons by the U.S. Geological Survey (USGS).[44] This statistical approach is known to be resistant to outliers because the method is based on median, 25th percentile, and 75th percentile values rather than mean values in parametric statistics. All data were first trimmed to exclude values that were reported as zero or below detection limits. Thereafter, the 25th percentile (Q_1), median, and 75th percentile (Q_3) concentrations for all analytes in the three O&G wastewaters and four solid samples were calculated. $F_{\text{psuedosigma}}$ (mg L^{-1}), an approximation for standard deviation, was calculated for each analyte according to:

$$F_{\text{psuedosigma}} = \frac{Q_3 - Q_1}{1.349} \quad (1)$$

where 1.349 is the number of standard deviations encompassing 50% of the data (*i.e.*, $Q_3 - Q_1$).[44]

To perform all desired statistical processing tests, a full suite of data with a high number of total reported values (>7 reported values per analyte) and low $F_{\text{psuedosigma}}$ was required. For analytes with over seven reported values and with $F_{\text{psuedosigma}}$ values less than the median, the median value of all the data was reported as the most probable value (MPV) for the analyte concentration within the sample. In this study, $F_{\text{psuedosigma}}$ values for analytes with over seven reported values were never greater than the median. Thereafter, the performance of the labs was evaluated by calculating their *z*-score (dimensionless) according to:

$$z = \frac{\text{Reported value} - \text{MPV}}{F_{\text{psuedosigma}}} \quad (2)$$

Interpretation of the *z*-scores were as follows: $|z| \leq 2$ is an acceptable result, $2 < |z| \leq 3$ is a questionable result, and $|z| > 3$ is an unacceptable result.[44] The range of acceptable results was compared to the MPV value for a given analyte to determine the % difference (*i.e.*, accuracy) of the measurements according to:

$$\%\ \text{Difference} = \left[\frac{\text{MV} - \text{MPV}}{\text{MPV}}\right] \times 100 \quad (3)$$

where MV is the measured value of an acceptable result.

In some cases, there were not enough reported values for specific analytes to do all the desired statistical tests. Therefore, the following modifications were made to the statistical processing methods above. When five or six values were reported for an analyte in a sample, the median and $F_{\text{psuedosigma}}$ values were reported with an asterisk (*) along with the 25th and 75th percentile concentrations. In this scenario, no *z*-scores or % difference calculations were performed. No summary statistics were calculated for analytes with <5 reported values. For these scenarios, the *z*-scores are represented as not calculable (n.c.) throughout the manuscript and are not included in data interpretations.

Results and discussion

Major cations, minor cations, and anions

Major cation (*i.e.*, Na, K, Mg, Ca, Sr, and Ba), minor cation (*i.e.*, Li, B, Al, Fe, and Mn), and anion (Br^-, Cl^-, SO_4^{2-}) concentrations in the three O&G wastewaters were measured using a variety of methods, including inductively coupled plasma with optical emission spectrometry (ICP-OES), direct plasma spectrometry (DCP), inductively coupled plasma with mass spectrometry (ICP-MS), triple quadrupole inductively coupled plasma with mass spectrometry (ICP-MS/MS), neutron activation analysis (NAA), X-ray fluorescence (XRF), and ion chromatography (IC). A summary of the instruments used by participating labs for measuring particular analytes is included in the ESI (Table S1†).

Approximately 50% of all major and minor element analyses were performed using an ICP-OES (*e.g.*, Perkin Elmer Optima 5300DV ICP-OES, Horiba Ultima Expert ICP-OES, Spectro ARCOS ICP-OES, Thermo Scientific iCAP 7400, and Thermo Scientific iCAP 6000). Prior to analyses, samples were diluted between 100–1000 times and measured in accordance with EPA method 200.7 [45] using internal standards (*i.e.*, Sc, In, Re, and Y), quality control samples, external standards [National Institute of Standards and Technology (NIST) 1640a, NIST 1643f, Ocean Scientific International Ltd (OSIL) seawater standard, USGS M-220, and NIST Standard Reference Material (SRM) 1640a], laboratory fortified blanks, matrix spikes, and/or laboratory reagent blanks to confirm the accuracy of the equipment. In one to three instances, labs using ICP-OES for major cation analyses switched to ICP-MS for Li, B, Ba, Al, Fe, or Mn measurements likely due to the lower concentrations of these cations relative to many of the major cations and lower detection limits of the ICP-MS (often less than 1 ppm after accounting for sample dilution). More complete descriptions of ICP-MS methods are included in the following section.

Other methods for analyses included NAA, XRF, DCP, and IC. One lab used a neutron activation analysis method for all analyses that consisted of drying samples into crystals, irradiating the crystals in a nuclear reactor core, and then comparing the emitted gamma rays to irradiated standard reference materials (*i.e.*, Montana soil 2711 SRM and Buffalo River SRM2704 sediments)[46,47] using a high purity germanium detector. Another lab used XRF for all analyses but no details were provided on the method other than the sample analysis time (21 minutes) and instrument manufacturer (*i.e.*, SPECTRO XEPOS XRF Spectrometer). In one case, an IC column (Dionex IonPac CS12A IC column with 15 mM methanesulfonic acid eluent) was used to separate major cations (*i.e.* Ca, Mg, Na, K, and Sr) for analysis using a Dionex ICS2000 Ion Chromatograph.

Over 80% of the labs used IC for anion analyses. Various columns and methods were referenced by participating labs, including AS11 HC, AS18, and AS19 columns with KOH eluent. With the exception of one lab who reported greater than 10 000 times dilution, all labs diluted samples approximately 100–1000 times prior to IC analyses. Referenced standards included the

Dionex 7 Anion Standard II and a diluted OSIL seawater standard. Two other labs used XRF or NAA for determining Cl^- and Br^- concentrations in the three samples.

All three O&G wastewaters had major cation, minor cation, and anion concentrations (Table 1) that were within the 25th to 75th percentile concentrations for wastewaters from the Appalachian Basin, U.S. (Table S2†).[48] The samples were nearly 100% charge balanced by chloride which had the highest concentration in sample 3 (MPV = 176 000 mg L^{-1} Cl^-) and the lowest concentration in sample 1 (MPV = 65 600 mg L^{-1} Cl^-). With the exception of SO_4^{2-} and Al, which had a low number of reported concentrations among the three samples (n < 5), summary statistics were calculated for all major cation, minor cation, and anion concentrations according to non-parametric statistics (Table 1).[44] $F_{psuedosigma}$ values for all these analytes were often orders of magnitude lower than the MPV, suggesting low variability among the reported results.

Greater than 80% of the reported values for major cation, minor cation, and anion concentrations were of acceptable or questionable quality (Fig. 1). For example, among all three samples, 433 values in total were reported (*e.g.*, 14 analytes per sample × 3 samples × number of values submitted by individual labs) and 365 of the values were determined to be of acceptable or questionable quality. Of the remaining 68 reported values, 56 were of unacceptable quality and 12 were not calculable because they were below method detection limits (*e.g.*, Al and SO_4^{2-} analyses). Unacceptable data quality was examined in more detail to determine if the data quality was influenced by the methods used for analyses.

Analyses of unacceptable quality data suggest that both the method and/or lab could have an influence on the reported major and minor cation concentrations submitted in this study. There were 48 total unacceptable quality values reported for major and minor cations (note that an additional 8 anion results were unacceptable) among all three O&G wastewaters. When grouped by method, the highest percentages of unacceptable values were for XRF and NAA (*e.g.*, 52% of the XRF and 33% of the NAA), while only 9% of the ICP results were unacceptable. NAA and XRF accounted for 40% of the total unacceptable values for all the submitted data. In addition, these two methods were each used by one lab.

The high percentage of unacceptable values for NAA could be attributed to analyses of a few cations. The NAA laboratory reported all detectable analytes, even though there was a strong likelihood that elements with activation products that have short half-lives (less than several days, *e.g.* ^{42}K and ^{82}Br) would be compromised by interference from the scattering of gamma rays from ^{24}Na in the high-purity germanium detector. Numerous factors influence NAA detection capabilities, including the isotopic abundance and neutron absorption cross-section of the target isotope, the gamma ray intensity and gamma ray energy from the activated isotope, and the presence of other elements in the sample. These last two factors are significant in the high salinity O&G samples. The very high Na concentration in these samples produces a large amount of ^{24}Na $\left(t_{\frac{1}{2}} = 14.997 \text{ hours}\right)$ during neutron irradiation. The high-energy gamma rays from ^{24}Na (1368.6 keV (99.99%) and 2754.0 keV (99.86%)) undergo Compton scattering in the high-purity germanium detector, creating a Compton plateau of increased counts at energies below approximately E_γ – 256 keV.[49] These increased counts in the lower-energy region of the gamma ray spectrum can alter and even completely obscure the gamma ray peaks from activated isotopes that emit lower energy gamma rays. Mainly because of this phenomenon, the most accurate elemental determinations in these types of O&G samples are for elements whose activation products have half-lives greater than several days, which allows for the full decay of the ^{24}Na and the elimination of the ^{24}Na Compton plateaus. For example, by excluding data from the shorter-lived isotopes (*e.g.*, ^{42}K and ^{82}Br), the percentage of acceptable data points reported by the NAA laboratory increases to 80%. Furthermore, it appears that three of the four remaining outliers of unacceptable quality are

Table 1 The most probable value (MPV), 25th percentile (Q_1), 75th percentile (Q_3), and $F_{psuedosigma}$ (F) for major cation, minor cation, and anion concentrations in O&G wastewater samples 1, 2, and 3. All values are represented in mg L^{-1}. When there were only 5 or 6 reported values submitted, summary statistics are noted with an asterisk (*).When there were less than 5 reported values for a given analyte, summary statistics were not calculable (n.c.)

	Sample 1			Sample 2			Sample 3		
Analyte	MPV	Q_1–Q_3	F	MPV	Q_1–Q_3	F	MPV	Q_1–Q_3	F
Br^-	746	652–773	90.4	1270	1180–1440	189	1890	1630–2060	320
Cl^-	65 600	63 900–68 300	3300	117 000	113 000–120 000	5470	176 000	160 000–180 000	15 000
SO_4^{2-}	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	170*	130–172*	33.0*
Na	27 000	24 900–28 600	2710	47 500	43 600–49 300	4260	66 850	64 600–68 900	3170
K	336	276–383	79.3	716	621–765	107	2190	1770–2310	402
Mg	1230	1200–1300	69.3	2168	2100–2270	127	3100	2990–3130	104
Ca	10 000	9280–10 200	686	19 800	18 600–20 600	1480	31 400	30 000–33 200	2350
Sr	2160	2130–2200	49.7	3710	3580–3940	270	1540	1410–1620	156
Ba	659	641–690	37.2	1320	1280–1380	72.8	6.12	6.07–6.33	0.20
Li	32.1	30.3–34.3	3.00	50.3	48.0–51.0	2.19	71.7	68.0–74.2	4.60
B	5.00	3.95–5.09	0.85	7.00	6.76–8.05	0.95	15.3	14.7–16.0	0.99
Al	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
Fe	64.8	58.7–69	7.61	94.9	85.8–98.5	9.44	169	158–181	17.0
Mn	6.10	5.75–6.7	0.70	14.4	13.7–14.9	0.93	47.8	41.5–48.3	5.06

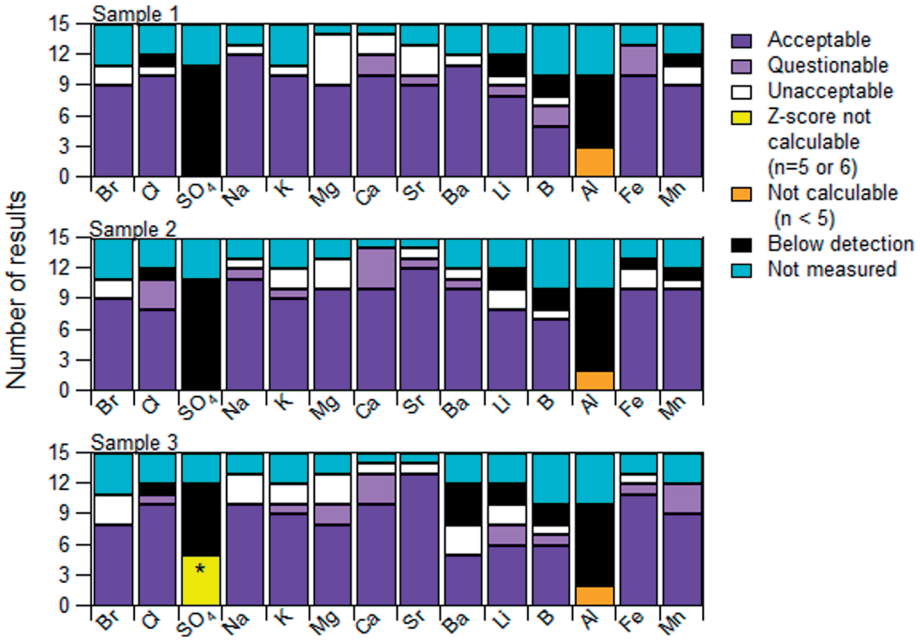

Fig. 1 Data quality for major cation, minor cation, and anion concentrations reported in O&G wastewater samples 1, 2, and 3. Acceptable, questionable, and unacceptable quality were based on *z*-score calculations when the number of values were ≥7 for a given analyte. When 5 or 6 values were reported, no *z* score was calculated but is noted with an asterisk as a MPV and $F_{psuedosigma}$ were still calculated (*i.e.*, Table 1). When less than 5 values were reported, no statistics were calculated.

from sample 3, which has the highest Na concentration of the three samples; the exact reason for the concentration of outliers in sample 3 is not known, but the high Na concentration could be the cause. Overall, NAA performs well for elements with longer-lived activated isotopes such as Sr, Ba, Fe.

Other values reported by labs using ICP-OES suggest that the lab also has an influence on the quality of data that was submitted. For instance, 17% and 27% of the reported values by two labs using ICP-OES had unacceptable quality while each of the other six labs using ICP-OES never had more than 4% of their data rejected due to unacceptable quality. As another comparison, one lab using ICP-MS for all analyses had 40% of their reported values rejected for data quality issues while another lab using ICP-MS had less than 6% rejected. These examples illustrate that each of these ICP methods can likely be used to generate acceptable quality data when measuring major and minor cation concentrations in O&G wastewaters and that a large portion of the variability observed in the current study is likely a result of quality control issues and internal lab protocols for specific analytical methods.

The only analytes that were particularly challenging for all participating labs were SO_4^{2-} and Al. For instance, only five total detectable SO_4^{2-} concentrations and seven total detectable Al concentrations were measured in the three O&G wastewaters (Fig. 1). All the reported SO_4^{2-} values were for sample 3 which had a median value of 170 mg L^{-1} and $F_{psuedosigma}$ value of 33.0 mg L^{-1}. While the median value was 170 mg L^{-1}, seven labs reported that this was below their detection (*i.e.*, 200 to 500 mg L^{-1}) indicating that SO_4^{2-} analyses of O&G wastewaters are challenging for labs when concentrations are below 200 to 500 mg L^{-1}. The reasons for the challenges associated with measuring Al are unresolved as the number of reported values ($n = 2$ or 3 per sample) and large variations in detection limits (0.02 to 14 mg L^{-1}) prevent drawing any conclusions from the data.

Major cation, minor cation, and anion concentrations in O&G wastewaters were within ±10% of the MPV, with the exception of Br^- and K which sometimes exceeded ±20%. These accuracies are very similar to recent inter-laboratory comparisons of freshwaters where acceptable quality data for major cations had ±8.5% difference from the MPV and minor cations had up to ±14.2% difference (Table S3†).[44] The range in the percent difference is based on comparisons of the reported minimum and maximum concentrations of acceptable quality data to the MPV. Results among the three samples indicate that the most deviation from the expected MPV occurred for Br^- and K. If these differences were a result of dilution errors during sample preparation, then similar % differences would be expected for analytes diluted to the same dilution factors. This was not observed among the data submitted by several of the labs. For instance, one lab diluted sample 2 by 50 times for K and Ca analyses by ICP-OES yet Ca concentrations were within 5% of the MPV while K concentrations were 23% greater than the MPV. Some of these differences could be attributed to the challenges of analyzing easily ionizable cations such as K and Na that can have large relative standard deviations in analyses by ICP.[50] In another case, one of the labs diluted sample 3 by 100 times and measured Cl^- concentrations that were within 2% of the MPV while the bromide concentrations were 20% greater than the MPV. All Br^- values reported with acceptable quality were measured using ion chromatography; therefore, these differences are not necessarily instrument-specific but could be

related to differences in calibration standards (*e.g.*, use of certified standards *versus* standards made from NaCl or NaBr salts, *etc.*), matrix-matching calibration standards (*e.g.*, high Cl^-/Br^- ratios in standards), or methods accounting for matrix interferences (*e.g.*, peak overlap with chloride or peak broadening by CO_2 or carbonate anions) (Fig. 2).[51]

From a regulatory perspective, ±10% to 20% differences in any of the measured analytes will not have a significant impact on the management or treatment of O&G wastewaters but could influence geochemical interpretations made about O&G reservoirs based on wastewater chemistry. For instance, some states that regulate the use of O&G wastewater spreading on roads require the wastewaters to meet standards for Cl^-, Ca, Mg, Na, Ba, or Fe.[15] Other facilities that treat these same wastewaters are also required to meet effluent discharge standards and permitted total maximum daily loads for analytes; these standards often include Cl^-, Ba, and Fe.[52] Based on the results from this inter-laboratory comparison, academic, commercial, and government labs can analyze each of these analytes with relatively high accuracy following a dilution step and the ±10% differences in measured *versus* expected values will likely have very little influence on how the wastewaters are managed. Other ions such as Br^- may have large percent differences between measured and expected values. However, there are currently no surface water or groundwater standards for Br^- despite evidence that it can lead to the formation of carcinogenic disinfection byproducts in drinking water.[17] However, monitoring of Br^- loads from treatment facility discharges may be required in future permits and, therefore, accurate Br^- measurements should be a goal of every laboratory.[53]

Differences in major and minor cations and anion concentrations between the measured value and MPV will influence the calculation of elemental ratios, which are commonly used to explain the origin of O&G wastewaters or are used as tracers for fingerprinting potential contamination events.[54,55] For instance, Cl^-/Br^- ratios (mass/mass) for reported results with acceptable quality ranged from 79 to 105 in sample 1 and 78 to 100 in sample 3 (Table S4†). O&G wastewaters throughout the Appalachian Basin are believed to originate from a common ancient seawater source; however, the range in Cl^-/Br^- ratios (<50 to 110) reported in the literature suggests that these fluids likely underwent varying degrees of evaporation (ranging from 20–40% evaporation).[55–57] As a comparison, the range in Cl^-/Br ratios reported for any one of the three samples in this study could be interpreted as a wastewater that originated from a seawater evaporated by 27% to 39%. Therefore, some of the variability in Cl^-/Br^- ratios in existing literature could be related to the challenges in measuring Br in these fluids. Other ratios commonly used to trace O&G wastewaters in the environment (*e.g.*, Sr/Ca and B/Cl^-)[23–25] showed much less variability (Table S4†).

Trace metal(loid) measurements

Trace metal(loid)s (*i.e.*, Cr, Ni, Cu, Zn, As, and Pb) were measured using many of the same methods highlighted for

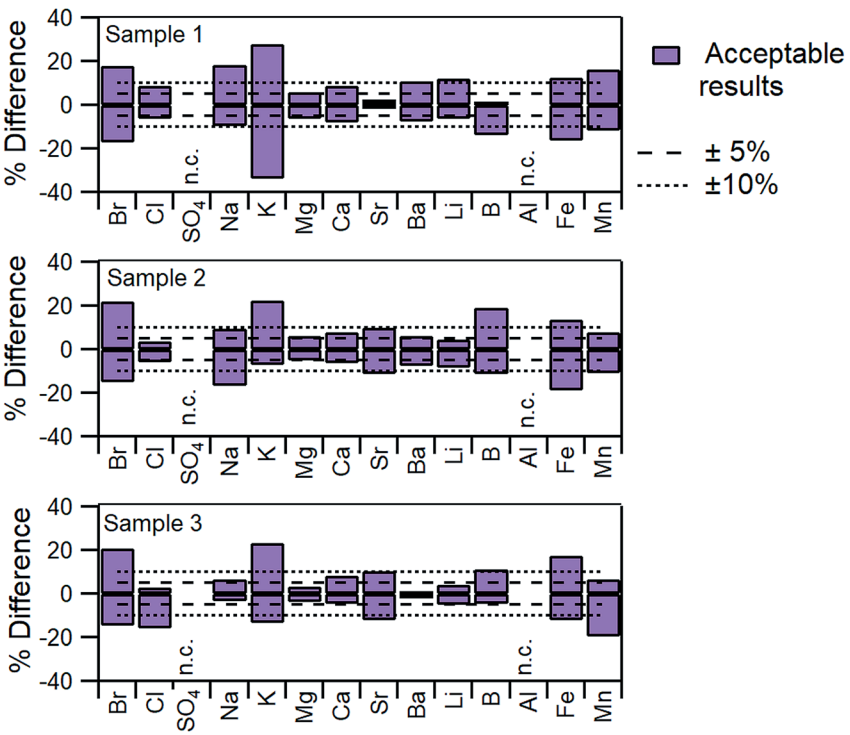

Fig. 2 Range in accuracy of reported values with acceptable quality for major cation, minor cation, and trace cation concentrations in O&G wastewater samples 1, 2, and 3 based on comparisons to the MPV. Values with a *z* score that was between −2 and 2 were considered of acceptable quality. No accuracy calculations were performed for SO_4^{2-} or Al due to the low number of detectable values and are represented as not calculable (n.c.).

major and minor cations. However, most analyses (60–75%) were performed using ICP-MS. ICP-MS equipment included an ICP-MS Element2XR, VG PlasmaQuad3 ICP-MS, Agilent 7500 ICP-MS ($n = 2$), Agilent 7900 ICP-MS, Thermo X series 2 ICP-MS, and Agilent 8800 ICP-MS/MS. Samples prepared for the ICP-MS Element2XR were measured against a 2-point calibration curve and with a In internal standard. Samples measured on the VG PlasmaQuad-3 ICP-MS were diluted ~1000 times prior to analyses. The equipment was calibrated with the NIST 1643e/1643f standard, which was measured at varying concentrations before, after, and throughout sample runs. Internal standards of In, Th, and Bi were spiked into all the samples prior to analyses. Analyses on the Agilent 7500 ICP-MS were diluted 100 to 1000 times prior to measurements. The equipment was calibrated using NIST traceable standards and Sc, Ba, Ge, Rh, In, Pt, and Bi were used as internal standards. All analyses on the Agilent 7900 ICP-MS were measured according to EPA 200.8. Samples were diluted ~10 times prior to analyses. Calibration check standards and laboratory control samples were measured before all samples and four internal standards were used (Tb, Rh, Ge, and Sc) to account for instrument drift. All analyses on the Thermo X series 2 ICP-MS were diluted ~100 times prior to analyses. Mass interferences and matrix complications were accounted for by using internal standards (Sc, In, Re, Y) and high-salinity, matrix-matched standards. Calibration curves for all analyses were verified by confirming <5% differences between measured and known metal(loid) concentrations in check standards (USGS M-220, USGS T-227, and SRM1640a). Lastly, analyses performed on the Agilent 8800 ICP-MS/MS were analyzed under a variety of conditions (*i.e.*, no gas, He 5 mL, H_2, and O_2 gas). To account for instrumentation drift, a mix of internal standards including Sc, Ge, In, Lu, and Bi were run in a variety of acquisition modes. Dilution factors for all metal(loid)s measured by this method were approximately 70.

Trace metal(loid) determinations in the O&G wastewaters were challenging for all laboratories (Table 2). There were only four analytes among the three wastewaters (Zn in sample 2, and Cu, Zn, and Pb in sample 3) that had sufficient data for performing non-parametric statistics and calculating *z*-scores. The

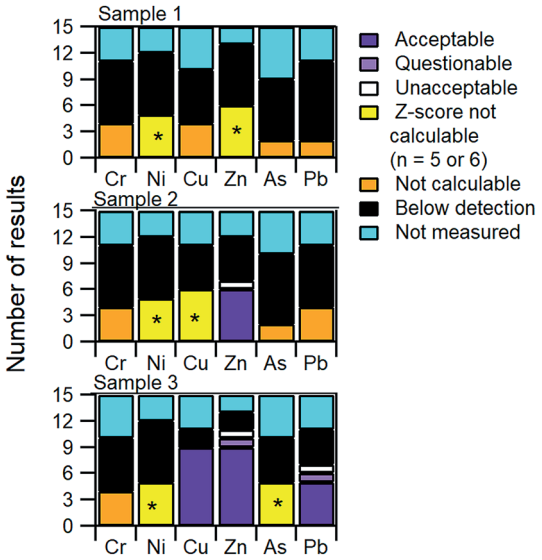

Fig. 3 Data quality for trace metal(loid) concentrations reported in O&G wastewater samples 1, 2, and 3. Acceptable, questionable, and unacceptable designations were based on *z*-score calculations when the number of reported values was ≥7 for a given analyte. When 5 or 6 values were reported, no *z* score was calculated but is noted with an asterisk as a MPV and $F_{psuedosigma}$ were still calculated (Table 2). When less than 5 values were reported, no statistics were calculated.

remaining analytes either had too little data to perform any statistics ($n < 5$) or not enough data ($n = 5$ or 6) to perform all statistical analyses (Fig. 3). Even in samples where 5 or 6 values were reported, the 25th (Q_1) to 75th (Q_3) percentile ranges were highly variable. For instance, Q_1 to Q_3 for Ni ranged from 0.009 to 0.345 mg L^{-1} and Zn ranged from 0.108 to 0.358 mg L^{-1} in sample 1 (Table 2). In every analyte with 5 or 6 values reported, $F_{psuedosigma}$ was greater than the MPV indicating that there was a large amount of variability among the data.

High method detection limits relative to the trace metal(loid)s concentrations within the wastewaters reduced the number of reported values. The reported MPVs for trace metal(loid)s measured in the three O&G wastewaters for this study (Table 2)

Table 2 The most probable value (MPV), 25th percentile (Q_1), 75th percentile (Q_3), and $F_{psuedosigma}$ (F) for trace metal(loid) concentrations in sample 1, 2, and 3. All values are represented in mg L^{-1}. When there were less than 5 reported values for a given analyte, summary statistics were not calculable (n.c.). When there were only 5 or 6 reported values submitted, summary statistics are noted with an asterisk (*). A Grubbs test was also performed on analytes with 5 or more reported values to remove any outliers[58]

	Sample 1			Sample 2			Sample 3		
Analyte	MPV	Q_1–Q_3	F	MPV	Q_1–Q_3	F	MPV	Q_1–Q_3	F
Ni	0.01*	0.01–0.35*	0.25*	0.03*	0.03–0.14*	0.08*	0.03*	0.03–0.17*	0.11*
Ni minus outliers	0.01*	0.01–0.35*	0.25*	0.03*	0.03*	0.00*	0.03*	0.030*	0.00*
Cu	n.c.	n.c.	n.c.	0.26*	0.12–0.69*	0.42*	1.53	1.34–1.92	0.43
Cu minus outliers	n.c.	n.c.	n.c.	0.26*	0.12–0.69*	0.42*	1.53	1.34–1.92	0.43
Zn	0.16*	0.11–0.36*	0.19*	0.33	0.18–0.55	0.27	1.86	1.43–1.97	0.41
Zn minus outliers	0.13*	0.10–0.19*	0.07*	0.28	0.16–0.35	0.14	1.83	1.36–1.93	0.42
As	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	0.07*	0.06–5.10*	3.75*
As minus outliers	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	0.07*	0.06–0.10*	0.03*
Pb	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	0.21	0.20–0.45	0.18
Pb minus outliers	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	0.20	0.20–0.21	0.01

are within the 25th to 75th percentile concentrations for Appalachian brines (Table S2†). However, often greater than 50% of the participating labs were unable to measure detectable concentrations within the samples (Fig. 3). Trace metal(loid) analyses are often required for certificates of analysis of O&G wastewaters, but there are no Federal trace metal(loid) standards that limit O&G wastewater disposal. Therefore, trace metal(loid) concentrations in O&G wastewaters are often compared to the drinking water standards.[22] Of the analyzed trace metal(loid)s, the most important to detect are Cr, Cu, As, and Pb since they have primary drinking water standards of 0.1 mg L^{-1}, 1.3 mg L^{-1}, 0.01 mg L^{-1}, and 0.015 mg L^{-1}, respectively. While all the reported instrument detection limits (IDL's) for labs using ICP-MS were below these standards, the labs diluted the samples 10 to 1000 times to reduce potential matrix effects from analyzing the high salinity brines, resulting in method detection limits (MDLs) (*e.g.*, dilution factor times instrument detection limit) that were sometimes greater than the drinking water standards. Methods other than dilution, such as resins or chelating agents, are often used to remove trace metals from high-salinity solutions and increase method detection limits.[59] However, these methods are not necessary if the method detection limits for analyzing O&G wastewaters are at or below the regulatory standards. ICP-MS MDLs for these trace metal(loid)s were 0.05 to 0.6 mg L^{-1} for Cr, 0.01 to 2.76 mg L^{-1} for Cu, 0.01 to 0.1 mg L^{-1} for As, and 0.01 to 0.06 mg L^{-1} for Pb. Therefore, the MDLs were less than one-to-six times above the drinking water standard for Cr, less than one-to-two times above for Cu, one-to-ten times above for As, and one-to-seven times above for Pb. In other words, all labs were able to achieve MDLs that were close to the primary drinking water standards; the concentrations in the O&G wastewaters were simply low and challenging to detect after the samples were diluted.

Only samples that had more than 0.2 mg L^{-1} of Pb or 1.5 mg L^{-1} Cu were detectable by more than 50% of labs. Of the reported values for Pb in sample 3, five were of acceptable quality while the other two values reported by labs using XRF or ICP-OES were determined to be of questionable or unacceptable quality. The lab using ICP-OES performed no sample dilution. Therefore, matrix interferences from the high salinity wastewater could have influenced their reported Pb concentrations.[26] All the reported values with acceptable quality were by labs using ICP-MS with measured Pb concentrations ranging from 0.2 mg L^{-1} to 0.22 mg L^{-1}, approximately 10 times above the drinking water standard. Pb measurements by ICP-MS were accurate, only deviating ±5% from the MPV (Fig. 4). In comparison, other methods that produced questionable or unacceptable quality values for sample 3 (*i.e.*, XRF and ICP-OES) measured Pb concentrations that were 200 to 11 000% different than the MPV. Therefore, we strongly encourage using ICP-MS for Pb analyses of O&G wastewaters. This method might be limited by MDLs, but appears to be accurate among the five labs using ICP-MS at concentrations approximately 10 times above the drinking water standard. Due to the low number of measured Pb values in other samples, we could not assess the data quality and performance at lower Pb concentrations.

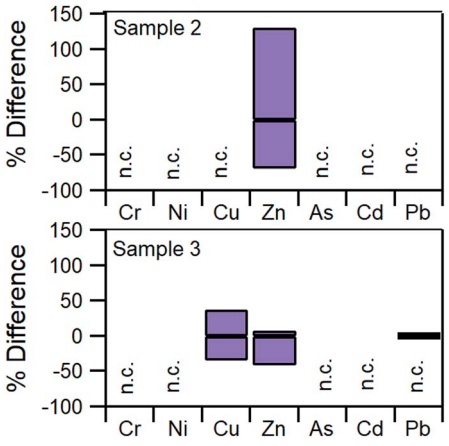

Fig. 4 Range in accuracy of reported values with acceptable quality for trace metal(loid)s based on comparisons to the MPV. No accuracy calculations were performed for sample 1 due to the low number of detectable concentrations. Other metal(loid)s where statistics were not calculable (n.c.) due to the low number of detectable values ($n < 7$) are shown for O&G wastewater samples 2 and 3.

Cu was the only other metal on the EPA's list of metals in drinking water that had a sufficient number of reported values to assess the data quality. All of the reported Cu values in sample 3 were determined to be of acceptable quality with concentrations ranging from 1.0 to 2.1 mg L^{-1}; values that are close to the EPA standard for drinking water quality (1.3 mg L^{-1}). These measurements were also relatively accurate, ranging from ±40% difference in comparison to the MPV (Fig. 4). In other samples with Cu concentrations less than 1.5 mg L^{-1}, there was a high amount of variability with $F_{\text{psuedosigma}}$ often greater than the median value (Table 2).

A significant amount of variability was observed in reported values for all other trace metal(loid)s that could be related to the methods used by a few participating labs. For many of the trace metal(loid)s, less than seven measured values were reported, thus limiting our ability to use the non-parametric statistics method (*i.e.*, the *z*-score method by Hoaglin *et al.* (1983) and in USGS inter-laboratory comparisons)[43,44] to identify unacceptable or questionable quality data. Therefore, the Grubbs statistical test for identifying outliers[58] was performed on analytes with five or more detectable values to determine if there were any statistically significant outliers ($p < 0.05$) in the trace metal data. When outliers were detected, the MPV, Q_1 to Q_3, and $F_{\text{psuedosigma}}$ values were recalculated (Table 2). For all trace metal(loid)s with five or more measured values, 10 outliers were identified out of the 66 total values reported for trace metal(loid)s. All outliers came from results submitted by four labs who used ICP-OES, XRF, NAA, or ICP-MS. When compared to the total number of trace metal(loid) values determined by each method, 57% of the data submitted by XRF (4 outliers out of 7 measured values), 50% of the data submitted by ICP-OES (3 outliers out of 6 measured values), and 33% of the data submitted by NAA methods (1 outlier out of 3 measured values) were outliers. For NAA, both reported Zn values were

acceptable, but the single As value was not. These NAA results are consistent with the previously identified trend of longer-lived activated isotopes $\left({}^{65}\mathrm{Zn},\ t_{\frac{1}{2}} = 243.93\ \mathrm{days}\right)$ providing more accurate data than shorter-lived activated isotopes $\left({}^{76}\mathrm{As},\ t_{\frac{1}{2}} = 26.24\ \mathrm{hours}\right)$, as the longer-lived isotopes can be measured after the decay of ^{24}Na. In contrast, less than 4% of the data (2 out of 53) submitted by ICP-MS were considered outliers. After removing these outliers, the recalculated $Q_1 - Q_3$ values became smaller and the $F_{\mathrm{psuedosigma}}$ values were reduced to below the median values (Table 2).

Removing all ICP-OES, XRF, and NAA data from the measured values submitted for sample 3 influenced interpretations of the submitted data. Therefore, we performed additional calculations for sample 3 where all the reported values of Ni, Cu, Zn, As, and Pb by ICP-MS were compared to the median values submitted by ICP-MS. After making these adjustments, the % differences from the median were −5% to 30% for Ni, −34 to 38% for Cu, −30% to 65% for Zn, −37% to 9% for As, and −1% to 9% for Pb. While we acknowledge that this is not a standard method for statistical analyses, the example simply illustrates that after excluding methods other than ICP-MS, most of the measured values deviated by ±40% from the median values. Similar % differences were reported for acceptable quality data in recent inter-laboratory comparisons by the USGS (*e.g.*, up to 30% difference for trace metal(loid)s).[44] While the high percentage of outliers in NAA, ICP-OES, or XRF could be attributed to lab protocols for each technique, we encourage using ICP-MS for measuring trace metals in O&G wastewaters as there is some evidence to suggest that ICP-MS measurements are accurate to within approximately ±40%.

Analyzing trace metal concentrations in O&G wastewaters requires a dilution factor that is enough to reduce potential matrix interferences without diluting analytes below their method detection limits. Results from this inter-laboratory comparison suggest that most labs using ICP-MS can detect metal(loid)s on the EPA list of regulated metals in drinking water at concentrations as low as 1 to 10 times above the primary standards. For instance, labs using ICP-MS were able to measure Cu, As, and Pb concentrations to within ±40% difference when the median values for these analytes were 1.5 mg L^{-1}, 0.06 mg L^{-1}, and 0.2 mg L^{-1}, respectively. Many labs struggled to report values below these concentrations. From a regulatory perspective, the question then becomes what are the method detection limits and accuracy that are needed for trace metal determinations in O&G wastewaters. Additionally, how necessary are these measurements since the majority of these measurements appear to be below detection limits that are above the standards set for trace metal concentrations in drinking water. If the goal of trace metal(loid) analyses is to only identify wastewaters that may have trace concentrations approximately 1 to 100 s of times above the drinking water standard, then simply diluting the wastewaters and analyzing by ICP-MS methods can result in accurate measurements (to within ±40% from the true value). If there is a need to measure lower concentrations for regulatory purposes or to understand trace metal geochemistry, then other methods that use resins or chelating agents to concentrate these metals are likely required.[60]

Radium measurements in liquids

Participating labs ($n = 11$) analyzed the O&G wastewaters for radium activity using a diversity of methods, including gamma ray spectroscopy, beta particle spectroscopy, Rn emanation counting in a scintillation cell, and alpha particle spectroscopy. A summary table with each of the methods used is included in the ESI (Table S5†). Gamma spectroscopy analyses were performed by the majority of the labs (70%) at geometries consistent with internal standards or certified reference materials. A common method for gamma spectroscopy analyses was to seal the samples in Marinelli beakers or polypropylene containers for 21 days to allow the ingrowth of ^{226}Ra daughter products (^{214}Pb or ^{214}Bi) that were measured at 295.2 keV, 351.9 keV, or 609.3 keV. In some cases, labs also analyzed the ^{226}Ra without ingrowth by direct measurements at 186.2 keV. One lab (Lab 7b; Table S5†) also co-precipitated ^{226}Ra from the wastewaters along with a ^{133}Ba tracer to estimate Ra recoveries prior to analysis by gamma spectroscopy. Complete details of the method were not reported but similar methods have been reported previously.[61] This same lab also measured Ra directly in the samples using gamma spectroscopy (Lab 7a; Table S5†).

Two labs used modified versions of EPA methods to pre-concentrate radium from the samples before analyses by alpha particle spectroscopy, Rn emanation counting in a scintillation cell, or beta particle spectroscopy (*e.g.*, EPA methods 903.0, 903.1, and 904.0, respectively). One lab added a ^{225}Ra tracer to the samples and then pre-concentrated radium using manganese oxide (MnO_2) and a Diphonix resin. Radioactivity measurements were performed by alpha spectrometry and the ^{226}Ra activity was corrected for chemical yield based on the observed activity of the alpha peak at 7.07 MeV (^{217}At, a progeny of ^{225}Ra). Complete details of the method were not provided by the lab but similar methods have been included elsewhere.[38] Another lab used co-precipitation methods to remove and concentrate ^{226}Ra from the samples according to EPA method 903.1. Radium was co-precipitated with barium-sulfate and the precipitate was then dissolved with ethylenediaminetetraacetic acid (EDTA) and stored for ingrowth of ^{222}Rn. ^{222}Rn alpha activity measured by scintillation counting was used to determine the ^{226}Ra activity. These two labs also precipitated ^{228}Ra with barium and lead sulfate according to EPA method 904.0. Lead sulfate precipitates were re-digested with EDTA and precipitated with yttrium oxalate, which was then purified, and transferred to a planchet for gas proportional counting of ^{228}Ac, a daughter of ^{228}Ra. One lab also noted that sub-aliquots of the dissolved precipitate were saved to determine the barium yield and estimate radium recovery from the sample.

All but one of the participating labs were able to report detectable Ra concentrations in the three oil and gas wastewaters (Fig. 5). The only method that reported below detectable concentrations was NAA; Ra is not considered a detectable element using NAA. The rest of the values reported had ^{226}Ra and ^{228}Ra activities that were within the 25th to 75th percentiles

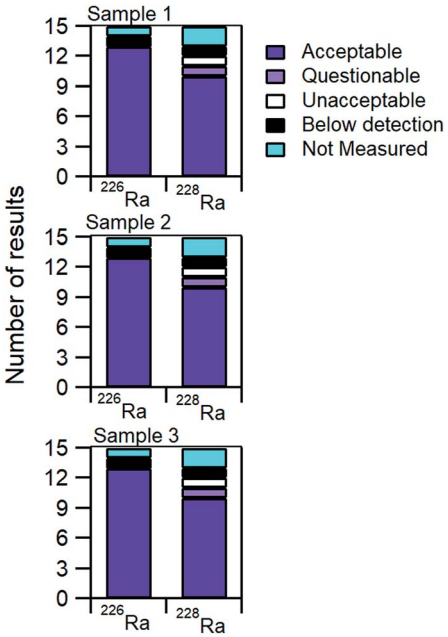

Fig. 5 Data quality for Ra concentrations reported in O&G wastewater samples 1, 2, and 3. Acceptable, questionable, and unacceptable quality were based on *z*-score calculations when the number of values were ≥7 for a given analyte.

for O&G wastewaters from the Appalachian Basin and were generally of acceptable quality (Table 3 and Fig. 5); all ^{226}Ra results were considered to be of acceptable quality while one ^{228}Ra value was considered to be of questionable quality along with another value that was of unacceptable quality. Both ^{228}Ra values that were of questionable or unacceptable quality were from gamma ray spectroscopy methods. Due to the large number of other acceptable quality analyses ($n = 7$) by gamma ray spectroscopy methods, the unacceptable or questionable Ra measurements do not appear to be a result of using gamma ray spectroscopy and could instead be attributed to lab-specific methods or other potential sources of bias.

Results from this inter-laboratory comparison suggest that reported Ra activities in O&G wastewaters could be within ±50% of the MPV (Fig. 6). Comparisons of the reported values to the MPV for radium activity in the three samples suggest that there is likely more inaccuracy in ^{226}Ra measurements than ^{228}Ra measurements, as ^{226}Ra values were approximately ±50% from the MPV while ^{228}Ra values were approximately ±30% from the MPV. As a comparison, ±20% accuracy has been estimated for ^{226}Ra in drinking water assessments.[62] In another study, up to ±60% accuracy for ^{226}Ra and ±20% for ^{228}Ra were reported in seawater samples.[63]

The differences in ^{226}Ra and ^{228}Ra activities measured by labs also influenced the Ra isotope ratios. The 25th to 75th percentile ratios for ^{228}Ra/^{226}Ra ranged from 0.8–1.5 in sample 1, 0.8–1.4 in sample 2, and 1.4–2.4 in sample 3 (Table 3). As a comparison, ^{228}Ra/^{226}Ra ratios for all produced waters from the Appalachian Basin can range from 0 to 4.[64] These ratios are often used to fingerprint wastewaters produced from unconventional shale reservoirs compared to conventional oil and gas reservoirs as the higher ^{238}U (parent isotope for ^{226}Ra) concentrations in organic-rich shales relative to conventional sandstone formations can result in low ^{228}Ra/^{226}Ra ratios (*e.g.*, median value for Marcellus Shale is 0.12)[57] that are traceable in suspected contamination events.[7,65] None of the wastewaters analyzed in this study were from O&G wells drilled into the Marcellus Shale, which was also reflective of the higher ^{228}Ra/^{226}Ra ratios (*e.g.*, all MPVs greater than 0.9) measured by the participating labs. The range in ^{228}Ra/^{226}Ra ratios reported by the labs did not influence the ability of this tracer to confirm that the fluids were not from the Marcellus Shale. However, there could be instances where labs that under-reported ^{226}Ra and over-reported ^{228}Ra activities (*e.g.*, Lab 4, Lab 12, and Lab 14) in the three samples could measure higher ^{228}Ra/^{226}Ra activities in a Marcellus Shale wastewater, which could be interpreted as fluids from conventional oil and gas reservoirs. This variability in ^{228}Ra/^{226}Ra ratios and radium activities could have implications for how wastewaters are identified or managed and it is therefore important to determine why these inaccuracies exist.

There are several factors that could influence the variability in the reported ^{226}Ra activities including (1) Rn leakage, (2) gamma photon attenuation, or (3) calibration inconsistencies.[37,40–42] Rn diffusion through storage containers and inconsistent preparation procedures between samples and standards can result in inaccurate measurements of ^{226}Ra daughter products.[40] Potential concerns with losses of daughter products can be resolved by measuring ^{226}Ra directly at 186 keV with gamma ray spectroscopy or at 4.8 MeV using alpha particle spectroscopy. In this study, reported values by labs using either of these methods were compared to determine if these indirect or direct counting techniques influenced the ^{226}Ra activities. However, there was no consistency in the reported Ra activities by labs using either of these methods. For instance, Lab 13 measured ^{226}Ra activities using daughter products and had average *z*-scores of −1.24 (−45% from MPV) for the three O&G wastewaters, while Lab 3 also measured ^{226}Ra using daughter products but had average *z*-scores of 0.67 (24% from MPV). In

Table 3 The most probable value (MPV), 25th percentile (Q_1), 75th percentile (Q_3), and $F_{psuedosigma}$ (F) for radium activities and isotope ratios in O&G wastewater samples 1, 2, and 3. All values are represented in pCi L^{-1} except ^{228}Ra/^{226}Ra (dimensionless)

	Sample 1			Sample 2			Sample 3		
Analyte	MPV	Q_1–Q_3	F	MPV	Q_1–Q_3	F	MPV	Q_1–Q_3	F
^{226}Ra	676	513–916	299	1420	1170–1840	497	526	425–659	173
^{228}Ra	722	616–780	122	1520	1280–1630	256	928	765–998	173
^{228}Ra/^{226}Ra	0.86	0.75–1.39	0.47	0.82	0.74–1.45	0.52	1.41	1.32–2.17	0.63

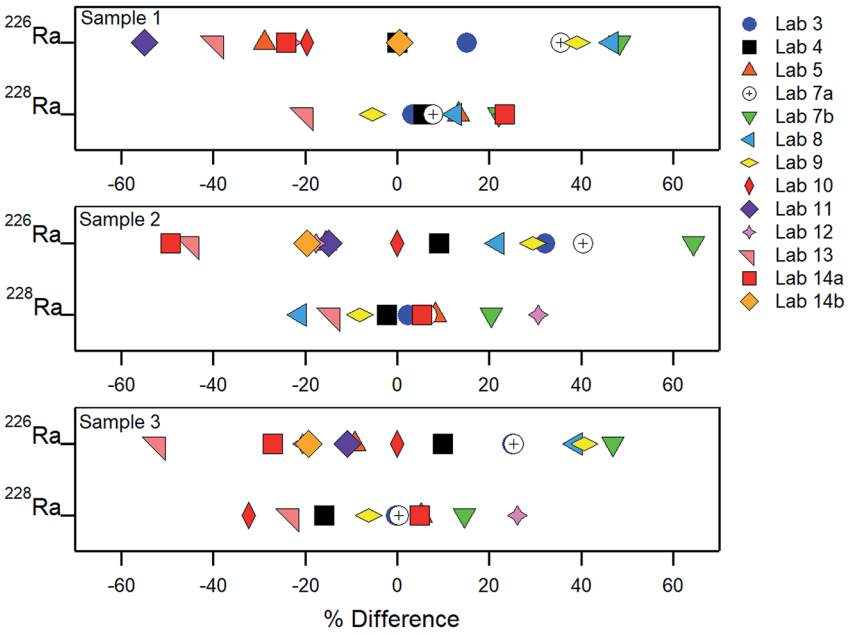

Fig. 6 The % difference of measured Ra activities in O&G wastewater samples 1, 2, and 3 by individual labs based on comparisons to the MPV. A summarized description of each lab's methods is included in Table S5.†

other words, both labs used similar methods but values reported by Lab 3 were often two times higher than the values reported by Lab 13. Interestingly, labs that measured ^{226}Ra directly also showed significant variability despite being unaffected by potential biases from Rn leakage. Among the labs that used direct measurements, average *z*-scores were −0.5 (−20% from MPV) for Lab 11 and 14b, 0.2 (∼5% from MPV) for Lab 3, and 0.9 for Lab 7a (34% from MPV). Because these *z*-scores span almost the entire range of calculated values, it does not appear that indirect *vs.* direct counting methods had a significant influence on the accuracy of the results. However, an inter-laboratory comparison performed with a greater number of laboratories could examine this possibility with greater statistical certainty.

Other potential sources of bias could occur by not accounting for photon attenuation in samples relative to the O&G wastewaters.[41,42] Specifically, the attenuation of photons by solutions with different densities or chemical matrices relative to standard solutions can result in negative bias (*i.e.*, under-reporting of Ra activities). While attenuation effects are well known in the literature, they are often unaccounted for in O&G wastewaters.[40,41] In the current study, only one lab (Lab 7a) accounted for photon attenuation by using a high-salinity matrix-matched radium standard to calibrate gamma ray spectroscopy equipment. Additionally, other wet-chemical methods used by labs 8 and 9 were not affected by attenuation biases since Ra was separated from solution prior to analysis. When grouped together, these labs (Labs 7a, 8, and 9) consistently reported ^{226}Ra activities that were 20 to 50% higher than the MPV. It is possible that these labs are closer to the true ^{226}Ra activity of the wastewaters as they are likely unaffected by attenuation bias or bias from Rn leakage. However, this is uncertain as other methods by Lab 3 and Lab 7b that were likely influenced by these potential sources of bias also over-reported Ra activities by >20%.

Regardless of the source and magnitude of these potential sources of bias, they appear to have a consistent influence on the Ra activities reported by individual labs in this inter-laboratory comparison. This is supported by the calculated *z*-scores for each of the labs which indicated that if a lab reported high or low activity for one of the samples, they reported high or low activity for all of the samples. For instance, calculated *z*-scores for Lab 13 were −0.9 (−39% from MPV), −1.3 (−44% from MPV), and −1.5 (−52% from MPV) for samples 1, 2, and 3 respectively. In other words, the similar *z*-scores for all samples analyzed by individual labs suggests that lab methods were precise but inaccurate. The precision of the labs is encouraging in suggesting that the inaccuracies in reported ^{226}Ra activities could be resolved by (1) confirming that the standards used for calibrating equipment are accurate, (2) ensuring consistent Rn entrapment between standards and samples, and (3) accounting for potential attenuation differences in standards and samples. However, future work is needed to identify which of these factors has the most impact on the reported activities in O&G wastewaters. We recommend that a high-salinity solution with certified Ra activities be developed (*e.g.*, NIST standard) to help alleviate the potential sources of bias from attenuation. Labs could also correct for potential negative bias from attenuation by making their own high-salinity, matrix-matched Ra standards. We also recommend that labs measuring ^{226}Ra activities in O&G wastewaters by ^{214}Bi or ^{214}Pb should perform simple quality control metrics such as verifying potential bias from Rn leakages by confirming that measurements using 186 keV or 352 keV, 609 keV, *etc.* are comparable.

Radium measurements in solids

Most of the labs (9 of 10) measured radioactivity in the solid samples by gamma spectroscopy. Of these nine labs, eight labs directly measured radioactivity without chemically separating radium from the solids, *i.e.*, radium activities were directly measured on the solids as received. One lab did not describe their sample preparation, but stated that they performed direct measurements using gamma spectroscopy. Because the study was anonymous, only the sample preparation procedures described when the data was submitted could be used for data interpretations. Radioactivity was determined in varying geometries that were often incubated for >21 days prior to analysis. However, only two labs reported performing a self-attenuation correction based on the Cutshall method or with any other attenuation method.[42,66,67] ^{226}Ra activity was often determined based on the average of the daughter products (^{214}Pb at 295.2 keV and 351.9 keV, ^{214}Bi at 609.3 keV) but also directly at 186.2 keV with a correction factor. ^{228}Ra activity was determined based on its daughter product activity, ^{228}Ac at 911.2 keV or at 463 keV. Detector efficiencies were determined using various standards, including ores from the Canadian Certified Reference Materials Project (CCRMP) (BL4a ore, DL1a ore, BL5 ore, and Oka2 ore), and other traceable standards (IAEA-385 and NIST 4353a).

One lab did not perform their analysis by gamma spectroscopy. Instead, they digested 0.25–0.5 grams of solid using nitric acid, hydrogen peroxide, and hydrochloric acid according to EPA method 3050B. Thereafter, ^{228}Ra was pre-concentrated with barium/lead sulfate and then purified by precipitation from EDTA solution. After an ingrowth period for ^{228}Ac from ^{228}Ra, yttrium oxalate carried ^{228}Ac, which was then purified, and measured for beta activity using a gas-flow proportional counting system according to EPA method 904.0. Likewise, ^{226}Ra was pre-concentrated with barium sulfate, sealed for ^{222}Rn ingrowth, after which the ^{222}Rn alpha activity was determined using alpha spectrometry (EPA method 903.1). A summary table with each of the methods used for determining the radium activities in the solids is included in the ESI (Table S6†).

Table 4 The most probable value (MPV), 25th percentile (Q_1), 75th percentile (Q_3), and $F_{psuedosigma}$ (F) for Ra activities and isotope ratios in solid samples 1, 2, 3, and 4. All values are represented as pCi gram^{-1} except ^{228}Ra/^{226}Ra (dimensionless)

Solid sample	Analyte	MPV	Q_1–Q_3	F
SS1	^{226}Ra	1.82	1.67–1.97	0.22
	^{228}Ra	1.04	0.97–1.19	0.16
	^{228}Ra/^{226}Ra	0.59	0.53–0.66	0.09
SS2	^{226}Ra	10.3	10.2–11.8	1.21
	^{228}Ra	0.55	0.50–0.65	0.10
	^{228}Ra/^{226}Ra	0.05	0.05–0.06	0.01
SS3	^{226}Ra	6.50	6.20–7.22	0.75
	^{228}Ra	1.18	1.16–1.31	0.11
	^{228}Ra/^{226}Ra	0.19	0.16–0.21	0.04
SS4	^{226}Ra	3.00	2.95–3.36	0.30
	^{228}Ra	1.09	1.03–1.25	0.17
	^{228}Ra/^{226}Ra	0.36	0.33–0.40	0.05

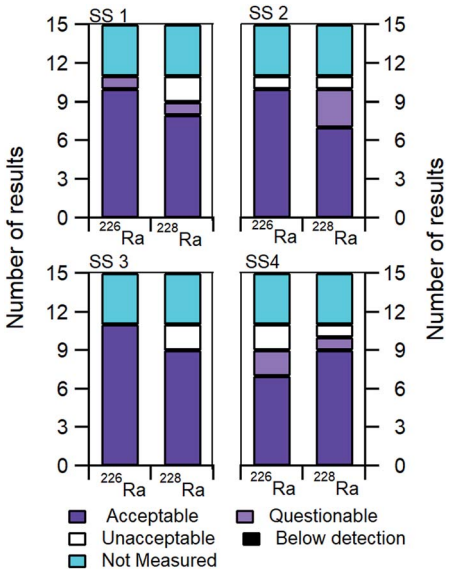

Fig. 7 Data quality for Ra activities reported in solid samples (SS) 1, 2, 3, and 4. Acceptable, questionable, and unacceptable designations were based on z-score calculations when the number of values were ≥7 for a given analyte.

All labs reported measurable activities of ^{226}Ra and ^{228}Ra in the solid samples (Table 4) that were generally of acceptable quality (Fig. 7). Ra data quality was comparable to a previous inter-laboratory comparison performed by the International Atomic Energy Agency (IAEA) on a sea sediment.[68] In our study, 14% (6 of 44) of the reported ^{226}Ra values were questionable or unacceptable which compares well to 18% from the IAEA study; while 25% (11 of 44) of the reported ^{228}Ra values were questionable or unacceptable, compared to 56.5% from the IAEA study.[68]

All ^{226}Ra activities that were questionable or unacceptable were determined by gamma spectroscopy methods; three of these analyses were performed with 2 hours of counting time (and two of these analyses were performed in an unknown geometry), while the other three analyses were counted for over 16 hours. It is likely that these questionable or unacceptable measurements were because of lab-specific methods (*i.e.*, sample preparation, counting time, and efficiency calibration), and not because of the use of gamma spectroscopy. For ^{228}Ra, eight of the eleven questionable or unacceptable data were determined by gamma spectroscopy. The other three were determined by beta counting after chemical separation. Amongst the questionable or unacceptable data determined by gamma spectroscopy, six analyses were likely performed after short counting times (<24 hours).

The results from this inter-laboratory comparison suggest that the reported Ra activities of O&G impacted solids could be within ±20% from the MPV (Fig. 8). Variations in the reported Ra measurements in the solids could be attributed to a number of factors, including (1) sample geometry (fill height), (2) unintentional differences in Rn sealing between samples and

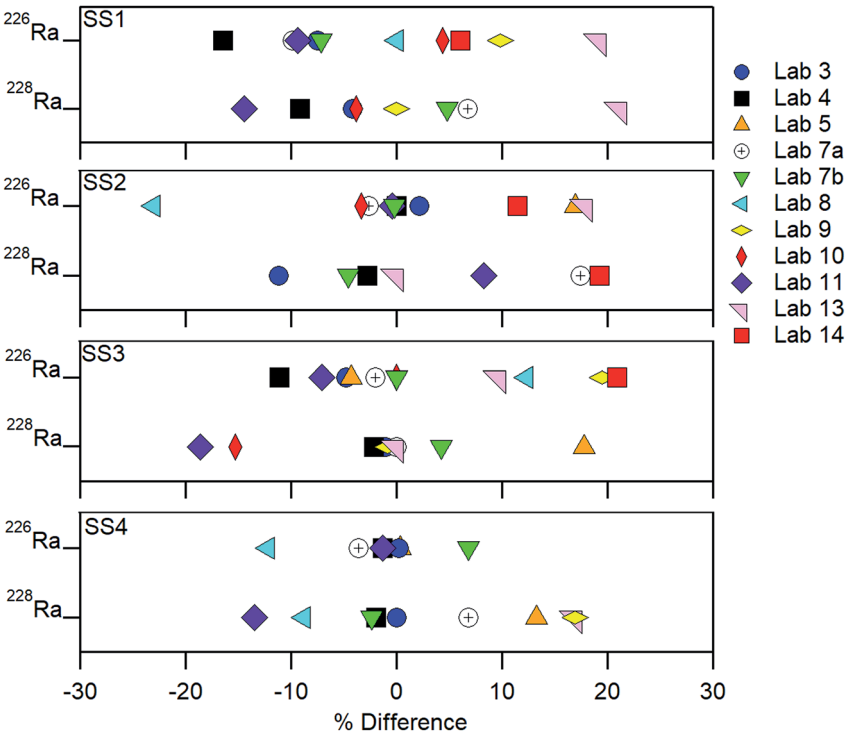

Fig. 8 Range in the % difference of reported radium activities in solid samples (SS) 1, 2, 3, and 4 with acceptable quality based on comparisons to the MPV.

standards, (3) insufficient counting time, and (4) sample attenuation.[42,67,69] All the reported ^{226}Ra activities in solid samples SS1 and SS3 were of acceptable or questionable quality. SS1 had the lowest activity, while SS2 had the highest activity. Yet SS2 and SS4 both had reported values that were unacceptable. There was therefore no reason to believe that the quality of the data was influenced by the activity of the samples. Furthermore, the densities and matrix/chemical composition of these solids were different, yet analysis of the *z*-scores showed no systematic influence on the reported activities by sample type. Some labs over-estimated the radium activities in one solid sample, but under-estimated it in another sample. As such, it was difficult to conclude if the questionable or unacceptable data were solely due to density and matrix differences. However, large % differences in the reported activities by labs that did not account for density or potential matrix differences with attenuation corrections suggest that this was likely still an issue.

As with gamma spectroscopy measurements of liquid samples, another potential cause of discrepancy could be whether Ra activity was determined directly at 186 keV, or indirectly from the daughter products (^{214}Pb or ^{214}Bi). Direct measurement at 186 keV can result in erroneous data, if there is U in the sample, as the gamma decay of ^{235}U (185.7 keV) interferes with ^{226}Ra measurements at 186.2 keV. An interference correction must be performed if this is the case. If the daughter products are used instead, then improper sealing of counting vessels will lead to escape of Rn gas, which will result in inaccurate measurements of ^{226}Ra decay products.[37]

Alpha spectrometry following chemical separation of Ra produced data of acceptable quality for ^{226}Ra; however, 3 out of 4 measurements for ^{228}Ra using beta particle counting were of unacceptable quality. This suggested that beta counting by the gas-flow proportional counting system following chemical separation was not a reliable method for determining the ^{228}Ra activities of the solids.

Close inspection of the *z*-scores allows us to identify methods and labs that produced data of consistently high quality. These labs reported values with low *z*-scores, indicating that the measured activities were likely accurate, and none of the reported values were rejected across the four solid samples. We were able to identify that for reliable Ra measurements, gamma spectroscopy produced the most accurate results. In addition to this, labs that used ores from the CCRMP reported values that were of acceptable quality. The labs, Lab 3 and Lab 7, that also accounted for attenuation using a point-source correction by the Cutshall technique, produced the highest quality data. When these methods were used, the reported Ra activities were often within $<\pm 5\%$ of the MPV. We therefore recommend gamma spectroscopy methods that incorporate certified Ra standards, such as the ores from CCRMP, and account for the self-attenuation in solid samples that result from density and matrix differences between the calibration standard and the unknown sample. Furthermore, we recommend longer counting times for samples with activities close to environmental background (>24 hours), and a close attention to the sample preparation concerning the geometry, fill height, and Rn gas entrapment.

Limitations of the inter-laboratory comparison

There were several limitations of the current study that the authors would like to acknowledge. First, none of the labs were required to analyze samples multiple times. Therefore, there was no way to adequately assess how precise individual labs were in analyzing the O&G wastewaters. We also explored several methods for analyzing the precision of the data; however, these methods are heavily dependent on how outliers are excluded from the data. Therefore, we relied on comparisons to the median (*i.e.*, most probable value) to show how much agreement there was among the reported values. Using the median as the MPV could influence our interpretations of the accuracy of these measurements; however, this is a viable statistical method that is commonly used in inter-laboratory studies.[44] Testing the accuracy of each lab's measurements could be resolved by requiring all labs to analyze certified standards for the analytes in this study but the availability and cost of these standards prevented this comparison. A well characterized check standard from the Spring 2018 USGS inter-laboratory study[70] was sent to participating labs for cation and anion analyses. However, not all of the labs analyzed the sample. Because most labs did not report concentrations for the USGS sample, results for these reference materials were not used to assess the accuracy of the labs. Another limitation of the study was that statistical comparisons between various methods were not possible due to the majority of labs performing one method of analysis. In some cases there were also not enough reported values to determine the accuracy of the measurements (*e.g.*, most of the trace metal(loid)s) using the MPV method. Other potential factors that could influence the results, such as dilution errors, were not explored but could be resolved by spiking internal standards into all samples sent out for inter-laboratory comparisons and requiring labs to measure analytes within the standard. Regardless of these limitations, there was relatively good agreement among the reported values and we were able to comment on the accuracy of many of the methods used for analyzing solid and liquid wastes from O&G development.

Conclusions and recommendations

Major cations, minor cations, and anions

The majority of laboratories that participated in this study reported values for major and minor cations and anions in the O&G wastewaters that were in good agreement with the MPVs. Accuracies for these cations and anions were similar to other inter-laboratory comparisons analyzing freshwaters. Depending on the detection limits of the analytical equipment, we recommend diluting samples approximately 10–1000 times before analysis on an ICP-OES, ICP-MS, or IC, and using internal standards to correct for potential matrix interferences along with check standards to verify calibration curves. Combined major and minor cation and anion chemistry data support the use of Sr/Ca and B/Cl^- ratios for tracing O&G wastewaters. However, the range in reported Cl^-/Br^- values in this inter-laboratory comparison indicate that geochemical interpretations using this ratio could have uncertainty and should be acknowledged when using data sets with Cl^-/Br^- ratios from multiple laboratories.

Trace metal(loid) measurements

In contrast to the major and minor cations, few reliable values were reported for trace metal(loid)s. The number of reported values were also limited by high method detection limits relative to the trace metal(loid) concentrations in the wastewaters. Reporting limits for trace metal(loid)s were often above or near drinking water standards, which could lead to difficulties regulating high-salinity oil and gas wastewaters based on trace metal concentrations.

Radium measurements in liquids

Most of the laboratories were able to report values for Ra activities in high-salinity brines, but values showed greater variability between laboratories than major and minor cations or anions. Compared to previous inter-laboratory studies of naturally occurring radioactivity in seawater and freshwater, the accuracy of reported values in this study were very similar, demonstrating that many participating laboratories using a variety of methods for O&G wastewater analyses can produce acceptable quality data. However, the range in values reported also suggests that individual laboratories are over-reporting or under-reporting Ra activities by ±50% likely due to calibration inconsistencies among labs, radon leakage, or self-attenuation. We recommend that a high-salinity brine Ra standard be developed to help eliminate these sources of bias.

Radium measurements in solids

Ra analyses of solid samples were more accurate than liquid measurements, deviating by ±20% from the MPV, but had less consistency in the % differences reported by individual labs; *i.e.*, labs over-estimated the Ra activities in one sample, but under-estimated it in other samples. Some of this variability could be minimized by longer counting times for samples with activities close to environmental background (>24 hours), correcting for gamma attenuation, and paying close attention to sample preparation procedures (*e.g.*, geometry, fill height, and radon gas entrapment).

Conflicts of interest

There are no competing financial interests.

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Supporting information for accuracy of methods for reporting inorganic element concentrations and radioactivity in oil and gas wastewaters from the Appalachian Basin, U.S. based on an inter-laboratory comparison

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Table S1. Methods used for cation and anion analyses. Numbers below each lab identification represents the different types of equipment used by individual labs including ICP-MS/MS (identified as 1), ICP-MS (2), Direct Plasma Spectrometry (3), ICP-OES (4), XRF (5), Neutron Activation (6), or Ion chromatography (7).

Analyte	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10	L11	L13	L13	L14	L15
Li	1	2		2	4	4	4	4	2	4		4		2	6
B	1			2	4	4		2	2	4		4		2	6
Na	1		7	3	4	4	4	4	2	4	5	4		4	6
K	1	2	7		4	4	4	4	2	4	5	4			6
Mg	1	2	7	3	4	4	4	4	2	4	5	4		4	6
Ca	1	2	7	3	4	4	4	4	4	4	5	4		4	6
Sr	1	2	7	3	4	4	4	4	2	4	5	4		4	6
Ba	1			3	4	4	4	2	2	4	5	4		2	6
Al	1			2	4	4		4	2	4		4		2	6
Fe	1	2		3	4	4	4	4	2	4	5	4		2	6
Mn	1	2		3	2	4	4	4	2		5	4		2	6
Cr	1	2		2	2	4		2	2		5	2	4	2	6
Ni	1	2		2	2	4		2	2	4	5	2	4		6
Cu	1	2		2	2			2	2		5	2	4	2	6
Zn	1	2		2	2	4		2	2	4	5	2	4	2	6
As	1	2			2	4		2	2		5	2	4	2	6
Cd	1	2		2	2			2	2		5	2	4	2	6
Pb	1			2	2	4		2	2		5	2	4	2	6
Cl	7	7		7	7	7		7	7	7	5	7		7	6
Br	1	7		7	7	7		7	7	7	5	7		7	6
SO4	7	7		7	7	7		7	7	7	5	7		7	6

Table S2. Chemistry of Appalachian Basin O&G wastewaters as reported in the United States Geological Survey's produced water database[1].

Analyte	Median	Q1	Q2
Br	841	327	1580
Cl	99600	51300	159000
SO4	115	20.3	337
Na	38900	22400	57500
K	840	221	1740
Mg	1920	871	3530
Ca	13600	5360	27800
Sr	813	175	1290
Ba	331	45.7	1130
Li	50.0	23.0	81.6
B	18.1	6.77	30.6
Al	0.80	0.25	4.00
Fe	45.0	9.48	131
Mn	11.7	3.00	41.0
Ni	0.15	0.03	0.40
Cu	0.23	0.04	0.25
Zn	0.80	0.12	2.00
As	0.10	0.05	0.10
Pb	0.03	0.02	0.03
226Ra	658	190	1780
228Ra	248	39.4	821

Table S3. Range in percent difference for various analytes in the most recent USGS inter-laboratory comparison for freshwaters[2]. The range in percent difference is based on reported data with acceptable quality (i.e., $z < 2$ or $z > -2$).

Element	Sample	Units	MPV	F	Acceptable quality concentration range	% difference
Br	M-226	mg/L	0.06	0.03	0 - 0.12	>±109
Cl	M-226	mg/L	26.2	0.96	24.3 – 28.1	±7.36
SO4	M-226	mg/L	14.2	0.45	13.3 – 15.1	±6.27
Na	T-233	mg/L	16	0.46	15.1 – 16.9	±5.70
K	T-233	mg/L	1.58	0.07	1.45 – 1.71	±8.48
Mg	T-233	mg/L	6.71	0.15	6.41 – 7.01	±4.53
Ca	T-233	mg/L	16.7	0.45	15.8 – 17.6	±5.33
Sr	T-233	µg/L	94	3.22	87.6 – 100	±6.85
Ba	T-233	µg/L	27.4	0.74	25.9 – 28.9	±5.41
Li	T-233	µg/L	2.57	0.03	2.52 – 2.62	±2.02
B	T-233	µg/L	22	1.56	18.9 – 25.1	±14.2
Al	T-233	µg/L	481	21.5	438 – 524	±8.94
Fe	T-233	µg/L	279	10.6	258 – 300	±7.60
Mn	T-233	µg/L	18.5	0.96	16.6 – 20.4	±10.3
Ni	T-233	µg/L	1.99	0.27	1.44 – 2.54	±27.5
Cu	T-233	µg/L	3.98	0.19	3.60 – 4.36	±9.60
Zn	T-233	µg/L	19.7	1.85	16.0 – 23.4	±18.8
As	T-233	µg/L	4.10	0.22	3.66 – 4.54	±10.7
Pb	T-233	µg/L	0.33	0.02	0.29 – 0.38	±12.6

Table S4. Elemental ratios (mass/mass) as measured by labs in this study that reported acceptable quality values (i.e., z score that was between -2 and 2 was considered acceptable quality). In instances where no ratios are reported for a lab, the reported values were either of unacceptable or questionable quality or they did not analyze one of the cations or anions needed for calculating the ratio. S1, S2, and S3 represent samples 1, 2, and 3.

	Cl/Br			Sr/Ca			B/Cl		
	Sample #			Sample #			Sample #		
LAB	S1	S2	S3	S1	S2	S3	S1	S2	S3
1	99.1	95.1	96		0.19	0.05		5.36E-05	8.60E-05
2	79.5	82.7	78.5						
3				0.22	0.19	0.05			
4	92.8		92.6	0.21	0.18	0.05	7.01E-05		9.76E-05
5	87.0	85.7	85.7		0.20	0.05			
7				0.23	0.19	0.05			
8	86.7	90.6	87.2	0.21	0.18	0.05	7.73E-05	6.09E-05	8.65E-05
9	105	75.4	86.6		0.17	0.04	7.72E-05	5.98E-05	8.57E-05
10				0.22	0.19				
11			90.4						
13	90.9	92.9		0.20	0.18	0.05	7.43E-05	7.01E-05	
14	87.7	95.9	100	0.22	0.19	0.05	7.47E-05	6.83E-05	8.71E-05

Table S5. Methods used for radium analyses in liquids.

Lab	Equipment	Sample prep	Measurement
Lab 3	Gamma Spectroscopy	Samples sealed in 55 mL polypropylene jars. Jar threads sealed with vacuum grease. >21 day storage	^{226}Ra (609 keV and 351 keV) and ^{228}Ra (911 keV)
Lab 4	Gamma Spectroscopy	>21 day storage. >48 hour counting time. Sealed in 2 oz sediment jar to prevent ^{222}Rn gas release.	^{226}Ra (186 keV) and ^{228}Ra (911 keV)
Lab 5	Gamma Spectroscopy	3 L of sample sealed in 4 L Marinelli beaker. 30 day storage.	^{226}Ra (weighted average of 609 Kev, 351 keV, 295 keV, and 242 keV), ^{228}Ra (911 keV)
Lab 7a	Gamma Spectroscopy	No sample prep. Direct counting in 125 mL geometry	^{226}Ra (186 keV) and ^{228} Ra (911 keV)
Lab 7b	Gamma Spectroscopy	Co-precipitation with barium sulfate. ^{133}Ba yield monitor. Precipitate filtered onto 47 mm filter and analyzed on gamma spec.	^{226}Ra (186 keV) and ^{228} Ra (911 keV)
Lab 8	Low-level proportional counters (^{228}Ra) and radon flask counters (^{226}Ra)	Co-precipitation with barium sulfate (^{226}Ra and ^{228}Ra). EPA methods 904.0 and 903.1	^{226} Ra (^{222}Radon scintillation counting) ^{228}Ra (^{228}Ac daughter counted with low background proportional counter)
Lab 9	Canberra LB5100 gas flow counter (^{228}Ra) and EG&G Ortec alpha detectors	Pre-concentrated with MnO_2 and traced with ^{225}Ra (^{226}Ra) and co-precipitation with barium sulfate (^{228}Ra)	^{226}Ra (alpha spectrometry) and ^{228}Ra (gas flow proportional counter)
Lab 10	Gamma Spectroscopy	Evaporation and analysis of 6 grams of solid.	^{226}Ra (186 keV) and ^{228}Ra (911 keV)
Lab 11	Gamma Spectroscopy	3.5 L of sample sealed in 4L Marinelli beaker for 21 days. EPA method 901.1.	Not reported
Lab 12	Gamma Spectroscopy	500 mL. 24 hour counting time.	^{226}Ra (186 keV) and ^{228}Ra (911 keV)
Lab 13	Gamma Spectroscopy	20 mL of sample sealed in liquid scintillation vial. EPA method 901.1. Counting time of 4-10 hours.	^{226}Ra (351 keV and 609 keV) and ^{228}Ra (911 keV)
Lab 14a	Gamma Spectroscopy	3 L of sample sealed in a 4 L Marinelli beaker. >21 day storage. Counting time of 3 to 18 hours.	^{226}Ra (609 keV), ^{228}Ra (911 keV)
Lab 14b	Gamma Spectroscopy	3 L of sample sealed in a 4 L Marinelli beaker. Direct counting with no storage. Counting time of 3 to 18 hours.	^{226}Ra (186 keV)
Lab 15	Neutron activation followed by gamma spectroscopy	Sample evaporation. Counting time of 3 to 18 hours.	Not reported

Table S6. Methods used for Radium analyses in solids.

Lab #	Method	Sample prep	Measurement
Lab 3	Gamma Spectroscopy	Samples were packed into 40 mL jars	Count time of 48 hours. Detector calibrated using Canadian Certified Reference Materials Project. Attenuation correction was performed using the Cutshall point-source technique[3]
Lab 4	Gamma Spectroscopy	Samples were packed in petri dishes and incubated (>21 days)	Count time of 24-48 hours. Detector calibrated using Canadian Certified Reference Materials Project
Lab 5	Gamma Spectroscopy	Samples were packed into 200 mL HDPE vials	Count time of 16.7 hours. Detector calibrated using NIST standards (Eckert and Ziegler)
Lab 7a	Gamma Spectroscopy	Samples were packed into petri dishes	Count time of 48 hours. Detector calibrated using Canadian Certified Reference Materials Project. ^{226}Ra (weighted average of 295, 352, 609 keV) and 463 keV for ^{228}Ra. Attenuation correction was performed using the Cutshall point-source technique[3]
Lab 7b	Gamma Spectroscopy	Samples were packed into petri dishes	Count time of 48 hours. Detector calibrated using Canadian Certified Reference Materials Project. ^{226}Ra at 186 keV and ^{228}Ra at 911 keV. Attenuation correction was performed using the Cutshall point-source technique[3]
Lab 8	Low-level proportional counters (^{228}Ra) and radon flask counters (^{226}Ra)	Digestion according to EPA 3050B. Final liquid volume of 100mL	Count time of 100 min. ^{226} Ra (^{222}Radon scintillation counting) ^{228}Ra (^{228}Ac daughter counted with low background proportional counter)
Lab 9	Gamma Spectroscopy	Not described	Count time of 120 min. Detector was calibrated with NIST traceable soil (500g geometry)
Lab 10	Gamma Spectroscopy	Samples were packed into petri dishes	Count time of 24 hours.
Lab 11	Gamma Spectroscopy	Samples were packed into 0.5L Marinelli beakers	Count time of 1,000 min.
Lab 13	Gamma Spectroscopy	Samples were packed into 0.5L Marinelli beakers	Count time of 2 hours. Detector calibrated using Eckert and Ziegler standards. ^{226}Ra at 186 keV, ^{228}Ra at 911 keV
Lab 14	Gamma Spectroscopy	Samples were packed in scintillation vials and incubated (>21 days)	Count time of 7-36 hours. Detector calibrated using Canadian Certified Reference Materials Project. ^{226}Ra by average of ^{214}Bi at 609.3 keV, ^{214}Pb at 295.2 keV and 351.9 keV; ^{228}Ra by ^{228}Ac at 911.2 keV

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