Application of ICP-OES for Evaluating Energy Extraction and Production Wastewater Discharge Impacts on Surface Waters in Western Pennsylvania

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Abstract

Oil and gas extraction and coal-fired electrical power generating stations produce wastewaters that are treated and discharged to rivers in Western Pennsylvania with public drinking water system (PDWS) intakes. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to quantify inorganic species in wastewater and river samples using a method based on EPA Method 200.7 rev4.4. A total of 53 emission lines from 30 elements (Al, As, B, Ba, Ca, Cd, Ce, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, Ti, Tl, V, and Zn) were investigated. Samples were prepared by microwave-assisted acid digestion using a mixture of 2% HNO_3 and 0.5% HCl. Lower interferences and better detection characteristics resulted in selection of alternative wavelengths for Al, As, Sb, Mg, Mo, and Na. Radial view measurements offered accurate determinations of Al, Ba, K, Li, Na, and Sr in high-brine samples. Spike recovery studies and analyses of reference materials showed 80–105% recoveries for most analytes. This method was used to quantify species in samples with high to low brine concentrations with method detection limits a factor of 2 below the maximum contaminant limit concentrations of national drinking water standards. Elements B, Ca, K, Li, Mg, Na, and Sr were identified as potential tracers for the sources impacting PDWS intakes. Usability of the ICP-OES derived data for factor analytic model applications was also demonstrated.

Keywords
Conventional and unconventional oil and natural gas wastewaters, electric power generating stations wastewaters, hydraulic fracturing, public drinking water intakes, inorganic elemental composition.

1. Introduction

Oil and gas production and coal-fired electric generation in Western Pennsylvania produce wastewater with elevated bromide concentrations and the discharge of high bromide wastewater to the Allegheny River increases bromide levels at public drinking water system (PDWS) intakes (States et al., 2013). There is evidence to suggest that elevated river bromide levels from oil and gas wastewater discharges may result in increased brominated disinfection byproducts in drinking water (States et al., 2013, Parker et al., 2014).

All of the unconventional wells and most of the conventional wells in Pennsylvania are hydraulically fractured (PA DEP 2014). Unconventional wells are drilled horizontally into low permeable shale formation below the base of the Elk Sandstone or its geologic equivalent and conventional vertical wells extract gas from sandstone (PA DEP 2014). Oil and gas extraction can produce large amounts of contaminated produced and flowback wastewater (Simon and Fleming, 2011; Fontenot et al., 2013; Veil, 2010; Abualfaraj et al., 2014). Wastewater from conventional and unconventional oil and gas (CUOG) extraction can contain inorganic salts, radioactive substances, heavy metals, and volatile organic substances originating from the producing formation, which require subsequent treatment and disposal or recycling (Vengosh et al., 2014; Keister, 2009; Balaba and Smart, 2012; Warner et al., 2013). Centralized wastewater treatment facilities (CWTFs) in Pennsylvania are designed to precipitate and filter heavy metals in CUOG wastewater, but total dissolved solids (TDS) still range from 70,000 to 90,000 mg/L in treated wastes discharged into surface waters (Ferrar et al., 2013). A recent study by Hladik et al. (2014) reports that outfalls from CWTFs that accept CUOG produced waters are a source of disinfection by-products to receiving streams in PA.

In Western Pennsylvania, both CWTFs and electric power generating stations discharge into the Allegheny River and its tributaries. Generating stations have multiple water contaminant sources including storm water runoff of coal and ash storage, cooling towers, and air pollution scrubber discharge (U.S. EPA, 2013; Thorneloe et al., 2010). The contaminants discharged from these sources include bromide, bioaccumulative metals (mercury, arsenic), sulfur and nitrogen compounds, and total dissolved solids (U.S. EPA, 2013; U.S. EPA, 2014).

For multi-elemental analysis of these high salt samples, ICP-MS is a preferred method due to its high sensitivity, and it has been used to quantify metals in CUOG produced waters (Johnson et al., 2008) and in drinking water wells near CUOG extraction sites (Fontenot et al., 2013). Nonetheless, analysis of high TDS samples by ICP-MS results in narrowing of sampler and skimmer cone orifices through salt deposition and eventual reduced measurement sensitivity requiring increased maintenance and instrument down time (Thomas, 2013). On the other hand, ICP-OES methodology can handle relatively high levels of TDS. The EPA has set guidelines for drinking water and wastewater analysis using ICP-OES Method 200.7 (U.S. EPA, 1994). Besides technical notes from instrument manufacturers (Chausseau and Lebouil, 2013; Jones, 2014), only a few publications have been found in our literature search that used ICP-OES for the analysis of CUOG wastewaters (Haluszczak et al., 2013; Ferrar et al., 2013). However, no article was found in our search that presented potential ICP-OES analytical challenges and methodological solutions for total recoverable elemental determinations in CUOG wastewaters that contains up to five times the salinity of contemporary ocean water.

This manuscript describes our efforts to optimize EPA Method 200.7 for total recoverable determination of inorganic elements in high-saline CUOG wastewaters. The optimized method was applied for the quantification of elements in water samples with varying levels of salinity, collected as part of the EPA's study of bromide sources and their contributions at river sampling locations and PDWS intakes (U.S. EPA, 2012a; U.S. EPA, 2014). Elemental signatures of treated and untreated CUOG wastewaters are presented and discussed. Baseline surface water characteristics of the Allegheny River and Blacklick Creek were also statistically characterized using the generated data.

2. Experimental methods

2.1 ICP-OES

Samples were analyzed using a PerkinElmer (PE; Sheldon, CT, USA) Optima 4300 DV ICP-OES instrument in conjunction with a PE AS93 Plus autosampler and PE WinLab32 software for ICP (version 3.0.1). Plasma optimization involved adjustment of the plasma power between 1300 and 1600 W while observing best signal strengths for Sc (0.1 ppm), Mn (1.0 ppm), K (5.0 ppm),

and Ba (0.1 ppm) in the continuous graphics window. Nebulizer flow was adjusted incrementally between 0.9 and 0.5 L/min to find an optimum setting. The torch was aligned using PE's automated Align view procedure. Sample and internal standard flow rates were set to 0.35 mL/min using a peristaltic pump. An internal standard mixing block (ESI, NE) was connected after sample solutions were pumped but before they entered the nebulizer. Optimized instrumental parameters used throughout this study are presented in Table 1.

All elements listed in EPA Method 200.7, with the exception of silver (Ag), beryllium (Be), and mercury (Hg), were included in the analysis method. Sulfur (S), which is not included in Method 200.7, was added to the analytical ICP method since it is an important species in coal-fired power generating wastewater. Measurement wavelengths, points per peak, and number of background correction points used for each wavelength are listed in Table 2. Some elements were viewed both axially (to attain better detection) and radially (to evaluate coexisting ion interferences). Alternate wavelengths were also investigated. The best measurement was chosen as the primary wavelength for reporting the analytical concentrations of each element based on sensitivity, dynamic range, and relative freedom from common spectral interferences.

2.2 Reagents and standards

Certified calibration standards (44CS1Y and 44CS1Z) from VHG Labs, Inc. (Manchester, NH, USA) produced specifically for the U.S. EPA 200.7 methodology were used to prepare working standards. Seven working standards were prepared and used to establish daily analytical calibrations. A certified quality control (QC) check standard (QCS-26-R) was purchased from High-Purity Standards (HPS; Charleston, SC, USA). Certified single-element standards from HPS were used to study spectral interferences. Yttrium (VHG Labs Inc.) at 2 mg/L was used as an internal standard. All reagents and standards were prepared in acid-cleaned (Landis and Keeler, 1997) PTFE bottles. An acid matrix composition of 2% (v/v) nitric acid (ultrapure grade, Fisher Scientific, USA) and 0.5% (v/v) hydrochloric acid (ultrapure grade, Sigma Aldrich) was maintained in all standards, QC checks, and samples.

National Institute of Standards and Technology (NIST) Standard Reference Materials (SRM) SRM1640a and SRM1643e, U.S. Geological Survey (USGS) Reference Water M-172, and HPS

CRM-TMDW were used as reference samples. ERA (Golden, CO, USA) certified waters (WatR ERA-500 and a custom mix) performance evaluation samples were treated as unknowns and analyzed along with the collected samples.

2.3 Quality control

U.S. EPA Method 200.7 requires that every laboratory establish its linear dynamic range (LDR) for each wavelength used and the method detection limit (MDL) for each analyte, as well as conduct a comprehensive spectral interferences study as part of its initial demonstration of capability. An average of MDLs, calculated from data collected over three nonconsecutive days, were used to categorize the elements that had concentrations above the MDL (Table 2). Method 200.7 defines LDR as the highest concentration at which an observed signal deviates by less than 10% from that extrapolated from lower standards. For the purpose of this study, however, a more restrictive definition of LDR as the highest calibration concentration was used. Minimum reporting limit (ML) concentration was set as the lower of either the lowest calibration standard or the lowest known concentration analyzed and determined within 15% accuracy. Single-element standards of all analytes were analyzed at levels of 10, 100, and 1000 mg/L to evaluate spectral interferences. Inter-element correction (IEC) factors were calculated and are summarized in Table 2.

Routine checks such as laboratory reagent blanks, laboratory-fortified blanks, instrument performance checks, continuing calibration verifications (CCVs), continuing calibration blank (CCB) verification solutions, spectral interference check solutions, and laboratory-fortified matrices were also performed during each analytical sequence per the quality assurance project plan (QAPP) (US EPA, 2012b). The type, purpose, and frequency of these checks and the criteria for acceptable data are summarized in Supporting Information (SI) Table S1.

2.4 Sample collection and preparation

Teledyne Isco (Lincoln, NE, USA) model 6712 computer-controlled automatic sequential water samplers simultaneously collected daily 800 mL composite river and CWTF samples along the Allegheny River and Blacklick to Kiskiminetas River System sampling sites within the designated study area (U.S. EPA, 2012b). In brief, daily river samples were collected for two

weeks during spring, summer, and fall of 2012 at sites upstream and downstream of a CWTF on both river systems. Outfall samples from the CWTFs, coal-fired electrical generating stations, and industrial sources were also collected to obtain profiles of species (U.S. EPA, 2012b).

Samples were prepared for ICP-OES analysis according to U.S. EPA Method 3015A, "Microwave Assisted Acid Digestion of Aqueous Samples and Extracts" (U.S. EPA, 2007). Ultrapure-grade acids were used throughout the study. All samples were acidified to 2% (v/v) nitric acid concentration and allowed to leach for 7 days. Following this passive leach, known aliquots of H_2O_2 and HCl were added to each sample to attain final solution concentrations of 0.05% (v/v) and 0.5% (v/v), respectively. Samples were then microwave digested using a CEM Corporation MARS 5000 system (Matthews, NC, USA) and MARS Xpress vessels at 170^{o}C for 35 min. After digestion, samples were vacuum filtered through pre-cleaned 0.45 µm cellulose nitrite membrane filters (Whatman #7184-004) into a 50 mL acid cleaned and dried polypropylene (PP) tube. Approximately 10 mL of the filtrate was decanted into a 15 mL acid cleaned and dried PP tube for ICP-OES analysis. All of the above mentioned total acid digestion (AD) sample preparation steps are shown in Figure 1A. Unless specified, concentration data discussed and presented in this manuscript are AD sample results. For the determination of filtered acid leach (AL) concentrations of elements in PDWS samples (n=76), a 50 mL aliquot was filtered prior to acidification, and steps shown in Figure 1B were followed.

A reagent blank solution of 2% HNO_3 and 0.5% HCl was prepared and used for sample dilutions. Calibrated pipettes (Eppendorf, Hauppauge, NY, USA) and analytical balances (Scout Pro SP202, Ohaus Corp., Parsippany, NJ, USA; Sartorius Genius ME 235P, Germany) were used for sample dilution. Typically, 0.5 mL of a sample (v1) was volumetrically transferred into a pre-weighed (wt1), labeled, and dried 15 mL PP tube. The tube was then weighed (wt2). Next, 9.5 mL of reagent blank (v2) was volumetrically transferred into the same sample tube, and it was weighed again (wt3). The gravimetric dilution factor was calculated as (wt3 – wt1) / (wt2 – wt1), and the volumetric dilution factor was calculated as (v2 + v1) / v1. Specific conductivity (hereinafter conductivity) of samples was determined using a Mettler Toledo (Columbus, OH) model S47-K meter equipped with an InLab731 probe.

3. Results and discussion

3.1 Measurement interferences

CUOG produced wastewaters from middle Devonian geological shale formations are relatively new sample matrices (Dresel and Rose, 2010), and thus required a thorough spectral interferences study. High concentrations of alkali and alkaline earth elements in the CUOG wastewaters and CWTF discharge presented particular challenges in axial view measurements. For instance, K (766.490 nm) concentrations were approximately 80% higher than in the radial measurements. Signal enhancements of atomic emission lines due to coexisting, easily ionizable elemental concentrations have been documented in the literature. Morishige and Kimura (2008), in their study of ionization interferences, found that the axial view was strongly affected when the first ionization potential of analytes or coexisting elements was below 6 eV. Since our experimental results exhibited similar findings, elements Al, Ba, K, Li, Na, and Sr were measured only in radial view.

The LDR of Ba was limited by the presence of sulfur (as sulfate), a behavior that is a common ion effect of sulfate (Vogel and Jeffery, 1989). The effect of sulfur matrix on Ba measurements was studied under our experimental conditions. Ba concentrations at two levels, 0.5 mg/L and 5.0 mg/L, were analyzed in the presence of sulfur concentrations ranging between 0 and 5000 mg/L. Study results showed salting out of Ba as $BaSO_4$ above 100 mg/L of sulfur (SI Figure S1). Major elements Na and Mg did not affect measurements of other elements up to the studied concentration of 1000 mg/L. While sulfur can be quantified at 180.669 or 181.975 nm emission lines, neither line was free of interference. Ca spectrally interfered with S at 180.667 nm in axial mode. Sr interfered with S at 181.975 nm in both axial and radial modes. The interference-free P emission at 178.221 nm was interference free but showed less sensitivity and inconsistent background emission levels. Hence, P at 214.914 nm was used with an IEC for Cu. IEC factors were calculated for all interferents and are listed in Table 2.

In addition to the common spectral interferences listed in U.S. EPA Method 200.7, we also observed that Tb spectrally interfered with Al308.215 and Ti334.940 nm measurements; La had an overlapping peak at As 188.970 nm; and Sm and Nd interfered with S180.669 nm and Sr460.733 nm, respectively. While interfering elements were observed, the actual concentration

of these rare-earth elements (REE) in the CUOG samples from the study region were too low to impart significant interference effects (< 0.3 μg/L in PDWS and < 70 μg/L in effluent waters). For the benefit of readers, a table with summary statistics of REEs in CUOG waters, analyzed by ICP-MS, is provided in the Supplemental Information (SI) Table S2.

3.2 Method performance

To ensure accuracy of elemental concentrations in the collected samples, certified reference materials were analyzed immediately after the analytical calibration was verified with a CCV and quality control standard (QCS). SI Table S3 summarizes average and 1-sigma recoveries of all certified reference materials studied. In general, 95–105% recoveries were obtained for all elements for which measured concentrations were above the ML. Concentrations near the ML were determined within 25% accuracy. Pre- and post-digestion recovery tests were performed with NIST SRM1640a, SRM1643e and laboratory fortified blank samples to study any potential recovery issues. Recoveries of > 90% for most analytes indicated no analyte loss in the sample preparation step. Cd and Zn recoveries were 86%.

Since certified brine solution was not available, matrix spike recovery studies were carried out. Table 3 summarizes spike concentrations, sample background concentrations, and recovered concentrations in moderate- to high-saline wastewater samples. Concentration-weighted measurement uncertainty of all species for this study is < 20.2% (SI Table S4), and therefore spike recoveries were calculated only when the spiked concentrations were more than 20% of the sample background concentrations. Most elements were recovered at > 80%. Salinity appears to affect recoveries of Sn. While the exact mechanism is unknown, formation of an insoluble calcium stannate complex in acidified brine is speculated to cause the lower recovery of Sn. As discussed in section 3.1, Ba measurements suffered when the sample matrix contained high sulfate concentrations.

Analysis precision was estimated from analyzing sequentially collected triplicate high-brine source samples with specific conductivities in the range 120–200 mS/cm. Average relative standard deviation (RSD) from all of these samples was < 5% for Al, Ba, Fe, K, Li, Mn, Sr, Zn, Ca, Mg, and Na. Low levels of B and Si resulted in higher estimates (RSD < 8%). Since

concentrations of most elements in all investigated samples were determined at two wavelengths, linear regression analysis was performed between those pairs of measurements. Regression analysis showed excellent agreement between the emission lines, with most slopes equal to 1, intercepts equal to 0 (at the 95% confidence interval), and coefficients of determination (r^2) > 0.99 (SI Table S5). The use of an internal standard was necessary since samples from multiple sources with varying saline composition were analyzed. CCV analysis was used to evaluate the stability of the method performance over a period of time. Recoveries from the CCVs in each sequence were plotted against analysis run time. All elements measured in this study met the 15% criterion specified in the QAPP for up to 30 hours of run time.

3.3 Analytical blanks

Analysis of microwave acid digestion (AD) and acid leach (AL) reagent blanks showed no evidence of contamination from any species measured except Na, for which AD concentration was 0.27 ± 0.16 mg/L (n = 32). A total of 51 AD field blanks showed an average Na concentration of 0.37 ± 0.08 mg/L. Mg and Sr were measured between their MDL and ML values in approximately 25% of the field blanks. AL field blanks showed an average concentration of 0.17 mg/L Na. These results indicate that no blank correction was required for field blanks except for Na. While 0.10 mg/L of Na appears to be the contribution from the field, 0.20 mg/L was from the AD process itself.

3.4 Sample dilution

Preliminary analytical concentration ranges of CWTF-treated wastewater discharge from the study facilities showed levels from parts per billion (µg/L) up to parts per thousand (g/L) levels for Ca, Na, Mg, and Sr. Higher ion concentrations can cause analytical problems such as plasma quenching, ionic interference, and memory effects. Conductivity measurements have been used in industrial and environmental applications as a fast, inexpensive, and reliable way of measuring ionic content in a solution (Gray, 2005). Conductivity electrode measurements are nonspecific and will respond to all ions present in a solution. This study used conductivity data as a screening tool for identifying samples unsuitable for analysis without dilution and for estimating required dilutions.

When samples with conductivity over 100 mS/cm were analyzed, the ICP plasma color changed from blue to yellow, the internal standard recovery fell abruptly from 100% to approximately 75%, and prolonged rinsing (more than 30 min) was required to return blank signals to the background level. These observations emphasize the unsuitability of high-conductivity samples for analysis without dilution. Also, higher sample conductivity indicates higher ion content and, in turn, higher sample density. Therefore, gravimetric dilution is appropriate for these samples. To determine when gravimetric dilution is essential, we performed both volumetric and gravimetric dilutions and plotted the results as a function of sample specific conductance (Figure 2). Significant differences were observed between the two dilution approaches when sample conductivity exceeded 10 mS/cm, and thus we used only gravimetric dilutions when specific conductance exceeded 10 mS/cm. For samples < 10 mS/cm, volumetric dilutions can be used safely. In general, the established calibration range for this study was found to be sufficient for samples with specific conductance < 0.5 mS/cm.

Serial dilution can potentially introduce analytical artifacts in the way of contamination. In such instances, poor charge balance in the chemical analysis data will indicate either missing species or potential problems introduced by the dilution steps (Dresel and Rose, 2010). The principle of electro-neutrality requires that the sum of mass equivalence (eq/L) of the positive ions (cations) equals the sum of negative ions (anions) in solution. Anion data from IC analysis were used for this evaluation (EPA, 2012b). The determined differences were within ± 3% (SI Table S6) for produced waters from conventional and unconventional wells, which proved that major ions were accurately quantified by the optimized ICP-OES method.

3.5 ICP-OES sample analysis to resolve sources

The sample preparation and the ICP-OES procedure described above were used to analyze CUOG produced water, treated produced wastewater, samples collected upstream and downstream of CWTFs, and samples collected at PDWS intakes. These samples represent a range of matrices, and the ICP-OES procedure was able to generate data that could be used for evaluating source impacts.

3.5.1 Baseline conditions of the study domain

Percent detectability and mean elemental concentrations of upstream river sampling domains are shown in Table 4. In general, concentrations found in Blacklick Creek (acid mine drainage impacted) samples were significantly higher than in Allegheny samples. Particularly, the S concentration was 21 times higher in Blacklick than in Allegheny samples. Li and Ni were quantifiable only in Blacklick samples. Upstream elemental concentration measurements were statistically analyzed with respect to conductivity and river discharge volume (flow rate) for variations in baseline conditions. Varimax principle component analysis (PCA) of Allegheny samples extracted three principle components (PCs) with eigenvalues ≥ 1 (Table 5). The first PC (PC-1A, identified as suspended sediments) showed a positive correlation (> 0.7) with river discharge, Al, Mn, P, Si, Zn, Fe, and Ba; and inverse correlation with sample conductivity. The second PC (PC-2A), identified as dissolved species showed a positive correlation with conductivity and negative correlation with river discharge with Ca, Mg, Na, Sr, and K. PC-3A (B and S) was not associated with sample conductivity or discharge conditions. Blacklick samples had only two PCs with eigenvalues ≥ 1. PC-1B resembled PC-2A (dissolved species), but explained a much larger fraction of the total variance (73% *versus* 15%, respectively), indicating the importance of a dissolved species contribution at the upstream Blacklick Creek location. Like PC-1A, PC-2B (suspended sediments) is characterized by positive correlations with Al, Mn, P, Si, Zn, Fe, and Ba.

Acid digestion (AD) analysis data (total species) were compared against acid leach (AL) analysis data (soluble species) in order to elucidate the factors resolved by PCA. Of the elements measured over MDL concentrations in > 50% of the samples, two groupings were resolved based on AD/AL ratios: AD/AL > 1 and AD/AL ~ 1. The elements B, Ba, Ca, K, Mg, Na, S, and Sr displayed AD/AL ratios of ~1. These dissolved species factors (PC-2A and PC-1B) are positively correlated with sample conductivity and not correlated with river flow rate (discharge volume). The elements Al, Mn, P, Fe, Si, Ba, and Zn were in AD/AL >1 group. Concentrations of these elements with a measureable particulate fraction are positively correlated with river flow rate (discharge volume) which is consistent with observed increases in suspended sediment load (turbidity) due to turbulence. Therefore, the ICP-OES analytical data were sufficient in deriving PCA factors indicative of soluble anthropogenic discharges and natural resuspended sediments.

3.5.2 Produced water and CWTF discharges

Elemental concentrations determined in CUOG produced waters and treated CWTF discharges are presented in Table 6. Specific conductivities of treated (effluent) and untreated (influent) waters were approximately 100 and 200 mS/cm, respectively, hence dilution was necessary. Elements that are regulated by national drinking water standards (U.S. EPA, 2006), such as As, Cd, Cr, Cu, Pb, Se, and Tl, were measured below their respective MDL at the minimum required dilution level ($\leq$ 20 times). As can be seen in Table 6, concentrations of the most common elements contributing to salinity (Na, Mg, and Ca) were relatively constant in shallow and deep formation waters. Sulfur concentrations were low in all produced waters analyzed, as observed elsewhere (Haluszczak et al., 2013). High concentrations of B, Li, and Sr were found for the Marcellus and Oriskany unit sandstone samples. Haluszczak et al. (2013) also observed enriched levels of B and Li in the Marcellus shale formation.

Effluent elemental concentrations were largely consistent from each CWTF in all three sampling seasons (Table 6). While transition series elements (Fe, Mn, and Zn) were apparently removed when comparing the treated and untreated effluents, only approximately 50% of the alkali and alkaline elements seem to be removed by the treatment process. S was found enriched in the effluent water. As part of the CWTF treatment process, sulfate salt is added to precipitate elements like Ba (Ferrar et al., 2013); hence, S is elevated in facility discharges. In addition, coal mine discharges add S to river water and alter Ba and S levels in the dissolved phase such that these two elements are not conserved in river waters. From our analysis of produced water and CWTF discharges, we were able to narrow down the potential tracers of CWTF input into PDWS to B, Ca, K, Li, Mg, Na, and Sr.

Zero discharge facilities enable shale gas drillers to reduce their waste disposal costs by recycling CUOG wastewaters after treatment. Typically, recycled water from a zero discharge facility is blended with fresh water and transported back for reinjection into other hydraulically fractured well completions. This study also analyzed treated CUOG wastewaters from a zero discharge facility for inorganic constituents (Table 6). Results indicate that the treatment process can apparently reduce Ca, Mg, and Na levels. Concentrations of Li, B, Sr, and Ba were found in the treated waters in concentrations similar to the influent concentrations. Recently, Sr isotopic

characterization has been shown to be a useful tool for the identification of Marcellus formation brines (Chapman et al., 2012). Use of recycled wastewaters (with mixed Sr abundances and other species) might potentially limit isotopic and chemical characterization studies of shale formation sources.

3.5.3 PDWS intakes

A total of 84 PDWS intake samples from two collection points in the Allegheny River were analyzed (Table 4). The second collection point, Intake-2, was ~98 km downstream of Intake-1 and just downstream of the confluence of the Kiskiminetas River with the Allegheny River. These PDWS intake samples did not require dilution as sample specific conductance was mostly < 400 µS/cm. Concentrations of As, Cd, Ce, Cr, Mo, Sb, Se, Sn, Ti, Tl, and V were below their respective MDL values. Ba, Ca, Fe, K, Mg, Mn, Na, S, Si, and Sr were quantifiable in > 97% of the samples. Elements B, Ca, K, Mg, Na, and Sr were enriched in Intake-2 as compared to Intake-1. The S concentration was particularly high (5.6 times), possibly due to coal-fired electrical generation facility and historical acid mine drainage discharges. Li was found only in Intake-2, which indicates CUOG wastewater contribution. These observations explicitly show the Blacklick-Kiskiminetas River as a significant contributing source of B, Ca, K, Li, Mg, Na, S, and Sr to Allegheny Intake-2.

Although standards under the Safe Drinking Water Act (SDWA) are relevant to treated drinking water, rather than the source waters measured in the current study, they provide a useful (and conservative) point of reference (U.S. Government Publishing Office, 40 CFR 141, 40 CFR 143). There are six elements (i.e. As, Ba, Cd, Cr, Pb, Se) that we measured with SDWA primary standards (i.e. Maximum Concentration Limit, MCL, for protection of public health). Of those, only Ba was measured above the detection limit at median concentration levels 42 times lower than the MCL. Elements with secondary standards (for aesthetic properties including smell and taste) including Al, Fe, and Mn, were measured at concentrations that exceeded the standard in 35, 48 and 85% of the samples, respectively.

4. Conclusions

- CUOG produced water, treated produced wastewater, industrial outfall (electric generating stations) wastewater, and river water samples were analyzed using ICP-OES for a total of 53 emission lines from 30 elements. In general, EPA Method 200.7 guidelines were adequate for most elements studied. This study found the following: Radial measurements offer accurate results for Ba, Ca, K, Mg, Na, and Sr in a high-saline matrix. The LDR and the solution-phase concentration of Ba are very limited in the presence of S. Spectral interferences not documented in Method 200.7 were also identified. Nevertheless, concentrations of the interfering elements Tb, Sm, La, and Nd in the CUOG wastewater samples were too low to cause significant effects.
- Conductivity measurements were helpful in achieving high analytical throughput. Overloading of the plasma and consequent memory effects were eliminated by not analyzing samples with conductivity > 100 mS/cm. For these samples, dilution by gravimetric means is preferred to yield levels of <10 mS/cm in samples as analyzed. At the same time, dilutions of high-saline CUOG wastewaters affected ICP-OES measurement sensitivity for analysis of elements regulated by national primary drinking water standards.
- Analytical sensitivity of ICP-OES was sufficient to capture underlying variability in species concentrations in PDWS intake samples. This work has demonstrated applicability of the data for factor analytic models such as PCA to successfully resolve suspended sediment and dissolved species in baseline river water.
- Inorganic chemical signatures of a range of CUOG wastewaters have been developed using ICP-OES for possible application in constraint-based source-receptor modeling approaches. Elements B, Ca, K, Li, Mg, Na, and Sr were identified as potential tracers of CWTF input into PDWS. Even though Ba is enriched in CUOG wastewaters (up to 2000 mg/L), wastewater treatment processes and sulfur chemistry prevent it from being used in multivariate statistical model applications.

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Figure 1. Illustrated diagram of sample preparative steps used in the study.

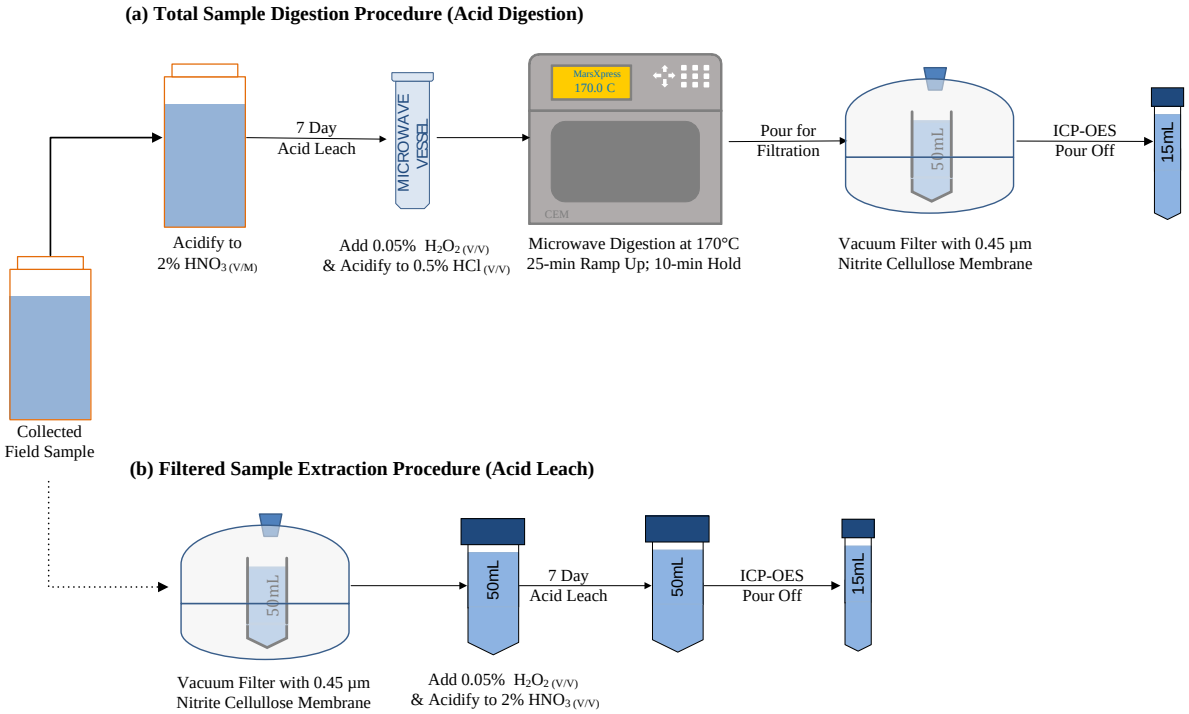
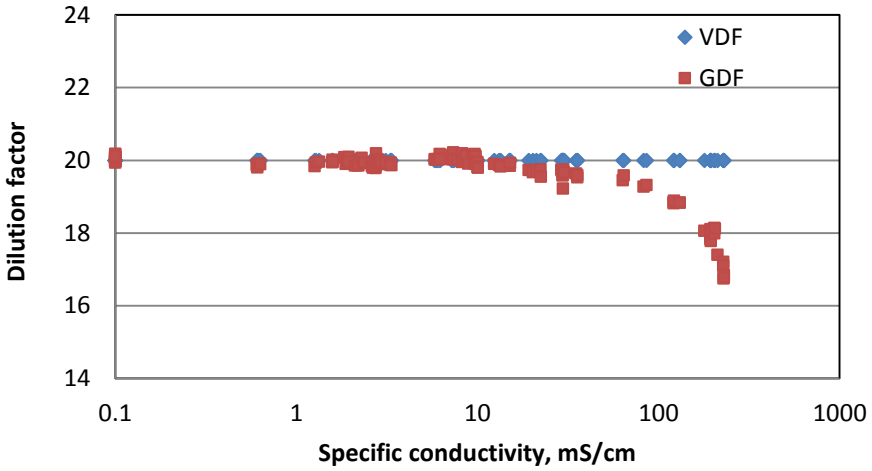


Figure 2. CUOG wastewater dilution as a function of specific conductivity.



VDF - volumetric dilution factor; GDF - gravimetric dilution factor. VDF values were calculated based on 0.5 mL in 9.5 mL v/v dilution.

Table 1. ICP-OES optimized instrumental parameters.

Parameter	**Condition**
Plasma gas flow	15.0 L/min
Auxiliary gas flow	0.2 L/min
Nebulizer gas flow	0.6 L/min
RF power	1500 watts
Nebulizer	Meinhard type C
Spray chamber	Cyclonic
Injector	Alumina, 2.0 mm ID
Sample uptake rate	0.35 mL/min, pumped, orange-green polypropylene (PP) tubing
Internal standard uptake rate	0.35 mL/min, pumped, orange-green PP tubing
Drain tubing	Black-black PP tubing, pumped
Sample flush time	90 s (for PDW samples) or 160 s (for high-saline samples) at 0.6 mL min^{-1}
Rinse time between analysis	60 s for any concentration < 50 mg/L; 120 s for any concentration > 50 mg/L
Read time	Automatic
Read delay time	90 s
Plasma view	Axial and radial (as needed); refer to Table 2
Resolution	High for Na and Zn; normal for the rest
Measurement	Integration, background
Number of replicates	3

Table 2. Measurement wavelengths, plasma view selected, points/peak, background correction points, MDL, ML-LDR, and inter-element correction factors.

Element	Wave-length (nm)	Plasma View	Points/ peak	Bkgd. corr. points	MDL (µg/L)	ML–LDR[c] (µg/L - mg/L)	Report[e]	Interference (IEC)[h]
Al	308.215[a]	Radial	3	2-pt	20	100–50		Ce (12), Mo (16), V (13), Tb (33)
Al	396.153	Radial	2	2-pt	16	50–50	Primary	Mo (31)
As[b]	188.980	Axial	2	2-pt	5	25–25	Primary	La (39)
B	249.677[a]	Axial	3	2-pt	13	100–20	Primary	
B	249.772	Radial	3	2-pt	12	100–20		Fe (1.5)
Ba	233.527	Radial	3	2-pt	17	20–100[d]		Tb (3)
Ba	493.408[a]	Radial	3	2-pt	1	10–100[d]	Primary	
Ca	315.887[a]	Radial	3	2-pt	12	50–200	Primary	Ti (5)
Ca	396.847	Radial	3	2-pt	2	100–50		Ti (5.5)
Cd	226.502[a]	Axial	3	2-pt	1	10–10		Fe (0.16)
Cd	228.802	Axial	3	2-pt	1	10–10	Primary	As (20)
Ce	413.764[a]	Axial	3	2-pt	3	10–10	Primary	
Ce	418.660	Axial	2	2-pt	5	20–10		
Co	228.616[a]	Axial	2	2-pt	1	10–10	Primary	Ti (2)
Cr	205.56[a]	Axial	2	1-pt	1	10–10	Primary	
Cr	357.869	Axial	2	2-pt	3	10–2		Ti (2), Ce (2), Tb (4)
Cu	324.752[a]	Axial	2	2-pt	5	20–10	Primary	
Cu	327.393	Axial	2	2-pt	7	20–10		
Fe	238.204	Radial	3	2-pt	30	100–50		
Fe	259.939[a]	Radial	3	2-pt	3	50–50	Primary	
K	766.49[a]	Radial	3	2-pt	59	100–100	Primary	
Li	670.784[a]	Radial	2	2-pt	3	25–50	Primary	
Mg	279.077[a]	Radial	2	2-pt	18	50–100		
Mg	285.213	Radial	3	2-pt	2	50–100	Primary	
Mn	257.61[a]	Axial	3	2-pt	1	20–10	Primary	
Mn	257.610	Radial	3	2-pt	1	20–10		
Mo	202.031	Axial	3	2-pt	3	50–50	Primary	
Mo	203.845[a]	Axial	3	2-pt	3	50–50		
Na	588.995[a]	Radial	2	2-pt	27	100–200		
Na	589.592	Radial	2	2-pt	12	100–200	Primary	
Ni	231.604[a]	Axial	2	2-pt	1	10–20	Primary	
Ni	232.003	Axial	2	1-pt	2	10–20		Cr (16), Mo (3)
P	213.617	Axial	2	1-pt	8	100–100		Cu (44), Mo (13)
P	214.914[a]	Axial	2	1-pt	9	500–100	Primary	Cu (26)
Pb	217.000	Axial	2	2-pt	7	100–2		
Pb	220.353[a]	Axial	2	2-pt	3	20–2	Primary	
S	180.669	Axial	2	1-pt	35	500–100	Primary	Ca (8)
S	180.669	Radial	2	2-pt	382	500–1000		Sm(67)

S	181.975	Axial	2	2-pt	47	500–100	Primary[f]	Sr(4)
S	181.975	Radial	2	2-pt	684	5000–1000	NR [g]	Ca (20), Sr (198),
Sb	206.836[a]	Axial	2	2-pt	3	25–25		
Sb	217.582	Axial	2	2-pt	3	25–25	Primary	
Se	196.026[a]	Axial	2	2-pt	7	50–25	Primary	
Se	203.985	Axial	2	2-pt	20	50–25	NR [g]	Cr (24), Ca (0.2–1.5)
Si	251.611[a]	Axial	3	2-pt	4	24–48	Primary	Mo (16), Sn (44), Ti (11)
Si	251.611	Radial	3	2-pt	27	47–48		Mo (16), Sn (40), Ti (9)
Sn	189.927[a]	Axial	3	2-pt	3	10–20	Primary	
Sr	421.552[a]	Radial	3	2-pt	1	20–10	Primary	
Sr	460.733	Radial	3	2-pt	22	50–50		Nd (36), Sm (-22)
Ti	334.940[a]	Axial	3	2-pt	3	50–50	Primary	Tb (18)
Ti	334.940	Radial	3	2-pt	3	50–50		Tb (18)
Tl	190.801[a]	Axial	2	1-pt	6	25–25	Primary	
V	292.402[a]	Axial	2	1-pt	1	10–10	Primary	
Zn	206.200	Axial	3	2-pt	3	50–25		
Zn	213.857[a]	Axial	3	2-pt	3	25–5	Primary	Cu (2), Ni (4)

[a] Method 200.7 recommended wavelength

[b] Method 200.7 recommended wavelength was not used as the chosen wavelength is free of interferences

[c] ML is minimum limit concentration (ppb) and LDR is linear dynamic range or upper calibration range (ppm)

[d] Linearity of Ba is limited to 2 ppm when sulfur concentration in solution >100 ppm

[e] Wavelengths not marked as 'Primary' were used as backup measurements for reporting analytical concentration

[f] Data not collected for all samples analyzed

[g] NR: Not Recommended

[h] Inter-element Correction (IEC) factor was calculated as apparent analyte concentration in ppb due to interfering element measured at analyte wavelength / Actual interfering element concentration in ppm measured at wavelength characteristic of interfering element

Table 3. Spike recovery analysis of high-saline samples. Percent recovery is not calculated if the spiked concentration was less than 20% of the sample background concentration.

		Treated Sanitary Sewage 1,024 µS/cm			FGD Scrubber Wastewater 29,900 µS/cm			CUOG Treated Discharge 160,900 µS/cm		
Ele.	Spike Conc. (mg/L)	Sample Bkgd. Conc. (mg/L)	Fortified Sample Conc. (mg/L)	% Recovery	Sample Bkgd. Conc. (mg/L)	Fortified Sample Conc. (mg/L)	% Recovery	Sample Bkgd. Conc. (mg/L)	Fortified Sample Conc. (mg/L)	% Recovery
Al	39.8	<MDL	38.5	97	<MDL	39.6	100	0.9	36.9	91
As	19.9	<MDL	19.0	96	<MDL	19.2	97	<MDL	18.4	92
B	8.0	0.2	7.6	93	59.2	67.6		3.1	10.6	94
Ba	8.0	0.1	6.9	85	<MDL	1.2	15	1.3	8.2	86
Ca	39.8	60.5	95.2	87	2325.7	2355.0		10823.8	10852.8	
Cd	8.0	<MDL	7.1	90	<MDL	6.9	86	<MDL	6.7	84
Ce	8.0	<MDL	7.7	96	<MDL	7.4	93	<MDL	6.5	82
Co	8.0	<MDL	7.5	95	<MDL	7.5	94	<MDL	6.5	82
Cr	8.0	<MDL	7.5	94	<MDL	7.3	92	<MDL	6.7	85
Cu	8.0	0.0	7.2	90	<MDL	7.5	94	<MDL	7.8	99
Fe	39.8	0.1	40.0	100	<MDL	38.4	97	<MDL	35.6	90
K	39.8	9.1	47.8	97	93.6	132.4	97	239.6	278.2	
Li	19.9	0.0	20.0	101	1.0	20.1	96	47.8	66.3	93
Mg	39.8	11.2	50.1	98	1729.7	1790.7		671.2	711.6	
Mn	8.0	0.0	7.6	95	203.7	215.0		<MDL	6.3	80
Mo	39.8	<MDL	39.3	99	<MDL	37.7	95	<MDL	34.3	86
Na	39.8	89.4	129.3	100	980.0	1023.0		28289.0	28373.3	
Ni	8.0	<MDL	7.2	90	0.6	8.0	93	<MDL	7.3	92
P	39.8	2.4	39.1	92	<MDL	39.0	98	<MDL	39.3	99
Pb	8.0	<MDL	6.6	84	<MDL	5.9	75	<MDL	6.5	82
S	198.5	9.7	192.7	92	649.9	833.0	92	191.5	353.1	81
Sb	19.9	<MDL	19.4	97	<MDL	18.8	95	<MDL	17.6	88
Se	19.9	0.0	18.9	95	<MDL	19.5	98	<MDL	18.1	91
Si	18.6	4.3	21.4	92	2.7	19.9	92	0.5	16.1	84
Sn	8.0	<MDL	7.5	95	<MDL	5.6	70	<MDL	4.7	60
Sr	8.0	0.2	7.9	97	27.9	34.5	83	874.7	892.9	
Ti	39.8	<MDL	38.6	97	<MDL	37.6	95	<MDL	34.7	87
Tl	19.9	<MDL	19.1	96	<MDL	18.2	92	<MDL	16.1	81
V	8.0	<MDL	7.5	95	<MDL	7.5	95	<MDL	6.9	87
Zn	19.9	0.0	18.2	91	<MDL	18.0	91	<MDL	17.8	90

Table 4. Percent detectability and mean concentrations of upstream and PDWS intake samples.

Elements	Allegheny Upstream Samples (n=46)		Blacklick Upstream Samples (n=42)		PDWS Intake-1[(a)] (n=41)		PDWS Intake-2 [(b)] (n=43)	
	%>MDL	mean, mg/L	%>MDL	mean, mg/L	%>MDL	mean, mg/L	%>MDL	mean, mg/L
Al	89	0.251	100	1.477	100	0.201	100	0.282
B	89	0.017	100	0.028	63	0.014	91	0.041
Ba	100	0.046	100	0.053	100	0.048	100	0.046
Ca	100	14.087	100	43.837	100	17.313	100	26.210
Fe	100	0.537	100	3.367	100	0.398	100	0.389
K	100	1.105	100	3.087	100	1.209	100	1.754
Li	7	<MDL	100	0.029	2	<MDL	63	0.006
Mg	100	2.905	100	12.380	100	3.517	100	7.569
Mn	100	0.103	100	0.646	100	0.096	100	0.109
Na	100	9.886	100	18.495	100	11.088	100	16.748
Ni	28	<MDL	100	0.019	34	0.001	72	0.007
P	70	0.027	52	0.019	71	0.025	70	0.018
S	100	2.859	100	59.118	100	3.545	100	19.953
Si	100	1.430	100	3.973	100	1.445	100	1.468
Sr	100	0.056	100	0.262	100	0.069	100	0.151
Zn	37	<MDL	100	0.038	100	0.007	63	0.004

(a) - Intake-1 is located 51.8 km downstream of Allegheny upstream sampling point.
(b) - Intake-2 is located 97.8 km downstream of Intake-1 and 1.35 km downstream of the confluence of the Blacklick to Kiskiminetas River with Allegheny.

Table 5. Principle component analysis of baseline samples. Rotated component scores >0.5 are bold faced.

Species	Alleghany Site 1 (n=46)			Blacklick Site 1 (n=42)	
	PC-1A (Suspended sediments)	PC-2A (Dissolved species)	PC-3A (unknown)	PC-1B (Dissolved species)	PC-2B (Suspended sediments)
Explained Variance	76%	15%	5%	73%	23%
Al	**0.9**	-0.38	-0.01	-0.04	**0.9**
Ca	-0.46	**0.85**	0.13	**0.97**	0.08
Mg	-0.38	**0.88**	0.18	**0.97**	0.07
Mn	**0.86**	-0.43	0.07	**0.85**	**0.42**
Na	-0.47	**0.74**	0.27	**0.95**	-0.01
P	**0.74**	-0.26	0.02	-0.39	**0.72**
Si	**0.84**	-0.4	0.08	**0.74**	**0.57**
Sr	-0.58	**0.71**	0.24	**0.98**	0.06
Zn	**0.82**	-0.39	0.06	0.45	**0.8**
K	-0.14	**0.82**	0.18	**0.95**	-0.07
Fe	**0.9**	-0.4	-0.08	-0.38	**0.42**
B	-0.02	0.26	**0.69**	**0.9**	0.06
Ba	**0.86**	-0.06	0.2	0.33	**0.86**
Li (a)				**0.96**	0.11
S	0.1	0.09	**0.67**	**0.97**	0.08
SC (b)	**-0.62**	**0.74**	0.13	**0.98**	0.03
Discharge(c)	**0.79**	-0.41	-0.25	**-0.5**	0.35

(a) - Li concentrations in Allegheny are <MDL, hence variable not included
(b) - Sample specific conductivity (SC)
(c)-Flow rate of river at the time of sampling

Table 6. Average concentrations of treated and untreated CUOG wastewaters.

Species (meas. unit)	Conventional Produced Waters		Unconventional Produced Waters			Zero Discharge	CWTF Discharge in Allegheny Sampling Domain			CWTF Discharge in Blacklick Sampling Domain		
	SC1(a) n=3	SC2 (b) n=3	RES1 (c) n=3	RES2 (d) n=2	ORIS (e) n=3	RES3 (f) n=3	Fall n=13	Summer n=10	Spring n=13	Fall n=14	Summer n=15	Spring n=12
SC (mS/cm)	193.9	206.6	206.7	191	229.7	121.6	135.1	133.6	109.9	168.1	164.4	167.5
Al (mg/L)	4.836	11.32	0.2891	1.57	1.305	0.1009	0.0801	0.0182	0.1807	0.2298	0.0273	<MDL
B (mg/L)	1.284	1.414	15.9	16.22	28.66	9.595	4.572	4.307	2.142	4.015	2.531	3.555
Ba (mg/L)	218.8	64.68	2008	2927	861.2	2150	10.58	8.652	2.241	7.999	4.898	3.978
Cu (mg/L)	1.215	0.0389	0.3104	0.2472	<MDL	0.1335	0.0811	0.1774	0.2678	0.0914	0.0689	0.2036
Fe (mg/L)	133.2	248.6	117.2	113.8	227.4	0.0875	0.3776	0.1884	0.4295	0.3672	0.3027	0.4449
K (mg/L)	158.7	110.7	893.4	603.5	1784	344.7	417.5	495.4	334.7	290.0	238.9	314.5
Li (mg/L)	13.31	25.30	155.2	128.4	168.4	51.32	19.62	18.38	12.00	68.55	83.97	54.16
Mn (mg/L)	8.387	12.43	9.175	9.931	5.567	3.570	0.2072	0.2888	0.0681	0.1363	0.0907	0.2748
P (mg/L)	0.8089	1.225	2.994	2.795	3.521	1.339	0.078	0.1101	0.2039	0.4572	0.5200	0.4138
S (mg/L)	<MDL	43.79	<MDL	2.659	<MDL	<MDL	91.78	97.10	266.6	202.9	232.2	368.2
Si (mg/L)	6.763	9.935	5.568	11.47	4.209	0.8579	0.7581	0.7115	0.8290	0.5451	0.4266	0.7224
Zn (mg/L)	0.3039	0.7392	0.8478	0.6251	1.143	0.2004	0.0739	0.0634	0.0449	0.0894	0.0688	0.0612
Ca (g/L)	13.94	14.99	17.70	15.27	29.49	7.877	9.374	9.392	7.613	12.16	12.03	12.77
Mg (g/L)	2.058	2.017	1.628	1.419	1.913	0.689	0.992	0.9373	0.7754	0.7145	0.7814	0.803
Na (g/L)	41.81	39.74	45.95	38.07	54.35	20.91	23.74	23.29	18.81	30.94	31.64	32.82
Sr (g/L)	0.5865	0.6889	4.386	4.928	7.442	2.182	0.3558	0.4431	0.2639	1.118	0.9165	1.197

(a) - Shallow conventional-1; IDs GRAB-431, 432, 433
(b) - Shallow conventional-2; IDs GRAB-437, 438, 439
(c) - Closed Loop Recycling Facility provided; IDs GRAB-245, 246, 247
(d) - Closed Loop Recyling Facility provided; IDs GRAB-249, 250
(e) - Oriskany sandstone formation; IDs GRAB-434, 435, 436
(f) - Treated produced waters at a zero discharge facility; IDs GRAB-242, 2

Supporting Information

Application of ICP-OES for Evaluating Energy Extraction and Production Wastewater Discharge Impacts on Surface Waters in Western Pennsylvania

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SI Table S1. Routine quality control checks for the ICP-OES analysis.

No.	Check name	Purpose	Frequency	EPA HF QAPP limits	Method 200.7 limits
1	Calibration	Establish linear range	At beginning of each analytical sequence	$r^2 > 0.99$	
2	Internal standard (IS) recovery	Check for any sample transport issues	100% of samples	80–120%	80–120%
3	Quality control standard (QCS)	Checks accuracy of calibration with a second source standard	Post-calibration	85–115%	95–105%
4	Standard/certified reference material (SRM/CRM)	Checks accuracy of calibration with a certified reference sample	At start and end of an analytical sequence	85–115%	85–115%
5	Spectral interference check sample (SIC)	Commercially available certified samples for ICP to verify absence of interferences	No QAPP-specified criteria	20% user-defined criteria	Not specified
6	Continuing calibration blank verification (CCB)	Continuing check of the blank level by remeasuring the CCB	Every 10 samples analyzed	≤ MDL	≤ IDL
7	Continuing calibration verification (CCV)	Instrument performance check at beginning; then continuing check of instrument accuracy by remeasuring a CCV	At start, then every 10 samples analyzed, and at end	85–115%	90–110%
8	Laboratory Control Sample (LCS)	Continuously track recoveries of elements of interest using certified waters as samples	One per analytical batch	85–115%	
9	Duplicate analysis (Dp)	Continuing precision check by reanalyzing a sample	One reanalysis for 10 samples analyzed	80–120%	80–120%
10	Laboratory reagent blank (LRB)	Checks laboratory reagents and sample preparation process for contamination	One per analytical batch	< MDL	< 2.2 x MDL
11	Laboratory-fortified blank (LFB)	Matrix-matched sample with known concentration to verify accuracy of method	One per analytical batch	Not specified	85–115 %
12	Laboratory-fortified matrix (LFM)	Checks recovery of analyte in a matrix by spiking a known quantity into a sample	One per analytical batch	Not specified	85–115 %

SI Table S2. Rare-earth elemental concentrations in µg/L in CUOG wastewaters as compared to PDWS waters, determined by HR-ICPMS. Refer to U.S. EPA, 2015 for method information.

Sample type	Metrics	La	Nd	Sm	Tb
	MDL (µg/L)	0.029	0.029	0.011	0.015
Effluent waters	% over MDL	100	100	100	*
	median	68.5	30.6	31.9	*
	range	32.1 – 108	14.9 – 41.6	7.38 - 262	*
PDWS waters	% over MDL	70	87	65	26
	median (µg/L)	0.246	0.287	0.112	0.040
	range	0.020 – 1.150	0.020 – 1.531	0.011 – 0.467	0.020 – 0.079

*Species not detected at 100 times dilution

SI Table S3. Percent recoveries of certified reference materials analyzed.

	SRM 1640a (n = 31)				SRM1643e (n = 31)				HP-TMDW (n = 14)				M-172 (n = 31)				ERA-500 (n = 3)				ERA custom mix (n = 3)			
Element	Certified, µg/L	Recovery %, mean	±	SD, %	Certified, µg/L	Recovery %, mean	±	SD, %	Certified, µg/L	Recovery %, mean	±	SD, %	Certified, µg/L	Recovery %, mean	±	SD, %	Certified, µg/L	Recovery %, mean	±	SD, %	Certified, mg/L	Recovery %, mean	±	SD, %
Al	50.7	96	±	16	138.8	99	±	6	120.0	96	±	5					530.0	102	±	3				
As	4.4 (a)	92	±	24	59.0	95.5	±	4.4	80.0	99	±	3					753.0	101	±	2				
B	318.1	106	±	4	154.0	104.7	±	5.7					97.1	123	±	15	859.0	99	±	1				
Ba	151.4	101	±	4	531.0	99.8	±	3.4	50.0	100	±	2					827.0	101	±	2				
Ca	5542.7	100	±	4	31500.0	96.5	±	3.1	35000.0	100	±	3	8360.0	106	±	5								
Cd	3.9	100	±	15	6.4	103.8	±	12.6	10.0	98	±	8					689.0	91	±	1				
Ce																					45.4	101.5	±	1.8
Co	19.6	98	±	3	26.4	95.1	±	3.1	25.0	97	±	2					215.0	104	±	2				
Cr	39.7	99	±	2	19.9	101.0	±	4.0	20.0	100	±	3					214.0	100	±	1				
Cu	83.7	98	±	4	22.2	115.9	±	17.4									842.0	92	±	1				
Fe	36.4	100	±	8	95.7	101.4	±	8.9	100.0	100	±	3					795.0	102	±	2				
K	562.8	98	±	4	1984.0	96.8	±	3.2	2500.0	99	±	2	3800.0	105	±	4								
Li					17.0	105.8	±	12.0	20.0	98	±	7												
Mg	1031.5	98	±	4	7841.0	97.1	±	2.9	9000.0	99	±	3	4730.0	104	±	5								
Mn	39.4	98	±	3	38.0	99.8	±	3.2	40.0	101	±	2					1850.0	101	±	2				
Mo	42.6	94	±	7	118.5	100.9	±	3.0	100.0	99	±	2					575.0	102	±	1				
Na	3075.7	99	±	4	20230.0	98.0	±	3.0	6000.0	100	±	2	12500.0	104	±	5								
Ni	22.2	89	±	5	1984.0	94.0	±	0.1	60.0	92	±	1					1720.0	97	±	2				
P													1350.0	102	±	3								
Pb	11.7 (a)	97	±	20	19.2	94.7	±	12.3	40.0	97	±	3												
S													4105.7	109	±	3	460.0	98	±	1				
Sb	4.1 (a)	82	±	33	56.9	94.9	±	4.0	10 (a)	84	±	18					632.0	100	±	1				
Se	18.9 (a)	95	±	17	11.7 (a)	125.9	±	27.0	10.0 (a)	108	±	20					291.0	101	±	2				
Si	5231.1	101	±	3									5697.4	104	±	2								
Sn																								
Sr	124.5	100	±	4	315.2	97.8	±	4.6	250.0	100	±	2	54.0	105	±	5	65.1	99	±	3				
Ti																					56.8	102.0	±	0.6
Tl									10.0 (a)	135	±	37					744.0	101	±	2				
V	14.7	99	±	6	36.9	99.4	±	2.2	30.0	99	±	3	10.3	100	±	9	931.0	100	±	1				
Zn	55.8	101	±	5	76.5	101.7	±	5.5	70.0	101	±	2					1330.0	96	±	2				

Empty cells denote certified/reference concentrations for that particular element does not exist.
(a) - Certified concentration is below ML but above MDL.

SI Table S4. Analytical and sampling precision of river water analysis.

Element	ICP-OES Analysis Precision[a], % difference	Overall Sampling Precision[b], % difference
Ba	3.0	4.2
K	4.6	6.7
Sr	3.2	4.9
Mg	3.6	5.7
Cu	8.0	14.1
Ca	3.4	6.0
S	2.8	5.4
Na	3.4	7.0
Al	7.3	20.1
Fe	3.3	9.5
Mn	3.1	8.8
Si	3.2	10.5

[a] Data from 87 duplicate ICP-OES analysis of river samples were used.
[b] Data from 78 concurrently collected sample pairs from one of the PDWS sampling sites were used.

Method: A total of 78 concurrently collected PDWS sample pairs with concentration data within the reporting range (ML – LDR) was used to estimate overall uncertainty. Also, species with low % detectabilities (B, Co, Li, Ni, Pb, Zn) were excluded from this precision analysis. Relative percent difference (RPD) in the concentration pairs, a measure of precision, was calculated as the percent of absolute concentration difference divided by the mean concentration. For instrumental analysis uncertainty, a total 87 duplicate sample analyses, available from all of the PDWS analyses were used. Table S4 presents the results of this uncertainty study. It was found that 'sampling' was a major contributor to the overall uncertainties of Al, Fe, Mn, and Si. Analysis precision is approximately half of overall precision for Sr, Mg, Cu, Ca, S, and Na measurements. Measurement uncertainties of Ba, K, and Sr appear predominantly controlled by the analysis method.

SI Table S5. Regression analysis of elements measured at two different emission wavelengths.

Element	x variable	y variable	r^2	Slope	Intercept
Al	308.215 nm radial	396.153 nm radial	1.00	1.00	-0.01
B	249.677 nm axial	249.772 nm radial	0.99	0.91	0.07
Ba	233.527 nm radial	493.408 nm radial	1.00	1.02	0.00
Ca	396.847 nm radial	315.887 nm radial	1.00	0.98	1.14
Fe	238.204 nm radial	259.939 nm radial	1.00	1.00	0.00
Mg	279.077 nm radial	285.213 nm radial	1.00	1.01	0.16
Na	588.995 nm radial	589.592 nm radial	1.00	1.03	0.24
Mn	257.610 nm axial	257.610 nm radial	1.00	1.00	-0.20
Zn	213.857 nm axial	206.200 nm axial	1.00	1.00	0.01

SI Table S6. Electro-neutrality in the high-saline produced water samples analysis.

Species	Unit	Produced Water from Conventional Wells		Produced Water from Unconventional Wells		CUOG Wastewater before CWTF	
Conductivity	$mS.cm^{-1}$	203	205	82.8	179	228	228
Cl-	meq/L	3257.5	3008.5	932.7	2528.7	4228.2	4225.4
NO_3^-	meq/L	0.4	0.3	5.9	8.4	0.0	0.0
Br^-	meq/L	8.2	10.7	1.5	6.8	23.9	23.7
F^-	meq/L	0.0	0.0	0.0	0.0	0.6	0.6
SO_4^-	meq/L	0.8	0.3	0.1	0.0	2.0	2.1
B	meq/L	13.6	14.1	7.3	18.5	9.0	9.1
Ba	meq/L	24.4	24.8	10.5	68.6	0.0	0.0
Ca	meq/L	847.4	855.5	257.9	672.3	1419.6	1419.2
Fe	meq/L	5.8	5.8	3.6	7.0	14.4	14.5
K	meq/L	20.2	20.0	8.7	11.0	33.1	33.5
Li	meq/L	24.3	23.6	5.4	13.1	6.9	6.9
Mg	meq/L	137.7	136.0	34.6	98.9	223.2	225.8
Mn	meq/L	0.6	0.6	0.1	0.8	3.4	3.4
Na	meq/L	1930.2	1925.2	614.3	1432.3	2285.9	2296.4
Si	meq/L	4.9	4.9	0.7	21.4	0.0	0.0
Sr	meq/L	86.8	87.9	21.5	138.2	22.9	21.8
∑anion	meq/L	3266.9	3019.9	940.2	2543.9	4254.6	4251.6
∑cation	meq/L	3082.2	3084.3	957.4	2463.5	4009.4	4021.5
diff,%		2.9	-1.1	-0.9	1.6	3.0	2.8

SI Figure 1. Effect of sulfur concentrations on barium measurement.