

TRACE ELEMENTS AND NATURALLY OCCURRING RADIOACTIVE MATERIAL ASSOCIATED WITH PRODUCED WATERS IN COAL SEAM GAS AND SHALE GAS RESOURCES AND THEIR POTENTIAL RELATIONSHIP TO MINERAL GROUPS

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SUMMARY

The focus of this study is to determine the geochemical properties of formation, produced and flowback fluids and correlate the findings to geochemical properties of different mineral groups. This analysis can be achieved by: (a) investigating the occurrence and abundance of trace elements and naturally occurring radioactive material associated with different mineral groups, (b) determining the geochemical composition of produced water associated with these compositionally different formations using a comparative study between hydrocarbon resources and individual basins, and (c) determining the mineral origin of these trace elements and NORM associated with produced water. The geochemical NORM and trace element composition associated with produced water depends on the characteristics of the original depositional environment, the composition of the source rock, post depositional genesis processes, type/grade of the hydrocarbon and the ability for these trace elements and NORM to become mobile. The USGS produced water database was used to compare the variation of geochemical properties of produced water between the various energy generating types and basins. This was achieved by developing a statistical analysis for each trace element and NORM and comparing the results between the various hydrocarbon types and basins. The results of this study illustrates; (a) that certain trace elements have an overall higher concentration within certain hydrocarbon resources, and (b) there is a correlation of trace elements concentration associated with compositionally different formation and is related to the formations unique mineralogy. The information contained in this study and studies on mechanism that impact fluid migration and well integrity will provide decision-makers the framework to develop a more detailed PWMP during the initial exploration phase that can be part of their requirements when applying to the land owners for an exploration licence.

Key words: produced water, trace elements, NORM, CSG, shale gas

INTRODUCTION

The rise in energy requirements for societies and the increase in prices of conventional fossil fuels have led many countries to develop new mining techniques to extract previously non-economical fossil fuels, known as unconventional energies (Kurthet *et al.* 2010). The further development of hydraulic fracturing and horizontal drilling has allowed the extraction of unconventional hydrocarbons, such as coal seam gas (CSG), and shale gas (SG) (Hamawand *et al.* 2013). Hydraulic fracturing is a technique that facilitates the development of fractures within low permeable rock formations. This technique facilitates the release of gases and formation waters trapped from within the rock formations pore structure, thus allowing them to flow freely to the surface via the constructed wellbore. The increase in production has led to a greater volume of produced water requiring treatment before reuse or disposal and not every wastewater treatment facility have the appropriate technologies to treat highly contaminated produced water to a satisfactory standard. Therefore, there has been reported studies that produced water has been released into the environment with little to no treatment, thus causing environmental impact to freshwater ecosystems (Erakhrumen 2015). Furthermore, due to the variation in produced water toxicity some wastewater has been purified to a standard that is not cost effective for the applied purpose, thus costing mining companies more than required (Erakhrumen 2015). Therefore, developing an appropriate produced water management plan (PWMP) for the applied purpose will ensure a cost effective way in utilising or disposing produced water without causing environmental harm. Conventional and unconventional hydrocarbons contain naturally occurring radioactive materials (NORM) and trace elements (TE) in the reservoir's formation water (Chermak and Schreiber 2013). The mixing of formation water and fracturing fluids creates what is known as produced waters (Engle and Rowan 2014). The geochemical composition of formations water can be influence by the following; (a) surface and sub-surface condition that provide detrital and authigenic minerals into the original and post depositional environment, (b) hydrogeological mechanism that influence the mobilisation, transfer and retention of TE and NORM, and (c) the infiltration of meteoric and circulation of groundwater that promotes fluid migration and/or fluid mixing into/out of the formation (Authority, S.C., 2012; Ali *et al.* 2010).

The process of diagenesis is an important factor that determines formation water geochemical characteristics and occurs from deposition to the process of compaction and lithification. (Ali *et al.* 2010). Diagenesis occurs during low temperature and pressure and once these two variable exceed a certain undefined threshold; metamorphisms takes the role in changing the properties within the rock structure (Ali *et al.* 2010). The material within the environment are subjected to compaction, cementation, recrystallization, replacement, dissolution and authigenic chemical alteration (Ali *et al.* 2010). In addition, there are a number of sedimentary and environmental conditions that influence diagenesis. These sedimentary factors include; fluid and organic material present, grain size and mineralogical composition (Ali *et al.* 2010). The environmental factors that influence diagenetic alterations include; chemical properties, temperature and pressure gradients during burial (Ali *et al.* 2010). These changes occur because the material within the depositional environment are in chemical disequilibrium with the local sub-surface environment (Ali *et al.* 2010). This disequilibrium causes changes to chemical properties of the formation from the processes illustrated above, thus altering it to equilibrate with the surrounding environment (Ali *et al.* 2010). Therefore, the rate and extent of alteration from diagenetic processes is related to how much the sedimentary structure and composition of the depositional environment is in disequilibrium with its surrounding environment. The formation can equilibrate by precipitating minerals from the mineral structure, thus mobilising them into an aqueous form. This process of mobilisation changes the chemical composition of the formation water by adding or removing precipitants (Ali *et al.* 2010).

The incorporation of detrital and authigenic minerals during deposition influences the composition of the source rock, thus ultimately influencing the composition of the formation water. These detrital minerals can originate from eroded sedimentary, igneous and metamorphic crustal material and from volcanic activity, which contain vastly different mineral composition (Ali *et al.* 2010). This volcanic activity promotes the incorporation of volcanoclastic materials that originate from compositionally different magma. Authigenic minerals can also be incorporated into the formation during and post deposition (Huston *et al.* 2006). These authigenic minerals are transported within groundwater or hydrothermal fluid and can precipitate minerals into the formation. The concentration of these minerals can range and depend on the properties of the groundwater such as, what minerals the groundwater has interacted with, chemical properties of the fluid (e.g. pH and temperature) and its geological origin (Huston *et al.* 2006). These environmental and geological processes illustrated above impact the composition of the source rock and ultimately the formation water, thus facilitating the diverse chemical and mineralogical composition of formations waters associated with different SG, CSG and conventional O&G formations.

The composition of the source rock is an important factor that influences the composition of formations waters and is dictated by the properties stated above (Chermak and Schreiber 2014; Ali *et al.* 2010; Huston *et al.* 2006). The source rock mineral composition is different between SG, CSG and conventional O&G, thus producing a variation of TE and NORM within their formations water. Shale gas source rock can be sub-divided into black shale or traditional shale, where black shales have a high degree of organic matter compared to traditional shale formations. Shale rocks are composed of organic material, clays, quartz with minor amounts of feldspar, carbonates, sulphide and oxide minerals with varying proportion within different regions around the world (Chermak and Schreiber 2014). Black shales are defined by their bulk composition being enriched in organic carbon. Furthermore, black shales commonly have higher concentration of TE compared to the average shale (Chermak and Schreiber 2014). The variation of minerals associated with shales depends on the detrital and authigenic input, which is a function of the detrital and authigenic TE composition within the surrounding environment. The addition of volcanoclastic materials can elevate TE concentration within the formation. For example, high Cr content can be incorporated into formations from ultramafic volcanic material during detrital and authigenic transport processes of chromium rich minerals such as, Cr-rich spinel (Boyd 2004). Coal rank is important in understanding TE and NORM concentration in CSG formations. Coal rank is an important aspect because it defines the degree of modification of organic matter from environmental conditions such as, temperature and pressure gradient during coalification (Vassilev *et al.* 1996). The coal rank is also determined by the amount of volatile material, which include ash and sulphide minerals present in varying degree. Furthermore, the ashes content associated with coal rank can affect the occurrence of TE and NORM within the coal formation, thus impacting the properties of the formation waters (Vassilev *et al.* 1996).

METHODOLOGY

The approach used to achieve a comparative study between CSG, SG and conventional O&G produced water properties with compositionally different source rocks was achieved by determining the mode of occurrence of TE and NORM associated with different mineralogical groups and correlate these findings with the United States Geological Survey (USGS) produced water geochemical database collected from various resource production zones (Table 1). The USGS developed a produced water database that illustrates the variation of TE and NORM for a variety of CSG, SG, and conventional O&G formations. I sub-divided the USGS produced water sample data into their respective hydrocarbon type and basin to illustrate, which, basin and hydrocarbon type contained the highest concentration of each TE and NORM (Figures 1-10). Furthermore, I calculated the minimum, maximum and averages for each produced water samples associated with different source rock composition to illustrate the statistical range of TE and NORM concentration associated with the different hydrocarbon source rock properties. In addition, I determined the number of samples used to calculate the statistical analysis illustrated above for each analyte to demonstrate the degree of certainty of the results. The results illustrated that certain TE and NORM are associated with different mineral groups and these mineral groups are one of the driving factor in determining the range of TE and NORM concentration within produced waters (Table 1; Figures 1-10).

DISCUSSION AND RESULTS

This section will now attempt to correlate laboratory analysis of various produced water samples submitted to the USGS to the mode of occurrence of trace elements associated with different minerals. This was done to develop techniques to predict the expected variation of contaminants in produced water, thus providing decision-makers with a tool to predict which TE and NORM will be dominant during the initial exploration phase, so that they can develop a PWMP, which should include developing partnerships with treatment facilities that have the adequate technologies to purify the highly contaminated wastewater. This is needed because not all treatment facilities have the adequate resources/technology to treat highly contaminated produced water to a satisfactory safe disposal/reuse standard. The information provided will provide valuable information on the potential impact of produced water to the environment and provide methods to determine toxicity values to adequately classify this wastewater, thus allocated wastewater to an appropriate treatment facility that has the required technologies to adequately purify these fluids for safe reuse or disposal practices. This will provide the means to adequately developing standards and techniques for future transport, treatment, reuse and disposal based on mineralogical composition of the formation. Initially, the target area can be investigated using academic literature to determine geological history before drilling and later can be verified from laboratory analysis from core sampling drilling. This data produced can be interpreted using the information provided in this topic, thus developing a more detailed PWMP. The predicted results can later be verified from laboratory analysis done on produced water samples during the extraction phase. This process stated above can become a standard for a PWMP report, thus improving on current standards. Currently, mining companies do not provide enough detail on the sustainable disposal/reuse of produced water.

Mineralogical Results:

The mineralogical composition of the source rock plays an important role in determining TE and NORM concentration within the rock formation. These contaminants can become incorporated into formation water under the right chemical conditions. The amount of TE and NORM within the source rock is a factor that illustrate the degree of TE and NORM within the formation water. Therefore, having

an understanding of the mineralogical origin of TE and NORM within produced water will give scientist a better framework on predicting which geological formation will contain higher concentration of TE and NORM within produced water. This will ultimately provide a framework to predict the toxicity of produced water during the initial stages, thus giving decision makers the means to develop an adequate PWMP.

Ash material are an important aspect in determining the concentration of TE and NORM within CSG formation waters. Coals with a higher rank will have ash content with greater concentrations of SiO₂, Al₂O₃, Fe₂O₃, K₂O, Na₂O and TiO₂ from the enrichment of minerals such as, illite, mica, spinel, chlorite, siderite, dolomite and to some degree quartz, kaolinite and iron-rich oxyhydroxides (Vassilev *et al.* 1996). These minerals are generally associated with detrital processes at the time of deposition and are the ash forming minerals associated with CSG formations (Vassilev *et al.* 1996). In Australian coals, the Mn content produced from siderite within the Tongarra coal measures is about 3000 mg/kg and in Bentley Tops is 10,000mg/kg. Furthermore, the Mn concentration in calcite within coal measures in Queensland is approximately 2240 mg/kg, 10,000 mg/kg in Wallarah and 4650 mg/kg within the Hunter Valley coal measures (Swaine 2015). Lastly, the Mn content in New South Wales coal measures can be attributed by the mineral ankerite and has a statistical range between 500 – 17700 mg/kg with a mean of 7500 mg/kg (Swaine 2015). Furthermore, there is evidence that higher rank coals have smaller concentration of Cu, As, Mn, Cr, V and Mo (Boyd 2004). In the US, coals with a rank between lignite to anthracite have lower concentration of Mg, Ca, Ba, B, Sr and Na and higher concentration of Cl (Boyd 2004). Coals with a lower rank will have an ash content composed of feldspar, calcite, gypsum, pyrite and Fe or Al or Ba rich sulphide minerals. These minerals are associated with an authigenic origin and have higher total organic carbon (TOC) (Vassilev *et al.* 1996). The most common authigenic minerals associated with coal formation are: pyrite, quartz, calcite, siderite and ankerite (Boyd 2004). Pyrite is a very important mineral in determining TE within CSG formations as they are generally associated with As, Co, Hg, Mo, Se, Fe, Zn and Pb (Vejahati *et al.* 2010; Boyd 2004). This is illustrated by certain Chinese coals containing concentration of As up to 32,000mg/kg (Boyd 2004). Furthermore, CSG formation contain organic sulphur within the organic matter and also contain inorganic sulphur that is present in the mineral pyrite (Boyd 2004). Generally, coals that are influenced by marine environment have greater concentration of pyritic sulphur, iron, zinc and sulphate sulphur (Boyd 2004). During deposition if the formation is influenced by fluvial mechanism then the coals can have higher concentrations of Cu, Cr, Ti, K, Si and Al (Boyd 2004). Carbonate minerals are also important as they generally have high concentration of Mn. The carbonate minerals associated with CSG formations that have high Mn content include; siderite, calcite and ankerite (Swaine 2015). Groundwater rich in Mn can be incorporated into the CSG formation from mixing of Mn-rich groundwater and formation waters that originated from nearby carbonate-rich formations, thus increasing the Mn concentration within the CSG formation waters (Boyd 2004). Seawater, clays, organic matter and on occasionally tourmaline contain B (Table 1). These materials influence the B concentration within the coal formations (Swaine 2015). The concentration of B is influenced by the salinity levels of fluids that interact with the original deposition environment (Boyd 2004). CSG formations that were dominantly influenced with freshwater have B concentration of up to 50 mg/kg. Furthermore, if the original depositional environment was influenced by brackish water than the B concentration will range between 50 – 110 mg/kg and if highly saline fluid interacted with the formation than the concentration of B will be above 110 mg/kg (Boyd 2004). These are some examples of how salinity and the minerals pyrite, siderite, calcite and ankerite play an important role in B, Mn and As content within CSG formation waters. Furthermore, hydrological mechanism influences the enrichment and distribution of TE within coal seams. Within freshwater environments the circulation of groundwater influences the distribution and enrichment of Na, B, Ca and Ba (Boyd 2004). The cementation of authigenic minerals such as pyrite or sphalerite can influence the permeability of the formation and the composition of formation water, thus ultimately impacting the variation of authigenic minerals and the associated TE that could be incorporated or circulated into the formation water (Boyd 2004). For example, brown coals in Victoria, Australia have elevated concentration of Na, B, Ca and Br within the top layer of the coal formation, which was associated with groundwater transporting and facilitating bonding mechanism of these TE to the upper section of coal formation (Boyd 2004). Furthermore, the infiltration of meteoric water within some Chinese coals has facilitated the enrichment of U, Mo and germanium within the upper section of the coal formation (Boyd 2004). There have been studies conducted regarding Chinese coals that illustrated epigenetic carbonates within groundwater depositing Mn, Zn, Ca, Cd, Sr and Ba into the coal formation (Boyd 2004). The trace element Cd is generally not associated with organic and inorganic material or clay or carbonate minerals but can be associated with sulphide or other minerals (Table 1). The mobilisation of Ba, Ca, Cl and Na can be incorporated within coal formations from gypsum, halite, anhydrites and carbonates (Vejahati *et al.* 2010; Boyd 2004). These studies illustrate that the occurrence of certain TE within rock formations are associated with the local composition of the source rock and the surrounding geological environment that groundwater has interacted with. Furthermore, due to the heterogeneity of rock formations the concentration of different TE will vary within the same coal measure, thus illustrating that certain sections will have a variation of formation water composition associated with the same formation. (Boyd 2004; Table 1). Shale formations can have a range of organic material and the amount of organic material present within the SG formation will illustrate which TE will be found in high concentration. Using the mode of occurrence, the major trace elements associated with organic material include; Be, B and Cl (Table 1). Calcite and dolomite are carbonate mineral that is associated with shale formation. Calcite and dolomite can drastically vary between shale formation and this variation will impact the concentration of Ba and Mn, as they are the dominant TE associated with carbonate rocks. Furthermore, carbonifous carbonates, chert and terrigenous material contain high concentration of Zn with carbonifous carbonates and chert containing the highest amount of Zn, while terrigenous rocks impact the formation to a lesser degree (Ketris and Yudovich 2009). Black shales can contain a significant amount of pyrite, which formed under anoxic condition. The pyrite can become oxidised during oxic conditions induced by hydraulic fracturing fluid, thus forming sulphuric acid within the sub-surface strata (Chermak and Schreiber 2014). This sulphuric acid can induce the mobilisation of other TE within the formation, such as carbonates, thus increasing the Ba and Mn content within the formation water (Chermak and Schreiber 2014). In the US, a study determined that Cr concentration was the highest from 40 black shale samples compared to the worldwide average from thousands of samples and that the dominant TE within black shales around the world include; Ba, V, Zn, Cr, Cu, Ni, As, Mo, La, Pb, Co, An and Be with Ba as the highest constituent and Be the lowest.

NORM material occur within various minerals, as they are able to chemically bond under the right environmental conditions. These NORM increase the radioactivity of the formation water during exposure from the natural process of radioactive decay. The sulphate

mineral barite readily incorporates Ra isotopes and is the primary constituent of NORM in O&G formations. During the extraction of produced water Ra is brought to the surface and incorporates into barite (Zielinski and Otton 1999). The concentration of Ra within produced water can be determined by having an understanding of the formation waters salinity concentration and the amount of Cl within the fluid (Zielinski and Otton 1999). Therefore, the more Cl and saline rich the formation water the more Ra is found (Zielinski and Otton, 1999). Thorium can become incorporated into a sedimentary basin by its ability to be absorbed by hydroxide and clay particles during deposition. Therefore, rocks with high clay mineral content are more likely to have high concentrations of Th (Zanin *et al.* 2016). U can become incorporated into a sedimentary basin authigenically by fluids that contained dissolved U when entering the basin (Zanin *et al.* 2016). Clay and silicate minerals such as, feldspar, mica and quartz contain ^{40}K , which are incorporated into the formation by alluvial and fluvial mechanisms from eroded crustal material and volcanic activity (Zanin *et al.* 2016). These minerals are common in sedimentary rocks associated with O & G production, thus is the origin of ^{40}K within their formation water (Adams and Weaver 1958). Black shales contain trace levels of ^{238}U , ^{235}U , ^{40}K and ^{232}Th and generally have a higher concentration than shales with less organic material. This is due to ^{40}K and ^{232}Th having preference in bonding with clay material and the preference of ^{238}U and ^{235}U to chemically bond with organic material (Adams and Weaver 1958). Therefore, the composition of organic material within shale rock can determine the amount of NORM within shale lithologies (Schmoker 1981). The concentration of U and Th contained within organic rich shale can range from 10 to 100 mg/kg, which is much higher compared to the average crustal concentration of 2 – 3 mg/kg (Adams and Weaver 1958). These types of organic material associated with black shales contain different concentration of U with humic material containing far more U than sapropelic material (Swanson 1960). Therefore, if the SG formation contains high amount of humic material than the formation will be elevated in U compared to sapropelic. The dissolution of the highly radioactive minerals can increase the radioactivity of the formation water. Therefore, radioactivity of produced water depends on the minerals incorporated from detrital and authigenic processes.

Produced Water Results:

The information provided in the previous section illustrates the potential origin of TE and NORM within produced waters. This section will illustrate TE associated with the three hydrocarbon types and then with different basins, thus illustrating the variation of TE within compositionally different source rocks. The overall analysis of CSG produced water samples in the U.S. illustrates that Ca, Na, Mg and Cl were the four most dominant trace elements associated with CSG produced water with Ca being the most concentrated and Cl being the least out of these dominant T.E. Furthermore, the overall analysis of SG samples in the U.S. illustrates that Na, Cl, Sr, Br, K, and Mg were the six most dominant trace elements associated with SG produced water with Na being the most concentrated and Mg being the least out of these dominant T.E (Figure 1-4). In regards to a comparative study between the three hydrocarbon types, the results indicate that: (a) Ba and Sr are more concentrated in SG compared to CSG and conventional O&G, (b) Al, B, Br, K, Na, Pb and Zn are more concentrated in conventional O&G compared to SG and CSG produced water, and (c) CSG has the lowest average concentration of all TE compared to the SG and conventional O&G (Figures 1-4). Therefore, CSG on average will impact groundwater the least from the same volume of produced water contamination compared to the other two. However, CSG generated far more produced water because the formation requires dewatering before the resource can be extracted, thus greater volumes of produced water is transported to wastewater treatment facilities than SG and conventional O&G. The average produced water concentration of Ca and Cl within the Michigan SG basin is significantly higher compared to the Green River and Appalachian basin. Furthermore, the Na content within the Appalachian is significantly higher than the Green River Basin (Figure 5). The Mg produced water content within the Michigan SG basin is significantly higher than the Green River, Appalachian, and Anadarko – Southern Oklahoma Basin with the Appalachian Basin containing the second highest Mg concentration compared to the other two (Figure 6). The concentration of Sr, Ba, Br, and K associated with SG produced water within the Appalachian Basin is the highest compared to the Green River, Michigan, and Anadarko – Southern Oklahoma Basin. However, comparing the K content between the Appalachian and Michigan basin illustrates that they have almost similar average concentrations with the Appalachian basin containing slighter higher values (Figure 6). In addition, I, B, and Mn concentrations within Appalachian SG produced water is higher than the Michigan Basin (Figure 7). The high Mn concentration could have originated from a source rock mineralogy that composed of a high degree of carbonate mineral. Furthermore, the high B levels could indicate that highly saline groundwater interacted with the Appalachian basins source rock, thus depositing B from an authigenic origin. The average concentration of Cl, Na and Sr associated with CSG produced water is highest within the Green River Basin compared to the Black Warrior, Powder, Raton, San Juan, and Uinta–Piceance, and Wind River Basin. In Addition, the Ca concentration associated with the San Juan Basin is the highest compared to the other six basins (Figure 8&9). The average Ba, Cr, Fe, and K concentration associated with CSG produced water is highest within the Wind River basin compared to the other six basins. However, there is a lack of available data for Cr for the Green river and Uinta–Piceance CSG basin. The origin of the Fe could be attributed to high sulphide mineral composition within the source rock derived from an authigenic origin. Furthermore, the average concentration of Mg associated with the Uinta–Piceance CSG basin is the highest compared to the other six basins (Figure 9). The average B, Br, and Li concentration within the Raton Basin is highest compared to the other six basins. However, there is an exception for Li for the San Juan and Winder river basin, as no sampling data is available for these basins (Figure 10).

Discussion and Limitations:

The degree of NORM and TE concentrated in wastewater is important as it illustrate if the wastewater is able to be reused for other purposes such as, reinjection into the well or irrigation purposes post treatment. However, not all treatment facilities have adequate treatment technologies to remove the hazardous material to the adequate standards for disposal or reuse. Therefore, having an understanding of the toxicity of produced water will felicitate allocation of produced water to appropriate, thus developing standards for the handling of produced water post extraction. In the US, produced water was initially sent to wastewater treatment facilities that was not equipped to achieve the required standards for safe disposal of contaminated produced water and eventually refused to accept produced water for treatment purposes. Therefore, determining the degree of toxicity is important because it will ensure that wastewater treatment facilities are able to achieve the safety standards by developing a more effective wastewater classification similar to waste classification standards for general solid or restricted waste by developing defined toxicity thresholds limits and assigning them to the facility with adequate treatment technologies. Inadequate treatment of produced water derived from the Appalachian basin that contained high concentration of NORM's had impacted freshwater ecosystems even though the results indicated that it was treated to

a satisfactory standard. This occurred from a number of disposal cycles that led to NORM accumulation in the sediment at the point of discharge, thus directly impacted nearby aquatic biota and potentially impacting humans who consumed seafood from that water system. The high level of NORM concentration within produced water can also impact infrastructure during extraction, transport and treatment by increasing radiation levels, thus requiring decontamination procedures to ensure that health and safety legislative standards could be achieved. The USGS produced water database is lacking any form of laboratory testing relating to Be, I, Mo, Rh, S, Th, and Ti associated with CSG produced water sample. In addition, the USGS produced water database is lacking any form of laboratory testing relating to Bi, Rh, Sc, Th, U, and V associated with SG produced water sample. Furthermore, there is minimal overall Cs, I and Rb, produced water data collected for SG formations within the U.S., thus doesn't illustrate the complete variation of these trace elements (Figure 1-10). Lastly, the USGS produced water database is lacking laboratory data relating to ^{40}K , $^{238/234}\text{U}$, $^{226/228}\text{Ra}$, $^{222/220}\text{Rn}$, ^{210}Pb , ^{210}Po , and ^{232}Th NORM concentration within conventional O&G, CSG and SG. Therefore, a comparative study between produced water NORM and source rock mineralogy is not possible within this research topic. However, using the information contained within the mineralogical results section can facilitate predicting NORM concentration. It is important to have future testing done on the trace elements and NORM stated above to determine their concentration and their potential impact on water quality and therefore is an aspect that can be a topic for further research.

Table 1 illustrates the mode of occurrence of likely trace elements associated with different mineral groups (in %) generated from global case study averages (Boyd 2004, p.49).

Trace Elements	Organic Material	Inorganic Material	Sulphide Minerals	Clay Minerals	Carbonate Minerals	Other Minerals
As	15	14	69	1	0	1
Ba	21	19	0	21	35	4
Be	75	0	0	25	0	0
B	81	0	0	25	0	0
Cd	0	0	32	0	0	68
Cl	61	0	0	0	0	39
Cr	22	28	0	30	0	20
Co	33	19	23	14	6	5
Cu	22	20	38	13	0	7
Pb	5	13	65	0	0	17
Mn	18	19	10	0	37	16
Hg	0	8	78	0	0	14
Mo	34	6	49	0	0	11
Ni	23	11	36	0	0	31
Se	25	7	43	0	0	24
Th	1	40	0	0	0	59
Sn	9	30	33	0	0	28
U	39	32	0	22	0	7
Zn	7	16	35	0	0	42

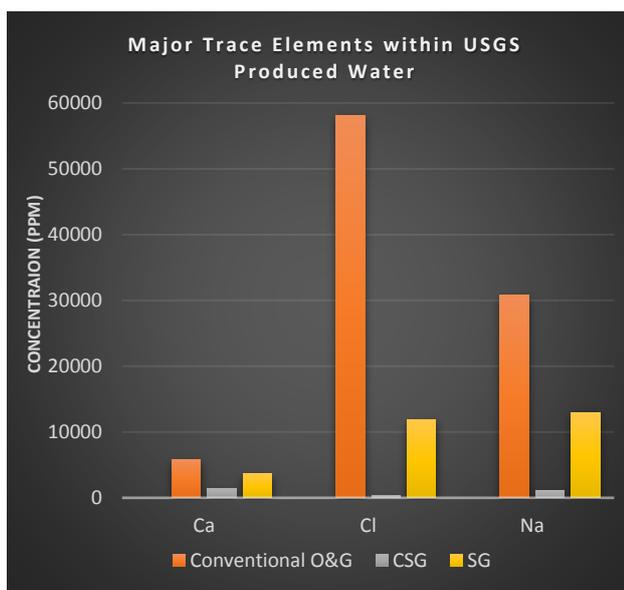


Figure 1 illustrates the average concentration of major trace elements within produced water associated with conventional and unconventional O&G (derived from the USGS produced water

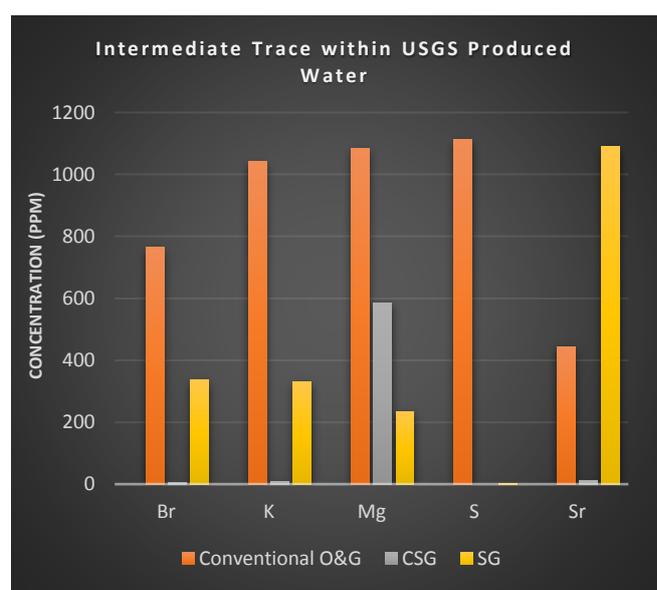


Figure 2 illustrates the average concentration of intermediate trace elements within produced water associated with conventional and unconventional O&G (derived from the USGS produced water

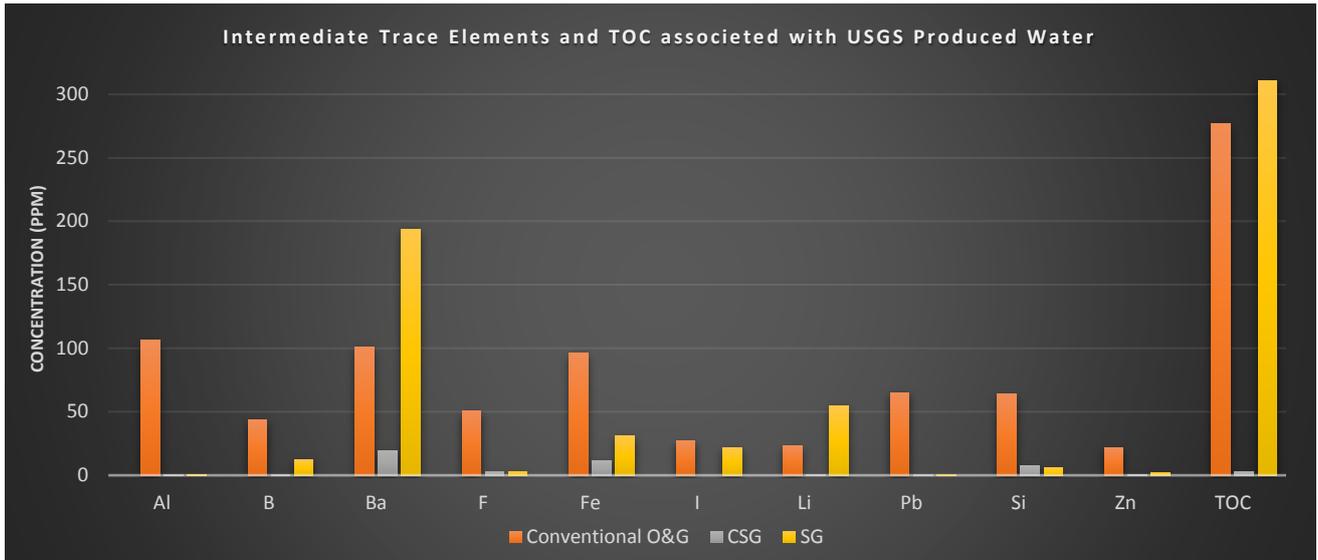


Figure 3 illustrates the average concentration of intermediate trace elements and TOC within produced water associated with conventional and unconventional O&G (derived from the USGS produced water database).

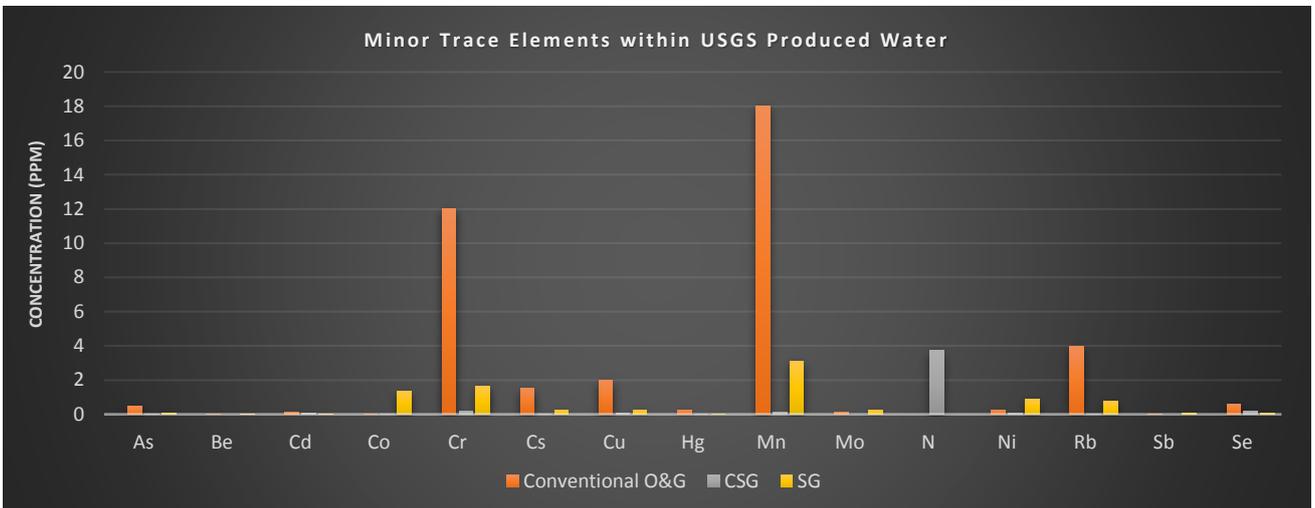


Figure 4 illustrates the average concentration of minor trace elements associated with conventional and unconventional O&G produced water (derived from the USGS produced water database).

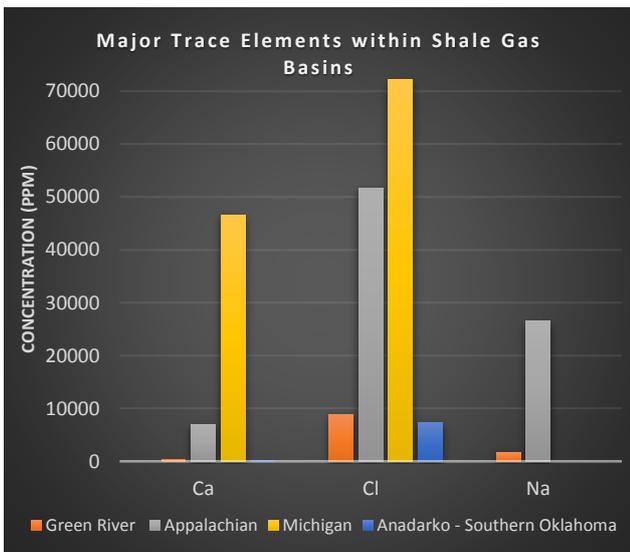


Figure 5 illustrates the average concentration of major trace elements within produced water associated with different shale gas basins (derived from the USGS produced water database).

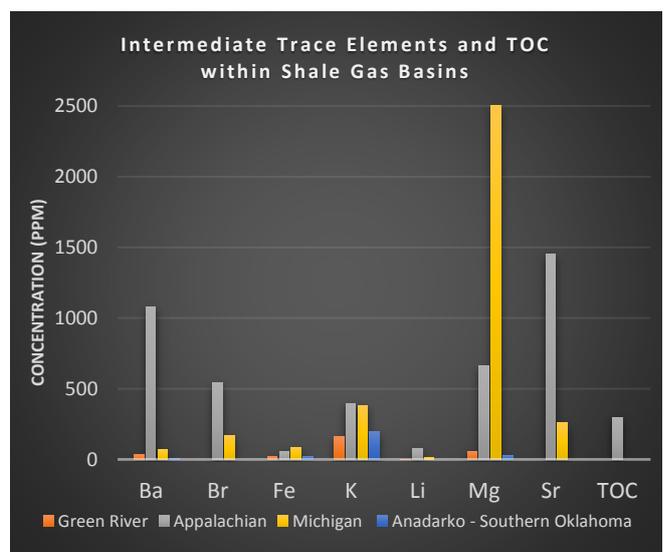


Figure 6 illustrates the average concentration of intermediate trace elements and TOC within produced water associated with different shale gas basins (derived from the USGS produced water database).

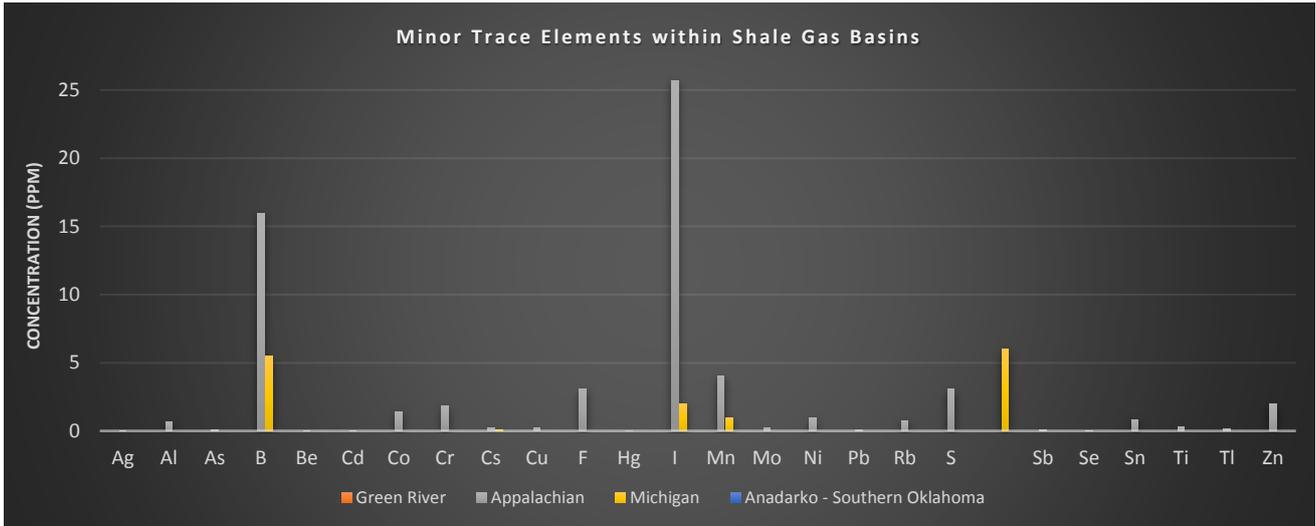


Figure 7 illustrates the average concentration of minor trace elements within produced water associated with different shale gas basins (derived from the USGS produced water database).

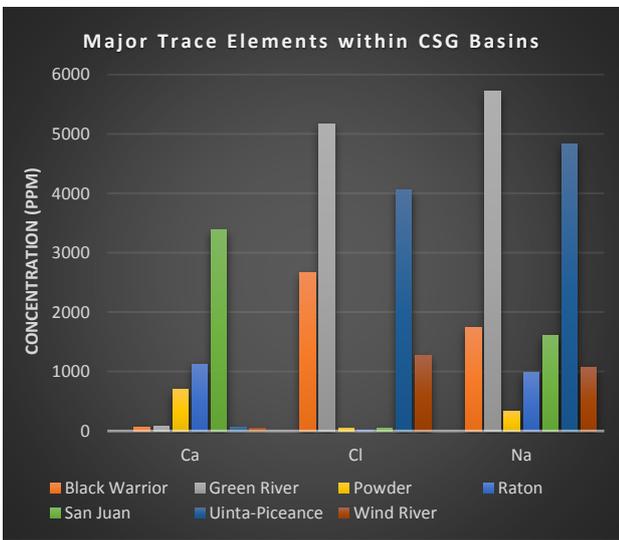


Figure 8 illustrates the average concentration of major trace elements within produced water associated with different CSG basins (derived from the USGS produced water database).

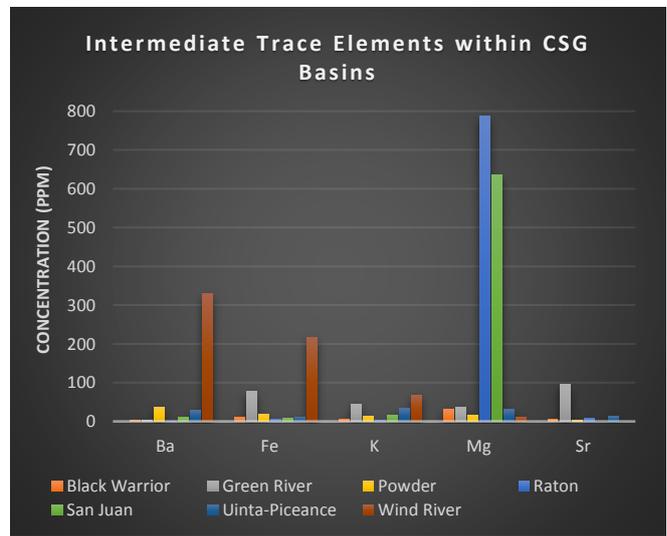


Figure 9 illustrates the average concentration of intermediate trace elements within produced water associated with different CSG basins (derived from the USGS produced water database).

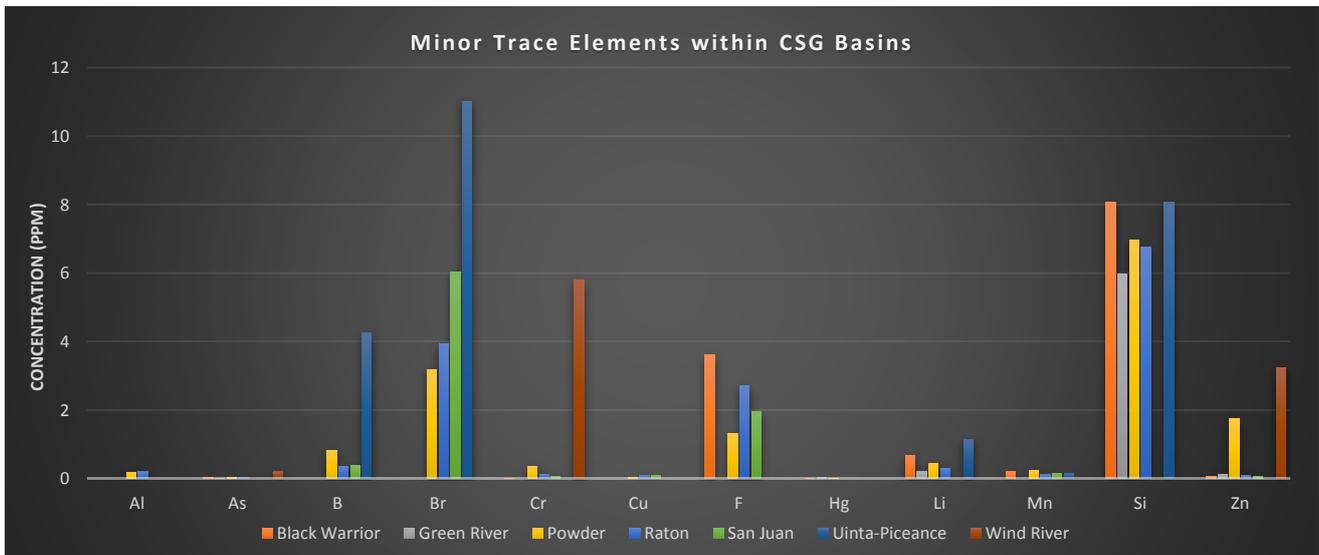


Figure 10 illustrates the average concentration of minor trace elements within produced water associated with different CSG basins (derived from the USGS produced water database).

CONCLUSIONS

This analysis has developed a possible correlation between source rock mineralogy groups and the concentration of trace elements within produced water. This data illustrates potential sources of trace elements from mineralogical studies using the mode of occurrence of trace elements associated with different mineral groups. This was achieved by comparing the USGS geochemical produced water results from figures 1-10 to the mode of occurrence of trace elements from different mineral groups from table 1. This geochemical data compiled was the foundation of this research topic and is a guide for future research regarding geochemical composition and TE mineralogical origin of trace elements and NORM's. However, geochemical concentrations can vary between formations (as illustrated from figures 5 - 10) and therefore a detailed study is required for individual formations through a number of investigative techniques such as core and produced water sampling analysis, to confirm or reject the results illustrated in this topic. This variation of produced water toxicity will require different treatment techniques to remove contaminants at a cost effective price. This can be achieved by; (a) developing a more detailed geochemical analysis of TE's and NORM's associated with different mineral groups, (b) developing a more detailed produced water database, (c) confirming results with geochemical analysis of core samples for a more detailed understanding of the formation of interest and improving on the methods stated within this topic and (d) ensuring that highly contaminated produced water is allocated to facilities with purification techniques that will achieve the disposal standards for the target purpose at a lesser cost. These studies will ultimately lead to a greater understanding of formation water and the mineralogical source of TE and NORM, thus illustrating the degree of impact of produced water to the environment from accidentally seepage or during disposal practices post treatment. However, this produced water database is lacking in many countries and currently only reside within the United States, which is impacting the overall scientific understanding of the potential impact of produced water to the environment from fluid migration and inappropriate allocation of produced water to facilities that cannot achieve the safety standards for disposal. The utilisation of the information provided will provide decision-makers the means to develop a produced water management plan during the initial exploration phase by review scientific literature, laboratory analysis of core samples (during initial drilling) and later validate the expected values with laboratory analysis of produced water samples, thus developing a detailed PWMP to adequately deal with the growing concern of produced water. This will ensure that standards for produced water generated from mining are effective to adequately deal with the rise in quantity of produced water being extracted from the increase in unconventional hydrocarbon extraction.

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