Approval to defend

THE USE OF IODINE TO CHARACTERIZE FORMATION WATERS IN OIL AND GAS FIELDS

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Abstract
Hydrologists and geochemists commonly use the solutes chloride and bromide and their ratio to distinguish sources of salinity in waters. These halogens neither precipitate from solution nor react with aquifer minerals and ideally can trace solute migration in both surface and ground waters. However, where bromide and chloride ratios are similar in multiple aquifers, it can be difficult distinguishing water sources from wells that tap them. Similarly, discriminating waters produced with hydrocarbons from only bromide and chloride concentrations can be difficult if the origin of salinity is the essentially the same (e.g. evaporation of sea water or fresh water). This thesis explores how to characterize formation waters within both a non-marine hydrocarbon producing basin and a marine sourced hydrocarbon basin by using a combination of halogens and stable water isotopes.

Chapter 1 explores interpretation of the chemical composition of samples of water collected with oil produced from lake derived Triassic-aged Karamay (T2k) and Jurassic-aged Badaowan (J1b) and Qigu (J3q) formations in the northwestern margin of the Junggar Basin, located in western China. Scatter plots of deuterium (2H) and Oxygen-18 (18O) isotopes of oil-field waters from this basin show a trend below and deviating to the right of modern evaporated surface waters in the region, which may reflect paleoevaporation from ancient Junggar Lake from which oil derived. Br/I ratios from the waters produced with oil separate formation waters and identify lacustrine (Br/I from 2.9 to 8.2) from marine origins (Br/I from 1.2 to 2.4). The Br/I ratios can also show where formation waters from multiple formations naturally mix or mix in production wells.

Environmental concerns regarding the potential for shallow aquifer contamination has led to controversy on hydraulic fracturing of the Marcellus formation in the Appalachian Basin. Chapter two of this thesis explores how bromide and iodide ratios I measured from 60 shallow
ground water samples in the southern Tier of New York suggest that solutes potentially derived from deep organic rich Marcellus formation water can be distinguished by Br/I ratios. Water with a Br/I ratio of ~19 are consistent with that associated with Marcellus shale production waters whereas higher or lower Br/I ratios may suggest a different organic rich source rock. Combined, the work on iodide and other halogens in China and southern New York highlight the potential value of iodide as an environmental tracer associated with oil and gas production in general.
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Chapter 1. Characterizing and Distinguishing oil-field brines and sources in the
Northwestern Margin, Junggar Basin: The use of halogens and stable water isotopes
(Note: This manuscript is written in the style of the journal Applied Geochemistry)

1. Introduction

Geochemical analyses of oil-field brines can be used to understand the origin and
evolution of waters in oil and gas fields because hydrocarbon bearing formations in sedimentary
basins typically contain water with high salinity, exceeding 100 g/L. In marine basins this solute
enrichment usually is caused by seawater evaporation coupled to halite precipitation (e.g. Hanor,
1994; Carpenter, 1978; Dellwig and Evans, 1969; Dollar et al., 1991), whereas in non-marine
basins, lake evaporation controls salinity of original formation waters (i.e. Jones et al., 2009;
Ortega-Guerrero et al., 1997; Horita et al., 2009) with differences of chemistry dependent upon
climate during deposition (Carroll and Bahacs, 2001).

With compaction, residual brines associated with the hydrocarbons disperse into other
parts of sedimentary basins through geologic time, sometimes many kilometers from the source
(Bethke, 1985). Produced water occurs with oil and gas (Collins, 1975) and contains various
natural tracers in formation waters that can fingerprint hydrocarbon source formations and
geochemical evolution of the waters. Common geochemical tracers include dissolved bromide
and chloride (i.e. Walter et al., 1990; Davis et al., 1998; Gupta et al., 2012), strontium
concentrations and isotopes (i.e. Warner et al., 2012; Osborn et al., 2012; Chapman et al., 2012),
and stable water isotopes (i.e. Cai et al., 2001; Smalley et al., 1992; Lowry et al., 1988).
Geochemists widely use chloride and bromide in formation water geochemical studies
(Carpenter, 1978) because of their conservative chemical behavior. Ratios of chloride to bromide
can trace groundwater and surface water flow and distinguish sources of salinity; formation
brines, road salt, and septic effluent (i.e. Panno et al., 2006; Richter et al., 1993; Siegel and Knight, 2011). Iodide and fluoride are occasionally analyzed in formation waters but uncommonly used to trace oil-field waters (Worden, 1996). Iodine geochemistry in oil and gas field studies may give additional information on sources of brines which other tracers cannot distinguish.

Iodide shares similar chemical behaviors with chloride and bromide but its distribution in rocks and waters differs. Iodide uncommonly occur in rock-forming minerals and concentrations of iodine typically are smaller in freshwater than in the marine environment. Iodide concentrations in shallow ground water and surface waters are generally <0.05 µM (Panno et al., 2006), whereas the average iodine concentration in seawater is about 0.5 µM (Krauskopf, 1979).

Marine organic-rich sedimentary rocks are a major source of iodine and have distinctive Br/I ratios. Consequently due to its biophillic nature, high concentrations of iodine occur in oil and gas field brines (Moran et al., 1995; Bottomley et al., 2002; Panno et al., 2006; Dresel and Rose, 2010; Osborn et al., 2012) and in some cases, iodine rich salts are mined from these fluids (ex: Krukowski, 2008). The amount of organic matter decomposition during hydrocarbon generation in marine environments influences the amount of iodine released (Fuge and Johnson, 1986).

In terrestrial settings, iodine in sediments and organic matter mostly derives from rainfall (Fuge and Johnson, 1986) and sorbes onto organic matter if present. Thus hydrocarbons and associated formation waters derived from organic-rich sediments originally deposited in terrestrial environments will have higher concentrations of iodine than found in non-organic sediments (Worden, 1996; Fuge and Johnson, 1986). Potentially, iodine should be useful as a tracer for sedimentary basin brines wherever it is associated with organic-rich rock, independent
of marine or terrestrial setting. The use of Br/I ratios could serve as a means to distinguish marine versus terrestrial source rocks in organic rich settings since it is unlikely Br/I ratios will be the same between marine and terrestrially derived organic matter (Fuge and Johnson, 1986).

This paper presents the results of a study on formation fluids sampled from oil wells in the Junggar Basin, northwestern China. Here, Chinese petroleum companies extract asphalitic oil by injecting fresh water into reservoirs into which oil migrated from both marine and lacustrine organic rich sources. Geologic faulting controls oil accumulation in the basin (Cao et al., 2010, 2012; Rhodes et al., 1996; Chen et al., 2001, 2011; Wu et al., 2011) and details of the petroleum geochemistry in different reservoirs are well known. (Cao et al., 2006; Hu et al., 2010). However, no clear characterization of the original source beds for the oil has been done based on analyses of associated formations fluids. Herein I show the effectiveness of using halogens (Br⁻, Cl⁻, I⁻) and stable water isotopes to characterize the sources of formation waters in the northwestern margin Junggar Basin and the degree to which injection waters mix with oils.

2. Study Area

2.1 General overview on Junggar

The Junggar Basin covers an area of 1.3 x 10⁵ km² in the northern part of the Xinjiang Uygur Autonomous Region, Northwest China, (Fig.1) and is well known for its crude oil (Ulmishek, 1984; Cao et al., 2005). The Northwestern margin of the basin contains more than 40% of the basin reserve (Cao et al., 2006). To increase oil production, Chinese oil companies inject water to displace the waxy crude towards the producing well.

Samples of produced water for this study came from three production “blocks” in the Chepaizi and Hongshanzui oilfields along the Hongche fault in the Northwestern margin of the
basin (Fig. 1). Each of the three blocks varies in structure, production/injection trends and producing reservoir. Block 29 (B29) consists of three producing formations into which separate injection wells are placed (Fig. 2). Parallel NW-SE thrust faults compartmentalize the field. Production occurs from the Lower Jurassic Badaowan (J1b) and Triassic Karamay (T2K1, T2K2) formations (Fig. 3). In B29 block, these formations form a symmetrical homocline with a structural high uplift that steepens to the northwest. Four wells inject 103 m$^3$ of water per day approximately 1800 m deep into the J1b. Eight wells inject 119 m$^3$ water per day 2050 m deep into T2k1 and two wells inject 39 m$^3$ of water per day into T2k2.

Block 67 (B67) consist of a 3.4 km$^2$ triangular shaped area bounded by two S-N and NE-SW trending normal faults, the Hongche and Well Che7 (Fig. 4a) formed before Jurassic time, and by reverse faults formed after the Jurassic in the E-W and NW-SE direction. B67 produces from the Jurassic (J1b) formation. Compared to B60 and B29, this production area has lower porosity and permeability and larger well spacing between injection and production wells. Three wells inject 41 m$^3$ water per day approximately 2560 m deep into the J1b. Block 60 (B60) within the Chepaizi oilfield (Fig. 1) covers 3.7 km$^2$ (Fig. 4b) and formed between normal faults formed during the Jurassic Period. B60 produces oil from the Upper Jurassic Qigu (J3q) formation (Fig. 3) at an average depth of 2400 meters. Fourteen wells inject 395 m$^3$ of water per day approximately 2325 m into the J3q formation.

2.2 Geologic Background

2.2.1 Structure and Tectonic History

The Junggar (Fig. 1) formed as a continental sedimentary basin evolving from the compression between the Altai fold orogenic belt, Siberian Plate, Kazakhstan plate, and
Tianshan fold orogenic belt (Chen et al., 2001, 2002). Four orogenies (Hercynian, Indosinian, Yenshanian and Himalayan) contribute to the complex tectonic framework during the last 410 million years (Chen et al., 2002). Fan delta, lake, and swamps deposited accumulated sediment throughout the Paleocene into Pleistocene, during which a stable shallow lake formed (Wang and Kang, 1999, 2001). The tectonic and litho-stratigraphy have been subdivided into four generalized sequences (Chen et al., 2001, 2002): (1) foreland oceanic basin during Late Carboniferous to Early Permian, (2) Foreland continental basin during Middle to Late Permian, (3) intracontinental depression during the Triassic to Cretaceous, and (4) a rejuvenated foreland basin during the Paleogene to Quaternary (Cao et al., 2006). The Himalayan orogeny of the Late Mesozoic did not extend to the northern Junggar (Chen et al., 2001, 2002).

Oil and gas fields occur throughout the basin, mainly located along fault zones (Fig. 5), (Cao et al., 2006) of which the Hongche Fault serves as a prime example (Cao et al., 2010), trending NE-SW to N-S, along the southern flank of the northwest margin of the basin.

2.2.2 Oil Reservoir and Source Rock Geology

Oil and gas migrated from Permian source rocks and accumulated mostly in alluvial conglomerates and sandstones of Permian, Triassic, and Jurassic age and in some deltaic sandstone of Upper Jurassic and Lower Cretaceous (Chiyi, 1981; Cao et al., 2005, 2010).

Wells sampled produce from Triassic Karamay (T2k), the Lower Jurassic Badaowan (J1b), and the Upper Jurassic Qigu (J3q) reservoir. The reservoir rocks consist of intercontinental depression deposits (Fig.3). The T2k has been divided into two members: T2k1 was deposited by a braided stream whereas the T2k2 member was deposited by a piedmont river.
The Middle and Lower Jurassic deposits in the northwestern Junggar Basin consist of alternating gray carbon-rich sandstones and conglomerate argillite containing thin layers of coal deposited in swampy, riverine and shallow lacustrine environments (Yunkhun and Burlin, 2007). The lower Jurassic Badaowan formation (J1b) consists of arkose sandstone with kaolinite deposited in a distributary lake deltaic channel and braided fluvial system. The Upper Jurassic Qigu formation (J3q) was deposited by alternating cycles of braided rivers and lake deltaic deposits.

Geochemical and sedimentological data show there are three sets of hydrocarbon source rocks, the Lower Permian Jiamuhe formation (P1j) and Fengcheng Formation (P1f), and the Middle Permian Lower Wuehe Formation (P2w) (Fig.3; Jiang and Fowler, 1986; Jiang et al., 1988; Graham et al., 1990; Carroll et al., 1990, 1997; King et al., 1994; Clayton et al., 1997; Pan and Yang, 2000), with the main source generally believed to be dark shales of the Lower Permian Fengcheng and Middle Permian Wuerhe formations (Chen et al., 2004). The Lower Permian Jiamuhue and Middle Permian Wuerhe formations are dark grey and tuffaceous mudstones deposited in a fairly fresh lacustrine environment.

In contrast, the Lower Permian Fengcheng formation was deposited in a hypersaline lagoonal environment and consists of dark grey, dolomitic tuffaceous mudstones and carbonate rocks (Cao et al., 2005). Oil generation occurred from the Permian Fengcheng and Jiamuhe source rock formations during the Late Triassic (Cao et al., 2006) and then migrated with faulting into reservoirs in the Upper Triassic (i.e. Karamay formation). Multiple source rocks could have generated oil now found in the same formation.

The oil source rocks for the reservoirs have been explored using geochemical analysis of free and inclusion oil-bearing fluids from reservoir rocks (Cao et al., 2005, 2006; Pan and Yang,
Oil produced from the T2k formation probably came from the Fengcheng formation, whereas oil in the J3q formation appears to consist of mixed sources from the Lower Wuerhe and Fengcheng oils (Cao et al., 2006, 2010). Different oils can be distinguished by kerogen type suggesting both terrestrial and marine sources contributing organic matter (Cao et al., 2005, 2006). Type III kerogen indicates terrestrial plant material contributed the organic matter necessary for hydrocarbon generation and is observed in oils from P1j and P2w formations. Oil from the P1f formation show kerogen types I and II and suggest the organic matter was derived from algal remains in anoxic lake conditions and plankton in marine environments (Cao et al., 2005).

Oil and gas in the Junggar Basin was generated from different source rocks and then either migrated into the same reservoir, or into different reservoirs (Cao et al., 2005). This has led to some debate on which hydrocarbon source contributed oil to reservoirs in the NW margin of the Junggar Basin. Cao et al., (2006) propose the Fengcheng source rock contributes the most oil to the reservoirs in the Northwest margin, whereas the Jiamuhe contributes the least. The Triassic reservoir rock (T2k) had at least two separate charging events from the Fengcheng and Jiamuhe formations during the Late Triassic to Early Triassic and the Cretaceous. Whereas the Jurassic reservoir rock (J3q) has had only one charging event during the Cretaceous with hydrocarbons from the Fengcheng and Lower Wuerhe formations (Cao et al., 2006).

3.0 Methods

3.1 Sampling Procedure

Oil and water samples from 65 production wells and 26 injection wells from three blocks in the Junggar Basin were collected (Fig.1). Employees of PetroChina collected oil/water mix
samples from free-flowing well, swapping pump jack production wells, and water injection wells into 500mL high density Nalgene plastic bottles. Production of the thick asphaltic oil is enhanced by injecting fresh to brackish water collected from overlying shallow formations into the oil bearing units to help mobilize the oil.

If the water-oil sample visually contained more than 30% water, a course silicon filter was used to separate the water out. When the matrix contained more than 70% oil, the sample was placed into a water bath for about 5 minutes at 75 degrees Celsius. Afterwards a centrifuge was used to coarsely separate oil and water. The water was then collected using a Leur Lock syringe fitted with a 0.45 µm filter.

For anion and stable water isotopic analyses, the sample was filtered again through a 0.45-µm nylon filter and collected in a HDPE bottle, filled with no headspace. Samples for metal analyses were filtered in the same manor and then acidified with nitric acid to a pH <2. All samples were stored at 4°C until analysis was complete.

3.2 Analytical Methods

Specific conductance and pH were completed in lab using a WTW Multiline meter. Total dissolved iodine and bromine concentrations were measured on ICP-MS, a Bruker Aurora M90 at Syracuse University following methods by Muramatsu and Wedepohl, 1998. Instrumental error for iodine and bromine concentrations were below one percent and are not reported individually. Anion concentrations (F⁻, Cl⁻, SO₄²⁻, NO₃⁻, PO₄³⁻) were measured by ion chromatography (IC) using a Dionex ICS-2000 with a AS18 column at Syracuse University. The IC was calibrated with five internal laboratory standards and the calibration quality was validated
using three external USGS standard reference samples (N103, M178, and P50, http://bqs.usgs.gov/srs/). The relative percent error for replicate samples is under 3%.

Trace metal concentrations (Ba, B, Ca, Mg, Mn, K, Na, Sr, Li, Fe) were measured with an Elan DRC-e Inductively Coupled Plasma Mass Spectrometer (ICP-MS) equipped with an S-10 auto sampler through the Analytical and Technical Services Department at SUNY College of Environmental Science and Forestry (error bars, probably within 3%). Stable water isotopes were determined under contract with Isotope Tracer Technologies Inc. located in Ontario, Canada. The results were reported relative to SMOW with an average repeat error of ±0.10‰ for δ¹⁸O and ±0.30‰ for δ²H.

4.0 Results

The water extracted from the produced oils for this study is designated “formation water”. The samples were grouped by production reservoir formation, independent from the producing area. However the producing reservoir and block generally coincide. For example, B60 produces from Late Jurassic formation, B67 from the Early Jurassic formation, and B29 from the Triassic and Early Jurassic formations.

4.1 General Chemistry

The sodium (Na⁺), chloride (Cl⁻), bromide (Br⁻), and iodide (I⁻) concentrations for oil-field waters and injection waters are presented in Tables 1 and 2. For comparison Shallow groundwater (SGW) data from a previous study (D. Han et al., 2011) for the Karamay Agricultural District is summarized in Table 3. Only Na⁺, Cl⁻, and stable water isotopes (δ¹⁸O, δ²H) were available.
Injection waters from B60 and B67 have low concentrations for all solutes (Table 2). The B29 injection water has Total Dissolved Solid (TDS) concentrations comparable to the formation waters and is difficult to distinguish solely based on chemistry (Fig.6; fig.7). Shallow groundwater reported from Han et al., (2011) can have TDS concentrations higher than that in formation waters. Samples from the T2k1, T2k2 and J1b reservoirs, injection waters, and SGW fall closely on a one to one mixing line for Na\(^+\) and Cl\(^-\) (fig.6). The Na/Cl ratios of formation waters from T2k and J1b, injection waters, and SGW are 1.0, 2.5, and 1.3, respectively. Formation water from J3q has higher Na/Cl ratios (1.8) and lower Cl\(^-\) concentrations plotting to the right of the 1:1 mixing line for Na\(^+\) and Cl\(^-\) (Fig.6). The ratios of Cl/Br for formation water (~1373) are higher than that in seawater (639) and have a trajectory above the seawater dilution trend (fig.7). Samples from the T2k and J1b reservoir have higher concentrations of Cl\(^-\) and Br\(^-\) compared to waters from the J3q reservoir (Table 1).

Bromide and iodine concentrations of injection waters are less than 0.15 mM and 0.02 mM, respectively. In contrast, Br and I concentrations in formation water samples vary depending upon producing reservoir. The T2k reservoir waters have higher concentrations of I\(^-\) (0.008mM to 0.1mM) and less variability of Br\(^-\) concentrations (0.03mM to 0.2mM), leading to Br/I ratios less than 4.0 (fig. 8; table 1). The oil waters from the J1b formation have Br/I ratios greater than 4.0 and distinctively lower concentrations of I\(^-\) (less than 0.04mM) and greater variability of Br\(^-\) concentrations (0.03mM to 0.35mM). Only four samples from the J3q formation were analyzed for iodine. The J3q formation water samples do not show any trend reflective of the other reservoir formations (fig. 8). Overall, two separate linear relationships in bromide versus iodine are apparent in the formation water samples. The dashed line on figure 8 represents a generalized
theoretical marine end member based on iodine and bromide concentrations from organic-rich shale extractions.

4.2 Stable Water Isotopes

Stable water isotopes, $\delta^{18}$O and $\delta^2$H, are reported in table 1 for formation waters and tables 2 and 3 for injection and shallow ground waters. The local meteoric water line (LMWL; $\delta^2$H=7.2 $\delta^{18}$O+4.3; D. Han et al., 2011) is similar to the global meteoric water line (GMWL; $\delta^2$H=8$\delta^{18}$O+10; Craig, 1961).

Injection waters fall along the LMWL showing similarities to other shallow ground waters from the region (Fig. 9). The SGW are more depleted in $\delta^{18}$O and $\delta^2$H with increasing TDS whereas formation waters are depleted with respect to $\delta^2$H (fig.9). Slight differences in isotopic signatures occur between formation waters from different reservoirs. The T2k reservoirs have average $\delta^{18}$O and $\delta^2$H of -7.1‰ and -80.2‰, respectively. Average $\delta^{18}$O and $\delta^2$H for J1b are -6.1‰ and -87.7‰ and J3q are -4.3‰ and -71.3‰, respectively. The J3q formation shows enrichment of $\delta^{18}$O, and the J1b formation shows $\delta^{18}$O depletion (fig. 9). The oil waters all fall to the right of the LMWL (fig. 9).

5.0 Discussion

5.1 Characterization of oil-field waters

Groundwater can be classified into three categories based on the salinity: fresh, brackish, and salt, with TDS values of <1 g/L, 1-10 g/L, and 10-100 g/L, respectively (Fetter, 1994). The majority of formation water samples collected from the Junggar Basin are salt or brackish in composition (Table 1). These waters were likely more saline in the past and later diluted by
meteoric or injection waters. The samples with higher TDS are less likely altered by injection water.

The salinity of samples broadly appears similar to modern evaporated shallow groundwater occurring in the basin (Fig. 6). The Na/Cl molar ratios increase with younger reservoir age, which does not reflect the increasingly dryer conditions since the Triassic (Ashraf et al., 2010). Most samples show a linear relationship between sodium and chloride when injection waters have mixed with a formation water end-member.

The J3q formation waters from B60 deviate to the right of this mixing relationship (Fig. 6). B60 is a new production area and the Na-Cl relationship observed in these wells, compared to others, probably reflects formation water which has not been altered or mixed extensively with injection waters.

Injection waters for B60 and B67 are mostly fresh, with TDS values between 0.3 and 14.2 g/L (Table 2). These waters are extracted from a shallow aquifer geochemically comparable to other shallow groundwater from the area. However high TDS concentrations occur in samples from B29 injection wells and it is likely these waters are obtained from a different aquifer. In arid regions, shallow ground waters typically have high TDS due to evaporation (Han et al., 2011). For example the SGW data reported from Han et al. (2011), are significantly evaporated, with the majority of samples having TDS concentrations above 10 g/L.

Stable water isotopes are commonly used as tracers for determining the origin of groundwater and sources of groundwater salinity (Clark and Fritz, 1997). The trends of the shallow ground water data and formation water samples deviate to the right of the LMWL representing local evaporation lines (LEL) with modern LEL represented by the shallow ground
water trajectory (Han et al., 2011). Both water types have different isotopic compositions but show isotopic enrichment in $\delta^{18}$O with respect to TDS (Table 1).

The Junggar Basin has been located at relatively constant latitude since the Permian; therefore any change in climate zones that could lead to a different LMWL can be largely excluded (Ashraf et al., 2010). The formation water samples fall below and to the right of the LMWL, reflecting modification typical for waters having been affected by evaporation in closed-basin lakes (Kharaka and Carother, 1986). The isotopic signature differences between formation waters from different reservoirs may reflect small changes in climate over time (Ortega-Guerrero et al., 1997; Ashrat et al., 2010).

5.2 Mixing Characteristics

Tracing injection and formation waters is a useful method for understanding fluid movement, reservoir connectivity, and structural oil traps. The conservative tracers Cl$^-$, Br$^-$, and I$^-$ are ideal since their ratios stay constant during mixing of formation water with less concentrated waters. Since different signatures are observed between injection and formation waters, halogens were used to calculate the amount of mixing during water injection methods.

For each block, a formation water end member was chosen based on the highest Cl$^-$ concentration. For each reservoir within a block, theoretical mixing lines were calculated between the average halogen concentration of injection water and formation water end-member. These mixing lines give some insight on the connectivity within the block, between reservoirs, and potentially between oil source rocks.
5.2.1 Mixing relationships using bromide and chloride

After the Late Permian, the Junggar Basin was a lake (Carroll et al., 1990). The chemical compositions of oil water samples are typical for formation waters from terrestrial basins with higher Cl/Br ratios than expected from seawater dilution (fig. 7). In B29, of the 34 formation water samples, three do not follow the theoretical mixing line between injection water and the end member (fig. 10a). According to the well location map for B29 provided by Petro China (fig. 2), these wells (H218, H229, and H242) are disconnected by faults from the normal injection and production patterns. Well H0218 produces water and no oil, has low concentrations of the major ions and low TDS. Since the well is not hydraulically connected to injection wells, it may reflect evaporated meteoric recharge which has recharged along faults. The chemistry is similar to shallow ground waters from the Karamay agricultural district (Table 2 and 3), evidence of a different water source.

H0229 and H0242 both produce oil and do not show mixing with injection waters, indicating low connectivity within the location area of those wells (fig.2). Of the wells which do lie along the theoretical mixing line, approximately 39% have 50% or less injection water influence (fig.10a). There are no geographic patterns observed for these wells, reflecting independence for injection pattern and flows.

In B67, three of the ten wells do not show influence of injection waters (Fig. 10b; H49, H58, H82). These samples have high ion concentrations compared to others (Table 1). Wells H58 and H82 have similar halogen ratios to the end member and indicate connectivity to the formation water end member. H49 has a lower Cl/Br ratio, compared to other samples from B67 (Table 1) and likely not connected to any injection/production patterns. The high density of
faults within B67 likely causes injection waters to move through the high conductivity zones (Fig. 4a) and mix in areas far from the site of injection.

In B60, three wells in close proximity to faults do not show mixing with injection waters (Fig. 10b). These wells are also isolated from the injection and production patterns by faults (Fig. 4b) and possibly connect to other oil reservoirs. Approximately 65% of the wells have 50% or less injection water influence and are observed to be closer to faults than wells with a higher percentage of injection water mixing. Observing higher oil percentage in wells along fault zones is expected since oil production is largely associated with faulting in the Junggar Basin (Zhang, 2002).

Bromide and chloride are useful tracers for determining mixing between injection and formation waters. However similar ratios between formation waters from different oil reservoirs in the Junggar (i.e. average Triassic Cl/Br = 1210, average Jurassic J1b Cl/Br = 1640, average Jurassic J3q Cl/Br = 1640) leads to difficulty in discriminating these waters from only bromide and chloride concentrations when the origin of salinity is the same. For example Cl/Br ratios cannot distinguish formation waters from Jurassic-aged reservoirs separately. Other conservative tracers may prove more useful for tracing oil sources to reservoirs and distinguishing mixing between reservoirs. Organic signatures in formation waters can be traced using bromide and iodine concentrations and their ratios

5.2.2 Mixing relationships using bromide and iodine

Iodine can distinguish organic matter sources and has been used successfully in previous studies to trace the origin of methane rich pore fluids (ex. Martin et al., 1993; Moran et al., 1995; Fehn et al., 2000; Fehn et al., 2007; Muramatsu et al., 2007; Lu et al., 2008; Lu et al., 2011 ).
During the degradation of organic matter, bromide and iodine are released leaving a signature which is useful for tracing the fluid’s origin. Iodine is higher in the marine environment and less available in terrestrial settings. Using both iodine and bromide concentrations a marine signature will show low Br/I ratios, whereas a terrestrial signature will likely have higher Br/I ratios. The source rocks in the Junggar were deposited in various environments, and various Br/I ratios are observed reflecting differences in organic sources.

Two linear relationships are apparent with iodine versus bromide in formation water samples (Fig. 8). A theoretical mixing line was created using a T2k end member with the highest iodine concentration (fig.8), indicating a marine source (P1f source rock). A second mixing line was created for J1b formation using a Jurassic end member from B67. The iodine concentrations in formation waters are lower in the J1b and have different Br/I ratios (Table 1), indicating a non-marine source.

In B29, formation waters from the Triassic and Jurassic reservoirs have different Br/I ratios (2.9 and 5.4, respectively). Higher iodine concentrations occur in formation water samples from the T2k, whereas samples from the J1b have lower iodine and higher bromide concentrations. Three of 26 Triassic samples do not follow the same mixing trend (H0218, H0518, and H0216) and 2 of 8 Jurassic samples do not show mixing with Jurassic or Triassic formation water (H0702, H0708). With the exception of sample H218, the others fall between the mixing line for the Triassic (T2k) and Jurassic (J1b) reservoir waters (Fig. 8). This trend indicates that mixing has likely occurred between P1f (marine) and P1j or P2w (lacustrine) oil sources. Some J1b oil water samples from B29 do not have the same Br/I as other samples from the J1b reservoir, and it’s possible that connectivity between T2k and J1b reservoirs exists or other oil sources charged the J1b reservoir.
The similar chemistry of sample H218 and injection waters from B60 and B67 (fig. 8) shows that well H218 receives a significant recharge of shallow ground water. Faults and fractures create a conduit for less saline ground water to migrate towards the vicinity of well H218 and no mixing with injection waters appears to occur within the well. All samples from B67 lie close to the theoretical mixing line for the J1b reservoir. These wells have higher Br/I ratios, characteristic of a lacustrine source rock. Only four wells from B60 were analyzed for iodine and have great variability in Br/I ratios, which possibly represents a mixture of oil sources in the J3q reservoir as proposed by others (Cao et al., 1996).

The Br/I ratios of formation waters can aid in distinguishing possible oil source rocks. According to Cao et al., (2005), oil from Jiamuhe (P1j) and Fengcheng (P1f) formations accumulated in Permian and Triassic reservoir rocks, especially the T2k formation, whereas oil from the Wuerhe (P2w) formation migrated into Jurassic reservoirs during the Late Permian. J1b oil water samples have high Br/I ratios following a trend similar to injection waters, having a stronger terrestrial organic signature.

The T2k formation water samples have a more marine organic signature with lower Br/I ratios. These samples additionally show a mixing relationship with oil derived from lacustrine sources (fig.8). After the Late Permian, the generation of new secondary faults caused the regeneration of pre-existing oil pools resulting in mixing between oil sources (Cao et al., 2005). Formation water samples from the J3q do not show distinctive Br/I relationships. Since previous studies have suggested that Late Jurassic reservoirs contain a higher degree of mixed oil sources, it is possible the varying Br/I ratios reflect this mixing.
5.3 Geographic relationships

Geographic relationships using total dissolved solids, chloride concentrations and other chemical constituents are sometimes observed in oil-field wells. The observations can approximate direction of fluid flow and migration of injected waters. In the Junggar, throughout geologic history multiple orogenies caused generation, then migration of oils from source rocks southeast of the present day reservoir location (Fig.5). TDS values do not show depth relationships among the reservoirs in the study area. Therefore, lateral patterns of chloride concentrations may provide more evidence related to the connectivity between reservoirs and sources.

Wells closer to the west fault in B29 (Fig. 2) have the lowest concentrations of chloride. In contrast wells which are located on the southern end of the production area have higher concentrations of chloride and produce a greater percentage of oil. Wells located close to faults show lower solute concentrations and it is likely injected waters naturally flow along faults and mix with formation waters.

B67 shows a significant relationship between well placement and fault locations. The wells located near the north-south fault (fig. 4a) show about 50% less chloride than the other wells. This relationship can also be observed with iodine concentrations, indicating a significant relationship with injection water pathways and faulting within the block. In contrast to B29 and B67, B60 is a new production area and has had very little water injection activity. No correlation is observed between fault locality and well placement.
6.0 Conclusions

In tectonically complex areas it is especially pertinent to have an understanding of fluid migration and mixing. Through the use of conservative tracers, more insight on the connectivity between reservoirs and source rocks can be gained. Bromide and chloride are reliable for determining sources of salinity and for calculating mixing between injection and formation waters. The Br/Cl ratios of Junggar oil waters show that salinity was not derived from seawater evaporation, however this method cannot fully distinguish between samples from various production reservoirs. Bromide and iodine on the other hand can serve as sensitive tracers in sedimentary basins by distinguishing between oil sources and mixing. Br/I ratios are able to separate oil water samples by production reservoirs (fig. 8), likely reflecting the various oil source rocks and can determine between terrestrial and marine sources. Coupled with other techniques (i.e. groundwater flow modeling, basin modeling) conservative tracers yield a better understanding of fluid migration in oil-fields.

Cross formation and lateral fluid flow of both formation and injected waters has occurred. Injected water influence is evident in blocks 29 and 67, where water injection has been occurring for some time to increase well productivity. Production from B60 is relatively recent and the samples do not show significant influence of injected waters. Mixing occurs between injection and formation waters. However faults create conduits for fluid movement between reservoirs and also compartmentalize areas adding to the complexity of formation water origin.

Cross formation flow is also evident through the use of bromide and iodine concentrations. Oil generated from organically different source rocks accumulated in reservoirs during various times in geologic history, leading to a separate Br/I observed for formation waters. The different signatures are reflective of either a lacustrine or marine like source. This
suggests that accumulated oil in the Jurassic, J1b formation likely migrated from either the Jiamuhe (P1j) or Wuerhe (P2w) formation. Formation waters from Triassic reservoir rocks have different organic signatures which suggest a more marine organic source. It is plausible that oils from the T2k reservoir are a mixture of oils from both the P1f and P1j or P2w formations. Mixing of oil sources is apparent from the varying Br/I ratios observed from each reservoir.

Stable water isotopes are commonly used in groundwater studies to help determine the origin and source of salinity. A paleoevaporation trend is apparent from the samples obtained for this study and different than modern day evaporation. The variation in isotopic composition of samples from different reservoirs is reflective of slight changes in climate during the time of formation.

Different approaches to tracing fluid movement in the NW Junggar should be considered to account for the many sources of mixing which occur. The usefulness of bromide and iodine is relative to identify organic signatures associated with source rocks. However few studies have utilized Br and I in oil-field fluid tracing. Difficulty also arises in non-marine sedimentary basins due to the complex depositional environments of source rocks which generated the hydrocarbons.

Future work utilizing iodine and bromide in non-marine basins should be considered. With the availability of more data a better understanding of iodine trends in terrestrial sedimentary basins would be possible.
Tables

Table 1.1. Chemical analyses and halogen ratios of oil-field waters. Table continued on next page.

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Table 1.2. Injection water analyses and halogen ratios

| Well ID | Injection Formation/Block | TDS (g/L) | Br (mM) | I (mM) | Cl (mM) | Na (mM) | 61RO | 62H | Na/C | CI/B | Br/I |
|---------|--------------------------|-----------|---------|--------|---------|---------|-------|-----|------|------|------|------|
| H505    | TJK2/block 29            | 14.1      | 0.15    | 0.022  | 175.9   | 243.5   | -11.0 | -84.2| 1.22 | 1210 | 6.5  |
| H0202   | TJK1/block 29            | 13.9      | 0.15    | 0.009  | 176.1   | 199.8   | -10.8 | -83.6| 1.13 | 1172 | 17.1 |
| H205    | -                        | 14.1      | 0.20    | 0.008  | 177.7   | 218.3   | -11.0 | -84.0| 1.23 | 910  | 29.6 |
| H229    | -                        | 14.1      | 0.15    | 0.019  | 178.7   | 224.4   | -10.9 | -83.7| 1.26 | 1196 | 7.9  |
| H236    | -                        | 14.2      | 0.16    | 0.009  | 178.9   | 214.1   | -10.0 | -84.0| 1.20 | 1138 | 17.1 |
| H701    | J1a/block 29             | 14.1      | 0.15    | 0.022  | 175.7   | 208.8   | -10.8 | -83.6| 1.18 | 1200 | 0.7  |
| H703    | -                        | 14.1      | 0.15    | 0.023  | 175.9   | 212.8   | -11.1 | -84.0| 1.21 | 1187 | 6.6  |
| H705    | -                        | 14.1      | 0.15    | 0.010  | 178.4   | 213.5   | -10.9 | -83.8| 1.20 | 1175 | 15.2 |
| H707    | -                        | 14.1      | 0.15    | 0.018  | 175.9   | 207.3   | -10.1 | -81.5| 1.18 | 1205 | 8.0  |
| H1111   | J1b/block 67             | 0.5       | 4.5E-04 | 5.6E-04| 1.1     | 9.9     | -12.6 | -84.1| 9.05 | 2212 | 0.9  |
| H121    | -                        | 0.5       | 5.0E-04 | 5.2E-04| 1.0     | 9.8     | -12.6 | -84.9| 9.38 | 2112 | 1.0  |
| H131    | -                        | 0.5       | 5.0E-04 | 4.5E-04| 1.0     | 9.9     | -12.7 | -85.4| 9.43 | 2083 | 1.1  |
| H602    | J1a/block 60             | 0.3       |         |        | 1.2     | 5.6     | -12.7 | -86.2| 4.80 |      |      |
| H6002   | -                        | 0.8       |         |        | 6.9     | 5.8     | -12.9 | -87.7| 0.85 |      |      |
| H6010   | -                        | 0.3       | 1.5E-03 | 4.7E-04| 1.1     | 5.7     | -13.0 | -87.8| 5.00 | 777  | 5.1  |
| H6015   | -                        | 1.5       | 2.9E-04 |        | 13.7    | 7.0     | -12.9 | -87.6| 0.51 | 47833|      |
| H6016   | -                        | 0.3       |         |        | 1.2     | 6.0     | -12.7 | -87.4| 5.01 |      |      |
| H6020   | -                        | 1.4       |         |        | 15.3    | 6.0     | -12.9 | -87.9| 0.59 |      |      |
| H6023   | -                        | 1.4       | 1.7E-04 |        | 15.3    | 10.2    | -12.5 | -85.4| 0.67 | 87707|      |
| H6025   | -                        | 1.2       | 2.0E-04 | 2.8E-04| 13.3    | 5.9     | -11.9 | -84.4| 0.44 | 67495| 0.7  |
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| H6035   | -                        | 0.3       |         |        | 1.1     | 5.6     | -12.7 | -85.2| 4.96 |      |      |
| H6042   | -                        | 1.0       | 1.6E-04 | 1.8E-04| 9.4     | 5.9     | -12.1 | -85.9| 0.43 | 57271| 0.9  |
| H6048   | -                        | 0.9       |         |        | 8.0     | 5.9     | -11.9 | -83.5| 0.74 |      |      |
| H605    | -                        | 1.0       | 7.4E-04 |         | 12.3    | 6.6     | -12.3 | -84.0| 0.54 | 16576|      |
| H6051   | -                        | 0.8       |         |        | 7.5     | 5.6     | -12.2 | -84.0| 0.74 |      |      |
Table 1.3. Chemistry of shallow ground waters from Karamay Agricultural Development Area (KADA) reported by D. Han et al., 2011.

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Figure 1.1 Map showing location of production blocks (Modified from Cao et al., 2005)
Figure 1.2. Well placement in Block 29 (Modified from maps provided by PetroChina).
Figure 1.3. Generalized stratigraphy of Junggar Basin. Thickness of sequences varies depending on location. See Figure 1.5 for cross section across the northwestern margin.
Figure 1.4. Well placement in a) Block 67 and b) Block 60 (Modified from maps provided by PetroChina)
Figure 1.5. Simplified cross section of northwestern margin into the slope area (Modified from Cao et al., 2006)
Figure 1.6. Plot of chloride verse sodium concentrations for oil-field, injection, and shallow ground waters (KADA).
Figure 1.7. Plot of chloride and bromide concentrations. All formation waters follow a trajectory above the expected seawater dilution line, with lower concentrations than modern seawater.
Figure 1.8. Plot of iodine and bromide concentrations. Theoretical marine end-member data comes from known iodine and bromide concentrations from organic-rich shale extractions. The blue diamond’s represent injection waters.
Figure 1.9. Plot of stable water isotopes showing a modern evaporation trend and paleo-evaporation evident from oil-field waters. The depletion of $\delta^2$H in oil-field waters may represent climate differences during formation water origin.
Figure 1.10. Bromide and chloride mixing models for a) Block 29 and b) Blocks 67 and 60. Black tics on mixing line represent increments of 10% mixing.
Chapter 2. *Iodine as a sensitive tracer for detecting influence of organic-rich shale in shallow groundwater*

*(Note: This manuscript is written in the style of the journal Applied Geochemistry)*

1. Introduction

Shale gas extraction from the Marcellus formation in the Appalachian Basin has increased with technological improvements in horizontal drilling and hydraulic fracturing (Soeder, 2012; Kerr, 2010; PADEP Year End Report, 2009). The increase in hydraulic fracturing has led to environmental concerns regarding potential for shallow aquifer contamination. Two primary concerns are the potential for contamination of groundwater and surface water from hydraulic fracturing fluids and produced brines during their transport, drilling, and disposal (Dresel and Rose, 2010; Rowan et al., 2011), and stray gas migration to shallow aquifers (Osborn et al., 2011).

Hydrocarbon bearing formations in sedimentary basins typically contain water with high salinity, which can exceed 100 g/L, due to seawater evaporation during the basin’s evolution, which leads to halite precipitation (e.g. Hanor, 1994; Carpenter, 1978; Dellwig, L., and Evans, R., 1969; Dollar et al., 1991). With compaction, residual brines disperse into other stratigraphic layers of the sedimentary basin as it evolves through geologic time. Hydraulic fracturing of organic-rich shale produces waters, called flow-back, with high salinity and high concentrations of dissolved solids, trace metals, and organic compounds.
Geochemically, halogens are relatively conservative and therefore chloride and bromine have been used to trace groundwater and surface water flow for decades and distinguish different sources of salinity, such as road salt and septic effluent in streams and groundwater. For example, Townsend and Whittemore (2005) used chloride and bromine to distinguish contamination of drinking water from oil-field brines, halite dissolution, and other sources. Other studies show that Cl/Br ratios can effectively distinguish saline water coming from road salt, halite dissolution brines, and household water softeners (e.g. Davis et al., 2004, 1998; Richter et al., 1993; Panno et al., 2006; Rittenhouse, G., 1967; Whittemore, D.O., 1995; Walter et al., 1990; Knuth et al., 1990; Siegel, D. et al., 1991; Townsend. and Whittemore, 2005; Alley et al., 2011; Siegel and Knight, 2011). Halogen ratios are potentially effective for distinguishing formation water from other sources of salinity because halite precipitate excludes bromine from its crystal structure, causing the remaining formation waters to have low Cl/Br ratios compared to the seawater they originated from (Carpenter, 1978).

Fresh water overlies saline water in almost all sedimentary basins (Feth, 1970). During dry times, drinking water wells over 150 meters in depth can develop elevated salinity if they intersect the freshwater-formation brine subsurface interface, which commonly occurs less than 300 meters deep in shallow aquifers (Feth et al., 1965; Richter and Kreitler, 1991). In particular, water wells in valleys, where groundwater discharges from local to regional scale flow systems, can develop naturally high salinity because of their close proximity to the saltwater-freshwater interface (Warner et al., 2012; Panno et al., 2006). This saline groundwater can have about the same Cl/Br value as deeper groundwater in formations that commercially produce gas and oil (e.g. Haluszczak et al., 2013). For example, bromine and chloride could not distinguish between Appalachian Basin brines as a whole from Marcellus Formation or older brines (Warner et al.,
Another non-reactive solute, in addition to bromine and chloride, needs to be considered that can potentially distinguish and “fingerprint” brines from deep gas producing formations from those in shallow gas producing formations.

Iodine has been used to trace water movement in methane-rich settings (ex. Martin et al., 1993; Moran et al., 1995; Fehn et al., 2000; Fehn et al., 2007; Muramatsu et al., 2007; Lu et al., 2008; Lu et al., 2011) because pore water iodine and methane mostly derive from organic matter (Lu et al., 2011). Organic-rich rocks and associated pore waters in marine sedimentary basins contain elevated iodine and low Br/I ratios (Worden, 1996). Therefore iodine is a potentially sensitive tracer for sedimentary basin brines where it is associated with geologic formations enriched in organic matter deposited in marine environments, such as the Marcellus Shale.

In this chapter, the results of an initial geochemical background study showing the utility of iodine as a tracer for fluids associated with the Marcellus Formation of the Appalachian Basin of the eastern United States are presenter. Iodine concentrations, in conjunction with other halogens and isotopic systems, may be able to distinguish the presence of deep fluids that migrate upwards into shallow groundwater or spilled on the land surface from other sources of salinity.

1.1 Iodine Geochemistry

Similar to other halogens, iodine is a conservative solute and iodine concentrations in freshwater are smaller than those in the marine environment (Fig. 1) because iodine is virtually absent from rock-forming minerals (Fig. 1a). Iodine concentrations in shallow ground water and surface waters are generally <0.05 µM (Panno et al., 2006), whereas the average iodine concentration in seawater is ten times higher, about 0.5 µM (Krauskopf, 1979). Some rare
contaminated surface water and shallow ground water have iodine concentrations averaging 11 µM (Panno et al., 2006) derived from municipal landfill leachate incorporating disinfectants, medical products, and animal feeds/additives (Panno et al., 2006). Iodized salt is a potential anthropogenic source of iodine; however, elevated iodine concentrations in ground water due to such contamination have not been reported, to our knowledge.

Marine origin organic-rich sedimentary rocks and halite are the two major natural sources of iodine in the terrestrial environment, and these have distinctive Br/I ratios (Fig. 1a). Iodine is a biophillic element, strongly enriched in marine organic matter, such as kelp, and consequently accumulates in marine sediments (Elderfield and Truesdale, 1980; Muramatsu and Wedepohl, 1998). When marine organic matter is buried, microbial/thermal decomposition produces methane and releases iodine. This process leaches out iodine from the sediments, and concentrates it in interstitial fluids, along with methane. These methane-rich and iodine-rich fluids escape to the surface, in modern seeps/gas fields, or get trapped within sedimentary strata which are now located in terrestrial settings. High concentrations of iodine in groundwater occur in oil/gas field brines (Moran et al., 1995). Iodine concentrations are enriched in the Appalachian Basin brines similar to those found in other oil/gas fields (Moran et al., 1995; Bottomley et al., 2002; Panno et al., 2006; Dresel and Rose, 2010; Osborn et al., 2012; Fig. 1b).

1.2 Geologic Background

A stratigraphic cross section of the southern tier of NYS is shown in figure 2. The Marcellus Formation is Middle Devonian organic-rich black shale, the oldest and basinal unit of the Hamilton Group. The remainder of the Hamilton group consists of some black shales but mostly dominated by marine gray shales and limestone representing bases of formations (Reeves
and Davies, 1937). Along with the Marcellus shale’s organic rich black shale, there is the Geneseo shale formation part of the Geneseo group, present in the subsurface in the study area. The remainder of the Upper Devonian in the region is interbedded black and gray shales with sandstone and thin limestone (NYS DEC, 2011). The Western section has the black shales of the Middlesex and Rhinestreen present in the subsurface (Bradley et al., 1941). The lower Devonian through Silurian consists of carbonates and sandstone (Medina, Clinton, and Salina Formations) with embedded evaporite units and minor organic-rich shale (Boswell, 1996). The Middle Ordovician Trenton/Black River group is inter-bedded limestone and shale. This group is confined by Upper Ordovician shales such as the Utica, Reedsville, and Queenstone formations (Boswell, 1996; Dresel and Rose, 2010; Osborn and McIntosh, 2010). The Upper Silurian Salina group consists of inter-bedded shale, dolomites, and salt deposits. The Lower Devonian carbonates and sandstones separate the Lower Silurian Medina group from the upper organic-rich shales (Dresel and Rose, 2010).

The Appalachian Basin formed as elongated foreland basin west of the ancestral Appalachian Mountains with relatively un-deformed sedimentary rocks deposited throughout the Paleozoic era (Colton, 1970). About 350 million years ago, the basin contained a tropical inland sea from New York to Alabama, with a warm climate and conditions favorable for generating organic matter. Erosion of the Appalachian highlands provided clastic material for deposition (Colton, 1970). Repeating sequences of carbonates, shales, siltstones, and sandstones occur through the Paleozoic section (Roen, 1984) reflecting several marine transgressions and regressions. The black shales present throughout the Appalachian Basin contain high levels of organic matter. The fine grained material and organic matter accumulated in a deep, warm,
quiescent marine basin. The organic matter was incorporated into accumulating sediments and buried (Roen, 1984; NYDEC, 2011).

2. Methods

2.1 Sampling strategy and protocol

We completed a systematic sampling of landowner drinking water wells and streams from four counties located in the southern tier of NYS (Fig. 3). Waters from 60 drinking water wells and 20 headwater streams were sampled. An aerial grid of 49 km$^2$ was placed over the counties of interest (Steuben, Tioga, Broome, and Chemung) with the explicit goal of collecting one sample within each grid cell to optimize uniform spatial coverage. The NYS water well contractor program database, containing data on all water wells drilled since April 2000 in a GIS format, was combined with GIS-based county cadastral data to identify potential sampling targets. We preferentially targeted the deepest depth and maximum penetrating wells within each grid cell. Wells sampled for this study range in depth from 20 m to 122 m. In addition to shallow groundwater samples, surface water samples were collected from headwater streams in the counties of interest with upstream drainage areas between 50 and 100 km$^2$.

Standard quality control procedures were followed for field measurements and sampling based on Boyer et al (2011). All well waters were collected upstream of water treatment equipment at either outdoor spigots or at the water pressure tank. Before sampling, water was purged from the well until the temperature stabilized. Measurements of pH, specific conductance, and temperature were made in the field using a WTW 340i Multiprobe, which was calibrated daily. Field blanks were also taken daily. Water samples were collected in prewashed
HDPE bottles that were triple-rinsed with sample and filled until there was no headspace. Water samples were filtered with a 0.45 µm nylon filter and split into aliquots for various analyses. All samples were stored at 4°C until analysis was complete.

2.2 Analytical Methods

Chloride concentrations were measured at Syracuse University via ion chromatography (IC) using a Dionex ICS-2000 with column AS18 for anions. The IC was calibrated with five internal laboratory standards and the calibration quality was validated using three external United States Geological Survey Standard Reference Samples (N103, M178, and P50, http://bqs.usgs.gov/srs/). Percent error for chloride is less than 3%. Total dissolved iodine and bromine concentrations were measured on a Bruker Aurora M90 ICP-MS at Syracuse University following established analytical methods (Muramatsu and Wedepohl, 1998). Calibration standards for bromine and iodine were prepared before the measurements. Blanks were monitored every three samples and standard ran every six samples. Instrumental error for iodine and bromine concentrations are typically below one percent and are not reported individually.

To better constrain the source rock halogen composition, two shale samples were collected from the Marcellus interval in the Morton Salt core drilled near our study area (Fig. 3). Iodine and bromine associated with the organic matter were extracted with an alkaline solution from well-homogenized shale powder. The solutions were then diluted for concentration measurements on ICP-MS.

Spatial patterns in iodine concentrations were compared to geologic variability of the source rocks using GIS. Available GIS resources included the Finger Lakes sheet of the 1:250,000 geologic map of NYS (NYS Museum, 1999). Contour lines were derived from 10 m
resolution National Elevation Dataset data (http://ned.usgs.gov) and isopach maps for the Marcellus Shale. Contour lines for total organic carbon (TOC), depth, thickness, and thermal maturity of Marcellus Shale were obtained from the NYS Museum and overlaid over the study area. The values TOC, depth, thickness, and thermal maturity at each water well were calculated by measuring the distance from well to nearest contour line and calculating the approximate value at that location through the use of extrapolation. The depth and TOC values were multiplied to calculate the values for figure 9.

3. Results and Discussion

Histograms for bromine and iodine of all samples are shown in figure 5. Samples with concentrations <1 µM for bromine and <0.1 µM for iodine are considered to be a representation of relatively pristine surface and shallow ground water in the study area. 35 of the 56 drinking water wells fall in this category and are grouped together as Type I water regardless of their geographic location. The remaining wells have elevated concentrations and are grouped as Type II and III waters with distinct Br/I ratios of 19.3 and 5.6, respectively defined by linear regressions. The majority of the waters from streams sampled for this study have bromine concentrations between 0.2 and 0.8 µM, except for two samples with concentrations between 1 and 1.3 µM (Fig. 4a). Iodine concentrations in stream waters range between 0.01 and 0.04 µM, a range slightly higher than iodine concentrations reported in an earlier study in western NY (Rao and Fehn, 1999).

3.1 Mixing relationships
From our water analyses, two separate linear relationships in bromine versus iodine are apparent in the samples with elevated iodine and bromine concentrations (Fig. 4a). Nine of the 10 wells located in Steuben County fall on a line defined by higher Br/I ratios (17.5 to 26.9), which we classify as Type II waters. Nine of 11 wells located throughout the remaining three counties, Chemung, Tioga, and Broome, form the other linear relationship, which is defined by lower Br/I ratios of 1.7 to 6.9 which we classify as Type III waters. In three wells, Br/I ratios differ from that found in their geographic grouping (Fig. 3 and 4).

We compared the linear relationships in Fig. 4a to mixing relationships expected if freshwater were mixing with formation water derived from halite or Appalachian Basin sedimentary units (Osborn et al., 2012). The ratios of Br/I in NYS gas formation waters sampled from Devonian organic rich shale, Bradford sandstone, and the Marcellus Shale formations ranged from 17.5 to 49. Extractions completed on Marcellus Shale core samples (Fig. 4a) had average iodine concentrations of 0.32 µM and bromide concentrations of 0.19 µM, which equates to a Br/I ratio of 0.59. Water chemistry data from the Salina Formation, a major halite bed of Silurian age (Dresel and Rose, 2010), was used to derive the halite dissolution mixing line.

The I/Cl ratios in Type II and Type III water are elevated relative than expected if halite dissolution was the sole source of salinity (Fig. 4b) and are more consistent with salinity derived from formation waters. In contrast to Type II and Type III groundwater samples, streams have trends more consistent with halite dissolution, averaging $4.0 \times 10^{-5}$. I/Cl ratios are consistently one to two orders of magnitude smaller than shallow ground waters. A plot of Cl versus Br shows similar relationships between Br-Cl and I-Cl (Fig. 3c).
The two linear trends in shallow groundwater suggest mixing between surface water and solutes from deep groundwater, which are originally derived from halite and organic-rich shale. Salt deposits are common in the Appalachian Basin (i.e. Salina Formation; Fig. 2) due to evaporation of seawater during the basin’s origin (Carpenter, 1978; Hanor, 1994). Halite salt has a high Br/I ratio with relatively little iodine (0.1 to 10 mg/kg) compared to bromine (12.6 to 1584.9 mg/kg) (Schijf, 2007). Among the four groups of water samples (Type I, II and III well waters and streams), the stream waters seem more influenced by the halite end-member than the organic source (Fig. 4), even though the stream waters do not show perfect halite dissolution mixing. The stream water halogen system may also be influenced by residual road salt applied during winter.

Both Type II and III water groups have Br/I ratios between that of halite and shale extractions (Fig. 4). Waters that fall closer to the shale extraction mixing line should have stronger influence by organic sources, thus Type III waters have a stronger organic signature compared to Type II, which falls closer to the halite mixing line (Fig. 4a).

3.2 Formation water halogen chemistry

To pinpoint the source of excess halogens in Type II and III shallow groundwater, it is important to know the formation water compositions at various depths and also the spatial heterogeneity of groundwater chemistry in the same geologic formation across the study area. Iodine historically has not been used as a natural tracer in deep groundwater in NY State. Only one study reported iodine and bromine concentrations in formation waters from several deep wells in New York State (Osborn et al., 2012; shaded area in Fig. 3). Mixing between these formation waters and freshwater would result in mixing relationships bracketing the Type II
group, whereas the Type III group has a significantly lower Br/I ratios and cannot be explained by these known formation water compositions (Fig. 4a).

One of the formation water wells, D60 (Osborn et al., 2012), is located 15 to 45 kilometers from the Type II group samples in Steuben County (Fig. 3). The calculated mixing line between D60 and freshwater is nearly identical to the linear relationship shown for the Type II group (Fig. 4a). The elevated bromine and iodine in the Type II waters may be contributed by Marcellus formation waters. However, assuming that Marcellus formation water is indeed the source of excess halogens, a simple two-component mixing model indicated only a trace amount of formation water has entered the shallow groundwater aquifer. It is not clear whether formation waters associated with other shale units (i.e. Middlesex and Utica Shale; fig. 2) may have similar Br/I ratios to the Marcellus.

There are noticeable depth and spatial patterns of halogen ratios in the formation waters sampled within NYS (Osborn et al., 2012). Formation waters appear to have decreasing Br/I and Br/Cl and increasing I/Cl with depth. Type II shallow groundwater has average Br/I and Br/Cl ratios similar to D60, the deepest Marcellus well from which we obtained analytical data (Fig. 6). The Type III group has lower Br/I (4.0±1.7) and Br/Cl ratios (1.2±1.7), but higher I/Cl (0.50±0.89) ratios than Type II and any of the formation water samples. These differences may suggest these samples have solute contributions from different formation waters than the Marcellus Shale (Fig. 6).

On the other hand Br/I ratios in formation water decrease from west to east across NY State (Fig. 7). D60 is the deepest and easternmost sample of NY formation waters with reported iodine values. It is located geographically close to the Type II group of samples (Steuben County) and west of the Type III group. Current knowledge on halogen compositions of
formation waters in NYS does not conclusively allow any arguments on whether the Type III group is affected by a deeper source or an eastern source, compared to Type II waters.

3.3 Potential geological controls

The Br/I ratios show there is a stronger organic signature influence in Type III waters (fig. 4a). By examining any spatial differences of source formations (fig. 8), we can potentially pinpoint a likely source of the excess halogens. For the purpose of this thesis, I use the Marcellus formation as an example, acknowledging the possibility that other shale units may contribute the excess halogens to Type II and III waters.

The thickness of the Marcellus shale increases from approximately 50 feet in the west to greater than 550 feet in the east (fig. 8a). Nine of the ten wells in the Type II group are located where the thickness ranges between 50 and 100 feet in Steuben County. The thickness of the Marcellus Shale underlying the Type III water group varies from 50 to over 550 feet. Nine of the eleven wells identified as Type III water are located where the Marcellus thickness is greater than 100 feet in Chemung, Tioga, and Broome Counties.

The total organic carbon (TOC) of the Marcellus is highest in western Chemung/Eastern Steuben counties and decreases to the east (fig. 8b). We multiplied the thickness of the shale by the total organic carbon (TOC) to quantitatively reflect the size of the pool of organic matter and iodine that is available for Type II vs. Type III waters. Type III waters with lower Br/I ratios in shallow groundwater appear to be associated with a stronger organic source in the underlying Marcellus (fig. 9). For instance, it is possible the thicker shale unit and larger amounts of TOC show stronger organic signatures in overlaying groundwater; thus Type III waters have a stronger organic signature than Type II waters. Additionally Type III waters fall closer to the
Organic shale end member mixing line (fig. 4a), and the thermal maturity of the Marcellus shale is highest in the eastern section of the study area (fig. 8c).

It is plausible that organic-rich shale formations may have similar spatial patterns as the Marcellus. To further test whether Marcellus formation water may be responsible for the Type III group signature, we obtained Marcellus flow-back waters (Chapman et al., 2012) from Bradford County, PA, which borders Broome County, NY. These flow-back waters have a Br/I (23 to 27), similar to that of the Marcellus formation waters in NYS (Fig. 4a) and higher than the ratios found in Type III waters. However it is unclear whether this ratio reflects Marcellus formation water in eastern NY, since the initial halogen compositions in hydraulic fracturing fluids are unknown. Currently, the Type III signature cannot be conclusively tied to any shale formation. More information on Br/I ratios of organic shale formations above and below the Marcellus and the associated formation waters would yield better insight into the higher iodine concentrations observed in the Type III samples.

4. Conclusions

Distinct iodine and bromine concentrations and ratios occur in shallow groundwater wells located in southern NYS. Iodine and bromide concentrations in multiple wells in Steuben County may be related to mixing between small amounts of solutes derived from Marcellus formation water and freshwater (Type II water). In Chemung, Tioga, and Broome Counties (Type III water) the source for excess halogen is likely not the Marcellus.

Source rocks across the southern tier of NYS vary in shale thickness, TOC and thermal maturity which may cause the differences observed between Type II and Type III halogen composition. There are also possible scenarios which may explain excess halogens in shallow
wells, including existing faults and fractures creating conduits for deep groundwater migration to shallow aquifers and available excess halogens picked up during groundwater recharge. Currently there is not enough available information to pinpoint a specific source formation. Once iodine measurements in formation waters cover a broader array of shale units, a more detailed study could offer better insight on halogen sources in shallow groundwater in NYS. Additionally, a denser sampling across the southern tier will allow future evaluation of the possible scenarios for the migration of excess halogens to shallow groundwater wells. Further study of more formation waters from greater depth range and spatial coverage may allow iodine to be used as a sensitive and unambiguous tracer for quantifying the degree and source of groundwater contamination associate with organic-rich shale.
Figure 2.1. Iodine compilation and comparison for a) solid materials and b) surface and groundwater (Balcone-Boissard et al., 2009; Bottomley et al., 2002; Carpenter, 1978; Davis, et al., 1998; Dresel and Rose, 2010; Fehn et al., 2007; Gupta et al., 2012; Katz et al., 2011; Lu et al., 2008; Moran et al., 2005; Muramatsu et al, 2004; Muramatsu and Wedepohl, 1998; Osborn et al., 2012; Panno et al., 2006; Richter et al., 1993; Schnetger et al., 1998; Warner et al., 2012; Worden, 1996).
Figure 2.2. Simplified geologic cross section across the southern tier NYS
Figure 2.3. Sampling locations. NYS formation water from Osborn et al., 2012. Shale sample from ESO-GIS, NYS Museum.
Figure 2.4. a) I vs Br b) I vs Cl and c) Br vs Cl. Appalachian Basin formation waters in NYS are represented in figure 3 by the shaded region. Refer to fig. 3 legend.
Figure 2.5. Histograms for iodine and bromine concentrations in all samples
Figure 2.6. Depth profiles of NYS formation water for a) Br/I vs Depth b) I/Cl vs Depth and c) Br/Cl vs Depth. Shallow groundwater is represented as mean and error bars as standard deviation for each group. The standard deviations for the halogen ratios in Type II waters are shown as error bars in Fig 6.
Figure 2.7. Spatial Distribution of NYS formation water and shallow groundwater. Shallow groundwater for Type II water represented as mean and standard deviation.
Figure 2.8. a) Marcellus Shale Thickness (larger symbol represents higher I/Br), b) Total Organic Carbon, and c) Thermal Maturity
Figure 2.9. I/Br vs TOC*Shale thickness (values were estimated from figs. 6 and 7a by approximating between given contour lines through extrapolation)
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