SITE-SPECIFIC INDUSTRIAL TRACER APPLICATION TO THE PETROLEUM INDUSTRY

FINAL REPORT

Submitted To:

Robert Phillips and Pierre Boucher
Environment Canada
Oilsands & Downstream
Oil, Gas and Alternative Energy Division
351 St. Joseph, Gatineau QC. KIA 0H3

Contributors:
Cathy Main, Don Jones

Submitted By:

Cathy Main
Alberta Innovates – Technology Futures
3608 – 33 Street N.W.
Calgary, AB
T2L 2A6
Cathy.main@albertainnovates.ca
AITF # 8785031

January 2014

TABLE OF CONTENTS

LIST OF TABLES

1. INTRODUCTION

1.1 Background

Tracers have long been used for determining the fate and flow pathways of air and water sources in the environment. Present concern over the oil sands stems from a need to understand what is natural to the oil sands environment, what has been created due to anthropogenic activities, what is harmful to the environment, what portion of total concentrations of specific compounds come from which sources and what portion they make up of the total concentration. Tracers are being used to determine the age and source of specific compounds and, in some instances, the portion of the entire concentration of specific compound that is from a specific source.

A groundwater tracer has been defined as “matter or energy carried by ground water which will give information concerning the direction of movement and/or velocity of the water and potential contaminants” (Davis et al., 1986). Tracers extend beyond the realm of groundwater studies. In this report, the application tracers to surface water and atmospheric studies will also discussed. Tracers can be classified into two general categories: environmental tracers that are monitored as part of existing environment, in the case of this study as part of the water or atmosphere; and, introduced tracers that have been added to the existing environment. Important properties of a tracer include:

- If an introduced tracer is used, it can be added to a fluid or atmosphere in small concentrations without affecting the properties of the fluid or atmosphere itself.
- Nontoxic properties assumed release to the environment.
- Easily detectable and quantifiable at very low concentrations over a short period of time.
- Low cost.
- Easy handling and use.
- Available commercially and easy enough to obtain.
- Conservative in nature (i.e. not absorbing or adsorping to soils, not degrading by chemical or biological processes in the subsurface, not reacting with soils or matrix medium) so that it remains present in the medium within which it is transported.
- No or low background concentrations/sources of tracer other than the source being studied.

(Davis et al, 1986 and IAEA, 2004).

When evaluating tracers it is necessary to determine if the tracer acts conservatively or if the tracer transforms or reacts with matrix through which it travels. It is important to determine the rate of change or the processes involved in the change of a tracer (e.g. partitioning coefficients, biodegradation rates and chemical transformations).

This review presents a summary of tracers use in environmental applications and the potential for tracer use in the Athabasca oil sands. An extensive literature search was conducted accessing articles in refereed journals, theses and unpublished studies conducted by AITF.

2. HISTORY OF TRACER TECHNOLOGY IN ENVIRONMENTAL APPLICATIONS

2.1 Environmental Tracers

Environmental tracers are either naturally or anthropogenically derived compounds or isotopes whose variations in the environment can be used to determine sources, pathways, timescales and/or environmental processes. Environmental isotopes are defined as the naturally occurring isotopes commonly found within our environment (H, C, N, O, S) that are found within hydrological, hydrogeological, geological and biological systems (Clark and Fritz, 1997). Of particular use are the stable isotopes that serve as tracers for water, carbon, nutrient and solute cycling (Clark and Fritz, 1997). Radioactive isotopes are effective in determining age of waters and allow an understanding of the water cycle and rate of circulation through the system. More recently, isotopic tracers have been used in hydrogeological applications to:

- Study water origin, evolution and age.
- Study mixing of water types and water balance.
- Determine the hydrodynamics of surface and subsurface reservoirs.
- Determine the transportation of contaminants.

A summary of isotopes and their applications are found in Table 1.

Isotopic tracers are considered powerful tools when applied as tracers in hydrologic and geochemical processes. Bullen et al. (1998) recommends that isotopes be used in a multi-isotope approach to constrain and supplement models developed from hydrologic data and chemical data. Bullen et al. (1998) cautions against the use of only one isotope when interpreting processes or systems to explain natural systems observed in the environment.

Environmental isotopes include the following:

- Stable isotopic ratios.
- Radioactive atoms or molecules.
- Non-radioactive chemical species.

Commonly analyzed stable isotopes include those of oxygen, carbon, nitrogen, hydrogen and sulphur. These lighter isotopes have been measured for years partially due to the fact that they are easier to measure than the isotope ratios in the heavier stable elements. In addition to ease of measurability, the analyses is carried our routinely in a number of laboratories and therefore is considered a more common and accessible isotope method.

Table 1: Major Applications of Natural and Anthropogenic Radionuclides in Earth Sciences

USES	**ISOTOPES**
Studies of Atmosphere	
Dispersion, transport, and mixing processes on local, regional, and global scale.	tritium, krypton-85, radon-222, carbon-14
Transport of water vapour.	tritium
Stratosphere-troposphere exchange.	tritium, carbon-14, krypton-85, beryllium-7, beryllium-10
Sources and sinks of CO_2 and CH4.	tritium, carbon-14
Atmospheric deposition.	chlorine-36, berylhum-7, beryllium-10, strontium-90, caesium-137
Studies Continental Hydrosphere	
Replenishment of groundwater resources.	tritium, chlorine-36
Dispersion studies in surface waters.	tritium
Aeration studies.	krypton-85
Interaction between surface and groundwaters.	tritium, radon-222, carbon-14
Groundwater dating.	tritium, carbon-14, krypton-85, argon-39, chlorine-36, krypton-81
Rock-water interactions.	uranium-238, uranium-234, radium-226, radium-228
Sedimentation rates in lakes and reservoirs.	caesium-137, lead-210
Radioactive waste disposal.	chlorine-36, iodine-129
Studies of Ocean	
Circulation and mixing processes.	tritium, carbon-14, krypton-85
Age of water masses.	tritium, carbon-14, argon-39, krypton-85
Transfer of anthropogenic CO_2 into the ocean.	carbon-14
Dating of oceanic sediments.	carbon-14, potassium-40
Variations of sea level in the past.	carbon-14, uranium-234, thorium-230
Studies of Lithosphere	
Dating of rocks and minerals.	potassium-40, argon-39, rubidium-87, lutetium-176, hafnium-174, samarium-147, neodymium-143, rhenium-187, radionuclides of uranium and thorium decay series
Dating of carbonate deposits.	carbon-14, uranium-234, thorium-230
Dating of lacustrine sediments.	caesium-137, lead-210, carbon-14, uranium-234, thorium-230
Surface exposure dating.	beryllium-10, carbon-14, aluminum-26, chlorine-36
Soil erosion.	caesium-137, lead-210, beryllium-10
Mineral exploration.	radionuclides of uranium and thorium decay series
Earthquake monitoring.	radon-222
Paleoseismicity and volcanic eruptions.	chlorine-36, aluminum-26, beryllium-10

Adapted from Rozanski et al., 1996.

2.1.1 Water Isotope Hydrology – Water Balance, Mixing and Age

Water tracers consist of isotopes that form water molecules (i.e. those with oxygen and hydrogen), include both stable and radioactive tracers and are ideal since they are integral components of the water molecule not a dissolved constituent. Stable isotopes include the water tracers of ^{18}O and ^{2}H. These are often used to determine water balance since they produce quantifiable, measureable changes between phases within the water cycle such as precipitation, surface water and groundwater recharge (Gibson and Birks, 2008). Variations in precipitation are usually correlated to the strong linear relationship that exists between $\delta^{18}O$ (oxygen) and $\delta^{2}H$ (deuterium) (Gibson et al., 2005). If both $\delta^{18}O$ and $\delta^{2}H$ data is available, the deuterium excess can be calculated which provides an indication of evaporation that is associated with surface water features.

Water isotopes provide information about water residence times and relative contributions from various sources that can be used to make hypothesis of the water flow paths (Kendall and Caldwell, 1998). Applications of these tracers include regional analysis of lake water balance (Bennett et al, 2008), groundwater recharge, water sources and mixing, flow pathways and water age dating (Gibson and Birks, 2008). Common water isotopes and potential applications are summarized in Table 2.

Table 2: Common Water Isotopes

Water Tracers	Isotope	Isotopic Ratio	Use
Stable	^{2}H	$^{2}H/^{1}H$	Water cycle
Stable	^{18}O	$^{18}O/^{16}O$	Water cycle
Radioisotope	^{3}H		Age of recent waters – anthropogenic input since 1960s

Modified from Clark and Fritz, 1997

The water-based isotopes have a long history for use in environmental applications. Tritium (^{3}H), when measured today, is usually less than 10 tritium units (TU) but generally ranges between 10 to 30 TU. However in 1952 to 1963, nuclear weapons testing provided a large anthropogenic input of tritium into the environment (Wolkersdorfer, 2007). Peak concentration inputs of up to 10,000 TU were observed between 1963 and 1965. Tritium is a short-lived radioisotope (i.e. half-life of 12.43 years) that enters the hydrologic cycle though precipitation (Clark and Fritz, 1997). Tritium is effective in dating waters that have relatively recently been recharged (i.e. the 1950s onward). Tritium is produced naturally as well as from anthropogenic sources and the monitoring of tritium is affected by seasonal variations.

2.1.2 Solute Isotope Biogeochemistry – Flow Path and Water Source

The term solute tracers refers to the interaction of water with airborne emissions, rock and unconsolidated sediments and the evolution of the water chemistry as a result of these interactions. It includes constituents that are dissolved within water or are carried in the gas phase. The solute tracer can be used to determine the chemical evolution or changes that occur to water as it flows through the catchment or along its subsurface flow path.

Solute isotopes (e.g. ^{13}C, ^{34}S, ^{87}S) provide information on the water flow paths not the water sources themselves; they reflect the reactions that typically take place along specific flow paths (Kendall and Caldwell, 1998). The composition of solute isotopes in water flowing along a specific mineralogically distinct horizon can be used with information regarding the chemical composition of the water to fingerprint or label waters from the distinctive geological formation. These tracers, when used with major and minor ions, are instrumental in determining water sources and water-rock interactions. Examples of stable solute tracers and potential applications are summarized in Table 3.

Table 3: Common Stable Solute Tracers

Solute Tracers	**Isotope**	**Isotopic Ratio**	**Use**
Stable	^{11}B	$^{11}B^{10}B$	Water evolution, source and mixing, including saline waters
Stable	^{13}C	$^{13}C/^{12}C$	Water evolution, source and mixing, inorganic and organic carbon
Stable	^{15}N	$^{15}N/^{14}N$	Airborne nitrates, organic nitrogen
Stable	^{34}S	$^{34}S/^{32}S$	Airborne sulphur, sulphur organics
Stable	^{37}Cl	$^{37}Cl/^{35}Cl$	Saline waters, evaporates, solvents
Stable	^{81}Br	$^{81}Br/^{79}Br$	Saline waters source, mixing, evolution
Stable	^{87}Sr	$^{87}Sr\ /^{86}Sr$	Dating of sedimentary rocks
Stable	^{6}Li	$^{7}Li/^{6}Li$	Saline waters source, mixing, evolution

Modified from Clark and Fritz, 1997.

An example of the use of isotopes for water source travel time and estimating dilution was a study conducted by Quast et al., 2006. The study used ^{10}B (enriched boric acid) as an artificial tracer to determine groundwater travel times from a reclaimed water infiltration basin to nearby monitoring wells. The results confirmed that ^{10}B is an effective tracer. This conclusion was further reinforced by intrinsic tracers of $^{18}\delta O$, δ^2H , B/Cl ratio and xenon isotopes ^{124}Xe and ^{136}Xe that were injected with xenon gas as part of the study.

2.1.3 Radioactive Tracers – Source Water Age and History

Environmental radioactive tracers consist of three basic types:

- Primordial radionuclides – originate from a time before the earth was formed
- Cosmogenic radionuclides – originate as products from the interaction of cosmic rays
- Anthropogenically influenced radionuclides – formed or enhanced as part of activities conducted by humans.

Often a specific type of radionuclide originates from more than one source. For instance, ^{129}I can be found locked in rocks, however, it is also found in atmospheric deposition in the form of precipitation due to its association with radiation emitted during weapons testing and the operation of fission reactors.

A variety of tracers are often used to constrain the age of groundwaters. Isotope ^{14}C of dissolved inorganic carbon (DIC) is used for dating groundwater less than 60,000 years old such as that found in the Quaternary units (Gibson and Birks, 2008). Both ^{36}Cl and ^{129}I become part of the hydrological cycle through either precipitation or dry fallout and therefore can be used to date more recent waters recharge and infiltration into the subsurface. These tracers are also useful for dating ancient waters 50,000 to 2 million years old with ^{36}Cl (Ingebritsen and Sanford, 1998) and the 3 to 80 million years old with ^{129}I (Ingebritsen and Sanford, 1998) and therefore are useful for studying old source waters found in geological units from the Cretaceous and Devonian (Gibson and Birks, 2008).

Surface water studies benefit from the study of ^{222}Rn. The isotope ^{222}Rn has a short half-life of 3.8 days and is produced by decay of radium and uranium in groundwaters (Gibson and Birks, 2008). It is useful in providing an indication of the connectivity of groundwater and surface water in lake systems. It also is useful in determining and mapping of groundwater discharge zones.

2.1.4 Primordial Radionuclides

The primordial radionuclides are tracers that remain since the world was formed. These radionuclides are characterized by very long half-lives (Table 4). Note that the daughter products, also included within the tables, have much shorter half-lives. These primordial radionuclides were trapped in the rocks at the time of the earth's formation. The daughter decay products were also trapped within the closed rock system and accumulated over time. By comparing the amount of parent and daughter products, and by knowing the half-life of the parent material, we can calculate the age of a specific rock formation.

Table 4: Common Primordial Radionuclides used in Earth Sciences

Primordial Radionuclides	**Isotope**	**Half-life (years)**	**Origin**
uranium 235	^{235}U	7.04×10^{8}	Primordial
uranium 234	^{234}U	2.46×10^{5}	Daughter of ^{234}Pa in ^{238}U decay series
uranium 238	^{238}U	4.47×10^{9}	Primordial
thorium 230	^{230}Th	7.54×10^{4}	Daughter of ^{234}U in ^{238}U decay series
thorium 232	^{232}Th	1.41×10^{10}	Primordial - crustal rock
chloride 36	^{36}Cl	301,000	Surface Cl-- based salts origin
radon 222 (noble gas)	^{222}Rn	3.82 days	Daughter of ^{226}Ra in ^{238}U decay series
potassium 40	^{40}K	1.28×10^{9}	Primordial

Adapted from: EI, 2013 and RIN, 2013.

Therefore, these tracers are good for determining source water age and history of the solutes in the water.

2.1.5 Cosmogenic Radionuclides

The cosmogenic radionuclides form as a result of irradiation of protons and neutrons of gases in the atmosphere. The irradiation results in the formation of radionuclides that reach the earth surface in the form of precipitation. Generally the half-lives of the cosmogenic radionuclides are shorter than those of the primordial nuclides. , These tracers are also good for determining source water age and history of the solutes in the water (See Table 5).

Table 5: Common Cosmogenic Nuclides

Cosmogenic Radionuclides	**Isotope**	**Half-life (years)**	**Use**
carbon 14	^{14}C	5730	Age dating in organic matter and groundwater
hydrogen 3 (tritium)	^{3}H	12.43	Groundwater dating
chloride 36	^{36}Cl	301,000	Surface Cl^-- based salts origin
beryllium 7	^{7}B	53.28	Atmospheric studies

Modified from Clark and Fritz, 1997.

2.1.6 Anthropogenically Influenced Radionuclides

Human activity has influenced the abundance of radionuclides in the environment. Many of tracers (e.g. ^{14}C, ^{3}H, ^{36}Cl, ^{129}I,) produced from cosmic radiation have been influenced by weapons testing in the 1950s and 1960s (Clark and Fritz, 1997). In addition to weapons testing, fission reactors, nuclear weapons manufacturing and medical use has increased the prevalence of radioactive material in our environment (See Table 6).

Table 6: Common Anthropogenically Influenced Radionuclides

Human Influenced Radionuclides	**Isotope**	**Half-life (years)**	**Use**
tritium	^{3}H	12.43	Age dating in organic matter and groundwater
strontium 90	^{90}Sr	28.78	Groundwater dating
iodine 131	^{131}I	8.04	Groundwater dating
iodine 129	^{129}I	1.57×10^{7}	Groundwater dating

Modified from Clark and Fritz, 1997.

2.1.7 Chemical Tracers

Chemicals tracers have been used successfully in surface water, groundwater and airborne tracer studies. Usually the study has required that the chemical that is being traced has a unique chemical composition. In airborne studies, plume studies have been successful in identifying the distribution of atmospherically derived contaminants based on soil, snow, rainfall and dry fallout when the emissions have a unique chemical signature. Groundwater and surface water also use chemical tracers to study the fate and transport of contaminants in the environment when the chemical composition of the source is unique (e.g. caffeine or pharmaceuticals downstream from water treatment plants).

Tracers have been used in geothermal reservoirs to determine inter-well subsurface interconnectivity to establish the potential for thermal breakthrough (Acuna et al., 2008). Addition of naphthalene sulfonate was found to resemble the fate and transport of reservoir chlorides, and therefore is thought to be a potential tracer in high-temperature thermal regimes. Previous use of fluorescein was found to be ineffective as a tracer since it thermally degrades. Polyaromatic sulfonates have been tested for use in tracing in geothermal applications and were found to be thermally stable (Acuna et al., 2008 and Gunderson et al., 2002).

2.2 Fluorescent Dyes

2.2.1 Groundwater/Surface Water

Dyes have been used to trace groundwater flow since the late 1800s. The first dye to be used for hydrogeological studies was Fluorecein and has become the most commonly used dye in groundwater studies (Flury and Wai., 2003). Dyes can be found in both the fluorescent and non-fluorescent dye varieties. Dyes have been used extensively in surface water and groundwater studies. The detection of fluorescent dyes is up to 10^4 times lower than for non-florescent dyes (Wolkersdorfer, 2007).

The use of non-fluorescent dyes has largely fallen into disuse within field-based applications due to the potential perception of individuals observing coloured surface or groundwaters as indications of significant pollution and impact to the environment. As such, although both have been used in the past, this study will only discuss the use of fluorescent dyes. The exception to this is their application in small-scale vadose zone studies where Brilliant Blue FCF has become most prominent (Flury and Wai, 2003).

The use of fluorescent dyes for intentional labeling of waters has been applied for over 100 years (Moser, 1995). The main advantage in using fluorescent dyes to trace groundwater or surface water is that they usually has a low or nonexistent background concentrations, can be detected up to a dilution of 10^{-12} depending of the tracer chosen, are inexpensive and easily sampled with automatic samplers. However, care must be exercised in the choice of fluorescent dye as each has varied properties related to sorption and decomposition (see Table 7). It should be noted that no “ideal dye tracer” has been found due to retardation in soils. In addition, dyes decompose by chemical degradation, photodegradation and biochemical degradation, although this often takes place slowly (Flury and Wai, 2003).

Studies indicate that fluorescent dyes behave as a passive or conservative tracer in most environments whereas other dyes can exhibit characteristics of active tracers and are more prone to be affected by the local site conditions. Table 7 summarizes the sorptive properties of fluorescent dyes. In particular, Rhodamine B has very high sorptivity (Wolkersdorfer, 2007). However, in highly saline groundwater, Sulfo-Rhodamine B and Eosin strongly adsorb onto pure minerals and sediments (Magal et al., 2008). Therefore, Sulfo-Rhodamine B and Eosin are not suitable for use as conservative tracers in saline groundwater. In addition, Uranine and Pyranine sorption is found to increase in highly saline conditions and therefore these dyes are only recommended for use in waters that have low to moderate salinity (Magal et al., 2008). Although Sodium Naphthionate was found to be the least sorbed of dyes tested in fresh and saline conditions, it still was found to sorb significantly onto minerals with high clay contents (Magal et al., 2008).

Table 7: Fluorescent Dyes and Their Properties

Tracer	Colour Index	Detection Limit, µg/L	Sorptivity
Uranine, Na- fluoresceine	45 350	0.002	very low
Eosin	45 380	0.01	Low
Pyranin	45 040	0.008	very low
Sulforodamine G	45 220	0.005	Weak
Sulforodamine B	45 100	0.007	Weak
Rhodamine B	45 170	0.006	Strong
Rhodamine WT	AR 388	0.006	Medium
Lissamin FF	56 205	0.03	Medium
Tinopal CBS-X	FB 351	0.07	Medium
Sodium Naphthionate		0.01	Low

Modified from Magal et al., 2008 and Wolkersdorfer, 2007.

All fluorescent dyes summarized in Table 7 have low detection limits and can be easily used applying traditional injection methods to surface water bodies or groundwater units. These dyes are good for small-scale studies but are not suitable for regional studies.

2.2.2 Air Particulate Distribution

Fluorescent tracers have also been used to provide field-based data to calibrate particulate matter transport in atmospheric models. These models have been used for the study of regional acid deposition to improve the understanding of transport and dispersion processes. The use of chemical tracers in the past has required in-situ sampling by aircraft (Uthe et al., 1985). A series of studies were initiated using an airborne Lidar system to remotely track the concentration distribution of fluorescent dye particules (FDP) employed in the atmosphere via a cropduster aircraft. The use of airborne Lidar to remotely monitor FDP distribution 3-dimensionally for long-range atmospheric transport was found to be successful (Uthe et al., 1985).

2.3 Salts

The use of salts as groundwater tracers is not a new application and can be found to have been used in the late 1800s. Original studies using salts were conducted as part of health related studies to determine water sources responsible for the spread of epidemics. Since salts tend to be conservative as they travel in the environment, they generally are considered to be an ideal tracer. An exception to their proficiency as tracers occurs in environments where background salt concentrations are high such as in areas impacted by mine waters or areas where the aquifer material is composed of highly saline rock or unconsolidated matrix materials.

Salts have been used primarily in research-based studies involving groundwater. The studies often involve the intentional injection of tracers into the surface thereby controlling the doses, locations and times of release. The studies have been primarily involved with either understanding of physical flow or understanding of fate and transport of solutes (often contaminants) in the subsurface. Physical assessment studies include determination of flow rates and dispersion studies. The salts are also used as a conservative tracer to assess in-situ groundwater flow rates, residence times, hydrodynamic dispersion and to assess the rate at which solutes are attenuated through absorption, adsorption and biodegradation.

Intentional labeling of groundwaters through injection techniques is a well-developed method and has included the use of NaCl as well as LiCl and KCl (Moser, 1995). Although NaCl was the first salt to be used in tracer applications, LiCl was used in 1907 in Notranjska Teka near St. Kanzian Solvenia (Wolkersdorfer, 2007). The advantage to using Li as an anion is that it has a very small ionic radius and therefore is less affected by ion exchange than other cations associated with salts. It has the potential to impact animal life at high concentrations. Although KCl can also be used as a tracer, it is more sorptive and has a greater potential for ion exchange than NaCl.

Applied studies have often resulted from the unintentional release of salt tracers into the environment. In particular, salts have been used as an effective method to identify plume extent, travel pathway and rate of travel. Such plumes have been associated with landfills, salt storage facilities, spills or releases of produced water from activities associated with the oil and gas industry, flare pit plumes associated with oil and gas industry or sewage effluent releases. Through the application of water sampling techniques and geophysical techniques, the configuration of existing plumes have been identified. Groundwater studies often determine travel times of the plumes and travel distances to nearby surface water features.

2.4 Noble Gases

Noble gases when dissolved in water can act as an ideal tracer since they do not interact chemically with the aquifer matrix materials and they can easily be dissolved in water (Moser, 1995). Both natural tracers and injected tracers can be and have been used. Difficulties can arise with injected tracers as a result of diffusion and outgassing when injection pressures are high. Past studies have used ^{3}He, ^{4}He, ^{22}Ne, ^{39}Ar and ^{85}Kr ^{85}Kr for natural labeling in water cycle for determinations in groundwater age and origin (Clark and Roberts, 2000).

Noble gases are conservative tracers in the subsurface and as such, have been used to assess and track movement of CO_2 in the subsurface during Carbon Capture and Storage (Stalker and Boreham et al., 2006 and Stuart and Stuart et al., 2007). Perfluorocarbons (PFC), krypton (Kr), xenon (Xe) and sulfur hexafluoride (SF_6) have been also used.

Yang and Goldberg et al., (2011) used noble gases bromide (Br) and SF_6 in conjunction with geochemical monitoring of trace metals, bacterial abundance and community diversity to assess potential leakage of CO_2. Although the tracer tests indicated a weak ambient background flow of CO_2 into the near-surface aquifer aquifer, monitoring of the geochemistry and microbial community confirmed change due to leakage. Therefore, use of more than one technique is seen as effective in confirming changes in conditions.

3. APPLICATION OF TRACER TECHNOLOGY IN THE OIL SANDS

Isotopic tracers coupled with geochemical tracers are by far the most commonly used tracers in the oil sands today. Tracer applications are frequently a part of in-situ operations and including defining of reservoir geology and reservoir configuration, determining the source of oil reserves, fingerprinting of oil reserves and tracking movements of hydrocarbons (petroleomics) and providing information to optimize the recovery of heavy oil. In addition\, isotopic procedures are used in exploratory drilling during the logging of boreholes and frac configuration definition.

The use of isotopic and geochemical tracers in the oil sands is also used for defining systems specifically for groundwater – surface water interactions, monitoring of potential environmental impacts and interpreting the difference between background water quality and flow systems and impacts due to anthropogenic activities. Present uses of isotopic and geochemical tracers in the oil sands includes but is not limited to the following applications:

- Determining water yields to lakes in ungagged basins;
- Assessment in sulphate in lakes;
- Tracing and labeling oil sands constituents;
- Defining particulate matter source and effects (i.e. snow, bulk dry and flow through deposition, precipitation);
- Tailings pond water balance;
- Labeling pond water seepage;
- Regional aquifer hydrodynamics – age dating, aquifer mixing, recharge rate estimation;
- Surface runoff and discharge mapping;
- Wetland hydrology and biochemistry;
- Measurement of lake-groundwater exchange;
- Calibration of numerical groundwater models; and,
- Identification of source receptors and source water partitioning.

(Modified from Gibson and Birks, 2008). Additional information is provided in this chapter on uses of tracers in the oil sands and information obtained from those uses.

3.1 Petroleum Industry Application of Tracers for Operations

3.1.1 Tracers for Logging of Boreholes and Fractures During Well Production

Tracers have been used by the oil and gas industry for many years during production logging of the wells. A tracer is injected into the flow stream of a production or in an injection well so that the flow velocities can be determined as well as the pathways injected fluids take within the subsurface.

Radioactive tracers have been used as part of the production logging process for oil and gas since the 1940s (IAEA, 2004). Today radioactive tracers are still commonly used to determine flow profiles in injection wells. The radioactive tracer is injected as a slug flow into the flow stream of a well. The time it takes the slug to travel from the injection point to a detection device is measured and the flow velocity between the two points is calculated. Water-soluble tracers (such as iodine) are the most common tracers to be used for velocity studies although oil and gas soluble tracers have been used. The use of radioactive tracers to calculate flow velocities are believed to provide more accurate indications of flow than flow meters when the substance is traveling at low flow rates. There are issues with disposal of the tracers used and thus the tracers are not usually used in production wells.

Radiotracer technology has been used to determine inter-well communication in oilfields since the1950s. The use of tracers in the inter-well assessment allows for an understanding of fluid dynamics within a specific reservoir. The injected fluids are tagged with a specific nuclide. Samples are measured from the production well to determine response curves that can provide information regarding:

- Presence of high permeability channels such as fractures and barrier to flow.
- Communication between layers.
- The fraction of injected waters reaching the production well.
- Geometry of the reservoir (i.e. stratification within a specific geological layer).
- Preferential flow paths/directions within the reservoir.

(IAEA, 2004).

In the 1970s, tracers with high neutron capture characteristics were used for the creation of neutron logs for injection wells (IAEA, 2004). Tracers used at this time included borax and highly saline water. In the 1990s new tracers were used to track individual phases of multi-phase flow and are usually run with the continuous phase to create a phase-velocity log.

The oil gas industry also uses multiple isotope logging techniques where radioactive tracers are added to mark various stages of a process. The processes include such activities as gravel pack placement, squeeze cementing, hydraulic fracturing, acid treatment. By measuring the tracers released at different stages, it is possible to determine the history of the impacts of the various processes. In this application the most common radioactive tracers are ^{110}Ag, ^{135}I, ^{192}Ir, ^{124}Sb and ^{46}Sc.

Tracer types typically used can be categorized as being a passive or conservative tracer, or an active tracer. The conservative tracer is chosen because of its properties and ability to flow as part of the fluid it was injected with into the subsurface. Active tracers are injected to measure specific properties directly related to interaction with the reservoir which include partitioning, sorbing to formation rock, thermally and microbial degradation (IAEA, 2004). Tracer types include stable isotopic ratios, non-reactive chemical species and radioactive nuclides.

3.1.2 Frac-Pack Evaluations in Fracing Operations

Isotopes are used by the oil and gas industry to effectively tag fluids and solids placed down hole during fracing operations (Gadeken and Fox, 1997). Gamma ray emitting isotopes are used so that gamma-logging sondes can be run down the hole to determine the precise locations of the frac fluids. In addition, the information supplied by the produced gamma ray spectroscopy logs can provide details reading the placement of the frac pack and allow for adjustments to enhance frac-pack placement.

3.1.3 Dating of Petroleum Systems

The use of rhenium (Re) – osmium (Os) geochronology has been recently been explored for applications to date sedimentary rocks, petroleum and sulphide minerals in the oil sands. Selby, 2011 used $^{187}Os/^{188}Os$ of petroleum to date petroleum generation as well as trace it to the source rock. The $^{187}Os/^{188}Os$ signature of the petroleum was used with Pt/Pd to fingerprint the source of petroleum in the oil sands. Results suggest that the petroleum in the oil sands originates from the Jurassic Gordondale Formation not the Exshaw Formation as previously believed (Selby, 2011). In addition, direct dating of the sulfide mineralization using Re-O has been proven viable using molybdenite, pyrite, chalcopyrite and bornite. Additional studies by Creaser, 2005 and Creaser et al., 2006) support this technique.

3.1.4 Petroleum Recovery Optimization

Geochemical and isotopic tools have been used for dating and fingerprinting the oil source and history of heating and biodegradation for heavy oils and oil sand bitumen. Balliache (2011) looked at proxies for assessing thermal processing temperatures so that chamber temperatures of SAGD operations could be determined. Balliashe found that the $\delta^{34}S$ and $\delta^{15}N$ signatures of were unaffected by the biodegradation process involved in the formation of heavy oils therefore they remained stable source signatures for the heavy oils.

Two proxies were examined as indicators for in situ upgrading of heavy oil and bitumen:

- Molecular transformations to the oil during catalytic and non-catalytic upgrading (i.e. under hydrous pyrolysis and hydrocracking conditions);
- Hydrogen isotope signatures for assessing hydrogen transfer to oil from water during heating.

The study found that the type of anthracenes formed during heating were indictors of the heating history of the oils and that δ^2H hydrogen transferred to the oil by exchange/addition increased with the increase in heating temperature. Therefore both proxies were found effective for understanding steam chamber temperature histories.

The findings of this work have implications for optimization of operations and controlling environmental impacts. The ability to understand in-situ temperature conditions of the steam chamber through monitoring could potentially result in better control of required temperatures to optimize the production (i.e. in situ recovery) of products potentially reducing energy requirements and improving steam/oil ratios. In addition, it would aid in the understanding of the generation and distribution of newly formed pollutants. For instance, a higher amount of naphthenic products are produced with catalytic versus non-catalytic procedures. Finally, understanding the variability in oil quality in individual reservoirs can help with assessing well placements and recovery strategies and methods.

3.1.5 Petroleomics

Petroleomics has been used in the petroleum industry to track the movement of hydrocarbons in the subsurface. This supports optimization of resource extraction and has been used since the 1950s to manage operations. Inherent in this approach is the use of geochemical fingerprinting of the oil type.

Critical to the petroleum industry is the understanding of the crude oil composition and its potential to be refined in to desired compounds for market. Petroleomics involves the study of the components of crude oil and how these components affect the properties and reactivity of that specific crude oil (Marchall and Rodgers, 2004). Boiling point fractionalization has been used to as a method to separate and classify the compounds present within crude oil. These are known as distillation cuts and are based on the knowledge of the types of compounds that can be removed at specific temperatures. Also, crude oils have been classified based on solubility of the compounds within various solvents.

The Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (ESI FT-ICR MS) has provided the potential to analyze extremely complex chemical compositions such as those found in heavy crude oils at a level of complexity that was not before available. More than 15,000 chemically distinct species can be detected and analyzed from one single sample (Klein et al., 2005). The oil and gas industry use this molecularly-based characterization method to define more efficient extraction methods and refining processes.

Environmental applications of this technique allow for identification of polar species of compounds (e.g. many, such as nitrogen/sulphur/oxygen (NSO) containing polar species, which are detrimental to the environment) that are unique to a specific crude oil much like fingerprints are unique to individuals. Molecular-based characterization of non-polar species using the FT-ICR MS coupled with Gas Chromatography and Flame Ionization Detector will allow for characterization of all compounds within crude. An understanding of the crude at the molecular level will allow for us to predict the behaviour of the crude oil and allow for the removal of deleterious substances prior to processing. This is a newly developing field of study.

3.2 Tracers for Monitoring of Environmental Impacts

In the oil sands, the primary concerns regarding environmental impact stem from the following:

- Oil Sands Process Waters (OSPW) primarily characterized by the presence of naphthenic acids, chlorides, polyaromatic hydrocarbons and trace/heavy metals.
- Deposition of airborne particulate matter containing polycyclic aromatic hydrocarbons (PAHs) and NOx and SOx emissions in both wet and dry forms.

Isotopic techniques and geochemistry have been in the forefront in helping assess impacts and natural systems in the Athabasca oil sands.

3.2.1 Isotopic Tracers for Industrial Emissions

In the Athabasca oil sands region, industrial emissions to the atmosphere are monitored on a continual basis for the concentrations of specific compounds as well as particulate matter. In particular, there is a concern regarding nitrogen oxides (NOx) and sulfur dioxide (SO_2) emissions because of the potential of increased nitrogen and sulphur deposition. The increases in nitrogen and sulphur result in increases in biomass in the short term. However, over the long term there is a concern of changes to plant communities as well as potential eutrophication and acidification of surface water features such as lakes and wetlands (Allen, 2004)

Recent studies have included isotopic tracing of oil sands atmospheric emissions (Proemse et al., 2012a, 2012b, 2012c, 2012d). A study involved an assessment of unique and emerging tools to monitor impacts of industrial emissions (Proemse, 2012c). The study compared background nitrate (NO_3), ammonium (NH_4) and sulphate (SO_4) deposition with industrial stack emissions. This was accomplished through comparing stack emission samples and atmospheric bulk and fall-through deposition samples from various sites located specific distances from the emission stack. Samples were analyzed for:

- $\delta^{15}N\text{-}NO_3$, $\Delta^{17}O\text{-}NO_3$, $\delta^{18}O\text{-}NO_3$ (of nitrate)
- $\delta^{15}N\text{-}NH_4$, (of ammonium)
- $\delta^{34}S\text{-}SO_4$, $\delta^{18}O\text{-}SO_4$ (of sulphate)

The results of the study indicate that the following have distinct isotopic characteristics and can be successfully used as quantitative industrial tracers for airborne emission contributions to deposition:

- nitrate emissions are associated with distinct values of $\Delta^{17}O\text{-}NO_3$, $\delta^{18}O\text{-}NO_3$.
- sulphate emissions are associated with distinct values of $\delta^{18}O\text{-}SO_4$.

Although variable, $\delta^{15}N\text{-}NO_3$ contents of industrial ammonium and nitrate emissions were found to be variable but offered value as a qualitative tracer.

Note that $\delta^{34}S\text{-}SO_4$ of sulphate from the stack emissions were not found to have a distinctly different isotopic signature from background atmospheric sulphur deposition, therefore it could not be used as an isotopic tracer for the industrial emissions.

Proemse and Mayer et al. (2012d) also conducted studies to evaluate N deposition and the N cycle in the Athabasca oil sands region. Recent concerns have been identified regarding increases in N deposition due to oil sands activities. Stable isotope techniques involving ^{18}O, ^{17}O and ^{15}N of nitrate and ammonia were collected via bulk deposition. The study found that ^{15}N values varied based on season and distance from the source. Biogenic nitrogen emissions appeared to have the greatest effect on isotopic composition of nitrate in the summer and vehicle exhaust had the greatest contribution in the winter months. The use of ^{15}N for tracing anthropogenic influences of N deposition appear to an effective method of evaluation. Subsequent work by Proemse et al. (2012b) found that ^{18}O and ^{17}O of nitrate and sulphate are excellent monitoring tools for tracing N and S emissions from industry.

Promese also completed studies evaluating the radius of influence of SO_4 deposition and found that bulk and throughfall deposition rates were elevated within the 29 km radius of the industrial source. Bulk and throughfall deposition of SO_4 is highly dependent on distance from the source with the highest amounts falling within 29 km from the source (Promese et al., 2012a). The work finds that that monitoring of ^{18}O values of SO_4 is an effective approach for quantifying industrial atmospheric SO_4 contributions in the oil sands.

3.2.2 Environmental Receptors

There is a significant area of study linked to the use of isotopes to study impact to receptors within the environment. Although this is not within the main scope of this study, it is noted as an important emerging field for tracer work.

Air emissions can successfully be linked to environmental receptors. Proemse, (2012c) found that elevated nitrogen and sulphur concentrations in lichens located 16 km from the emission sources with $\delta^{15}N$ of total nitrogen indicated industrial origins 3 km from the emission stacks. Conifer needles sampled within local forests for $\delta^{15}N$ and δ34S did not provide indication of industrial impact. Landis et al. (2012) also identified the effects and distribution of air pollution in the oil sands through the study of lichens.

The effects of nitrogen deposition on boreal bogs and peatlands were studied by Xu (2011). Isotopes $^{15}NH_4$ and $^{15}NO_3$ were used as tracers to examine the effects of increased nitrogen deposition on nutrient pools associated with oligotrophic bogs. Fertilizer was applied to the bog three times and the effects on plants and microbial communities were examined. The responses in production of biomass were monitored and uptake of ^{15}N with plants, mosses and lichens were assessed. The use of isotopes was effective in determining nutrient uptake and release in the system. However, temporal variations were not taken into account during the study methods and therefore results were not as clear as hoped.

3.2.3 Tracking of Process Affected Waters

The characteristics of process-affected waters (OSPW) have been examined through many studies. These studies have indicated that the waters have the following characteristics (Abolfazlzadehdoshanbehbazari, 2011):

- organic compounds: residual bitumen, naphthenic acids (NA), humic and fulvic acids, ashphaltenes, polycyclic aromatic hydrocarbons (PAHs), creosols, phenols, phthalates, toluene.
- elevated concentrations relative to local surficial waters: calcium, magnesium, bicarbonate, sodium, chloride, ammonia, sulphate.
- TDS is reported to range from 1900 -2221 mg/L (MacKinnon and Retallack, 1981; MacKinnon and Sethi, 1993; McKinnon, 2004).
- trace metals: aluminum (Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), molybdenum (Mo), titanium (Ti), vanadium (Va), zinc (Zn) .

Naphthenic acids are the noted as being the most toxic organic in the OSPW when found at usual concentrations (50 to 70 mg/L).

Abolfazlzadehdoshanbehbazari (2011) used $\delta^{18}O$ and $\delta^{2}H$ stable oxygen isotopes to track the fate and transport of OSPW in the clay till located below an infiltration pond over a period of 2 years. The geochemistry of the porewaters, including heavy metals and major ions, was also examined. The results suggest that over a 2 year period, process water infiltrated 0.9 m into the till. The OSPW was found to be enriched in $\delta^{18}O$ and $\delta^{2}H$ compared to other sources of water (e.g. river and groundwater). The breakthough curves of metals and ions in the OSPW lagged behind those of the chlorides and isotopes, and is attributed to ion exchange, precipitation and microbiological processes. The geochemical changes noted in the cation concentrations revealed that ion exchange was the dominant factor controlling the transport of cations. Chloride behaved conservatively as illustrated by the concentration versus depth profiles when compared to stable isotope tracers. Diffusion is considered to be the dominant transport process of the OSPW and advective transport is considered minimal.

Stable isotopes and geochemistry have been used to determine:

- Effectiveness of engineering controls for OSPW.
- Fate and transport of OSPW in the subsurface.

Geochemical tracers have been used in the oil sands to determine whether a dyke and associated collection systems are working correctly. Process affected water (OSPW) was used as a chemical tracer to determine whether the dyke system and seepage collection system was effective at capturing and containing the OSPW of the Muskeg River Mine tailings pond (Yasuda, 2006). As with other studies and determinations, alternative tracer techniques are also applied to provide credibility to the study results. In this instance, stable O and H isotope water analyses were conducted which in turn supported the geochemical results.

A study was conducted along a length of the Athabasca River (i.e. Firebag River to Fort McMurray) to identify seeps and to determine whether the seeps represented natural waters or waters impacted by anthropogenic activities (Gibson et al., 2011). The electromagnetic survey of the Athabasca River identified 10 zones of elevated salinity in porewater located in the river bed sediments. Waters collected from the river, groundwater and river bed seepage were compared to signatures of waters collected from 4 tailings ponds, 3 course tailing samples and 1 tailings seepage.

The results of the study (Gibson et al., 2011) indicate that some of the OSPW signatures differed from some of the natural high salinity groundwater seeps in isotopic signatures but that in general the OSPW compositions overlapped with the overall ranges found in natural waters in the survey, with the exception of some trace metals. In this study, the greatest potential for identifying OSPW, was using ultra-high resolution mass spectrometry profiling of the dissolved organic fraction in OSPW using electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR MS). The technique allows individual compounds in complex organic mixtures to be identified. The results suggest that based on the 23 samples that included natural groundwater and surface water from the region as well as OSPW, there was a strong clustering of the OSPW samples based on operator.

3.2.4 Carbon Capture and Storage

Concerns with reducing carbon footprints associated oil and gas operations have resulted in the study and operation of carbon capture and storage facilities. A great number of studies have been initiated to determine fate of CO_2 emissions using different monitoring techniques and tools. Below two case studies are summarized.

A study conducted by Pekney and Wells et al. (2009) used a controlled release of CO_2 with perfluorcarbon (PFT) tracer. Oil reserves are routinely mapped by injecting PFT down a borehole and measuring concentrations in adjacent boreholes. It allows for an image of the reservoir to be produced. In addition, PFT are used to follow air movement and tracing pollutants. PFT is a non-toxic, chemically inert, clear, colourless liquid that does not occur in nature. It can be detected at very low concentrations. The study found it was an effective tracer for the use of plume delineation.

3.2.5 Assessing Water Balance in Lakes

Many studies have been conducted by Gibson (e.g. Gibson et al. 2005) examining the water balance in lakes in both the Athabasca oil sands area and across Canada using isotopes. The combined use of $\delta^{18}O$ and $\delta^{2}H$ isotopes is effective in providing distinction between precipitation and evaporation effects. It is most effective when combined with water quality and quantity surveys to support work on long-term monitoring of precipitation and river discharge.

In addition, work with $\delta^{18}O$ and $\delta^{2}H$ isotopes for water balance in the Peace Athabasca Delta lake area was conducted by Falcone (2007). The studies allow for establishing existing conditions and allowing for tracking of potential future impacts to the ecological conditions due to climatic variations and development impacts.

3.2.6 Unpublished Tracer Studies Completed by AITF for the Oil Sands.

AITF has completed numerous published reports for clients based on the needs for the oil sand. These studies are summarized in this section.

Specific water resources applications for the water isotope tracers have included:

- $\delta^{18}O$ and $\delta^{2}H$ for regional analysis of lake water balance, estimation of water yield (runoff) to lakes in ungauged basins
- $\delta^{18}O$ and $\delta^{2}H$ as a tailings-pond seepage indicator
- $\delta^{18}O$ and $\delta^{2}H$ for isotopic labeling of constitutents in oil sands
- D-excess as an indicator of wetland water cycle function
- $\delta^{18}O$ and $\delta^{2}H$ for establishing meteoric origin of groundwater
- $\delta^{18}O$, $\delta^{2}H$,^{3}H for surface-groundwater interaction
- $\delta^{18}O$ and $\delta^{2}H$ for partitioning water sources in stream hydrographs

- $\delta^{18}O$ and $\delta^{2}H$ for evaporation/transpiration partitioning in wetlands
- ^{3}H for detection of post-1950s recharge in groundwater wells
- Absence of ^{3}H used to exclude site as process-water affected

Specific water resources applications utilizing the solute tracers have included:

- $\delta^{34}S$ and $\delta^{18}O$ in sulphate for emission source labeling in lakes
- major-ion characterization of groundwater sources (historical, industry from 1950s to present) and groundwater-surface water interaction
- $\delta^{13}C$, $\delta^{34}S$, $\delta^{15}N$, $^{87}Sr/^{86}Sr$, $\delta^{11}B$, $\delta^{81}Br$, and $\delta^{37}Cl$ for labeling of groundwater sources i.e.Quaternary aquifers, buried channels, formation waters
- $\delta^{13}C$, $\delta^{34}S$, $\delta^{15}N$, $^{87}Sr/^{86}Sr$, $\delta^{11}B$, $\delta^{81}Br$, and $\delta^{37}Cl$ for labeling of OSPWtrace elements (fluoride, vanadium, titanium) for labeling water/hydrocarbon sources
- $\delta^{13}C$ in DIC and strontium for labeling of solute origin, reactions: bacterial SO_4 reduction and methanogenesis and for establishing mixing zones in formations
- $\delta^{13}C$ in dissolved gas (CH_4 and CO_2) for estimating biodegradation of hydrocarbon
- ^{15}N as artificial tracer of nitrogen fate in bogs and soil

Specific source water and water age studies that have been conducted using radioactive tracers include:

- ^{14}C in DIC for age dating of groundwaters, southern Athabasca
- ^{14}C in DIC for estimating recharge rates to Mannville
- ^{14}C in DIC for calibration/evaluation of numerical groundwater models
- ^{222}Rn for lake-groundwater exchange studies and groundwater discharge points in streams

Hydrocarbon tracer applications have included:

- naphthenic acids for tracing process water
- ^{13}C in DOC as a tracer of groundwater sources
- ESI-FTICR MS organic profiling of dissolved constituents in OSPW, groundwater and produced water.

4. EMERGING TECHNOLOGIES AND TRENDS IN TRACER APPLCATION

4.1 Nanotechnology

Nanotechnology is fast becoming a leading edge technology for addressing any needs within the environmental sector. It is being considered for water treatment including OSPW and water high in salinity. Patents exist for new technologies that use magnetic nanoparticles in frac waters to trace frac fluid distribution. Nanocomposite polymer membranes are being considered for enhanced water treatment (Alpatove et al., 2011). Downhole treatment of compounds that could be considered contaminants once they reach the surface are being considered, such as the oxidation of napthenic acids (Alpatove et al., 2011). As well, the creation of nanomembranes for water treatment is an active field of study.

Potential applications for nanoparticles in oil and gas field range enabling characterization of hydrocarbons in place and sensors to be used downhole to collect information regarding temperature, pressure and stress of formation (Matteo et al., 2012). The vision is to develop "smart fluids" for drilling, production and stimulation applications. The hope is that a nanosensor will be able to provide direct, in-situ information about the subsurface system. Remote applications could help determine the amount of oil in the reservoir as well conditions (e.g. temperature, pressure, salinity) within the reservoir.

Studies have been conducted to evaluate the potential for using nanomaterials as tracers to sense in-situ the properties of the reservoirs both near well bores as well as at distances from the well bore (Alaskar et al., 2010). Preliminary testing of nanofluid suspensions, including that of nanoparticles and nanowires, was conducted to determine the potential for transport of the nanomaterials through the porous medium. Various detection devices have been evaluated to determine breakthrough detection of the nanotracers. These methods included:

- Dynamic light scattering (DLS) for the detection of nanoparticles.
- Ultra-visible spectroscopy (UV-visible spectroscopy) for detection of nanowires.
- Scanning electron Microscopy (SEM) and Optical Microscopy – used to confirm findings.

Results of the study found that the spherical nanoparticles successfully navigated through pore spaces in the host rock whereas the nanowires were found to bridge the pore spaces, clogging the pores and therefore not allowing transport of nanowires through pore spaces.

Therefore, potential exists for nanotechnology in tracing potential contaminants in the environment perhaps to specific operations or activities.

4.2 Petroleomics with the Use of the Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

One of the areas of development that hold promise is the use of ultra-high resolution profiling of dissolved organics to establish tailings and process water fingerprints. The potential use of these techniques would allow for an understanding of the unique water types (influences by source geology and aquifer conditions and processing) so that natural versus industrial waters can be distinguished. Defining unique fingerprints for different OSPW would allow for the following:

- establishing source, pathway linkage;
- labelling water leakage from such sources as end-pit lakes, tailings deposits, injected saline waters.

ESI FT-ICR MS allows complex mixtures, such as heavy crude oils, to be analyzed. More than 15,000 chemically distinct species have been detected from a single sample (Klein, 2005). Analysis with the ESI FT- ICR MS has allowed for detailed fingerprinting of porewater OSPW from oil sands. The techniques hold great promise for future fingerprinting of water sources and distinguishing natural waters from anthopogenically influenced waters.

4.3 New Isotopic Tracer Applications for the Oil Sands

One of the areas of development that hold promise is the use of isotopic and geochemical tracers to establish tailings and process water fingerprints. The potential use of these techniques would allow for an understanding of the unique water types (influences by source geology and aquifer conditions and processing) so that natural versus industrial waters can be distinguished.

There are still some isotopic tracers whose full potential for oil sands applications are not yet known, and require additional research. Water tracers still have not been tested in their full potential for such applications as steam-assisted gravity drainage (SAGD) applications for assessing water leakage or breakthrough including the potential for tritium for labeling SAGD impacted groundwater zones. Water cycle analyses in reconstructed wetland and end-pit lake constructed environments could better be explored through the use of water isotopes. In addition, understanding of the water balance for evaporation and evapotranspiration losses in vegetated versus non-vegetated tailings has not been fully examined (Gibson and Birks, 2008). Also, potential impacts to wells due to fracing operations can be examined through the use of isotopes.

Additional applications of isotopes could include ^{36}Cl and ^{129}I dating of older groundwater and ^{14}C isotopes could be used for regional surveys of groundwater-surface water interactions. The isotope ^{14}C could be used for distinguishing tailings pond seepage from natural seepage. Isotopes such as ^{222}Rn could be used for end-pit lake water balance and groundwater exchange analysis.

5. POTENTIAL PILOT PROJECTS AND PARTNERS

There are many areas of study involving tracers that would allow for an increase in knowledge of the natural environment, of impacts that anthropogenic activities may have on the natural environment, of how much water can be used and when it can be used to minimize impact on the environment, of understanding of systems and the many linkages between cause and effect, of how specific geological formation water and bitumen treatment processes may produce specific compounds that may be harmful to the environment if not managed in an appropriate manner. The knowledge gained by understanding what environmental contaminant concerns there may be, how we can perhaps change operations to avoid or minimize creation of these contaminants of concern and how much water we have and what is the most cost effective and efficient method to monitor the environment will allow improved management decisions and reduction of potential remediation costs in the future.

Although numerous opportunities exist to study and develop tracer technology to meet the objectives noted above, the following projects are put forth for discussion purposes:

- Nanotechnology tracers for tracking of SAGD fluids;
- Petroleomics-based tracers to fingerprint specific natural waters and waters impacted by anthropogenic activities;
- Tracers use in distinguishing water source and water balance; and,
- Tracer use in monitoring at receptors using key targets such as lichens.

Nanotechnology is now being considered for use in tagging injection fluids. SADG operations would benefit from knowledge about flow pathways, conditions within the reservoir (i.e. such as heating) to control operations. It would be advantageous to look at how isotopes could be used in conjunction with nanotechnology to tag injected fluids to trace flow as well as to look at formation waters and understand how waters are flowing within the reservoir area (inputs and leakages). Numerical models often use estimates of leakage from tailings ponds or end pit lakes and it would be advantageous to calibrate these assumptions with data for real world operations.

Petroleomics can be applied in conjunction with isotopes and geochemistry to determine specific compounds in complex mixtures as seen in OSPW. If a fingerprint unique to a specific operation is obtained (i.e. varies based on targeted geological formation and processing methods), the waters can be distinguished from natural water sources with high salinity and/organics.

Isotopic tracers have been used for a long time to determine the water balance and source waters for lakes, rivers and wetlands. Often when this is done in the Athabasca oil sands region it is completed on a project by project basis by individual companies. A regional understanding of water balance is required if the entire region is to proceed with well-managed development. Isotopes can provide answers to initial baseline characterization of water balance and monitoring of water source and flow during operations in a cost effective and efficient manner.

When monitoring potential impact on natural ecosystems the question is often asked whether you spend time and resources monitoring the emissions or the receptors or both. If you monitor receptors, which ones should be monitored and how does that relate to impacts to the entire ecosystem? One method of measuring the distribution of impacts is to look at isotopic uptake by plants such as lichens. The uptake can be correlated to emissions from particular sources and overall changes in biomass can be associated to these biomarkers. Note that background sites would also have to be monitored to allow for calibration based on temporal effects on results.

The partners suitable for the research described above would depend on the specific project. Generally it is recommended that funded studies be supported by the Canadian Oil Sands Innovative Alliances (COSIA) that has 14 members and represents up to 90% of activity within the oil sands. Support will require finding a suitable industry partner who believes in the proposed study and will support it within COSIA. It is recommended that an information workshop be conducted on a specific proposed study with invited guests from industry, COSIA, government, academia and AITF. It is anticipated that the work scope and project could then be refined and potential interested research and industry partners could be found. It would be beneficial if government would be a part of this initiative.

6. REFERENCES

Abolfazlzadehdoshanbehbazari, M. 2011. Characterizing the Transport of Process-Affected Water Contained in Oil Sands Tailings Ponds into the underlying Pleistocene Clay Till in Northern Alberta's Athabasca Oil Sands Region: A Field Study. University of Alberta Thesis. 2011.

Allen, E. 2004. Effects of Nitrogen Deposition on Forests and Peatlands: A Literature Review and Discussion of the Potential Impacts of Nitrogen Deposition in the Athabasca Oil Sands Region. Wood Buffalo Environmental Association, Fort McMurray, BC. pp.114.

Alpatova, A. and E. Kim, P. Drzewicz, Y. Liu, M. El-Din. "Application of Nanotechnology for Treatment of Oil Sands Process-Affected Water." University of Alberta.

Balliache, N. 2011. Isotopic and Molecular Studies of Biodegraded Oils and the Development of Chemical Proxies for Monitoring In Situ Upgrading of Bitument. University of Calgary Thesis: Calgary, Canada. pp. 389.

Bullen, Thomas and Carol Kendall. 1998. "Tracing of Weathering Reactions and Water Flowpaths: A Multi-isotope Approach." Isotopes Tracers in Catchment Hydrology. Elsevier Science B.V: Amsterdam, Netherlands.pp. 611-646.

Clark, I. and P. Fritz. 1997. Environmental Isotopes in Hydrogeology. Lewis Publishers: New York.

Clark, I.D. and R.J. Phillips. 2000. "Geochemical and ^{3}He/^{4}He evidence for mantle and crustal contributions to geothermal fluids in the western Canadian continental margin". Journal of volcanology and Geothermal Research, Vol 104 (1-4), pp 261-266.

Creaser, D. 2005."Direct Radiometric Dating of Hydrocarbon Deposits using Rhenium – Osmium Isotopes". Science. Vol 308. p. 1293.

Creaser, R. and D. Selby. 2006. "Re-Os Elemental and Isotopic Systematics in Petroleum; a Potentially Powerful Tracer. Geochimica at Cosmochimica Acta. Vol 70 (18S): 1-A116.

Davis, S., D. Campbell, H. Bently and T. Flynn. 1986. Introduction to Groundwater Tracers: Project Summary. US EPA/600/2-85/022. Ada, Oklahoma: US EPA.

Environmental Isotopes (EI). 2013. Chapter 1. University of Ottawa. http://www.science.uottawa.ca/eih/ch1/htm

Falcone, M. 2007. Assessing Hydrological Processes Controlling the Water Balance of Lakes in the Peace-Athabasca Delta, Alberta, Canada. University of Waterloo Thesis: Waterloo, Ontario. pp 201.

Flury, M and N. Wai. 2003. "Dyes as tracers for vadose zone hydrology". Reviews of Geophysics. American Geophysical Union. Vol 41 (1). pp 2-1 to 2-37.

Gadeken, L. and P. Fox. 1997. "Enhancing frac-pac evaluations with directional and spectral gamma ray measurements." Proceedings – SPE Annual Technical Conference and Exhibition: San Antonio, Texas. pp. 241-253.

Gibson, J.J. and T.W. Edwards, S.J. Birks, N.A. Amour, W.M. Buhay, P. McEachern, B. B. Wolfe and D.L. Peters. 2005. "Progress in isotope tracer hydrology in Canada." Hydrological Processes. Vol. 19. pp. 303-327.

Gibson, J.J. and S.J. Birks. 2008. Application of Isotopic and Geochemical Tracers in the Oil Sands Industry and Potential for Establishing Tailings and Process-Water Fingerprints: A Working Paper for Discussion. Alberta Research Council.

Gibson, J.J. and S.J. Birks, M.M. Moncur, Yi Yi, K. Tattrie, S, Jasechko, K. Richardson, P. Eby. 2011. "Isotopic and Geochemical Traces for Fingerprinting Process-Affected Waters in the Oil Sands Industry: A Pilot Project." Report prepared for the Oil Sands Research and Information Network.

Ingebritsen, S. and W. Sanford.1998. Groundwater in Geologic Processes. Cambridge University Press: Cambridge, United Kingdom. pp 335.

International Atomic Energy Agengy.2004.Radiotracer Applications in Industry – A Guidebook. Technical Report Series No. 423. Vienna, Austria. ISBN 92-0-114503-0.

Kendall, C. and E. Caldwell. 1998. Fundamentals of Isotopic Geochemistry. Elsevier Science B.V.: Amsterdam.

Klein, Geoffrey Christoffersen, "Petroleomics: Applications in the Fingerprinting of the Acid and Base Crude Oil Componenets Detected by Electrospray Ionization Fourier Transform Cyclotron Resonance Mass Spectrometry" (2005). Electronic Theses, Treatises and Dissertations. Paper 2822.

Landis, M. and J. Pancras, J. Graney, R. Stevens, K. Perry, S. Krupa. 2012. "Receptor Modeling of Epiphytic Lichens to Elucidate the Sources and Spatial Distribution of Inorganic Air Pollution in the Athabasca Oil Sands Region". Chapter 18, Alberta Oil Sands: Energy, Industry and the Environment. Elsevier BV, AMSTERDAM, Netherlands, 11:427-467.

MacKinnon, MD and JT Retallack. 1981. Preliminary Characterization and Detoxification of Tailings Pond Water at the Syncrude Canada Ltd. Oil Sands Plant. pp. 185-210.

MacKinnon, MD and A. Sethi. 1993. A Comparison of Physical and Chemical Properties of Tailings Ponds at the Syncrude and Suncor Oil Sands Plants.

MacKinnon, MD. 2004. Oil Sands Water Quality Issues: Properties, Treatment and Discharge Options. Canada Oil Sands Network for Research and Development of Oil Sands Water Usage Workshop. Edmonton: February 2005.

Magal, Einat and Noam Weisbrod, Alex Yakirevich, Yoseph Yechieli. 2008. “The use of fluorescent dyes as tracers in highly saline groundwater”. Journal of Hydrology. Elsevier. Vol 358. pp 124-133.

Marchall, A. and R. Rodgers. 2004. “Petroleomics: The next grand challenge for chemical analysis”. Accounts of Chemical Research. Vol 37 (1). pp.53-59.

Matteo, C. and P. Candido, R. Vera, V. Francesca. 2012. “Current and Future nanotech Applications in the Oil Industry.” American Journal of Applied Sciences. Vol 9(6): pp. 784-793.

Moser, H. 1995. Groundwater Tracing. Tracer Technologies for Hydrological Systems Proceedings, July, 1995. Boulder, Colorado. IAHS Publ. No. 229. Pp. 119 – 124.

Pekney, N. and A Wells, etc. al. "Atmospheric monitoring of perflurorcarbon tracer at the 2009 ZERT Center experiement." Atmospheric Environment. Vol. 47. pp 124-132.

Proemse, Bernadette and Bernhard Mayer, Mark Fenn. 2012a. “Tracing industrial sulfur contributions to atmospheric sulfate deposition in the Athabasca oil sands region, Alberta, Canada.” Applied Geochemistry. December 2012. Vol 27 (12). pp. 2425-2434.

Proemse, Bernadette and Bernhard Mayer, Judith Chow, John Watson. 2012b. “Tracing industrial nitrogen and sulfur emissions in the Athabasca Oil Sands Region using stable isotopes.” Developments in Environmental Science. Vol 11. pp. 243-266.

Proemse, 2012c. Tracing industrial emissions in the Athabasca Oil Sands region using stable isotope techniques δ^{15}N-NO$_3$,Δ^{17}O-NO$_3$, δ^{15}N-NH$_4$, δ^{34}S-SO$_4$, δ^{18}O-SO$_4$ and $\delta^{98/95}$Mo. Thesis: University of Calgary. March 2012. pp.279.

Proemse, B., B. Mayer, et al.2012d ”Tracing anthropogenic nitrogen in the vicinity of industrial emitters in the Athabasca oil sands region, Alberta, Canada.” Mineralogical Magazine. Vol 75(3). p. 1670.

Quast, K. W., K. Landsey, et. al. 2006. "Boron Isotopes as an Artifical Tracer". Ground Water. Vol.44. No.3. pp. 453-466.

Radiation Information Networks. 2013. Radioactivity in Nature. Idaho State University. http://www.physics.isu.edu/radinf/natural.htm

Rogers VV and K. Liber, MD MacKinnon. 2002. “Isolation and characterization of naphthenic acids from Athabasca oil sands tailings pondwater”. Chemosphere. Vol 48(5) pp 519-527.

Rozanski, Kazimiera and Klaus Frohlich. 1996. “Radioactivity and Earth Sciences: Understanding the Natural Environment.” International Atomic Energy Agency: Vienna, Austria. Vol 38(2). pp. 9-15.

Selby, D., 2011 “A history and future insights of the rhenium-osmium geochronology of sedimentary rocks, petroleum systems and ore deposits.” Geological Society of America GSA Annual Meeting and Exposition; Minneapolis. Vol 43(5). pp. 144.

Stalker, L. and C. Boreham, et al. 2006. “The role of chemical tracers in the monitoring and verification of carbon storage.” American Association of Petroleum Geologists International; Conference.

Stuart, G. and R Stuart et al. 2007. “Natural and artificial noble gases as tracers of injected CO2 migration within a deep reservoir.” Mineralogical Magazine. Vol 75 (3): 916.

Uthe, Edward. and William Viezee, Bruce Morley, Jason Ching. “Airborne lidar tracking of Fluorescent tracers for atmospheric transport and diffusion studies.” Bulletin American Meteorological Society. Vol. 66 No. 10. pp. 1255 – 1262.

Wolkersdorfer, C. 2007. Hydrogeological Tracer Techniques for Groundwater, Surface Water and Mine Water. Technische Universitat Bergakademie Freiberg.

Xu, B. 2011. “Effects of nitrogen deposition on boreal bogs: A three year nitrogen fertilization and tracer experiment.” University of Carbondale Thesis: Southern Illinois.

Yang, Q.. Goldberg et al. “Biogeochemical reactions in response to CO_2 leakage in a test well in the Newark Basin.” Geological Society of America, Fall Meeting 2011. Vol43(5). pp.126.

Yasuda, N. 2006. Hydraulic performance of seepage collection ditches at the Albian Sands Muskeg River Mine. MASc. Thesis. University of Waterloo (Canada). pp.186.