Ligand-Based Partial Extraction of Near-Surface Soil Samples: An Innovative Geochemical Approach to Shallow Gas Exploration, Southwestern Manitoba

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Summary
Mobile Metal Ion (MMI®) Technology is a surficial geochemical exploration tool that was applied to exploration for unconventional shallow shale gas reservoirs. An historic capped gas well situated southwest of the community of Manitou, Manitoba, was chosen as the test site for this methodology. Results from multi-element geochemical surveys conducted along a north-south transect centered on the gas well indicate that multi-element geochemical anomalies are developed directly over the site and that MMI technology can be used for this type of hydrocarbon exploration. The method is rapid, simple and cost-effective.

Introduction and Application to Hydrocarbon Exploration
Surficial geochemical exploration has a long and varied history in its application to the search for petroleum. Much of the current geochemical exploration focuses on the collection and analysis of soil gases and the integration of the chemical expression of hydrocarbon micro-seepage with geological and geophysical (seismic) databases. Based on historical precedent the seismic approach is unsurpassed for the definition of oil and gas reservoirs. Surficial geochemical techniques, however can identify metals associated with hydrocarbon micro-seepage from the same reservoirs and discriminate “productive” versus “non-productive” reservoirs or seismic targets. The approach can be used to re-assess active fields for extensions of known resources or to delineate by-passed resources of oil and gas in “exhausted” oilfields. It can also be utilized to evaluate seismic targets for their prospectivity or pioneer areas for the presence of oil and gas potential.

The trace element content of petroleum, natural gas, associated brines and coal has been established by sophisticated analytical procedures by hydrocarbon producers and the academic community. These trace element contents or “fingerprints” can be used to differentiate and characterize hydrocarbons originating from oil fields in different geological environments. In effect, the various hydrocarbon reservoirs represent “metal-sources” of variable geochemical characteristics, i.e. they contain different trace elements in varying amounts. These same trace elements can also be used to define exploration targets by measuring their concentrations in near-surface soils subsequent to ligand-based partial extraction, a new and innovative approach to geochemical exploration. This technique is referred to as Mobile Metal Ions Process Technology.

Mobile Metal Ions or “MMI” is a term used to describe ions, which have moved from buried metal-source to near-surface environments where they become weakly or loosely attached to
the surface of soil particles. These are the ions that are measured by the MMI geochemical technique to target metal-sources at depth. The weakly attached ions are at very low concentrations in soil. Because the ions have recently arrived at the surface they provide a precise ‘signal’ on where the sources of metal/hydrocarbons are located. When the Mobile Metal Ions arrive in the near-surface environment they have a limited lifetime as ‘mobile’ ions. At the surface the ions are subject to weathering and are bound up by soil forming processes (i.e. they become part of the soil during pedogenesis). Bound ions are subject to lateral movement away from the source region. The mobile ions, however, do not move away from the metal source because they have a limited lifetime before they are converted to a bound form.

By measuring Mobile Metal Ions in surface soils, the MMI technology and additional related geochemical determinations can document the presence of focused apical responses (anomalies) directly over the source regions. The source may be any accumulation of metals that is in contrast with surrounding rocks such as oil and gas within reservoirs and coal. Chemical analysis of petroleum has documented characteristic trace elements within the oil and its surrounding host rocks. These trace elements will move to surface and be indicative of a buried hydrocarbon accumulation. Regardless of the type of metal-enriched zone at depth, metal ions that comprise that zone will be mobilized to the surface under a variety of mechanisms. These include vapor phase transport by light hydrocarbon gases, Hg-vapor and carbon dioxide, convection, diffusion, evapo-transpiration and electrochemical mechanisms.

The relative importance of each of these mechanisms can be variable depending on the nature of the source region, presence of “plumbing systems” to channel metal-rich gases, depth to water table and numerous other variables. Nevertheless, research and case studies over known metal/hydrocarbon-bearing zones have shown that mobile metal ions and additional compounds accumulate in surface soils above these metal sources. Hydrocarbons that are present in the subsurface also “leak” from their structural and stratigraphic traps and move upward to the surface or along geological pathways. Hydrocarbons can move vertically through thousands of metres of rock without obvious fractures or faults in a period spanning weeks to years. Hydrocarbon micro-seepage has been documented at less than 1 to tens of metres per day. This is evidence for an ongoing and dynamic geochemical system. Published studies documenting zoned mineralogical and geochemical “haloes” developed in association with plumes above oil and gas reservoirs (cf. Sikka and Shives, 2002) are present in the literature.

**Current Study Geological Setting and Gas Exploration**

In this initial study, an orientation soil geochemical survey was undertaken within the Pembina Hills and Pembina Valley region located in southwest Manitoba, west of the Manitoba Escarpment at the northeastern edge of the Williston Basin. In this region the Cretaceous strata is approximately 320 m thick with a southwesterly dip of 1.5 to 1.9 m/km. Lithologies include the basal sandstone of the Swan River Formation, with overlying shale sequences of the Ashville, Favel, Carlile formations and Pierre Shale. Jurassic, Triassic and Paleozoic strata underlie the Cretaceous sequence, and extend east beyond the Manitoba Escarpment. Cretaceous shale is near-surface in many parts of the Pembina Hills region, outcropping along the Manitoba Escarpment and in the Pembina Valley. Gas occurrences in the Cretaceous shale have been documented in the Pembina Hills region for over a century.

Two known capped gas wells are still present today and have reservoir pressures of about 276 kPa and methane concentrations of over 85%. The gas reservoir in this area is estimated to be between 180 and 200 m below surface (approximately 230 m asl) and likely originates from the Assiniboine Member of the Favel Formation.
Sample Collection And Analysis
Soil samples were collected from hand-dug 40 cm deep pits along a 512 m north-trending transect with sample stations centered on the shallow gas occurrence. At each pit, four samples were collected at 10 cm intervals along one wall of the pit. This sampling approach is designed to assess the upper 40 cm of the soil profile for the presence of vertical differentiation of metals in an ascending metal-rich plume. Results determine at what level in the soil profile metals reach their maximum and most representative concentrations, and therefore the location of the optimum sampling position. Approximately 200 g of soil were collected from four positions in each of 25 pits along the transect. Samples were analyzed by inductively coupled plasma–mass spectrometry (ICP-MS) after MMI-ME partial extraction. Additional parameters included I, Br, Cl, Hg, S and pH.

Results – Vertical Profiles
Vertical profiles for samples collected from top to bottom of an individual sample pit over the shallow gas occurrence indicates the majority of elements have maximum concentrations in samples collected between 0 and 10 cm with a few select elements concentrated in samples from the 30-40 cm depth. The elements Ca, Co, Ni, Zn, Cd, Mo, Sb, S, Th and Tl have maximum concentrations in the 0-10 cm samples and are characterized by a steady, progressive decrease in concentration with an increase in sample depth. The elements Cu, Li, Mg, rare earth elements (“REE”) and I are maximized in samples collected from the 30-40 cm depth. These elements gradually increase in concentration between 0 and 40 cm. These patterns suggest that differentiation in elements occurs through the upper 40 cm of the soil profile where no obvious changes in soil type occur. At most sample stations the soil was a black, featureless silt-clay with occasional gritty laminae of platy shale fragments dispersed though the wall of the pit. There were no pedogenic horizons observed in any of the sample pits along the sampling transect.

Results – Lateral Profiles
Analysis of samples collected between 0 and 10 cm indicate the presence of a diagnostic suite of elements enriched in the soil directly above the shallow gas occurrence. These include Mo, Tl, Co, Ni, Th and Br. Maximum extent of the anomalous responses is 50 m. Samples collected between 10 and 20 cm and 20 and 30 cm gave no diagnostic responses over the shallow gas vent site. The 30 to 40 cm sample suite documented Br, and I anomalies over 50 m of the sampling transect.

Discussion
This orientation survey was designed to assess the potential for partial extractable soil geochemical signatures associated with a shallow gas vent site near Manitou. The survey has demonstrated that multiple diagnostic responses for elements determined using the Mobile Metal Ion multi-element extraction (MMI-ME) are present in the soil profile. The most representative are to be found in the 0-10 cm samples whereas subsidiary elements Br and I are also diagnostic of the shallow gas vent site.

The Br response in the 30-40 cm samples produces the most extensive halo-effect around the vent site at 50 m and as such should be considered as an extremely valuable pathfinder element in shallow gas soil geochemical surveys. The drawback may be the requirement to sample at a depth of 30-40 cm versus 0-10 cm for the remainder of the elements as the 0-10 cm Br response, albeit high-contrast is somewhat less diagnostic.

If the location of shallow gas vent sites can be shown to be localized along geologic features such as faults or in general terms “lineaments” then the MMI-ME approach will have merit in the exploration for vent sites along these linears.

The presence of a multi-element high-contrast anomaly at the shallow gas vent site is indicative
of metals being mobilized from the origin of the gas along with the gas itself. The gas therefore may be acting as a “carrier” for these metals bringing them “source to surface” or the gas may be liberating these metals from bedrock sources during its ascent to surface. The metals are then fixed on the surfaces of individual soil particles and stripped by the MMI-ME partial extraction, held in solution by a complex suite of ligands until measured with an ICP-MS.

Conclusions
A multi-element signature consisting of Mo, Tl, Co, Ni, Th, I and Br characterizes the immediate area of the shallow gas vent site. This anomaly is documented on the basis of the partial extraction of soil samples using Mobile Metal Ions extraction MMI-ME and separate determinations for I and Br. The anomaly at the vent site has maximum dimensions of 50 m. The optimum sample position for the delineation of this anomaly is between 0 and 10 cm although diagnostic responses were obtained for Br in 30-40 cm samples. The optimum distance between sample sites based on this limited survey is 25 m. Changes in pH are minimal in soils collected vertically through the soil profile and laterally along the sampling transect.

The discovery of new oil and gas resources has become challenging in recent years, and the increased need for natural gas has prompted a worldwide search for unconventional reservoirs previously bypassed. Unconventional shale gas occurrences require new techniques to find the best site to drill an economic well since these types of resources tend to be expansive but not necessarily economical over their entire expanse. The application of MMI technology could assist in locating gas sweet-spots prior to investing heavily in drilling a potentially marginal gas well. Application of this technology opens up shallow gas exploration opportunities in southwestern Manitoba, particularly where shallow stratigraphic test drilling is expensive and commonly has poor and non-reliable drill chip or core recovery.

References