Hydrogeological Study of the Cold Lake Air Weapon Range, Alberta

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ABSTRACT

A hydrogeological study has been accomplished at the Cold Lake Air Weapon Range (CLAWR), Alberta. Various measurements were performed in order to characterize the groundwater flow pattern. Water samples were collected and analyzed for several compounds including metals, routine anions, perchlorates, energetic materials and nitrates. Surface water was found to be uncontaminated with respect to freshwater guidelines. Localized contamination by some metals and perchlorate was found in groundwater. TNT, TNT-byproducts and RDX have been detected in soils and groundwater. Nitrate was also found in groundwater, with concentrations up to 20 mg/L N-NO3. N and O isotopic results indicate that nitrates in high concentrations in shallow wells are not of natural origin and their specific source is currently under investigation.

RÉSUMÉ

Une étude hydrogéologique a été réalisée à la Base Aérienne de Cold Lake (CLAWR), Alberta. Diverses activités ont été réalisées afin de caractériser l'écoulement souterrain. Des échantillons d'eau ont été prélevés et analysés pour divers composés, incluant des métaux, anions, perchlorates, matériaux énergétiques, et nitrates. L'eau de surface semble non contaminée par rapport aux critères en vigueur. Une contamination localisée par le perchlorate et certains métaux a été détectée dans l'eau souterraine. Du RDX, TNT et des sous-produits du TNT ont été détectés dans les sols et l'eau souterraine. Des nitrates ont également été détectés à des concentrations atteignant les 20 mg/L de N-NO3. Les résultats isotopiques de l'azote et de l'oxygène suggèrent que les nitrates en hautes concentrations présents dans les puits peu profonds ne sont pas d'origine naturelle. Leur source potentielle est présentement investiguée.

1. INTRODUCTION

In the last decade an increased environmental awareness has lead the Canadian Forces to complete studies in order to evaluate the impact of various military activities. A better understanding of those impacts on groundwater and surface water is important in order to ensure sustainability and long-term availability of training ranges. Within this context, the hydrogeological study of the Cold Lake Air Weapon Range (CLAWR) has been accomplished. This site is different from the other studied Canadian military bases in that it is an Air Force base, and thus, the activities going on are different from those taking place on regular military bases.

The four main training ranges of the CLAWR were thus studied for their groundwater flow system and potential contamination. Various measurements were performed in order to determine the groundwater flow direction and velocity, as well as the interactions between groundwater and surface water. Surface water and groundwater samples were also collected and analyzed for energetic materials, metals, routine anions, nutrients and perchlorates. Those are the main contaminants expected to be found on such a site. Explosive residues may be found in the soil and groundwater as a result of incomplete detonation of bombs, whose casing may be broken or eventually eroded, and whose exposed contents may be leached to the water table. In addition to the danger pertaining to their explosive nature, many energetic materials and their degradation by-products are toxic and potentially carcinogenic (US EPA 2003a). Metals such as iron are expected to be found in the same areas, originating from the corrosion of buried casings. Perchlorates, which are used extensively in rocket fuels, are also a common contaminant on military bases and have been linked to various health disorders, affecting primarily the thyroid gland (US EPA, 2003b). They are not easily degraded or adsorbed, and are therefore persistent in the environment.

It has been previously demonstrated that nitrates were commonly found at military sites (Beller et al. 2004, DiGnazio et al. 1998, Spalding and Fulton 1988), and that their origin might be linked to the degradation of explosives (Fournier et al. 2002, Hawari et al. 2002). Isotopic analyses of N and O have therefore been performed to try to determine the origin of nitrates on the site.

2. OVERVIEW OF THE SITE

The Cold Lake Air Weapon Range (CLAWR) covers an area of approximately 10, 373 km^2 straddling the Saskatchewan-Alberta border (Martel et al. 2006). The range has been used over the years for the training of Canadian and Allied pilots. The two main areas of interest are Primrose Lake Evaluation Range (PLER) and Jimmy Lake Range (JLR), which are located in the south central part of the CLAWR.

PLER contains drop zones Alpha and Bravo, which are used for air-to-ground operations including live weapons. JLR, adjacent to the northern boundary of PLER, contains drop zones Jimmy Lake and Shaver Range. Jimmy Lake is mostly used for strafe and factice bomb drop, while Shaver Range is used intensively for live explosive training and destruction of obsolete ammunition. Figure 1 shows nearly all of JLR, where most of the research has been focused. The area in shades of grey, where all the monitoring wells are located, covers both training ranges (Shaver Range and Jimmy Lake Range) and will later be used for numerical modeling.

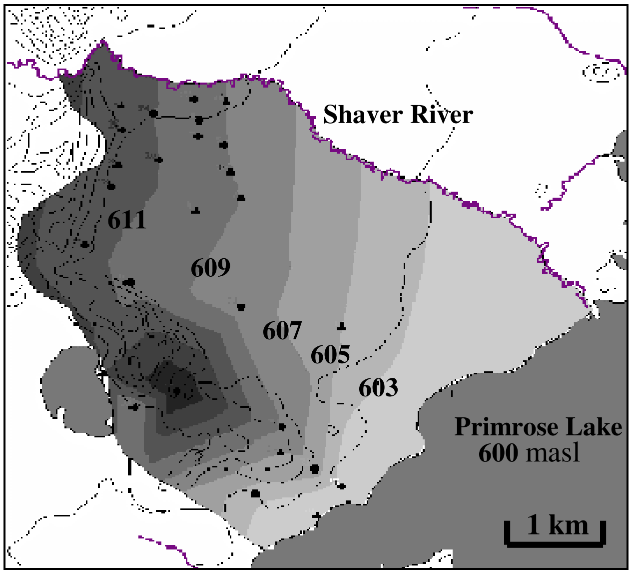

Figure 1. The JLR area of CLAWR, with hydraulic heads (masl) and sampling wells represented as dots.

Primrose Lake is the largest and deepest water body within the CLAWR. The Primrose Lake watershed plays an important role in providing the water supply for the city of Cold Lake, which serves as the principal industrial and municipal water for the region (Martel et al., 2006).

The Lea Park Formation is the major bedrock aquitard in this region and the top of this formation, located at 50 to 120 m depth, essentially marks the lower limit of groundwater supplies in the area. The glacial drift on top of the bedrock (consisting of sand, sand and silt or gravel, and till) is the most common shallow aquifer (Martel et al., 2006).

Commercial fishing occurs within the CLAWR and is centered mainly on Primrose Lake. The groundwater and surface water at CLAWR is not used by military personnel for consumption. The PLER training area is located 46 km north of CFB Cold Lake, and the JLR area is located even further north, while the town of Cold Lake lies south of CFB Cold Lake.

3. METHODOLOGY

3.1 Hydrogeological Characterisation

The hydrogeological study of CLAWR took place in three phases, spread over five field campaigns between March 2004 and November 2005. Each subsequent phase was done with the objective of getting more precise information on the areas where contamination was detected.

A total of 64 wells were drilled, installed and developed during the study, with depth varying between 1.5 and 10 meters. When a clay layer was encountered, two wells were drilled (shallow and deep), to characterize the different layers of sand below and above the clay. Of all the sites, 13 have 2 wells installed at different depths, and two have 3 wells, the third one being installed within the clay layer. Well locations were selected based on past and present activities on the ranges. The maximum drill depth was set at 10 m due to UXO hazards and limitations in the ability to detect hazards deeper than 10 m. The drilled wells were completed according to ASTM-D5092-02 (American Society for Testing and Materials). All wells were surveyed for location and elevation, with a precision of +/- 2 cm.

Slug tests were performed in 26 wells by the removal of a volume of water and recording of pressure during well recovery. Data were analyzed with the Bouwer and Rice (1976, in Butler, 1998) method where the aquifer was unconfined, and with the Cooper (1967, in Butler, 1998) method where confined conditions were found. Water level was recorded in each well within the shortest time possible, to provide a ‘snapshot’ overview of the piezometry on the site. These data were used for the creation of piezometric maps. Standard decontamination procedures were applied to all equipment being transferred between wells.

3.2 Environmental Characterisation

119 groundwater samples have been collected throughout the study using different methods. In March 2004, the set-up used for development was also used for sampling. Low-flow sampling (Pulse and Barcelona, 1996) was performed in August and November 2004, as well as in August 2005. In November, the temperature was too low to allow for low-flow sampling, even with a tent and heater set-up. For this reason, the wells were sampled either with the mechanical pump technique or with a bailer. Physiochemical properties were always measured using a multiparameter probe capable of recording dissolved oxygen, conductivity, temperature, pH and oxygen redox potential (ORP). Samples were collected for the analysis of energetic materials, routine anions and nutrients, routine metals and perchlorate. In August and November 2005, certain sites were also sampled for isotopic analysis of N and O in nitrates. Surface water sampling was made by grabbing samples manually, directly with the sampling bottles. Physiochemical parameters were measured from the water body, and samples were collected for the same analytes as groundwater samples.

For surface water and groundwater collected via the development set-up or with a bailer, samples for metal analysis have been filtered. All metal samples were acidified to pH 2.0 by addition of HNO_3, and samples for nutrients were preserved with H_2SO_4. Appropriate sampling bottles and preservatives were provided by the labs performing the analyses. For energetic materials, approximately 2 grams of sodium bisulfate were added to amber glass bottles to ensure the stability of samples with respect to microbial degradation and photodegradation. Quality control was attained by duplication of the sample collection and measurement of physiochemical for about 15% of the samples. Additional replication of analysis was performed by the laboratories involved. In addition, many field blanks and trip blanks were gathered to detect any contamination coming from the field manipulations or the lab distilled water, respectively.

3.3 Nitrate Isotopic Analysis

31 water samples collected for nitrate isotopic analyses have been passed through 0.45 µm filters, and frozen within 24 hours. Samples containing at least 1 mg/L of nitrates were analyzed at the Delta-Lab of the Geological Survey of Canada (Québec) using the ion-exchange resin and Silver nitrate methods for nitrate extraction from waters. Combustion and pyrolysis on-line systems were used to analyze N and O isotope ratios, respectively. The ion-exchange resin technique, however, does not permit an easy treatment of samples with nitrate concentration lower than 1 mg/L. Therefore, samples with lower concentrations were sent to an external lab and analyzed using the denitrifier method described by Sigman et al. (2001) and Casciotti et al. (2002). The standards used for comparison with our results are atmospheric N_2 for nitrogen, and Vienna Standard Mean Ocean Water (VSMOW) for oxygen. In addition, a sample of RDX was put into solution (18,89 mg/L, solution saturated at 4°C) and photodegraded at 350 nm for 22 hours. The produced nitrates have been analyzed as well using the ion-exchange/Silver nitrate method. Precision on the analyses were better than 0.2 ‰ for both isotopes at both laboratories.

4. RESULTS AND DISCUSSION

4.1 Hydrogeological Characterization

The water table varies from being at or near the soil surface in some areas, and deeper than 10 m in others. Shaver Range has the shallowest water table with an average of 2.7 m depth. Jimmy Range has the highest variation, because it is the only range which comprises a series of hills. The aquifer is recharged from precipitation, which amounts to 452 mm/yr. Aquifer recharge was estimated from climate data, long-term pressure sensors in wells and hydrograph data, and the average obtained from each method varies between 25 and 119 mm/yr (Martel et al., 2006). The groundwater yield of the aquifer is around 25 to 100 L/min (Wallick, 1984 in Martel et al., 2006).

Hydraulic conductivity has been calculated from slug tests and grain size analysis. The average is in the order of 10^{-5} m/s for Alpha and Bravo, 10^{-6} m/s for Jimmy, where till was often encountered, and 10^{-4} m/s for Shaver Range, where essentially only sand has been found, with the exception of a thin clay layer. Values from both techniques agreed very well. On PLER and JLR, the groundwater flows eastward, towards Primrose Lake. Groundwater velocities have been calculated from the mean hydraulic conductivities, the hydraulic gradients and an estimated porosity of 0.3. Jimmy Range has a high gradient but its low hydraulic conductivity yields a velocity of 0.75 m/year. Alpha and Bravo Ranges are in the order of 8 m/year, while Shaver, with a higher hydraulic conductivity, produces a groundwater velocity of 26 m/year.

4.2 Environmental Characterisation

Groundwater results have been compared to the Health Canada (2004) guidelines for drinking water. For surface water, the Canadian Council of Ministers of the Environment (CCME, 2003) guidelines for aquatic life were used, and energetic material results were compared to the US EPA (2003a) criteria, since neither Health Canada nor the CCME has guidelines for those compounds. To discuss the chemical results that exceed the established criteria, it is helpful to have a comparative baseline, or background water composition indicative of the natural chemical composition found in the area. The only background well that was not later found to be dry was drilled in November 2004, near Primrose Lake between JLR and PLER. However, due to time and access constraints, it was only sampled once.

4.2.1 General Chemistry

PH is below the guideline in many wells spread out on Shaver, Jimmy and Bravo Ranges. In Shaver Range, for most wells with pH below the guideline, there is a tendency of gradually increasing pH from the first sampling campaign to the last one. However, the background well was found to have a pH of 5.28, suggesting that groundwater in the area is naturally acidic. Surface water tends to be normal to slightly acidic. Total dissolved solids are above the aesthetic objective in two wells on Alpha, and one well on Bravo range. Arsenic was detected in one well on Shaver Range, with concentrations above the guideline in two out of three sampling campaigns.

4.2.2 Heavy Metals

Iron and manganese are exceeding the guidelines in 17% and 35% of the wells, respectively. It is possible that the background concentrations of iron and manganese are high in this area due to natural processes. The sample taken from the background well GW-BG-2-1 has a very low Mn concentration, and an iron concentration just below the guideline. However, guidelines for Fe and Mn are only an aesthetic objective. This is not the case for the surface water iron guidelines, which 48% of the samples exceeded. Only two surface water samples exceeded the tentative guideline proposed by the British Columbia Government to the CCME for manganese. As for aluminum, until November 2004 only one groundwater sample had exceeded the guideline. In the last study phase (Aug. and Nov. 2005), 13% of the wells, most of which had not been sampled before, showed Al concentrations above the guideline.

Because this situation was only observed in one phase, it is difficult to draw any conclusion. In August 2004, copper was also detected above the guideline in many surface water samples. Although it was still present in the November 04 and August 05 samples, the levels went down, with only one location per sampling campaign exceeding the guideline. Zinc was detected in surface water in August 2004 and August 2005. However, the only sample from August 2004 exceeding the guideline had very low Zn levels in the following campaigns, and the two samples exceeding the guideline in August 2005 have only been sampled once.

4.2.3 Perchlorates

Perchlorates have been detected above the preliminary guideline of 6 ppb recommended by Health Canada (2004) in five wells, four of them located on Shaver Range. In two of those wells, the concentration significantly increased from the first until the last sampling campaign. It seems that perchlorate is present in groundwater on all training ranges at concentrations below the guideline. It has been detected in wells at different depths, but generally in significantly lower amounts in deep wells compared to shallow or clay wells. Finally, perchlorate was detected below the guideline level in two surface water samples during one campaign.

4.2.4 Energetic Materials

Energetic Materials were analysed in both groundwater and surface water, and the results were compared with the Lifetime Health Advisory for Drinking Water of the US EPA (2003a). Those guidelines are presented in Table 1.

Table 1. Drinking Water Guidelines for E.M. (US EPA 2003a)

Compound	(µg/l)
TNT	1,0
RDX	2,0
HMX	400
2,4-DNT	0,17
2,6-DNT	0,0068
2-A-4,6-DNT	no guideline
2-A-2,6-DNT	no guideline
1,3,5-TNB	1,0
NG	5,0

As shown in Table 2, most of the contamination was found on Shaver Range, where RDX has been detected in six wells, four of which had concentrations above the guideline. All samples presented there are groundwater samples, except SW-Lake-4, which is a surface water sample from Primrose Lake near the Bravo training range. GW-SR-11 has been sampled for energetic materials in each campaign, and RDX was always detected above the guideline. GW-SR-10 also contained RDX above the guideline concentration, but only in one sampling campaign. The other two wells with RDX levels above the guideline on Shaver Range were only sampled once. RDX was also found in one well on Bravo Range and one on Jimmy Range. However, it was only detected in one sampling campaign out of two for the well on Bravo, and the one on Jimmy was only sampled once. TNT was detected in two wells on Shaver Range. One of them was only sampled once, and the other contained amounts of TNT which were increasing during the last three sampling campaigns (Nov. 2004, Aug. 2005 and Nov. 2005). TNT was also detected in a surface water sample in Aug. 2004, but not later. This could be due to contaminated sand from nearby Bravo Range being blown into the lake from the wind.

Table 2. Energetic Materials Detected in Water Samples at CLAWR

Compound	Site	Mar. 04	Aug. 04	Nov. 04	Aug. 05	Nov. 05
RDX (ppb)						
	SR-4	n.d.	n.d.	n.d.	n.d.	0.51
	SR-10	n.d.	n.d.	n.d.	25.8	n.d.
	SR-11	3.2	-	3.12	n.d.	4.09
	SR-111*	-	7.02	1.96	3.9	-
	SR-3-1(S)	-	-	-	-	1.59
	SR-3-2(S)	-	-	-	-	2.55
	SR-3-5	-	-	-	-	1.38
	JL-3-9	-	-	-	-	0.42
	B-2-2(S)	-	-	-	2.38	n.d.
TNT (ppb)						
	SR-4	n.d.	n.d.	7.43	78.98	97.02
	SR-3-1(S)	-	-	-	-	72.19
	SW-Lake-4	-	-	1.81	n.d.	n.d.
1.3.5-TNB (ppb)						
	SR-3-1(S)	-	-	-	-	0.32
2.4-DNT (ppb)						
	SR-3-1(S)	-	-	-	-	3.71
2-A-4.6-DNT (ppb)						
	SR-4	n.d.	n.d.	n.d.	n.d.	2.37
	SR-3-1(S)	-	-	-	-	6.16
2-A-2.6-DNT (ppb)						
	SR-4	n.d.	n.d.	n.d.	n.d.	3.81
	SR-3-1(S)	-	-	-	-	8.17

\- not sampled or bottle broken   n.d. not detected
* Duplicate of SR-11

Products of TNT degradation were detected in two wells on Shaver Range in November 2005. The 2,4-DNT concentration exceeded the guideline, and there exists no guideline for 2-A-4,6-DNT and 2-A-2,6-DNT. The concentration of 1,3,5-TNB was below the guideline. All the wells on Shaver Range, Bravo Range, and the lake sample location, where explosives have been detected are located downgradient of their respective range target. The well on Jimmy Range (JL-3-9) was not expected to be contaminated, considering its location. However, it is possible that a target has been located in this area many years ago, and that some buried UXO's are still present. In summary we observed increasing concentrations of dissolved energetic materials in well SR-4 over two years. TNT and its metabolites are a concern in groundwater in wells SR-4 and SR-3-1(shallow), and RDX in wells SR-10, SR-11, SR-3-1(shallow) and SR-3-2(shallow).

4.2.5 Nitrates

Nitrates are present on the sites at relatively high levels. Although only six wells (five of them located on Alpha and Bravo ranges) had N-NO_3 levels above the drinking water maximum acceptable level of 10 mg/L, many wells have groundwater with concentration above 2 mg/L, a level that we consider the upper limit for the natural background. It is therefore clear that many wells carry groundwater that has been affected by anthropogenic contamination. On Shaver Range, 61% of the wells have N-NO_3 concentrations above 2 mg/L, with one well reaching 11.69 mg/L. In almost all cases, for double level wells the nitrate content was considerably lower in the deep well than in the shallow well, indicating a surface source. However, the concentration of 11.69 mg/L was found in a deep well, while the shallow well at the same location had a concentration of 2.2 mg/L. On Jimmy range, only two wells had nitrate contents above 2 mg/L.

On Alpha and Bravo ranges, the nitrate contents are much higher, with five out of 16 locations having concentrations above 10 mg/L, and more than half of the locations having concentrations above 2 mg/L. The two deep wells located on Bravo Range have very low nitrate contents. The two wells installed in clay at the same location, however, have higher concentrations, one of them reaching 19.17 mg/L. In both cases the clay well had higher nitrate concentration than the shallow and deep well. Duplicate samples from four of the wells show constancy in their nitrate concentrations. This constancy and the presence of much lower concentrations in the other wells (below detection limit to 1.4 mg/L) suggest that high nitrate contents are not a punctual situation, and that they are not originating from natural sources. Finally, all of the surface water samples had very low nitrate contents, the highest being 0.18 mg/L.

It was proposed that the high nitrate concentrations found on the site may come from the degradation of explosives. While it is unlikely for chemical reasons that they come from TNT, it is possible that they be the result of the degradation of RDX (Hawari, pers. comm.). Indeed, TNT transformation generally involves the reduction of a nitro group to an amino group, while transformation of RDX involves the removal of a nitro group from the molecule (Brannon and Myers, 1997). It has been demonstrated in several studies that degradation of RDX could be important in anaerobic conditions, but much less pronounced in aerobic conditions (Price et al., 1998). However, Fournier et. al (2002) and Coleman et. al (1998) have found that biodegradation of RDX by Rhodococcus sp. Strain DN22 was possible, and produced significant amounts of NO_2. Furthermore, photodegradation of RDX in water has been shown to mimic biodegradation, with NO_2 and NO_3 as resulting products (Hawari et. al, 2002). When RDX is photodegraded, nitrites and nitrates are produced by denitration of the molecule, which precedes ring cleavage (Fournier et. al, 2002 and Hawari et. al, 2002). In the case of biodegradation, no nitrates have been directly formed, but under aerobic conditions it is expected that the nitrites will be oxidized to nitrate.

The highest concentrations of nitrates in groundwater have been found on Alpha and Bravo Ranges. Shaver Range had medium concentrations (between 3.5 and 5.0 ppm) in almost all wells sampled, and generally very low levels of nitrates have been found on Jimmy Range. Although RDX has only been detected in groundwater on Shaver Range, it has also been detected in soils in relatively high amounts all over Alpha Range, and in lower amounts on Bravo Range and Shaver Range (Ampleman et al., 2004). There is therefore an available source of RDX that could be transformed into nitrates at the locations where high concentrations have been found.

With the exception of the two deep wells on Bravo Range, all wells sampled were located in aerobic (dissolved oxygen levels between 2.5 and 9.3 mg/L) and moderately to highly oxidizing (redox potential between +100 and +400 mV) environments. These conditions are excellent for nitrification (Stenstrom and Poduska, 1980) and can support RDX biodegradation (Price et al., 1998). It is also possible that RDX residues present at the soil surface be photodegraded, and that the resulting nitrates migrate into the aquifer through leaching. Confined wells on Bravo Range could very well support the degradation of RDX due to their anaerobic conditions, but explosives were never found in deep wells, where nitrate levels were always very low.

4.3 Nitrate Isotopic Analysis

The degradation pathways for RDX have not yet been extensively characterized. Except for two photodegraded RDX samples, there is no data available concerning the isotopic composition of nitrates produced as a result of the various degradation processes affecting explosives. It is therefore difficult to clearly relate our results to a RDX source. For this reason, to investigate the source of nitrates at CLAWR we proceeded by elimination. The site is surrounded by a very large forested area, and there are no fertilizers used on the training ranges, and pesticides were applied only once in 2000, in the PLER area. However, the herbicides applied contained only 0.65 kg of N, spread over 6.15 ha, five years before the sampling campaigns. Moreover, the results from JLR, where no herbicide was applied, are not significantly different from those at PLER. Therefore, the only possible source of nitrates other than the explosives is soil natural nitrate, coming from the degradation of plant material.

Most of samples from Shaver Range form a cluster of results with $\delta^{15}N$ values between 0 and 3.5 and $\delta^{18}O$ values around -10 (Fig. 2). Another cluster with similar $\delta^{18}O$ values and slightly heavier $\delta^{15}N$ values comprises all results obtained for the Alpha Range wells, the Jimmy Range well, and half of the Bravo Range group. To the right of this cluster, a Shaver Range point stands alone. This well is located in the forest, outside the training range, and is therefore not exposed to contaminants. The points within the circle and the squares, as well as in the squares include all results for samples from the deeper confined aquifer, plus a surface water sample (Figs. 2 and 3). These GW samples do not carry nitrate loads altered by denitrification because they do not form a linear N and O isotopic trend with a slope equal to 0.51 which is typical of denitrification residual nitrates (Kendall and Aravena, 2000; Chen and MacQuarrie, 2005). The same can be written for the Shaver Range samples, and the Bravo ones. Moreover, the conditions in the Shaver Range deep aquifer are aerobic, and could therefore not support denitrification. It is rather thought that nitrates at those locations are of a different origin than nitrates in the shallow aquifer. Indeed, no explosives have ever been detected in the deep aquifer, hence the low nitrate concentrations found in those wells are not expected to come from the degradation of explosives.

The photodegraded RDX samples analyzed in our study and in the study from Beller et al. (2004) have similar δ^{15}N values, but very different δ^{18}O values (-3.4 vs -25.7, reported in VSMOW). However, the RDX from Beller et al. (2004) was degraded at 254 nm for 2 hours, while our sample was degraded at 350 nm for 22 hours. In both cases, the δ^{15}N is significantly lower than the δ^{15}N of our field samples. The δ^{18}O of our photodegraded RDX corresponds to the upper limit of our two shallow-well sample clusters (Shaver, and Alpha/Bravo/Jimmy clusters), but the RDX sample of Beller et al. (2004) has a much lower value. In both cases, only one photodegraded RDX sample has been analyzed for isotopic composition. More RDX samples need to be characterized before we can use those values to draw conclusions.

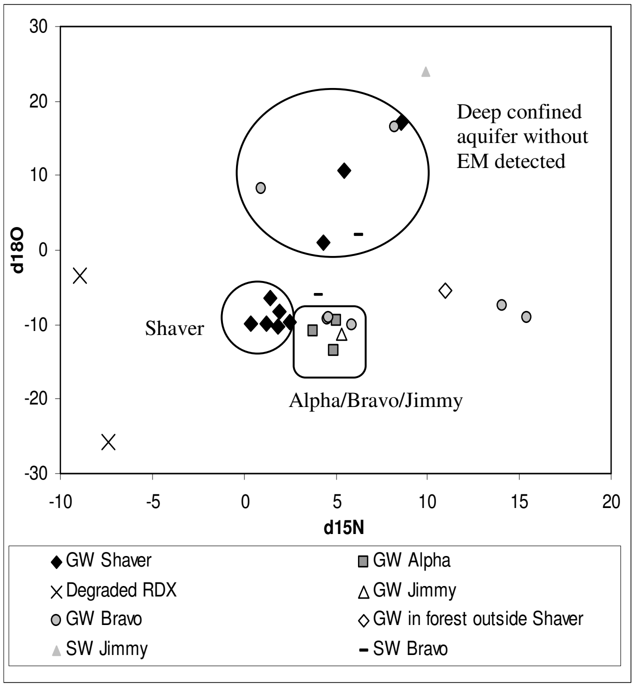

Figure 2. Isotopic Values for N and O in Groundwater (GW) and Surface Water (SW) at CLAWR, and for Photodegraded RDX samples

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The δ^{15}N values from deep, low nitrate-concentration samples (within the square) overlap with the values found in the clusters of higher nitrate concentrations (Fig. 3). However, the values for wells with higher nitrate concentrations tend to form tighter δ^{15}N clusters, indicating a specific nitrate source. Shaver Range, where RDX has been detected in the groundwater from several wells, has lower δ^{15}N values than the three other training ranges. The values on Shaver Range are lower than what would be expected for soil natural N (plant residues), which should be between +4 and +9 ‰ (Kendall and Aravena, 2000). The δ^{15}N values in the Alpha/Jimmy/Bravo cluster could correspond to soil natural N. However, Bravo Range has δ^{15}N values that are variable, and only two of those values fall within the cluster. The well located outside of Shaver Range has a δ^{15}N value much higher than both clusters, and higher than the values from the deep wells.

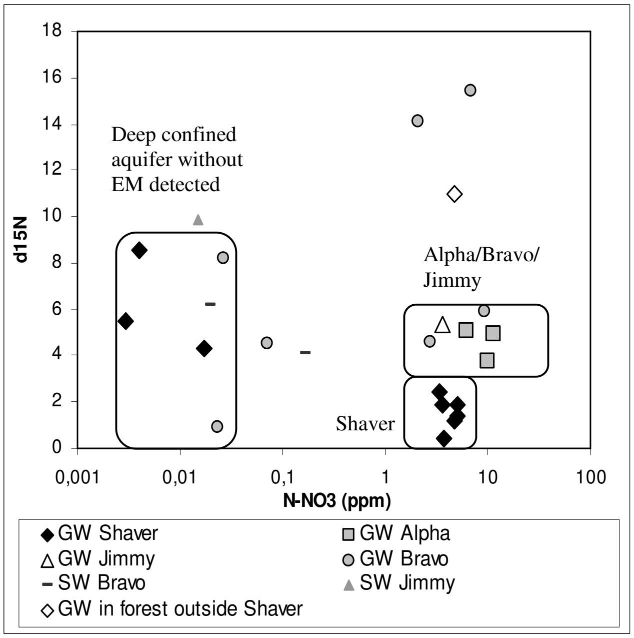

Figure 3. N-NO$_3$ Concentration vs d^{15}N for Groundwater and Surface Water at CLAWR

The $\delta^{18}O$ results seem to show a clear distinct values for deep and shallow wells (Fig. 4). All samples from shallow wells form one single cluster including samples from Shaver Range. Samples from the deep wells have $\delta^{18}O$ between 0 and +19‰, the latter end-member suggesting a greater contribution of atmospheric O_2, which has a value of +23.5‰. The average yearly $\delta^{18}O$ value of precipitation in Edmonton between 1962 and 1965, which are the only data currently available for the area, is -17.7‰. If the nitrates present at CLAWR were mediated by bacteria which use two oxygen atoms from water and one from air in soil pores to make nitrates, the resulting value should be around -4‰ This roughly corresponds to the upper limit of the shallow-well cluster. The $\delta^{18}O$ value of photodegraded RDX samples depends on the isotopic signature of the water used to make the RDX solution. Indeed, if a NO_2 group is detached from the RDX molecule, the last oxygen atom required to form nitrate should come from the water and influence one third of the final result. This information was not provided by Beller et al. 2004), and is not yet available for our experiment. Until more data is available on the isotopic signature of nitrates from degraded RDX and the processes affecting it, it is difficult to use the two results available.

The results for the three surface water samples suggest, in the case of Jimmy Lake, a strong contribution from atmospheric oxygen, resulting in a high $\delta^{18}O$ value. In the case of Primrose Lake (named SW Bravo on the graphs), the $\delta^{18}O$ values are lower and suggest a mixture of atmospheric source and of the source that causes the nitrate contamination in groundwater.

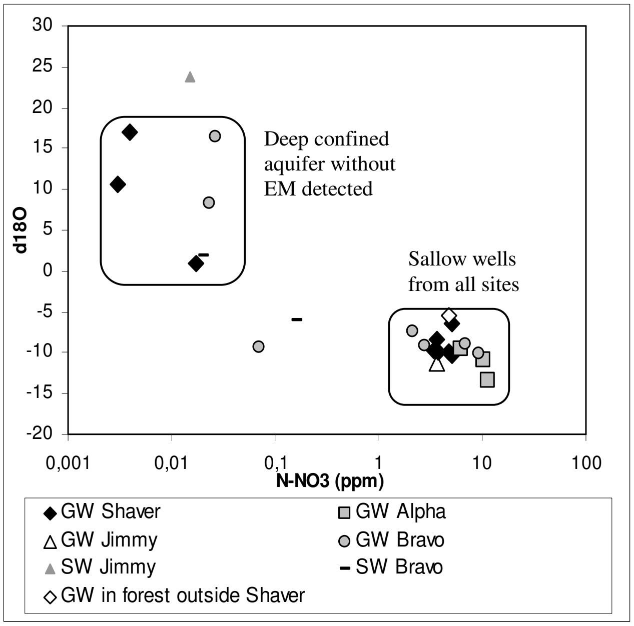

Figure 4. N-NO_3 Concentration vs $d^{18}O$ for Groundwater at CLAWR

Considering that the high nitrate concentrations in GW and explosive residues in soils and GW have been detected in the same areas, that the isotopic values of our samples do not correspond to any known natural source, and finally that the isotopic composition of nitrates coming from explosives are not yet well characterized, we suggest that the high nitrate concentrations at CLAWR may come from the degradation of RDX. This research is still in progress, and we will try to better characterize the isotopic composition of photodegraded and biodegraded RDX in the very near future.

6. CONCLUSION

Overall, it seems that lead, manganese, aluminum, copper, zinc, perchlorates, energetic materials and nitrates are present in many areas on the site. Lead is generally high in surface water samples, but could come from natural sources, as was indicated by the background sample. In groundwater, lead and manganese were often above the guideline, but this guideline is an aesthetic objective. Mn levels were low in surface water. The groundwater on the different training ranges at CLAWR seem to be sensitive to Al, Cu and Zn contamination. However, the levels of those elements were fluctuating, and no persistent contamination was found. Unlike metals, nitrates and perchlorate do not seem to originate from natural sources. Perchlorate levels are often above the preliminary guideline on Shaver Range, but are present at lower levels in groundwater on all other ranges. Surface water was generally free of perchlorate, but those have been detected at low levels in the PLER tap water, coming from Primrose Lake. Energetic materials have been mostly detected on Shaver Range, the area most intensively used for live explosive training. RDX, as well as TNT and its metabolites, were consistently detected in wells located generally downgradient from the target. RDX has also been detected once in a well located on the northern border of Jimmy Range, near Shaver Range, as well as once on Bravo Range. TNT was found in one sampling campaign at one sampling location in Primrose Lake, just east of Bravo Range. This contamination may come from the sand being blown from Bravo Range from strong winds.

Nitrate levels range from undetected to almost 20 mg/l (as N-NO_3). The highest nitrate concentrations correspond to areas where explosive residues have been detected in the soils or groundwater. For the shallow wells, the $\delta^{18}O$ values form one cluster containing results from all training ranges, while the $\delta^{15}N$ values are separated in two clusters: one containing results obtained for Alpha, Jimmy and some of the Bravo samples, and one containing the Shaver samples, with lower $\delta^{15}N$ values. The deep wells located in the lower confined aquifer have isotopic values distinct from those of the shallow wells. In the deep wells, nitrates have always been detected at very low concentrations, and explosives residues were never detected. For this reason, we believe that the nitrates in the confined aquifer are of natural origin. The isotopic composition of the nitrogen and oxygen in shallow wells do not correspond to any known natural source. For these reasons, and until the isotopic composition of nitrates coming from the degradation of RDX are better known, we suggest that the nitrates in excess of natural background levels in shallow wells might come from the photodegradation and/ or biodegradation of RDX.

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