Investigation of Hydrogen Sulfide Concentrations in Hudgeon Lake at the Abandoned Clinton Creek Asbestos Mine

- Interim Report 2 -

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Prepared by:
Werner Liebau
Indian and Northern Affairs
Waste Management Program
Yukon Region

Background

Hudgeon Lake was created in 1974, when waste rock deposited on the north-facing slope of the Clinton Creek valley failed. The blockage caused the flooding of the valley bottom to form a lake with an estimated surface area of 115 ha, an approximate volume of $1.2 \times 10^7 m^3$, and a maximum depth of 27 m (Royal Roads University, 1999). The lake lies within the operational area of the abandoned Clinton Creek Asbestos Mine, about 100 km northwest of Dawson City, Yukon, 9 km upstream of the confluence of Clinton Creek and the Forty Mile River.

During the environmental review of the Clinton Creek Asbestos Mine in September of 1998, the presence of hydrogen sulfide odour was noted from a water sample taken at a depth of about 10 m. The sample analysis confirmed this with an elevated concentration of sulphate at 307 mg/L (Royal Roads University, 1999).
In July of 1999, DIAND Water Resources staff used a Hydrolab® water sampler at Hudgeon Lake and found dissolved oxygen levels at 90% (8.3 ppm) in the first metre of the water column and a rapid decrease at four metres to below 10% (1 ppm). The surface water temperature was recorded at 20°C and a rapid drop of temperature was also noted below four metres. The conclusion of the study was that environmental conditions in regard to fish habitat would be supportive only within the 2 to 3 m range of the water column, because surface waters are too warm during the summer and water below is anoxic. Year-round conditions for a fish population, so the study concluded, would likely be precluded by ice cover and poor water quality (Royal Roads University, 1999).

The Royal Roads University environmental review included, among other recommendations, the need to assess the chemical behaviour of the anoxic hypolimnion and the study of the lake stratification. Due to the most likely scenario that the lake is seasonally dimictic, there may be a risk of temporary intoxication to ecological receptors by the downstream movement of sulfide-rich water.

While remediation work on site in September of 2002 was in progress (stabilization of the stream channel of Clinton Creek at the outlet of Hudgeon Lake), Waste Management personnel sampled the waters of the lake to investigate its stratification and hydrogen sulfide levels. The sampling was repeated in March of 2003 (through the ice) and in July of 2003 to gain some insight in seasonal changes.

Hydrogen Sulfide

Hydrogen sulfide (H_2S) is produced naturally through nonspecific and anaerobic bacterial reduction of sulfates and sulfur containing organic compounds. At atmospheric pressure, H_2S exists as a gas and partitioning to the air is likely when released. However, it may also partition

to surface water, moist soils and plant foliage (ATSDR, 2002).
H_2S solubility is one gram in 187 ml water at 10°C, in 242 ml water at 20 °C and in 314 ml water at 30 °C (Merck Index, 2000).

At 0 °C and at 1 atm pressure, the solubility is given as 4.37 ml/ml (Creighton University, 2002). At a density of H_2S at 0 °C and 1 atm of 1.5392 g/l, the maximum solubility is calculated to amount to **6,726 mg/l.**
High water temperature and low pH increase the evaporation of H_2S.

H_2S in air is oxidized by molecular oxygen and hydroxide radicals to form the sulfhydryl radical (SH^-) and finally sulfur dioxide or sulfate compounds. These end products are removed from the atmosphere through absorption by plants and soils or through precipitation.
In water, H_2S oxidation occurs in surface waters and the sulfhydryl radical (SH^-) is found to be more abundant with increasing pH. SH^- is believed to be a lesser toxicological hazard, since it is not as readily absorbed across biological membranes as H_2S. There is evidence however, that SH^- may produce toxic effects in fish in hydrogen sulfide-contaminated water at higher pH levels (ATSDR, 2002).
H_2S is extremely toxic to aerobic organisms because it reacts with the heavy metal groups of the cytochrome systems (Atlas and Bartha, 1998). Cytochromes are complex protein respiratory pigments within cells, functioning as electron carriers in biological oxidation.

Methods

September 28, 2002:

Hudgeon Lake was accessed by boat (ZODIAC inflatable).
Weather: Partly cloudy, wind light W, temperature 10°C.
The sample location was determined with a GPS (BRUNTON, Multi-Navigator^{TM}):
N 64° 27.081' W 140° 44.376'
This location is only an approximation for subsequent sampling due to drifting caused by the wind and correction measures (Figure 1).
Water samples from various depths were retrieved with an eight litre Van Dorn sampler (Wildco Instruments - Saginaw, Mich.). The line used was marked in 5 m intervals.
The water temperature was taken in a designated 500 ml bottle filled with retrieved water from the Van Dorn sampler with a Fisher Scientific Traceable® (-50°C - 250°C) thermometer.
Water samples for sulfide analysis were preserved with sulfuric acid (for hydrogen sulfide dissociation) and directly filled into 500 ml plastic bottles from the spout of the Van Dorn sampler. The samples were labelled and listed in a chain of custody form and shipped in a cooler with ice packs by air freight to Norwest Labs, Surrey,BC.

March 18, 2003:

The mine site was accessed by helicopter from Dawson City and the sampling site on the lake on foot over lake ice.

Weather: Mostly cloudy, wind light SE, temperature -5.6°C.
To obtain water samples from the lake, a hole was drilled through the ice with a motorized ice auger.
Water samples from various depths were retrieved with a 1.5 litre water sampler (The Science Source - Waldoboro, Maine: Model # 15010). The line used was marked in 5 m intervals.
The water temperature was taken in a designated 500 ml bottle filled with retrieved water from the water sampler with a Fisher Scientific Traceable® (-50°C - 250°C) thermometer.
Attempts were made to take pH and DO readings, however, problems with the instruments due to cold conditions were encountered causing the data set to be incomplete.
Dissolved oxygen measurements were taken with a YSI DO meter (Yellow Springs Instrument Co. Inc. - Model 55/12) and pH readings with a microcomputer pH meter (Hanna Instruments - Model HI 8424).
Water samples for sulfide analysis were preserved with sulfuric acid (for hydrogen sulfide dissociation) and directly filled into 500 ml plastic bottles from the spout of the water sampler. The samples were labelled and listed in a chain of custody form and shipped in a cooler with ice packs by air freight to Norwest Labs, Surrey,BC.

July 23, 2003
Hudgeon Lake was accessed by boat (ZODIAC inflatable).
Weather: Partly cloudy, light wind W, temperature 27°C.
Water samples from various depths were retrieved with an eight litre Van Dorn sampler (Wildco Instruments - Saginaw, Mich.). The line used was marked in 5 m intervals.
Temperature, pH, dissolved oxygen and conductivity measurements at corresponding depths were taken with a submersible YSI 6600 Bulkhead Sonde with a YSI 650 Multiparameter Display System (Yellow Springs Instruments Co. Inc.).
Not all water samples for sulfide analysis could be properly preserved with sulfuric acid, since some of the vials were found to have leaked their contents into the absorbent material provided for transport. The laboratory results for this sample set are therefore doubtful and the sampling should be repeated for the early to mid summer period.

The total sulfide in water analysis was carried out using Gas Dialysis, Automated Methylene Blue Method, 4500-S2-E with a detection limit of 0.005 mg/L by Norwest Labs, Surrey, BC.(Appendix A).

Observations

An increase of the characteristic rotten egg odour from the water samples was noticed with the depth the water was taken from (H_2S is perceptible in air at concentrations of 0.02 - 0.13 ppm).

Although the appearance of the lake water is brownish, the sample water was generally clear and only slightly darker from the deepest sampling points with some visible but small, suspended organic materials.

The winter site visit in March, 2003 revealed that the ice cover on Hudgeon Lake contained numerous bubbles of trapped gas throughout its thickness (approx. 2 ft.). This may indicate that hydrogen sulfide is bubbling off over time in a gradual fashion rather than during short periods; should the lake turn over at all.

Along with bubbles in the ice, there were also some small areas of the lake with open water, adding the hazard of winter travellers or wildlife breaking through the ice to the overall health and safety concerns at the site (a snowmobile track on the lake and caribou tracks at the lake outlet were observed during the site visit).

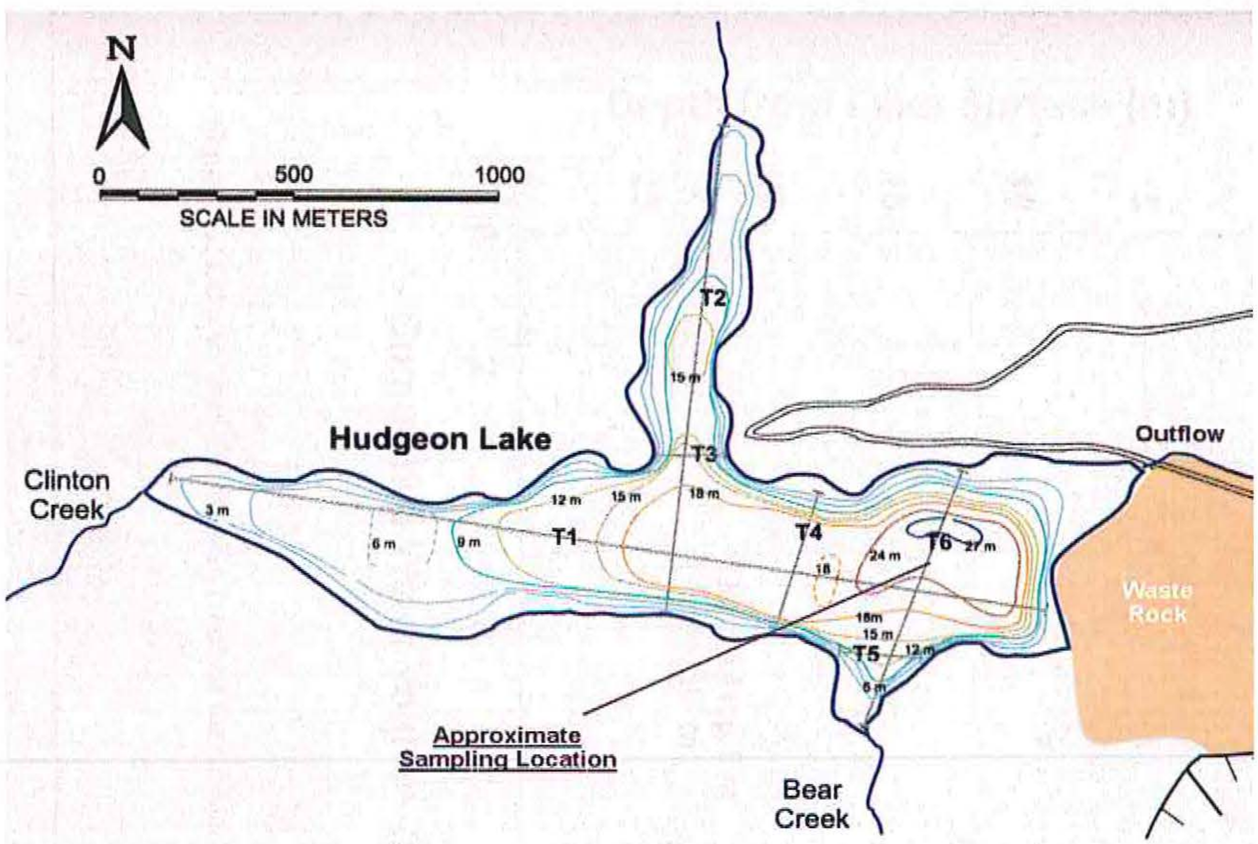

Figure 1: Sampling location Hudgeon Lake (Bathymetry Map: Royal Roads University, 1999)

Data Tables

Depth	**Sept. 28/02** Sulfide mg/L	Water Temp. °C	**March 18/03** Sulfide mg/L	Water Temp. °C	**July 23/03*** Sulfide mg/L	Water Temp. °C
Surface	n/a	n/a	n/a	n/a	n/a	19.7
1 m	<0.005	7.1	<0.005	-0.2	<0.005	14.4
5 m	<0.005	6.1	<0.005	1.6	<0.005	3.7
10 m	0.190	2.4	0.940	0.9	0.027	1.6
15 m	0.160	1.2	0.740	0.3	<0.005	1.2
20 m	0.420	0.5	1.220 1.440	0.1 0.2	0.005	0.6
21 - 25 m	0.390 0.700	0.0 -0.2	1.340	-0.2	<0.005	0.6

Table 1: Sulfide Concentrations and Temperature Regime at Specific Depths of Hudgeon Lake in 3 Seasons.
*Sulfide Concentrations may not be valid since water samples could not be properly preserved at the time of sampling (see: Methods, July 23, 03).

Depth	**March18/03** pH	Dissolved Oxygen %	Dissolved Oxygen mg/L	**July 23/03** pH	Dissolved Oxygen %	Dissolved Oxygen mg/L	Conductivity µS/cm	Salinity ppt
Surface	n/a	n/a	n/a	8.0	100.0	9.2	392	0.21
1 m	7.5	n/a	n/a	7.7	85.4	8.7	457	0.22
5 m	n/a	n/a	n/a	7.2	25.7	3.1	384	0.31
10 m	n/a	n/a	n/a	7.0	3.2	0.45	652	0.57
15 m	n/a	17.0	2.45	6.9	4.7	0.67	709	0.64
20 m	7.08	13.4	1.90	6.9	3.7	0.54	919	0.86
21-25 m	n/a	6.5	0.87	6.9	3.9	0.55	931	0.87

Table 2: Various Parameters at Specific Depths of Hudgeon Lake for 2 Seasons.

Discussion

Sulfide concentrations in Hudgeon Lake are increasing with depth (below 5 m), although in a non-linear fashion. No detectable sulfide concentrations were evident in surface waters. The highest concentrations observed so far were found in winter and may be attributed to reduction of out-gassing by ice cover and absence of physical mixing by wind/wave action and flushing by

incoming, oxygen rich water from tributaries.
The sulphide concentrations are low compared to the solubility potential of H_2S in water at 0 °C (6,726 mg/L), but above the Yukon Contaminated Sites Regulations water standards for aquatic life - **0.020 mg/L** and drinking water - **0.050 mg/L** (YCSR, 2002).
There are currently no CCME water quality guidelines for aquatic life[1] regarding hydrogen sulfide, however, a criterion has been established by the U.S. Environmental Protection Agency for fish and other aquatic life in fresh and marine water. A safe level of undissociated H_2S in water was established to be 2 µg/L, or **0.002** mg/L (EPA, 1986).
Normally, low levels of H_2S in water would not present a problem because the smell renders it unfit for drinking and anoxic conditions associated with the presence of H_2S would preclude aerobic life forms from exposure and intoxication. If seasonal turnover or other sudden disturbances of the waters of Hudgeon Lake would occur however, the release of H_2S and its product of rapid oxidation (SH^-) may pose a temporary risk of intoxication to fish and macro benthos in parts of the lake and the outlet.

Evidence to date does suggest that the release of H_2S happens gradually (bubbles in the ice) and that it may be largely dependant on the intensity of spring run-off, rainfall events and surface agitation by wind. Another factor may be occasional small land-slides (above or below the water surface). Several slides on steep slopes around the lake can be found, showing sloughing of soils and organic layers at locations underlain by permafrost. Since the lake acts as a water body capable of absorbing and retaining solar energy, more land-slides near the lake can be expected in the future as permafrost is retreating.

The stratification of the lake according to recorded temperatures initially suggests high instability (highest density of fresh water at 4 °C). The temperature decrease from the surface down to zero, however, and the increase of conductivity and salinity toward the lake bottom indicate that the temperature of the densest water in the lake is colder than 4 degrees. Also, unfrozen water at the bottom of zero and slightly below zero degrees seem to enforce the theory of a salinity effect, where the freezing point is somewhat depressed. If the cold water at the bottom is unusually dense due to a "salinity effect" (content of high levels of dissolved anions such as chloride, fluoride and sulfate, and due to high total alkalinity), a seasonal turnover may not occur at all - at least in the deepest sections of the lake (below 5 - 10 m).

Temperatures around zero degrees at the bottom of the lake may be the result of contact with permafrost, which is discontinuous but widespread in the region, with medium ice content in fine-textured valley deposits (UMA, 2000).

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[1] The only guideline for sulphide in water (as H_2S) in the Canadian Environmental Quality Guidelines is an aesthetic objective of $\leq 50 \mu g \cdot L^{-1}$ for drinking water (CCME, 2002).

Recommendations

- Continued depth sampling is recommended to be repeated for all seasons to confirm findings to date and monitor changes in the hydrogen sulfide concentrations.
- In situ recordings should include temperature, pH, conductivity and dissolved oxygen content of the water column and may be extended to other locations of interest around the lake.
- Laboratory analysis should be extended to include dissolved metals in the water column, as recent water quality investigations in the Clinton Creek area have pointed out that elevated levels of aluminum, iron, magnesium and low levels of cadmium are present in the surface waters of Hudgeon Lake (UMA, 2003).
- Measured water samples from the water column could be processed on site to determine density (= mass/volume) at various depths to gather more evidence on stability, mixing or seasonal turn-over issues.
- A record of land-slide activities (mapped, photographed, measured) around the lake may be established to assess the thermal influence of the lake body on permafrost and slope stability.
- Several studies of Hudgeon Lake and its tributaries could be initiated to answer questions, such as:
    - do any species of fish winter in the upper Clinton Creek system?
    - what life forms do exist in the lake?
    - what is the extent of biological productivity in Hudgeon Lake?
    - what are the geochemical processes at the lake and its tributaries and how do these processes influence the water quality?

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