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# BIOGEOCHEMISTRY OF HYDROCARBON IMPACTED ARCTIC WATERS

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## ABSTRACT

Microbial mats, composed of cyanobacteria, algaes and non-photosynthetic bacteria, appear where arctic surface waters are contaminated with hydrocarbon impacted groundwater and sediments. These mats may have potential for remediation of hydrocarbons. Hydrocarbon impacted groundwater and sediments are usually anaerobic or anoxic in comparison to unimpacted arctic surface waters. The higher dissolved carbon dioxide related to, and often present in, hydrocarbon impacted groundwater and sediments, may benefit photosynthetic cyanobacteria and diatom found in oligotrophic, lower alkalinity arctic waters. Redox fronts, conducive to the formation of bacterial slime consortia, also occur where oxygen depleted and hydrocarbon impacted waters enter arctic streams. Potentially, anaerobic and aerobic bacteria can take advantage of both the hydrocarbon substrate and the nitrogen fixing abilities of the cyanobacteria. The toxicity of the impacted groundwater may also kill off the zooplankton predators of bacteria and algae. A combination of several or all of these factors could explain the apparent dominance of microbial mats in contaminated arctic streams and waters.

## INTRODUCTION

In late summer 2001, EBA Engineering Consultants Ltd. (EBA) staff conducting an environmental assessment of hydrocarbon impacted soil at Repulse Bay, Nunavut found a recent diesel spill flowing from groundwater into a creek, in low flow conditions, leading to Hudson Bay. This spill was unreported. A mat colonised the creek for a distance of about 50 m, beginning at the location where contaminated groundwater discharged into the creek. The microbial mat was several millimetres in thickness and was yellow at the surface of the creek and reddish-brown and black at depth. Further downgradient, the microbial mat was green at the surface and increased in thickness. Along the banks of the creek where the mat was found, iron sulphide deposition was occurring and a reddish-brown benthic mat colonised saturated soils. A few millimetres below the sediment-water interface, free phase diesel product was found. Significant sulfate reduction (200 ppm to 80 ppm) appeared to be occurring within the stream through impacted areas, along with iron reduction and a drop in oxygen (8 to 3.5 ppm) (EBA 2002). On the basis of this initial finding, EBA and Nunavut Power had an interest in determining whether these mats were commonly associated with hydrocarbon impacted sediments and waters in the arctic.

## BACKGROUND

Early research into the effects of hydrocarbons on microbial and algae populations in arctic freshwater lakes often found changes in these communities when oil was spilled. An experimental crude oil spill into Mackenzie Delta lakes found high mortality of zoobenthic populations, attributed to the toxicity of the lighter fractions of the oils used. Periphytic blue-green algae increased in abundance in the oil spill lakes in comparison to control lakes. (Snow and Rosenberg 1975). A similar experimental oil spill using Prudhoe Bay crude oil added to pond water collected from the Prudhoe Bay region found increases of several orders of magnitude in bacterial populations when the oil was added. Diatom populations, coccoid green algae populations and algae diversity increased in one of the pond waters when low concentrations (0.1 ml/100 ml) were added. At higher concentrations (1.0 ml/ 100 ml), diatom concentrations increased, but coccoid green algae populations decreased. (Atlas et al 1976). In a study of the effects of oil spills on phytoplankton, there was a small increase in algal biomass and a virtual elimination of zooplankton following an experimental oil spill into thaw ponds and a morainal lake near Pt. Barrow, Alaska. The aromatic fraction of the oil was believed to be toxic to the grazing population, which increased the biomass of the ponds (Miller et al 1978).

In recent years, mats have been observed in association with crude oil contamination on the Arabian Gulf coasts (Al Hasan et al, 1993), and cyanobacteria, Microcoleus chthonoplastes and Phormidium sp. within these mats were believed to be degrading n-alkanes. These cyanobacteria grew phototrophically better within a crude oil medium than in a medium without the crude oil. Offshore waters of the Arabian Gulf had picocyanobacteria that were found to absorb hydrocarbons in their thylokoid spaces (Al Hasan et al 2001). A benthic cyanobacterial mat, dominated by Phormidium and Oscillitaria-like cyanobacterial morphotypes, from the Wadi Gaza, Gaza Strip, Palestine, was found to have bacterial communities associated within it that could degrade several model hydrocarbon compounds in slurry experiments: n-octadecane, pristane, dibenzothiphene and phenanthrene. Communities of bacteria and cyanobacteria underwent changes with degradation of these compounds (Abed et al, 2002).

Natural mat communities, differentiated from biofilms and other microbial communities (based on thickness), have some of the highest microbiological metabolic rates. Slimes found in organically polluted streams and slimes in trickling filters in aerobic sewage treatment plants are also microbial mats that are similar to naturally forming mats. The structure of a natural cyanobacterial mat is a yellow or brown surface layer composed of diatoms together with filamentous and unicellular cyanobacteria. Deeper layers can be green, purple and black created by filamentous blue-greens, purple and green sulphur bacteria and black iron sulphide sediments (Fenchel et al 1998). Natural cyanobacterial mats develop as a result of extreme conditions that eliminate grazing metazoans and eucaryotic organisms (Cohen 1990). Microbial consortia that include a variety of organisms such as photosynthetic, heterotrophic and strict anaerobic bacteria are synergistic. Growth, reproduction and biogeochemical cycling are done more efficiently than with individual populations. Strict anaerobes can obtain protection from oxygen within mat niches and these niches support transformations not found in surrounding waters. Microbial communities are initially formed by colonies of heterotrophs, such as pseudomonas, that consume oxygen and form anoxic microzones. Within these microaerophilic and anaerobic microzones nitrogen fixing, fermentative and chemolithotrophic organism can thrive (Paerl and Pinckney 1995).

Microbial mats have gradients of oxygen that peak at surface and decrease with depth, and hydrogen sulphide concentrations, formed by sulfate reduction, which do the reverse. There is a diurnal migration of the oxic/anoxic interface that releases Fe from FeS deposits within the mat. The released Fe can be a good potential donor for photosynthetic cyanobacteria. Efficient oxidation and trapping of sulfide, through deposition of FeS, allows diatoms to form at the surface of the groundwater (Cohen 1990).

Up to 50% of organic carbon in sediments may go through a microbiologically mediated sulphur cycle. Organic carbon can be oxidized through dissimilitory sulfate reduction (Chappelle 2001 and Hamilton 1998) or iron reduction (Ghiorse 1990). Petroleum are a class of organic carbon known to undergo these reduction processes. For oxidation of BTEX compounds, 4.6 mg of sulfate is required to completely metabolise 1 mg of total BTEX (Wiedemeier et al 1995).

Water bodies at higher latitudes may be as effective as water bodies at lower latitudes in dealing with man-made organic impacts. A study conducted in lakes in sub-antarctic Marion Islands found these lakes to be responsive to increases in organic loads. Hetrotrophic microbial populations in Marion Island's lakes were found to be similar in size, activity and production to lakes of similar trophic status found in lower latitudes (Robarts et al 1991).

## BIOGEOCHEMISTRY OF CONTAMINATED ARCTIC WATERS

### Grise Fiord

In 2002 while conducting environmental site assessments in various Nunavut communities, other microbial mats were discovered associated with hydrocarbon-impacted sediments and waters. Reddish-brown benthic mats were found colonizing shallow diesel impacted waters in Grise Fiord, Resolute Bay and Iqaluit. A red benthic mat overlaid sediments with concentrations of hydrocarbons ranging from 500 to 14,000 ppm (EBA Grise Fiord 2003) at Grise Fiord (see Photograph 1). Ground and surface waters in the hydrocarbon impacted areas, and where the mats colonized, had lower concentrations of oxygen, lower pH, higher electrical conductivity and higher dissolved iron than in unimpacted waters upgradient to it. Upgradient water had pH, conductivity, oxygen and iron concentrations of about 8.05, 217 uS, 8 ppm and 0 ppm, respectively. Within impacted waters, these values at their extreme were 6.96, 422 uS, 1 ppm and 1 ppm, respectively.

### Iqaluit

In an Iqaluit stream and pond, old diesel spills from the mid 1970s and earlier had sediments contaminated with up to 3% oil by dry weight, as determined through GC/FID analysis (EBA 2000). A relatively thick 1 to 2 cm red-brown cyanobacterial mat covered these sediments (see Photograph 2). The chemistry of impacted waters in comparison to unimpacted waters is given in Table 1.

## Table 1: Water Chemistry at Iqaluit Pond

| Sample Location | Time | DO | $CO_2$ | Carbonate Alkalinity | Sulfide | Iron | Sulfate | Nitrate | Phosphate | Ammonia | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A[1] | 14:30 | 6.5 | >100 | 350 | 0.02 | 23.4 | 83 | 0.18 | 0.90 | 0.14 | 7.11 |
| B[2] | 14:30 | 10 | >100 | 300 | 0.03 | 10.25 | 28 | 0.11 | 0.31 | 0.09 | 7.70 |
| C[3] | 14:30 | 12.4 | <10 | <50 | 0.01 | 0.16 | 16 | 0.07 | 0.11 | 0.10 | 7.43 |
| D[4] | 14:30 | 12.3 | <10 | <50 | 0.01 | 0.10 | 17 | 0.12 | 0.44 | 0.13 | 7.18 |
| E[5] | 14:30 | 12.4 | <10 | <50 | 0.01 | 0.25 | 12 | 0.08 | 0.73 | 0.02 | 7.18 |
| F[6] | 14:30 | 12.3 | <10 | <50 | 0 | 0.25 | 9 | 0.09 | 0.08 | 0.03 | 7.12 |
| G[7] | 14:30 | 12.1 | <10 | <50 | 0 | 0.22 | 7 | 0.10 | 0.10 | 0.06 | 7.20 |
| A | 22:30 | 4.2 | 50 | 350 | 0.1 | 26.4 | 64 | 0.10 | 1.03 | 0.10 | 7.05 |
| B | 22:30 | 2.9 | 25 | 300 | 0 | 14.35 | 30 | 0.09 | 0.33 | 0.14 | 7.31 |
| C | 22:30 | 11.9 | <10 | <50 | 0 | 0.42 | 7 | 0.08 | 0.09 | 0.01 | 7.31 |
| D | 22:30 | 11.7 | <10 | <50 | 0 | 0.26 | 4 | 0.10 | 0.03 | 0.14 | 7.15 |
| E | 22:30 | 11.6 | <10 | <50 | 0 | 0.75 | 8 | 0.08 | 0.07 | 0.06 | 7.05 |
| F | 22:30 | 11.6 | <10 | <50 | 0 | 0.33 | 5 | 0.09 | 0.62 | 0.21 | 6.99 |
| G | 22:30 | 10.8 | <10 | <50 | 0 | 0.15 | 18 | 0.13 | 0.27 | 0.07 | 6.92 |

Note: All results except pH in mg/L

[1] Within impacted stream
[2] Within impacted stream, downgradient of Point A
[3] Unimpacted stream 1 upgradient location
[4] Unimpacted stream 1 downgradient location
[5] Unimpacted stream 2 upgradient
[6] Unimpacted stream 2 downgradient location
[7] Within pond receiving waters from these three streams

The chemistry was conducted in the field using a Lamotte spectrophotometer, for the majority of the parameters. Chemets mini-titrets were used to measure concentrations of dissolved carbon dioxide and carbonate-alkalinity. An Oakton pH meter was used to measure pH.

There was a difference in water chemistry between samples obtained and tested during the day and samples obtained and tested at night. The hydrocarbon impacted stream had lower dissolved oxygen, lower dissolved $CO_2$ and pH at night than in the daytime. The higher dissolved oxygen concentrations are likely the result of photosynthetic cyanobacteria and algae. The higher dissolved oxygen concentrations are likely used by hetrotrophic bacteria, and indirectly by dissimilatory sulfate reducing bacteria taking advantage of sulfate produced abiotically, as anaerobic iron sulfide deposits, underlying the mats, become aerobic. Higher dissolved carbon dioxide and lower pHs result from greater daytime respiration from the non-photosynthetic bacteria. pH, of course, can also be lowered by production of organic acids by dissimilatory sulfate reduction or by the production of sulfides. To a lesser extent, these processes are also occurring diurnally in the unimpacted creeks. The hydrocarbon impacted creek, however, is eutrophic and likely has greater productivity, respiration, and greater concentrations and fluctuations of nutrients than in the unimpacted streams.

pH, dissolved oxygen and sulfate concentrations within the impacted and unimpacted streams were determined six times throughout a 24-hour period to qualitatively assess the fluctuations of these parameters. This work was done on August 30 and 31, 2003. The following table summarizes the results. The stream locations are the same as in the previous table.

**Table 2: DO, $SO_4$ and pH Fluctuations Throughout a 24-Hour Period**

| Status | Time of Day | pH | DO | $SO_4$ |
|---|---|---|---|---|
| A | 7:30 | 6.88 | 6.5 | 61 |
| | 10:30 | 7.03 | 5.6 | 67 |
| | 14:15 | 7.02 | 2.6 | 76 |
| | 18:00 | 7.09 | 2.6 | 80 |
| | 22:15 | 6.92 | 2.0 | 14 |
| | 7:30 | 7.06 | 4.2 | 92 |
| B | 7:30 | 7.22 | 5.6 | 24 |
| | 10:30 | 7.53 | 8.1 | 22 |
| | 14:15 | 7.70 | 6.6 | 17 |
| | 18:00 | 7.63 | 5.7 | 21 |
| | 22:15 | 7.25 | 4.8 | 27 |
| | 7:30 | 7.27 | 5.8 | 26 |
| C | 7:30 | 7.22 | 12.2 | 6 |
| | 10:30 | 7.96 | 12.3 | 4 |
| | 14:15 | 7.56 | 12.3 | 3 |
| | 18:00 | 7.68 | 7.5 | 6 |
| | 7:30 | 7.15 | 11.7 | 3 |
| D | 7:30 | 7.15 | 12.1 | 14 |
| | 10:30 | 7.01 | 12.5 | 5 |
| | 14:15 | 7.67 | 12.5 | 5 |
| | 18:00 | 7.43 | 8.2 | 2 |
| | 7:30 | 7.52 | 11.9 | 4 |
| E | 7:30 | 7.08 | 12.2 | 14 |
| | 10:30 | 7.50 | 12.5 | 6 |
| | 14:15 | 7.38 | 12.3 | 6 |
| | 18:00 | 7.58 | 7.9 | 3 |
| | 7:30 | 7.25 | 12.0 | 3 |
| F | 7:30 | 6.67 | 11.9 | 6 |
| | 10:30 | 7.40 | 12.5 | 4 |
| | 14:15 | 7.37 | 12.4 | 5 |
| | 18:00 | 7.41 | 8.1 | 3 |
| | 7:30 | 7.25 | 11.8 | 4 |
| G | 7:30 | 7.01 | 12 | 5 |
| | 10:30 | 7.37 | 9.7 | 6 |
| | 14:15 | 7.36 | 12.4 | 3 |
| | 18:00 | 7.51 | 8.5 | 4 |
| | 22:15 | 7.85 | 8.9 | 3 |
| | 7:30 | 7.07 | 11.7 | 4 |

* All concentrations in mg/L except pH.

An interesting observation of the above data is the variability of sulfate concentrations throughout the day at Station A, where it is 14 ppm at its lowest measured concentration at 22:30 at night and is at its highest concentration the following morning at 7:30 at 92 ppm. Sulfate reducing bacteria may play a prominent role in chemical cycling of this impacted stream.

Previous work by EBA Engineering Consultants Ltd. (Ziervogel, et al, 2003) characterized the Iqaluit mat being dominated by cyanobacteria *Phormidium sp.*, with lesser numbers of *Anabaena aequalis Borge and Oscillatoria nigra Vacher*. Diatom species were also present in the mat.

## Resolute Bay

Resolute Bay has had several large spills in association with its fuel pipelines, dispensers and tank farms. A reddish-brown benthic mat (see Photograph 3) formed in waters overlying contaminated sediments (1 to 4% oil) adjacent to one of the main tank farms, referred to as Parcel 6 and 7 in the community (EBA 1993). Red and green mat colonies were forming downgradient of a 2002 gasoline spill from a fuel dispenser (see Photograph 4). Much further downgradient of the tank farm and fuel dispenser area, below an old landfill, various mats were growing within red and green sphagnum mosses (see Photograph 5).

Underlying the microbial mats in hydrocarbon impacted areas were extensive deposits of iron sulfides. Typically, mats and iron sulfide deposits occur where seepage is near the surface. Iron sulfide deposits were not noticeably significant where impacted groundwater was more than approximately 30 cm below ground elevation.

### Repulse Bay

Repulse Bay was revisited in 2002 and it was found to have higher flow conditions than in 2001, but microbial mats still colonized the area where impacted groundwaters entered the creek. A red-brown to green mat colonized quieter waters on the bank, but within more turbulent waters a green to dark green diatom-dominated mat was prevalent (see Photographs 6 through 8). Unimpacted upgradient waters had pH and conductivity readings in the 8.0 to 8.2 range and 500 to 550 range, respectively. Conductivity rose to as high as 900 uS and pH dropped to as low as 6.7 ppm within the impacted sediment and mat colonized areas.

## DISCUSSION

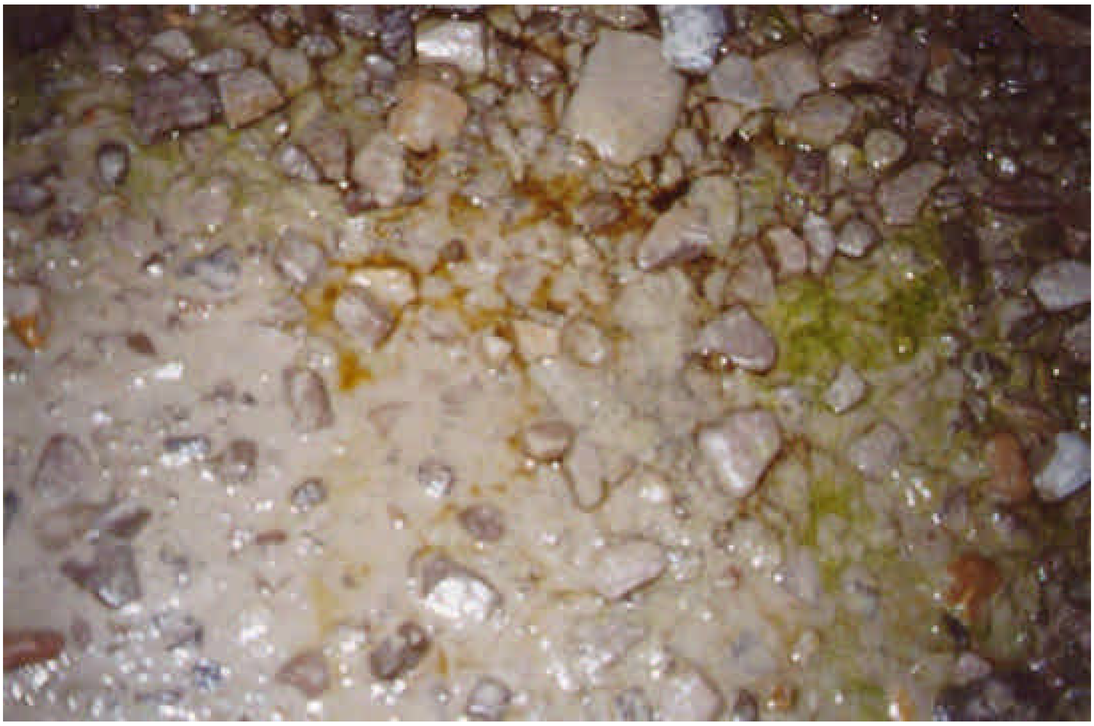
Hydrocarbon impacted waters and saturated soils with dissolved hydrocarbons are commonly colonized by microbial mats. Underlying these mats are extensive iron sulphide deposits. Observations and some limited geochemical data is consistent with an interpretation of links between the photosynthetic production of oxygen and the abiotic cycling of iron sulphide and sulfate.

Arctic streams impacted by hydrocarbons become eutrophic with greater concentrations and fluctuations of nutrients and electron acceptors that can by used by this microbial community. The hydrocarbons change both the ecosystem and geochemistry of the stream. These hydrocarbon impacted streams have lower dissolved oxygen concentrations higher dissolved $CO_2$, carbonate alkalinity, dissolved phosphate and dissolved iron concentrations. There is high sulfate concentrations and fluctuations of sulfate that appear linked to the production and use of oxygen within the mat.

This limited data set is not definitive and more work is necessary to determine both the chemical cycling within this ecosystem and whether this ecosystem can be beneficial in remediating hydrocarbon contaminated waters.

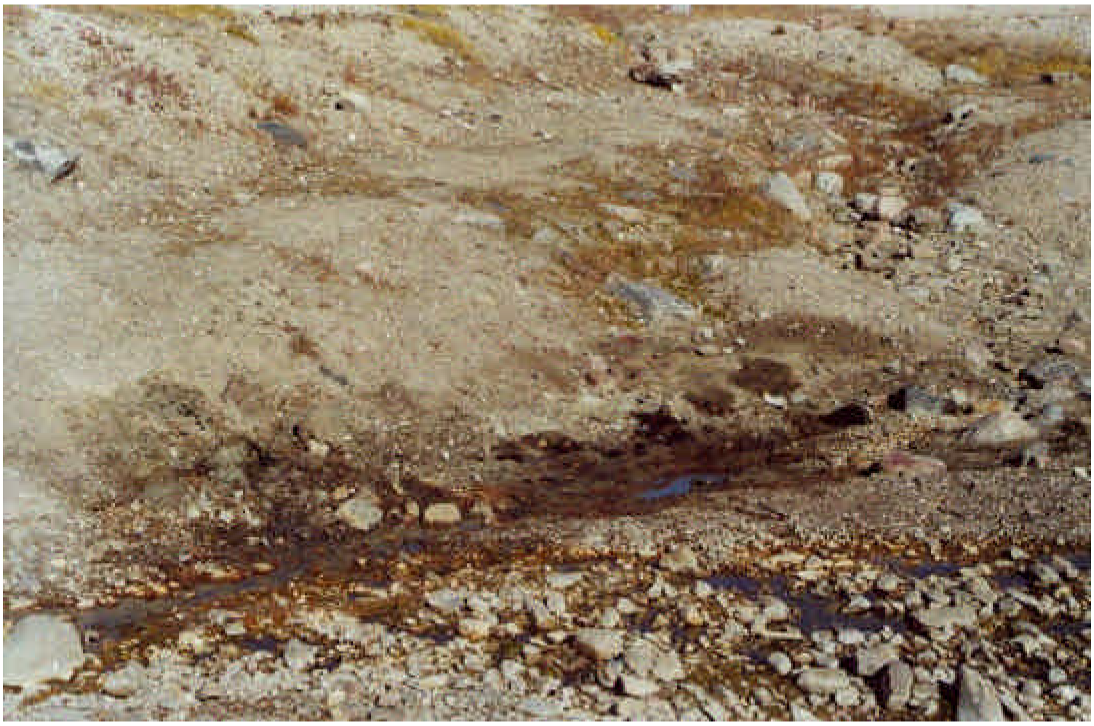
Photograph 1:  Microbial Mat at Grise Fiord

Photograph 3:  Microbial Mat adjacent to Tank Farm at Resolute Bay



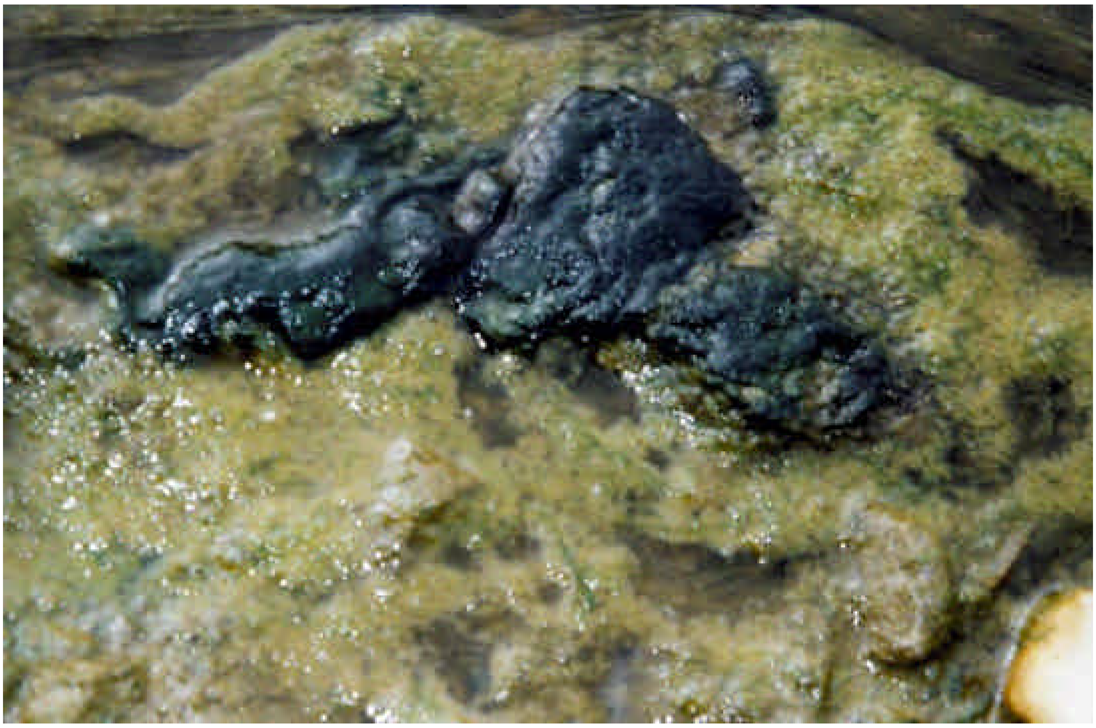
Photograph 4:  Colonies growing in contaminated waters on road at Resolute Bay near fuel dispenser

Photograph 5:  Mat growing below landfill within sphagnum moss at Resolute Bay



Photograph 6:  Mat at stream at Repulse Bay 2001

Photograph 7: Mat on banks of Repulse Bay in 2002



Photograph 8: Diatom dominated mat in turbulent water in stream at Repulse Bay 2002

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