Potential Impacts to Water during Exploration at the Pebble Prospect, Alaska

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SCOPE OF REPORT

The scope of this report is limited to assessment and analysis of chemical reactions related to drilling and seismic surveys that have the potential to impact water resources.

In general, contamination of surface water may occur through

- fuel spills from drills and water pumps
- surface discharge of drilling fluids
- breakdown products of drilling chemicals
- chemical reactions with drill cuttings
- ammonia from seismic charges

Contamination of groundwater may occur through

- introduction of grout, clay, fuel, and drilling additives into holes and wells
- improper closure of drill holes, particularly in sulfidic host rock
- direct infiltration of drilling chemicals and drill cutting metals from unlined mud pits excavated within or in immediate proximity to shallow aquifers

SECTION A GENERAL SUBJECT MATTER

1.0 Introduction to chemistry related to exploration drilling

Hardrock mining exploration involves (i) extracting rock cores or chips to determine vertical and horizontal extent of a resource; (ii) drilling "geotechnical" holes to determine features such as density and fracturing in the ore body; (iii) installing wells to determine groundwater quality, quantity, and flow rates at different elevations; (iv) setting off charges to determine changes in density underground; and digging trenches to assess subsurface rock. Rotary core drill rigs require water, fuel, and various drilling additives. Use of specific additives and their quantities may depend on the material the hole is drilled in (sand/gravel, bedrock), the depth of the hole, and the degree of fracturing in the rock.

It is important to understand that most chemical impacts related to drilling do not arise necessarily from the type of metal that is sought after (copper, gold, etc.) but rather from introduction of drilling chemicals or disturbance of the rock the minerals are "hosted" in: oxides, silicates, sulfides and so forth. Different "host rock" has different potential to introduce material to the environment when brought to the surface or exposed to oxygen and water. Sulfide rock is particularly problematic in that it becomes sulfuric acid upon contact with water and oxygen; this process may occur quite quickly or may take several decades depending on the other material in and around the rock.

Additionally, deeper holes have more potential to contaminate surface water through discharge of greater quantities of drill fluids and rock cuttings to the surface, and more potential to contaminate groundwater due to more rock surface area exposed and subject to chemical reactions underground.

While some contamination may be obvious on the surface (e.g. sheens at fuel spills), virtually all effects will occur in water and underground and, while not visible to the naked eye, have the potential to cause direct and indirect disruptions to aquatic life.

1.1 Natural water chemistry

The main constituents within water are salts (cations and anions), dissolved metals, metals attached to sediment (referred to as "total" or "unfiltered" metals in a laboratory), and nutrients (carbon, nitrogen, phosphorous). These drive the defining parameters of water, such as pH and alkalinity. Organic carbon provides both potential food sources and can provide a surface for metals to attach to, potentially moderating their toxicity. Nitrogen can be a stimulus for growth, but too much nitrogen can stimulate algal and plant growth to the degree that they remove oxygen from the water; nitrogen may also occur in the toxic ammonia form. Therefore, while metals, salts, and nutrients are natural components, changes in them can cause negative impacts to stream and pond environments.

Exploration activities have the potential to release organics,¹ ammonia, cations (e.g. sodium, calcium), anions (e.g. sulfate), change concentrations of total and dissolved metals, and change water pH, but natural events can also drive these and other changes. In order to determine whether the water that aquatic life depends on has changed, the nature of that water and the processes that drive water chemistry need to be understood.

1.1.1 Natural processes in surface water

Surface water does not have a static, unchanging chemistry, but rather fluctuates, particularly with rain, snowmelt, and erosion.

Trace metals – particularly iron, aluminum, and manganese, derive from erosion of surface rocks and are most commonly observed in elevated concentrations during erosional events or when dust and dirt enter surface water. These may be attached to sediment or dissolved. In general, "dissolved" metals (from filtered water samples; commonly filters that remove all particles larger than 0.45 um are utilized) are considered to be the most bio-available, while "total" metals (from unfiltered water samples) contain both dissolved metals and metals attached to sediment or part of the sediment particle's physical matrix. Metals on or within sediment are generally considered less bio-available, although under certain conditions they can enter the food chain.

Soluble salts² (calcium, sodium, potassium, magnesium, barium cations; sulfate, chloride, fluoride anions) commonly derive from underground material. Having washed off surface rocks long ago, they remain in the subsurface and are picked up by groundwater.

Because most metals that enter water originate above ground and cations and anions from below ground, a seasonal pattern can be discerned in surface water.

- *Late summer and fall.* Rains cause erosion, and total metals on sediment increase in streams (particularly iron, aluminum, and manganese) along with some dissolved metals; salts decrease with the intrusion of freshwater, diluting the effect of groundwater in streams.
- *Winter*. Due to lack of surface runoff, stream water tends to be low in trace metals. Salts increase as groundwater makes up a larger percentage of the surface water. Trace metals, meanwhile, sequester in pore-water (the water that fills the cracks and crevices of stream bottom gravel and sediment) in winter.

¹ Fuels, oils, antifreeze and many drilling additives are hydrocarbon based. The term "organics" refers to carbonbased compounds such as are used in exploration (or their breakdown products e.g. benzene, toluene, anthracene) but it may also refer to natural tannic acids, humic acids, and other material. Natural organic material can be discerned from likely anthropogenic material through chemical analysis of water and other sample media.

² A salt is a cation and an anion loosely joined by an ionic bond; e.g. table salt is sodium (cation Na^+) and chloride (anion Cl⁻). Although technically sodium, potassium, magnesium, and calcium are metals, they are very soluble and are referred to as cations in this paper to distinguish them from copper and other metals. The term "salts" is also used in this paper to refer to soluble cations and anions distinct from dissolved cationic metals.

- *Spring*. Melting snow "pushes" old pore-water up into the stream water column, increasing dissolved trace metals in surface water, while melting snow and ice deposit sequestered dust and dirt into streams, increasing sediment-based metals. A "spike" in metal concentrations, particularly of dissolved metals, may be observed. At the same time that trace metals increase, salts (typically sourced from groundwater) decrease with dilution.
- *Summer*. Surface runoff dries up; trace metals decrease and salts increase as stream discharge volume decreases and groundwater makes up more of the stream flow.

In Figure 1, seasonal increases in total trace metals are evident, as are smaller increases in dissolved metals. For example, the spike in August 2006 is correlated with a precipitation event, as recorded by precipitation gages at the Iliamna airport.



Figure 1. Seasonal surface water chemistry at Pebble. (Above) UT100B is a surface water sampling site on Upper Talarik Creek established by PLP. The plot shows total iron (Fe_T) and total copper (Cu_T) concentrations increasing with precipitation events (snowmelt or late summer rains); dissolved metal concentrations (Fe_D, Cu_D) do not increase as much, indicating the increase is due to sediment entering the water. The chart was developed from PLP, 2008. Pre-Permit Report F; all PLP data is preliminary and subject to change. (**Right**) Increases in metals correlate with precipitation (recorded at the Iliamna airport). Note precipitation events July 2005 and August 2006 and the consequent increases in total copper and total iron in stream water. Precipitation data is from Weather Underground, http://wunderground.com

The location of the site can also influence its water chemistry. The surficial geology, size of the watershed being drained, and elevation all affect the patterns and timing observed in water chemistry. This is illustrated in Figure 2; sampling site UT100E is located in the upper reaches of the Upper Talarik watershed and drains a small area while sampling site UT100D is located in the lower reaches and receives water from a larger watershed.

Nutrients may change seasonally or with location. Organic carbon tends to be most available in wetland environments, where water moves slowly through vegetation towards streams and ponds; nitrogen may be most available during significant die-offs, such as salmon spawning events.

July 24

Aug 11

Aug 12

Aug 13

Aug 14

Aug 15

0.3

0.9

0.5

0.2

0.6

0.1



Figure 2. Effect of watershed drainage on surface water chemistry. (Top) Concentrations of iron and aluminum at PLP surface water sampling sites UT100E and UT100D (Upper Talarik Creek). Al_T and Fe_T refer to total aluminum and iron at UT100D; Al_T UT100E and Fe_T UT100E refer to the metals at site UT100E. (Bottom) Discharge volumes; note different scales of vertical axis. UT100D receives water from a larger watershed drainage area and has higher flows, which likely contributes to the higher concentrations of metals observed relative to UT100E. From PLP, 2008. Pre-Permit Reports B and F; all PLP data are preliminary and subject to change.

1.1.2 Natural processes on groundwater

Groundwater chemistry is influenced by interactions with soils and aquifer materials and infiltration of precipitation (shallower groundwater systems) or stream water. Deeper soils and rock may receive some material transported downward. Groundwater commonly contains soluble anions (sulfate, chloride, fluoride), soluble cations (calcium, magnesium, potassium, sodium) and dissolved metals, but not total metals. Groundwater tends to be most concentrated in cations and anions during periods where there is little contribution from surface water (which dilutes groundwater), such as mid-winter.

Groundwater is generally less susceptible to the seasonal fluctuations observed at the surface, although there may be some seasonal changes if surface water readily infiltrates into and mixes with groundwater.

Groundwater level fluctuations can affect water chemistry by changing the type of rock groundwater is in contact with or the length of time water is in contact. There may also be redox reactions associated with fluctuating groundwater levels (e.g. as water drains out of a fracture, the rock may become oxidized; as water fills in fractures and pathways, it may create a reduced environment).

Clusters of monitoring wells may be clustered in the same location but completed at different depths (deep, medium, and shallow) and may show similar or dissimilar water chemistry depending on the material they are screened in. For instance, in one study, pH, alkalinity, and calcium increased in water samples collected from further downslope or from deeper soil.³

1.2 Blasting

Blasting is conducted during development of seismic lines. Explosions generate seismic waves which move through layers of rock at different speeds, characterizing the geologic structure and providing information on faults and subsurface density, which can assist in identifying potential mineral resources. Although sound waves can be generated using less obtrusive methods, dynamite is the preferred method when the soil is loose and unconsolidated. Explosives can leave behind nitrogen residues such as ammonia and nitrates/nitrites, and may leave barium residue depending on the type of explosive utilized; ammonia and barium are toxic to aquatic life in certain concentrations.

1.2.1 Sediment

Blasting may increase suspended sediment if conducted in close proximity to water bodies; large sediment increases can subsequently transport attached metals which may be lethal and/or detrimental to fish, and fine sediment can suffocate fish eggs.

1.2.2 Barium

Blasting compounds may contain barium nitrate; barium is acutely and sub-lethally toxic to plants and animals. Although the state of Alaska only lists drinking water standards for barium (2000 ug/L) and not aquatic-based standards,⁴ according to the EPA:⁵

Acute toxic effects may include the death of animals, birds, or fish, and death or low growth rate in plants. Acute effects are seen two to four days after animals or plants come in contact with a toxic chemical substance.

³ Aastrup and Axelsson 1984

⁴ ADEC. 2008. Water Quality Criteria Manual.

http://www.dec.state.ak.us/water/wqsar/wqs/pdfs/Alaska%20Water%20Quality%20Criteria%20Manual%20for%20 Toxic%20and%20Other%20Deleterious%20Organic%20and%20Inorganic%20Substances.pdf ⁵ http://www.ndcrt.org/data/EPA_Chemical_Fact_Sheets/Barium-Azide.html;

http://gis.dep.wv.gov/tri/cheminfo/csfs206.txt

Barium and its salts have moderate acute toxicity to aquatic life. Insufficient data are available to evaluate or predict the short-term effects of barium or its salts to plants, birds, or land animals. Chronic toxic effects may include shortened lifespan, reproductive problems, lower fertility, and changes in appearance or behavior. Chronic effects can be seen long after first exposure(s) to a toxic chemical.

Barium is "released to water and soil in the discharge and disposal of drilling wastes".⁶ Barium salts may move into groundwater or surface water. Despite potential toxicity, barium is not regulated for chronic or acute effects to aquatic life. Toxic effects on aquatic life appear to occur above 1 mg/L.⁷

1.2.3 Ammonia and Nitrate

Ammonia, which is toxic to fish, forms from nitrogen compounds found in blasting and drilling products. Testing on trout and salmon suggest total ammonia-nitrogen is acutely toxic to them at concentrations from 11-48 mg/L when they are migrating,⁸ and concentrations as low as 40-80 ug/L un-ionized ammonia (NH₃) have sublethal effects; ⁹ the EPA considers concentrations of un-ionized ammonia over 20 ug/L to be potentially harmful to salmon reproduction. Total ammonia is the sum of un-ionized ammonia (NH₃) and ionized ammonia (NH₄⁺). Virtually all total ammonia is in the ionized form at natural stream water pH; ionized ammonia will be in the un-ionized form at natural stream pH. The un-ionized NH₃ form can cross from water into fish, and once inside, convert to the ionized form (NH₄⁺) which then causes cellular damage.

Dissolved oxygen in the water can render both forms of ammonia into non-toxic nitrate (NO₃). Most surface water and groundwater are highly oxygenated and most ammonia is expected to oxidize to nitrate quickly. However, potential exists for ammonia to remain in less oxygenated environments such as some groundwater, stagnant surface water, and sediments. It was noted by the USGS that many of the ponds in the Pebble region had reducing atmospheres,¹⁰ and these environments may retain ammonia.

Nitrate, while not toxic, can stimulate aquatic plant and algae growth, causing dramatic diurnal swings in dissolved oxygen and pH. These diurnal swings can directly affect aquatic organisms or indirectly impact these organisms by causing a direct physical change in the stream ecosystem (stream bottom gravel and cobble environments being choked with rooted macrophytes).

1.3 Drilling

Drilling is conducted for a variety of purposes, including retrieval of rock cores to determine mineral content (coring holes), investigation of subsurface faulting and material (geotechnical holes), and development of wells to measure water quality, quantity, and elevation (monitoring wells and piezometers). Coring holes are generally deeper (500 to more than 6000')¹¹ than geotechnical holes and hydrology wells (less than 400' deep) at the Pebble prospect.

Contamination can occur from use of improper casing material (iron or other metal casing), surface water moving down the outside of the casing if the annular space is improperly sealed, sediment sloughing,

⁶ EPA fact sheet <u>http://www.epa.gov/OGWDW/contaminants/dw_contamfs/barium.html</u>

⁷ http://www.inchem.org/documents/ehc/ehc/ehc107.htm#SectionNumber:8.4; http://www.epa.gov/EPA-

TOX/1997/January/Day-03/pr-24225DIR/pr-24225.html; LC50 for *Hyalella azteca* zooplankton was determined to be 1 mg/L, see <u>http://www.pesticideinfo.org/List_AquireAll.jsp?Rec_Id=PC41174</u>

⁸ Randall and Tsui 2002; Thurston and Russo 1983

⁹ Wicks et al 2002

¹⁰ Fey et al 2009

¹¹ Holes to 6,000' were being drilled in 2007 (ADNR Field Inspection Report July 2007); the 2009-2010 Alaska Multi-Agency Permit Application allows drilling to 7,000' (ADNR 2009a)

grout/cement, or reactions with drilling additives found in the pore spaces in the screened interval of the aquifer.

1.3.1 Hole and well development

Drilling techniques may change depending on the subsurface material. Air hammer and rotary drilling are common. An air hammer utilizes compressed air to break up rock and blow the crushed rock fragments out of the hole, along with any water that comes in. Rotary drills utilize a drill bit that looks similar to a "hole saw" and allows a "core" of rock material to be drawn up through the center of the bit while cuttings exit in the space within the hole outside of the bit (called the "annular space") (Figure 3). Rotary drills may use air alone, air and water, or drilling muds. A casing may need to be installed in coring holes when unstable material such as sand and gravel are encountered to prevent the hole from caving in.

Monitoring wells are constructed in the same manner as coring holes, except they must allow repeated access for water chemistry analysis and need casings to prevent the walls of the well from caving in; cement, sodium bentonite, or a combination may be used to stabilize the casings (Figures 4 and 5). Using only bentonite is discouraged - the expanding lattice structure holds water and never sets up completely.¹²



Figure 3. Example of rotary drilling. From "How Wells are Drilled", American Groundwater Trust, http://www.agwt.org/info/pdfs/welldrilling.pdf



Figure 4. Typical groundwater monitoring well. From North Carolina Division of Water Resources, November 2001.

The Alaska Department of Environmental Conservation (ADEC) suggests specific protocols be followed when a monitoring well is developed, primarily to prevent contamination of water samples, which would generate data not representative of true water quality.¹³ In particular ADEC cautions that drilling muds should never be used unless there is no other way to develop the well; PLP appears to be utilizing mud

¹² Mikkelsen 2002

¹³ ADEC 1992

rotary drilling for monitoring wells and geotechnical holes.¹⁴ Drilling muds may be required for deep wells or wells developed in highly fractured rock.



Figure 5. Hydrology well construction at the Pebble prospect. From PLP 2008 Draft Sampling Plan, Figure 2.

1.3.2 Purpose of drilling muds

Drilling muds serve three primary purposes. (1) Like water, they can be used to remove drill cuttings. Drill fluid is pumped down the center of the bit and carries cuttings up in the annular space. The drilling fluid must circulate or the cuttings would engulf the bit and hamper or stop drilling. The type of drilling fluid used, and the consistency, changes with the depth of hole and may change with the density of the rock. Large cuttings, higher density cuttings, or deeper drilling require mud with higher specific gravity to bring the cuttings to the surface. Specific gravity of the mud can be adjusted as necessary.

(2) The mud also maintains fluid circulation; without circulation, the cuttings won't rise. Loss of circulation occurs when the subsurface material is permeable or contains fractures. Drilling through fractured rock requires the addition of dense drilling additives that are able to flow into the fractures and seal them. If there is too much fracturing, circulation cannot be maintained and the hole may need to be abandoned. When drilling is conducted through sand and gravel, a casing needs to be installed to prevent the walls from caving in. For instance, at the Pebble prospect, the top 50 m or so above bedrock is often

¹⁴ ADNR 2009a

loose gravel and sand and casings may need to be installed in the upper section of the hole. Drilling muds may also help to prevent weak rock from sloughing off and hindering circulation.

(3) Lastly, chemical additives in drilling muds are required to keep the drill bit cool. Returning drill fluid contains metals from both the rock and from the drill bit as friction grinds both.

1.3.3 Composition of drilling additives

Drilling additives may include polysaccharides, polyacrylamide, and additives such as surfactants, fluid loss control additives, salts, fibers, silica, and bentonite (Table 1). It is known that PLP used many types of drilling additives (Table 2 and Attachment 1). Drilling muds can potentially change alkalinity and pH (they are mixed at pH 8.5 or higher), ammonia, barium, and stimulate of bacterial growth (Attachments 2 and 3).

Product Name	Purpose	Description	
AQUAGUARD®	Subsurface grouting material	sodium bentonite grout	
BENSEAL®	Sealing and plugging agent	sodium bentonite	
PEL-PLUG	Sealant	sodium bentonite	
QUIK-GEL [®]	High-yield gelant / viscosifier	sodium bentonite	
Bentonite	Sealing and plugging agent	Bentonite clay	
Cellophane	Circulation control	Cellophane	
Nylon	Circulation control	Nylon	
EZ-MUD®	Borehole stabilizer/Viscosifier	PHPA polymer	
LIQUI-TROL	Filtration control/viscosifier	cellulosic polymer	
PAC-L	Filtration Control	Polyanionic cellulose	
MF-1	Well-bore stablizer	Polyacrylamide	
TORKease	Lubrication	Polymer	
QUIK-FOAM®	Foaming agent	biodegradable surfactant	
N-SEAL	Circulation control	mineral fiber	
Magma Fiber	Circulation control	mineral fiber	
Soda ash	pH and hardness control	Sodium carbonate	

Table 1. Typical drilling additives.From Shanahan 2004.

EZ-Mud and Penetrol bear labels warning users to prevent the material from entering waterways.¹⁵ According to the Material Safety Data Sheets (MSDS), EZ-Mud is toxic at concentrations exceeding 1000 mg/L for fish and 16.7 mg/L for algae (diatoms). These toxicity limits address only lethal, rather than potentially sublethal effects on aquatic life. The MSDS from the makers of EZ-Mud and Penetrol were examined to determine the source of toxicity (Attachments 4 and 5). The potential toxics include

- acrylamide
- DEA
- ammonia

¹⁵ <u>http://www.muddirect.net/MSDS/PDFs/EZ-Mud.pdf</u> for MSDS on drilling muds; product information for several drilling fluids available at <u>http://www.muddirect.net/Products/Products.htm</u>

Table 2. Some drilling additives used at Pebble. A full list is provided in Attachment 1. From Exhibit 3, pgs 51-53, Pebble Partnership. PureVis product is not listed on Attachment 1 but has been used according to ADNR Inspection Report October 15, 2009. Chemical descriptions are from MSDS sheets, product information sheets, and/or the Baroid Fluids Handbook dc99.4shared.com/download/x0GARm2i/Baroid_Fluids_Handbook.pdf

MSDS File Name	Product	Chemical Description	
Baro-Seal Classic	Lost circulation material	fibers	
Hy-Seal	Lost circulation material	not available	
Penetrol	Wetting Agent	diethanolamine	
Con Det	Wetting agent	surfactant	
EZ-MUD	Borehole stabilizer	polyacrylamide/polyacrylate polymer	
EZ-MUDPlus	Borehole stabilizer	polyacrylamide/polyacrylate polymer	
Clear-Bore	Drilling Fluid	polysaccharides	
Prima-Seal	Lost circulation material	vegetable and polymer fibers	
PureVis	Drilling fluid additive	acrylamide polymer	
PAC-R	Viscosifier; solids-enhanced fluid	polymer; type not specified	
Xtragel	Viscosifier	not available	

EZ-Mud is a polyacrylamide product with a slippery consistency that aids in lubrication. There is some evidence that polyacrylamide can break down to acrylamide under acid-neutral conditions when ferric iron is present.¹⁶ Acrylamide is a neurotoxin, and can also cause damage to DNA resulting in mutations.¹⁷ Due to the high pH at which drilling muds are used, it is unlikely that acrylamide is formed during exploration. Residual acrylamide is likely present, although probably in less than toxic concentrations.

Penetrol is primarily a diethanolamine (DEA) product. Unless DEA is released in large quantities, it is unlikely to be directly toxic.¹⁸ However, it is listed as "incompatible" with acids, copper, and zinc. It is possible that Penetrol could contact all of three. "Incompatible" is undefined by the MSDS; one definition of incompatible is materials which may react violently or explosively if they are mixed or brought together. These materials should be stored separately and should not be mixed unless special procedures are followed.¹⁹

EZ-Mud and Penetrol have not had toxicity testing conducted on cold-water fish. The MSDS for Penetrol lists all ecotoxicological information as "not determined," suggesting that toxicity tests with this product have never been performed. For EZ-Mud, the species used in lab tests to determine toxicity was the commonly used fathead minnow (*Pimephales promelus*), which is a warm-water fish that survives well in muddy ponds with high turbidity and little oxygen and is likely less sensitive than cold-water fish such as salmon and other species present at the Pebble site.

1.3.4 Closing drill holes

After cores are removed, the State of Alaska requires that drill holes be filled in the following manner:

¹⁶ Woodrow et al 2008; Smith et al 1997

¹⁷ Josephy and Mannervik 2006

¹⁸ Craciunescu et al 2009

¹⁹ <u>http://ccinfoweb.ccohs.ca/help/msds/msdsINTGUIDE.html</u>

All drill holes shall be plugged by the end of the exploration season during which they are drilled, unless otherwise specifically approved by the Division of Mining, Land, and Water. All drill holes shall be plugged with bentonite hole plug, a benseal mud, or equivalent slurry for a minimum of 10 feet within the top 20 feet of the drill hole. The remainder of the hole will be backfilled to the surface with drill cuttings. If water is encountered in any drill hole, a minimum of 7 feet of bentonite hole plug, a benseal mud, or equivalent slurry shall be placed immediately above the static water level in the drill hole. Complete filling of the drill holes, from bottom to top, with a bentonite hole plug, a benseal mud, or equivalent slurry is also permitted and is considered to be the preferred method of hole closure.²⁰

Examination of DNR documents found the wording above in the 2007 "Plan of Operations" but the 2009 plan omitted the last sentence.²¹ PLP protocol requires filling holes with grout by pumping it down rods to the bottom of the hole or, if an artesian aquifer is encountered, pumping grout to the plug (placed to keep water out of the hole).²² Grout is to be subsequently pumped until mud flows out of the rods.²³

Bentonite is used as both a drilling additive to seal fractures in rock and assist in bringing cuttings to the surface, and when mixed more thickly it can be used to install casings or to seal drill holes; several bentonite compounds are utilized at Pebble (Table 3). Bentonite is a type of clay formed when volcanic ash falls on seawater. Different bentonites have high concentrations of sodium, potassium, calcium, and/or aluminum. As such, they have a high cation exchange capacity and the ability to contribute salts to natural water. Although a natural product, bentonite can be toxic to plants due to its high shrink/swell properties and the salt content. Reclamation of old bentonite mines has been problematic in Montana; vegetation was difficult to establish due in part to the salt content of bentonite.²⁴ Additionally, cement or cement-bentonite grout utilized to install monitoring well and piezometer casings or to close a coring hole are mixed at a high pH (over 9) and introducing alkaline material into holes may mobilize some elements such as molybdenum and uranium.

MSDS File Name	Chemical Description		
Benseal	crystalline silica and bentonite		
Quik-Gel	sodium bentonite		
Pel-Plug	sodium bentonite		
CETCO 1/4 Coated Tablets	sodium bentonite		
Premium Gel	sodium bentonite		
Super Gel-X	sodium bentonite		
PureGold Grout	bentonite clay grout		
PureGold Medium Chips	sodium bentonite		
Volclay Granular Grout	sodium bentonite grout		
Volclay Grout One Step	sodium bentonite grout		
Aquaguard	sodium bentonite with inorganic additives		
Oil well G Cement	Cement		
Portland Cement	Cement		

Table 3. Bentonite products used in drilling at Pebble. From Exhibit 3, pgs 51-53, Pebble Partnership. Chemical descriptions are from MSDS sheets, product information sheets, or the Baroid Fluids Handbook.

²⁰ ADNR 2009b

²¹ 2007 Plan of Operations, Pebble Copper Project Permit #AO76118; 2009-2010 Plan of Operations, Pebble Exploration Project, Permit #AO86118

²² Å well plug is cement placed to prevent water from flowing up

²³ Brommeland 2007; Cole 2008

²⁴ Schuman et al 2000

1.4 Chemical mechanisms

In addition to the direct toxicity of drilling and blasting breakdown products, there are broad chemical mechanisms that affect biology and may be changed by exploration processes. Chemical mechanisms on water chemistry can be complex and interactive. For instance, dissolved oxygen, redox, pH, and alkalinity may all be related.

1.4.1 pH and alkalinity

The pH of natural waters is generally 6.5-8; pH lower than 6 (acidic) or higher than 9 (alkaline) can be directly toxic to fish, fish eggs, and other aquatic life.²⁵ However,

"There is no definite pH range within which a fishery is unharmed and outside which it is .damaged, but rather, there is a gradual deterioration as the pH values are further removed from the normal range. The pH range which is not directly lethal to fish is 5 - 9; however, the toxicity of several common pollutants is markedly affected by pH changes within this range, and increasing acidity or alkalinity may make these poisons more toxic. Also, an acid discharge may liberate sufficient CO_2 from bicarbonate in the water either to be directly toxic, or to cause the pH range 5 - 6 to become lethal."²⁶

Trace metals (e.g. copper, cadmium, zinc) naturally bound up in soil and sediment may be released when pH changes; these metals, when mobile, can move into pore-waters of soil/sediment and into the water column, exposing aquatic life. Aluminum and iron, some of the most abundant trace metals in soil, will dissolve at low pH but then form problematic solids when the dissolved metals re-enter neutral pH waters: aluminum forms a floc that suffocates fish and iron forms an oxide solid that can "cement" stream bottoms, suffocating benthic life and sequestered fish eggs.²⁷ Increased acidity can also affect fish reproduction by lowering calcium levels in female fish to the point where she does not produce eggs, or they are produced abnormally.²⁸ Naturally low pH environments occur when soil organic humic and tannic acids enter surface water, decreasing stream pH to as low as 4.5 but not below that; when waters reach pH below 4.5, virtually all fish die. Mineral acidity can be much more extreme than soil acidity and accelerate the dissolution and desorption of trace metals and, as mentioned above, shift naturally low pH water into a lethal range.

Trace metals that enter the environment may accumulate in sediments in concentrations several times higher than in overlying water. From sediment, metals move into aquatic plants and macroinvertebrates, and from there into fish.²⁹ Macroinvertebrates can be particularly good indicators of water toxicity as they are sensitive to very low levels of metals and to surges of metals.³⁰ At the abandoned Leviathan mine in the Sierra Nevada mountains, California, mine drainage that was treated year-round had a recovery in macroinvertebrates; this recovery was not observed in drainage from the same mine treated only in the summer and fall. The partial treatment did not occur until after snowmelt. Snowmelt released a slug of metals into receiving waters every spring. The effect was most noticeable on the macroinvertebrate population, which was not able to fully recover due to the periodic releases.³¹

²⁵ US EPA 1976; <u>http://www.lenntech.com/aquatic/acids-alkalis.htm</u>

²⁶ ibid

²⁷ National Research Council 1999

²⁸ US EPA 2000 "Generalized Short-Term Effects of Acidity on Fish," in *National Water Quality Inventory: 1998 Report to Congress,* U.S. Environmental Protection Agency, Washington, DC, June 2000

²⁹ National Research Council 1999

³⁰ ibid

³¹ Herbst 2004

The introduction of high pH (alkaline) material can also cause contamination. High pH environments encourage the mobility of oxyanions of arsenic (arsenate, AsO_4^{3-}), selenium (selenite, SeO_3^{2-} and selenate, SeO_4^{2-}), and molybdenum (molybdate, MoO_4^{2-}). High pH can also strip fish of their protective slime coating and cause an increase in un-ionized ammonia, if total ammonia (ionized + un-ionized) is present.

Both Penetrol and EZ-Mud have alkaline pH. EZ-Mud has a pH of 8.5 when mixed as 1 quart to 100 gallons of water. Some applications require mixing 2 quarts to 100 gallons of water, in which case the pH could be even higher.³² Penetrol has a pH of 9.5 when mixed as a 1% solution, and possibly a higher pH when mixed as a 10% solution according to common practice.

Total alkalinity refers to the ability of the water to resist changes in pH. In surface water, this is controlled by the atmosphere contributing CO_2 , which, in water, becomes mostly bicarbonate (HCO₃⁻). In water, CO_2 takes on three forms simultaneously, and buffering occurs because a change in pH shifts the ratio of the three forms. At neutral pH in water, CO_2 exists primarily as HCO_3^- ; if acid is introduced, the ratio shifts to increasing H₂CO₃ (carbonic acid) and off-gassing of water and CO_2 back to the atmosphere (Figure 6)



Figure 6. Buffering in natural water.

In groundwater, alkalinity is primarily provided by dissolution of carbonate minerals (CaCO₃, MgCO₃, FeCO₃, etc), therefore an increase in alkalinity can be accompanied by an increase in carbonate minerals $(Ca^{2+}, Mg^{2+}, Fe^{3+}, etc)$.

In addition to the possible mobilization of oxyanions and cations, a pH greater than 8 inhibits microbial growth (biocide) and poses risks to soil and sediment microbes, which are a vital part of nutrient cycling in aquatic and wetland environments.

1.4.2 *Redox*

While pH is a measure of the gain and loss of protons (hydrogen ions), redox is the measure of the gain and loss of electrons. It is often affected by pH, and can be driven by microbial activity.

"Redox" is shorthand for "oxidation-reduction". A "reduced form" of a metal is one that has more electrons, and an oxidized form has fewer electrons; e.g. Fe^{2+} is reduced and Fe^{3+} is oxidized.

A change in the redox environment can have strong effects on the mobility of metals. Metal ions commonly exist in ratios of reduced and oxidized forms; an "oxidizing environment" will have more Fe³⁺

³² Product information for several drilling fluids available at <u>http://www.muddirect.net/Products/Products.htm</u>

than Fe^{2+} . Because Fe^{2+} is more mobile than Fe^{3+} , changing the environment from oxidative to reductive is likely to increase the concentration of dissolved soluble cationic metals such as iron (Fe^{2+}), copper (Cu^{2+}), cadmium (Cd^{2+}), zinc (Zn^{2+}) and so forth. Contrarily, when metals are moved from a reducing environment to an oxidative one, they may precipitate. For instance, pumping water from a monitoring well may pull water from reduced environments in bedrock into an oxygenated one in the well if water is pumped faster than recharge; in this situation, metals that are in the dissolved form in groundwater may precipitate in the monitoring well water sample, causing samples to have suspended solids in concentrations that are not found in natural groundwater.³³

Oxyanions are more mobile in an oxidizing environment than a reducing one.

Oxidation-reduction potential (ORP) is measured in millivolts (mV) or microvolts (uV) and is a measurement of the affinity of a substance for electrons, and runs from +800 mV to -400 mV. An environment with a highly positive ORP is a highly oxidizing environment in which aerobic bacteria are likely active, cationic metals tend to be insoluble and immobile, and oxyanions tend to be mobile. An environment with a highly reducing atmosphere favors anaerobic bacteria and causes cationic metals (Cu^{2+}, etc) to become soluble and mobile while oxyanions (AsO₄³⁻, etc) become less mobile. By way of illustration, swamp sediments are highly reducing environments and may reach -300 mV while the sediment in bubbling streams is more likely near +100 to +300 mV.

1.4.3 Microbial activity and water chemistry

Microbes consume hydrocarbons in order to use the carbon for growth. Essentially, this is a redox reaction. As hydrocarbons are oxidized (electrons lost), something must accept the lost electrons and become reduced. In a normal oxygen atmosphere, oxygen accepts electrons and water is formed. In the microbial community, there is a sequence of reactions in which microbes can use a variety of electron acceptors, and obtain different amounts of energy in doing so. The "energetics", from the most energy gained (left hand side) to the least (right hand side) is shown in Figure 7.



Figure 7. Microbial energetics sequence. Oxidized compounds and elements are on the top; their reduced counterpart is on the bottom line. The most energy is gained by reducing oxygen to water (oxygen receives the electrons "dumped" when hydrocarbons are oxidized for food); the least energy is gained by reducing carbon dioxide to methane.

In moving from left to right, the following will be observed: dissolved oxygen will decrease, the reducing atmosphere will increase, dissolved concentrations of manganese and iron will increase, the presence of Fe^{2+} will be observed, and eventually a "rotten egg" smell will be evident if sulfate reduction is occurring (although S²⁻ is the waste product, there will be some H₂S, or hydrogen sulfide, present).

³³ McCarthy and Shevenell 1998

Where hydrocarbons, such as fuel, are present, the microbial activity can reduce the dissolved oxygen content of the water, which may have an impact on aquatic life. If metals are mobilized due to changing redox conditions, they may also impact aquatic or plant life.

Chemical reactions that indicate microbial activity include low dissolved oxygen, decreasing ORP, increased concentrations of iron (particularly Fe^{2+}) and manganese, and possibly a "rotten egg" hydrogen sulfide smell.

1.4.4 Sulfide rock and acid drainage

One of the primary reactions in mining chemistry is the oxidation of sulfide rock and subsequent generation of acid. Depending on the other material in the rock, such as carbonates, the development of acid may be delayed by several decades; however, once started, it may continue unabated for hundreds to thousands of years. There are old mining sites in Europe that have been generating this "acid mine drainage" for thousands of years,³⁴ and a former iron mine in California that is expected to generate acid for about 3,000 years.³⁵

Exposing sulfide rock to oxygen and water causes the rock to form sulfuric acid; the rock, in fact, dissolves. This can occur by simply bringing rock or drill cuttings to the surface, or by drilling a hole and not sealing it. This usually begins as a simple abiotic weathering reaction (Equation 1)³⁶ and is then catalyzed by bacteria to a more aggressive reaction.

$$2 \text{ FeS}_2 + 2 \text{ H}_2\text{O} + 7 \text{ O}_2 \rightarrow 2 \text{ Fe}^{2+} + 4 \text{ SO}_4^{2-} + 4 \text{ H}^+$$
 Equation 1

Microbial activity from aerobic "iron oxidizing" bacteria accelerates the reaction (Equations 2 and 3), by converting "reduced" iron (Fe^{2+}) to "oxidized" iron (Fe^{3+}) ; Fe^{3+} is able to oxidize sulfide minerals and release a much greater amount of acid than simple exposure to oxygen:

4
$$Fe^{2+} + O_2 + 4H^+ \rightarrow 4 Fe^{3+} + 2 H_2O$$
 Equation 2

$$FeS_2 + 8 H_2O + 14Fe^{3+} \rightarrow 15 Fe^{2+} + 2SO_4^{2-} + 16H^+$$
 Equation 3

This becomes a perpetual cycle that cannot be broken unless one of the "legs" of the reaction (oxidant, water, sulfide) is removed (Equation 4).

28
$$Fe^{2+}$$
 + 7 O_2 + 28 H^+ \rightarrow 28 Fe^{3+} + 14 H_2O
 \uparrow Equation 4
30 Fe^{2+} + 4 SO_4^{2-} + 32 H^+ \leftarrow 28 Fe^{3+} + 16 H_2O + 2 FeS_2

As acid forms, minerals in the rock also dissolve. Rock contains multiple metals in its structure, and acid forming at the rock face will dissolve copper, iron, and other metals present in the rock.

The reaction also produces sulfate (oxidized sulfide, SO_4^{2-}) which, if released into streams in high enough concentration, has the potential to negatively affect fish eggs.

³⁴ Thornton and Abraham 1984; Davis et al 2000

³⁵ Alpers et al 2003; also personal conversation with Eric Marchand, Ph.D, Civil Engineering professor at the University of Nevada, Reno

³⁶ Although sulfate ($SO_4^{2^-}$) and hydrogen (H^+) are separated in the equation, they are essentially sulfuric acid (battery acid, H_2SO_4)

Chemical measurements that indicate acid rock reactions are occurring include an increase in concentrations of sulfate, Fe²⁺, and dissolved metals, and a decrease in pH.

1.4.5 *Cation exchange*

Soils have different degrees of electrical charge at their surface. Clays in particular have a strongly negative electrical surface charge. This attracts ions with a positive charge, such as calcium, sodium, and dissolved cationic metals (e.g. Cu^{2+} , Cd^{2+} , Fe^{3+}), and clays are referred to as having a high "cation exchange capacity" (CEC) as compared to sand.

Clays may release sodium (Na^+) in exchange for binding calcium (Ca^{2+}) . This will increase the sodium content of the soil, and increase the sodium content of groundwater that moves through it. In a reducing atmosphere, clays also release positive ions, increasing the sodium and metal content of the environment; in an oxidizing atmosphere, clays may sorb (attract) soluble cationic metals and prevent them from becoming mobile. Introduction of clay can change the alkalinity and pH of natural waters as well as the cation content.

1.4.6 Summary

Redox, pH, alkalinity, and dissolved oxygen can be related to each other, depending on the chemical drivers in the environment. In particular, microbial activity can consume oxygen and change the redox environment. Redox and pH are intimately related, as they refer to the movement of protons and electrons. Alkalinity, the buffering capacity of water, may be related to pH, but also changes with the type of rock that water moves through.

Because metal species may originate from or be changed by different sources, one must be careful in interpreting measured metal concentrations in water, particularly iron and manganese.

- In surface water, iron and manganese may originate from erosional material, and will often be accompanied by aluminum. Depending on the surficial geology, copper, arsenic, lead, and other elements may also present as erosional material; these will all be primarily be attached to sediment and while elevated "total" metals are observed, "dissolved" metals concentrations are unlikely to increase much.
- Microbial activity may increase the concentrations of dissolved iron and manganese, but not the "total" forms, and aluminum won't increase; iron will be in the Fe²⁺ form.
- If acid is the cause for measured amounts of iron and manganese, iron will likely be in the Fe²⁺ form (which is more mobile than Fe³⁺), but the water sample is also likely to contain dissolved copper, cadmium, zinc, and so forth, with nearly all metal observed as "dissolved", not "total" just the opposite of what would be observed if the metals originated as erosional material.

Additionally, metals may go through series of dissolution and precipitation reactions and may change diurnally and seasonally, and with changes in UV light, pH and redox, and with changes in concentrations of dissolved organic matter,

Given the controls on natural water chemistry and the chemical changes that can be expected from exploration, it is important to measure chemical components of the natural environment prior to drilling to ensure that the "true" or baseline chemistry is characterized, and to measure specific chemical indicators – such as pH, redox, dissolved oxygen, hydrocarbons/organics, cations, anions, and metals – at drill holes and in environmental media downgradient to assess whether indicators change with drilling. This is particularly important given that impacts to natural resources are likely to be subtle and not visually observable.

2.0 Water Quality Standards

The State of Alaska recognizes water quality standards for fresh water are based on uses: drinking water, irrigation, livestock watering, aquaculture, industrial, recreation, growth and propagation of aquatic life, and harvesting aquatic life for consumption. All waters are, by default, considered of adequate quality for all uses unless demonstrated otherwise.³⁷ The most stringent water quality standards are generally those protective of drinking water or aquatic life. These standards must be met when permits are provided for discharges to freshwater, unless specific exceptions – referred to as "site specific criteria" – are imposed. The term "benchmark criteria" is used to refer to the most stringent water quality standard of any use as listed in the ADEC 2008 Alaska Water Quality Toxic Manual.³⁸

Some standards vary with the hardness of the water. Commonly 25 mg/L is utilized (Table 4).

Table 4. Analytes and Relevant Standards. Standards pertain to a particular use. The most stringent standards of all possible uses may also be referred to as "benchmark criteria". DW= drinking water; CCC = freshwater aquatic life, chronic criteria; IRR = irrigation; HC = human consumption of aquatic organisms. The standard for alkalinity is 20 mg/L "unless natural conditions are less". A hardness of 15 mg/L is used in calculations. All standards come from ADEC 2008, except sulfate is from ADEC 2009. * hardness dependent **pH dependent T=total, D=dissolved fraction for metals.

Analysis	ADEC standards	Use category
Dissolved organic carbon (mg/L)	no standard	
Nitrate + nitrite as N (mg/L)	10	DW
Total Ammonia as N** (mg/L)	0.18	CCC
Alkalinity as CaCO ₃ (mg/L)	20	CCC
Chloride (mg/L)	230	DW
Fluoride (mg/L)	1	IRR
Sulfate (mg/L)	250	DW
Aluminum (μg/l)	87	CCC
Iron (μg/l)	1000	CCC
Calcium (µg/l)	no standard	
Magnesium (µg/l)	no standard	
Sodium (µg/I)	no standard	
Potassium (μg/l)	no standard	
Antimony (µg/l)	6	DW
Arsenic (μg/l)	10	DW
Cadmium* (µg/I)	0.10	CCC
Chromium (µg/I)	100	DW
Copper* (µg/l)	2.85, 2.74 D	CCC
Lead* (µg/l)	0.54	CCC
Manganese (µg/l)	50	HC
Molybdenum (µg/l)	10	IRR
Nickel* (µg/l)	16.1	CCC
Selenium (µg/I)	5	CCC
Uranium (µg/l)	30	DW
Zinc* (μg/l)	37.0T, 36.2D	CCC
Mercury* (µg/l)	0.05	HC

³⁷ ADEC 2008; ADEC 2009

³⁸ ADEC 2008. The benchmark for sulfate is taken from ADEC 2009.

3.0 Potential contamination of surface water

In areas where groundwater and surface water are closely linked and exchanged, any contamination to one may potentially contaminate the other. The Pebble prospect has permeable soils,³⁹ extensive wetlands,⁴⁰ innumerable tundra streams, kettle ponds fed by surface water and groundwater,⁴¹ and several ponds and lakes, making it a region at risk.

The most likely sources of contamination to surface water is from fuel spills, drilling discharge, and breakdown chemical products from blasting.⁴² All material brought to the surface during drilling is considered "drilling discharge". This includes the rock cuttings, metal from friction on the drill bit, drilling mud and additives, and discharged water. Drilling discharge may

- be transported by groundwater in the borehole via conductive aquifer zones
- be intentionally discharged to tundra or lakes or
- unintentionally overflow to the surface from the borehole or from drilling mud recirculation tanks

The discussion below is theoretical; whether actual contamination occurs depends on the concentration and rate of toxic material release, potential pathways to receptors (plants, aquatic life), dilution, sorption, and other factors.

3.1 Fuel spills

Drill rigs and water-extraction pumps require gasoline, diesel, and hydraulic fluids. Spills may be directly toxic to soil or aquatic organisms. Because all are hydrocarbon-based, soil microbes will consume them over time, using them as carbon sources. These microbes all require oxygen. As they consume hydrocarbons in the surface soil, they also consume oxygen, potentially changing the environment from an oxidative to a reductive one, which could allow cationic metals to mobilize.

3.2 Drill cuttings

Virtually all of the mineral resources found to date at the Pebble prospect have been hosted in sulfidic rock,⁴³ and cuttings from the mineralized zones would therefore be sulfidic. The Pebble Limited Partnership (PLP) has been testing the acid generation potential of different material in order to develop a waste management plan, should the mine proceed, and has determined that acid is expected to develop within anywhere from a few years to several decades after removal from the ground.

Cuttings may be dry, chipped rock (from air drilling) or mixed with water or drilling additives. Dry cuttings can be used by geologists to characterize the subsurface environment. PLP documents suggest that drill cuttings from monitoring wells were to be collected and bagged.⁴⁴ However, documents for the Pebble Project demonstrate that cuttings have been disposed of in sump pits.⁴⁵

Cuttings from core drilling can be considerable. For example, a standard drill core has an outside hole diameter of 3 inches and a core sample diameter of 1.9 inches; what isn't core is cuttings. This means that

³⁹ Wobus 2009; Moran 2007

⁴⁰ Moody 2008

⁴¹ Rains 2008

⁴² Moran 2007

⁴³ Day 2009

⁴⁴ PLP 2008 Draft Field Sampling Plan, Section 6.1.3

⁴⁵ ADNR Field inspection reports July 2007, April 2008; Loeffler 2009

for every 1,000 linear feet of core hole there will be approximately 29 cubic feet (1.07 cubic yards) of cuttings brought to the surface.⁴⁶

The cuttings, if they consist of sulfide rock, will generate acid and leach metals; depending on the amount of acid and the concentration and type of metals in the leachate, plant life could be affected. Additionally, the leachate may reach groundwater or surface water, particularly if transported by rain or melting snow through permeable soils. Metals and metalloids⁴⁷ leached from cuttings, due to either acid rock reactions or weathering, that enter the hyporheic zone or surface water can pose risks for aquatic life. Most metals are toxic to aquatic life at low concentrations and can cause both lethal impacts and subtle impacts such as reduced growth and development, changes in community structure, or changes in movement to avoid metal contaminated waters.⁴⁸

Drilling muds 3.3

Drilling muds themselves are relatively benign with regards to human health hazards, but do have some potential to contaminate surface water through changing pH and introducing sodium, calcium, barium, and ammonia. Many of them may also represent carbon sources that can stimulate bacterial growth, and as such they have been known to change the redox environment within a drill hole, creating reducing conditions that can mobilize cationic metals.⁴⁹

Drilling muds are mixed at a high pH. Soil and rock in the Pebble area contains metalloids such as arsenic, antimony, uranium and molybdenum⁵⁰ that can be released into the environment when in contact with alkaline material.

3.4 Ammonia

Blasting can produce nitrogen residues, including ammonia, and ammonia is the most likely toxic breakdown product of the drilling additives EZ-Mud and Penetrol. Amides⁵¹ (as are present in EZ-Mud) break down into ammonia, a reduced form of nitrogen Penetrol is a diethanolamine (DEA) product, and although ammonia is not listed in MSDS sheets as a hazardous breakdown product of Penetrol, bacteria can and do break DEA into ammonia. Therefore, Penetrol also presents potential for ammonia toxicity.

However, the impact of introduced ammonia to surface water is complicated in that toxicity can vary with the characteristics of the stream and the fish present. Ammonia is the natural breakdown product of organic material such as spawned-out salmon carcasses. Ammonium (NH_4^+) increases during salmon migration due to decomposition of carcasses (external source) and due to breakdown of protein in swimming salmon (internal source). Ammonium has been found to increase from near 5 ug/L to near 60 ug/L in water where many carcasses are present.⁵² The form is highly dependent on pH, so that a concentration of non-toxic NH₄⁺ of 60 ug/L is likely to have only about 2 ug/L of the toxic un-ionized ammonia form (NH_3) in natural streams. With increasing pH, ammonia moves towards the toxic NH_3 form; at pH 9.5, water will contain 50% NH₃ and 50% NH₄⁺. Water with concentrations of less than 20

⁴⁶ Volume of cuttings will be the outer hole dimensions minus the core hole. V=length * $\prod r^2$. The volume of an outer hole 3" in diameter and 1000' linear feet is 49 cubic feet; the volume of the core would be 20 cubic feet; cuttings represent the remainder.

⁴⁷ Metalloids refer to elements such as arsenic, antimony, molybdenum, selenium, uranium and vanadium that form oxyanions and tend to mobilize under neutral to alkaline conditions.

⁴⁸ National Research Council 1999

⁴⁹ Gilkeson 2004; Shanahan 2004

⁵⁰ Fey et al 2008; Fey et al 2009; Kellev et al 2010

⁵¹ An amide is an organic molecule (R) bonded to carbon, oxygen, and nitrogen; the general formula is written as R-C(=O)-NH₂. The structure R-C=O is referred to as an acyl group. ⁵² Mitchell and Lamberti 2005

ug/L un-ionized ammonia (NH₃) is considered safe for fish reproduction.⁵³ Temperature also affects the form of ammonia/ammonium.

The natural streams at Pebble have high levels of oxygen. Oxygen converts ammonia, a reduced form of nitrogen, to nitrate and nitrite (NO_3^- , NO_2^-), oxidized forms of nitrogen that have considerably less toxicity. Therefore ammonia is only likely to persist in low-oxygen environments such as marshes, stagnant ponds, and where organic material such as salmon carcasses is being rapidly consumed by microbes that use up oxygen in the water.

The physical characteristics of the water body, the nutrients already in the water body, and the physical state of any fish present are factors in any actual impacts nitrogen products may have. Studies need to be examined closely when being used for interpretation of data. Given that ammonia toxicity can vary with the characteristics of the stream and the fish itself, toxicity testing of Penetrol and EZ-Mud, and other drilling additives with nitrogen compounds, should be done on salmonids in different life stages and stress levels.

4.0 Potential contamination of groundwater

Groundwater may come in contact with drilling muds and sulfide rock in a drill hole, and be subject to the same potential contamination as surface water, including increases in ammonia. Unlined sumps used to hold drilling fluids can directly contribute constituents to groundwater when the sump either directly intercepts a shallow groundwater zone or is in close vertical proximity to the groundwater table (Figure 8). Sealing drill holes also may result in the introduction of cement and/or bentonite into aquifers.



Figure 8. Typical sump. Sump is located at the Pebble prospect. From ADNR Field Inspection Report, July 2007, photo 12.

The greatest potential contamination of groundwater, particularly in holes developed in sulfide material, is through acid rock reactions. This can occur in improperly or unfilled holes. Holes that encounter artesian water could be susceptible to long term acid rock reactions in that these holes cannot be

⁵³ US EPA 1976

completely filled, but rather are closed by placing a plug above the aquifer and filling the hole above the plug. There have been references to NDM using water from "previously drilled holes" to supply active drilling rigs,⁵⁴ and these open holes could also be susceptible to acid rock reactions, particularly in the Pebble West zone, where sulfidic rock is found all the way to the surface.

In the West zone, "50% of Cominco holes in Pebble West bottomed in sulfide mineralization with grades of 0.6% $CuEQ^{55}$ and 96% bottomed in mineralization with grades higher than 0.30% $CuEQ^{;56}$ demonstrating that sulfide is a major component of the ore body. The USGS also found sulfide material at the surface in Pebble West.⁵⁷ There is also pyrite (FeS₂) beneath the overburden material of the East zone (Figure 9).⁵⁸



Figure 9. Potentially acid generating rock at Pebble deposit. Green symbols represent overburden above the Pebble East zone, others represent rock from which cores are taken. NP= neutralizing potential AP= acid potential A ratio of NP/AP less than 1 is likely to make acid. The only material not likely to generate acid is the Tertiary overburden which does not contain ore. This chart represents Pebble West, but Pebble East ore is expected to be similar. From Stephen Day and Claire Linklater, SRK Consulting, Pebble Project Geochemical Characterization. PLP Agency Meetings, November 2008.

Given the large number of boreholes and their depth, it is possible that hundreds to thousands of feet of sulfide rock could remain un-sealed and susceptible to oxidation and acid rock reactions. Should an aquifer have access into and out of these holes, acid and associated cationic metals could move into the aquifer; this reaction could potentially continue for decades.

⁵⁴ ADNR 2007

⁵⁵ CuEQ refers to the "copper equivalent" of ore; i.e. the combination of gold, molybdenum, and copper resource as if they were all in the value of copper.

⁵⁶ Rebagliati et al 2009 Section 13.1

⁵⁷ Fey et al 2009

⁵⁸ Rebagliati and Payne 2005 Section 10.2.8

There are about a dozen seeps in Pebble West that are clearly producing acid drainage based on my interpretation of data released on PLP's webpage.⁵⁹ However, available information does not provide data on seep water quality prior to drilling, therefore there is no way to assess whether these seeps are in fact historic un-sealed exploration drill holes or have developed post-drilling.

While some aspects of acid rock drainage may be directly observable – such as when water flowing from a monitoring well or drill hole runs red from acid rock reactions and dissolution of iron – most will be under the surface in drill holes and potentially moving into aquifers. Determining whether this is occurring and, if so, to what extent it represents natural reactions or ones initiated by opening up sulfide rock requires measurements before and after drilling.

Whether contamination of groundwater or of surface water fed by groundwater occur under such situations will depend on whether there are connections to surface water through springs, seeps, or the hyporheic zone; dilution effects; and neutralization effects if the aquifer passes through carbonate or feldspar rock.

5.0 Identifying contamination

Identifying "contamination" requires differentiating natural water chemistry from water chemistry that has been changed due to chemical reactions initiated by exploration or direct introduction of chemicals. Contamination from direct introduction of fuel or hydrocarbons could be measured, but commonly is not. Changes in pH, metals, cations, anions, oxygen, and other indicators can be observed, but it is extremely difficult to determine whether they occurred due to natural events, due to issues that occurred inside the monitoring well from which the water sample was collected, or originated from exploratory work.

If one is to trace contamination directly to exploration drilling, it is most helpful to have

- a) Baseline data (natural chemistry of soil, water, sediment) prior to drilling
- b) Samples of media downgradient of drilling discharge sites (soil, sediment, water) before, during, and after active drilling.
- c) Basic water chemistry (pH, conductivity, dO, ORP) from inside drill holes (commonly recorded in drilling logs or driller's field notes)
- d) Lithology of material holes are drilled in and, for monitoring wells, screened in.

This set of data will allow researchers to know the constitution of the natural environment, whether drill holes are a potential source of contamination and if so what kind of contamination, and whether environmental media near drilling had chemical changes.

5.1 Analytes that indicate contamination

As mentioned in the introduction, several analytes must be examined to determine the source of water chemistry.

• Sediment. Increase in "total" metals, particularly iron, aluminum, and manganese, may originate from natural sources or disturbances from exploratory activity. It also may originate from the monitoring well itself: gravel packing is often used to prevent sediment from entering the screen where water is sampled in monitoring wells but sediment can enter the screen on occasion, causing the water sample to contain high sediment-related metals. If un-filtered water has much higher metals than filtered, it indicates sediment is in the sample.

⁵⁹ PLP 2008 Pre-Permit Report F

- Acid rock reactions. Increased sulfate, increased concentrations of dissolved (but not "total") cationic metals, increased Fe²⁺, and decreased pH are indicators that sulfidic rock is reacting to form acid, which can occur naturally or be initiated in drill cuttings or open drill holes.
- **Microbial activity.** Decreased ORP, decreased dissolved oxygen, and decreased nitrate with increased concentrations of ammonia, dissolved iron and dissolved manganese indicate microbial activity that is creating a reducing atmosphere; a highly reducing atmosphere will also have decreasing sulfate and a "rotten egg" hydrogen sulfide smell. These can originate naturally or be catalyzed by introduction of hydrocarbons from fuel or drilling muds.
- Blasting. Increased ammonia and barium originate from blasting residue.
- Salts. Increase in cations (calcium, sodium, potassium), the relative nature of salt concentrations (sodium adsorption ratio SAR), alkalinity, and pH may indicate groundwater in contact with clay, which can be natural or from bentonite used in drilling and grouting. Increase in cations (calcium, sodium, magnesium, potassium) and anions (sulfate, chloride, fluoride) may also indicate increasing contribution of groundwater to surface water.
- **Metalloids.** Increase in oxyanion metalloids (arsenic, antimony, selenium, molybdenum, uranium, vanadium) may occur when the environment becomes more alkaline or more oxidizing, which can occur naturally or through introduction of high pH drilling materials that cause metalloids in the natural rock to dissolve and mobilize.

5.2 Fate and transport of contaminants

In all environments, the potential impact to plants, animals, birds, and fish is dependent on the exposure to and sensitivity of the receptor. Receptors may be terrestrial plant and animal life, or aquatic plant and animal life. Terrestrial organisms could be exposed through drilling discharge on tundra or through windblown contamination if discharge dries and contains fine metal particles. Aquatic organisms can be exposed through contact with direct discharge to surface waters, through infiltration of material into soil and transport to surface water, or through groundwater-surface water exchange.

As a larger concept, hydrocarbons can be degraded into water and CO_2 , while metals do not degrade and therefore remain in the environment. Metals may change form from solid to dissolved and become more or less mobile.⁶⁰

- The soil composition will dictate the rate at which material infiltrates into the ground; soils with high silt or clay content will allow much slower infiltration than sand and gravel.
- As material infiltrates, organic matter or clay in soil may remove some dissolved metals through adsorption, and clay may become a site for future cation exchange. Sorbed metals remain in place and may become bioavailable to soil organisms; dissolved metals may sequester in pore-waters or migrate downgradient.
- The lighter components of fuel hydrocarbons will vaporize, particularly in warm weather, but the heavier components will not, sequestering heavy hydrocarbons in the soil where they become available to bacteria and other organisms.
- Hydrocarbons may be consumed by soil and sediment bacteria, particularly if the flow path is long and slow, but little microbial activity is expected in winter. Long-chain hydrocarbons in cold environments can persist and possibly remain bioavailable for years.
- Contaminants may move through changing redox zones with depth, with deeper zones having more reducing environments. Metals such as copper, zinc, iron, and manganese that enter reducing environments become more mobile; they are less likely to remain sorbed to soil and more likely to move along flow paths.

⁶⁰ A summary of fate and transport issues can be found at <u>http://www.clu-in.org/contaminantfocus/default.focus/sec/Sediments/cat/Fate_and_Transport_of_Contaminants/</u>

- Dissolved metals discharged to tundra or in an aqueous environment may precipitate as hydroxides, carbonates, etc. and remain in the environment. This can occur at the point of discharge or at a later point along a flow path as the redox zone and available ligand groups change.
- Fluxes in groundwater may cause sorbed metals in soil and sediment to go through cycles of release and precipitation/binding.

5.2.1 Discharge to tundra

At the Pebble prospect, drilling muds are discharged to unlined tundra depressions. This discharge has the potential to impact tundra vegetation, and to reach some shallow aquifers, small streams and ponds. Although small headwater streams, such as the intermittent trickles that are found in tundra landscapes, may appear to be too small to be important components of the ecosystem, they are a major source of organic material, nutrients, and the insects and invertebrates that fish require.⁶¹

High or low pH, or elevated salts, barium, and metals can be directly toxic to tundra plants. The extent of plant death can be assessed with photos and contaminant measurements in soil, water, and vegetation. This would provide a basis for researching potential repercussions due to loss of food for terrestrial animals and birds and for determining pathways through the food chain. Food chain effects to migratory animals such as caribou and waterfowl would likely be negligible.

Other impacts cannot be so readily assessed with visual inspection. Some plants may take up metals through root systems; lichen may complex (bind) metals too small to see at the vegetation surface.⁶² As sediment and periphyton accumulate metals and metalloids, metals become available to macroinvertebrates.⁶³ Macroinvertebrates, benthic animals and insects living in soil and sediment can bioaccumulate toxic concentrations of metals.⁶⁴ The fate and transport of contaminants through soil or sediment is complex. Depending on composition and pH, soil and sediment may sorb or bind metals, or may go through fluxes of binding and release;⁶⁵ the actual activity and transformations cannot be determined without measurements. Metals are generally considered most available when dissolved in water in the pores between soil or sediment particles rather than attached to soil or sediment.

If drilling material dries and metals remain on the tundra surface, there is potential for them to be carried by the wind and settle in other ground or water locations. The impact of wind-borne contamination will depend on the mass of material transported, the toxicity of the material, the sensitivity of receptors at the new site, and factors mentioned above such as dilution and sorption effects once the material has relocated.

Material that moves into aquifers and surface water will likely have subtle impacts that cannot be identified without measurements. For instance, fish may avoid areas with high copper or macroinvertebrate population structures may shift.

5.2.2 Discharges to surface water

If drilling discharge reaches surface water such as kettle ponds and intermittent tundra streams, contaminants may affect aquatic life, particularly benthic organisms, algae, and aquatic insects. The interactions of hydrocarbons, salts, and metals in sediment are the same as those in soil, discussed above.

⁶¹ They also may contribute a significant volume of water to second order streams. However, disruption of water volume, while critical, is not discussed in this review.

⁶² Askaer et al 2008; Richardson 1995; Pucket et al 1973

⁶³ National Research Council 1999

⁶⁴ Besser et al 1995

⁶⁵ ibid

The lighter components of fuel hydrocarbons will vaporize, and some will remain at the surface of the water temporarily until wind and wave action break them up; heavier components will sink to sediment. Lighter components may remain as droplets in the water and be available to aquatic organisms. Some components of hydrocarbons are toxic (e.g. benzene, toluene). Salts will dissolve; potential changes in salinity will depend on the mass of salts introduced, the volume of water entered, and rate of water flow. High concentrations of "total dissolved solids"⁶⁶ can be toxic to fish eggs, reducing hatch and having long term effects on growth and development.⁶⁷ The degree and rapidity of dilution may be important in moderating toxicity. For all contaminants, the rate and degree of dilution will affect potential toxicity; for hydrocarbons, the rate of microbial consumption may also affect toxicity.

Clay particles from high sodium drilling fluids can remain in suspension in kettle ponds, directly impacting aquatic organisms by increasing pond turbidity and eventually coating periphyton and other food sources.

5.2.3 Groundwater-surface water interactions

When areas with a high water table have surficial material consisting primarily of gravel and sand, discharges to the ground surface may enter shallow groundwater aquifers. Additionally, contaminants that enter surface water may reach groundwater when surface water "recharges" aquifers during rain and snowmelt events. Contaminants entering deep groundwater aquifers may have no connection to surface water and thus not pose a biological risk. Groundwater feeds surface waters in the following ways:

- The phreatic zone is the subsurface region in which rock is saturated with water. Water from the phreatic zone of hills and mountains may travel long distances to discharge into valley streams.
- The hyporheic zone is groundwater that flows underneath a stream bed and exchanges freely with surface water. It provides vital habitat to sediment life and fish eggs due to oxygen and nutrient exchange. It also provides interstitial pathways below the stream bottom through which benthic life and fish fry may move when the stream itself is frozen solid.⁶⁸
- Springs and seeps are groundwater that "daylights" and may feed surface waters.
- Some kettle ponds are fed by groundwater; this is evidenced by ponds with vegetation at the water line year round. Kettle ponds fed by surface runoff dry up as runoff declines, and may have long banks of mud or soil between vegetation and the water line.⁶⁹

Therefore, contaminants entering soil and surface water have the potential to reach groundwater, and contaminants entering groundwater may reach soil and surface water. Contaminants that enter one surface water body may have the potential to be transported to another through groundwater, and contaminants entering groundwater may move into several surface water bodies, depending on the flow path.

Contaminants entering groundwater are subject to the same sorption, precipitation, and transformation reactions as contaminants entering surface water, as discussed above, although contaminants moving along groundwater flow paths through bedrock have little opportunity for sorption or precipitation.

A summary of transport interactions is shown in Figure 10.

⁶⁶ Total dissolved solids (TDS) are the sum of inorganic salts, organic matter, and other dissolved material; the toxicity is related to concentrations of potassium, calcium and other ions that change salinity.

⁶⁷ Stekoll et al 2003a, 2003b; Weber-Scannell and Duffy 2007

⁶⁸ Garrett et al 1998; Godin 1981

⁶⁹ Rains 2008

Source

Media

5.3 Advanced versus *de minimus* exploration on water resources ore processing

Discharges that are temporary and small in nature will affere receptors less than discharges that are larger and sustained over time. Drilling material will be discharged on Underground the drill hole is being developed, although discharge material has the potential to remain on site for long periods if not removed and has the potential to continue to contaminate the encirpotential by being carried on wind and by water. The mass of discharge material will not increase and exposure will generally be limited to the local area at the discharge point. Entry to surface water and shallow aquifers will be controlled by infiltration rates, rainfall and snowmelt events, and sorption/precipitation reactions. Small discharges expose the environment to smaller masses over shorter periods of time than larger or more constant discharges. Bioavailability to some material, such as hydrocarbons, is partly a function of the rate at which they are added to the environment and the rate at which they are degraded (e.g. by microbes) or removed (e.g. by surface runoff or wind).



Figure 10.Potential routes of
transport in
environmental media.of
transport in
Mapted fromWilkin 2000

Metals do not degrade; the total mass introduced, extent of area over which they are introduced (including dispersal by wind and water), length of time over which they are introduced, and environmental properties make them more or less bioavailable. Toxicity is a function of both exposure and the ability of an organism to eliminate the contaminant from its system or detoxify the contaminant.

Large scale discharges place more mass of material in a localized area over a longer period of time. Degradation and dispersal can be expected to take longer, and biota is exposed to more material over more time. Increased exposure can overwhelm an organism's detoxifying mechanisms, allowing the contaminant to bioaccumulate, potentially to toxic levels.

Deeper holes, a greater number of holes, and holes in close proximity to each other have the potential to magnify drilling contamination through both greater material discharge to the surface, opening of more sulfide rock to oxygen and oxygenated groundwater, and development of more potential pathways between aquifers. There is greater risk of acid rock drainage occurring, more paths for mobilized elements to move through, and higher potential to contaminate groundwater and impact aquatic life.

For instance, at the Pebble prospect, Cominco, during exploration 1987-1988, reported spacing their holes in Pebble West about 330-650' apart, and closer in high grade ore. Holes were relatively shallow at 330-650' deep, with only 5 greater than 900'.⁷⁰ Cominco also explored outside Pebble West, south of the deposit and between the South Fork and Upper Talarik (Sill Prospect) although holes were more sparse. After Cominco, Northern Dynasty Minerals (NDM)⁷¹ extended the drilling east and along the South Fork (32, 38, 55 zones)⁷² and drilled deeper, to 2000' in the West zone and to over 6000' in the East zone.⁷³

⁷⁰ Rebagliati et al 2009 Section 13.1; Rebagliati and Payne 2005

⁷¹ NDM obtained the mining claims from Cominco in 2002. In 2007, NDM joined with Anglo-American to form the Pebble Limited Partnership (PLP). In this review, activity conducted by NDM prior to 2007 is often lumped in with activity conducted after PLP formed and referred to as PLP activity.

 $^{^{72}}$ The 37 zone appears as the 32 zone, the 55 zone as the 66 or 52 zones in different publications.

⁷³ Rebagliati et al 2008

By the end of 2008, the Pebble deposit was drilled intensively, with 1125 holes (Table 2 and Attachment 6),⁷⁴ and permits allowed drilling to as deep as 7,000'.⁷⁵ PLP considers the property "open" to the northwest, south, east and southeast, meaning drilling could continue in the future in those directions.⁷⁶

Drilling in 2004 represented a considerable increase in activities. Exploration drilling was increased from 20-40 holes a year to over 250. The increase in depth is significant. This is dramatized by the addition, in every year from 2003 on, of cumulative drilling distance exceeding what Cominco drilled in ten years of exploration; in each of 2007 and 2008, cumulative drilling distances were twice what Cominco achieved in ten years.

Actual impact of these larger scale discharges would be dependent on dilution and sorption/precipitation effects, and access of contaminated groundwater to surface water or the hyporheic zone where aquatic life is present.

Table 5. Exploration holes at the Pebble deposit. Available information reveals over 160 cumulative miles of holes were drilled 1988-2008. The term "cores" as used below refers to holes drilled to delineate the resource; metallurgical drilling obtains samples to test resource concentration; geotechnical drilling fractures, density, etc.; environmental drilling installs wells to determine water quality and flow. Data are taken from Technical Reports; however the sum of reported wells does not add up to the total well sum (1125) listed in Table 13.1 of Rebagliati et al 2009, although the meter length does sum correctly. They list NDM/PLP as having drilled 450 holes within the deposit and 511 outside the deposit while Cominco drilled 117 within the deposit and 47 outside the deposit. Sources: Rebagliati and Payne 2005, 2007; Rebagliati et al 2008, 2009. Cominco data is from Rebagliati and Payne 2005 Tables 6.1-6.3.

		No.	Cumulative	Cumulative	
Company	Drill dates	Holes	length (m)	length (miles)	Purpose
Cominco	1988	26	2,317	1.4	2 in Pebble deposit, 24 in Sill Prospect
Cominco	1989	27	2,256	1.4	7 in Pebble deposit, 15 in Sill
Cominco	1990	25	2,991	2	in Pebble deposit
Cominco	1991	48	8,414	5	in Pebble deposit
Cominco	1992	14	2,014	1	in Pebble deposit
Cominco	1993	4	382	0.2	outside Pebble deposit
Cominco	1997	20	4,479	3	in Pebble deposit
Cominco cumulative total	1988- 1997	47 117	3,905 18,702	2 12	outside the Pebble deposit inside Pebble deposit
NDM 2002		68	11,350	7	cores
NDM 2003		67	21,717	14	cores
					151 cores
	May Oct	250	E0 100	21	32 environmental
NDIVI 2004	May-Oct	259	50,199	51	50 geotechnical
					26 metallurgical
					20 cores
NDM 2005	April-Dec	45	23,180	14	15 geotechnical
					10 metallurgical
					17 cores
NDM 2006	April-Dec	50	23,930	15	14 environmental
					17 geotechnical
					37 exploration
NDM 2007	Feb-Dec	72	53,374	33	26 geotechnical
					9 metallurgical
					32 cores
		23/	54 645	3/	15 metal
1 El 2000		234	54,045	54	105 geotechnical
					82 environmental
Total		(1125)		162	
within deposit		567			
outside deposit		558			

SECTION B DETAILED SUBJECT MATTER

6.0 Assessing contamination of the natural environment at the Pebble prospect

As mentioned in the previous section, there was a significant increase in drilling intensity and depth in and after 2004, and much of the drilling is in close proximity to streams, tributaries, kettle ponds,⁷⁷ and lakes in an area with permeable soils and shallow aquifers. Because much of the mineral resource is associated with sulfidic rock, it is possible that many drill holes are undergoing acid rock reactions. Should an aquifer have access into and out of these holes, acid and associated cationic metals could move into the aquifer; this reaction could potentially continue on the scale of decades. In particular, holes that encounter artesian water could be subject to acid rock reactions and transport of contaminants.⁷⁸ Documents indicate that artesian water is encountered in exploratory holes, and that some core holes are left open as water sources for new drilling.⁷⁹

Additionally, the extensive drilling results in increased amounts of drilling muds to be discharged. These contain alkaline material and potentially sulfidic drill cuttings. Some documents specify these were to be discharged to upland tundra depressions⁸⁰ and over 100' away from fish-bearing water.⁸¹ The Corps of Engineers Nationwide Permit specifies that the minimum distance from a drill site to flowing water would be 100', and that drilling water discharge and blasting would occur 200' from flowing water.⁸² Documents also mention that "no bore runoff will be allowed to enter streams or wetlands",⁸³ however other documents indicated that drilling mud has entered water bodies.⁸⁴ In addition, because drilling rigs must have access to water and are therefore located proximate to water,⁸⁵ there is risk that both tundra and surface water resources could be contaminated. The 2008 USGS map shows some drilling may have occurred in water bodies (Figure 11).⁸⁶

6.1 Ability to determine actual site contamination using PLP baseline data

Collection of baseline environmental data for the purposes of characterizing the natural environment does not serve the same function as collecting data for the purposes of determining whether contamination has occurred due to exploration activities. The goal of environmental baseline data collection is to collect uncontaminated media and analyze for elements and compounds expected in the natural environment; the goal of contaminant assessment is to collect media proximate to potential sources and analyze for likely contaminants.

In order to determine whether contamination occurred or not, there need to be methods that identify a possible contamination source, identify potential pathways, and identify potential receptors. Additionally, lab analysis must be conducted on the potentially affected environmental media for the potential contaminants.

⁷⁷ The USGS maps produced in Fey et al 2008 and Fey et al 2009 provide a good indication of the proximity of drill holes to water bodies.

⁷⁸ Moran 2010

⁷⁹ ADNR Field Inspection Reports, July 2007; Crafford 2007

⁸⁰ ADNR Field Inspection Report April 2007; PLP Pebble Drilling Program Backgrounder 2009

⁸¹ Loeffler 2009; ADNR Field Inspection Report April 2007

⁸² Memo from Mike Smith of NDM to Don Kuhle, US Army Corps of Engineers, February 15 2006.

⁸³ PLP 2007 Plan of Operations Pebble Copper Project for permit #AO76118; PLP Pebble Drilling Program Backgrounder 2009

⁸⁴ ADNR Field Inspection Report July 2007; Fey et al 2009, Excel spreadsheet "FieldSite", USGS sites PB071, PB132

⁸⁵ Fey et al 2009 Excel spreadsheet "FieldSite"

⁸⁶ Fey et al 2008, maps 2007 sampling sites. The drill holes situated in lakes do not appear on the map of 2008 sampling sites.





Figure 11. Drilling proximity to Pebble lakes. The USGS plotted water bodies, drill holes, and USGS sampling locations. Shown above are subsets of the 2007 sampling map. (**Left**) the Lincoln Lakes (three large bodies near the bottom of the map) and (**above**) ponds near the discovery outcrop with drill hole locations that appear to be in water bodies, indicated by arrows. These sites are not shown on the map depicting 2008 sample locations. White dots are drill hole locations and black dots are USGS sample sites.

6.1.1 Ideal baseline data

The full data necessary to assess whether potential contamination of water resources has occurred at the Pebble prospect is not available. An ideal data set would define the natural background before anthropogenic activity, define potential sources of contamination, define potential receptors (e.g. insects, macroinvertebrates, fish, caribou, waterfowl, plants), define potential links between them, and monitor both source and receptor through the period of potential impact.⁸⁷

The first step would be to collect baseline data prior to extensive drilling to ensure true characterization of the natural environment, particularly on water resources, given that water resources are at risk with drilling operations. Surface water locations should be mapped and field notes should include information on depth, color, and basic field chemistry (pH, dissolved oxygen, temperature, specific conductance). Anomalies in readings that indicate potential groundwater intrusions should be noted. Samples should be collected from seeps, ponds, and tributaries from mineralized and un-mineralized areas, and analyzed for analytes that affect biotic life and ecosystem integrity such as nutrients (dissolved organic carbon, nitrogen compounds, phosphorous), cations, anions (particularly sulfate and sulfide), dissolved and total metals, sulfate, acidity, and alkalinity. Additionally, samples should be analyzed for chemical contaminants that could be released during exploration or mining, including cyanide, thiocyanate, fuel hydrocarbons and other organics. This should be done prior to deep drilling or significant density of drill holes.

Samples should be collected on a regular monthly basis from surface water to determine seasonal flux; on – site precipitation and any incidents, natural or anthropogenic, which could potentially affect the water chemistry should be noted in field books. Groundwater would be collected quarterly, except more frequently at sites where groundwater made significant contribution to surface streams or when sampling showed inconsistency, and should include the period of rapid snowmelt in regions where groundwater and surface water are closely linked. Particular care should be noted in the database. Groundwater color, turbidity, pH, dissolved oxygen, ORP, temperature, and specific conductivity data should be collected with every sample to determine if the nature of groundwater was changing, and if so, why.

This data should be correlated with hydrology studies to determine aquifer locations and pathways, and in particular surface water sites with significant groundwater contributions. Hydrology and chemistry should be followed at surface water and groundwater stations during and after drilling.

Additionally, environmental media (soil, sediment, water) should be collected as drill rigs are set up (prior to drilling), when the rig is removed, and downgradient of the drilling discharge location. These samples should be analyzed for possible contaminants in addition to the chemistry that all sites would be subject to. Dates of drill rig operation should be noted, and maps should include the location and dates of drill rigs, hole depth and depth of aquifers, locations of discharge sites, and locations of water sampling sites for spatial and temporal correlations with water quality.

Baseline environmental field sampling at Pebble could have been modified to include a contaminant impact and assessment data set to determine whether water resources were contaminated during exploration. This would include:

- Soil, sediment, and water samples taken downgradient of drilling discharge before and after drilling to assess whether chemical changes occurred in environmental media.
- Analysis of environmental media, including groundwater from monitoring wells, for potential contaminants not expected to be in the natural environment, such as fuel hydrocarbons, acrylamide, and other organic material found in drilling muds and additives.

⁸⁷ US EPA 1992; US EPA online training in watershed ecological risk management

- Measurements of water chemistry over a period of time while the drill hole is open would provide information on whether groundwater chemistry changed over time. Groundwater chemistry could be used in conjunction with elevation, topography, and hydrology to determine if surface water or hyporheic zone resources could potentially have been contaminated.
- A map with clear topographic markings of drill sites and discharge locations, with water bodies and surface water sampling sites also indicated.

Data that may have been collected at the Pebble site but have not been released to the public:

- Drilling logs and driller's field notes. These should contain the location coordinates, elevation, and dates of drilling. It is expected that most, if not all, drill holes would encounter groundwater, and logs should contain details of the depth of aquifers encountered and basic field chemistry (ORP, dissolved oxygen, pH, conductivity, temperature).
 - Dates of drilling and locations of discharge sites could be compared to dates of surface water sampling to determine if water samples near discharge or downgradient experienced changes in chemistry during drill dates.
 - Logs and field notes containing dates and methods of closing holes could be used to verify that holes were in fact closed, and whether they were sealed from top to bottom or not. These, however, should be corroborated with eyewitness accounts by regulators or independent third parties.
- Dates and locations of seismic runs, where explosives were used and at what depths has not been provided, and could be used to compare with dates and locations where high ammonia concentrations were observed.
- Results of seismic runs and drill logs and driller's field notes could indicate fractures or aquifers and be used to determine whether subsurface transport pathways exist that link groundwater and surface water at specific locations.
- Field parameters (basic field chemistry) for surface water have not been made available except for 2004.
- Field notes from surface water sampling crews could be compared with sites and dates in which unusual chemistry was observed to determine if natural events (bank sloughing, rainfall, salmon carcasses, etc) could explain the chemistry.

6.1.2 PLP's baseline data

Cominco conducted very little analysis of surface water, and to date no analysis of groundwater, drill holes, soil, or sediment has been provided and samples may not have been taken.

PLP conducted extensive environmental baseline studies, but it should be noted that these studies began in 2004, approximately 16 years after the first drilling was conducted, and during the year in which there was extensive drilling. It is possible that much of the media was collected during or after drilling in proximity to the sampling location.

PLP's baseline studies included hydrology, surface water chemistry, groundwater chemistry, and trace metals in soil and vegetation. Analysis was typical of what would be examined for natural baseline: total and dissolved metals, cations (e.g. calcium), anions (e.g. sulfate), alkalinity, hardness, specific conductivity, and other analytes. However, the data was not put into context: whether samples were collected from a mineralized area, the monthly precipitation, recent precipitation or changes in temperature in the days prior to sample collection, and other factors that affect water chemistry. PLP did analyze for nitrogen compounds associated with mining (cyanide, thiocyanate, and ammonia) and for phosphorous but not for dissolved organic carbon until 2007, nor was there any analysis for total organic carbon. There was virtually no analysis for fuel hydrocarbons or anthropogenic materials found in drilling mud breakdown products but not expected to be found in the natural environment. Basic

field chemistry may have been collected, but has not been made available since 2004 for surface water (it is available for groundwater).

Groundwater studies included samples from monitoring wells and groundwater seeps. Most monitoring wells were installed in 2004 and are usually sampled quarterly. Much of the seep sampling was conducted after 2005, after drilling had significantly increased. In the region between the South Fork Koktuli River and Upper Talarik Creek, seeps were sampled multiple times, but on the ore body, each seep has only one to three samples, all collected in or after October 2006 except Seep 11 was sampled once in 2004. Whether this is due to the ephemeral nature of seeps or for some other reason has not been stated. Data from seeps collected prior to extensive drilling and subsequently, particularly on the ore body, would provide critical information on whether the nature of the groundwater has changed over time.

Stream surface water sampling was conducted on the three main rivers – the South Fork Koktuli, North Fork Koktuli, and Upper Talarik Creek – and some of their tributaries as well as a single site on the Koktuli River (main stem) and Kaskanak Creek, near the southern border of the mining lease. Streams that did not directly border the mining lease – such as Lower Talarik Creek, Chulitna River, and Stuyahok River – had no surface water sampling. Some tributaries to the main streams were sampled, but small headwater streams do not appear to have been sampled. Most surface water sites were sampled monthly.

There was only very minimal water sampling of lakes and ponds -- each site had only one or two samples each, and no ponds on top of the main ore body were sampled by PLP.⁸⁸ Extensive, regular sampling of pond and lake water, similar to sampling conducted at stream sites, would be useful in determining whether contamination from exploration occurred, as ponds and lakes would be more likely to sequester material in sediments than fast-running streams.

Sediment chemistry sampling at pond and lake sites in the mine area was minimal, with minimal field parameter (e.g. pH) information, no information on sediment character (silt, sand, organic content) that affects transport and sequestration, and minimal analysis for fuel hydrocarbons. This is in stark contrast to samples from the port site and Lake Iliamna, in which all samples collected for trace elements testing were also submitted to full or partial fuel organics analysis.⁸⁹

Maps of surface water sites (Attachment 7), groundwater sample sites (Attachments 8 and 9), and drill holes were all separate, not inclusive. The only drill hole maps, prior to the release of the map by ADNR in 2010, could only be accessed through SEDAR technical reports. Additionally, maps were not produced with clear topographic gradients to assist with determining whether surface water or water sampling sites were downgradient of drilling, nor have drilling discharge sites been indicated on any map produced to date. A clear topographic map with surface water bodies clearly drawn became available when the USGS released their report on sampling at Pebble (Attachment 10).

In summary, an accurate determination of contamination or lack thereof would require:

• field parameter data for surface water sites after 2004

⁸⁸ The USGS did sample many of the ponds on the ore body (Fey et al 2008; Fey et al 2009).

⁸⁹ Although this review focuses on the exploration area, the road and port may impact the environment during and after construction. In order to obtain good baseline natural characterization, surface water, groundwater, and sediment should be characterized prior to activity. Along the road corridor, where fuel will be transported and releases will likely occur, only two soil samples were analyzed for RRO and DRO (no GRO or BTEX testing); and although 97 samples of sediment from the road corridor were submitted to trace elements testing, none were analyzed for organics. This is inadequate for understanding the range of organics found naturally in order to distinguish anthropogenic releases in the future.

- extensive pond and lake water analysis, prior to 2004 and subsequently
- distinction between soil and sediment in reports
- sediment data that includes field parameters prior to 2004 and subsequently; extensive organics analysis, including fuel; discussion of the makeup of sediment (sand, silt, organic content, etc) which affects transport and sequestration of metals⁹⁰
- drill logs or driller's notes, including dates of drilling, location of discharge sites, and in-hole chemistry
- mineralogical information at drilling locations and regarding soil near surface water sampling sites

6.2 Methods used

A literature review and mapping were conducted. The methods utilized in the analysis were to

- Compare pond water and pond sediment data available from PLP (samples collected 2004-2007) and USGS (samples collected 2007-2008) to determine whether drilling compounds could be detected.
- Examine the chemistry of surface water adjacent to drilling with surface water distant from drilling.
- Examine available data on monitoring well siting and water chemistry
 - to determine chemical anomalies in monitoring wells for which data was available.
 - to determine the distance between coring/geotechnical holes and monitoring wells
 - o determine elevation between coring/geotechnical holes towards the monitoring well
- Examine seep and spring data for changes over time or differences in seeps located near drill holes.

6.2.1 Available data

Literature reviewed included

- Cominco data 1991-1993 (ADNR File 1033. Date unknown)
- NDM draft baseline environmental studies posted on ADNR website <u>http://dnr.alaska.gov/mlw/mining/largemine/pebble/index.htm</u>
- Preliminary data posted on PLP website
 <u>http://www.pebblepartnership.com/pages/environment/environment-pre-permitting.php</u>
- USGS reports from sampling in the region and just north of the region (Fey et al 2008; Fey et al 2009; Brabets 2002; Brabets and Ourso 2006)
- Map of drill hole locations (ADNR 2010)
- Maps available from technical reports submitted to SEDAR (the Canadian Securities and Exchange Commission) (Rebagliati et al 2005, 2008, 2009)

The earliest surface water sampling and analyses were conducted by Cominco. Of 20 surface water sites, data for a suite of metals and cations are available for four, abbreviated analyses for five more, and no water chemistry was made available for 11 sites. No field parameters,⁹¹ driller's logs, organics analysis, or groundwater chemistry has been made available by Cominco.⁹² Ten surface water sites (Cominco 1-10) sampled bi-weekly in June and July 1991 were replaced by ten sites (Cominco 11-20) presumed to be

⁹⁰ PLP 2008 Pre-Permit Report E; Zamzow 2008

⁹¹ Field parameters include pH, dissolved oxygen, oxidation-reduction potential, specific conductance, and temperature usually collected with a hand-held meter.

⁹² Å 1994 Cominco report on surface water was made electronically available by ADNR for one day. It contained chain of custody sheets and lab tables. Data were missing for Cominco sites 1, 2, 3, 4, 5, 7, 10, 15, 16, 18, 19 and 20.
sampled monthly August 1991- November 1993 for fewer analytes.⁹³ Analytes at all sites had such high (insensitive) method reporting limits relative to current benchmark water quality criteria⁹⁴ that this information is not useful for comparison with current samples.

NDM obtained the mine claims in 2002 and collected surface water and groundwater beginning in 2004,⁹⁵ consistent with the period when drilling was rapidly intensified. Some surface water sites established by Cominco were relocated and more monitoring wells were installed near the proposed mine area. NDM's 2005 report contained water chemistry data including field parameters, but did not include information on replicates or lab quality controls.

The only water chemistry data available from mining companies after 2004 is a PLP publication of tables with no field parameter data, no information on replicates or lab quality control results, and no context for the analytical data.⁹⁶ Surface water sampling occurred at 41 stream and river sites, 19 ponds, and 125 seeps.⁹⁷

The USGS also collected surface water from streams, ponds, seeps, and soil in 2007 and 2008 in the Pebble lease area and had extensive metals analysis conducted, as well as basic field chemistry. The sampling of ponds within and surrounding the main ore body was much more extensive than the PLP database, although the PLP database contained more seeps.

Reports by the United States Geological Survey (USGS) examining streams in Lake Clark National Park, north of the Pebble prospect, were reviewed as references for regional water quality pertaining to ammonia.

PLP published preliminary data on its website that included maps of surface water sample sites, monitoring well and piezometer locations, and seep locations (Attachments 7-9). Maps of coring holes were contained in reports submitted to SEDAR, the Canadian Securities and Exchange commission; from annually submitted reports, the location of new drill holes installed between 2005 and 2008 could be determined. Lastly, the 2010 Alaska Department of Natural Resources map with all drill holes was reviewed (Attachment 6), identified by year of installation, but this was not accompanied by a spreadsheet of coordinates and elevation; some coordinates are available in PLP's Pre-Permit Report D.

Drilling logs, driller's field notes, and chemistry in drill holes has not been made publically available. All existing hydrologic information was not examined for this report.

7.0 Evidence of contamination

7.1 Fuel

Exploratory holes are made using drill rigs, each of which requires up to 200 gallons of diesel per day for 24 hour drilling. Six to nine drills operated in 2007, requiring 1200 - 1800 gallons of fuel each day. Fuel deliveries were by float plane or helicopter to a lake just north of the deposit (Wiggly Lakes) each

⁹³ During the first two months: total Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Hg, Ni, Se, Ag, Th, V, Z, Ca, Mg, Na, K, CN. Later samples: total As, Ba, Cd, Cu, Pb, Hg, Mo, P, Se, Ag, Ca, CN. No dissolved metals, organics, nitrates, or ammonia.

⁹⁴ The term "benchmark criteria" is used to refer to the most stringent water quality standards that could apply.

⁹⁵ Groundwater: 11 separate locations for wells, or 21 sites if including shallow, medium, and deep screens as separate sites. Surface water: 5 sites at North Fork Koktuli, 12 at South Fork Koktuli, 10 at Upper Talarik, 1 at Kaskanak Creek, and 1 at the Koktuli River below the confluence of North and South Forks.

⁹⁶ Pebble Partnership 2008. Pre-Permit Report F

⁹⁷ ibid

carrying 100-200 gallons/trip.⁹⁸ All fuel was stored on-site in double-walled structures with berms surrounding the fuel area, and fuel containment is to be at least 100' from water bodies.⁹⁹ However, spills occur due to human error and have been documented in ADNR Field Inspection reports at the Pebble exploration site, as have hydraulic fluid spills. To date, reported spills have been from 1.5 to 30 gallons.¹⁰⁰

Contamination of water due to fuel contamination could not be assessed in that samples were only analyzed once for hydrocarbons, and there has been no regular monthly or quarterly monitoring of hydrocarbons in surface water, groundwater, vegetation, or sediment at any location, including sites downgradient of spills documented by ADNR. A frequent, consistent inspection program might have provided more evidence of spills, and sampling near spill sites would provide information on the extent of contamination.

7.2 Drilling discharge

Discharged drilling material has the potential to contaminate tundra and surface water bodies downgradient that received material flowing on the surface or in alluvial material just under the surface. Contamination and impacts could potentially occur through introduction of salts, ammonia, and petroleum or changes in pH and alkalinity. The petroleum distillate that is a constituent of drilling muds can be directly toxic,¹⁰¹ and potentially can stimulate bacterial growth, leading to low dissolved oxygen and potentially changing the redox environment to allow metals to become mobile – metals and low oxygen represent possible toxicity.

At the Pebble prospect, the federal US Army Corps of Engineers Nationwide Permit may require that drilling "water" be discharged within 100' of flowing water, and drill rigs must be at least 100' away from water bodies, ¹⁰² but the state permit does not appear to have any such stipulation.¹⁰³ Documents state that discharges are made to tundra depressions or to sump pits in order to prevent entry to surface water (Figure 12). Where discharge is allowed to stream onto the ground, rather than move through a sump pit, sediment can be dislodged into streams and ponds. Sediment can carry metals, and fine sediment can smother fish eggs.

7.2.1 Physical evidence

The USGS noted at least two ponds that appeared to have received drilling mud, and several others had the potential to be contaminated due to the proximity of drill rigs.¹⁰⁴ Additionally, ADNR photos show that discharges have been made close to water bodies, although reportedly PLP personnel use straw bales to prevent entry (Figure 13).¹⁰⁵ Discharge may disappear quickly into the tundra. Whether the discharged material remains in the soil or moves through shallow aquifers has not been determined; nearby water bodies and sediment are not tested for drilling mud chemical constituents – such as barium, ammonia, or hydrocarbons – to determine if drilling discharge has reached them.

Drilling muds can be re-circulated to decrease water withdrawal and reduce discharges to the ground, but even when such re-circulation methods were utilized inspection reports have noted drilling muds

¹⁰⁰ DEC Spill report information, SOA 023097-099 and SOA 023036-38, Nunamta Aulukestaii v State AN0909137; see also ADNR field inspection reports <u>http://dnr.alaska.gov/mlw/mining/largemine/pebble/reports.htm</u>

http://ADNR.alaska.gov/mlw/mining/largemine/pebble/fieldreports/pebble102808.pdf

⁹⁸ Fuel information from Brommeland 2007

⁹⁹ ADNR 2009a; PLP 2007 Plan of Operations Pebble Copper Project for permit #AO76118

¹⁰¹ Loeffler 2009

¹⁰² Memo from Mike Smith of NDM to Don Kuhle, US Army Corps of Engineers, February 15 2006

¹⁰³ ADNR 2009a

¹⁰⁴ Fey et al et al 2009

¹⁰⁵ ADNR Field Inspection Report October 28-29 2008

overflowing re-circulation tanks (Figure 14). As of October 2008, PLP was reportedly re-circulating drilling mud, and ADNR was suggesting a discussion on the relative merits of re-circulation versus direct discharge to ground.¹⁰⁶



Figure 12. Discharge to sump pits (top) or ground depression (bottom). Photos from ADNR Inspection Report October 2008 <u>http://ADNR.alaska.gov/mlw/mining/largemine/pebble/fieldreports/pebble102</u> <u>808.pdf</u>

¹⁰⁶ ADNR Field Inspection Report October 28-29 2008



Figure 13. Discharge flowing **toward pond.** Dark stains are discharge that has turned to ice. Photo from October 2008 ADNR Field Inspection Report. http://ADNR.al aska.gov/mlw/ mining/largemi ne/pebble/fieldr eports/pebble1 02808.pdf



Figure 14. Drilling mud overflowing re-circulation tank. Photo from October 2008 ADNR Field Inspection Report. http://ADNR.alaska.gov/mlw/mi ning/largemine/pebble/fieldrepo rts/pebble102808.pdf

7.2.2 Chemical Evidence

There is no pre-drilling data on pond and stream water and sediment, nor have any ponds or streams on the ore body – where the densest drilling has occurred – had water or sediment analyzed for fuels, polyacrylamide, DEA, or acrylamide, it is not possible to definitively identify by chemistry water bodies that drilling mud has entered or whether these bodies have been chemically altered. Anomalies in pond and stream water and sediment chemistry that may represent changes in water quality initiated by exploration are discussed in the next section.

7.3 Anomalies in surface water chemistry

Surface and groundwater throughout the mining claims area are pure: cold (less than 10 °C), with high oxygen content, low alkalinity, low mineral concentrations, and very low conductivity.¹⁰⁷ This is the condition for surface water throughout the claims area and for groundwater outside the mineral deposit site.¹⁰⁸ In waters this pure, introduction of contaminants may easily change water chemistry.

Water bodies located spatially and temporally near exploration activities are the best candidates for assessing potential contamination, although assessment of acid drainage may take longer because it may take several years to develop. Publicly available data on surface water sites - including ponds, lakes, and streams – were assessed for spatial and temporal association with drilling. This method was necessarily imprecise in that no map containing both water sampling sites and drill hole or drill discharge locations was available, nor was there information on hydrologic gradients at drill discharge locations. The USGS report noted specifically when drilling, either old or active, occurred near surface water and often noted whether the drilling was upgradient and/or the number of feet between the drill hole and the water body. PLP reports did not provide this information. To determine spatial association, maps in PLP preliminary reports showing sample sites were compared with the ADNR map showing drill hole sites; this, therefore, provides only a rough estimate of distance.

I limited my review to drill sites within 500 m of surface water bodies. Although drill rigs need to be located in close proximity to water, most surface water sample sites on the North Fork and South Fork Koktuli Rivers, and all sites on the lower section of Upper Talarik Creek appeared to be greater than 500 m from drill holes. This again highlights the difference in the manner in which sampling plans are designed – baseline water samples are likely to be collected away from drilling, while contaminant assessment studies should collect water, soil, and sediment in the drilling vicinity. The exceptions to the proximity of baseline surface water sample sites and drill locations were on South Fork Koktuli river tributaries at the south border of the ore deposit (SK136A, SK136B, and SK131A), each with a couple of drill holes nearby and on a single North Fork Koktuli river tributary (NK119A and NK119B, stream sites near geotechnical holes).

This review of surface water focused on the water and sediment chemical character of ponds inside and outside the ore body, where the greatest concentration of drilling occurred, and some adjacent surface water sites on the upper section of Upper Talarik Creek that had sample sites near drilling (within 500 m, or within 1 km of several drill holes) compared to some greater than 1 km from drilling.

7.3.1 Historical water quality

An attempt was made to compare Cominco water data to more recent data (PLP 2004-2007) but, in addition to the difficulties that were expected in disentangling natural variability from anthropogenic influence, so much information was lacking that no conclusions could be made regarding water chemistry between 1990 and 2008 and potential long term changes over time.

¹⁰⁷ Data from PLP 2008 Pre-Permit Report F

¹⁰⁸ "Mineral deposit site" refers to the location where an open pit and underground mining would likely occur. It does not refer to the broader claims area.

- No data is available for most of the Cominco sites.
- Cominco only measured total, not dissolved, metals.
- Cominco did not analyze for several metals commonly found above detection limit such as aluminum, iron, and manganese.
- Reporting limits used by Cominco for trace metals such as copper were higher than current reporting limits and benchmark criteria, so that comparison of trace metal concentrations were of limited use.
- Often barium was the only analyte Cominco detected.
- Cominco did not sample ponds and seeps.

7.3.2 Pond and lake sediment and water

Ponds are less likely to flush contaminants than streams are. Sediments and pond water data were reviewed for barium, sulfate, calcium, sodium, and copper as indicators of drilling discharge.

The majority of exploratory drilling occurred at the mineral deposit site, but PLP did not sample the numerous ponds at Pebble West and Pebble East. The only pond samples collected near the main ore body were upgradient of the majority of drilling, on the southwest border of the ore deposit (Figures 15, 16, and Attachment 7), sample sites WLP01, 28B2, and 28B1. The precise location of the ponds with respect to drill holes is difficult to determine in that no single map marked both pond sample sites and drill holes.¹⁰⁹ The USGS collected samples from several ponds within the main ore body (Attachment 10). Because USGS did not collect pond samples until 2008, there is no pre-drilling data.

The location of ponds and surface water sites in relation to mineralized areas is important, as the chemistry from natural mineralization can mimic some contamination from drilling in mineralized areas.

Only five pond sample sites sampled by PLP appeared to be located within 500 m of drilling (Table 6), and actual proximity of ponds to drilling discharge could not be determined through the public data available. Only pond site 335133 appeared to have pre- and post-drilling data (Table 7).

¹⁰⁹ Coordinates for surface water stream sites are available in 2008 PLP Pre-Permit Report B, and most drill hole coordinates are available in PLP Pre-Permit Report D, but no such coordinates could be located for ponds.



Figure 15. PLP surface water sampling sites near the main ore body in relation to USGS sample sites. The map is from the USGS 2009 report regarding USGS sampling at Pebble. A larger version is attached at the end of this report. The USGS sampled most water bodies on the ore deposit (small black labels). PLP only sampled 3 ponds in the southwest corner of Pebble West (WLP01, 28B1, 28B2 - these were actually considered to be outside the Pebble West area when sampled) and one stream (SK136B). Four other streams close to the ore body and sampled by PLP are shown in call-out labels. Data is from Fey et al 2009 and from PLP 2008 Pre-Permit Report F. Locations of PLP sites are estimated based on maps in that report.



Figure 16. PLP pond and stream samples near the ore body in relation to drill holes. (Top) The top map is taken from PLP 2008 Pre-Permit Report F published on their website. Pond sites are WL-P01, 28B2, and 28B1; the other sample sites are on streams. The light outline is the general outline of the ore body. The dotted box indicates the approximate region as shown on the ADNR drill hole map (bottom). On the drill hole map, monitoring well labels are outlined with a rectangular box. The figures illustrate the difficulty of locating water sampling sites relative to drill sites.

Table 6. Pond sample sites and spatial association with drill holes. All ponds from which PLP collected samples were reviewed for spatial proximity to drill rig locations. Spatial association is tentative, in that discharge site coordinates have not provided, nor has a map with drill sites, discharge sites and surface water bodies been provided, nor is the hydrologic gradient that may provide a flow path available. Spatial distances estimated by comparing the map of surface water sites on PLP's website (Pre-Permit Report F) and the 2010 ADNR drill hole map.

Region	Pond Name	Near drilling?
North of ore body	Black Lake	
	Lilly Lake	
	TPS4	
	Wiggly Lake	
	TPS3	
	TPS1	
Headwaters of the North Fork Koktuli	TPS2	
Upper section, Upper Talarik Creek	335133	x
Lower section, Upper Talarik	TPS5	
Creek	TPS6	
	TPS7	
	TPS8	
Ore body	WL-P01	х
	28B2	х
	28B1	х
Upper section, South Fork	Frying Pan	
Koktuli	WL-S04D	x
South of South Fork Koktuli	Chiquita Lake	
	Lake 2	

Table 7. Pond sample sites and temporal relation to drill holes. Ponds PLP sampled and that were potentially located near drilling are listed below. Temporal association is tentative, as the dates of drilling have not been made publicly available. Holes GH-04-27, GH-05-58, 121, and 9464 are up on Kaskanak Mountain, and may or may not be along a flow path towards ponds. GH = geotechnical hole, P = piezometer, water = water sample sediment = sediment sample, labels without alphabetical identifiers are presumed to be core holes. Only sample sites that appear to be near drill holes are shown in the table. Table developed through analysis of PLP's 2008 Pre-Permit Report F and the ADNR 2010 drill hole map.

Site	2003	2004	2005	2006	2007	2008
WL-P01	2003_470', 2001_301',	GH-04-27_129'	GH-05-58_155', P-05_07S_78', P-	water, sediment	water, sediment	121_500', 9464_1070'
28B2	2022_410', 4304_1000',		05-07D,_213'	water	water, sediment	
28B1	3124_1318'			water	water, sediment	
335133				water	P-07-46D water, sediment	
WL-S04D		GH-04-29_45', GH- 04_29A_159'	P-05-26S_30', P- 05_26M_80', P-05- 26D_130'	water, sediment		

Pond water. There are some indications of acid drainage in Pebble West. There are also at least two sites located near the ore body that chemical analysis indicates may have been contaminated by drilling mud, and one that is outside the ore body but near drilling. Pre-drilling data is needed to confirm whether contamination has occurred.

The USGS noted in its water samples which sites may have been contaminated by drilling through observation of drilling mud in water bodies and the location of drill rigs near water bodies. USGS analyzed water from several ponds, and only a subset is presented in the table below. The full data is available at Fey et al 2009 and Fey et al 2008. PLP and USGS did not analyze pond water for fuel hydrocarbons or drilling product organics.

Although visually there was evidence of drilling mud in ponds PB132 and PB139, the chemistry did not indicate contamination with cations and metals/metalloids: alkalinity, in fact, was low rather than elevated while sulfate, sodium, and barium were at the low levels normally found in the region (Table 8).

Some sites indicated acid drainage. Ponds PB254, 255, 256, 130, and 131 had high sulfate, acidity, cadmium, copper, manganese, zinc, nickel, potassium, and rare earth elements. Ponds sampled in 2007 in this location (PB025, PB026) were acidic (pH 4- 4.8) and warm (17 °C), indicating a possible geothermal source. They had, in addition to chemistry similar to PB254 et al, elevated cobalt, iron, manganese, aluminum, and barium. Pond PB070 due south of the acidic ponds, had chemistry similar to PB025 and PB026.

These sites are the only sites of those sampled by the USGS to have acidic, high dissolved metal chemistry typical of acid rock drainage. Except for PB070, these sites are all in an area of the discovery outcrop. Oxidation of pyritic material on the surface accounts for at least some of the chemistry. However, the area has been densely drilled and contains historical drill holes; the possibility that drilling has caused or exacerbated the poor water quality should be considered. Sites at adjacent ponds (PB133, PB134) do not have acid drainage; it is difficult to tell from the maps, but it appears that PB133 and PB134 are not located directly in the midst of dense drilling as the others are. Without pre-drilling data, it is not possible to confirm whether acid at any of the sites developed or was exacerbated due to drilling.

Of the five PLP-sampled ponds near drilling, 28B1, 28B2, and WL-P01 were near, but not actually in, Pebble West. Alkalinity was higher than in USGS sites noted as potentially contaminated with drilling muds, and generally higher than USGS pristine sites as well. Pond sites 28B1 and 28B2 had chemistry that is more indicative of exposure to drilling material than the USGS-noted ponds. However, the chemistry may also be a result of natural geologic material. It is not known whether theses water bodies are on located on a mineralized surface or not, nor their proximity to drilling discharge sites.

- All three ponds had copper and molybdenum significantly above the median for other ponds sampled by PLP; this may indicate the ponds are located in a mineralized area.
- Site 28B1 stands out as having elevated salts (sulfate, barium, calcium, sodium) and metals (copper, manganese) in water with respect to the median for all ponds sampled by PLP. High salts indicate a possible contamination from drilling muds.
- Site 28B2 had high alkalinity and sulfate relative to concentrations found at most Pebble sites and high iron and manganese which could indicate microbial activity, potentially induced by drilling additives. The ORP measurements that would verify this were not available, nor were field notes that could indicate whether drilling material or fuels which provide a carbon source could have entered the water body.
- Only copper and molybdenum were elevated relative to most ponds; other metals that could be mobilized by high or low pH were not elevated and neither sulfate, alkalinity, calcium, nor

sodium were elevated, indicating that neither bentonite, cement, nor acid drainage had contaminated the site.

Table 8. Pond water chemistry for Pebble West. A subset of the full data is presented, focusing on analytes that could inform whether sites were impacted by bacterial activity, introduction of alkaline material, or acid drainage. Blue shading indicates unusual chemistry. All metals are in the dissolved (filtered) form. Note that metals in the USGS data set were analyzed with high resolution ICP-MS; PLP data was analyzed with low resolution ICP-MS. USGS data is from Fey et al 2009 and Fey et al 2008; PLP data from PLP 2008 Pre-Permit Report F; all PLP data is preliminary and subject to change.

Pebble West, USGS data	Sites	рН	Alkalinity (mg/L)	Sulfate (mg/L)	Barium (ug/L)	Sodium (mg/L)	Fe (ug/L)	Mn (ug/L)	As (ug/L)	Mo (ug/L)	Cu (ug/L)
Possible drill	PB139	6.6	4	1	2	0.5	7	1	<0.04	0.04	0.9
mud contamination	PB132	5.9	3	2	2	0.3	13	5	<0.04	0.02	2
	PB130	3.6	nd	69	19	3	202	139	0.31	0.39	505
	PB131	4.5	nd	46	26	3	23	161	0.18	0.01	360
	PB133	6.1	4	1	3	0.4	21	4	<004	0.01	0.2
North of	PB134	6	7	2	4	0.8	108	3	<004	0.01	0.2
discovery	PB025	4.1	nd	85	26	3	161	445	<004	0.01	661
outcrop	PB026	4.8	nd	58	26	3	50	444	<004	0.01	240
	PB254	5.4	1	56	31	3	38	466	0.25	0.02	289
	PB255	4.4	1	60	30	3	67	531	0.29	0.01	306
	PB256	4.6	1	44	25	3	30	158	0.20	0.01	337
Other ponds	P070	5.8	5	63	28	4	58	81	0.07	0.07	49
anomalous	PB154	6.1	22	2	11	2	4440	176	0.26	0.23	1
water chemistry	PB158	6.5	15	2	6	3	2700	42	<0.04	0.23	2
	PB160	7.1	9	3	4	1	149	3	<0.04	1	4
Pristine	PB184	6.6	13	16	4	3	25	1	0.11	0.17	1
	PB185	6.2	nd	6	9	4	316	44	0.21	0.71	1
PLP data											
Ponds near	WL- P01	nd	18	5	5	2	137	12	0.4	1	3
Pebble West	28B2	nd	31	13	7	3	507	170	0.3	1	1
	28B1	nd	19	46	13	5	172	87	0.3	1	1
All other ponds (median/max)		nd	16/31	3/11	3/14	2/5	67/444	9/74	0.3	0.2/1.6	0.3/2

In pond water from Pebble East, alkalinity was generally higher than at Pebble West, sulfate lower, and copper lower, which is consistent with the Pebble West surface mineralization.

In the USGS field notes, no ponds were observed to have drilling mud in them at Pebble East. In 2007, the only water collected in Pebble East was from two seeps, one "groundwater flow" (spring?) and a stream. The highest alkalinity observed in all water samples collected that year was in the groundwater

flow (PB129, alkalinity 112 mg/L as CaCO₃); the other seep and the stream also had some of the highest alkalinities observed. In 2008, the only water sampled in Pebble East was from drill holes (PB191, 203, 219) and four ponds (PB138, 140, 141, 202). Three ponds had the low alkalinity typical of Pebble region waters (7-15 mg/L as CaCO₃) while one (PB202) had relatively high alkalinity. None had chemistry indicating contamination from drilling discharge or acid rock reactions. Only PB202 chemistry is shown in Table 9.

Table 9. Pond water chemistry at Pebble East and outside the ore body. A subset of the full data is presented, focusing on analytes that could inform whether sites were influenced by bacterial activity, introduction of alkaline material, or acid drainage. Shading indicates high or low concentrations. All metals are in the dissolved (filtered) form. Note that metals in the USGS data set were analyzed with high resolution ICP-MS; PLP data was analyzed with low resolution ICP-MS. USGS data is from Fey et al 2009; PLP data from PLP 2008 Pre-Permit Report F; all PLP data is preliminary and subject to change.

Pebble East, USGS data	Sites	рН	Alkalinity (mg/L)	Sulfate (mg/L)	Barium (ug/L)	Sodium (mg/L)	Fe (ug/L)	Mn (ug/L)	As (ug/L)	Cu (ug/L)
Pond inside Pebble East	PB202	6.7	35	0	10	3	365	7	0.3	0.2
Ponds just	PB145	6.7	11	3	2	2	12	1	<0.04	0.2
outside Pebble East	PB146	6.7	15	2	3	2	12	1	<0.04	0.2
PLP, Ponds r	near drillin	g								
outside Pe	bble West									
Near drilling	335133	nd	49	0.3	7	11	1445	19	1	2
(medians)	WL- SO4D	nd	2	0.5	1	0.5	21	2	0.2	0.4
Pristine (median/max)	all others	nd	16/31	3/11	3/14	2/5	67/444	9/74	0.3/7	0.3/4

Of the PLP sites in Pebble East, pond 331533 is the only one with possible pre- and post-drilling data. A single water sample was collected in 2006, and another in 2007, the same year a piezometer was installed nearby, although it is not clear if the water was collected prior to well installation. There were no other drill holes nearby. Most noticeable about this site is the high sodium, alkalinity, iron, manganese, and copper. The 2006 sample was higher in sodium than all other sites at 8580 mg/L, and it increased to 12,700 mg/L in 2007, significantly higher than the median of 2070 mg/L. There is no historical chain of sampling that would allow assessment of seasonal changes or a burden of evidence prior to drilling to determine that the water was naturally high in sodium.

Water at site WL-S04D, located on the northern reaches of the South Fork Koktuli, was notable for very low constituents, e.g. alkalinity at 2 mg/L. This does not appear to be an acid drainage site, as acidity is not elevated, and sulfate and metals are quite low.

Together, the information tells us that the sulfidic surficial nature of Pebble West is likely to cause ponds to have lower alkalinity and pH than ponds in Pebble East. However, only four ponds in Pebble East were sampled. Barium, sulfate, and metals were elevated in a set of ponds in a small area of Pebble West. They are potentially influenced by a geothermal source (two had high temperatures) and by runoff over the sulfidic surface. It is possible that intensive drilling in the area has exacerbated some of the chemistry; pre-exploratin data would be required to properly assess potential contamination. **Pond sediment.** Because there were no pre-drilling samples, few samples of any kind, and no testing for hydrocarbons, it is not possible to determine whether the elevated barium and sodium observed in some sediment was related to exploration.

Acidic ponds in Pebble West had elevated barium and sulfate in both sediment and water. Sediment was only collected after drilling occurred. No sediment was tested for organics such as diesel, benzene, or other fuel-related hydrocarbons. According to PLP data, sediment at Pond 28B1 (just southwest of Pebble West) was elevated in sulfate, barium, copper, and manganese; again, pre-drilling data is needed for comparison.

The USGS did not take sulfate measurements in sediment, so it cannot be compared with PLP data. Many ponds in Pebble West (Table 10), and all sampled ponds in Pebble East (Table 11, pond PB202 only), had high barium concentrations. This likely indicates that barium is naturally elevated in soil, rather than a drilling discharge contaminant. The "pristine" sites used in comparison were located, respectively, south of the ore body (PB160) and at ponds north of the ore body, just west of Upper Talarik headwaters (PB184, 185). Site PB160 had significantly higher copper, arsenic and molybdenum, in addition to the elevated barium, and should be investigated further to determine whether it is un-contaminated. There is no pre-drilling data, nor was sediment tested directly for organics, which would directly verify or dismiss whether drilling mud contamination was present.

Table 10. Pond sediment chemistry at Pebble West. A subset of the full data is presented; shading represents high concentrations of elements. Elements as average crustal abundance are: barium 250 mg/kg, copper 70 mg/kg, iron 50,000 mg/kg, zinc 132 mg/kg, and arsenic 5 mg/kg. All metals are in the dissolved (filtered) form. Note that metals in the USGS data set were analyzed with high resolution ICP-MS; PLP data was analyzed with low resolution ICP-MS.USGS data is from Fey et al 2009; PLP data from PLP 2008 Pre-Permit Report E; all PLP data is preliminary and subject to change.

Pebble West, USGS data	Sites	Sulfate (mg/kg)	Barium (mg/kg)	Copper (mg/kg)	Iron (mg/kg)	Zinc (mg/kg)	Arsenic (mg/kg)
Possible	PB139	nd	820	26	50,000	86	11
with drilling mud	PB132	nd	856	31	45,000	89	8
Sites identified	PB131	nd 755 272 28,000		28,000	53	8	
with high sulfate	PB254	nd	611	744	55,000	86	17
and barium in	PB255	nd	719	292	44,000	67	9
water	PB256	nd	662	703	44,000	59	13
Just north of	PB133	nd	795	18	51,000	87	10
sulfate/barium water	PB134	nd	836	11	58,000	74	9
	PB160	nd	815	228	50,000	84	23
Pristine	PB184	nd	713	21	29,000	63	4
	PB185	nd	117	19	12,000	23	6
PLP data							
	WL-P01	13	157	73	38,000	50	18
Ponds near Pebble Wes t	28B2	700	190	81	81,000	75	16
	28B1	171	150	92	25,000	71	11

Table 11. Pond sediment chemistry at Pebble East and outside the ore body. A subset of the full data is presented. Shading indicates high concentrations relative to average crustal abundance and relative to what is usually found in the Pebble region. USGS data is from Fey et al 2009; PLP data from PLP 2008 Pre-Permit Report E; all PLP data is preliminary and subject to change.

Pebble East,	Sites	Sulfate	Barium	Copper (mg/kg)	Iron (mg/kg)	Zinc (mg/kg)
Possibly contaminated (near PB203)	PB202	nd	nd	nd	nd	nd
Drictino	PB145	nd	671	14	38,000	67
Pristille	PB146	nd	595	19	43,000	81
PLP data						
Ponds near drilling outside	335133 (median)	13	150	20	28,000	76
Pebble West	WL-SO4D (median)	4	53	13	16,000	47
Pristine	all others (median/max)	7/150	62/170	8/35	14,000/49,000	37/88

7.3.3 Stream sediment and water

In addition to water and sediment from ponds, data from streams near the ore body – sites UT141A, UT146A, UT100E, SK136A, and SK136B – were examined (Tables 12-14). A tributary to the North Fork Koktuli with geotechnical holes (GH) near sampling sites was also included in this analysis. Site NK119A, furthest upstream, had one GH within 500 m, two within 800 m, and 5 within 1.5 km, all upgradient.¹¹⁰ Site NK119B, downstream, did not have drilling near it, except one piezometer set installed in 2007 about 1 km away.

The USGS took only a few stream samples, and this data was not included in the review.

After review, no definitive conclusions can be made as to whether exploration contaminated stream sites. No data from streams near intensive drilling were available.

- Drilling occurred near the main stem Upper Talarik site UT100E in 2002-2003, and the highest barium in sediments at this site was observed in May 2004; however, site UT100D, which had no drilling near it, had barium levels similar to UT100E in 2004. Barium may be found in drilling additives and in blasting material and in natural rock; the data examined was not enough to determine the source of the barium.
- A comparison of water chemistry at UT146A before and after the single piezometer well near the site was installed did not show a change in water chemistry. However, the single piezometer would not be representative of the possible contamination to a stream located near several deep core holes. Sediment was collected in 2004, but not in later years. Several deep core holes were drilled near UT146A in 2008; if water or sediment samples were collected in 2008 and 2009, the

¹¹⁰ The following geotechnical holes appear to be within 1 mile of NK119A: GH-06-67_123', GH-06-68 119', GH-07-082 215', GH-07-085 155', GH-08-136 120'; more are located further upgradient

data has not been made available. Due to the number and depth of the holes near the stream site, post-drilling data would be informative as to whether drilling has the potential to contaminate streams.

- Water and sediment collected at UT141A before and after two core holes and a piezometer set were drilled also did not show a change in chemistry, but most of the drilling near this site occurred in 2008 and no chemistry data has been made available since 2007.
- SK-136B had no samples prior to drilling
- SK-136A and SK-134A had samples prior to drilling but no data after drilling has been made available.
- NK-119A and NK-119B had similar medians for analytes in water, but NK-119A had stronger fluctuations. In particular, there was an increase in February 2006 at NK-119A in sulfate, TDS, conductivity, hardness; barium, calcium, magnesium, and sodium; total aluminum, copper, and lead; and total and dissolved cobalt, iron, manganese, nickel, and zinc. Although salts are expected to be highest in mid-winter, the concentrations were above any observed in other years. Additionally, while total metal concentrations can increase due to dust and sediment, there was also an increase in dissolved concentrations of metals. Again, it is not possible to determine if exploration influenced the chemistry. The spike in analytes in February 2006 was not sustained over time. No water samples were taken at NK-119B in 2006, so chemistry cannot be compared.
- Sediment at NK-119A was significantly elevated in copper; no sediment was collected at NK-119B. Sediment at NK-119A was also elevated in mercury and potassium compared to other NK sites for which sediment data was available, and had high concentrations of manganese and zinc in the first sample collected.

Table 12. Stream sample sites and temporal relation to drilling. The map of surface water sites in the PLP Pre-Permit Report F was compared with the ADNR 2010 drill hole map to estimate sites that might be near drilling. However, actual drilling discharge locations, as well as dates of drilling, have not been made public.: Sites potentially near drilling on the Upper Talarik include UT-100E, UT-146A, and UT-141A. Sites UT-100D and UT-138A, also located on the upper reaches of Upper Talarik Creek, were used as reference sites for comparison. NK-119A was on a tributary of the North Fork Koktuli and near geotechnical holes; NK-119B was downstream and not near drilling. PLP data from PLP 2008 Pre-Permit Report F; all PLP data is preliminary and subject to change.

Site	pre-2004	2004	2005	2006	2007	2008	2009
UT-100E	3109_769'	water sediment	water sediment	water sediment	water sediment		9460_1200'
UT-146A		water sediment	water P-05-35D-75'	water	water	8419_4332'	
UT-141A		water sediment	water sediment 5335_4358'	water sediment P-06-40D_20' P-06-40M_63' P-06-40S_145'	water sediment 7381_4589' (no label)	6343_5002' 6344_5700' 7377_4892' 8410_4337' 8419_4332' 8421_5078' 8423_5636' GH-08-119 165'	
NK-119A	water	water sediment GH-04- 07_110' GH-04- 23_120' GH-04- 25_185'	water sediment	water	water sediment		
SK-136B	3105_1438'	water	water 5329_1828'	water	water		
SK-136A	40_524' (Cominco) 2039_320'	water	water	water	water	P-08-55D_65' P-08-55S_15'	
SK-134A		water	water	water	water	P-08-56S_21' P-08-56M_100' P-08-56D_141'	9446_1002' 9447_1203'
		under a					
UT-100D		sediment	sediment	sediment	sediment		
UT-138A		water sediment	water	water	water		
NK-119B	water	water	water	water	water		

Table 13. Stream water chemistry. Only a small set of indicator analytes are presented. Blue shading indicates high concentrations relative to the data set; sulfate does not exceed relevant standards, copper could be greater than relevant standards depending on water hardness. Calcium, sodium, and alkalinity are indicators for contamination by bentonite or grout; barium may be an indicator of drilling mud; copper and sulfate are indicators for acid drainage (pH is not available). However, all are also naturally present in the geologic material at Pebble. Med = median, max = maximum concentrations. PLP data from PLP 2008 Pre-Permit Report F; all PLP data is preliminary and subject to change.

	Alkalinity		DC	DC	Sulf	ate	Bar	ium	Calc	ium	Sodi	um	Cop	oper
PLP data	(៣រួ	g/L)	(mg	5/L)	(៣រួ	5/L)	(ug	5/L)	(ug	;/L)	(ug/	/L)	(ប្អូ	g/L)
near														
drilling	med	max	med	max	med	max	med	max	med	max	med	max	med	max
UT-100E	42	49	1	5	7	8	5	8	10250	13700	3415	4490	0.3	2
UT-146A	19	36	2	6	30	42	10	13	10950	14800	3805	4640	2	5
UT-141A	31	50	2	5	2	4	4	6	8680	15800	2270	3040	0.2	0.4
NK-119A	13	26	2	2	1	7	2	13	3630	14000	1975	4510	0.3	2
SK-136B	16	30	2	3	22	29	6	13	9400	13500	3430	4990	3	20
Reference S	treams													
UT-100D	42	56	2	7	6	11	7	12	11150	16700	3630	5130	1	2
UT-138A	42	56	2	6	1	3	7	9	9320	12200	4230	5690	0.3	1
NK-119B	10	23	1	2	4	10	3	4	3490	4970	2075	3030	0.4	1
SK-134A	23	36	2	3	20	29	7	16	10200	13800	3540	4490	1	9
SK-136A	19	29	2	3	19	27	6	9	8800	11000	3620	4520	4	14

Table 14. Stream sediment chemistry. Only a small set of indicator analytes are presented. Blue shading represents high concentrations relative to the data set shown (but not necessarily relative to average crustal abundance). Med = median, max = maximum concentrations. Where only one number is listed, only one sample was taken. PLP data from PLP 2007 Pre-Permit Report E; all PLP data is preliminary and subject to change.

	Sulfate (mg/kg)		Barium (mg/kg)		Cal (mį	cium g/kg)	Sod (mg	ium /kg)	Copper (mg/kg)		
Stream sites near drilling	med max		med max		med	max	med	max	med	max	
UT-100E	6	41	105	239	3990	9700	270	423	8	12	
UT-146A	67 122		124	132	3650	3980	300	302	45	50	
UT-141A	5 148		87 100		4070	4170	221 283		7	8	
NK-119A	nd	nd	65	88	3050	4350	187	216	42	55	
SK-136B				n	o sedimer	nt samples					
Reference s	treams										
UT-100D	9	60	132	227	4830	10400	397	495	11	31	
UT-138A	14	26	112	124	4440	4730	328	351	9	9	
NK-119B				n	o sedimer	nt samples					
SK-136A				n	o sedimer	nt samples					
SK-134A				n	o sedimer	t samples					

7.4 Ammonia

Ammonia is a potential concern. Blasting is reportedly not to be conducted within 200' of any fishbearing stream or lake,¹¹¹ however the MLUP's allow for blasting as close as 37' under certain conditions.¹¹² Ammonia in surface water and groundwater in the mine lease area has been detected at much greater concentrations (up to 1500 ug/L total ammonia) than detected by the USGS in rivers of Lake Clark (28 ug/L as total ammonia)¹¹³ or in streams with spawned out salmon $(60 - 240 \text{ ug/L})^{114}$ total ammonia).¹¹⁵ Although the State of Alaska uses 5.9 mg/L total ammonia (NH₄⁺ + NH₃) as the standard (presuming 0-14C and pH of 7.0),¹¹⁶ the USGS uses the EPA recommendation of 0.02 mg/L (20 ug/L) of un-ioinized ammonia (NH₃), considered safe for fish reproduction.¹¹⁷

Lake Clark tributaries and rivers were well within the 20 ug/L NH₃ limit.

- The Tlikakila River had maximum total ammonia $(NH_3 + NH_4^+)$ of 28 ug/L and about 6 ug/L of un-ionized ammonia.¹¹⁸
- The highest total ammonia in the Kijik River system was 13 ug/L and 27 ug/L.
- The highest total ammonia in the Johnson River was 56 ug/L; the next highest 11 ug/L.

PLP reported higher concentrations of total ammonia (Table 15).¹¹⁹ Ammonia is pH dependent. For calculating ammonia (Table 15), a pH of 7 was utilized, along with the highest commonly observed temperatures and commonly observed conductivity. Total suspended solids were examined as a possible indicator of increased organic material in water and a possible source of ammonia; however, there was no correlation.

Total ammonia did not exceed the State of Alaska criteria based on relevant pH and temperatures at the Pebble sites. The toxic form of ammonia (NH₃) never exceeded the EPA recommendation for fish propagation, but a shift in pH from 7.5 to 8 with an increase of 1° C would cause the highest concentration (5.8 ug/L unionized ammonia) to reach 20 ug/L.

Exploration is not likely to be the sole source of ammonia, but may contribute to ammonia levels. Some sites of high ammonia concentrations were in areas not known to be near blasting or drilling – such as the transportation corridor and confluence of the South and North Fork Koktuli Rivers. Possibly the levels are due to influences of humic material and salmon carcasses. However, the highest reported total ammonia related to salmon carcasses is less than 300 ug/L in the literature reviewed, just 20% of the highest ammonia reported by PLP. Sporadic very high concentrations do raise questions about whether seismic lines or other activities may have been conducted in a manner that influenced the reported ammonia concentrations.

¹¹¹ US Army Corps of Engineers Nationwide Permit

¹¹² ADNR 2009a

¹¹³ Brabets 2002

¹¹⁴ Rice and Bailey 1980

¹¹⁵ Mitchell and Lamberti 2005; Rice and Bailey 1980

¹¹⁶ The total ammonia standard changes with temperature and pH. At 0-14C and pH of 6.5-7.5, the total ammonia standard is 4.4-6.7 mg/L; it decreases with higher temperature and higher pH.

¹¹⁷ US EPA 1976

¹¹⁸ Brabets and Ourso 2006; Brabets 2002

¹¹⁹ Method SM 4500-G is listed in PLP Field Sampling Plans

Table 15. Ammonia in surface water and groundwater. Only concentrations greater than 0.2 mg/L total ammonia are listed; several instances of concentrations near 0.1 mg/L have also been reported. Reported ammonia is presumed to be total ammonia, and un-ionized ammonia (NH_3) is calculated based on a theoretical pH and temperature using the American Fisheries Society calculator (<u>http://www.fisheries.org/afs/hatchery.html</u>); conductivity of 50 uS/cm was used for surface water and conductivity of 150 uS/cm was used for groundwater. PLP data from PLP 2008 Pre-Permit Report F; all PLP data is preliminary and subject to change.

	Total	Un-ionized				
Date	Ammonia	ammonia	Site	Location		
Surface water		NH₃ if pH=7.5, temp=10 ⁰ C				
	(mg/L)	(ug/L)				
July 23, 2004	0.45	2.53	GS14B			
Aug 17, 2004	0.41	2.30	GS12A			
Aug 17, 2004	0.23	1.29	GS14A	along the proposed road system		
Aug 17, 2004	0.45	2.53	GS14B			
Aug 19, 2004	0.18	1.01	GS3A			
Sep 25, 2004	0.25	1.40	GS3A			
Aug 15, 2005	0.20	1.12	SK131A	Tributary southeast of pit		
Aug 16, 2005	0.26	1.46	SK133A	Tributary, southwest of pit		
Aug 15, 2007	0.40	2.24	SK133A	Tributary, southwest of pit		
Aug 17, 2005	0.27	1.52	UT135A	Tributary of Upper Talarik		
Aug 17, 2005	1.03	5.78	UT138A	Tributary downstream of pit		
Sep 16, 2005	0.34	1.91	SK100A	Confluence of North and South Fork Koktuli		
Dec 12, 2006	0.22	1.23	UT100E	Upper Talarik upstream of pit		
April 24, 2007	0.50	2.81	UT100A	Upper Talarik, far downstream		
Groundwater		NH₃ if pH=7, temp=5 °C				
Mar 18, 2005	0.30	0.36	MW5S	south of pit		
Nov 10, 2005	0.28	0.33	MW14D	South Fork Koktuli below Frying Pan Lake		
Mar 23, 2006	0.29	0.35	MW14D	South Fork Koktuli below Frying Pan Lake		
May 21, 2006	0.21	0.25	MW14D	South Fork Koktuli below Frying Pan Lake		
Aug 21, 2006	0.22	0.26	MW9D	North Fork Koktuli tributary		
Aug 30, 2006	0.21	0.25	SWQ2 (1 of 2 samples)	transportation corridor		
Nov 2, 2006	0.70	0.84	MW3D	South Fork Koktuli below Frying Pan Lake		
Nov 3, 2006	1.11	1.33	P06-37S	North of pit		
Nov 4, 2006	0.73	0.87	P06-37D	North of pit		
Aug 23, 2007	0.18	0.22	P06-38D (1 sample)	North of pit		
Sep 7, 2007	1.51	1.81	SP57	spring on North Fork Koktuli		

7.5 Anomalies in groundwater chemistry

Surface water within the Pebble mine lease area generally receives both surface runoff and groundwater, in different ratios depending on the site. For instance, some kettle ponds are formed only from surface runoff and dry up in the summer while some are fed by groundwater and remain; gaining reaches of streams may be primarily groundwater while losing reaches receive water from surface runoff. Fluctuations with seasons, precipitation, and groundwater input make it difficult to distinguish natural chemistry from contamination, particularly when chemistry at and near the source has not been analyzed and the transport routes are not defined. To effectively define contamination, environmental media must be sampled prior to industrial activity, transport routes defined, and sampling conducted at sources and transport routes during activity.

Groundwater chemistry is generally more straightforward. However, most groundwater in the Pebble region is fully saturated in oxygen, indicating exchange with surface water and minimal residence time underground; recharge by surface water may cause some seasonal or storm fluctuations in groundwater chemistry. Groundwater data suffers from the same poor protocol for contaminant assessment as surface water – lack of data prior to intensified exploration, lack of definition of transport pathways or sampling along pathways during and after activity.

7.5.1 Groundwater collection

Groundwater is collected at seeps that daylight at the surface and at monitoring wells. Six monitoring wells were installed at the mineral deposit site where exploratory drilling was occurring and groundwater chemistry could potentially indicate aquifer contamination. Other monitoring wells were installed throughout the mine claims area, some adjacent to core holes or geotechnical holes and some located in areas with no drilling (drill holes greater than 1 km away).

In most cases, when groundwater appears contaminated, it will not be possible to determine whether the source was an exploratory drill hole or whether something occurred within the monitoring well itself. For instance, a monitoring well installed in a mineral zone could develop acid rock drainage the same as a coring hole.

In order to best analyze whether exploration has contaminated groundwater, chemistry of water within the drill hole itself is required. This could help distinguish when water chemistry that indicates types of contamination (from acid rock drainage, grout, etc) originates with exploratory holes or is due to chemistry occurring within the monitoring well itself. This data is not available. Historically, no Cominco groundwater data is available, nor are drill logs available. Additionally, logs or field notes for monitoring wells would clarify if and when there were problems with grout, cement, or drilling mud potentially contaminating groundwater samples.

This analysis proceeded by examining

- field and lab chemistry of seeps on the ore body and off
- which monitoring wells spatially and temporally had an opportunity to be contaminated by drilling and which did not (although actual drilling discharge locations were not made available)
- field and lab chemistry of monitoring wells within 500 m of drilling



Figure 17. Seeps inventoried by PLP. Over 4000 seeps have been identified by PLP, and water samples were collected from over 100. From PLP 2008 Pre-Permit Report D; all PLP data is preliminary and subject to change.

7.5.2 Seeps and springs

While pond water is affected by surface runoff, groundwater at seeps and springs provide information about the character of water below the surface.

There are thousands of seeps throughout the mine claims area (Figure 17 and Attachment 9), and several located on top of the ore body (Figure 18). PLP collected data on 125 seeps, including several on the ore body at Pebble West but only one at Pebble East. The USGS collected groundwater from 23 seeps and springs, and from three drill holes described as "free-flowing from a drill hole" with white precipitate substrate and "free flowing from capped rusted drill stems".¹²⁰ All the drill holes were located at Pebble East, as was a single spring. Both PLP and USGS sampled groundwater outside the ore body extensively.

Groundwater from drill stems. USGS sample PB191 is from coring hole 5332 (4206' deep) and was drilled in 2005. Coring hole 7365 (PB203) and 7367 (PB219), although clearly marked on the USGS map, could not be located on the ADNR 2010 map of drill holes. Other "73—" holes in the area are 4,000' to 5,000' deep, so it is likely that the three sampled holes were similar in depth. PB219 was noted as "barely dribbling".

The drill holes sampled are characterized by very high alkalinity (100-150 mg/L as CaCO₃), with elevated calcium, sodium, and metalloids. Two of the three (with free-flowing, rather than "dribbling" water) also had high barium and rare earth elements, with a pH of 6.4. The "dribbling" drill stem had a lower pH (5.3); barium and rare earth elements were not elevated. Only three other groundwater samples had an alkaline nature. Two were located in Pebble East and one was on a tributary to the Upper Talarik, far downstream in the area where the South Fork Koktuli and Upper Talarik run close together.

USGS data,				Sulfate	Barium	Calcium	Sodium	Aluminum	Conner
from drill holes	n	рH	ORP	(mg/L)	(ug/L)	(mg/L)	(mg/L)	(ug/L)	(ug/L)
PB191	1	6.5	nd	16	85	27	21	nd	2
PB203	1	6.5	nd	12	91	29	33	nd	0.1
PB219	1	5.3	nd	12	8	31	9	nd	0.2

 Table 16. Drill hole groundwater chemistry.
 Shaded boxes represent high concentrations relative to what is usually observed in the region.
 Collected by USGS in Pebble East, 2008. Fey et al et al 2009.

These drill stems could be monitored over time to determine whether sulfate increases and pH decreases, which would indicate the onset of acid rock drainage. Without data over time and lithological and mineralogical information, it is not possible to make an assessment as to whether the high cations and sulfate represent a natural condition or are the result of reactions initiated when the bedrock was opened up.

Historical groundwater at Pebble West. Only a single seep with a single sample from 2004 (Seep 11) was collected on the ore body; sampling of others began in late 2006. The seep water collected in 2004 had a neutral pH (7.0), low ORP (7 mV), and was high in dissolved oxygen (11 mg/L);¹²¹ nearby seeps sampled in 2006 had lower pH and higher ORP.¹²² Pre-drilling data could be utilized to determine whether groundwater in this small area had changed over two years; continuing to sample these seeps

¹²⁰ Fey et al 2009 Excel sheet "FieldSite"

¹²¹ PLP 2008 Pre-Permit Report F

¹²² The first samples (October 2006) for SRK17 and SP62, respectively were dissolved oxygen 8 mg/L, pH 5.5, and ORP 282 mV, and dissolved oxygen of 7, pH 5.8, and ORP 252 mV.

regularly, and re-instating sampling of Seep 11, could also provide information on potential groundwater changes over the long term.

Acid seeps at Pebble West. A cluster of seeps sampled by PLP in Pebble West have classic acid rock

chemistry: low pH, high sulfate, high ORP, and extremely high concentrations of copper and aluminum. There are twelve seeps with this type of chemistry, but each has only been sampled two to three times.

The single seep (PB266) sampled by USGS in Pebble West (for pH only) was located in the same section as the PLP acid seeps. It had a pH of 3.5 and may have been acid drainage.

Seep water has the potential to change over a period of years, but it also may change over a very short period of time. For instance, seep SRK17 (collected by PLP), located at Pebble West just north of the acid seep cluster, had water chemistry that was dramatically different in May than in the fall (Table 17).

A slug of obvious acid drainage – high acidity, sulfate, and dissolved metals came through in May, a time when snow is rapidly melting. In permeable soils, runoff will infiltrate into shallow aquifers, and the groundwater table may rise. The acid water may have resulted from surface reactions that infiltrated into groundwater or from changes in groundwater flow paths that may have brought deep water up or caused groundwater to contact different rock. Although the pH did not decline, the increase in dissolved metals was significant: copper is considered toxic to aquatic life by State of Alaska



Figure 18. Seeps at Pebble West. A cluster of seeps have acid drainage water. These are SP26, SRK06, SRK08-13, and SRK15. All have very high concentrations of copper, aluminum, and sulfate. The water chemistry develops as water spends time underground in contact with sulfide rock. Red outline encompasses the acid seeps. Figure is from PLP 2008 Pre-Permit Report F; all PLP data is preliminary and subject to change.

standards at near 2.7 ug/L¹²³ and aluminum at 87 ug/L; these levels were vastly exceeded (Table 18).

The USGS also collected water that trended acidic at three seeps west of the central discovery area, in Pebble West. However, none of these had the dramatic chemistry observed in the acid seep cluster sampled by PLP.

Clearly groundwater is mixing with surface water (becoming oxygenated) and allowing acid drainage reactions to occur in Pebble West. Of the seeps sampled by PLP on the ore body, all at Pebble West, all either had continual acid drainage or a slug of acid drainage in May 2007 (SRK-01 and SRK-04, both on the outskirts of Pebble West) or did not have samples collected in May of any year. It is possible that the density and depth of drilling is causing acid seeps to form or exacerbating flows already present. It is also possible that some seeps may be abandoned drill holes.

¹²³ The State of Alaska recognizes that copper toxicity changes with the hardness of the water; the regulatory standard (chronic criteria for aquatic life) for dissolved copper at a hardness of 25 mg/L is 2.7 ug/L of copper.

Table 17. Acid seep chemistry. PLP sampled acid seeps at Pebble West. The pH, ORP, sulfate, and metals in gray shaded boxes are classic signs of acid drainage. Although other metals at acid seeps were occasionally elevated, aluminum and copper were consistently in very high concentrations and greatly exceeded relevant standards. Barium is also elevated relative to what is usually found in the general Pebble area, but similar to what USGS found in some ponds at Pebble West near the discovery outcrop. Cation content was not elevated at acid seeps as it was in drill holes and some other seeps. PB266 is located near the acid cluster sampled by PLP; PB032, 034, and 035 are further east, although still within Pebble West. Yellow -- the highest concentrations of analytes. USGS data is from Fey et al 2009; PLP data from PLP 2008 Pre-Permit Report F; all PLP data is preliminary and subject to change.

	n	р	н	о	RP	Sulfate Barium (mg/L) (ug/L)		Calc (mg	ium g/L)	Sod (mg	ium g/L)	Alur (u	minum Ig/L)	Cop (ug	per :/L)		
PLP data, Acid seeps at																	
Pebble West	6	med	max	med	max	med	max	med	max	med	max	med	max	med	max	med	max
SP 26	0	4	7.	323	434	00	69	23	23	/	/	3	3	3750	4770	395	554
SRK 06	2	3./	3.8	413	415	102	104	12	3	10	1	0.	.5	6700	18200	2000	6410
SRK U8	3	3.3 2 E	3.4 2.7	247	540	193	194	22	22	10	10	4	4	3170	18200	2990	120
SRK 09	2	3.5	3.7	547	562	70	96	15	16	5	6	2	4	3170	4400	136	1/0
SRK 10	3	4.0	4.1	248	404	44	48	26	28	5	7	3	3	3240	3250	44	44
SRK 12	2	2.7	3.1	481	500	139	214	17	21	6	6	3	3	3365	3730	45	63
SRK 13	3	3.4	3.6	510	542	59	97	17	17	8	14	4	5	3940	7370	53	71
SRK 15	2	3.2	3.4	448	480	110	174	7	8	5	6	2	3	2430	3550	10	15
									l								
USGS data, red so	eep	1															
PB287 (North Fork Koktuli)	1	6	.4	n	d	2	2		6	3	3	2	2		nd	0.	.4
USGS data, acid s	seep	s at Pe	bble W	est													
PB266	1	3	.5	n	d	n	d	n	d	n	d	n	d		nd	n	d
PB032	1	5	.1	n	d	2	6	2	2	7	7	3	3		nd	4	6
PB034	1	5	.6	n	d	1	9	10		7		2			nd	6	6
PB035	1	6	.8	n	d	5	5	9)	3	0	3	3		nd	2	2

Table 18. Short term seep chemistry changes. Blue indicates elevated concentrations relative to other data collected at the site; copper and aluminum shift from within relevant standards to greatly exceeding relevant standards in May 2007. From PLP 2008 Pre-Permit Report F; all PLP data is preliminary and subject to change

enunge.								_
PLP data,								
seep SRK17	Alkalinity (mg/L)	Acidity (mg/L)	dO (mg/L)	pН	ORP	Conductivity (umhos/cm)	Sulfate (mg/L)	
Oct 2006	nd	2	8	5.3	282	80	30	
May 2007	nd	45	7	5.6	125	220	83	
Oct 2007	nd	1	6	6.1	146	123	44	

	DI I I		DI 1 1				
	Dissolved copper (ug/L)	Dissolved iron (ug/L)	aluminum (ug/L)	Dissolved molybdenum (ug/L)	Barium (ug/L)	Calcium (ug/L)	Sodium (ug/L)
Oct 2006	1	86	49	<0.3	9	10	3980
May 2007	65	444	5910	<0.3	16	6	3310
Oct 2007	1	25	35	<0.3	13	13	4800

Alkaline seeps at Pebble West. A set of two seeps (PB125, 126) sampled by USGS in the southern section of Pebble West had high sulfate, sodium, arsenic, and molybdenum (Table 19). The alkalinity was higher than most in the region (35 mg/L as CaCO₃) with pH 5.6 and 6.6. A third seep (PB127) had similar chemistry with even higher alkalinity and pH (88 mg/L as CaCO₃, pH 7.3). A fourth seep just outside the estimated boundary of the ore body had similarly high sulfate and sodium, but with very high barium, iron and manganese and no arsenic or molybdenum. This particular seep (PB128) was approximately one mile due south of the acid ponds in Pebble West.

USGS data, alkaline seeps	n	pН	Alkalinity (mg/L as CaCO3)	Sulfate (mg/L)	Barium (ug/L)	Calcium (mg/L)	Sodium (mg/L)	Arsenic (ug/L)	Molybdenum (ug/L)
PB125	1	5.6	23	38	3	12	5	3	14
PB126	1	6.6	24	39	4	11	6	36	16
PB127	1	7.3	88	64	15	26	12	11	13
PB128	1	6.8	36	32	25	12	5	2	<2

Table 19. Alkaline seeps. From Fey et al 2008.

Groundwater outside the ore body. A single seep on a tributary of the North Fork Koktuli draining Kaskanak Mountain was found running red and sampled by the USGS. Although it had very high iron as Fe^{2+} (6870 ug/L) and manganese (640 ug/L), it was low in sulfate and no other metals were elevated. The only other samples with similar chemistry was two ponds south of the ore body in a wetland near Lincoln Lakes; they each had elevated DOC (10-15 mg/L), and the elevated iron and manganese were likely due to bacterial activity. The red seep had slightly elevated DOC at 5 mg/L.

Except for the red seep, groundwater sampled from locations near the North Fork Koktuli and South Fork Koktuli tended to have low alkalinity and low to neutral pH while groundwater near the Upper Talarik tended towards more average alkalinity (near 20 mg/L as CaCO₃) and neutral pH. This is consistent with data on surface water, which tended to be more alkaline in the Upper Talarik.

Complex geology. The examples above demonstrate the complex nature of the subsurface in the Pebble region (Figure 19), which includes areas of alkali material as well as pyritic intrusions. The geologic structure contains potassium, sodium, and calcium in addition to suites of metals. USGS analysis of water bodies found that copper tended to group with potassium, nickel, rhenium, thallium and rare earth elements, while silver and zinc tended to group with metalloids (molybdenum, antimony, thorium, uranium, vanadium, tungsten).¹²⁴ Different material mobilizes depending on the nature of the rock and whether water moving underground contacts material that increases alkalinity or increases the acidity.



Figure 19. Subsurface geology at Pebble. This map indicates the subsurface distribution of mid-Cretaceousand older units. The map is interpretive and based almost exclusively on drill hole information. Red dashed line – boundaries of Pebble West; black dashed line – boundaries of Pebble East; green dashed line – western margin of post-Pebble cover rocks. From Kelley et al 2010.

These natural chemical reactions have the potential to be intensified by drilling operations: e.g. contamination of groundwater with grout may cause more metalloids to mobilize, and opening previously sealed sulfide rock to oxygenated groundwater and bacterial intrusion may allow acid generation to occur with consequential mobilization of copper, zinc, cadmium and other metals. This is relevant in that many of the elements that have been measured in soil and water in the Pebble region, and could be mobilized, are toxic to aquatic life.

¹²⁴ Kelley et al 2010

7.5.3 Monitoring wells

Seeps and springs provide access to groundwater without the necessity of drilling a well; however, they can be ephemeral and the depth from which the water arises may not be known. Monitoring wells are installed to provide information on groundwater at specific subsurface depths. Ten monitoring wells were installed by PLP at varying depths within the ore deposit: P-04S, PQ4, SRK2, SRK3, MW-05-12 D/S, SRK5 D/M/S, and KP-P4.

As the analysis of seeps indicated, groundwater moving through sulfide mineralized rock can develop indicators of acid rock reactions (high sulfate, acidity, low alkalinity and possibly low pH). If groundwater is located in mineralized areas and there is no pre-drilling data, it is not possible to determine if this represents the natural state of the groundwater, if the monitoring well is receiving aquifer water contaminated from drilling, or if the well itself has developed acid reactions. Data collection needs to consider all these possibilities and design sampling to determine influences on water chemistry.

The nature of the rock through which groundwater moves needs to be known before making definitive chemical assessment. The geologic nature is complex. Rock material could contribute alkalinity, cations (calcium, magnesium, potassium, sodium), and mobile oxyanions or it could contribute low alkalinity, high sulfate, and high cationic metals (copper, iron, etc.). Depending on depth, it may have low dissolved oxygen and a reducing environment, or, if in contact with surface water, could have high oxygen content and an oxidizing environment; these affect the mobility of metals and metalloids.

Table 20 provides a brief visual summary of the monitoring wells, whether they are adjacent to drilling, and whether they are likely in a mineral zone. Groundwater collected from a mineral zone naturally may have elevated minerals and acid rock indicators; potentially location adjacent to exploratory holes could increase the risk. Table 21 expands on the chemical indicators.

Table 20. Monitoring well spatial and temporal association with drill holes. This table is provides a visual of monitoring well chemistry and the factors that may affect it. Mineral zone: orange – in a mineral zone, yellow – might be in a mineral zone, green – is not in a mineral zone. Well ID: orange – signs of chemical or bacterial reactions, yellow – possible chemical or bacterial reactions but not clear, brown – sediment contamination, green – no sediment or bacterial or chemical reactions apparent. Wells near drilling: orange – monitoring well is located close to old coring holes and/or many drill holes, yellow – drill holes are at some distance and/or are geotechnical holes, green – no drill holes within 600 m of the monitoring well. Developed from analysis of PLP Pre-Permit Report F and the drill hole map provided by ADNR; all PLP data is preliminary and subject to change.

Located in a			Sample taken after
mineral zone?	Well ID	Well near drilling?	drilling?
	P-04-S *next to acid		
Yes	seeps	Many old holes	yes
Yes	PQ4	many old holes	yes
Yes	SRK2	1 Cominco <50m, 1 2004 hole < 50m; 1 2003 hole 400m	yes
Yes	SRK3	4 at 200m+ drilled 2007+	no
Yes	MW-05-12D	2 Cominco, 1 <50m	yes
	MW-05-12S	2 Cominco, 1 <50m	yes
Yes	SRK5D	1 Cominco <50m, new 400m	yes
	SRK 5M	1 Cominco <50m, new 400m	yes
	SRK 5S	1 Cominco <50m, new 400m	yes
			no, except one
Yes	KPP4	five 200m+	300m+
			don't know; both
No	MW-04-10	3 GH	2004
No	MW-05-14D	3 PW's	don't know
	MW-05-14S	3 PWs	
Yes	MW-04-1D	4 at 150m+	yes
	MW-04-1M	4 at 150m+	yes
	MW-04-1S	4 @ 150m +	yes
Maybe	MW-04-3D	2 GH	one maybe, one no
Maybe	MW-04-5D	1 GH 400m+ and two 2009	yes (one)
	MW-04-5M	1 GH 400m+ and two 2009	yes (one)
	MW-04-5S	1 GH 400m+ and two 2009	yes (one)
			don't know; both
No	MW-04-7D	1 GH <50m	2004
			don't know; both
	MW-04-7S	1 GH <50m	2004
			don't know; both
No	MW-04-9D	1 GH <50m	2004
NO	NIW-04-11D	No noies	
	WW-04-11M	No holes	
	NIW-04-115	No holes	
NO	WW-05-1155	No holes	
Tes	NIW-05-13D	No holes	
	WW-05-135	No holes	
NO	WW-04-2D	No holes	
NO	WW-04-6D	No noies	
NO	NIW-04-8D	1 in 2009, may not be upgradient	
	IVI VV-04-8IVI	1 in 2009, may not be upgradient	
D.d.a., h.a.	IVIW-04-85	L in 2009, may not be upgradient	
iviaybe	P-06-37D	No holes	
	P-00-37IVI	No holes	
	P-06-375	No holes	
NO	P-06-38D	No noies	

Table 21. Monitoring well chemistry. Groundwater with certain characteristics was noted as being "impacted". Well ID colors are the same as in Table 20, except that where chemical/bacterial reactions were indicated, those with acid indicators are orange and those with alkaline indicators are purple. *Indicators for:* Sediment: TSS, high concentrations of total metals; Microbial: low dissolved oxygen, potentially Fe^{2+} , H_2S , dissolved iron and manganese, low ORP; Acid rock: sulfate, acidity, pH, often with high concentrations of dissolved metals; Alkaline: alkalinity, high concentrations of salts (calcium, magnesium, potassium, sodium). The table was developed through analysis of PLP 2008 Pre-Permit Report F; all PLP data is preliminary and subject to change.

		Elevated		Acid rock	Elevated	Alkaline	
		metals	Microbial	reactions	metals	contamination	Elevated
Well ID	Sediment?	(total)	indicators	indicators	(dissolved)	indicators	salts?
P-04-S	No	No	x	x	Ni, V, Cu*, Zn*, Fe*, Mn*	No	x
PQ4	First sample	AI	x	x	Fe, Mn, As, Mo, Zn, Cu	No	x
SRK2	Several	No	х	No	Ni, As, Mo, Mn	х	х
SRK3	No	No	х	No	Fe, Mn	х	х
MW-05-12D	No	No	х	х	No	No	No
MW-05-12S	Several	х	х	х	Mn, Mo	х	х
SRK5D	First sample	Al, Fe	some	x	Cu, Mo Al, Fe, Mn, As,	No	No
SRK 5M	No	x	No	x	Co, Cu, Mo, Ni, Se, Si, Zn		No
SRK 5S	Occasional	Cu	No	No	No	No	No
KPP4	1 event	х	No	No	No	No	No
MW-04-10	No	No	No	No	No	No	No
MW-05-14D	First sample	х	х	No	No	х	х
MW-05-14S	Several	х	No	х	Cu	No	No
MW-04-1D	first sample	Al, Fe	No	No		No	No
MW-04-1M	1 event	х	No	No	Zn	No	No
MW-04-1S	1 event	х	No	No		No	no
MW-04-3D	First sample	х	No	No	Мо	x	First sample
MW-04-5D	Several	No	x	x	As, Mo, V, Fe, Mn	x	x
MW-04-5M	1 event	х	х	No	As, Mo, V	х	х
MW-04-5S	All	х	x	No	As, Mo	No	x
MW-04-7D	First sample	Al, Fe	No	No	Mn, Si	No	
MW-04-7S	First sample	Al, Fe	No	No		No	No
MW-04-9D	No	No	No	No	No	No	No
MW-04-11D	No	No	No	No	No	No	No
MW-04-11M	No	No	No	No	No	No	No
MW-04-11S	1 event	х	No	No	No	No	No
MW-05-11SS	First sample	х	No	No	No	No	No
MW-05-13D	Several	х	No	No	No	First sample	No
MW-05-13S	No	No	No	No	No	No	No
MW-04-2D	No	No	No	No	No	No	No
MW-04-6D	No	No	No	No	No	No	No
MW-04-8D	No	No	No	No	No	No	No
MW-04-8M	No	No	No	No	No	No	No
MW-04-8S	No	No	No	No	No	No	No
P-06-37D	No	No	x	No	As, Mo	х	х
P-06-37M	No	Cu	х	х	No	х	No
P-06-37S	No	No	No	No	No	х	Ca
P-06-38D	No	No	х	No	No	х	х

To summarize, of the ten monitoring wells on the ore body

- Nine had water chemistry indicating chemical reactions, such as stimulation of bacterial growth, acid rock drainage and/or introduction of highly alkaline material.
 - one appeared to be due to in-well reactions, rather than aquifer contamination from exploratory holes, in that water samples were collected prior to installation of nearby drill holes.
 - the other eight were all located near holes drilled prior to water sample collection and it could not be determined whether water chemistry was contaminated by exploratory holes or in-well reactions
- One had no chemistry indicating bacterial or chemical reactions; it did have one water sample contaminated by sediment. The drill holes near this well were installed *after* water samples had been collected and data reported; only a single drill hole 300m away was installed prior to sampling.

Although there are mineralized zones outside the mineral deposit, they do not have the same density of exploratory holes. Twenty eight monitoring wells have been installed outside the main deposit. Some monitoring wells are located in regions designated as mineral zones outside the main deposit, and some appear to be outside any mineral rock.

Of the 28 wells outside the main ore deposit

- ten had indications of chemical or bacterial reactions
 - eight were potentially within mineralized rock
 - six were located near drilling
- seven had samples contaminated by sediment
 - one was potentially within mineralized rock
- eleven had no indications of contaminated groundwater
 - nine were located greater than 600m from any drill holes
 - one was located near 3 geotechnical holes, but it is not clear if sampling occurred prior to GH hole installation
 - one was located less than 50 m from a single geotechnical hole
 - one was located in mineralized rock

This indicates that groundwater from wells located in mineralized rock and/or near drilling are more likely to be influenced by chemical or bacterial reactions. Eleven wells were installed that had no contaminated water samples, indicating that in-well reactions did not occur; most of these were in unmineralized zones and located away from drill holes.

However, locating wells in a mineral zone, near drilling, does not necessarily mean groundwater samples will be acidic.

- Monitoring well SK3, located in the mineral zone but which had water collected prior to the installation of nearby core holes did not have signs of acid rock reactions. It did have high alkalinity and high concentrations of salts, indicative of possible contamination by grout or cement, and there were signs of bacterial activity, which can be stimulated by hydrocarbons.
- Monitoring well MW-04-1D, located in a mineral zone but not close to drill holes, had no indications of chemical reactions.
- Monitoring well MW-05-13 D/S located in a mineral zone but not adjacent to drill holes had no contaminated groundwater samples.
- SRK2, near SRK3, had no acid indicators despite being located near drilling, but did appear to have bacterial activity and contamination with alkaline material.
- KP-P4 located at the main ore deposit near drilling had no chemical or bacterial indicators.

SRK3 is at Pebble West, and samples were collected prior to adjacent drilling; SRK2 and KP-P4 are also at Pebble West, north and south of SRK3 respectively, and had drilling occur prior to collecting samples. Therefore, locating a monitoring well in a mineralized zone, near drilling, does not always result in samples being acidic. Well chemistry may represent aquifers at specific depths or in specific lithologies – both SRK2 and KP-P4 were screened in sand at less than 60' deep. SRK3 appears to be an old drill hole screened in sand about 1000' down (hole 4250_998'). It may also mean that holes identified near SRK2 and KP-P4 were downgradient of the monitoring well.

Additionally,

- Monitoring well MW-04-7 D/S and MW-04-09D located close to geotechnical holes but outside the mineral zone did not have indications of chemical reactions; these wells are co-located.
- Monitoring well set P-06-37 which is not near any drilling had signs of chemical reactions; it is not known if the well is in mineralized rock. P-06-38, also not near drilling and not in a known mineral area had similar chemistry.

Together these indicate that geotechnical holes adjacent to monitoring wells may not influence well chemistry (MW-04-7 and -9), and some wells likely have water samples influenced by reactions initiated in the monitoring well itself (P-06-38, maybe P-06-37).

One monitoring well outside the mineral zone had particularly interesting chemistry. Monitoring well set MW-04-5 was a cluster of three wells - deep, medium, and shallow - that experienced somewhat different chemistry. Located between the main ore body and Frying Pan Lake, it appears that pH increased then decreased, and metals and salts fluctuated strongly. Manganese, iron, and salts were found in concentrations much higher than most wells outside the mineral deposit. It is possible that contamination with sodium bentonite slurry was followed by sulfide oxidation, contaminating at least a year of water samples.

- The pH of MW-04-5D was 10 when the first water sample was collected in September 2004, dropping to pH 9 by May 2005, and stabilizing at neutral pH after that. No other monitoring well had pH over 8, except MW-04-2D on the Upper Talarik, which has been stable near pH 8.5.
- Sodium was twice the concentration in the first two samples (20-30 mg/L) compared to later samples (near 12 mg/L).
- The oxidation-reduction potential indicates a change from a reducing environment (-360 mV) to an oxidizing one (near 130 mV) at the same time that pH is changing from pH 10 to pH 7. Although other wells in mineralized areas show fluctuations of redox around zero, from -120 to +150 mV, none have made such a dramatic shift from a clearly reducing environment to a clearly oxidizing one, with a corresponding change in pH.
- Iron (ferrous + ferric) was around 0.7 mg/L for the first year, and then increased to 1.5 mg/L, mostly as dissolved iron. Ferrous iron increased during the same period, from near 0 to about 1.5 mg/L. It is apparent that pyrite is oxidizing, releasing iron in the ferrous form to the point where nearly all of the iron was ferrous, not ferric. No other monitoring wells showed this pattern of ferrous iron change and no other wells had ferrous iron this elevated.
- Pyrite oxidation also influences the pH, decreasing it. Therefore pH is being influenced initially by the bentonite (becomes more alkaline than natural) and later by pyrite oxidation (potentially becoming more acidic than natural).

- As the pH changes from alkaline to neutral, the sulfide present in the well can be smelled. At very high pH it exists as S²⁻ and does not have the classic smell of hydrogen sulfide (H₂S), which cannot form until pH becomes near neutral.
- This alkaline pH mobilized several metals/metalloids, including selenium, molybdenum, copper, vanadium, and chromium. None exceeded benchmark criteria. After the change to the more oxidizing environment, manganese increased from near 500 mg/L (already highly elevated above criteria of 50 mg/L) to near 900 mg/L and remained steady at that concentration. Nitrate + nitrite was 4.2 mg/L at MW5D with the first water sample; this is significantly more elevated than in any other wells, although still below benchmark criteria of 10 mg/L.

7.5.4 Summary of groundwater

Groundwater samples may be contaminated by the introduction of fuels, drilling additives, grouting material, and sediment during drilling. Without direct measurement of fuel hydrocarbons and other organics, conjecture must often be used to hypothesize whether these materials have entered groundwater.

Acid rock reactions occur as oxygenated groundwater moves through sulfidic rock; the onset of the reactions may be delayed by several years, but once started they are likely to continue for decades. This may be directly observable as red or orange water, or may be determined through lab analysis, particularly where water is underground and not observable. All seeps in the Pebble West zone appear to have either continual or occasional acid drainage, and potentially acid groundwater may be contaminating ponds. Acid groundwater may be reflecting "true" water chemistry or may have been initiated or exacerbated by the movement of water along and through open drill holes or the open face of a monitoring well wall; changes in water level, either natural or induced through water withdrawal, may influence the chemistry. Additionally, it is possible that some seeps may be abandoned drill holes.

Utilization of monitoring well water to determine potential contamination that exploration has introduced into water resources is problematic because even when the source of contamination can be assessed as being anthropogenic, whether the source was from an aquifer contaminated by exploration or from inwell issues at the monitoring well is difficult to ascertain. In order to better assess contamination due to exploration, water chemistry and field notes from the exploratory holes themselves would be required, in addition to drill logs and field notes from monitoring wells that might include useful information such as lithology (to determine if the well was installed in sulfide minerals) and potential contamination from grouting. PLP field plans have a protocol to collect drill cuttings from monitoring wells as they are drilled, which could provide information on subsurface mineralization.

Table 21 summarizes my interpretation of the chemistry. These are preliminary assessments, and opinions could be changed as more information becomes available. It also should be noted that the term "elevated metals" refers to metals elevated over what is normally observed in the sample or normally observed in the region; it does not necessarily mean metals exceed potential regulatory standards, although in some instances they do. Of 38 total monitoring wells

- 20 wells had at least one sample contaminated by sediment
 - $\circ\,$ all but two had elevated concentrations of total (unfiltered) metals during the high-sediment event
- 14 wells may have had anthropogenic introduction of hydrocarbons, based on indications of bacterial activity
- 12 wells had indications of contamination by alkaline material
 - o 7 of these appeared to have mobilized at least one oxyanion, usually molybdenum
- 9 wells had indications of acid rock reactions

- 6 wells were at the main ore deposit; 2 wells outside the main deposit may have been in mineralized zones; 1 outside the main deposit was in a location that may not be mineralized
 - 2 wells released very high levels of copper (1000 ug/L); one well had a single sample with this very high level, in the other well all samples were very high
- all but two mobilized some metals in the dissolved (filtered) form; copper was almost always mobilized

8.0 Summary of Opinions

The preceding data has been presented to illustrate the futility of trying to conclusively establish impacts absent pre-drilling data. When acid drainage with dissolved metals and high sulfate, and alkaline drainage with elevated cations can develop through natural water running over and through natural rock, and the chemistry is identical to that occurring in a drill hole, pre-drilling data is required to distinguish natural from exploration-induced occurrences, frequency, or intensity. Difficulties in framing definitive conclusions are due to the lack of data available prior to exploration and prior to the dramatic increase in drilling in 2004. Conclusions related to the occurrence of acid drainage, ammonia, barium and other contaminants are based on limited data and could be more definitive if further information (e.g. natural soil content, location and water quality of seeps prior to 2004, salmon spawning locations, locations of seismic work) became available as part of the discovery process.

Surficial contamination obvious to the casual observer is rare, temporary, and/or undocumented given the data reviewed. In my area of expertise, impacts are likely to be ones that cannot be observed without chemical measurements, best corroborated by biotic data. The area of surface disturbance does not reflect the potential disturbance to aquifers and surface water bodies, which may be long-lasting due to the consistency, degree or timing of input. This is particularly true for acid drainage, the onset of which may be delayed for decades, or which may surface sporadically, as demonstrated by seeps on the ore body. The number, density, and depth of holes drilled by NDM after 2003 went well-beyond prior exploration efforts by Cominco. The subsurface has been perforated so extensively that it may have changed the groundwater pathways, and has almost certainly exposed significant sulfide rock to oxygenated water. This may have long-lasting effects to water resources, given the controls on acid generation, the shallow aquifers, and the permeable surface layer.

Lastly, contaminants need to be considered in context. The areas of heaviest drilling are in the headwaters of river systems, and as such provide habitat and nutrients to aquatic life, much of which is microscopic or quite small (e.g. benthic invertebrates, algae, and diatoms), which are sensitive to chemical fluctuations¹²⁵ and upon which species higher in the food chain depend. These aquatic organisms at the Pebble site have adapted to clear water with low metal content, extremely low electrical conductivity, and frequent upwellings of oxygen. Disruptions to this system through infiltration of drilling discharge or development of acid drainage may be difficult to assess without consistent, long-term data on macroinvertebrate and aquatic plant populations, but have potential long-term impacts nonetheless.

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¹²⁵ National Research Council 1999; Besser et al 1995

References

- Aastrup, M and C-L Axelsson. 1984. Representativeness of chemical analysis of groundwater. *Nordic Hydrology* 15: 195-204.
- Alaska Department of Environmental Conservation. 1992. Recommended practices for monitoring well design, installation, and decommissioning. Anchorage, AK. http://www.dec.state.ak.us/spar/csp/guidance/decom.pdf
- Alaska Department of Environmental Conservation. 2008. Water Quality Criteria Manual. http://www.dec.state.ak.us/water/wqsar/wqs/pdfs/Alaska%20Water%20Quality%20Criteria%20 Manual%20for%20Toxic%20and%20Other%20Deleterious%20Organic%20and%20Inorganic% 20Substances.pdf

Alaska Department of Environmental Conservation. 2009. Water Quality Standards. 18 AAC 70.

- Alaska Department of Natural Resources. 2009a. Multi-Agency Permit Application for Hardrock Exploration Operations, Miscellaneous Land Use Permit #A096118#1
- Alaska Department of Natural Resources. 2009b. Alaska Placer Mining Application. http://dnr.alaska.gov/mlw/forms/10apma/hardrock.pdf Accessed July 28, 2010.
- Alaska Department of Natural Resources. File 1033. Pebble copper water sample. (Data from Cominco water samples collected 1991-1993; publication date unknown).
- Alpers, CN,Nordstrom, DK., and Spitzley, J. 2003. Extreme acid mine drainage from a pyritic massive sulfide deposit: The Iron Mountain end-member. *Environmental Aspects of Mine Wastes*. Edited by JL Jambor, DW Blowes, and AIM. Ritchie. Vancouver: Mineralogical Association of Canada. **31**: 407-430.
- Askaer, L, LB Schmidt, B Elberling, G Asmund and IS Jónsdóttir. 2008. Environmental Impact on an Arctic Soil–Plant System Resulting from Metals Released from Coal Mine Waste in Svalbard (78° N). Water, Air and Soil Pollution 195 (1-4): 99-114.
- Besser, JM, JA Kubitz, CG Ingersoll, WE Braselton and JP Giesy. 1995. Influences on copper bioaccumulation, growth, and survival of the midge, *Chironomus tentans*, in metal-contaminated sediments. <u>Journal of Aquatic Ecosystem Stress and Recovery Vol 4 (3): 157-168.</u>

- Brabets, TP. 2002. Water Resources Investigations Report 02-4127. Water Quality of the Tlikakila
 River and Five Major Tributaries to Lake Clark, Lake Clark National Park and Preserve, Alaska,
 1999-2001. US Geological Survey and the National Park Service. Anchorage, Alaska.
- Brabets, TP and RT Ourso. 2006. Water Quality, Physical Habitat, and Biology of the Kijik River Basin,
 Lake Clark National Park and Preserve, Alaska, 2004-2005. Scientific Investigations Report
 2006-5123. US Geological Survey and the National Park Service. Anchorage, Alaska.
- Brommeland, L. 2007. Site Activities/Technical Overview. Presentation to Alaska State regulators for PLP, November.
- Craciunescu, CN, MD Niculescu, Z Guo, AR Johnson, L Fischer, and SH Zeisel. 2009. Dose response effects of dermally applied diethanolamine on neurogenesis in fetal mouse hippocampus and potential exposure of humans. *Toxicological Sciences* 107 (1): 220-226.
- Crafford, T. 2007. ADNR memo to Lena Brommeland; subject: Pebble site visit, October 4. October 8.
- Davis Jr., R.A., A.T. Welty, J. Borrego, J.A. Morales, J.G. Pendon, J.G. Ryan, 2000, Rio Tinto Estuary (Spain): 5000 Years of Pollution: Environmental Geology 39 (10) September, p. 1107-1116; Springer-Verlag. Available at: <u>http://www.uhu.es/dgeo/investigacion/gcostera/pdf/Tinto%205000%20year%20pollution-Davis2000.pdf</u>
- Day, S. 2009. Presentation to Pebble Geochemistry Technical Working Group. SRK Consulting. Anchorage, AK. November.
- Fey et al, David L., Matthew Granitto, Stuart A. Giles, Steven M. Smith, Robert G. Eppinger, and Karen D. Kelley, 2008, Geochemical Data for Samples Collected in 2007 Near the Concealed Pebble Porphyry Cu-Au-Mo Deposit, Southwest Alaska: USGS Open-File Report 2008–1132, 159 pg. http://pubs.usgs.gov/of/2008/1132/
- Fey et al, DL, M Granitto, SA Giles, M Smith, RG Eppinger, and KD Kelley. 2009. Geochemical data for samples collected in 2008 near the concealed Pebble porphyry Cu-Au-Mo deposit, Southwest Alaska. USGS Open File Report 2009-1239,120 pg. <u>http://pubs.usgs.gov/of/2009/1239/downloads/OF09-1239.pdf</u>

- Garrett, JW, DH Bennett, FO Frost, and RF Thurow. 1998. Enhanced Incubation Success for Kokanee
 Spawning in Groundwater Upwelling Sites in a Small Idaho Stream. North American Journal of
 Fisheries Management 18 (4): 925-930
- Gilkeson, R. 2004. Groundwater Contamination in the Regional Aquifer Beneath the Los Alamos National Laboratory. Robert H. Gilkeson, Registered Geologist, Los Alamos, New Mexico.
- Godin, JJ. 1981. Migrations of salmonid fishers during early life history phases: daily and annual timing. *In* EL Brannon and EO Salo (Eds). Salmon and trout migratory symposium. pgs 22-47.
- Herbst, DB. 2004. Bioassessment monitoring of acid mine drainage impacts in streams of the Leviathan mine watershed: an update for 2001 and 2002 surveys. Final report to the Lahontan Regional Water Quality Control Board.

Josephy, PD and Mannervik, B. 2006. Molecular Toxicology, 2nd edition. Oxford University Press p 322.

Loeffler, B. 2009 Memo to Lamar Cotton, Borough Manager. Subject: Drilling mud toxicity. August 10.

- Kelley, Karen D., Lang, James, and Eppinger, Robert G., 2010, Exploration Geochemistry at the Giant Pebble Porphyry Cu-Au-Mo Deposit, Alaska: Society of Economic Geologists SEG Newsletter (#80) January, 2010, pg. 17-23; available at: <u>http://www.segweb.org/publications/featuredarticles.aspx</u>
- Kresic, N. 2007. Hydrogeology and groundwater modeling. CRC Press, Taylor and Francis Group. Boca Raton, FL.
- McCarthy, J and L Shevenell. 1998. Obtaining representative groundwater samples in a fractured and karstic formation. *Groundwater* 36 (2): 251-260.
- Mikkelsen, PE. 2002. Cement-bentonite grout backfill for borehole instruments. *Geochemical Instrument News*, December, pgs 38-42.
- Mitchell, NL and GA Lamberti. 2005. Responses in dissolved nutrients and epilithon abundance to spawning salmon in southeast Alaska streams. *Limnol. Oceanogr.* 50 (1): 217-227.
- Moody, C. 2008. Wetlands study update. Presentation to Alaska regulatory agencies. 3 Parameters Plus consulting, Anchorage, AK. November.
- Moran, Robert, 2007 (September), Pebble Hydrogeology and Geochemistry Issues; submitted to Renewable Resource Coalition, Anchorage, Alaska. Available at: <u>http://www.renewableresourcescoalition.org/MoranSep07.pdf</u>
- Moran, RE. 2010. Expert report submitted to Trustees for Alaska, August.
- National Research Council, 1999. Appendix B, Potential Environmental Impacts of Hardrock Mining *in* Hardrock Mining on Federal Lands, National Research Council, National Academy Press. Washington, D.C.
- Puckett, KJ, E Nieboer, MJ Gorzynski, and DHS Richardson. 1973. The uptake of metal ions by lichens: a modified ion-exchange process. *New Phytologist* 72: 329-342
- Rains, M. 2008. Surface Water and Groundwater Interactions in Small Pools on the Pebble Property. Presentation to Alaska regulatory agencies. Coshow Environmental, Inc. Anchorage, AK. November.
- Randall, DJ and TKN Tsui. 2002. Ammonia toxicity in fish. Marine Pollution Bulletin (45): 17-23
- Rebagliati, CM and JG Payne. 2005. 2004 Summary Report on the Pebble Porphyry Gold-Copper Project. for Northern Dynasty Minerals, Ltd. March 31.
- Rebagliati, CM, J Lang, E Titley, D Gaunt, D Rennie, L Melis, D Barratt, and S Hodgson. 2008. Technical Report on the 2007 Program and Update on Metallurgy and Resources on the Pebble Copper-Gold-Molybdenum Project, Iliamna Lake area, Southwestern Alaska, USA. for Northern Dynasty Minerals, Ltd.
- Rebagliati, CM, J Lang, E Titley, D Rennie, L Melis, D Barratt, and S Hodgson. 2009. Technical Report on the 2008 Program and Update on Metallurgy and Resources on the Pebble Copper-Gold-Molybdenum Project, Iliamna Lake area, Southwestern Alaska, USA. for Northern Dynasty Minerals, Ltd.
- Rice, SD and JE Bailey. 1980. Ammonia concentrations in pink salmon, *Onchorynchus gorbuscha*, redds of Sashin Creek, Southeastern Alaska. *Fishery Bulletin* 78 (3): 809-811.

Richardson, DHS. 1995. Metal uptake in lichens. Symbiosis 18: 119-127.

Schuman, GE, LA King, and JA Smith. 2000. Reclamation of bentonite-mined lands. American Society of Agronomy. Agronomy monograph #41.

Shanahan, P. 2004. Review of Robert Gilkeson report. Memo to RACER project files.

- Smith, EA, SL Prues, FW Oehme. 1997. "Environmental Degradation of Polyacrylamides and its Effects of Environmental (Outdoor) Exposure." Ecotoxicology and Environmental Safety 37(1), 76-91.
- Stekoll, Michael S., William W. Smoker, Ivan A. Wang, and Barbi J. Failor, 3 February 2003a: Final Report for ASTF Grant #98-1-012, Salmon as a Bioassay Model of Effects of Total Dissolved Solids, JCSFOS 2003-002, for the Alaska Science and Technology Foundation, by the University of Alaska Fairbanks, Juneau Center School of Fisheries and Ocean Sciences.
- Stekoll, M., W. Smoker, I. Wang and B. Failor, 2003b. Final report for ASTF grant #98-1-012. Salmon as a bioassay model of effects of total dissolved solids. Juneau, Alaska, University of Alaska – Fairbanks, pp: 87.
- Thornton, I and P Abraham. 1984. Historical records of metal pollution in the environment. *In* J.O. Nriagu (Ed.) Changing metal cycles and human health. Springer-Verlag, New York.
- Thurston, RV and RC Russo. 1983. Acute toxicity of ammonia to rainbow trout. *Transactions of the American Fisheries Society* (112): 696-704.
- Weber-Scannell, PK and LK Duffy. 2007. Effects of total dissolved solids on aquatic organisms: a review of literature and recommendation for salmonid species. *American J Env Sci* 3 (1): 1-6
- Wicks, BJ, R Joensen, Q Tang, and DJ Randall. 2002. Swimming and ammonia toxicity in salmonids: the effect of sublethal ammonia exposure on swimming performance of coho salmon and the acute toxicity of ammonia in swimming and resting rainbow trout. *Aquatic Toxicology* 59: 55-69.
- Wilkin, RT. 2000. Fate and transport of contaminants from acid mine drainage. US EPA Scientist-to-Scientist meeting, Las Vegas, NV.
- Wobus, C. 2009. Initial comments on Pebble Mine hydrology and hydrogeology. Memorandum to CSP2 from Stratus Consulting, Boulder, CO

- Woodrow, J. E., Seiber, J. N., Miller, G. C. 2008, "Acrylamide release resulting from sunlight irradiation of aqueous polyacrylamide/iron mixtures." Journal of Agriculture and Food Chemistry, 56(8), 2773-2779
- U.S. Environmental Protection Agency. 1976. Quality criteria for water: U.S. Environmental Protection Agency, Washington, D.C., 256 p.
- U.S. Environmental Protection Agency. 1992. A Framework for Ecological Risk Assessment. Office of Research and Development, Risk Assessment Forum, Washington, DC. EPA/630/R-92/001. February 1992.
- U.S. Environmental Protection Agency. 2000. Generalized Short-Term Effects of Acidity on Fish in National Water Quality Inventory: 1998 Report to Congress, U.S. Environmental Protection Agency, Washington, DC, June 2000.
- U.S. Environmental Protection Agency. Watershed Risk Assessment. Online training and documents www.epa.gov/watertrain/ecorisk/ Accessed August 14 2010.
- Zamzow, K and R. Moran. 2008. Letter to John Shively and Ken Taylor of the Pebble Partnership and to Ed Fogels, ADNR. November 11.

Northern Dynasty and Pebble Limited Partnership reports used in this review:

Northern Dynasty Mines, Inc., November 2005c, Draft Environmental Baseline Studies 2004 Progress Reports, Chapter 6, Water Chemistry. http://www.ADNR.state.ak.us/mlw/mining/largemine/pebble/env_baseline_studies.ht m#2004 reports

- Northern Dynasty Mines, Inc., June 2005, Draft Environmental Baseline Studies 2004 Progress Reports, Chapter 8, Geochemical Characterization & Metals Leaching/Acid Rock Drainage.
- Pebble Limited Partnership. 2008. Pre-permitting Environmental/Socio-Economic Data Report Series. Report Series B: Surface Water Hydrology. HDR Alaska and Knight-Piesold.
- Pebble Limited Partnership. 2008. Pre-permitting Environmental/Socio-Economic Data Report Series. Report Series D. Section D-6. Water Management Consultants.

Pebble Limited Partnership. 2008. Pre-permitting Environmental/Socio-Economic Data Report Series. Report Series F: Surface Water and Groundwater Quality. HDR Alaska, SLR Alaska, Water Management Consultants, CH2M Hill, and Bristol Environmental & Engineering Services Corporation.

Pebble Limited Partnership. 2008. Pebble Project Environmental Baseline Studies, 2008 Field Sampling Plan, Groundwater Hydrology and Water Quality, Mine Study Area. Draft.

Please note that Pebble 2008 reports are drafts and have not been finalized. All Pebble Partnership reports are available on line at <u>http://www.pebblepartnership.com/pages/environment/environment-pre-permitting.php</u>