# APPENDIX 2
# DFO ATTACHMENTS

# *DFO 3.2.3 ATTACHMENT 1: TABLE 1 SHIP-BASED OBSERVER PROGRAM - MARINE MAMMAL OBSERVATIONS AND SURVEY TIME (2013 TO 2015)*

## Table 1 Ship-based Observer Program - Marine Mammal Observations and Survey Time (2013 to 2015)

| **Species** | **2013** | | **2014** | | | **2015** | | |
|---|---|---|---|---|---|---|---|---|
| | **Aug 06, 07** | **Oct 01** | **Aug 15** | **Sept 07** | **Sept 10** | **Aug 23** | **Sept 01** | **Sept 25** |
| Narwhal | 5 | 0 | 7 to 9 | 0 | 0 | 0 | 5 | 10 |
| Long-finned pilot whale | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Blue whale | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Minke whale | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Humpback whale | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Sei whale | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| White-beaked dolphin | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Ringed seal | 43 | 2 | 2 | - | - | - | - | 1 |
| Harp seal | 10 to 15 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Unidentified whale | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Unidentified dolphin | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Unidentified seal | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 |
| **Observation hours** | 4.5 | 1 | 6 | 1 | 2 | 3 | 2 | 4 |

# APPENDIX 3
# ECCC ATTACHMENTS

# *ECCC 4 ATTACHMENT 1: DETAILED EMISSION RATES CALCULATIONS FOR LOCOMOTIVES*

Detailed emission rates calculations for Locomotives

A locomotive in a railyard operates at various loads while idling and moving. As proposed in the table 4-6 of USEPA Locomotives emission standard (USEPA, 1997), a locomotive “switching” wagons in a railyard is idling approximately 60% of the time and moving at throttle notch between 1 and 2 approximately 25% of the time.

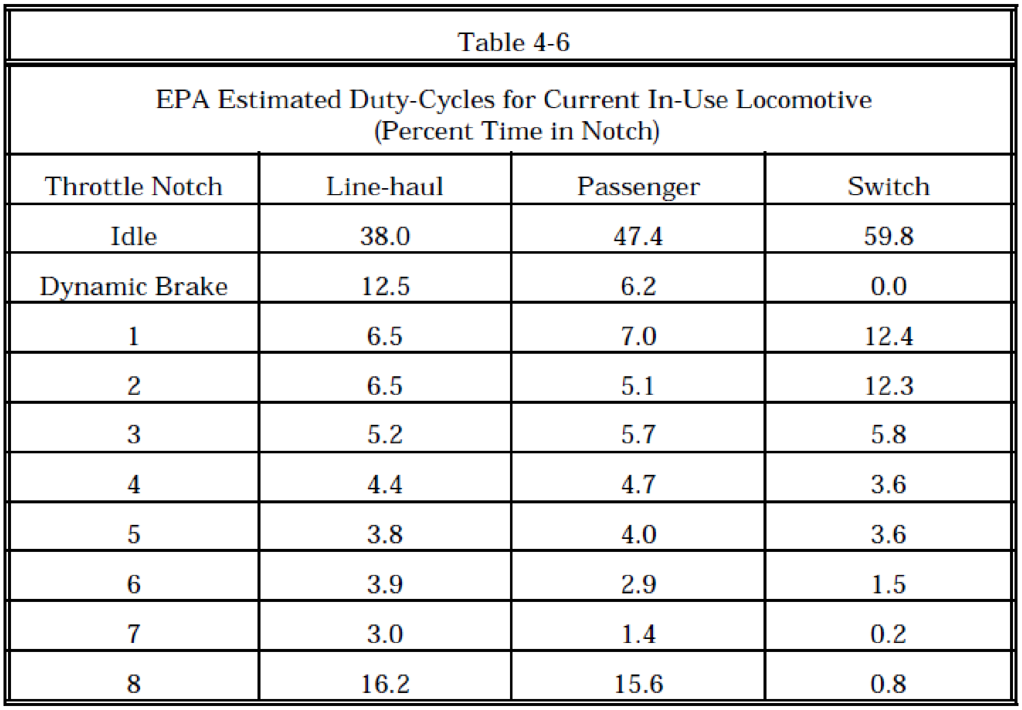


Table 4-6

EPA Estimated Duty-Cycles for Current In-Use Locomotive (Percent Time in Notch)

| Throttle Notch | Line-haul | Passenger | Switch |
|---|---|---|---|
| Idle | 38.0 | 47.4 | 59.8 |
| Dynamic Brake | 12.5 | 6.2 | 0.0 |
| 1 | 6.5 | 7.0 | 12.4 |
| 2 | 6.5 | 5.1 | 12.3 |
| 3 | 5.2 | 5.7 | 5.8 |
| 4 | 4.4 | 4.7 | 3.6 |
| 5 | 3.8 | 4.0 | 3.6 |
| 6 | 3.9 | 2.9 | 1.5 |
| 7 | 3.0 | 1.4 | 0.2 |
| 8 | 16.2 | 15.6 | 0.8 |

The maximum rated power of the locomotives is 4,400 HP. The following table 5-2 from the USEPA document was used to convert “throttle notch” into an average rated power of 364 HP, accounting for the fact that the locomotive is moving approximately 40% of the time.

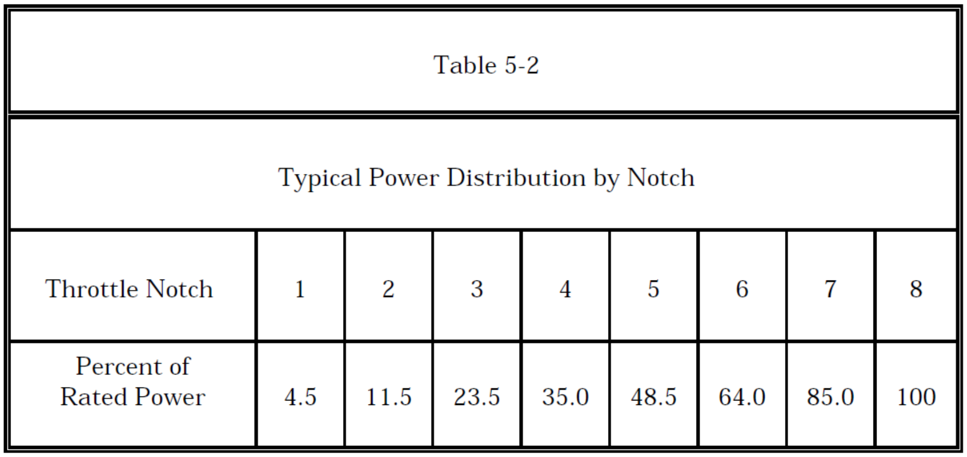
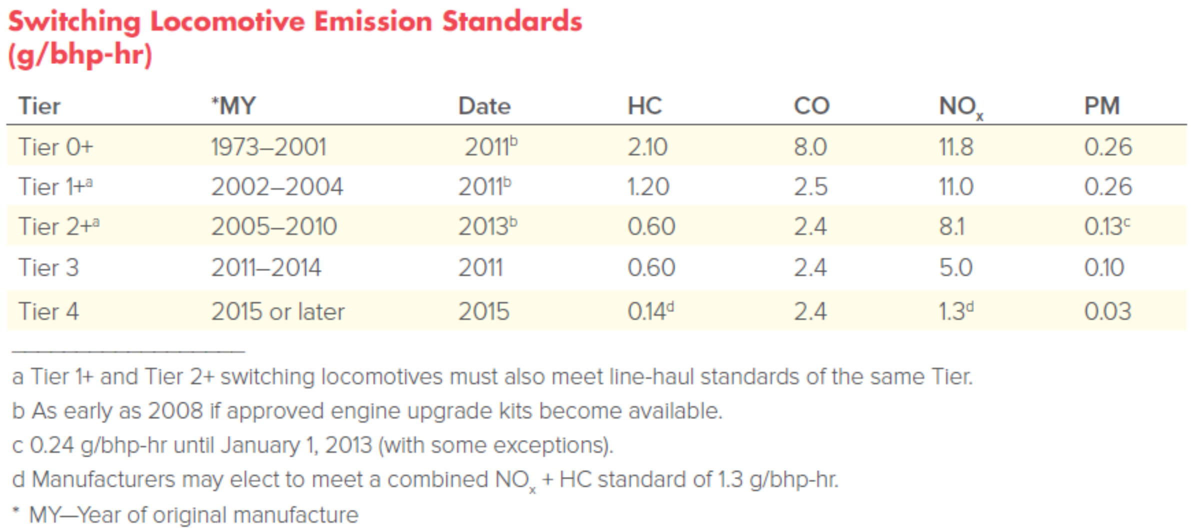


Table 5-2

Typical Power Distribution by Notch

| Throttle Notch | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Percent of Rated Power | 4.5 | 11.5 | 23.5 | 35.0 | 48.5 | 64.0 | 85.0 | 100 |

Tier 3 emission factors for $NO_X$, CO and PM, for a switching locomotive were taken from the Locomotive Emissions monitoring Program (Railway Association of Canada, , 2014), also shown below:



**Switching Locomotive Emission Standards (g/bhp-hr)**

| Tier | *MY | Date | HC | CO | $NO_x$ | PM |
|---|---|---|---|---|---|---|
| Tier 0+ | 1973–2001 | 2011[b] | 2.10 | 8.0 | 11.8 | 0.26 |
| Tier 1+[a] | 2002–2004 | 2011[b] | 1.20 | 2.5 | 11.0 | 0.26 |
| Tier 2+[a] | 2005–2010 | 2013[b] | 0.60 | 2.4 | 8.1 | 0.13[c] |
| Tier 3 | 2011–2014 | 2011 | 0.60 | 2.4 | 5.0 | 0.10 |
| Tier 4 | 2015 or later | 2015 | 0.14[d] | 2.4 | 1.3[d] | 0.03 |

---

a Tier 1+ and Tier 2+ switching locomotives must also meet line-haul standards of the same Tier.

b As early as 2008 if approved engine upgrade kits become available.

c 0.24 g/bhp-hr until January 1, 2013 (with some exceptions).

d Manufacturers may elect to meet a combined $NO_x$ + HC standard of 1.3 g/bhp-hr.

* MY—Year of original manufacture

An example calculation for the moving locomotive $NO_X$ emission rate is shown below (assuming no power losses):

$NO_X$ Emission rate = average locomotive power X Emission factor (g/bHp-hr)

$NO_X$ Emission rate (g/s) = 364 HP X 5.0 g/bHP-hr X 1 hour /3600 seconds

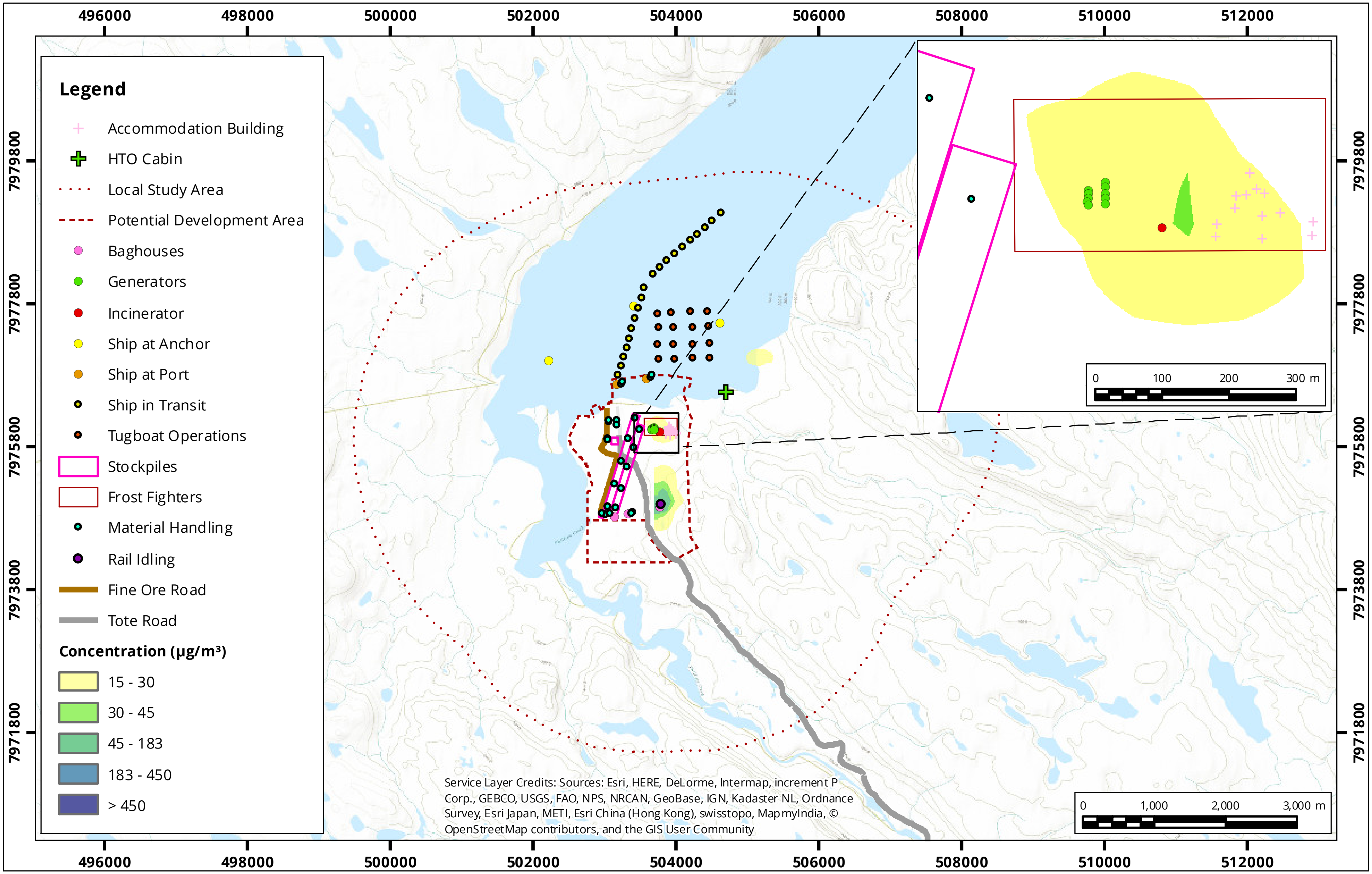
0.505 g/s

The locomotive idling emission rates were estimated based on measurements previously conducted by RWDI. The $NO_X$ emission rate for idling is 0.388 g/s. Since the locomotive is idling approximately 60% of the time, the average idling emission rate is 0.388 g/s x 60% = 0.233 g/s.

The total NOX emission rate for 2 locomotives in the railyard can be estimate by:

( 0.233 g/s + 0.505 g/s ) x 2 locomotive = 1.48 g/s

# *ECCC 5 ATTACHMENT 1: FIGURE D1B; FIGURE D3; FIGURE D4B; FIGURE D6; FIGURE D12B; FIGURE D15; FIGURE E1B; FIGURE E3; FIGURE E4B; FIGURE E6; FIGURE E12B; FIGURE E15; FIGURE F16B; FIGURE F19*



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# Predicted Maximum 1-Hour $SO_2$ Concentrations
## Milne Port

True North

| Drawn by: DJH | Figure: D-1b |
|---|---|
| Approx. Scale: | 1:75,000 |
| Date Revised: | Dec 13, 2018 |

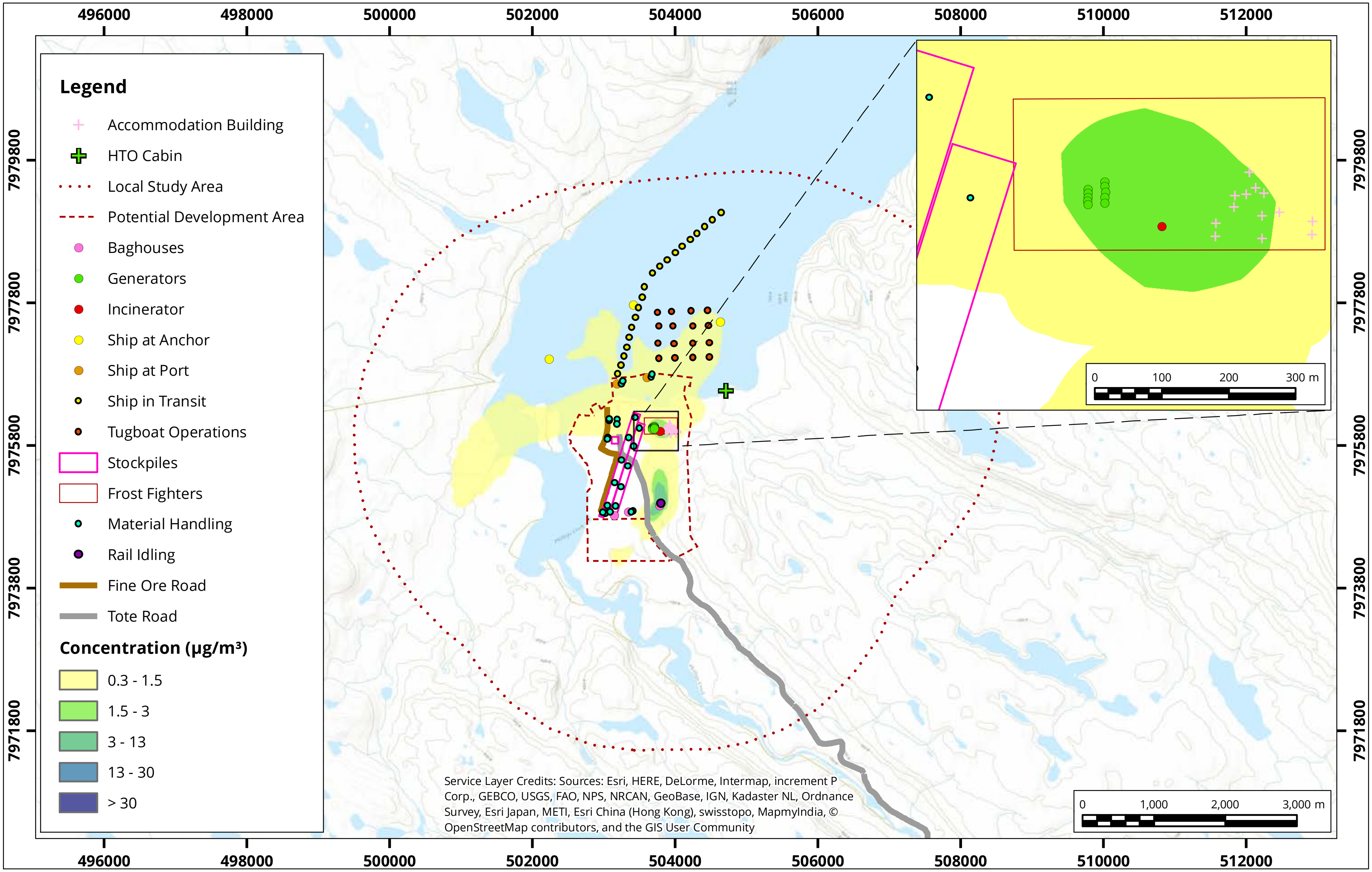
Map Projection: NAD 1983 UTM Zone 17N

1-Hour $SO_2$ CAAQS: 183 µg/m³

Baffinland Iron Mines Corporation - Nunavut, Canada

Project #: 1402090

Map Document: C:\Users\djh\OneDrive - ROWAN WILLIAMS DAVIES & IRWIN INC\GIS Temp\1402090\BK\Port\1402090 - Baffinland - AQ Milne Contour Plots_170419.mxd



Service Layer Credits: Sources: Esri, HERE, DeLorme, Intermap, increment P Corp., GEBCO, USGS, FAO, NPS, NRCAN, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China (Hong Kong), swisstopo, MapmyIndia, © OpenStreetMap contributors, and the GIS User Community

# Predicted Annual $SO_2$ Concentrations
## Milne Port

Map Projection: NAD 1983 UTM Zone 17N
Baffinland Iron Mines Corporation - Nunavut, Canada

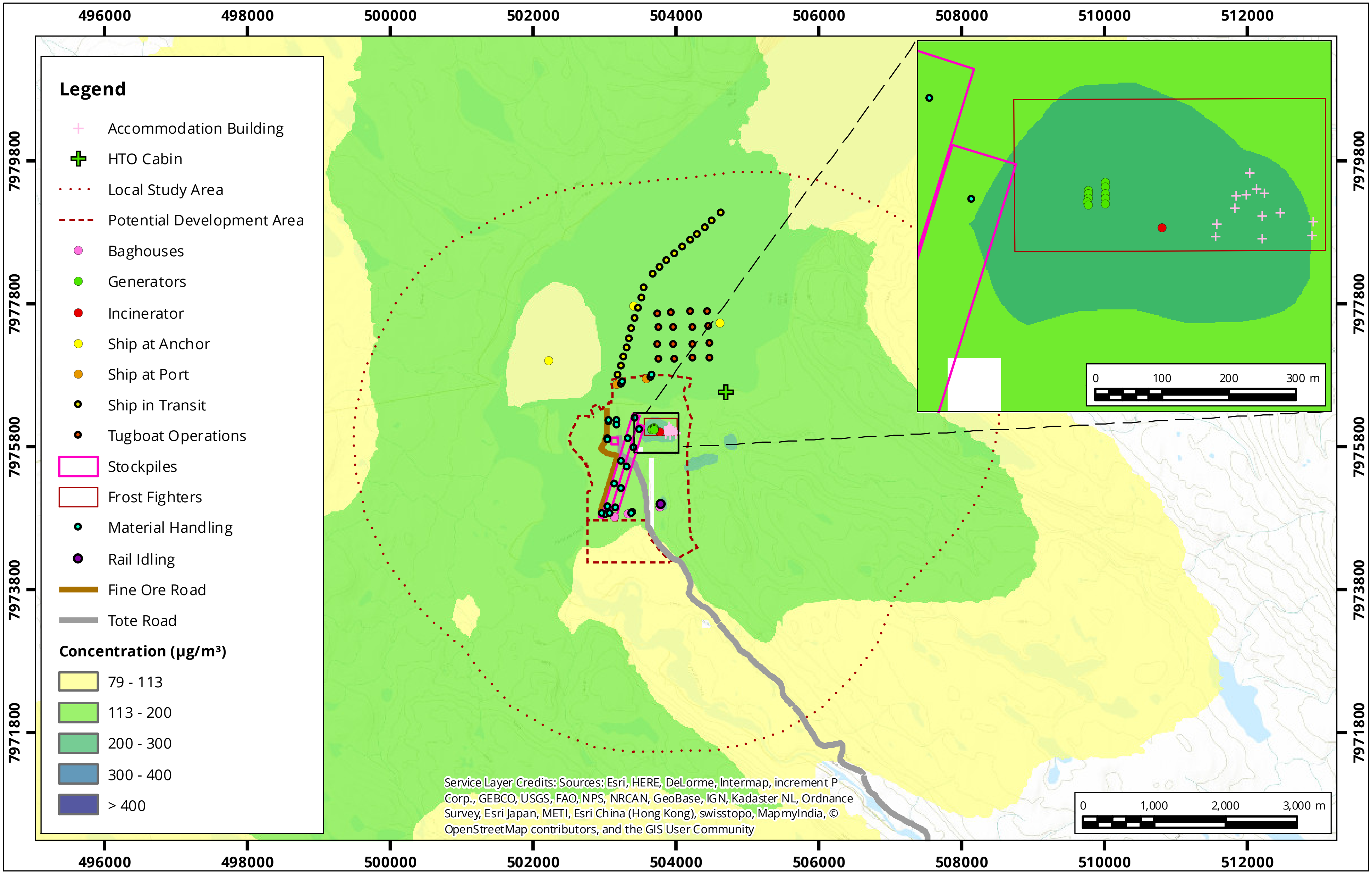
Annual $SO_2$ Indicator Threshold: 30 µg/m³
Annual $SO_2$ CAAQS: 13 µg/m³

True North

Project #: 1402090

| | |
|---|---|
| Drawn by: DJH | Figure: D-3 |
| Approx. Scale: | 1:75,000 |
| Date Revised: | Jan 3, 2019 |

Map Document: C:\Users\djh\OneDrive - ROWAN WILLIAMS DAVIES & IRWIN INC\GIS Temp\1402090\BK\Port\1402090 - Baffinland - AQ Milne Contour Plots_upd_181213.mxd



Service Layer Credits: Sources: Esri, HERE, DeLorme, Intermap, increment P Corp., GEBCO, USGS, FAO, NPS, NRCAN, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China (Hong Kong), swisstopo, MapmyIndia, © OpenStreetMap contributors, and the GIS User Community

# Predicted Maximum 1-Hour $NO_2$ Concentrations
## Milne Port

Map Projection: NAD 1983 UTM Zone 17N

Baffinland Iron Mines Corporation - Nunavut, Canada

1-Hour $NO_2$ 2020 CAAQS: 113 μg/m³

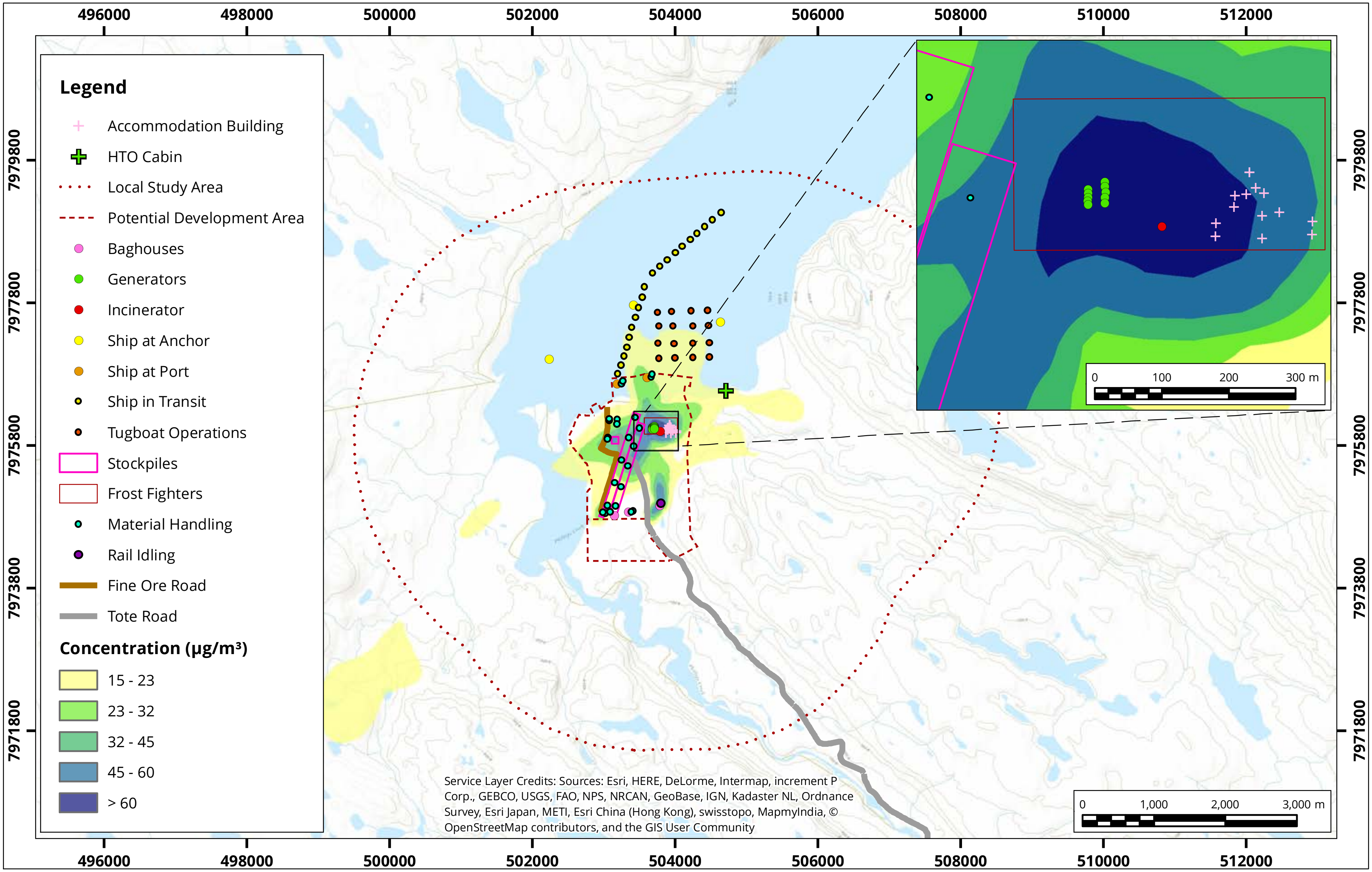
1-Hour $NO_2$ 2025 CAAQS: 79 μg/m³

True North

Project #: 1402090

| | |
|---|---|
| Drawn by: DJH | Figure:D-4b |
| Approx. Scale: | 1:75,000 |
| Date Revised: | Dec 13, 2018 |

Map Document: C:\Users\djh\OneDrive - ROWAN WILLIAMS DAVIES & IRWIN INC\GIS Temp\1402090\JBK\Port\1402090 - Baffinland - AQ Milne Contour Plots_170419.mxd



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# Predicted Annual $NO_2$ Concentrations
## Milne Port

Map Projection: NAD 1983 UTM Zone 17N
Baffinland Iron Mines Corporation - Nunavut, Canada

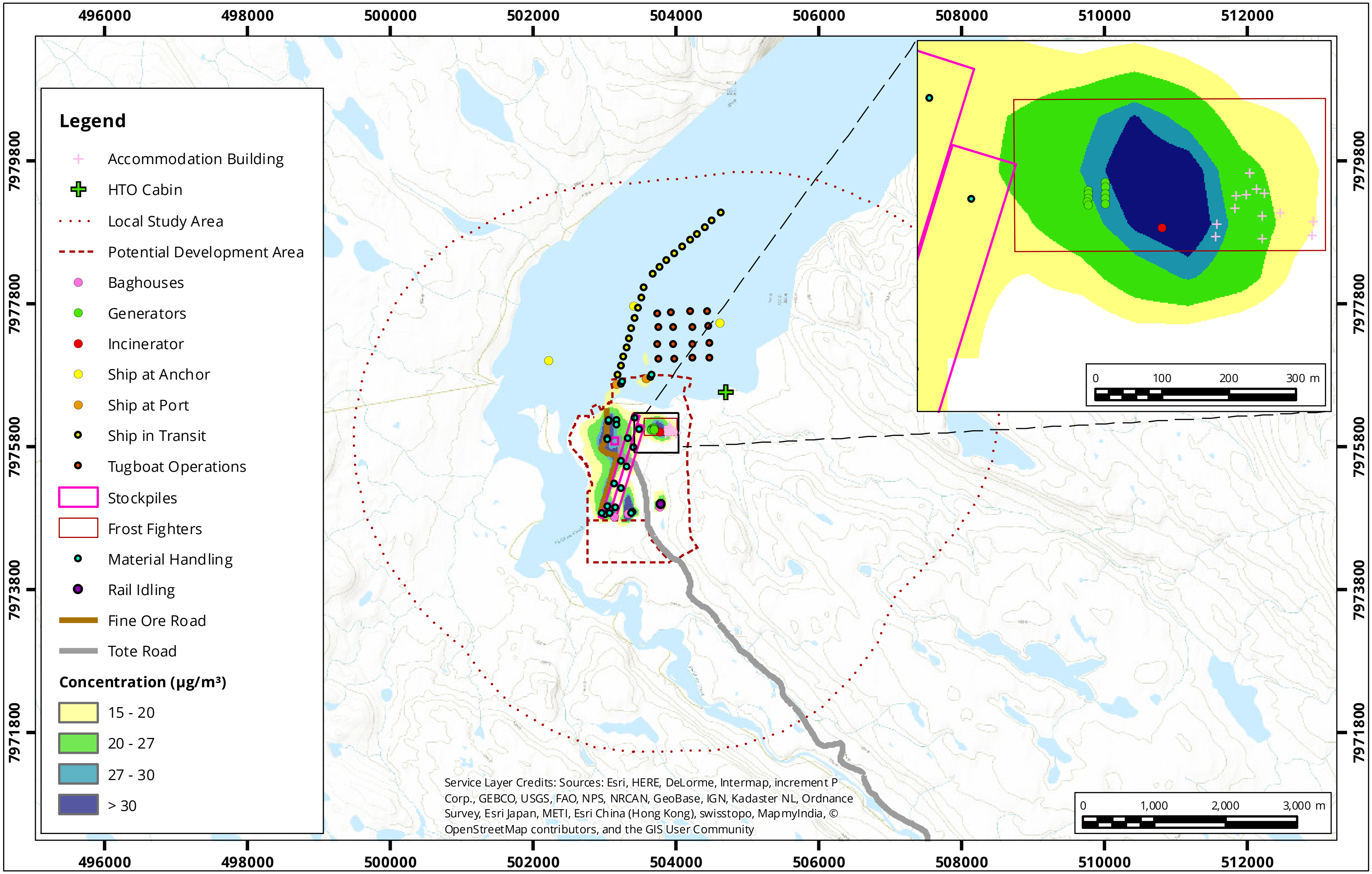
Annual $NO_2$ 2020 CAAQS: 32 μg/m³
Annual $NO_2$ 2025 CAAQS: 23 μg/m³

True North

Project #: 1402090

| | |
|---|---|
| Drawn by: DJH | Figure: D-6 |
| Approx. Scale: | 1:75,000 |
| Date Revised: | Jan 3, 2019 |

Map Document: C:\Users\djh\OneDrive - ROWAN WILLIAMS DAVIES & IRWIN INC-\GIS Temp\1402090\BIK\Port\1402090 - Baffinland - AQ Milne Contour Plots_upd_181213.mxd



Service Layer Credits: Sources: Esri, HERE, DeLorme, Intermap, increment P Corp., GEBCO, USGS, FAO, NPS, NRCAN, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China (Hong Kong), swisstopo, MapmyIndia, © OpenStreetMap contributors, and the GIS User Community

# Predicted Maximum 24-Hour $PM_{2.5}$ Concentrations
## Milne Port

Map Projection: NAD 1983 UTM Zone 17N

24-Hour $PM_{2.5}$ CAAQS: 27 µg/m³

Baffinland Iron Mines Corporation - Nunavut, Canada

True North

Project #: 1402090

Drawn by: DJH

Figure: D-12b

Approx. Scale: 1:75,000

Date Revised: Dec 13, 2018

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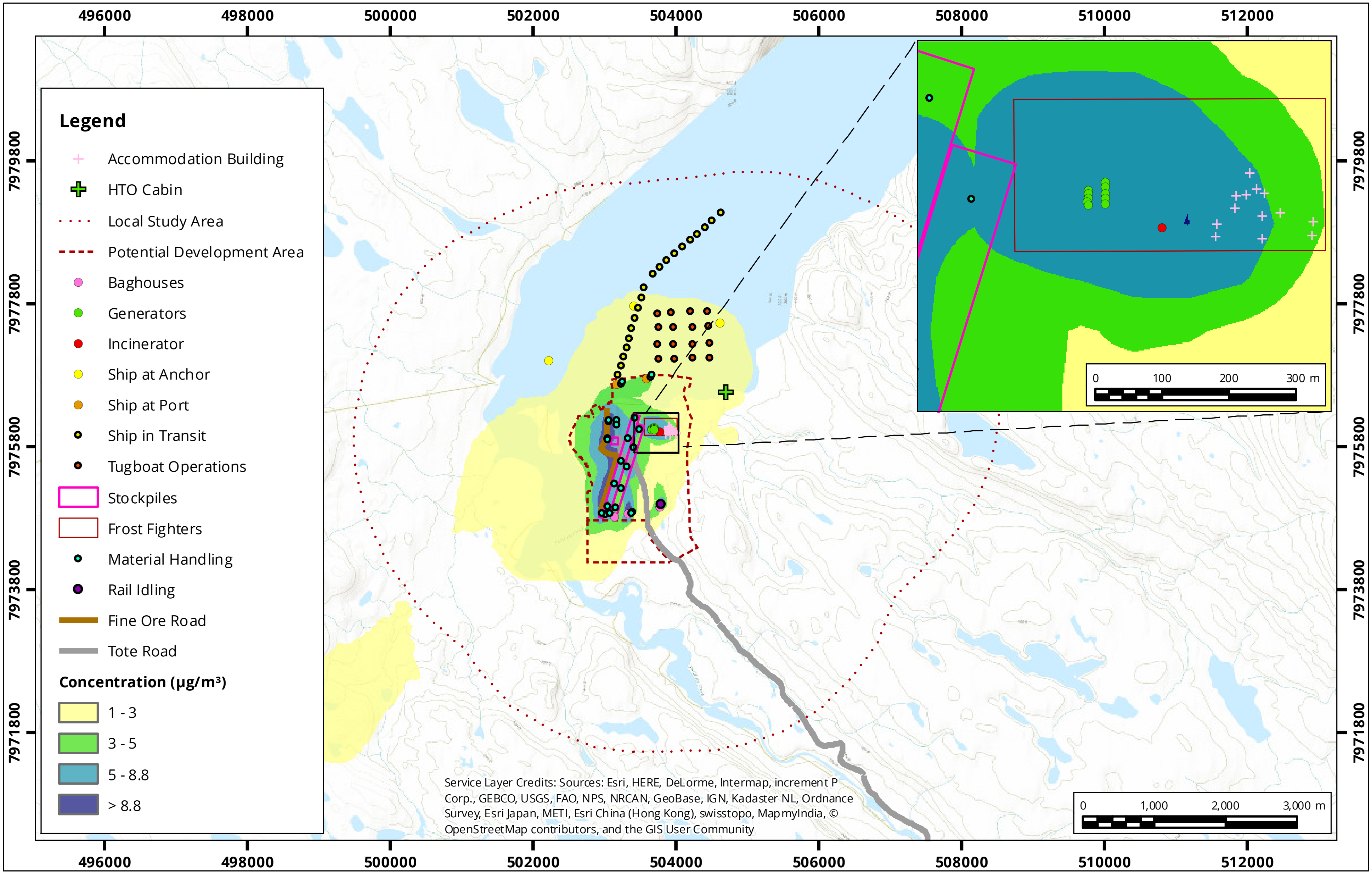

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# Predicted Maximum Annual $PM_{2.5}$ Concentrations
## Milne Port

True North

Drawn by: DJH | Figure:D-15

Approx. Scale: 1:75,000

Date Revised: Dec 13, 2018

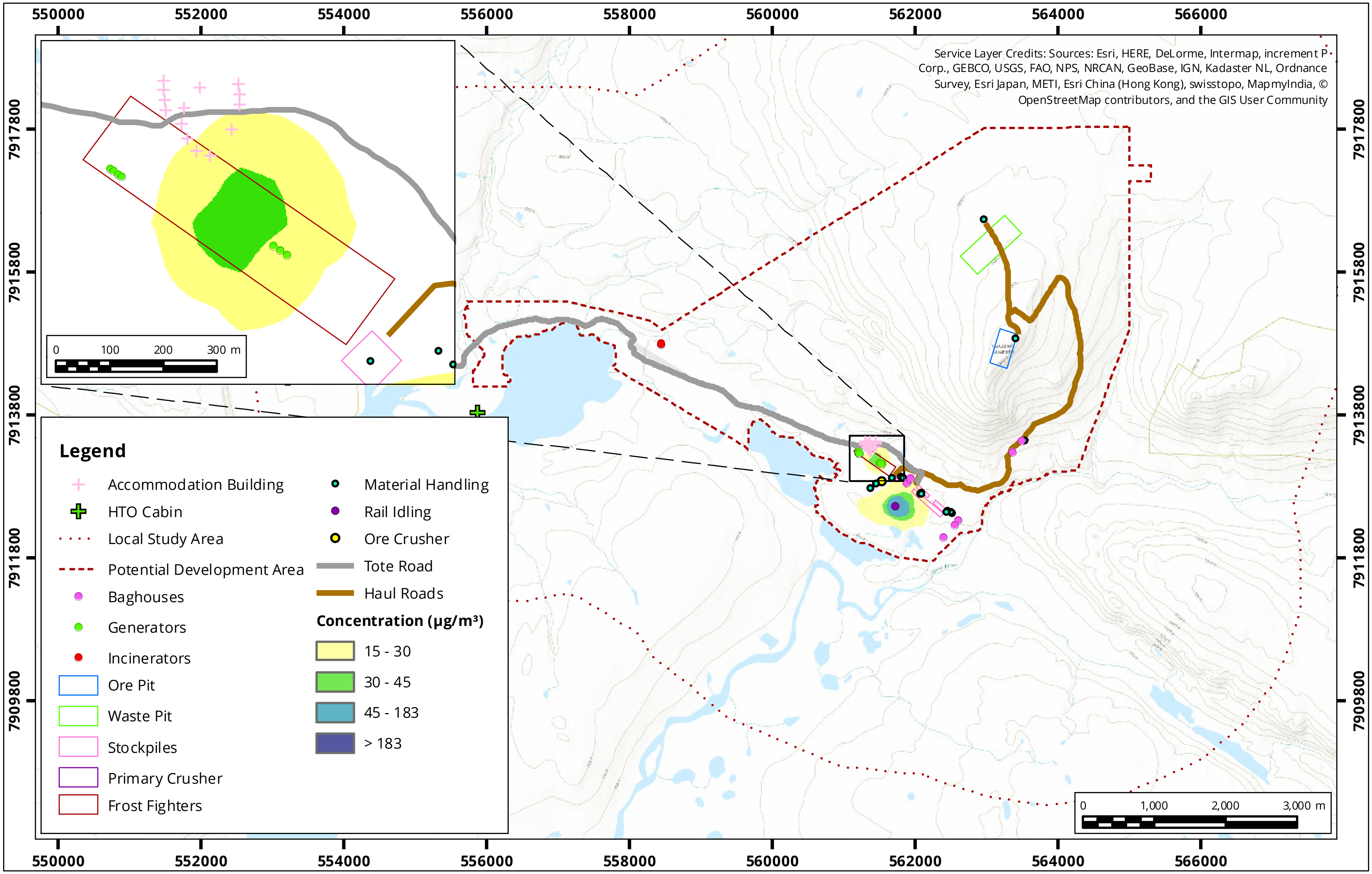
Map Projection: NAD 1983 UTM Zone 17N

Annual $PM_{2.5}$ CAAQS: 8.8 µg/m³

Baffinland Iron Mines Corporation - Nunavut, Canada

Project #: 1402090

Map Document: C:\Users\djh\OneDrive - ROWAN WILLIAMS DAVIES & IRWIN INC-\GIS Temp\1402090\BK\Port\1402090 - Baffinland - AQ Milne Contour Plots_170419.mxd



## Predicted 1-Hour $SO_2$ Concentrations
### Mine Site

True North

| Drawn by: DJH | Figure: E-1b |
|---|---|
| Approx. Scale: | 1:75,000 |
| Date Revised: | Dec 13, 2018 |

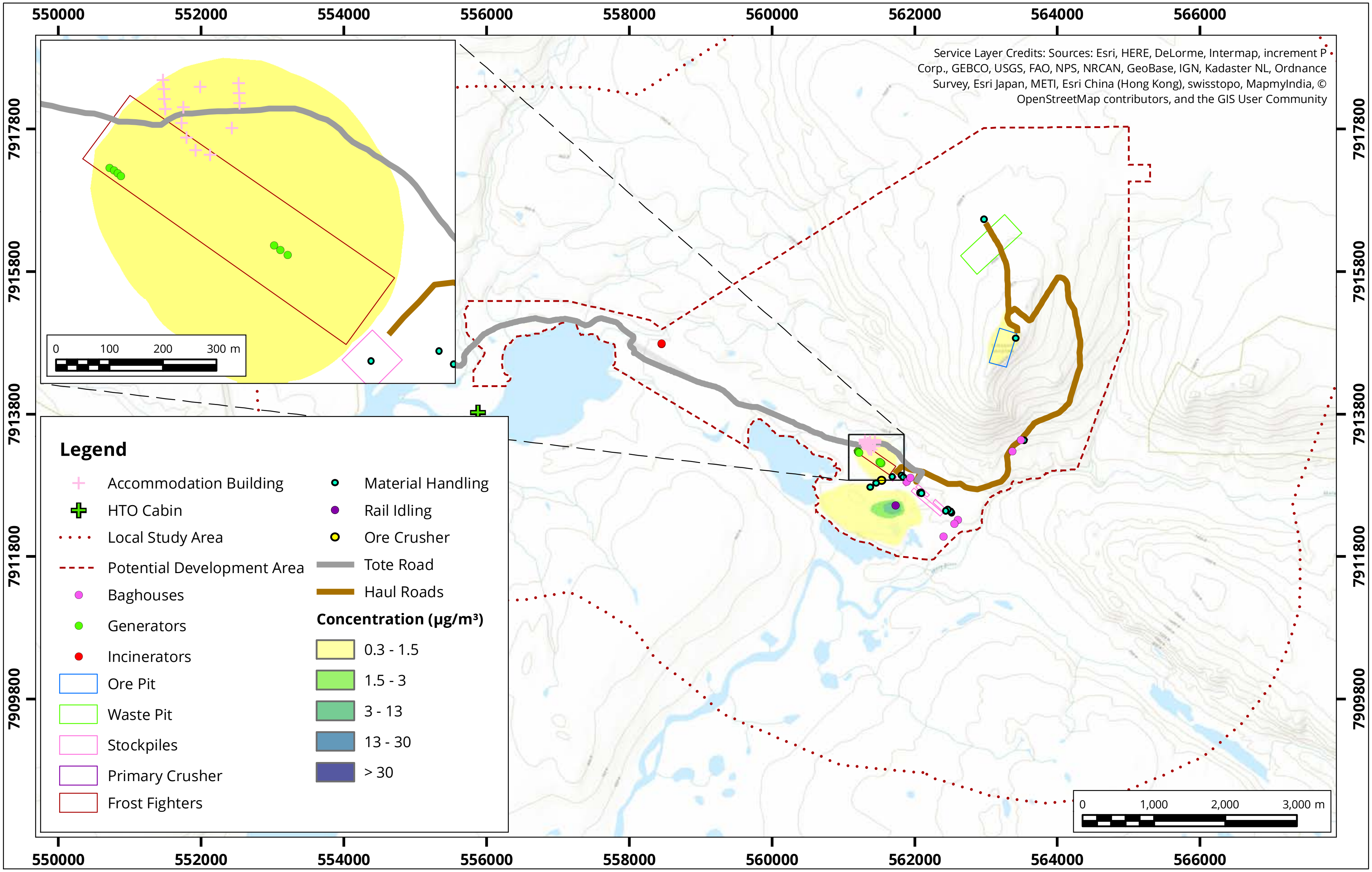
Map Projection: NAD 1983 UTM Zone 17N

1-Hour $SO_2$ CAAQS: 183 µg/m³

Baffinland Iron Mines Corporation - Nunavut, Canada

Project #: 1402090

Map Document: C:\Users\djh\OneDrive - ROWAN WILLIAMS DAVIES & IRWIN INC\GIS Temp\1402090\BK\Mine\1402090 - Baffinland - AQ Mine Contour Plots_upd_181213.mxd



# Predicted Annual $SO_2$ Concentrations

## Mine Site

Map Projection: NAD 1983 UTM Zone 17N

Baffinland Iron Mines Corporation - Nunavut, Canada

Annual $SO_2$ Indicator Threshold: 30 µg/m³

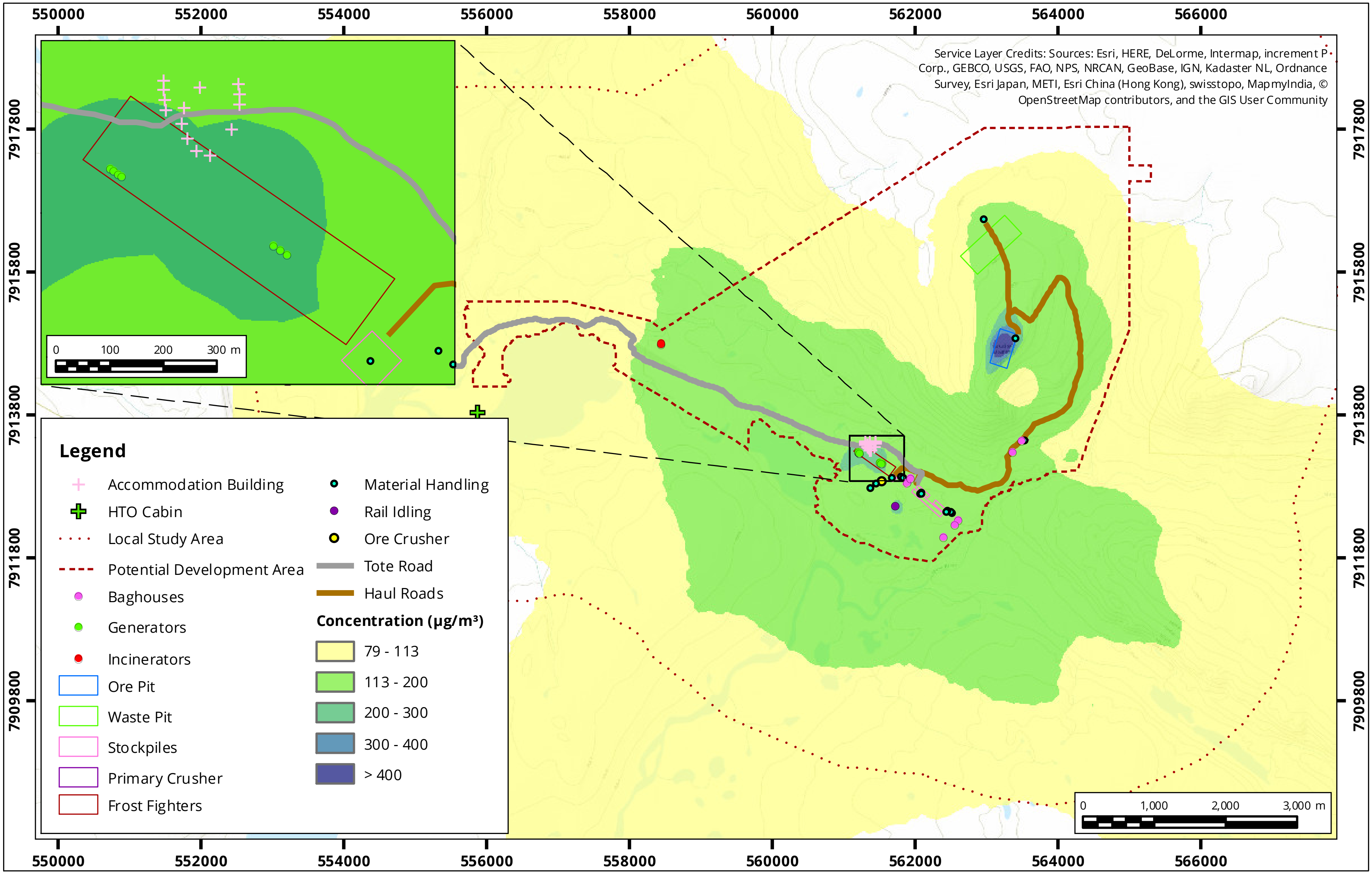
Annual $SO_2$ CAAQS: 13 µg/m³

True North

Project #: 1402090

| | |
|---|---|
| Drawn by: DJH | Figure: E-3 |
| Approx. Scale: | 1:75,000 |
| Date Revised: | Jan 3, 2019 |

Map Document: C:\Users\djh\OneDrive - ROWAN WILLIAMS DAVIES & IRWIN INC-\GIS Temp\1402090\BK\Mine\1402090 - Baffinland - AQ Mine Contour Plots_upd_181213.mxd



# Predicted 1-Hour $NO_2$ Concentrations

## Mine Site

Map Projection: NAD 1983 UTM Zone 17N

Baffinland Iron Mines Corporation - Nunavut, Canada

1-Hour $NO_2$ 2020 CAAQS: 113 µg/m³

1-Hour $NO_2$ 2025 CAAQS: 79 µg/m³

True North

Project #: 1402090

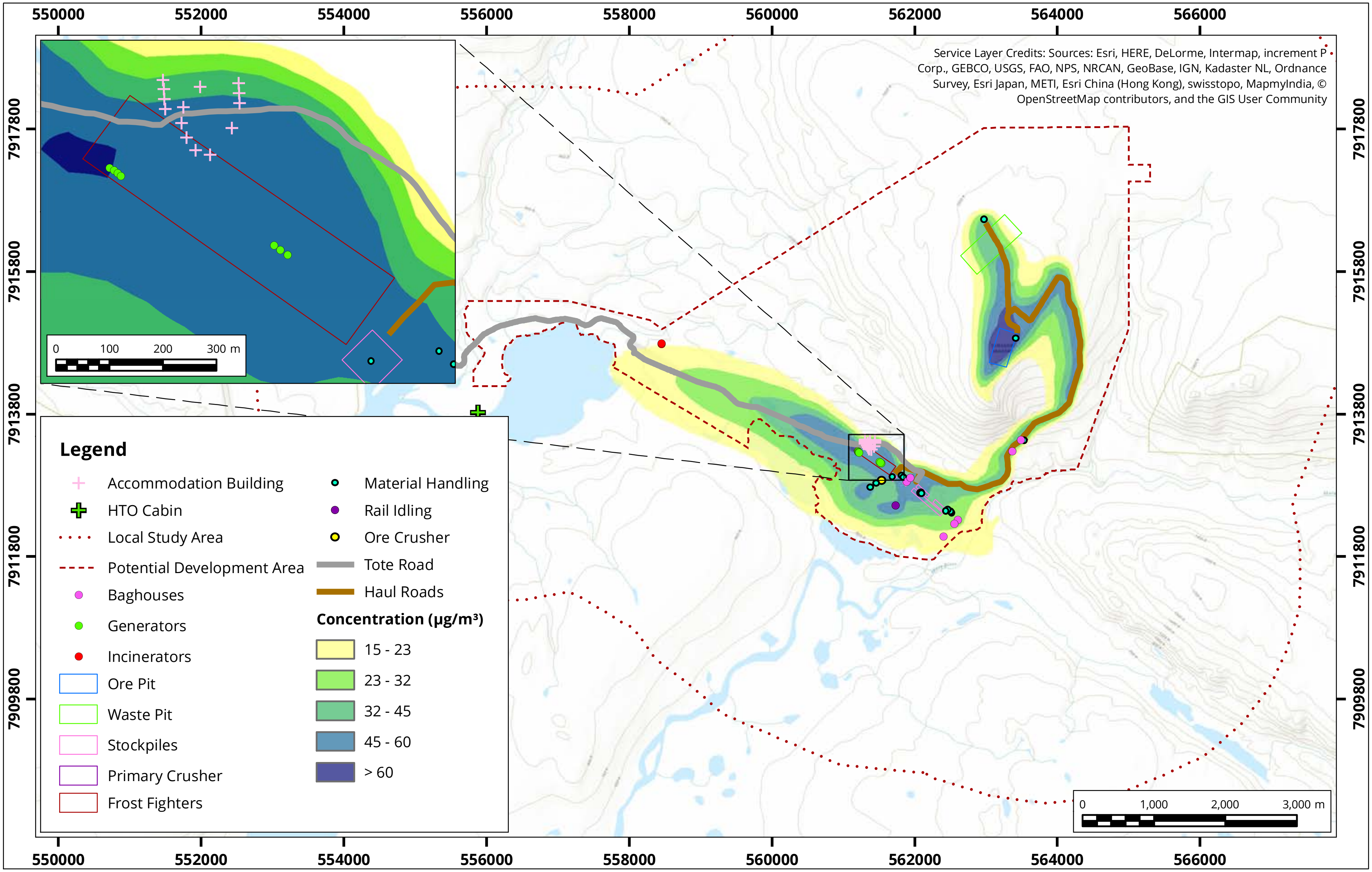
Drawn by: DJH

Figure: E-4b

Approx. Scale: 1:75,000

Date Revised: Dec 13, 2018

Map Document: C:\Users\djh\OneDrive - ROWAN WILLIAMS DAVIES & IRWIN INC\GIS Temp\1402090\BK Mine\1402090 - Baffinland - AQ Mine Contour Plots_upd_181213.mxd



# Predicted Annual $NO_2$ Concentrations
## Mine Site

True North

Drawn by: DJH

Figure: E-6

Approx. Scale: 1:75,000

Date Revised: Jan 3, 2019

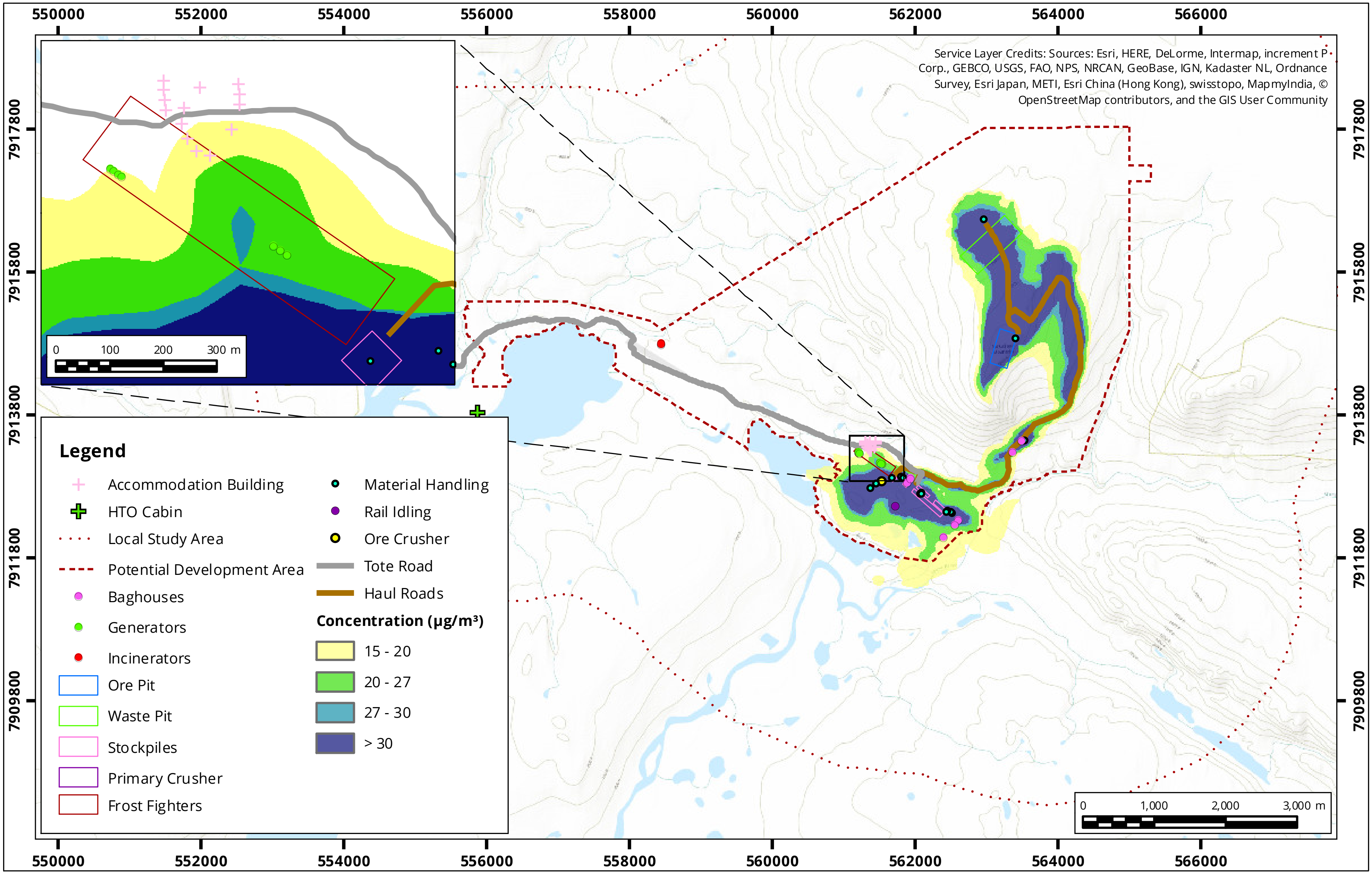
Map Projection: NAD 1983 UTM Zone 17N

Annual $NO_2$ 2020 CAAQS: 32 µg/m³
Annual $NO_2$ 2025 CAAQS: 23 µg/m³

Baffinland Iron Mines Corporation - Nunavut, Canada

Project #: 1402090

Map Document: C:\Users\djh\OneDrive - ROWAN WILLIAMS DAVIES & IRWIN INC\GIS Temp\1402090\BKMine\1402090 - Baffinland - AQ Mine Contour Plots_upd_181213.mxd



## Predicted 24-Hour PM$_{2.5}$ Concentrations
### Mine Site

Map Projection: NAD 1983 UTM Zone 17N

24-Hour PM$_{2.5}$ CAAQS: 27 µg/m³

Baffinland Iron Mines Corporation - Nunavut, Canada

True North

Project #: 1402090

Drawn by: DJH

Figure: E-12b

Approx. Scale: 1:75,000

Date Revised: Dec 13, 2018

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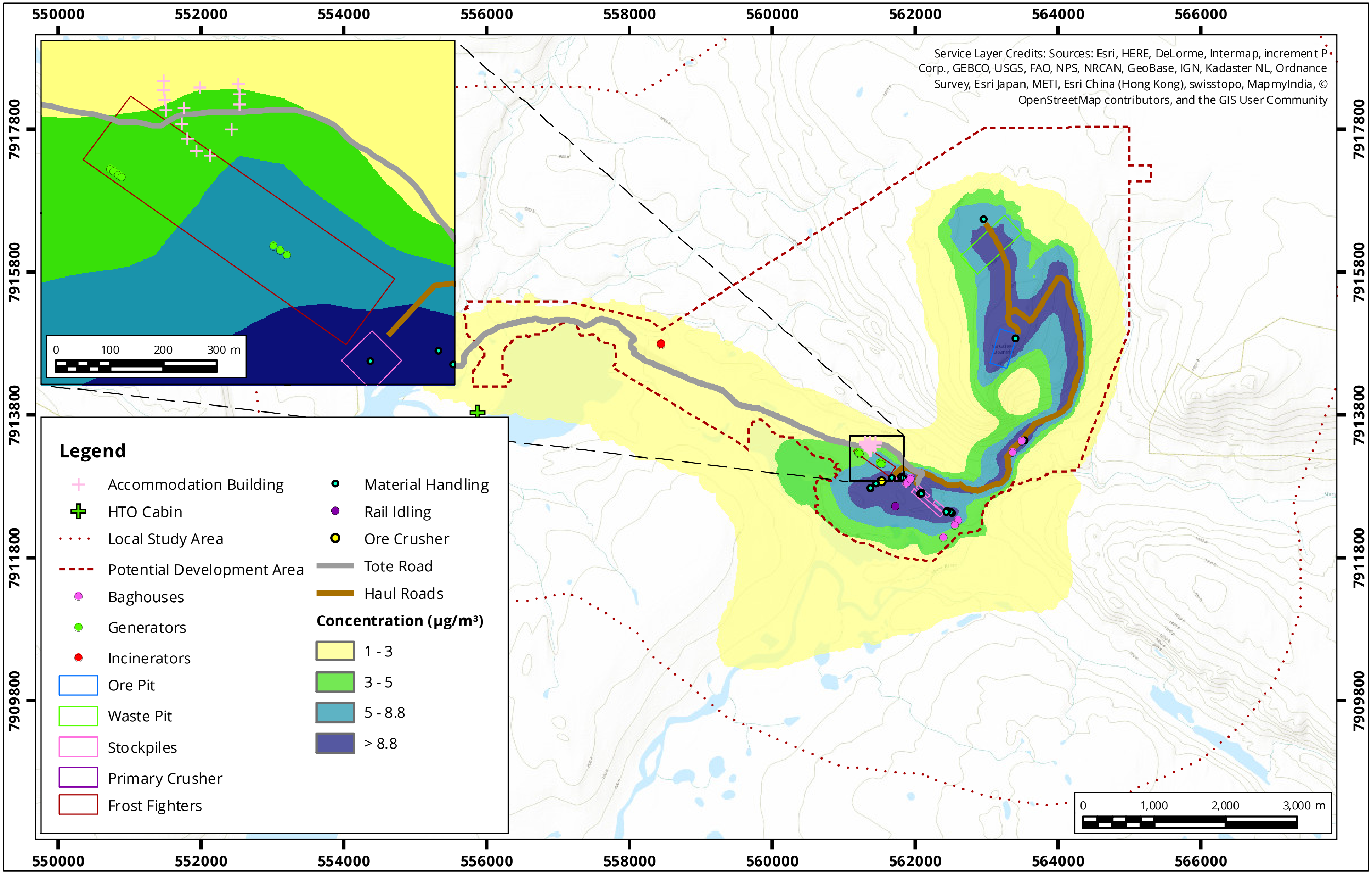

# Predicted Annual $PM_{2.5}$ Concentrations
## Mine Site

Map Projection: NAD 1983 UTM Zone 17N

Annual $PM_{25}$ CAAQS: 8.8 µg/m³

Baffinland Iron Mines Corporation - Nunavut, Canada

True North

Project #: 1402090

| | |
|---|---|
| Drawn by: DJH | Figure: E-15 |
| Approx. Scale: 1:75,000 | |
| Date Revised: Dec 13, 2018 | |

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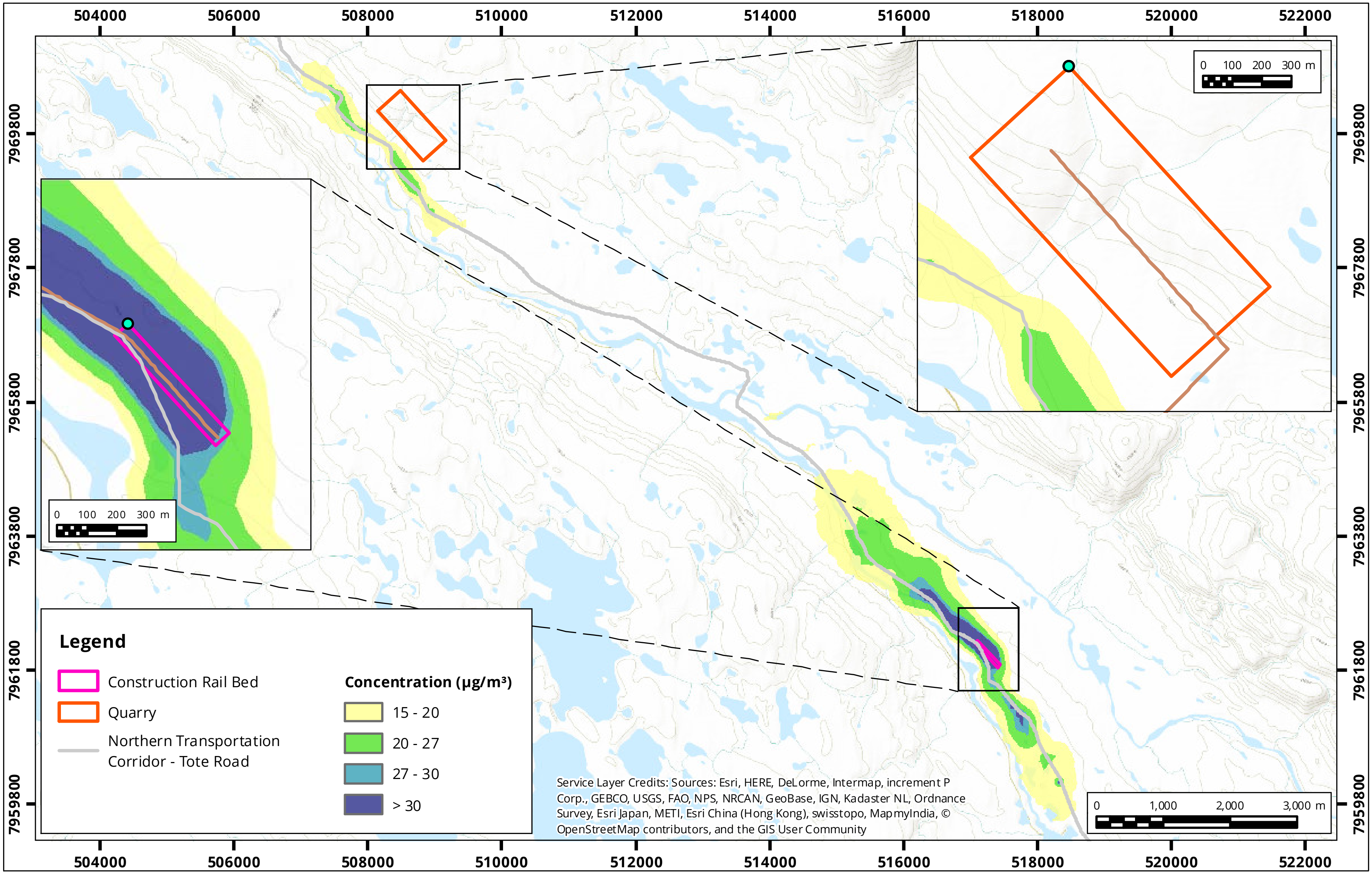

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# Predicted Maximum 24-Hour $PM_{2.5}$ Concentrations
## Northern Transportation Corridor - Tote Road and Construction Sources

Map Projection: NAD 1983 UTM Zone 17N

24-Hour $PM_{2.5}$ CAAQS: 27 µg/m³

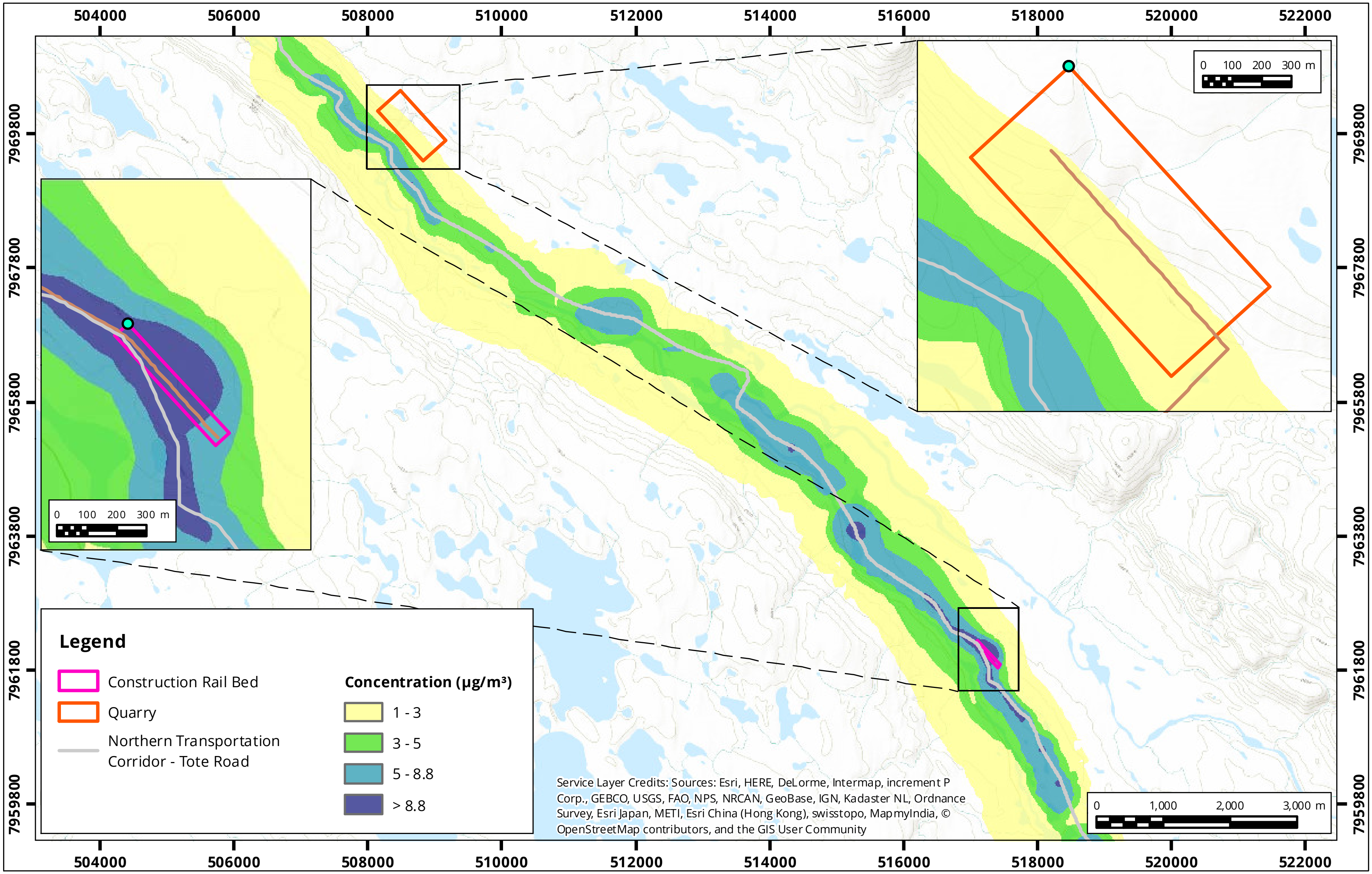
Baffinland Iron Mines Corporation - Nunavut, Canada

True North

Project #: 1402090

| | |
|---|---|
| Drawn by: DJH | Figure: F-16b |
| Approx. Scale: | 1:80,000 |
| Date Revised: | Dec 13, 2018 |

Map Document: C:\Users\djh\OneDrive - ROWAN WILLIAMS DAVIES & IRWIN INC-\GIS Temp\1402090\JBK\Cons\1402090 - Baffinland - AQ Construction Contour Plots_170529.mxd



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# Predicted Annual $PM_{2.5}$ Concentrations

## Northern Transportation Corridor - Tote Road and Construction Sources

Map Projection: NAD 1983 UTM Zone 17N

Annual $PM_{25}$ CAAQS: 8.8 µg/m³

Baffinland Iron Mines Corporation - Nunavut, Canada

True North

Project #: 1402090

Drawn by: DJH

Figure: F-19

Approx. Scale: 1:80,000

Date Revised: Dec 13, 2018

Map Document: C:\Users\djh\OneDrive - ROWAN WILLIAMS DAVIES & IRWIN INC\GIS Temp\1402090\JBK\Cons\1402090 - Baffinland - AQ Construction Contour Plots_170529.mxd

# *ECCC 6 ATTACHMENT 1: TABLES*

**Table 1: Wind erosion emissions at the Mine Site based on predicted wind at a level of 10 meters**.

| **Annual emissions (tonnes/year)** | | | | |
|---|---|---|---|---|
| **Wind speed (m/s)** | **Number of Hours in each bin** | PM$_{2.5}$ | **P** PM$_{10}$ | **TSP** |
| 10 | 22 | 0.002 | 0.013 | 0.025 |
| 11 | 13 | 0.005 | 0.036 | 0.071 |
| 11 | 10 | 0.008 | 0.053 | 0.106 |
| 12 | 0 | 0.000 | 0.000 | 0.000 |
| 12 | 3 | 0.005 | 0.035 | 0.070 |
| 13 | 0 | 0.000 | 0.000 | 0.000 |
| Sum: | | 0.020 | 0.137 | 0.273 |
| Total emissions at the facility: | | 234 | 1987 | 7839 |

**Table 2: Wind erosion emissions at the Milne Port based on predicted wind at a level of 10 meters**

| | | **Annual emissions (tonnes/year)** | | |
|---|---|---|---|---|
| **Wind speed (m/s)** | **Number of Hours in each bin** | PM$_{2.5}$ | PM$_{10}$ | **TSP** |
| 10 | 4 | 0.002 | 0.013 | 0.025 |
| 11 | 0 | 0.000 | 0.000 | 0.000 |
| Sum: | | 0.002 | 0.013 | 0.025 |
| Total emissions at the facility: | | 93 | 291 | 768 |

**Table 3: Wind erosion emissions at the Mine Site based on predicted winds at a level of 30 meters.**

| | | **Annual emissions (tonnes/year)** | | |
|---|---|---|---|---|
| **Wind speed (m/s)** | **Number of Hours in each bin** | PM$_{2.5}$ | PM$_{10}$ | **TSP** |
| 10 | 200 | 0.017 | 0.116 | 0.231 |
| 11 | 110 | 0.045 | 0.301 | 0.602 |
| 12 | 69 | 0.055 | 0.367 | 0.733 |
| 13 | 25 | 0.031 | 0.208 | 0.415 |
| 14 | 32 | 0.056 | 0.375 | 0.750 |
| 15 | 24 | 0.056 | 0.373 | 0.746 |
| 16 | 16 | 0.047 | 0.317 | 0.633 |
| 17 | 4 | 0.015 | 0.098 | 0.196 |
| 18 | 2 | 0.009 | 0.059 | 0.118 |
| 19 | 3 | 0.016 | 0.105 | 0.210 |
| 20 | 0 | 0.000 | 0.000 | 0.000 |
| Sum: | | 0.348 | 2.317 | 4.634 |
| Total emissions at the facility: | | 234 | 1987 | 7839 |

**Table 4: Wind erosion emissions at the Milne Port based on predicted winds at a level of 30 meters**

| | | **Annual emissions (tonnes/year)** | | |
|---|---|---|---|---|
| **Wind speed (m/s)** | **Number of Hours in each bin** | $PM_{2.5}$ | $PM_{10}$ | **TSP** |
| | | | | |
| 10 | 72 | 0.034 | 0.229 | 0.458 |
| 11 | 55 | 0.124 | 0.828 | 1.656 |
| 12 | 9 | 0.039 | 0.263 | 0.526 |
| 13 | 0 | 0.000 | 0.000 | 0.000 |
| Sum: | | 0.198 | 1.320 | 2.640 |
| Total emissions at the facility: | | 93 | 291 | 768 |

# *ECCC 12 ATTACHMENT 1: RESPONSE TO INFORMATION REQUEST ECCC-12 - PREDICTIVE METAL LOADING IN PHILLIPS CREEK FROM DUST DEPOSITION AT MILNE PORT MEMO*

Knight Piésold
CONSULTING

# MEMORANDUM

| | | | |
|---|---|---|---|
| **Date:** | December 12, 2018 | **File No.:** | NB102-00181/45-A.01 |
| | | **Cont. No.:** | NB18-00854 |
| **To:** | Mr. Lou Kamermans | | |
| **Copy To:** | | | |
| **From:** | Simon Foster | | |
| **Re:** | **Mary River Project – Phase 2 Proposal**<br>**Response to Information Request ECCC-12 - Predictive Metal Loading in Phillips Creek from Dust Deposition at Milne Port** | | |

## 1.0 INTRODUCTION

Baffinland Iron Mines Corporation (Baffinland) received the following information request from Environment and Climate Change Canada (ECCC):

*ECCC requests that the Proponent provide information on the expected water quality impacts on Phillips Creek due to dust deposition in the Milne Port Area, including predicted metal concentrations.*

Knight Piésold Ltd. (KP) has been requested by Baffinland to assist with the assessment.

The Phase 2 Proposal is expected to generate increased dust at Milne Port due to the increased ore throughput. Ore dust will arise from the unloading of ore from rail cars and conveyance to larger stockpiles, and from reclaimers and conveyance of ore to vessels (KP, 2018). It was assumed that the dust deposited on the land between the ore stockpiles and Phillips Creek would runoff to Phillips Creek, resulting in increased total suspended solids (TSS) in the last 1 kilometer of the creek. After which, the creek discharges into Milne Inlet and will be subject to considerable mixing and dilution due to the currents and tidal action in the inlet.

KP has utilized a series of baseline water quality, hydrology and dustfall datasets to complete the assessment. A description of the datasets and the results of the assessment are provided within this memorandum.

## 2.0 METHODOLOGY

The Surface Water Assessment (KP, 2018) presented a conservative estimate of the amount of TSS that would be introduced into Phillips Creek, based on the following inputs and assumptions:

- Dust will be deposited at rates ranging from 60 to 500 g/m$^2$/year over a 1.3 km$^2$ catchment area expected to report to Phillips Creek. A depiction of the catchment area is presented on Figure 1.
- All dust deposited on snow within the catchment area during winter will report to the creek evenly over 30 days during the freshet period. The mean monthly spring freshet discharge rate in Phillips Creek is approximately 43 m$^3$/s.

Based on the above assumptions, it was estimated that TSS concentrations in Phillips Creek adjacent to the stockpiles (at the mouth) could range from 1 to 9 mg/L.

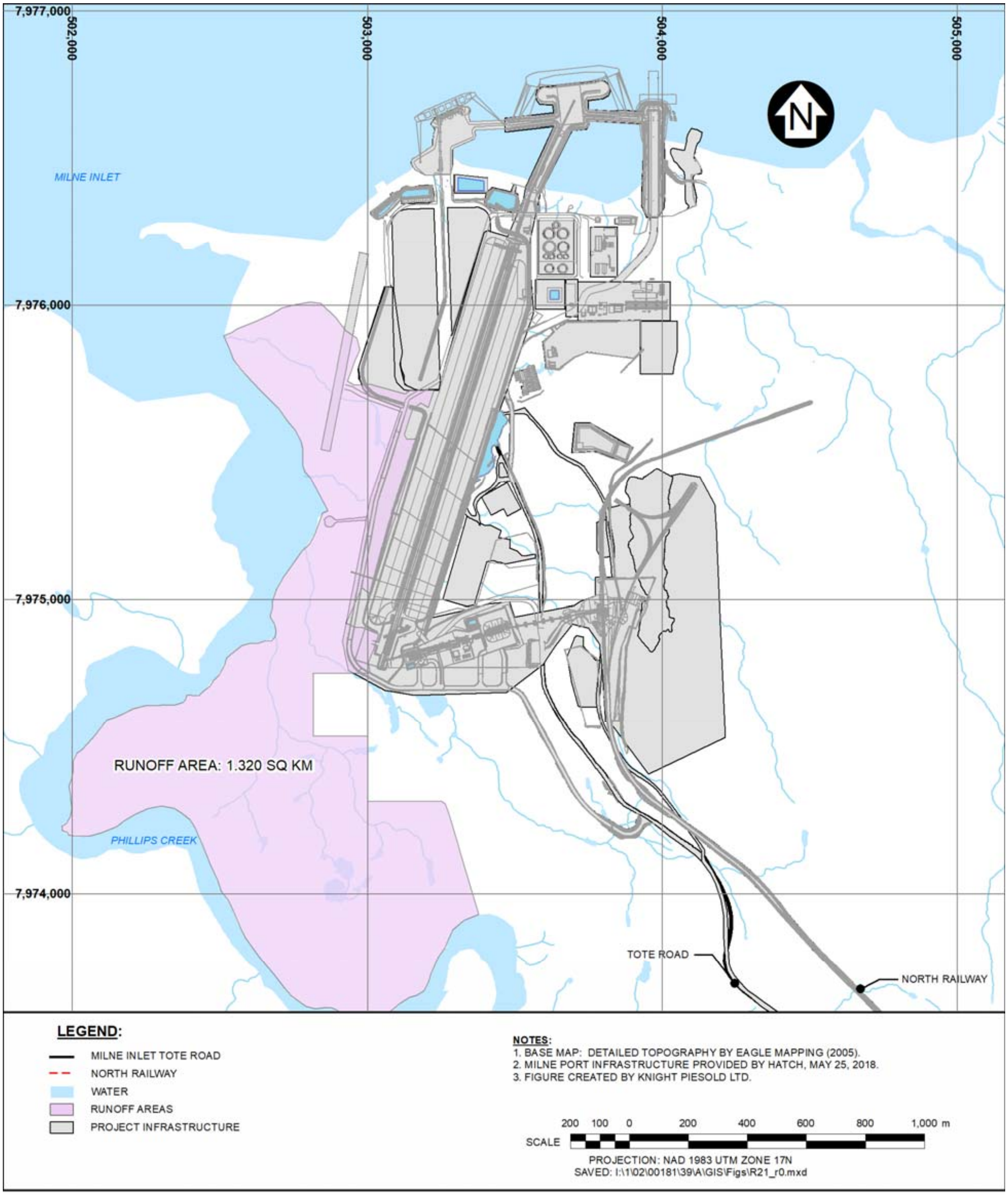

**Figure 1** Milne Port Phase 2 Project Infrastructure and Phillips Creek Catchment Area

Subsequent to this, KP reviewed recent satellite imagery and LiDAR-derived topography (for the Milne Port area) and determined that contrary to previous assumptions and mapping, most of the ponds located within and adjacent to the future Phase 2 Proposal ore stockpiles do not runoff to Phillips Creek. There is not a prevailing gradient across the area towards Phillips Creek, nor are there defined channels between most of the ponds or towards Phillips Creek. Hence, the estimate of 1 to 9 mg/L TSS in Phillips Creek is highly conservative. Figures 1 to 5 are provided in Appendix A to illustrate the basis of this conclusion.

KP has nevertheless utilized the original TSS estimate of 1 to 9 mg/L in the prediction of metal concentrations in order to ensure conservatism in the results.

Metals concentrations in Phillips Creek arising from contributions of dust deposition were estimated as follows:

- The percentages of metals measured in dustfall at the Mine Site presented in Table 2-1 of TSD-11 (Intrinsik, 2017) were applied to the predicted TSS concentrations (1 to 9 mg/L) estimated in Section 3.5.2.6 of TSD-13 (KP, 2018).
- These metals concentrations were added to the baseline water quality values for Phillips Creek (KP, 2011).

Metals percentages in dustfall collected at the Mine Site were found to contain a higher proportion of ore than dustfall collected at Milne Port. Since the proportion of ore in dustfall at Milne Port may increase due to a higher ore throughput, the geochemistry of the Mine Site dustfall was considered a better representation of future dustfall than recently collected dustfall at Milne Port.

The 90th percentile values of 8 samples collected between 2005 and 2011 at sample location N1-020, located at the lower reaches of Phillips Creek, was used to represent the baseline water chemistry of Phillips Creek for this assessment (KP, 2011).

## 3.0 RESULTS

Table 1 presents the estimated metals concentrations in Phillips Creek, compared to the CCME Canadian Water Quality Guidelines (CWQG) for Fresh Water Protection of Aquatic Life (FW PAL) (CCME, 1999).

The findings are as follows:

- **Aluminum, arsenic, cadmium, mercury, selenium, and zinc** - The 90th Percentile of baseline concentrations in Phillips Creek for these metals exceed CCME Canadian Water Quality Guidelines (CWQG) for Fresh Water Protection of Aquatic Life (FW PAL) (CCME, 1999).
- **Total iron** - At a dust deposition rate of 60 g/m$^2$/year, the concentration of total iron in Phillips Creek is estimated at 0.1 mg/L, but at a deposition rate of 500 g/m$^2$/year the total iron concentration increases to 0.34 mg/L, slightly above the CCME criterion for total iron of 0.3 mg/L.

In summary:

- The 90th percentile (baseline conditions) in Phillips Creek naturally exceed FW PAL for several metals.
- Dust deposition from Milne Port will increase metals concentrations in Phillips Creek.
- The highest dust deposition scenario will result in total iron slightly exceeding the FW PAL criterion for iron.
- The methodology used to calculate the TSS inputs from dust upon which this assessment is based, is highly conservative.

## 4.0 REFERENCES

Canadian Council of Ministers of the Environment (CCME). 1999. *Canadian Water Quality Guidelines for the Protection of Aquatic Life*. In: Canadian Environmental Quality Guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

Knight Piésold Ltd., 2011. *Surface Water and Sediment Quality Baseline Report*. December 22. North Bay, Ontario. Ref. No. NB102-181/30-5, Rev 0.

Knight Piésold Ltd., 2018. *Baffinland Iron Mines Corporation – Mary River Project – Phase 2 Proposal – Technical Supporting Document No. 13: Surface Water Assessment*. October 3. North Bay, Ontario. Ref. No. NB102-181/39-8, Rev 4

Intrinsik, 2017. *Evaluation of Exposure Potential from Ore Dusting Events in Selected VECS: Humans, Caribou and Blueberry*. October 25.

Yours truly,
**Knight Piésold Ltd.**

Prepared: Simon Foster, M.Sc., P.Geo.
Project Scientist

Reviewed: Richard Cook, P.Geo. (Ltd.)
Specialist Environmental Scientist | Associate

Approval that this document adheres to the Knight Piésold Quality System: RCS.

**Attachments:**

| | |
|---|---|
| Table 1 Rev 0 | Phillips Creek Predicted Water Quality - Milne Port Dust Deposition |
| Appendix A | Milne Port Pond Drainage (issued under NB18-00768) |

/sf

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CONSULTING

## TABLE 1

## BAFFINLAND IRON MINES CORPORATION
## MARY RIVER PROJECT

## PHILLIPS CREEK PREDICTED WATER QUALITY
## MILNE PORT DUST DEPOSITION

Print Dec/12/18 15:57:41

| Parameter | Average Percent of Metals in Total Insoluble Dustfall (Mine Site)[6] (%) (a) | Lower Limit - Concentration Increase from the addition of 1 mg/L TSS (mg/L)[7] (a) x (1 mg/l) = (b) | Upper Limit - Concentration Increase from the addition of 9 mg/L TSS (mg/L)[7] (a) x (9 mg/L) = (c) | Phillips Creek Baseline Water Quality (mg/L)[5] (d) | Baseline + Lower TSS Estimate (mg/L) (d) + (b) = ('e) | Baseline + Upper TSS Estimate (mg/L) (d) + ('c) = (f) | Percent Increase (Lower Limit) (%) (e)-(d)/(d)*100 | Percent Increase (Upper Limit) (%) (f)-(d)/(d)*100 | CCME Fresh Water Protection Aquatic Life - Short Term (mg/L)[8] | CCME Fresh Water Protection Aquatic Life - Long Term (mg/L)[8] |
|---|---|---|---|---|---|---|---|---|---|---|
| Hardness | - | - | - | 93.42 | - | - | - | - | - | - |
| pH | - | - | - | 7.84 | - | - | - | - | - | - |
| TSS | - | 1 | 9 | 2.00 | 3.0 | 11.0 | 50 | 450 | 25 (above background) | 5 (above background) |
| Aluminum | 1.58 | 0.02 | 0.14 | **1.65** | **1.66** | **1.79** | 1 | 9 | No data | 0.10 |
| Antimony | 0.00054 | 0.000005 | 0.00005 | 0.0004 | 0.0004 | 0.0004 | 1 | 12 | No data | No data |
| Arsenic | 0.018 | 0.00018 | 0.0016 | **0.005** | **0.0052** | **0.0066** | 4 | 32 | No data | 0.0050 |
| Barium | 0.013 | 0.00013 | 0.0012 | 0.754 | 0.754 | 0.755 | 0 | 0 | No data | No data |
| Cadmium | 0.00091 | 0.0000 | 0.0001 | **0.0001** | **0.0001** | **0.0002** | 9 | 82 | 0.001 | 0.00009 |
| Chromium | 0.0066 | 0.00007 | 0.0006 | 0.001 | 0.0011 | 0.0016 | 7 | 59 | No data | No data |
| Cobalt | 0.0013 | 0.00001 | 0.0001 | 0.0003 | 0.0003 | 0.0004 | 4 | 39 | No data | No data |
| Copper[1] | 0.022 | 0.0002 | 0.0020 | 0.001 | 0.0012 | 0.0030 | 22 | 198 | No data | 0.0022 |
| Iron | 3.06 | 0.031 | 0.275 | 0.07 | 0.1006 | **0.345** | 44 | 393 | No data | 0.30 |
| Lead[2] | 0.0017 | 0.00002 | 0.0002 | 0.001 | 0.0010 | 0.0012 | 2 | 15 | No data | 0.0029 |
| Manganese | 0.064 | 0.00064 | 0.0058 | 0.013 | 0.013 | 0.018 | 5 | 46 | No data | No data |
| Mercury | 0.0021 | 0.000021 | 0.0002 | **0.0001** | **0.0001** | **0.0003** | 21 | 189 | No data | 0.000026 |
| Molybdenum | 0.00045 | 0.0000 | 0.0000 | 0.005 | 0.0050 | 0.0050 | 0 | 1 | No data | 0.073 |
| Nickel[3] | 0.0062 | 0.00006 | 0.0006 | 0.005 | 0.0051 | 0.0056 | 1 | 11 | No data | 0.091 |
| Selenium | 0.0032 | 0.00003 | 0.0003 | **0.005** | **0.0050** | **0.0053** | 1 | 6 | No data | 0.0010 |
| Silver | 0.000044 | 0.00000044 | 0.00000396 | 0.0001 | 0.0001 | 0.0001 | 0 | 4 | NRG | 0.00025 |
| Strontium | 0.015 | 0.00015 | 0.0014 | 0.01902 | 0.0192 | 0.0204 | 1 | 7 | No data | No data |
| Thallium | 0.00032 | 0.000003 | 0.000029 | 0.0002 | 0.0002 | 0.0002 | 2 | 14 | No data | 0.00080 |
| Tin | 0.00071 | 0.00001 | 0.0001 | 0.01 | 0.0100 | 0.0101 | 0 | 1 | No data | No data |
| Uranium | 0.00071 | 0.00001 | 0.0001 | 0.00192 | 0.0019 | 0.0020 | 0 | 3 | 0.033 | 0.015 |
| Vanadium | 0.00416 | 0.00004 | 0.0004 | 0.001 | 0.0010 | 0.0014 | 4 | 37 | No data | No data |
| Zinc | 0.053 | 0.00053 | 0.0048 | **0.01** | **0.0105** | **0.0148** | 5 | 48 | 0.037 | 0.0070 |

I:\1\02\00181\45\A\Correspondence\NB18-00854 - Memorandum - Phillips Creek Metal Loading Effects from Dust\[Table 1 - Phillips Creek WQ.xlsx]Table 1

**NOTES:**

1. COPPER LONG TERM CCME FW PAL STANDARD DETERMINED USING CWQG (ug/L) = $0.2 * e^{\{0.8545[\ln(hardness)]-1.465\}}$
2. LEAD LONG TERM CCME FW PAL STANDARD DETERMINED USING CWQG (μg/L)= $e^{\{1.273[\ln(hardness)]-4.705\}}$
3. NICKEL LONG TERM CCME FW PAL STANDARD DETERMINED USING CWQC (μg/L) = $e^{\{0.76[\ln(hardness)]+1.06\}}$
4. NRG - No RECOMMENDED GUIDELINE.
5. PHILLIPS CREEK SAMPLING POINT N1-020 ($90^{TH}$ PERCENTILE) SOURCE: KNIGHT PIESOLD, 2012. FEIS: APPENDIX 7B-1, SURFACE WATER AND SEDIMENT QUALITY BASELINE REPORT. DECEMBER 22. NB102-181/30-5. Rev 0.
6. SOURCE: FEIS ADDENDUM NO. 2: TSD-11, INTRINSIK, 2017. EVALUATION OF EXPOSURE POTENTIAL FROM ORE DUSTING EVENTS IN SELECTED VECS: HUMANS, CARIBOU, AND BLUEBERRY, OCTOBER 25, 2017.
7. SOURCE: KNIGHT PIESOLD, 2018. FEIS ADDENDUM NO.2: TSD NO. 13, SURFACE WATER ASSESSMENT. OCTOBER 3. NB102-181/39-8.
8. BOLD VALUES ARE CONCENTRATIONS ABOVE CCME FW PAL STANDARDS.

| | | | | |
|---|---|---|---|---|
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| REV | DATE | DESCRIPTION | PREP'D | RVW'D |

# APPENDIX A

## Milne Port Pond Drainage (issued under NB18-00768)

(Pages A-1 to A-5)

**NOTES:**

1. COORDINATE GRID IS UTM NAD83, ZONE 17N.
2. CONTOURS ARE IN METRES. CONTOUR INTERVAL IS 0.5 METRES. CONTOURS PROVIDED BY HATCH MAY 2018.
3. IMAGERY PROVIDED BY BAFFINLAND OCTOBER 2018.

**LEGEND:**

➡ DIRECTION OF FLOW

**Baffinland**

MARY RIVER PROJECT

## OVERVIEW OF DRAINAGES ASSOCIATED WITH MILNE PORT PONDS ML-1 TO ML-8

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| P/A NO. | REF NO. |
|---|---|
| NB102-181/48 | NB18-00768 |

**FIGURE 1**

REV 0

| REV | DATE | DESCRIPTION | DESIGNED | DRAWN | REVIEWED |
|---|---|---|---|---|---|
| 0 | 30NOV'18 | ISSUED WITH TRANSMITTAL | RAC | MMD | RAC |

SAVED: I:\1\02\00181\48\A\Acad\FIGS\A07 R0, 11/30/2018 3:54:36 PM , MDEMERS PRINTED: 11/30/2018 3:55:10 PM, FIG 1, MDEMERS ACAD VERSION: 23.0S (LMS TECH)
XREF FILE(S): X-C-TOPO-MINE-MILN-FROM-OTHRS-FEB21-18; X-C-TOPO-FEAT-MILN-TO-MINE IMAGE FILE(S): GIS Baffinland Logo mary_river_wo3973_wv2_wv3_wv1_tile01

SAVED: I:\1\02\00181\48\A\Acad\FIGS\A07 R0, 11/30/2018 3:54:36 PM , MDEMERS PRINTED: 11/30/2018 3:55:47 PM, FIG 2, MDEMERS ACAD VERSION: 23.0S (LMS TECH)
XREF FILE(S): X-C-TOPO-MINE-MILN-FROM-OTHRS-FEB21-18; X-C-TOPO-FEAT-MILN-TO-MINE IMAGE FILE(S): GIS Baffinland Logo mary_river_wo3973_wv2_wv3_wv1_tile01

**NOTES:**

1. COORDINATE GRID IS UTM NAD83, ZONE 17N.
2. CONTOURS ARE IN METRES. CONTOUR INTERVAL IS 0.5 METRES. CONTOURS PROVIDED BY HATCH MAY 2018.
3. IMAGERY PROVIDED BY BAFFINLAND OCTOBER 2018.

**LEGEND:**

| | |
|---|---|
| ➡ | DIRECTION OF FLOW |

**Baffinland**

MARY RIVER PROJECT

**DRAINAGES ASSOCIATED WITH**
**MILNE PORT PONDS ML-1 AND ML-2**

| P/A NO. | REF NO. |
|---|---|
| NB102-181/48 | NB18-00768 |

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**FIGURE 2** REV 0

| REV | DATE | DESCRIPTION | DESIGNED | DRAWN | REVIEWED |
|---|---|---|---|---|---|
| 0 | 30NOV'18 | ISSUED WITH TRANSMITTAL | RAC | MMD | RAC |

**NOTES:**

1. COORDINATE GRID IS UTM NAD83, ZONE 17N.
2. CONTOURS ARE IN METRES. CONTOUR INTERVAL IS 0.5 METRES. CONTOURS PROVIDED BY HATCH MAY 2018.
3. IMAGERY PROVIDED BY BAFFINLAND OCTOBER 2018.

**LEGEND:**

| | |
|---|---|
| ➡ | DIRECTION OF FLOW |

**Baffinland**

MARY RIVER PROJECT

## DRAINAGES ASSOCIATED WITH MILNE PORT PONDS ML-3 TO ML-8

Knight Piésold CONSULTING

| P/A NO. | REF NO. |
|---|---|
| NB102-181/48 | NB18-00768 |

FIGURE 3

REV 0

| REV | DATE | DESCRIPTION | DESIGNED | DRAWN | REVIEWED |
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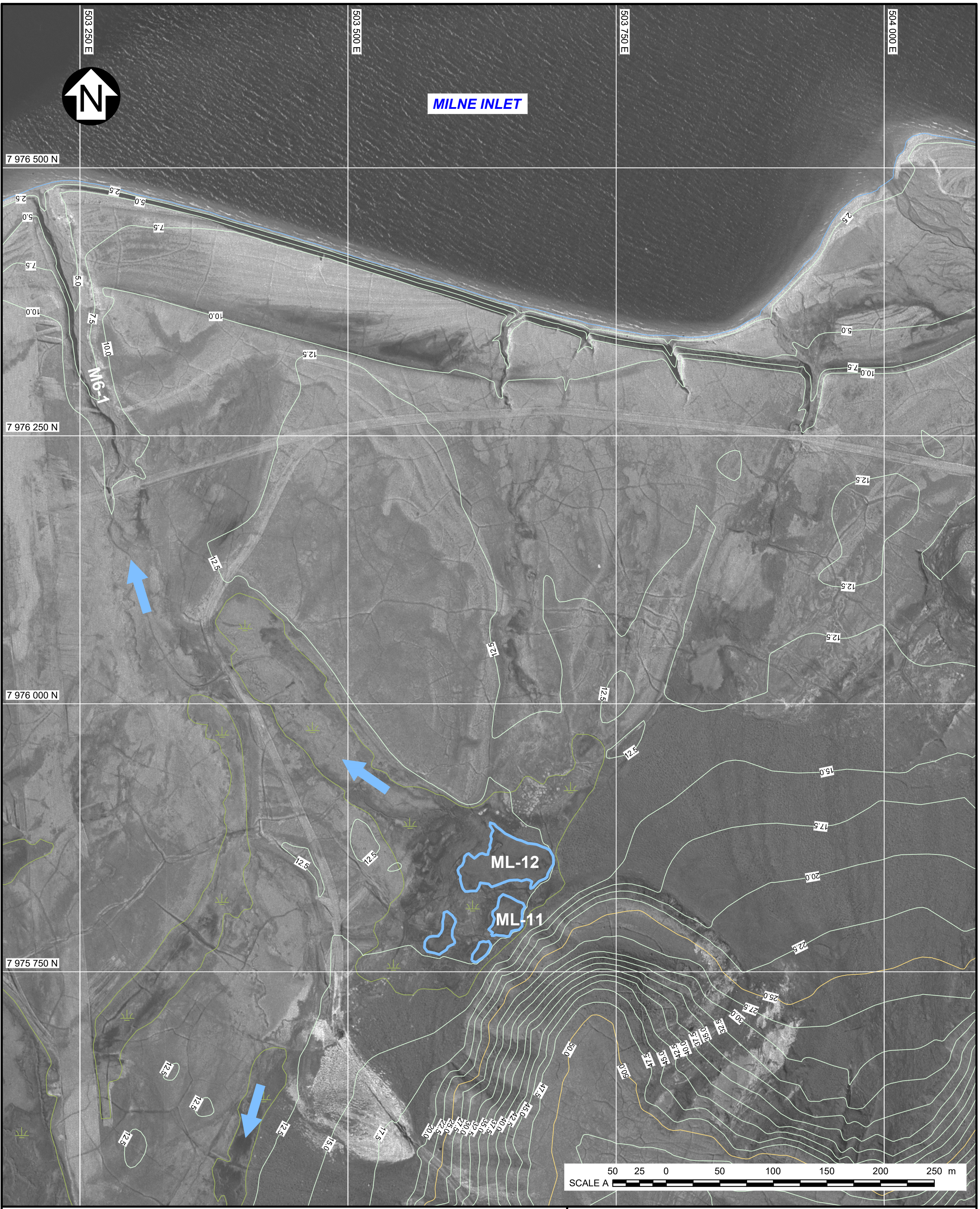
XREF FILE(S): X-C-TOPO-MINE-MILN-FROM-OTHRS-FEB21-18; X-C-TOPO-FEAT-MILN-TO-MINE IMAGE FILE(S): GIS Baffinland Logo mary_river_wo3973_wv2_wv3_wv1_tile01



## NOTES:

1. COORDINATE GRID IS UTM NAD83, ZONE 17N.
2. IMAGERY AND MAPPING PROVIDED BY EAGLE MAPPING 2005.
3. CONTOUR INTERVAL IS 2.5 METRES.

## LEGEND:

| | |
|---|---|
| ➡ | DIRECTION OF FLOW |

Baffinland

MARY RIVER PROJECT

## PRE-DEVELOPMENT DRAINAGE OF PONDS ML-11 AND ML-12

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| P/A NO. | REF NO. |
|---|---|
| NB102-181/48 | NB18-00768 |

FIGURE 4

REV 0

| REV | DATE | DESCRIPTION | DESIGNED | DRAWN | REVIEWED |
|---|---|---|---|---|---|
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## NOTES:

1. COORDINATE GRID IS UTM NAD83, ZONE 17N.
2. CONTOURS ARE IN METRES. CONTOUR INTERVAL IS 0.5 METRES. CONTOURS PROVIDED BY HATCH MAY 2018.
3. IMAGERY PROVIDED BY BAFFINLAND OCTOBER 2018.

| REV | DATE | DESCRIPTION | DESIGNED | DRAWN | REVIEWED |
|---|---|---|---|---|---|
| 0 | 30NOV'18 | ISSUED WITH TRANSMITTAL | RAC | MMD | RAC |

Baffinland

MARY RIVER PROJECT

## CURRENT DRAINAGE OF PONDS ML-11 AND ML-12

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CONSULTING

| P/A NO. | REF NO. |
|---|---|
| NB102-181/48 | NB18-00768 |

**FIGURE 5**

REV 0

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XREF FILE(S): X-C-TOPO-FEAT-MILN-TO-MINE IMAGE FILE(S): GIS Baffinland Logo mary_river_wo3973_wv2_wv3_wv1_tile01

# *ECCC 16 ATTACHMENT 1: CANADIAN WATER QUALITY GUIDELINES FOR THE PROTECTION OF AQUATIC LIFE – NITRATE ION*

ECCC 16 Attachment 1

# Canadian Water Quality Guidelines for the Protection of Aquatic Life

# NITRATE ION

The nitrate ion ($NO_3^-$) (CAS No. 14797-55-8, atomic mass 62.0049 $g \cdot mol^{-1}$) is the most oxidized form of nitrogen (N) present in the environment with an oxidation state of +5 (NRC 1978). It is the conjugate base of nitric acid ($HNO_3$), a strong acid which is completely dissociated in solution (NRC 1978). The nitrate salts of all common metals (e.g. $NaNO_3$, $KNO_3$, $Ca(NO_3)_2$, $AgNO_3$) are highly soluble in water, while the resulting free nitrate ion is chemically unreactive as it has little tendency to form coordination complexes with other metal ions in solution (NRC 1978).

Units used to report nitrate concentrations in the literature vary considerably. With the exception of the Canadian water quality guideline values presented in Table 2, all nitrate concentrations presented here will be for the ion only (i.e., as mg $NO_3^- \cdot L^{-1}$). Conversion factors for some of the commonly reported units in the literature are provided (Table 1).

**Table 1.** Conversion factors for various nitrate units to mg $NO_3^- \cdot L^{-1}$.

| Base Unit | Multiply by: |
|---|---|
| mg $NO_3^-$-N$\cdot L^{-1}$ | 4.43 |
| mg $NaNO_3 \cdot L^{-1}$ | 0.73 |
| mg $KNO_3 \cdot L^{-1}$ | 0.61 |
| mg $NH_4NO_3 \cdot L^{-1}$ | 0.78 |
| eq$\cdot L^{-1}$, *M*, N, or g-at.$\cdot L^{-1}$ * | 62.005 x $10^3$ |
| ppm $NO_3^-$ | 1 |
| ppb $NO_3^-$ | $10^{-3}$ |

* note: for these units, the conversion factor is the same whether expressed as $NO_3^-$-N or $NO_3^-$

***Sources to the environment:*** Natural sources of nitrate to surface waters include wet and dry deposition of $HNO_3$ or $NO_3^-$, which are formed through nitrogen cycling in the atmosphere. Atmospheric deposition of dissolved inorganic nitrogen (DIN = $NO_3^-$ + $NO_2^-$ + $NH_4^+$) in Canada is estimated to contribute 182 kt N$\cdot yr^{-1}$ to surface waters (Chambers et al. 2001). It should be noted, however, that some of this atmospheric nitrogen may have originated anthropogenically. Other natural sources of nitrate include igneous rocks and volcanic activity, mineralization of native soil organic nitrogen and the complete oxidation of vegetable and animal debris (Nordin and Pommen 1986). This latter nitrification process is the principle source of nitrate in terrestrial and aquatic environments (NRC 1978).

Anthropogenic discharges of N include point sources such as municipal and industrial wastewaters, and water discharges from mining (explosives) activity, and non-point sources such as agricultural runoff, feedlot discharges, septic beds, urban runoff, lawn fertilizers, landfill leachate, nitric oxide and nitrogen dioxide from vehicular exhaust, and storm sewer overflow (NRC 1972; NRC 1978). Organic forms of nitrogen (originating from living material, e.g. proteins, amino acids, urea) undergo ammonification and are eventually transformed to ammonia, ($NH_3$) or ammonium ($NH_4^+$) by a variety of micro-organisms. All forms of inorganic nitrogen, ammonia, ($NH_3$) or ammonium ($NH_4^+$), released into surface waters have the potential to undergo nitrification to nitrate.

**Table 2.** Canadian water quality guidelines for the nitrate ion for the protection of aquatic life[‡].

| | Long-Term Exposure [c] | Short-Term Exposure [d] |
|---|---|---|
| **Freshwater**[a] | 13 mg $NO_3^- \cdot L^{-1}$ | 550 mg $NO_3^- \cdot L^{-1}$ |
| | 3.0 mg $NO_3^-$-N$\cdot L^{-1}$ | 124 mg $NO_3^-$-N$\cdot L^{-1}$ |
| **Marine**[b] | 200 mg $NO_3^- \cdot L^{-1}$ | 1500 mg $NO_3^- \cdot L^{-1}$ |
| | 45 mg $NO_3^-$-N$\cdot L^{-1}$ | 339 mg $NO_3^-$-N$\cdot L^{-1}$ |

[‡] For protection from direct toxic effects; the guidelines do not consider indirect effects due to eutrophication.

[a] = derived from toxicity tests utilizing $NaNO_3$

[b] = derived from toxicity tests utilizing $NaNO_3$ and $KNO_3$

[c] = derived with mostly no- and some low-effect data and are intended to protect against negative effects to aquatic ecosystem structure and function during indefinite exposures (e.g. abide by the guiding principle as per CCME 2007).

[d] = derived with severe-effects data (such as lethality) and are not intended to protect all components of aquatic ecosystem structure and function but rather to protect most species against lethality during severe but transient events (e.g. inappropriate application or disposal of the substance of concern).

The 2008 National Pollutant Release Inventory calculated a total point source estimate of anthropogenic nitrate ion release from all reporting Canadian sources of 62.8 kt $NO_3^-$ to air, and surface and groundwaters, with a further 4.4 kt $NO_3^-$ transferred off-site for disposal (Environment Canada 2010). Although comprehensive national non-point source release estimates are not available for either nitrate or total nitrogen (Chambers et al. 2001), they are likely to exceed those of point sources; U.S. estimates for non-point source N discharges into receiving waters (9108 kt $N \cdot yr^{-1}$) greatly outweigh those for point sources (561 kt $N \cdot yr^{-1}$) (van der Leeden et al. 1990).

Nitrate metal salts such as potassium nitrate, calcium nitrate, silver nitrate and sodium nitrate are used in a variety of industrial applications, including: oxidizing agents in explosives, matches and pyrotechnics; photography; glass making; engraving; textile dyes; food processing (meat preservatives); and as a raw material for manufacturing nitric acid (Nordin and Pommen 1986; WHO 1996). Other industrial processes which are known to result in high nitrate concentrations in their wastestreams include the production of fertilizers, the production of nitroaromatic compounds, the synthesis of nitroorganic compounds in pharmaceuticals, and wastewaters from nuclear fuel processing (Pinar et al. 1997).

Intensive agricultural practices have resulted in a steadily increasing demand for nitrogen in Canada. Estimated annual nitrogen-based fertilizer consumption in Canada in 1975 was approximately 500 kt N; in 2000 this estimate rose to 1700 kt N (CFI 2001). Of the 1600 kt of N sold as fertilizer in Canada over a 12 month period in 1998 and 1999, 90 kt of N were nitrate compounds, with 82% as ammonium nitrate, and the remaining forms including calcium nitrate, calcium ammonium nitrate and potassium nitrate (Korol and Rattray 2000).

***Ambient Concentrations***: The form of N occurring in surface waters depends primarily on the levels of oxygen present. Systems saturated with dissolved $O_2$ will promote nitrification by autotrophic bacteria which oxidize reduced forms of inorganic nitrogen (e.g., $NH_4^+$, $NO_2^-$) to $NO_3^-$, while in $O_2$ deficient waters, auto- and heterotrophic denitrifying bacteria reduce $NO_3^-$ to $NO_2^-$, and ultimately to gaseous $N_2$ which is then lost to the atmosphere (Halling-Sorensen and Jorgensen 1993). Further information on the fate and behaviour of nitrate in the environment can be found in the scientific supporting document for the nitrate ion (Environment Canada 2012).

In general, nitrate constitutes two-thirds to four-fifths of the total available nitrogen in surface waters (Crouzet et al. 1999). Naturally occurring nitrate levels in Canadian lakes and rivers rarely exceed 4 mg $NO_3^- \cdot L^{-1}$. In oligotrophic lakes and streams nitrate concentrations are generally < 0.4 mg $NO_3^- \cdot L^{-1}$ (NRC 1978; Nordin and Pommen 1986). Average 1990 nitrate levels in raw (pre-treated) Canadian municipal drinking water supplies ranged from 0.1 to 3.3 mg $NO_3^- \cdot L^{-1}$ (Government of Canada 1996). In the U.S., concentrations exceeding 2.7 mg $NO_3^- \cdot L^{-1}$ are generally considered the result of anthropogenic inputs, and levels above 4 mg $NO_3^- \cdot L^{-1}$ in fresh waters are often associated with eutrophic conditions (NRC 1978; USGS 1999).

Anthropogenic inputs of inorganic nitrogen may lead to elevated freshwater nitrate levels. Nitrate concentrations downstream from open pit coal mining operations can exceed 44 mg $NO_3^- \cdot L^{-1}$ due to high nitrate levels in the residues from explosives (Nordin and Pommen 1986). Inorganic fertilizer use in rural areas can also result in excessive nitrate loading in localized areas. Mean nitrate concentrations of North American streams in agricultural landscapes generally range between 9 and 180 mg $NO_3^- \cdot L^{-1}$ and levels above 45 mg $NO_3^- \cdot L^{-1}$ can persist for several weeks (Rouse et al. 1999; Castillo et al. 2000). Nitrate concentrations ranging from 19 to 42 mg $NO_3^- \cdot L^{-1}$ were also found in the Cootes Paradise wetland in Dundas, Ontario in 1997, primarily as a result of anthropogenic loading from a sewage treatment plant (Rouse et al. 1999).

Naturally occurring nitrate concentrations in temperate region seawater can reach up to 2.4 mg $NO_3^- \cdot L^{-1}$ (Spencer 1975), the majority of which is due to nitrification processes (Muir et al. 1991). Coastal nitrate levels vary seasonally; for example, off the Canadian Atlantic coast higher concentrations occur during the winter months (up to 0.54 mg $NO_3^- \cdot L^{-1}$) than in the summer (< 0.03 mg $NO_3^- \cdot L^{-1}$) when nitrate is depleted in the surface waters due to biological assimilation (Petrie et al. 1999). Concentrations increase with depth in off-shore regions, with levels of up to 1.24 mg $NO_3^- \cdot L^{-1}$ occurring beyond 30 m on the Scotian Shelf (Petrie et al. 1999). Where coastal upwelling events occur, nutrient-rich waters from below can elevate surface water nitrate concentrations (Whitney 2001). Marine nitrate levels are also typically higher closer to shore. For example, on the Canadian Pacific coast, mean (± SD) winter nitrate levels in the upper 100 m were higher in the Strait of Georgia (1.7 ± 0.1 mg $NO_3^- \cdot L^{-1}$) than in the open ocean along an east-west transect near lower Vancouver Island (0.7 ± 0.2 mg $NO_3^- \cdot L^{-1}$) (Whitney 2001).

Where there are anthropogenic inputs, nitrate levels in marine and estuarine waters can be much higher. For example, nitrate levels in estuaries of rivers draining agricultural and urbanised areas can exceed 12 mg $NO_3^-\cdot L^{-1}$ (Sharp 1983).

Nitrate serves as the primary source of nitrogen for aquatic plants in well oxygenated systems, and as nitrate levels increase, there is an increasing risk of algal blooms and eutrophication in surface waters (Nordin and Pommen 1986; Meade and Watts 1995). Along with phosphorus, nitrogen plays a major role in eutrophication in both types of waters, depending on the underlying geology and anthropogenic inputs to a given water body (Dodds et al. 1998). Common ecological changes to aquatic systems undergoing nutrient enrichment may include an increase in algal and macrophyte production resulting undesirable blooms, a decrease in water clarity, a loss of cold water fisheries, shortened food chains and changes in species composition (NRC 1978).

***Toxicity***: The direct toxicity of nitrate ions to aquatic organisms is assessed using either $NaNO_3$, $NH_4NO_3$ or $KNO_3$ salts. Studies exposing aquatic test organisms to both $NaNO_3$ and NaCl have demonstrated the observed toxicity is a result of exposure to the $NO_3^-$ anion, rather than the $Na^+$ cation (Baker and Waights 1994). Therefore, studies using the $NaNO_3$ salt were included in the derivation of both freshwater and marine Canadian Water Quality Guidelines (CWQGs). Due to concerns about confounding toxicity of $NH_4^+$ ions in both freshwater and marine systems (Schuytema and Nebeker 1999a, 1999b), studies using these salts were excluded from CWQG development. Studies using potassium nitrate as the test compound were also not included in the derivation of the CWQG for freshwater environments due to the confounding toxicity of $K^+$. Potassium nitrate was shown to be 4.8 times more toxic to freshwater fish than $NaNO_3$ (Trama 1954), and other studies have demonstrated that potassium salts are more toxic to freshwater organisms than the corresponding sodium salt (Dowden and Bennett 1965; Khangarot and Ray 1989; Lilius et al. 1994; Calleja et al. 1994; Mount et al. 1997). As potassium ion concentrations used in marine toxicity studies with $KNO_3$ are generally within natural ranges of $K^+$ normally encountered in seawater, $KNO_3$ studies were not excluded from CWQG development for marine environments.

The mechanisms regulating nitrate uptake in aquatic biota are not fully understood. Limited accumulation of nitrate has been found in bodily fluids and tissues of invertebrates (crayfish and shrimp), and vertebrates (rainbow trout) exposed to high ambient nitrate levels (Jensen 1996; Stormer et al. 1996; Cheng et al. 2002). Mechanisms for nitrate uptake in amphibians have not been investigated, but there is potential for trans-dermal diffusion and uptake through the diet (Hecnar 2001).

Nitrate is considerably less toxic than ammonia or nitrite, with acute median lethal concentrations of $NO_3^-$-N being up to two orders of magnitude higher than for $NH_3$-N and $NO_2^-$-N (Colt and Armstrong 1981). Nonetheless, nitrate can produce toxic effects. There are two suspected mechanisms for the observed nitrate toxicity in aquatic animals: a) through methaemoglobin formation, resulting in a reduction in the oxygen carrying capacity of blood and b) through the inability of the organisms to maintain proper osmoregulation under high salt contents associated with elevated nitrate levels (Colt and Armstrong 1981).

***Toxicity Modifying Factors***: Recent work by Elphick (2011) investigated the effect of hardness on the toxicity of nitrate using both short-term and long-term toxicity tests. Short-term exposures were conducted using rainbow trout (*Oncorhynchus mykiss*) and an amphipod (*Hyalella azteca)*. Long-term exposures were conducted using the fathead minnow (*Pimephales promelas*), a water flea (*Ceriodaphnia dubia*), an amphipod (*Hyalella azteca*), and a midge (*Chironomus dilutus* – formerly *Chironomus tentans*). Tests with fish (rainbow trout and fathead minnow) were conducted using four hardness levels (approximately 15, 45, 90 and 160 $mg\cdot L^{-1}$ as $CaCO_3$). Tests with invertebrates (amphipod, water flea and midge) were not tested at the lowest hardness of 15 $mg\cdot L^{-1}$, and only tested at 45, 90 and 160 $mg\cdot L^{-1}$ as $CaCO_3$ hardness. In order to understand the relationship between hardness and nitrate toxicity, data were plotted into a regression of natural logarithmic (ln) of toxicant concentration as the dependent variable against the ln of hardness as the independent variable. Overall, the trend was one of decreasing toxicity with increasing hardness. However, in order to be able to derive a national hardness-adjusted guideline value, the calculated slopes for the hardness-toxicity relationships have to be compared to one other (e.g. comparison of slopes for short-term and long-term exposures separately). If it is concluded that the slopes for all species are not significantly different from one another, a pooled slope can be calculated, one using the short-term data and the second using the long-term data. This single pooled slope (one for short-term and a second for long-term exposures) is then used to derive hardness-adjusting equations for the development of a hardness-adjusted short-term and long-term guideline value. An F-test showed that the slopes for the two species (*O. mykiss* and *H. azteca*) for the short-term exposures were significantly different from one another (p=0.012). The slopes for the four species (*P. promelas, C. dubia, H. azteca* and *C. dilutus*) for the long-term exposures were also found to be significantly different from one another (F-test p value = 0.001). As a result, it was decided that the data would not be combined in order to generate a pooled slope, and there would be no derivation of either a hardness-dependant short-term or long-term equation for use in hardness-dependent short-term or long-term guideline derivation.

A long-term study evaluating the relationship between water hardness and nitrate toxicity was also conducted using a 40-day embryo-alevin-fry test with rainbow trout (*O. mykiss*) (Nautilus Environmental 2011). However, the results did not definitively demonstrate the relationship between increasing hardness and nitrate toxicity. In some cases, sensitivity appeared greater in the moderately hard water (92 $mg \cdot L^{-1}$ as $CaCO_3$) compared to the soft water (50 $mg \cdot L^{-1}$ as $CaCO_3$) and therefore this study was not included in the regression discussed above.

A short-term study conducted by Moore and Poirier (2010) evaluated the response of four species of salmonids to nitrate at three exposure temperatures (5, 10 and 15 deg C): *Oncorhynchus mykiss* (rainbow trout), *Salvelinus alpinus* (arctic charr), *Salvelinus namaycush* (lake trout), and *Coregonus clupeaformis* (lake whitefish). In this study, temperature did appear to have an effect on the 96-h $LC_{50}$ value, but not always in a predictable way. In the case of both *O. mykiss* and *C. clupeaformis*, nitrate was found to be most toxic (96-h $LC_{50}$ of 1690 and 4730 mg $NO_3^- \cdot L^{-1}$, respectively) when tested at the optimal metabolic temperatures for these fish (15 deg C for *O. mykiss* and 10 deg C for *C. clupeaformis*). Nitrate was found to be moderately toxic for *S. alpinus* at optimal metabolic test temperature of 10 deg C (96-h $LC_{50}$ of 6650 mg $NO_3^- \cdot L^{-1}$), and least toxic to *S. namaycush* at optimal metabolic temperature of 10 deg C (96-h $LC_{50}$ of 5230 mg $NO_3^- \cdot L^{-1}$). As for the influence of temperature on nitrate toxicity, species varied in their response, but this is likely due to species tolerance levels of temperature.

Water quality parameters such as pH and dissolved oxygen can influence the conversion of nitrate to other forms of nitrogen, or vice versa. Separate Canadian Water Quality Guidelines exist for some of these other forms of nitrogen (e.g., nitrite and ammonia).

***Water Quality Guideline Derivation:*** Both the freshwater and marine short-term benchmark concentrations and the long-term Canadian water quality guidelines (CWQGs) for the nitrate ion for the protection of aquatic life were developed based on the CCME protocol (CCME 2007) using the statistical (Type A) approach.

***Short-term Freshwater Benchmark Concentration:*** Short-term benchmark concentrations are derived using severe effects data (such as lethality) of defined short-term exposure periods (24 - 96-h). These benchmarks represent a concentration that may result in severe effects to the aquatic ecosystem and are intended to give guidance on the impacts of severe, but transient, situations (e.g., spill events to aquatic receiving environments and infrequent releases of short-lived/non-persistent substances). Short-term benchmark concentrations *do not* provide guidance on protective levels of a substance in the aquatic environment, as short-term benchmark concentrations are levels which *do not* protect against adverse effects.

The minimum data requirements for the Type A short-term benchmark concentration approach were met, and a total of 23 data points (all $LC_{50}$ values) were used in the derivation of the value (Table 3). Each species for which appropriate short-term toxicity data was available was ranked according to sensitivity, and its centralized position on the species sensitivity distribution (SSD) was determined using the Hazen plotting position (estimate of the cumulative probability of a data point). Intra-species variability was accounted for by taking the geometric mean of the studies considered to represent the most sensitive lifestage and endpoint.

The log-Gompertz model provided the best fit of the five models tested (Figure 1). The equation of the Gompertz model is of the form:

$$f(x) = 1 - e^{-e^{\frac{(x-\mu)}{s}}}$$

Where, for the fitted model: $x$ = log (concentration) of nitrate ($mg \cdot L^{-1}$), $f(x)$ is the proportion of species affected, $\mu = 3.6330$ and $s = 0.3019$. The short-term SSD is shown in Figure 1 and summary statistics are presented in Table 4. The 5th percentile on the short-term SSD is 545 mg $NO_3^- \cdot L^{-1}$. This value is rounded to 2 significant figures to generate the freshwater short-term benchmark concentration of 550 mg $NO_3^- \cdot L^{-1}$ (Table 4). The lower fiducial limit (5%) on the 5th percentile is 456 mg $NO_3^- \cdot L^{-1}$, and the upper fiducial limit (95%) on the 5th percentile is 652 mg $NO_3^- \cdot L^{-1}$. The concentration of 545 mg $NO_3^- \cdot L^{-1}$ is within the range of the data (to which the model was fit). Therefore, the 5th percentile and its confidence limits are interpolations.

**Table 3.** Endpoints used to determine the freshwater short-term benchmark concentration for the nitrate ion.

| Species | Endpoint | Hardness of Exposure water (mg·L$^{-1}$ as CaCO$_3$) | Concentration (mg NO$_3^-$·L$^{-1}$) | Reference |
|---|---|---|---|---|
| **Fish** | | | | |
| *Pimephales promelas*<br>Fathead minnow | 96h LC$_{50}$ | 156-172; 136-140 | 3304* | Scott and Crunkilton 2000; US EPA 2010 |
| *Oncorhynchus mykiss*<br>Rainbow trout | 96h LC$_{50}$ | 106-127; 90 | 3638* | Moore and Poirier 2010; Elphick 2011 |
| *Coregonus clupeaformis*<br>Lake whitefish | 96h LC$_{50}$ | 106-127 | 4730 | Moore and Poirier 2010 |
| *Salvelinus namaycush*<br>Lake trout | 96h LC$_{50}$ | 10-16 | 4968 | McGurk et al. 2006 |
| *Oncorhynchus tshawytscha*<br>Chinook salmon | 96h LC$_{50}$ | na | 5800 | Westin 1974 |
| *Notropis topeka*<br>Topeka shiner | 96h LC$_{50}$ | 210-230 | 5994 | Adelman et al 2009 |
| *Ictalurus punctatus*<br>Channel catfish | 96h LC$_{50}$ | 102 | 6200 | Colt and Tchobanoglous 1976 |
| *Salvelinus alpinus*<br>Arctic char | 96h LC$_{50}$ | 106-127 | 6650 | Moore and Poirier 2010 |
| *Lepomis macrochirus*<br>Bluegill | 96h LC$_{50}$ | 45-50 | 8753 | Trama 1954 |
| **Amphibians** | | | | |
| *Pseudacris regilla*<br>Pacific tree frog | 96h LC$_{50}$ | 70-80 | 2849 | Schuytema and Nebeker 1999a |
| *Xenopus laevis*<br>African clawed frog | 96h LC$_{50}$ | 21 | 7335 | Schuytema and Nebeker 1999c |
| **Invertebrates** | | | | |
| *Hydropsyche occidentalis*<br>Caddisfly | 96h LC$_{50}$ | 42.7 | 431 | Camargo and Ward 1992 |
| *Cheumatopsyche pettiti*<br>Caddisfly | 96h LC$_{50}$ | 42.7 | 503 | Camargo and Ward 1992 |
| *Hyalella azteca*<br>Amphipod | 96h LC$_{50}$ | 80-84; 110-124; 100 | 774* | US EPA 2010; Soucek and Dickinson 2011; Elphick 2011 |
| *Chironomus dilutus*<br>Midge | 48h LC$_{50}$ | 84-136 | 1582 | US EPA 2010 |
| *Lampsilis siliquoidea*<br>Fatmucket mussel | 96h LC$_{50}$ | 90-92 | 1582 | US EPA 2010 |
| *Sphaerium simile*<br>Fingernail clam | 96h LC$_{50}$ | 90-92 | 1644 | US EPA 2010 |
| *Ceriodaphnia dubia*<br>Water flea | 48h LC$_{50}$ | 156-172 | 1657 | Scott and Crunkilton 2000 |
| *Amphinemura delosa*<br>Stonefly | 96h LC$_{50}$ | 88-92 | 2020 | US EPA 2010 |
| *Daphnia magna*<br>Water flea | 48h LC$_{50}$ | 156-172 | 2047 | US EPA 2010 |
| *Allocapnia vivipara*<br>Stonefly | 96h LC$_{50}$ | 98-100 | 3703 | Soucek and Dickinson 2011 |
| *Megalonaias nervosa*<br>Washboard mussel | 96h LC$_{50}$ | 90-92 | 4151 | US EPA 2010 |
| *Potamopyrgus antipodarum*<br>New Zealand mudsnail | 96h LC$_{50}$ | 90.8 | 4616 | Alonso and Camargo 2003 |

*Value shown is the geometric mean of comparable values

**Table 4.** Short-term freshwater benchmark concentration for the nitrate ion resulting from the SSD Method.

| | **Concentration – as nitrate** |
|---|---|
| SSD 5th percentile | 550 mg·L$^{-1}$ |
| SSD 5th percentile, LFL (5%) | 456 mg·L$^{-1}$ |
| SSD 5th percentile, UFL (95%) | 652 mg·L$^{-1}$ |

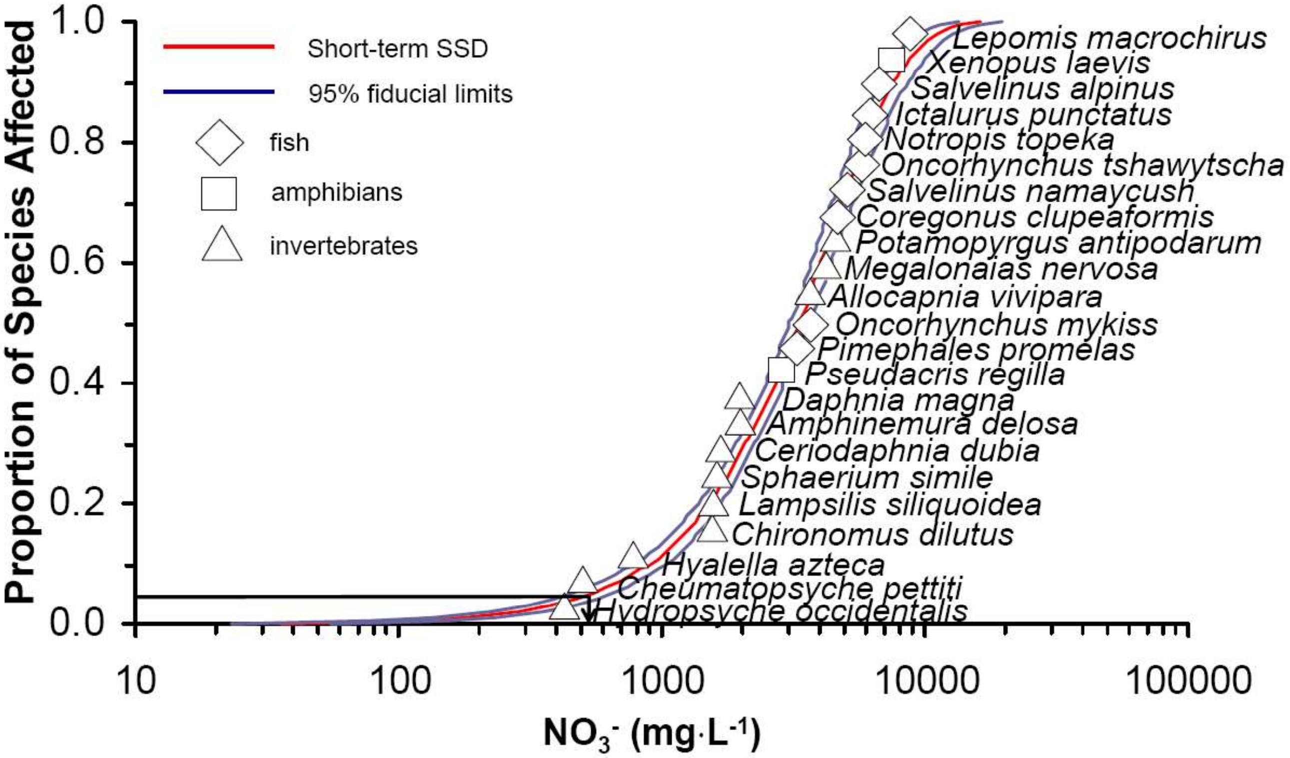

**Figure 1.** SSD of short-term LC$_{50}$ toxicity data for the nitrate ion in freshwater derived by fitting the Gompertz model to the logarithm of acceptable toxicity data for 23 aquatic species versus Hazen plotting position (proportion of species affected). The arrow at the bottom of the graph denotes the 5$^{th}$ percentile and the corresponding short-term benchmark concentration value.

Two data points fall below the short-term SSD 5$^{th}$ percentile value of 545 mg $NO_3^-$·L$^{-1}$. These include the 96-hour LC$_{50}$ of 431 mg $NO_3^-$·L$^{-1}$ for the caddisfly *Hydropsyche occidentalis (*Camargo and Ward 1992) and the 96-hour LC$_{50}$ of 503 mg $NO_3^-$·L$^{-1}$ for the caddisfly *Cheumatopsyche pettiti* (Camargo and Ward 1992). From all the invertebrate studies used in deriving the short-term benchmark value, these two caddisfly exposures were conducted in the exposure water of lowest hardness (CCME designated soft water, compared to the other exposures that used CCME moderately hard or CCME hard water). Based on the short-term SSD, short-term exposures to levels of nitrate exceeding the benchmark concentration of 550 mg $NO_3^-$·L$^{-1}$ *may* pose the greatest hazard to the sensitive caddisflies. Note that meeting the long-term guideline will protect from severe effects.

**Therefore, the short-term exposure benchmark concentration indicting the potential for severe effects (e.g. lethality or immobilization) to sensitive freshwater life during transient events is 550 mg $NO_3^-$·L$^{-1}$, for the nitrate ion.**

***Long-term Freshwater Quality Guideline:*** Long-term exposure guidelines identify a concentration of a parameter in the aquatic ecosystem below which of aquatic life are intended to be protected for indefinite exposure periods. Long-term exposure guidelines are derived using long-term data (≥7d exposures for fish and invertebrates, ≥24h for aquatic plants and algae).

The minimum data requirements for the Type A guideline approach were met, and a total of 12 data points were used in the derivation of the guideline (Table 5). Each species for which appropriate long-term toxicity data was available was ranked according to sensitivity, and its centralized position on the SSD was determined using the Hazen plotting position. Intra-species variability was accounted for by taking the geometric mean of the studies considered to represent the most sensitive lifestage and endpoint.

**Table 5.** Endpoints used to determine the freshwater long-term CWQG for the nitrate ion.

| Species | Endpoint | Hardness of Exposure water ($mg \cdot L^{-1}$ as $CaCO_3$) | Concentration ($mg\ NO_3^- \cdot L^{-1}$) | Reference |
|---|---|---|---|---|
| **Fish** | | | | |
| *Salvelinus namaycush*<br>Lake trout | 146-d MATC (delay to swim-up stage and growth as wet weight) | 10-16 | 14* | McGurk et al. 2006 |
| *Oncorhynchus mykiss*<br>Rainbow trout | 41-d MATC (proportion reaching swim-up) | 10 | 58 | Nautilus Environmental 2011 |
| *Pimephales promelas*<br>Fathead minnow | 32-d $EC_{10}$ (survival) | 132-180 | 207 | US EPA 2010 |
| *Notropis topeka*<br>Topeka shiner | 30-d MATC (growth) | 210-230 | 1594* | Adelman et al. 2009 |
| *Oncorhynchus tshawytscha*<br>Chinook salmon | 10-d $LC_{10}$ | na | 3142 | Westin 1974 |
| **Amphibians** | | | | |
| *Pseudacris regilla*<br>Pacific treefrog | 10-d $LC_{10}$ | 70-80 | 328 | Schuytema and Nebeker 1999c |
| *Xenopus laevis*<br>African treefrog | 10-d MATC (weight) | 21 | 404* | Schuytema and Nebeker 1999c |
| *Rana aurora*<br>Red-legged frog | 16-d MATC (weight) | 26 | 734* | Schuytema and Nebeker 1999b |
| **Invertebrates** | | | | |
| *Ceriodaphnia dubia*<br>Water flea | 7-d $IC_{25}$ (reproduction) | 44 | 50 | Elphick 2011 |
| *Hyalella azteca*<br>Amphipod | 14-d $IC_{25}$ (growth) | 46 | 57 | Elphick 2011 |
| *Chironomus dilutus*<br>Midge | 10-d $IC_{25}$ (growth) | 46 | 217 | Elphick 2011 |
| *Daphnia magna*<br>Water flea | 7-d MATC (reproduction) | 156-172 | 2244* | Scott and Crunkilton 2000 |

*Value shown is the geometric mean of comparable values.

The Normal model provided the best fit of the five models tested (Figure 2). The equation of the Normal model is:

$$f(x) = \frac{1}{2}\left(1 + \operatorname{erf}\left(\frac{x-\mu}{\sigma\sqrt{2}}\right)\right)$$

Where, for the fitted model: *x* = log (concentration) of nitrate ($mg{\cdot}L^{-1}$), *f(x)* is the proportion of species affected, $\mu = 2.4307$, $\sigma = 0.7992$ and *erf* is the error function (a.k.a. the Gauss error function). The long-term SSD is shown in Figure 2 and summary statistics are presented in Table 6. The 5th percentile on the long-term SSD is 13 mg $NO_3^-{\cdot}L^{-1}$. The lower fiducial limit (5%) on the 5th percentile is 7 mg $NO_3^-{\cdot}L^{-1}$, and the upper fiducial limit (95%) on the 5th percentile is 24 mg $NO_3^-{\cdot}L^{-1}$. The concentration of 13 mg $NO_3^-{\cdot}L^{-1}$ is outside the range of the data (to which the model was fit). Therefore, the 5th percentile and its confidence limits are extrapolations.

**Therefore the long-term exposure CWQG for the protection of freshwater aquatic life is 13 mg $NO_3^-{\cdot}L^{-1}$ for the nitrate ion.**

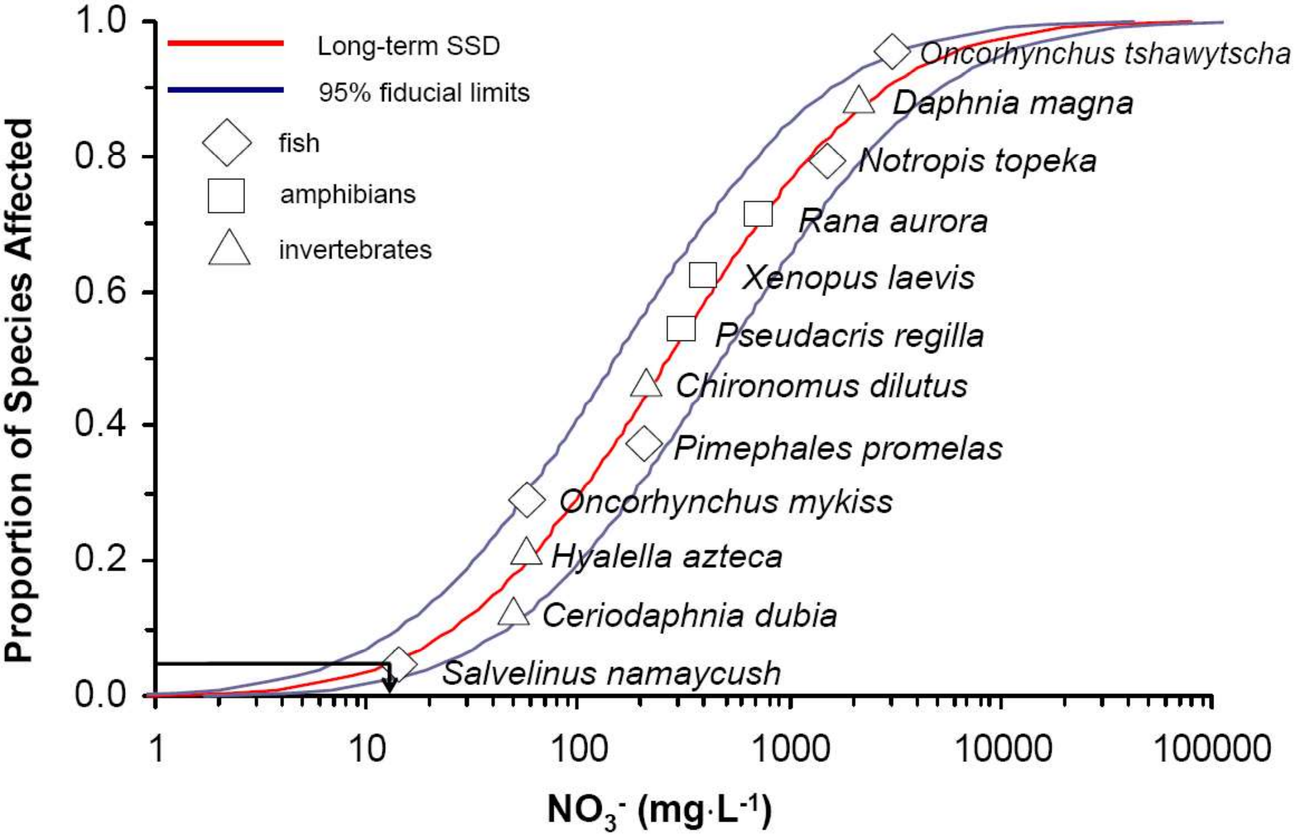

**Figure 2.** SSD of long-term no- and low-effect endpoint toxicity data for the nitrate ion in freshwater derived by fitting the Normal model to the logarithm of acceptable data for 12 aquatic species versus Hazen plotting position (proportion of species affected). The arrow at the bottom of the graph denotes the 5th percentile and the corresponding long-term Canadian Water Quality Guideline value.

**Table 6.** Long-term freshwater CWQG for the nitrate ion resulting from the SSD Method.

| | Concentration (as nitrate) |
|---|---|
| SSD 5th percentile | 13 mg·L$^{-1}$ |
| SSD 5th percentile, LFL (5%) | 7 mg·L$^{-1}$ |
| SSD 5th percentile, UFL (95%) | 24 mg·L$^{-1}$ |

***General Discussion Related to the Freshwater CWQG***: The use of the 5th percentile of the SSD as the environmental standard is designed to protect at least 95% of aquatic species from low-level effects. It is important to note that one toxicity endpoint lies just above the guideline value (Figure 2), which is the 146-d MATC of 14 mg $NO_3^-$·L$^{-1}$ for the lake trout swim-up fry (*Salvelinus namaycush*) (McGurk et al. 2006). McGurk et al. (2006) observed 2 endpoints that were impacted (or reduced compared to control) at 28 mg $NO_3^-$·L$^{-1}$ (low effect, or LOEC) whereas no effect (NOEC) was observed at 7 mg $NO_3^-$·L$^{-1}$. This was for both 1) growth, measured as wet weight, of lake trout swim-up fry, as well as 2) delay in development of lake trout alevin to the swim-up stage. Because the 2007 CCME protocol indicates that the inclusion of MATC values over LOEC and NOEC values, the geometric mean (MATC of 14 mg $NO_3^-$·L$^{-1}$) was included in the SSD calculations. The equivalent MATC endpoint for delay to swim-up stage for rainbow trout (*O. mykiss*) swim-up fry is 58 mg $NO_3^-$·L$^{-1}$ (Nautilus Environmental 2011) (Table 5). Since the CWQG value of 13 mg $NO_3^-$·L$^{-1}$ is below both the lake trout LOEC (delay to swim-up and growth) of 58 mg $NO_3^-$·L$^{-1}$ and lake trout MATC (mortality) of 886 mg $NO_3^-$·L$^{-1}$ (Environment Canada 2010), no direct effects on development delays, growth or survival are expected. The CCME guideline derivation protocol (CCME 2007) provides the option of implementing the Protection Clause in situations where a data point for a species at risk, a species of commercial or recreational importance, or an ecologically important species falls below the HC5 (CWQG) value on the long-term SSD. In this case, no data-points fell below the HC5 value.

This CWQG of 13 mg $NO_3^-$·L$^{-1}$ calculated using a species sensitivity distribution is the same value as the 2003 freshwater interim guideline of 13 mg $NO_3^-$·L$^{-1}$. In the case of the 2003 freshwater interim guideline, the value was based on a 10-day chronic study examining the toxicity of sodium nitrate to the Pacific treefrog (*Pseudacris regilla*; Schuytema and Nebeker 1999c). Test organisms exposed to 133 mg $NO_3^-$·L$^{-1}$ experienced a mean decrease in weight of 15% when compared to the control group. A safety factor of 0.1 was applied to the LOEC in accordance with CCME (1991) to derive the final interim guideline value. In the case of the 2012 full guideline value, all minimum dataset requirements for the development of a CWQG were fulfilled. It must be noted that the 2003 CWQG was interim, meaning that the required dataset was not fulfilled (one chronic invertebrate study on a non-planktonic organism was missing). A recommendation was also made in the 2003 scientific criteria document to "conduct additional toxicity tests for fish and invertebrate species that are known to be highly sensitive" to nitrate. For the derivation of the 2012 CWQG, additional testing was conducted using the amphipod *Hyalella azteca* (to ensure minimum dataset requirements were fulfilled). Testing was also conducted using the early life stage of the rainbow trout (Stantec 2006) and the lake trout (McGurk et al. 2006). Test results indicated that the CWQG of 13 mg $NO_3^-$·L$^{-1}$ would be protective of the lake trout, the most sensitive of the fish species tested.

***Short-term Marine Benchmark Concentration:*** Short-term benchmark concentrations are derived using severe effects data (such as lethality) of defined short-term exposure periods (24 - 96-h). These benchmarks represent a concentration that may result in severe effects to the aquatic ecosystem and are intended to give guidance on the impacts of severe, but transient, situations (e.g., spill events to aquatic receiving environments and infrequent releases of short-lived/non-persistent substances). Short-term benchmark concentrations *do not* provide guidance on protective levels of a substance in the aquatic environment, as short-term benchmark concentrations are levels which *do not* protect against adverse effects.

The minimum data requirements for the Type A short-term benchmark concentration approach were met, and a total of 10 data points (all $LC_{50}$ values) were used in the derivation of the value (Table 7). Each species for which appropriate short-term toxicity data was available was ranked according to sensitivity, and its centralized position on the species sensitivity distribution (SSD) was determined using the Hazen plotting position (estimate of the cumulative probability of a data point). Intra-species variability was accounted for by taking the geometric mean of the studies considered to represent the most sensitive lifestage and endpoint.

**Table 7.** Endpoints used to determine the marine short-term benchmark concentration for the nitrate ion.

| Species | Endpoint | Concentration ($mg NO_3^- \cdot L^{-1}$) | Reference |
|---|---|---|---|
| **Fish** | | | |
| *Monacanthus hispidus*<br>Planehead filefish | 96h $LC_{50}$ | 2538 | Pierce et al. 1993 |
| *Raja eglanteria*<br>Clearnose skate | 96h $LC_{50}$ | >4253[1] | Pierce et al. 1993 |
| *Oncorhynchus tshawytscha*<br>Chinook salmon | 96h $LC_{50}$ | 4400 | Westin 1974 |
| *Trachinotus carolinus*<br>Florida pompano | 96h $LC_{50}$ | 4430 | Pierce et al. 1993 |
| *Oncorhynchus mykiss*<br>Rainbow trout | 96h $LC_{50}$ | 4650 | Westin 1974 |
| *Centropristis striata*<br>Gulf black sea bass | 96h $LC_{50}$ | 10632 | Pierce et al. 1993 |
| *Pomacentrus leucostictus*<br>Beaugregory | 96h $LC_{50}$ | >13290[1] | Pierce et al. 1993 |
| **Invertebrates** | | | |
| *Strongylocentrotus purpuratus*<br>Purple sea urchin | 96h $EC_{50}$ (larval development) | 1384 | Stantec 2006 |
| *Penaeus monodon*<br>Tiger shrimp | 96h $LC_{50}$ | 7717* | Tsai and Chen 2002 |
| *Penaeus paulensis*<br>Prawn | 96h $LC_{50}$ | 9621 | Cavalli et al. 1996 |

[1] The use of toxicity data from a test where an insufficient concentration range on the higher end has been tested (i.e., where the results are expressed as "toxic concentration is greater than *x*"), are generally acceptable, as they will not result in an under-protective guideline. These studies can be used to fill the minimum data set requirements and in the actual guideline derivation (CCME 2007).

*Value shown is the geometric mean of comparable vlues.

The Logistic model provided the best fit of the five models tested (Figure 3). The equation of the Logistic model is:

$$y = 1/[1+e^{-((x-\mu)/\sigma)}]$$

Where for the fitted model: $x$ = log (concentration) of nitrate ($mg \cdot L^{-1}$), $y$ is the proportion of species affected, $\mu = 3.7290$ and $\sigma = 0.1881$. The short-term SSD is shown in Figure 3 and summary statistics are presented in Table 8. The 5th percentile on the short-term SSD is 1497 mg $NO_3^- \cdot L^{-1}$. This value is rounded to 2 significant figures to generate the marine short-term benchmark concentration of 1500 mg $NO_3^- \cdot L^{-1}$ (Table 8). The lower fiducial limit (5%) on the 5th percentile is 1046 mg $NO_3^- \cdot L^{-1}$, and the upper fiducial limit (95%) on the 5th percentile is 2141 mg $NO_3^- \cdot L^{-1}$. The concentration of 1497 mg $NO_3^- \cdot L^{-1}$ is inside the range of the data (to which the model was fit). Therefore, the 5th percentile and its confidence limits are interpolations.

**Table 8.** Short-term marine benchmark concentration for the nitrate ion resulting from the SSD Method.

| | Concentration (as nitrate) |
|---|---|
| SSD 5th percentile | 1500 $mg \cdot L^{-1}$ |
| SSD 5th percentile, LFL (5%) | 1046 $mg \cdot L^{-1}$ |
| SSD 5th percentile, UFL (95%) | 2141 $mg \cdot L^{-1}$ |

One data point falls below the short-term SSD 5th percentile value of 1497 mg $NO_3^- \cdot L^{-1}$, the 96-hour $EC_{50}$ of 1384 mg $NO_3^- \cdot L^{-1}$ for the purple sea urchin *Strongylocentrotus purpuratus* (Stantec 2006). Based on the short-term SSD, short-term exposures to levels of nitrate exceeding the benchmark concentration of 1500 mg $NO_3^- \cdot L^{-1}$ *may* pose the greatest hazard to the sensitive purple sea urchin. Note that meeting the long-term guideline will protect from severe effects.

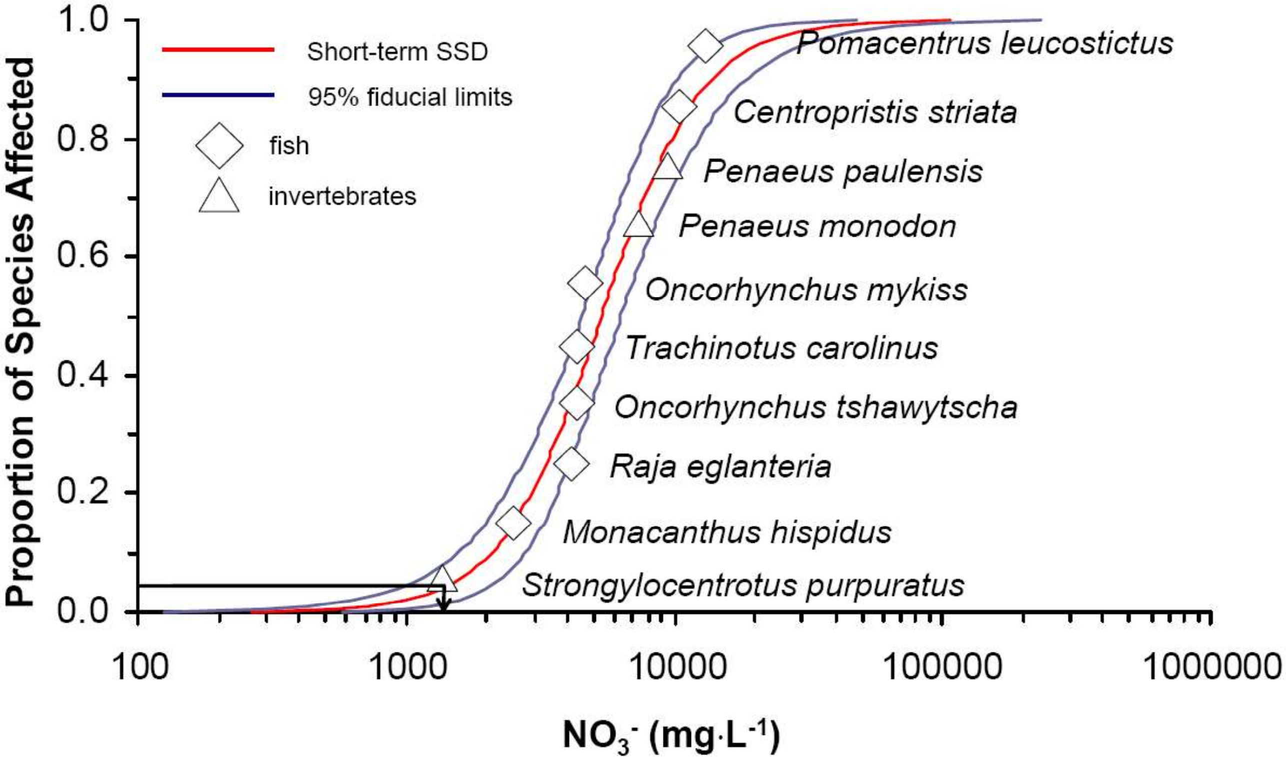

**Figure 3.** SSD of short-term L/EC$_{50}$ toxicity data for the nitrate ion in saltwater derived by fitting the Logistic model to the logarithm of acceptable toxicity data for 10 aquatic species versus Hazen plotting position (proportion of species affected). The arrow at the bottom of the graph denotes the 5th percentile and the corresponding short-term benchmark concentration value.

**Therefore the short-term exposure benchmark concentration indicating the potential for severe effects (e.g. lethality or immobilization) to sensitive marine life during transient events is 1500 mg $NO_3^-$·$L^{-1}$.**

***Long-term Marine Quality Guideline:*** Long-term exposure guidelines identify a concentration of parameter in the aquatic ecosystem below which all forms of aquatic life are intended to be protected, for indefinite exposure periods. Long-term exposure guidelines are derived using long-term data (≥7d exposures for fish and invertebrates, ≥24h for aquatic plants and algae).

The minimum data requirements for the Type A guideline approach were met, and a total of 12 data points were used in the derivation of the guideline (Table 9). Each species for which appropriate long-term toxicity data was available was ranked according to sensitivity, and its centralized position on the SSD was determined using the Hazen plotting position.

**Table 9.** Endpoints used to determine the marine long-term CWQG for the nitrate ion.

| Species | Endpoint | Concentration (mg $NO_3^-\cdot L^{-1}$) | References |
|---|---|---|---|
| **Fish** | | | |
| *Amphiprion ocellaris*<br>Anemonefish | 72-d LOEC (growth, mortality) | 443 | Frakes and Hoff Jr. 1982 |
| *Atherinops affinis*<br>Topsmelt | 7-d $LC_{25}$ | 2554 | Stantec 2006 |
| *Oncorhynchus mykiss*<br>Rainbow trout | 7-d $LC_{10}$ | 2954 | Westin 1974 |
| *Oncorhynchus tshawytscha*<br>Chinook salmon | 7-d $LC_{10}$ | 3510 | Westin 1974 |
| **Invertebrates** | | | |
| *Nereis grubei*<br>Polychaete | 28-d $LC_{10}$ | 214 | Reish 1970 |
| *Neanthes arenaceodentata*<br>Polychaete | 28-d $LC_{10}$ | 440 | Reish 1970 |
| *Capitella capitella*<br>Polychaete | 28-d $LC_{10}$ | 660 | Reish 1970 |
| *Dorvillea articulate*<br>Polychaete | 28-d $LC_{10}$ | 700 | Reish 1970 |
| *Haliotis tuberculata*<br>Abalone | 15-d LOEC (growth) | 1108 | Basuyaux and Mathieu 1999 |
| *Paracentrotus lividus*<br>Purple Sea Urchin | 15-d LOEC (growth / feeding) | 1108 | Basuyaux and Mathieu 1999 |
| *Strongylocentrotus purpuratus*<br>Pacific purple sea urchin | 4-d $IC_{25}$ (larval development) | 1178 | Stantec 2006 |
| *Cherax quadricarinatus*<br>Australian crayfish | 5-d LOEC (respiration) | >4430[1] | Meade and Watts 1995 |

[1] The use of toxicity data from a test where an insufficient concentration range on the higher end has been tested (i.e., where the results are expressed as "toxic concentration is greater than *x*"), are generally acceptable, as they will not result in an under-protective guideline. These studies can be used to fill the minimum data set requirements and in the actual guideline derivation (CCME 2007).

The Normal model provided the best fit of the five models tested (Figure 4). The equation of the Normal model is:

$$f(x) = \frac{1}{2}\left(1 + \operatorname{erf}\left(\frac{x-\mu}{\sigma\sqrt{2}}\right)\right)$$

Where, for the fitted model: $x$ = log (concentration) of nitrate ($mg\cdot L^{-1}$), $f(x)$ is the proportion of species affected, $\mu = 3.0385$, $\sigma = 0.4539$ and *erf* is the error function (a.k.a. the Gauss error function). The long-term SSD is shown in Figure 4 and summary statistics are presented in Table 10. The 5th percentile on the long-term SSD is 196 mg $NO_3^-\cdot L^{-1}$. This value is rounded to 2 significant figures to generate the marine Canadian water quality guideline of 200 mg $NO_3^-\cdot L^{-1}$ (Table 10). The lower fiducial limit (5%) on the 5th percentile is 141 mg $NO_3^-\cdot L^{-1}$, and the upper fiducial limit (95%) on the 5th percentile is 273 mg $NO_3^-\cdot L^{-1}$. The concentration of 196 mg $NO_3^-\cdot L^{-1}$ is outside the range of the data (to which the model was fit). Therefore, the 5th percentile and its confidence limits are extrapolations.

**Therefore the long-term exposure CWQG for the protection of marine life is 200 mg $NO_3^-\cdot L^{-1}$.**

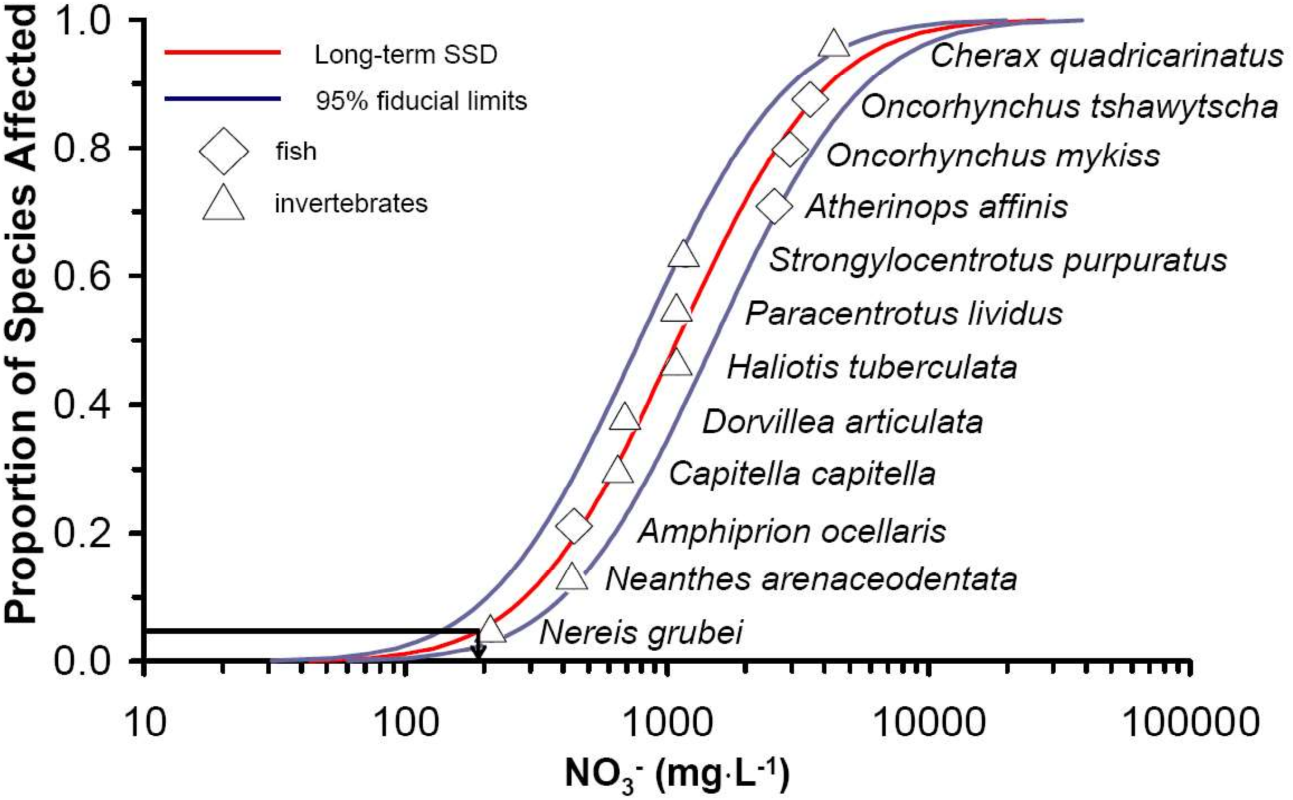

**Figure 4.** SSD of long-term no- and low-effect endpoint toxicity data for nitrate in saltwater derived by fitting the Normal model to the logarithm of acceptable data for 12 aquatic species versus Hazen plotting position (proportion of species affected). The arrow at the bottom of the graph denotes the 5th percentile and the corresponding long-term Canadian Water Quality Guideline value.

**Table 10.** Long-term Canadian Water Quality Guideline for the nitrate ion resulting from the SSD Method.

| | Concentration |
|---|---|
| SSD 5th percentile | 200 mg·L$^{-1}$ |
| SSD 5th percentile, LFL (5%) | 141 mg·L$^{-1}$ |
| SSD 5th percentile, UFL (95%) | 273 mg·L$^{-1}$ |

***General Discussion Related to the Marine CWQG:*** The ionic composition of marine water has resulted in nitrate guideline values much higher than the freshwater numbers. Cations in the water bind to dissolved $NO_3^-$ to offer protection to aquatic species against adverse effects of the nitrate ion (Environment Canada 2003, 2010b). $NO_3^-$ concentrations as high as the CWQG are rarely measured in water quality samples. Caution may be necessary when applying the marine nitrate guideline values in transitional environments such as estuaries and brackish-waters, in which salinity is lower than marine systems.

The newly derived guideline value of 200 mg $NO_3^-$·L$^{-1}$ (45 mg $NO_3^-$N·L$^{-1}$) has increased significantly when compared to the 2003 marine interim guideline of 16 mg $NO_3^-$·L$^{-1}$ (3.6 mg $NO_3^-$N·L$^{-1}$). In the case of the 2003 marine interim guideline, the value was based on 28-d TLm (= $LC_{50}$) of 329 mg $NO_3^-$·L$^{-1}$ (74 mg $NO_3^-$-N·L$^{-1}$) for the temperate marine adult-sized annelid *Nereis grubei*a (Reish, 1970). The guideline value was derived by multiplying the $LC_{50}$ for *N. grubei* by a safety factor of 0.05 (CCME 1991). A conservative safety factor was used for the marine guideline because: the polychaete in the critical study was not tested at its most sensitive life stage; the critical endpoint, although chronic, was based on a median lethal effect rather than a low sublethal effect; and adverse effects have been observed in nonindigenous tropical species exposed to much lower nitrate concentrations. For the derivation of the 2012 CWQG, additional testing was conducted using both the purple sea urchin (*Strongylocentrotus purpuratus)* and the topsmelt (*Atherinops affinis)* by Stantec (2006). A comparison of the marine CWQG of

200 mg $NO_3^-\cdot L^{-1}$ (45 mg $NO_3^-N\cdot L^{-1}$) to the data for temperate marine species in Appendix B of the scientific criteria document (CCME 2012) indicates that this value is protective. Therefore, even though the marine CWQG value has increased from the 2003 interim value, it is still considered to abide by the guiding principle of protecting all aquatic organisms at all life stages during indefinite exposure periods.

***Guidance on the Use of Guidelines:*** These guidelines for the nitrate ion are intended to protect against direct toxic effects of nitrate; indirect effects resulting from eutrophication may still occur at nitrate concentrations below these guideline values, depending on the total amount of bioavailable nitrogen and other site-specific factors (e.g., phosphorus, light availability). Further guidance on the application of these guidelines is provided in the scientific supporting document (Environment Canada 2010b).

The short-term benchmark concentration and long-term CWQG for nitrate are set to provide protection for short- and long-term exposure periods, respectively. They are based on generic environmental fate and behaviour and toxicity data. The long-term water quality guideline is a conservative value below which all forms of aquatic life, during all life stages and in all Canadian aquatic systems, should be protected. Because the guideline is not corrected for any toxicity modifying factors (e.g. hardness), it is a generic value that does not take into account any site-specific factors. Moreover, since the guideline is mostly based on toxicity tests using naïve (i.e., non-tolerant) laboratory organisms, it is going to be a conservative value, by design. If an exceedence of the guideline is observed, it does not necessarily suggest that toxic effects will be observed, but rather indicates the need to determine whether or not there is a potential for adverse environmental effects. In some situations, such as where an exceedence is observed, it may be necessary or advantageous to derive a site-specific guideline that takes into account local conditions (water chemistry, natural background concentration, genetically-adapted organisms, community structure) (CCME 2007). CCME has outlined several procedures to modify the national water quality guidelines to site-specific water quality guidelines or objectives to account for unique conditions and/or requirements at the site under investigation (CCME 1991; CCME 2003; Intrinsik 2010).

Fiducial limits (FLs) are reported along with the 5th percentile or guideline value, and are considered to be inverse confidence limits (CLs), since they are related to a concentration resulting in a specific effect (FLs are CLs around the independent varialble, as opposed to the dependent variable). FLs can be used to help interpret monitoring data, particularly if the guideline and method detection limit (MDL) are close. In general, when assessing the potential risk of chemical release and where the laboratory MDL is higher than the CWQG, water quality managers could look at the magnitude of the difference between the CWQG and the MDL (fiducial limits can be applied here), the size of the database used to develop the CWQG, and the toxicity of the substance. Note that only the 5th percentile is to be used as the guideline value.

In general, Canadian Water Quality Guidelines (CWQGs) are numerical concentrations or narrative statements that are recommended as levels that should result in negligible risk of adverse effects to aquatic biota. As recommendations, the CWQGs are not legally enforceable limits, though they may form the scientific basis for legislation or regulation at the provincial, territorial, or municipal level. CWQGs may also be used as benchmarks or targets in the assessment and remediation of contaminated sites, as tools to evaluate the effectiveness of point-source controls, or as “alert levels” to identify potential risks.

CWQG values are calculated such that they protect the most sensitive life stage of the most sensitive aquatic life species over the long term. Hence, concentrations of a parameter that are less than the applicable CWQG are not expected to cause any adverse effect on aquatic life. Concentrations that exceed the CWQGs, however, do not necessarily imply that aquatic biota will be adversely affected, or that the water body is impaired; the concentration at which such effects occur may differ depending on site-specific conditions. Where the CWQGs are exceeded, professional advice should be sought in interpreting such results. As with other CWQGs, the guidelines for nitrate are intended to be applied towards concentrations in ambient surface waters, rather than immediately adjacent to point sources such as municipal or industrial effluent outfalls. Various jurisdictions provide guidance on determining the limits of mixing zones when sampling downstream from a point source (see, for example, BC MELP 1986 and MEQ 1991), though Environment Canada and CCME do not necessarily endorse these methods.

## *References*

Adelman, I. R., L. I. Kusilek, J. Koehle and J. Hess. 2009. Acute and chronic toxicity of ammonia, nitrite and nitrate to the endangered topeka shiner (*Notropis topeka*) and fathead minnows (*Pimephales promelas*). Environ. Toxicol. Chem. 28(10):2216-2223.

Alonso, A. and J.A. Camargo. 2003. Short-term toxicity of ammonia, nitrite, and nitrate to the aquatic snail *Potamopyrgus antipodarum* (Hydrobiidae, Mollusca). Bulletin of Environmental Contamination and Toxicology. 70: 1006-1012.

Baker, J. and V. Waights. 1994. The effects of nitrate on tadpoles of the tree frog *(Litoria caerulea)*. Herpetol. J. 4(3): 106-108.

Basuyaux, O. and M. Mathieu. 1999. Inorganic nitrogen and its effect on growth of the abalone *Haliotis tuberculata* Linnaeus and the sea urchin *Paracentrotus lividus* Lamarck. Aquaculture. 174: 95-107.

BCMELP (British Columbia Ministry of Environment, Lands and Parks). 1986. Principles for preparing water quality objectives in British Columbia. British Columbia Ministry of Environment, Lands, and Parks, Water Management Branch, Resource Quality Section.

Calleja, M.C., G. Persoone, and P. Geladi. 1994. Comparative acute toxicity of the first 50 multicentre evaluation of *in vitro* cytotoxicity chemicals to aquatic non-vertebrates. Arch. Environ. Contam. Toxicol. 26: 69-78.

Camargo, J. A. and J. V. Ward. 1992. Short-term toxicity of sodium nitrate ($NaNO_3$) to non-target freshwater invertebrates. Chemosphere. 24(1): 23-28.

Castillo, M.M., J.D. Allan, and S. Brunzell. 2000. Nutrient concentrations and discharges in a midwestern agricultural catchment. J. Environ. Qual. 29: 1142-1151.

Cavalli, R. O., W. Wasielesky Jr., C. S. Franco, and K. M. Filho. 1996. Evaluation of the short-term toxicity of ammonia, nitrite and nitrate to *Penaeus paulensis* (Crustacea, Decopoda) broodstock. Arq. Biol. Tecnol. 39(3): 567-575.

Colt, J. and G. Tchobanoglous. 1976. Evaluation of the short-term toxicity of nitrogenous compounds to channel catfish, *Ictalurus punctatus*. Aquaculture. 8: 209-224.

CCME (Canadian Council of Ministers of the Environment). 1991. Appendix IX - A protocol for the derivation of water quality guidelines for the protection of aquatic life (April 1991). *In*: Canadian water quality guidelines. Canadian Council of Resource and Environment Ministers, 1987. Prepared by the Task Force on Water Quality Guidelines. [Updated and reprinted with minor revisions and editorial changes in Canadian environmental quality guidelines, Chapter 4, Canadian Council of Ministers of the Environment, 1999, Winnipeg.].

-----. 2007. A protocol for the derivation of water quality guidelines for the protection of aquatic life 2007. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, 1999, Winnipeg.

-----. 2012. Canadian water quality guidelines for the protection of aquatic life: Nitrate. *In*: Canadian Environmental Quality Guidelines, 1999. Canadian Council of Ministers of Environment. Winnipeg.

CFI (Canadian Fertilizer Institute). 2001. Canadian fertilizer information system 2001: Statistical compendium. Canadian Fertilizer Institute. Ottawa, ON. 11 pp. http://www.cfi.ca/

Chambers, P.A., M. Guy, E.S. Roberts, M.N. Charlton, R.A. Kent, C. Gagnon, G. Grove, and N. Foster. 2001. Nutrients and their impact on the Canadian environment. Agriculture and Agri-Food Canada, Environment Canada, Fisheries and Oceans Canada, Health Canada and Natural Resources Canada. 241 pp.

Cheng, S.-Y., S.-J. Tsai, and J.-C. Chen. 2002. Accumulation of nitrate in the tissues of *Penaeus monodon* following elevated ambient nitrate exposure after different time periods. Aquat. Tox. 56: 133-146.

Colt, J. and D.A. Armstrong. 1981. Nitrogen toxicity to crustaceans, fish, and molluscs. Bio-Engineering Symposium for Fish Culture 1: 34-37.

Crouzet, P., J. Leonard, S. Nixon, Y. Rees, W. Parr, L. Laffon, J. Bogestrand, P. Kristensen, C. Lallana, G. Izzo, T. Bokn, J. Bak, and T.J. Lack. 1999. Nutrients in European ecosystems. Thyssen, N. (ed.). Report no. Environmental Assessment Report no. 4. European Environment Agency. Copenhagen, Denmark.

Dodds, W. K., J. R. Jones, and E. B. Welch. 1998. Suggested classification of stream trophic state: Distributions of temperate stream types by chlorophyll, total nitrogen and phosphorus. Wat. Res. 32(5): 1455-1462.

Dowden, B.F. and H.J. Bennett. 1965. Toxicity of selected chemicals to certain animals. J. Waste Poll. Control Fed. 37(9): 1308-1316.

Elphick, J. 2011. Evaluation of the role of hardness in modifying the toxicity of nitrate to freshwater organisms. Nautilus Environmental. 4 April 2011.

Environment Canada. 2010. National pollutant release inventory. 2008 Reporting Year. http://www.ec.gc.ca/inrp-npri/

-----. 2010b. Canadian water quality guidelines for the protection of aquatic life: Nitrate ion. Scientific Supporting Document. National Guidelines and Standards Office, Environmental Quality Branch, Environment Canada. Ottawa, ON. Unpubl. draft.

-----. 2003. Canadian water quality guidelines for the protection of aquatic life: Nitrate ion. Ecosystem Health: Science-based solutions Report No. 1-6. National Guidelines and Standards Office, Water Policy and Coordination Directorate, Environment Canada. 115 p.

Frakes, T. and F. H. Hoff Jr. 1982. Effect of high nitrate-N on the growth and survival of juvenile and larval anemonefish, *Amphiprion ocellaris*. Aquaculture. 29(155): 158.

Government of Canada. 1996. The State of Canada's Environment: 1996. Environment Canada, State of the Environment Reporting. Ottawa, ON.

Halling-Sorensen, B. and S.E. Jorgensen. 1993. The Removal of Nitrogen Compounds From Wastewater. Elsevier Science Publishers. Amsterdam, NL. 443 pp.

Hecnar, S.J. 2001. Personal Communication. Department of Biology, Lakehead University, Thunder Bay, Ontario.

Intrinsik Science. 2010. Synthesis of research and methods for developing water quality guidelines for the Canadian environmental sustainability indicators (CESI) freshwater quality indicator. Prepared for Environment Canada, National Guidelines and Standards Office. February 2010.

Jensen, F.B. 1996. Uptake, elimination and effects of nitrite and nitrate in freshwater crayfish (*Astacus astacus*). Aquat. Tox. 34: 95-104.

Khangarot, B.S. and P.K. Ray. 1989. Investigation of correlation between physicochemical properties of metals and their toxicity to the water flea *Daphnia magna* Straus. Ecotoxicol. Environ. Saf. 18: 109-120.

Korol, M. and G. Rattray. 2000. Canadian Fertilizer Consumption, Shipments and Trade 1998/1999. Agriculture and Agri-Food Canada. pp. 1-32.

Lilius, H., B. Isomaa, and T. Holmstrom. 1994. A comparison of the toxicity of 50 reference chemicals to freshly isolated rainbow trout hepatocytes and *Daphnia magna*. Aquat. Tox. 30: 47-60.

McGurk, M. D., F. Landry, A. Tang, and C. H. Hanks. 2006. Acute and chronic toxicity of nitrate to early life stages of lake trout (*Salvelinus namaycush*) and lake whitefish (*Coregonus clupeaformis*). Environ. Toxicol. Chem. 25(8):2187-2196.

Meade, M.E. and S.A. Watts. 1995. Toxicity of ammonia, nitrite, and nitrate to juvenile Australian crayfish, *Cherax quadricarinatus*. J. Shellfish Res. 14(2): 341-346.

MEQ (Ministère de l'Environnement du Québec). 1991. Méthode de calculation des objectifs environnementaux de rejet pour les contaminants du milieu aquatique (Révisé 1996 et 2001). *In*: Direction du suivi de l'état de l'environnement. Ministerè de l'Environnement du Québec. Québec. 26 pp.

Moore, D and D. Poirier. 2010. The influence of temperature on the toxicity of nitrate and nitrite to 4 species of fish: lake whitefish (*Coregonus clupeaformis*), rainbow trout (*Oncorhynchus mykiss*), arctic char (*Salvelinus alpinus*), and lake trout (*Salvelinus namaycush*). Laboratory Services Branch, Ontario Ministry of the Environment. Unpublished data.

Mount, D.R., D.D. Gulley, J.R. Hockett, T.D. Garrison, and J.M. Evans. 1997. Statistical models to predict the toxicity of major ions to *Ceriodaphnia dubia*, *Daphnia magna* and *Pimephales promelas* (fathead minnow). Environ. Toxicol. Chem. 16(10): 2009-2019.

Muir, P.R., D.C. Sutton, and L. Owens. 1991. Nitrate toxicity to *Penaeus monodon* protozoea. Mar. Biol. 108: 67-71.

Nautilus Environmental. 2011. Evaluation of the role of hardness in modifying the toxicity of nitrate to rainbow trout. Final Report Submitted to Mining Association of BC. 12 September 2011.

Nordin, R.N. and L.W. Pommen. 1986. Water quality criteria for nitrogen (nitrate, nitrite, and ammonia): Technical appendix. Water Quality Criteria. Water Management Branch, British Columbia Ministry of Environment and Parks. Victoria, BC. 83 pp.

NRC (National Research Council). 1972. Accumulation of Nitrate. Committee on Nitrate Accumulation, Agriculture Board, National Academy of Sciences. Washington, DC.

-----. 1978. Nitrates: An Environmental Assessment. Scientific and Technical Assessments of Environmental Pollutants. National Academy of Sciences. Washington, D.C. 723 pp.

Petrie, B., P.A. Yeats, and P.M. Strain. 1999. Nitrate, silicate and phosphate atlas for the Scotian Shelf and Gulf of Maine. Can. Tech. Report of Hydrog. Ocean Sci. 203. Bedford Institute of Oceanography. Dartmouth, N.S. vii + 96 pp.

Pierce, R. H., J. M. Weeks, and J. M. Prappas. 1993. Nitrate toxicity to five species of marine fish. J. World Aquacult. Soc. 24(1): 105-107.

Pinar, G., E. Duque, A. Haidour, J.-M. Oliva, L. Sanchez-Barbero, V. Calvo, and J.L. Ramos. 1997. Removal of high concentrations of nitrate from industrial wastewaters by bacteria. Appl. Environ. Microbiol. 63(5): 2071-2073.

Reish, D. J. 1970. The effects of varying concentrations of nutrients, chlorinity, and dissolved oxygen on polychaetous annelids. Wat. Res. 4: 721-735.

Rouse, J.D., C.A. Bishop, and J. Struger. 1999. Nitrogen pollution: An assessment of its threat to amphibian survival. Environ. Health Perspect. 107: 799-803.

Schuytema, G.S. and A.V. Nebeker. 1999a. Comparative effects of ammonium and nitrate compounds on Pacific treefrog and African clawed frog embryos. Arch. Environ. Contam. Toxicol. 36: 200-206.

-----. 1999b. Effects of ammonium nitrate, sodium nitrate, and urea on red-legged frogs, Pacific tree frogs and African clawed frogs. Bull. Environ. Contam. Toxicol. 63: 357-364.

-----. 1999c. Comparative toxicity of ammonium and nitrate compounds to Pacific treefrog and African clawed frog tadpoles. Environ. Toxicol. Chem. 18(10): 2251-2257.

Scott, G. and R. L. Crunkilton. 2000. Acute and chronic toxicity of nitrate to fathead minnows (*Pimephales promelas*), *Ceriodaphnia dubia*, and *Daphnia magna*. Environ. Toxicol. Chem. 19(12): 2918-2922.

Sharp, J. 1983. The distribution of inorganic nitrogen and dissolved and particulate organic nitrogen in the sea. *In*: Nitrogen in the Marine Environment. Carpenter, E.J. and D.G. Capone (eds.). Academic Press. New York, NY.

Soucek, D.J. and A. Dickinson. 2011. Acute toxicity of nitrate and nitrite to sensitive freshwater insects, molluscs, and a crustacean. Arch. Environ. Contam. Toxicol. DOI 10.1007/s00244-011-9705-8.

Spencer, C.P. 1975. The micronutrient elements. *In*: Chemical Oceanography. (2nd Ed.). Riley, J.P. and G. Skirrow (eds.). Academic Press. London. pp. 245-300.

Stantec Consulting Ltd. 2006. Report on the toxicity of nitrate to Canadian fish and aquatic invertebrate species. Prepared for: Environment Canada, National Guidelines Standards Office. Stantec Project No. 162704276.

Stormer, J., F.B. Jensen, and J.C. Rankin. 1996. Uptake of nitrite, nitrate, and bromide in rainbow trout, *Oncorhynchus mykiss*: effects on ionic balance. Can. J. Fish. Aquat. Sci. 53: 1943-1950.

Trama, F. 1954. The acute toxicity of some common salts of sodium, potassium and calcium to the common bluegill (*Lepomis macrochirus* Rafinesque). Proc. Acad. Nat. Sci. Philadelphia 106: 185-205.

Tsai, S-J. and J-C Chen. 2002. Acute toxicity of nitrate on *Penaeus monodon* juveniles at different salinity levels. Aquaculture. 213:163–170.

US EPA (United States Environmental Protection Agency). 2010. Final report on acute and chronic toxicity of nitrate, nitrite, boron, manganese, fluoride, chloride and sulfate to several aquatic animal species. Report No. EPA 905-R-10-002. November 2010. US EPA Office of Science and Technology, Health and Ecological Criteria Division and US EPA Region 5 Water Division.

USGS (U.S. Geological Survey). 1999. The quality of our nation's waters: Nutrients and pesticides. Report no. 1225. U.S. Geological Survey. Reston, VA. pp. 1-82.

van der Leeden, F., F.L. Troise, and D.K. Todd. 1990. The Water Encyclopedia, 2nd Ed. Lewis Publishers. Chelsea, Michigan. 808 pp.

Westin, D. T. 1974. Nitrate and nitrite toxicity to salmonid fishes. Prog. Fish Cult. 36(2): 86-89.

Whitney,F. 2001. Personal Communication. Institute of Ocean Sciences, Department of Fisheries and Oceans Canada, Sidney, BC.

WHO (World Health Organization). 1996. Inorganic Constituents and Physical Parameters. *In*: Guidelines for Drinking-Water Quality: Volume 2 Health Criteria and Other Supporting Information. (2nd Ed.). World Health Organization. Geneva. pp. 313-322.

**Reference listing:**

Canadian Council of Ministers of the Environment. 2012. Canadian water quality guidelines for the protection of aquatic life: Nitrate. In: Canadian environmental quality guidelines, Canadian Council of Ministers of the Environment, Winnipeg.

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# *ECCC 16 ATTACHMENT 2: CANADIAN WATER QUALITY GUIDELINES FOR THE PROTECTION OF AQUATIC LIFE – AMMONIA*

# Canadian Water Quality Guidelines for the Protection of Aquatic Life

# AMMONIA

Ammonia (CAS # 7664-41-7, atomic mass 17.03) is a colourless alkaline gas which has a pungent suffocating odour at ambient temperature and pressure (WHO 1986; CCREM 1987). It freezes at -77.8°C and boils at -33.35°C, and is often stored or shipped in liquified form (Geadah 1985).

Ammonia is an important component of the nitrogen cycle and because it is oxidized in the environment by microorganisms (i.e., nitrification), it is a large source of available nitrogen in the environment (Raven & Johnson 1989). The complexity of the nitrogen cycle, various rate determining environmental conditions for nitrification (e.g., pH, temperature), and the physical behaviour of ammonia (e.g., volatilization, adsorption) make determining the fate of ammonia in the environment extremely complex. Ammonia can form explosive mixtures with air at concentrations between 16 and 27% by volume, but is generally regarded as non-flammable (WHO 1986; Geadah 1980). Ionized ammonium salts form when ammonia dissolves in dilute acids. Some of these salts are found in nature (water, soil, atmosphere) (WHO 1986).

Ammonia is highly soluble in water and its speciation is affected by a wide variety of environmental parameters including pH, temperature, and ionic strength. In aqueous solutions, an equilibrium exists between un-ionized ($NH_3$) and ionized ($NH_4^+$) ammonia species. Un-ionized ammonia refers to all forms of ammonia in water with the exception of the ammonium ion ($NH_4^+$) (Environment Canada 1997; CCREM 1987). Ionized ammonia refers to the ammonium ion. The term 'total ammonia' is used to describe the sum of ammonia ($NH_3$) and ammonium ($NH_4^+$) concentrations and may also be expressed as 'total ammonia-nitrogen', due to the slightly different relative molecular masses (Environment Canada 1997; CCREM 1987; WHO 1986).

In Canada, the Haber-Bosch process is the key commercial method of ammonia production. In this process, a catalyst is used to speed up the reaction between hydrogen and nitrogen (in a 3-to-1 ratio) combined under high pressure and high temperature (approximately 600°C) to produce ammonia (Harding 1959; Geadah 1985; Environment Canada 1997).

Total domestic demand for ammonia in Canada in 1996 and 1997 was approximately 3508 kt and 3535 kt, respectively. 1277 kt and 1226 kt of ammonia were exported in 1996 and 1997, respectively (CPI 1998). Ammonia is used in numerous applications in the refrigeration, pulp and paper, mining, food processing, refining, and animal husbandry sectors (Environment Canada 1997; Environment Canada 1992). The principal use of ammonia is the production of nitrogenous fertilizers (ammonium nitrate, ammonium phosphate, urea, and ammonium sulphate). In the agriculture industry, anhydrous ammonia is directly

**Table 1. Water quality guidelines for un-ionized ammonia for the protection of aquatic life.**

| Aquatic life | Guideline value (mg·L) |
|---|---|
| Freshwater | 0.019 |
| Marine | NRG[1] |

[1] No recommended guideline

**Table 2. Water quality guidelines for total ammonia for the protection of aquatic life (mg·L$^{-1}$ $NH_3$).**

| Temp (°C) | pH | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 6.0 | 6.5 | 7.0 | 7.5 | 8.0 | 8.5 | 9.0 | 10 |
| 0 | 231 | 73.0 | 23.1 | 7.32 | 2.33 | 0.749 | 0.250 | 0.042 |
| 5 | 153 | 48.3 | 15.3 | 4.84 | 1.54 | 0.502 | 0.172 | 0.034 |
| 10 | 102 | 32.4 | 10.3 | 3.26 | 1.04 | 0.343 | 0.121 | 0.029 |
| 15 | 69.7 | 22.0 | 6.98 | 2.22 | 0.715 | 0.239 | 0.089 | 0.026 |
| 20 | 48.0 | 15.2 | 4.82 | 1.54 | 0.499 | 0.171 | 0.067 | 0.024 |
| 25 | 33.5 | 10.6 | 3.37 | 1.08 | 0.354 | 0.125 | 0.053 | 0.022 |
| 30 | 23.7 | 7.50 | 2.39 | 0.767 | 0.256 | 0.094 | 0.043 | 0.021 |

[*] The guideline values and all reported total ammonia concentrations in this factsheet are reported in mg/L $NH_3$; measurements of total ammonia in the aquatic environment are often also expressed as mg/L total ammonia-N. The present guideline values (mg/L $NH_3$) can be converted to mg/L total ammonia-N by multiplying the corresponding guideline value by 0.8224.

[**] Values falling outside of shaded area should be used with caution.

[***] No recommended guideline for marine waters.

applied to fields and ammonia is injected into animal feed to increase its nutrient value (Environment Canada 1997; Environment Canada 1992).

In the textile industry, ammonia is used in the fabrication of synthetic fibres (such as nylon and rayon), and as a curing agent in leather making (Environment Canada 1997). The health care industry uses ammonia in the manufacture of pharmaceuticals, vitamins, amino acids, lotions, and cosmetics. The household chemical industry uses ammonia for the manufacturing of cleansing agents and detergents (Environment Canada 1999). In addition, ammonia is used in the production of many goods including explosives, rocket fuel, beer, plastics, rubber, nitrogen oxides required for manufacturing sulphuric acid, in sugar purification, and in the treatment and transformation of metals (Chemical and Engineering News 1980, as cited in WHO 1986; Environment Canada 1997).

Ammonia commonly enters the environment as a result of municipal, industrial, agricultural, and natural processes. Natural sources of ammonia include the decomposition or breakdown of organic waste matter, gas exchange with the atmosphere, forest fires, animal waste, human breath, the discharge of ammonia by biota, and nitrogen fixation processes (Environment Canada 1997; Geadah 1985).

Point sources of ammonia include emissions and effluents from a wide variety of industrial plants such as iron and steel mills, fertilizer plants, oil refineries, and meat processing plants (Environment Canada 1997; CCREM 1987; WHO 1986). The manufacturing of explosives and the use of explosives in mining and construction can also be significant point sources of ammonia (Pommen 1983, as cited in CCREM 1987). The largest non-industrial point sources are sewage treatment plants (Environment Canada 1999). Accidental ammonia spills are a major anthropogenic source of ammonia entering the Canadian environment (Environment Canada 1992). An ammonia spill can occur during the production, processing, storage, application, or disposal stage of the chemical's life cycle (Environment Canada 1992). Environment Canada ranked ammonia as the top priority on the Environment Canada 1990 Canadian Chemical Spill Priority List. Additionally, the Major Industrial Accidents Council of Canada (MIACC) has identified ammonia as a priority substance (Environment Canada 1992). From 1974 to 1984, there were 107 reported spills of anhydrous ammonia (a total of 46 t), which accounted for 5.5% of all chemical spills in Canada during that time. From 1985 to 1990 there were 92 reported ammonia spills. The number of spills may be higher, as spill reports to the National Analysis of Trends in Emergencies System (NATES) are voluntary (Environment Canada 1992).

Non-point sources of ammonia include agricultural, residential, municipal, and atmospheric releases. Major agricultural sources include areas with intensive farming, accidental releases or spills of ammonia-rich fertilizer, and the decomposition of livestock wastes (Environment Canada 1992; WHO 1986). Residential and municipal sources of ammonia include the use and disposal of cleansing agents that contain ammonia, improper disposal or accidental spills of ammonia products, and urban runoff (Environment Canada 1997; WHO 1986). Combustion processes such as the burning of municipal waste, emissions from sewage treatment plants, domestic heating, the decay of vegetation, and the production and use of chemical fertilizers increase atmospheric concentrations of ammonia. Mobile sources of ammonia to the atmosphere arise from all forms of transportation (Environment Canada 1997).

The National Pollutant Release Inventory (NPRI 1996) states that, in 1996, 32 037 metric tonnes of ammonia were released into the Canadian environment from reporting industries. Of all the substances reported, ammonia was ranked second in total amount released. Approximately 56% of the ammonia was released to air, 24% released underground, 18% to water, and 2% to land. Due to the reporting requirements of the NPRI, some large anthropogenic sources (municipal sewage treatment plants, transportation systems, and animal husbandry systems) are excluded from these totals.

The main factors that influence the equilibrium between un-ionized and ionized ammonia are pH and temperature (Environment Canada 1999; Jofre and Karasov 1999; EPA 1998). Raising pH by one unit can cause the un-ionized ammonia concentration to increase nearly tenfold, while a 5°C temperature increase can cause an increase of 40-50% (Environment Canada 1999). Emerson et al. (1975) examined data on ammonia-water equilibrium systems and prepared calculations for pKa at different temperatures and percent $NH_3$ in ammonia solutions as a function of pH and temperature. Two equations were developed:

EQUATION 1.

$$pKa = 0.0901821 + 2729.92 / T$$

Where,

$T$ = Temperature in K; Absolute zero = - 273.15 $^{o}$C

$T$ (in K) = T (in $^{o}$C) + 273.15

EQUATION 2.

$$f = 1 / [10^{(pKa - pH)} + 1]$$

Where,

$f$ = fraction of total ammonia that is un-ionized
pKa = dissociation constant from equation 1

Using the equations above, a table describing the percent of $NH_3$ in low ionic strength water for temperatures (0 – 30$^{o}$C) and pH (pH= 6 – 10) is presented (Table 3). The ionic strength of the water is also an important influence on the un-ionized ammonia concentration. As the ionic strength increases in hard or marine waters, there is a decrease in the un-ionized $NH_3$ concentration (Environment Canada 1997; Emerson et al. 1975). Freshwater systems with up to 200 - 300 mg· L$^{-1}$ total dissolved solids may have a negligible reduction in percent $NH_3$. The effect of ionic strength is much smaller than the effects of temperature and pH (Soderberg and Meade 1991).

**Table 3. Percent un-ionized aqueous ammonia solutions for 0-30$^{o}$C and pH 6-10 (Emerson et al. 1975)**

| **Temp ($^{o}$C)** | **pH** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **6.0** | **6.5** | **7.0** | **7.5** | **8.0** | **8.5** | **9.0** | **9.5** | **10** |
| **0** | 0.008 | 0.026 | 0.082 | 0.261 | 0.820 | 2.55 | 7.64 | 20.7 | 45.3 |
| **5** | 0.012 | 0.039 | 0.125 | 0.394 | 1.23 | 3.80 | 11.1 | 28.3 | 55.6 |
| **10** | 0.018 | 0.058 | 0.186 | 0.586 | 1.83 | 5.56 | 15.7 | 37.1 | 65.1 |
| **15** | 0.027 | 0.086 | 0.273 | 0.859 | 2.67 | 7.97 | 21.5 | 46.4 | 73.3 |
| **20** | 0.039 | 0.125 | 0.396 | 1.24 | 3.82 | 11.2 | 28.4 | 55.7 | 79.9 |
| **25** | 0.056 | 0.180 | 0.566 | 1.77 | 5.38 | 15.3 | 36.3 | 64.3 | 85.1 |
| **30** | 0.080 | 0.254 | 0.799 | 2.48 | 7.46 | 20.3 | 44.6 | 71.8 | 89.0 |

In surface waters, both nitrification and volatilization are important competitive fate processes for ammonia (Environment Canada 1999). Volatilization increases with increasing wind speed, temperature, and pH. In addition, the partial pressure of ammonia in solution increases with increasing pH, and in aqueous solutions, ammonia may form complexes with a number of metal ions. It may be sorbed onto suspended and bed sediments and to colloidal particles. Ammonia may also be exchanged between sediments and overlying water. Ammonia concentrations in water vary seasonally and regionally. In natural waters, concentrations of total ammonia are generally less than 0.1 mg·L$^{-1}$. Higher levels of ammonia are generally indicative of organic pollution (McNeely et al. 1979 as cited in WQB 1989).

The data on Canadian environmental concentrations presented below have been selected from a database prepared by Environment Canada in support of the Second Canadian Environmental Protection Act Priority Substances List (CEPA PSL II) assessment for ammonia (Environment Canada 1998). Detection limits were often not reported in the database.

From 1993 to 1996, concentrations of dissolved ammonia in twenty rivers sampled in the Northwest Territories ranged from 0.0002 to 0.294 mg·L$^{-1}$ (n=521), with an average concentration of 0.0148 mg·L$^{-1}$. Total ammonia sampled from two rivers in the Northwest Territories waters ranged from 0.002 to 0.19 mg·L$^{-1}$ (n=4) (Environment Canada 1998).

Concentrations of dissolved ammonia collected from 165 rivers and lakes across British Columbia between 1990 and 1996 ranged from ND (not detected) to 180 mg·L$^{-1}$ (n=5135), with an average concentration of 0.689 mg·L$^{-1}$. The maximum concentration was detected in the Fraser River at a hydro station south of Mission City in 1993. Total ammonia levels from 32 water bodies in British Columbia ranged from ND to 8.4 mg·L$^{-1}$ (n=2129), with an average concentration of 0.0858 mg·L$^{-1}$ (Environment Canada 1998). Similarly, concentrations of total ammonia sampled from 232 waterbodies in the province of Alberta between 1990 and 1996 ranged between ND and 10.2 mg·L$^{-1}$ (n=2599), with an average concentration of 0.183 mg· L$^{-1}$ (Environment Canada 1998). Dissolved ammonia concentrations from 414 rivers and lakes in Alberta ranged between ND and 8.8 mg·L$^{-1}$ (n=1929), with an average concentration of 0.110 mg·L$^{-1}$ (Environment Canada 1998).

In 1987, total ammonia concentrations in the South Saskatchewan River, 140 m below the outfall diffuser of Saskatoon's sewage treatment plant outfall, reached a maximum of 4.26 mg·L$^{-1}$ (WQB 1989). For five kilometres downstream of the sewage treatment plant outfall, a few of the transects had mean total ammonia concentrations within the effluent plume that surpassed the Saskatchewan Surface Water Quality Objective for total ammonia for the protection of aquatic life of 0.44 mg·L$^{-1}$ (WQB 1989).

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Total ammonia concentrations in Ontario between 1994 and 1996 ranged from 0.001 mg·L$^{-1}$ at several locations to 16.5 mg·L$^{-1}$ at Hayward Creek downstream from Molson and Lim Lakes, with an average concentration of 0.144 mg·L$^{-1}$, and an average pH of 7.92 (Environment Canada 1998). Concentrations of total ammonia ranged between 0.375 and 0.938 mg·L$^{-1}$ in stormwaters monitored in Ontario between 1985 and 1986 (Marsalek and Ng 1989). In 1987-88, distributions of ammonia, nitrite, and total dissolved nitrogen were measured in Hamilton Harbour, Lake Ontario. In the spring and summer seasons, levels of un-ionized ammonia in Hamilton Harbour surpassed the International Joint Commission (IJC) objective of 20 µg·L$^{-1}$ at all sampling sites (NWRI 1990). Loadings of total ammonia from multiple sources in Hamilton Harbour were estimated to be 7500 kg/day (DOE-MOE 1989, as cited in NWRI 1990). Approximately 70% (5300 kg/day) of the total loading in 1987 was released by the Hamilton sewage treatment plant. Other sources of ammonia to Hamilton Harbour include steel industries and combined sewer overflows (NWRI 1990). Since the late 1970s and early 1980s, total quantities of ammonia in Hamilton Harbour have been greatly reduced. For example, reductions in the total ammonia loading from steel industries, alone, decreased from 24000 kg/day in 1967 to 857 kg/day by 1987. However, the reductions from the municipal sewage treatment plants were less noticeable.

Water samples from 206 river sampling stations in Quebec indicated that total ammonia concentrations ranged from ND to 15.9 mg·L$^{-1}$ (n=2035), with an average concentration of 0.103 mg·L$^{-1}$. Samples of total ammonia collected from 62 lake sampling stations in Quebec ranged from 0.01 to 0.82 mg $^{-1}$, with an average concentration of 0.082 mg·L$^{-1}$ (Environment Canada 1998). No dates were reported for the samples collected in Quebec. Between 1981 and 1985, the average concentration of total ammonia sampled from 276 lakes in Nova Scotia was 0.09 mg·L$^{-1}$. Ammonia levels ranged from <0.01 mg·L$^{-1}$ to a maximum level of 0.3 mg·L$^{-1}$ (Environment Canada 1998).

Concentrations of ammonia in the atmosphere in urban areas typically vary from 5 – 25 µg·m$^{-3}$ and in rural areas between 2-6 µg·m$^{-3}$. Agricultural areas with a high use or production of manure may release ammonia concentrations between 100 - 200 µg·m$^{-3}$. Particulate ammonium concentrations have been detected above oceans at levels ranging from 0.01-0.1 µg·m$^{-3}$ (WHO 1986).

## Water Quality Guideline Derivation

The Canadian water quality guidelines for un-ionized and total ammonia for the protection of aquatic life (Tables 1 and 2) were developed using the CCME protocol (CCME 1991) and the community ecological risk criteria from Environment Canada (1999). It should be noted that due to the paucity of ammonia toxicity data on marine organisms; currently, there is insufficient information to adequately derive a full or interim guideline for the protection of marine life. As a result, no marine guideline is recommended.

### Freshwater Life

There are several factors that are known to affect the toxicity of ammonia in freshwater. These factors may have an effect on the concentrations of un-ionized ammonia in water or impact directly on the organism making it more or less susceptible to ammonia (Environment Canada 1999). Factors shown to affect ammonia toxicity include pH, temperature, dissolved oxygen concentration, ionic strength, salinity, previous acclimatization to ammonia, fluctuating or intermittent exposure, and the presence of other toxic substances (Environment Canada 1997). Of these, pH is thought to be the most important factor influencing ammonia toxicity.

The speciation of ammonia is very important to understanding ammonia toxicity. As un-ionized ammonia is known to be more toxic than the ammonium ion, the influence of pH and temperature, on the relative proportion of ionized and un-ionized ammonia, in particular is important. It is thought that un-ionized ammonia is more toxic to aquatic organisms because it is a neutral molecule and is therefore able to diffuse across biological membranes more readily than other forms (EPA 1998).

There is a substantial body of data available on the toxicity of ammonia to aquatic organisms, in particular acute, chronic, and sub-lethal effects of ammonia in fish. Less information is available on the toxicity of ammonia to invertebrates and benthic organisms. Mean 48- and 96-hr $LC_{50}$ values reported for freshwater invertebrates and fish ranged from 1.10 to 22.8 mg·L$^{-1}$ for invertebrates and from 0.56 to 2.37 mg·L$^{-1}$ for fish species (Environment Canada 1999). Several authors have suggested that the ammonium ion may contribute to the toxicity of total ammonia especially at low pH (Borgmann 1994; Thurston et al. 1981; Armstrong et al. 1978). However, the weight-of-evidence suggests that the un-ionized fraction is the best indicator of ammonia toxicity

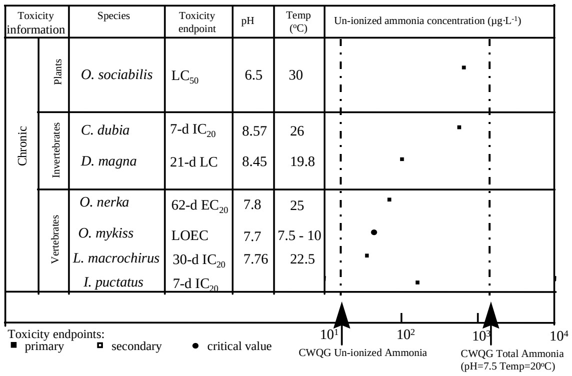
(Environment Canada 1999; Frias-Espericueta et al. 1999; EPA 1998).

*Ochromonas sociabilis*, a freshwater alga, was exposed to ammonia concentrations to observe the effect of ammonia on growth and mortality (Bretthauer 1978). Un-ionized ammonia concentrations ranging from 0.06 to 0.15 mg·L$^{-1}$ had an insignificant effect on growth. Concentrations of 0.015 to 0.03 mg·L$^{-1}$ were found to enhance alga growth. Development was reduced at 0.3 mg·L$^{-1}$ of $NH_3$ and mortality was observed at 0.6 mg·L$^{-1}$. Nimmo et al. (1989) conducted a 7-day life-cycle test on water fleas (*Ceriodaphnia dubia*). Test conditions included water from the St. Vrain River, Colorado at 25°C and pH 7.8. An $EC_{20}$ (# of neonates per original female) of 15.2 mg·L$^{-1}$ total ammonia was calculated using regression analysis and square root transformation (EPA 1998). The total ammonia concentration can be converted to un-ionized ammonia using the equations (EQ 1 & 2) from Emerson et al. (1975). Using this approach, the $EC_{20}$ is 0.525 mg·L$^{-1}$ for un-ionized ammonia.

Rainbow trout (*Oncorhynchus mykiss*) were tested for sensitivity to un-ionized ammonia ($NH_3$) concentrations ranging from 0.01 to 0.07 mg·L$^{-1}$ over a period of 5 years (Thurston et al. 1984). No correlation between ammonia concentration and number of eggs produced was observed in the parental generation. Pathological lesions in the gills and extensive tissue degradation in the kidneys were directly correlated with ammonia concentrations above 0.04 mg·L$^{-1}$, after 4 months of exposure.

Sockeye salmon (*Oncorhynchus nerka*) were exposed to total ammonia for 62 day from fertilization to hatching (Rankin 1979). Concentrations of un-ionized ammonia were calculated and ranged from 0.00097 - 4.92 mg $NH_3$ L$^{-1}$ at 10°C and pH 8.2 and hatchability was the measured endpoint. Hatchability was 63.3%, 49% and 0% in controls, at 0.12 mg·L$^{-1}$, and 0.46 mg·L$^{-1}$, respectively. An $EC_{20}$ was calculated for this study by Environment Canada (1999) with correction for control mortality. The reported $EC_{20}$ was 0.057 mg·L$^{-1}$ un-ionized ammonia. Bader and Grizzle (1992) exposed catfish (*Ictalurus punctatus*) fry to ammonia in a 7-day static renewal test. An $IC_{20}$ for fry growth was determined by Environment Canada (1999) at 0.162 mg·L$^{-1}$ un-ionized ammonia. There was no incremental mortality up to 0.490 mg·L$^{-1}$exposure. Smith et al. (1984) conducted a 30-day early life-stage test on bluegill sunfish (*Lepomis macrochirus*). The test exposed 28-day old embryos and monitored them to the swim-up fry life stage. No significant reduction was found in percent of hatch up to a concentration of 37 mg·L$^{-1}$ un-ionized ammonia, however, larvae were deformed and generally died within 6 days. An $IC_{20}$ (survival and growth) of 0.060 mg·L$^{-1}$ was calculated (Environment Canada 1998) for this study.

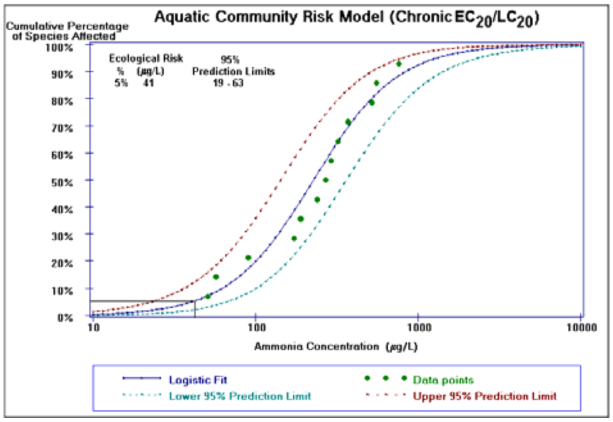
**Figure 1. Select freshwater chronic toxicity data for un-ionized ammonia.**



## Un-ionized Ammonia ($NH_3$)

The most sensitive freshwater study identified was for the rainbow trout (*O. mykiss*). The reported lowest observed effect concentration (LOEC) for un-ionized ammonia in a five year chronic study is 0.04 mg·L$^{-1}$, exposure to this and higher concentrations resulted in pathological lesions in the gills and tissue degradation in the kidneys (Thurston et al. 1984). Consistent with this study, Environment Canada's (1999) aquatic community ecological risk criteria on the impact of ammonia at the community level of both invertebrates and fish indicated that 5% of the species in an aquatic community would exhibit a 20% reduction in growth or reproduction at an un-ionized ammonia concentration of 0.041 mg·L$^{-1}$. Thus, an identical low toxic threshold of 0.4 mg·L$^{-1}$ was derived using two separate approaches namely the CCME Aquatic Life Protocol (CCME 1991) and a regression-based approach described in the ecological risk criteria for un-ionized ammonia (Environment Canada 1999). Following CCME protocol for the derivation of Water Quality Guidelines for the Protection of Aquatic Life (CCME 1991), the application of a safety factor to the designated low-threshold effects value should occur; however, the current protocol allows for deviation from the standard method of guideline development in cases where sufficient scientific weight of evidence permits. Such is the case for un-ionized ammonia. In the determination of the community ecological risk criteria (Figure 2), Environment Canada (1999) predicted 95% confidence intervals surrounding their sensitive ammonia data. The lower 95% prediction limit is 0.019 mg·L$^{-1}$ and the upper 95% prediction limit is 0.063 mg·L$^{-1}$ (Figure 2). Their analysis of the data using a two parameter logistic model produced an adequate model fit (i.e., < 5%) according to the goodness-of-fit statistic (G test). Therefore, based on this weight of evidence that has made use of the complete data envelope for un-ionized ammonia a safety factor is not applied to the most sensitive study (Thurston et al. 1984), but rather, the lower 95% prediction limit (0.019 mg·L$^{-1}$) will be set as the guideline.

**Figure 2. Aquatic Community Risk Model (Environment Canada 1999).**



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## Total Ammonia ($NH_3 + NH_4^+$)

In order to derive a Water Quality Guideline for the Protection of Aquatic Life for total ammonia, a series of calculations are required to convert un-ionized ammonia to total ammonia. Equations for these calculations are provided by Emerson et al. (1975) and EPA (1998). The variability of pH and temperature on a nation-wide basis is substantial. The impact of these factors on the speciation of ammonia is an important consideration when deriving a Water Quality Guideline for the Protection of Aquatic Life. As a result, the total ammonia guideline is not a specific value, but rather a range of values over various pHs and temperatures. Table 2 provides total ammonia guidelines over a range of pH (6.0-10.0) and temperature (0-30 ºC) based upon the un-ionized ammonia guideline of 0.019 mg·L$^{-1}$ and the equations presented in Emerson et al. (1975) and EPA (1998). It is recommended that the most conservative total ammonia guideline closest to the pH and temperature conditions of the waterbody be applied. Values falling outside of the pH and temperature ranges indicated in Table 2 should be used with caution because there was a lack of toxicity data to accurately determine the toxic effects at the low and high extremes of the reported ranges. In addition, results of the toxicity data that were available outside of the reported ranges (pH 6-10; temp. 0-30ºC) were often ambiguous and confounding. No safety factor is applied to these values based on the weight of evidence described above.

## References

Armstrong, D.A., D. Chippendale, A.W. Knight and J.E. Colt. 1978. Interaction of ionized and un-ionized ammonia on short-term survival and growth of prawn larvae, *Macrobrachium rosenbergii*. Biological Bulletin (Woods Hole) 154:15-31.

Bader, J.A., and J.M. Grizzle. 1992. Effects of Ammonia on Growth and Survival of Recently Hatched Channel Catfish. J. Aquat. Animal Health 4:17-23.

Borgmann, U. 1994. Chronic toxicity of ammonia to the amphipod *Hyalella azteca*: Importance of ammonium ion and water hardness. Environ. Pollut. 86:329-335.

Bretthauer, R. 1978. Some ecological limits of tolerance to *Ochromonas sociabilis*. Verh. Internat. Verein. Limnol. 20(3):1850-1854.

CCME (Canadian Council of Ministers of the Environment). 1991. Appendix IX—A protocol for the derivation of water quality guidelines for the protection of aquatic life (April 1991). In: Canadian water quality guidelines, Canadian Council of Resource and Environment Ministers. 1987. Prepared by the Task Force on Water Quality Guidelines. [Updated and reprinted with minor revisions and editorial changes in Canadian environmental quality guidelines, Chapter 4, Canadian Council of Ministers of the Environment, 1999, Winnipeg.]

CCREM (Canadian Council of Resource and Environment Ministers). 1987. Canadian Water Quality Guidelines. Prepared for the Task Force on Water Quality Guidelines.

Chemical and Engineering News. 1980. C and EN's top fifty chemical products. Am. Chem. Soc. 16.

CPI (CPI Product Profiles). 1998. Ammonia. June 1998. Camford Information Services Inc. 38 Groemsport Cr., Scarborough, Ontario, M1T 2K9.

DOE-MOE. 1989. Remedial Action Plan for Hamilton Harbour. Draft Summary Report, March 1989. 162p.

Environment Canada (Environment Canada). 1999. Canadian Environmental Protection Act Priority Substances List II – Supporting document for Ammonia in the Aquatic Environment. DRAFT –August 31, 1999.

Environment Canada (Environment Canada). 1998. Canadian Water Quality Data for Ammonia. Provided by Miles Constable, Toxic Substances Division, Environment Canada, Edmonton, Alberta.

Environment Canada (Environment Canada). 1997. Problem formulation for Ammonia in the aquatic environment. Canadian Environmental Protection Act Priority Substances List 2. Version 5.0, November 4, 1997.

Environment Canada (Environment Canada). 1992. Canadian Environmental Protection Act – Ammonia Spills Assessment

Report. Draft Assessment #3, August 24, 1992. Environmental Emergencies Branch, Environment Canada. Ottawa, Canada.

Emerson, K., R.E. Lund, R.V. Thurston and R.C. Russo. 1975. Aqueous ammonia equilibrium calculations: effect of pH and temperature. J. Fish. Res. Board Can. 32: 2379-2383.

EPA (U.S. Environmental Protection Agency). 1998. 1998 Update of Ambient Water Quality Criteria for Ammonia. Office of Water. EPA 822-R-98-008. Washington, D.C. 148 p.

EPA (U.S. Environmental Protection Agency). 1985. Ambient Water Quality Criteria for Ammonia – 1984. PB85-227114. Washington, D.C.

Frias-Espericueta, M.G., M. Harfush-Melendez, J.I. Osuna-Lopez, F. Paez-Osuna. 1999. Acute toxicity of ammonia to juvenile shrimp *Penaeus vannamei* Boone. Bull. Env. Contam. Tox. 62:646-652

Geadah, M., 1985. National Inventory of Natural and Anthropogenic Sources and Emissions of Ammonia (1980). Environmental Protection Programs Directorate, Environmental Protection Service, Environment Canada Report EPS5/IC/1.

Harding, A.J. 1959. Ammonia manufacture and uses. London, Oxford University Press.

Jofre, M.B. and W.H. Karasov. 1999. Direct effect of ammonia on three species of North American anuran amphibians. Environ. Toxicol. Chem. 18(8):1806-1812.

Marsalek, J. and H.Y.F. Ng. 1989. Evaluation of pollution loadings from urban non-point sources: Methodology and applications, Journal Great Lakes Research, 15(3): 444-451.

McNeely et al. 1979. Water Quality Sourcebook: A guide to water quality parameters. Environment Canada publication, Ottawa, Ontario. Cited in WQB 1989.

Nimmo, D.W.R., D. Link, L.P. Parrish, G.J. Rodriguez, W. Wuerthele, and P.H. Davies. 1989. Comparison of on-site and laboratory toxicity tests: Derivation of site-specific criteria for un-ionized ammonia in a Colorado transitional stream. Environ. Toxicol. Chem... 8:1177-1189.

NPRI (National Pollutant Release Inventory). 1996. Summary Report, 1996. Environment Canada, Minister of Supply and Services Canada, Catalogue #EN40-495/1-1996E, ISBN #0-662-2672F9-X.

NWRI (National Water Research Institute). 1990. Ammonia and nitrite contamination of Hamilton Harbour, Lake Ontario. NWRI Contribution No. 90-29.

Pommen, L.W. 1983. The effect on water quality of explosives use in surface mining. Vol. 1 Nitrogen Sources, Water Quality, and Prediction and Management of Impacts. British Columbia Ministry of the Environment, Victoria, British Columbia, Tech. Rep. 4. cited in CCREM 1987

Rankin, D.P. 1979. The influence of un-ionized ammonia on the long-term survival of sockeye salmon eggs. Technical Report 9-12. Department of Fisheries and Oceans, Nanaimo, British Columbia, Canada.

Raven, P.H. & G.B. Johnson. 1989. Biology. Times Mirror/Mosby College Publishing. New York ISBN 0-8016-4041-5

Smith, W.E., T.H. Roush, and J.T. Fiandt. 1984. Toxicity of Ammonia to Early Life Stages of Bluegill (Lepomis macrochirus).EPA-600/x-84-175. In-house report, U.S. EPA, Duluth, MN.

Soderberg, R.W. and J.W. Meade. 1991. The effects of ionic strength on un-ionized ammonia concentration. Prog. Fish-Cult. 53:118-120

Thurston, R.V., C. Chakoumakos, and R.C. Russo. 1981. Effect of fluctuating exposures on the acute toxicity of ammonia to rainbow trout (*Salmo gairdneri*) and cutthroat trout (*S. clarki*). Water Res. 15:911-917.

Thurston, R.V., R.C. Russo, R.J. Luedtke, C.E. Smith, E.L. Meyn, C. Chakoumakos, K.C. Wang, and C.J.D. Brown. 1984. Chronic toxicity of ammonia to rainbow trout. Trans. Am. Fish. Society 113:56-73.

WHO (World Health Organization). 1986. Environmental Health Criteria 54. Ammonia. IPCS International Programme on Chemical Safety. Geneva, Switzerland. ISBN 92-4-154194-6.

WQB (Water Quality Branch). 1989. Ammonia and residual chlorine monitoring study – South Saskatchewan River at Saskatoon. July and August 1987. Saskatchewan Environment and Public Safety. WQB 116. Saskatoon, Saskatchewan.

Reference listing:

Canadian Council of Ministers of the Environment. 2010. Canadian water quality guidelines for the protection of aquatic life: Ammonia. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

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