# 2006 Mercury Snowpack Report

**Idaho Department of Environmental Quality**

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# Acknowledgements

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# Introduction

This document reports findings from the 2006 field investigation of mercury contamination in snow in the Salmon Falls Creek watershed in southern Idaho. The study comprises one part of a multi-media sampling strategy designed to identify the source(s) of mercury contamination in Salmon Falls Creek Reservoir (SFCR).

Snow may be an important vector for atmospheric deposition of mercury to the Salmon Falls Creek watershed. This study attempts to characterize the concentrations of mercury in snow at a sample site near the Salmon Falls Creek watershed and at a background site in the Boise Mountains. These sites receive 92% - 95% of their annual precipitation in the form of snow, so the majority of the annual wet deposition of mercury at the study sites is collected in the snowpack, in addition to the dry deposition captured by the snow.

The objectives of the study were (1) to determine if mercury deposited in snow is a conduit for elevated mercury concentrations found in fish in the SFCR and (2) to determine the atmospheric source(s) of this elevated mercury in snow.

# Background: Behavior of Mercury in Snow

Atmospheric deposition to snow is thought to be an important pathway in the transport of mercury emissions from source to its uptake in fish. Atmospheric mercury, in the form of reactive gaseous mercury (RGM), deposits to snow within precipitation (*wet deposition)* or bound to particulates (*dry deposition*.) Such mercury not re-emitted to the atmosphere eventually leaves the snowpack in meltwater.

Mercury in the snowpack can also be *methylated* to methylmercury (MeHg), which is the bioavailable form of mercury that accumulates in the food web and poses health risks to humans who consume contaminated fish.

## Snowpack as Petri dish, not mercury reservoir

The behavior of mercury within snowpacks is important to ascertain if one wishes to use the concentrations measured there as an indicator for atmospheric deposition. Some suggest that snowpacks

are time-integrating reservoirs that collect a season's total mercury deposition and then release it to the watershed at snowmelt (Abbott, 2002). Others characterize snowpacks not as inert reservoirs but as vessels in which photochemical reactions take place to change the composition and concentrations of the originally deposited mercury (LaLonde, 2003).

Snowpacks were originally thought to be time-integrating sampling mediums that collect both wet and dry mercury deposition (Abbott, 2002, Susong, 2003). It was acknowledged that some loss of mercury to the atmosphere could occur, and some mercury could be added to the snowpack from soil re-emission, but concentrations measured in the snowpack were generally thought to reflect the concentrations entering waters through snowmelt. This hypothesis of the snowpack as a mercury reservoir supported research using the relative concentrations of mercury found in glacier ice cores to quantify historical mercury deposition (Schuster, 2002, Boutron, 1998) and sustained work done to determine the effects of industrial emissions sources on local and regional mercury deposition (Abbott, 2002, Susong, 2003).

More recent studies, however, suggest that mercury in snow is more volatile than previously thought (Dommergue, 2003b, Fain, 2006, LaLonde, 2002, LaLonde, 2003, Poulain, 2004, St. Louis, 2005), finding that the chemical reactions occurring within snowpacks *after* deposition change the concentration (and species) of mercury, so that the quantities measured are not directly representative of the amount deposited or released in meltwater. It is well known that snowpacks undergo physical and chemical transformations throughout the season as a result of temperature gradients and the physical loading of new snow on previously deposited snow (Colbeck, 1990, Hallett, 1984).

This snow chemistry metamorphosis during the winter may mask the original chemistry present when the mercury was deposited (St. Louis, 2005) and likely contributes to the chemical transformation of mercury over time. Factors affecting mercury retention in snowpacks include meteorological parameters (wind speed, short wavelength ultraviolet [UV-B] radiation, temperature, snow accumulation), residence time, and snow chemistry (presence of solutes).

Once deposited, the behavior of mercury within the snowpack is dynamic. Snowpacks are active laboratories for the transformation, reduction, oxidation, and dispersion of mercury and other chemical

elements. Snow metamorphosis, reduction-oxidation transformations, diffusion, and re-emission all occur over time.

## Chemical transformations of mercury in snow

Mercury typically deposits to snow in the form of Reactive Gaseous Mercury (RGM or Hg(II), divalent mercury) because RGM is more reactive and water-soluble than the predominant atmospheric form, gaseous elemental mercury (GEM or Hg(0), elemental mercury) (Dommergue, 2003b). Once in the snow, RGM is photo-reduced by UV-B radiation, producing GEM, some of which is then diffused, or re-emitted, back to the atmosphere (Ariya, 2004, Poulain, 2004, Amyot, 2003, LaLonde, 2002, St. Louis, 2005, Dommergue, 2003a, Fain, 2006).

Reduction of RGM to GEM occurs in the top few centimeters of the surface layers. Re-emission of GEM takes place within 24 - 48 hours of original deposition and has been observed in suburban and remote temperate locations and at both coastal and inland Arctic sites (Amyot, 2003, Ariya, 2004, Dommergue, 2003b, Kirk, 2004, LaLonde, 2003, Poulain, 2004, St. Louis, 1995, St. Louis, 2005).

The GEM that is not quickly exported from the snow undergoes photo-induced re-oxidation back to RGM (Poulain, 2004). If halides, such as sea salt or chloride, are present in the snowpack, more of the GEM may be photo-oxidized back to RGM form. This reduced mercury is more likely to remain in the snowpack to be released to meltwater as a pulse at snowmelt. Thus, coastal arctic snowpacks tend to retain higher concentrations of mercury than inland or temperate snowpacks without halides.

Dommergue (2003a) reports that reduction/oxidation (redox) reactions are accelerated at snowmelt, and a pulse of GEM is released to the atmosphere as well as to the meltwater. Volatile RGM can also travel *through* the snowpack, being redistributed by the influence of temperature gradients, and undergoing oxidation and reduction when it reaches the photo-penetrated surface layers (Poulain, 2004). Wind speeds at the air/snow interface can also influence the incoming and outgoing fluxes of mercury (Poulain, 2004).

## Bioavailable mercury in snow

Measured concentrations of total mercury (THg) in snowpacks do not necessarily represent bioavailable mercury. One objective of this study was to determine the environmental pathways that provide mercury in forms that can be taken up and bioaccumulated in fish in the SFCR. Therefore, the deposition or the production of bioavailable mercury species in snowpacks is important to consider.

The ratio of methylmercury (MeHg) to THg differs as reported in the literature. Hall (2005) reports MeHg is 1-6% of THg in the Upper Midwest. Values of 2-30% are reported from the high Arctic (St. Louis, 2005). The highest values of MeHg to THg are usually found at the top of the snowpack, because penetration of UV-B is restricted to the upper layers (~5 cm in dense Arctic snowpack, > 5 cm in less dense, drier Idaho snowpack) (LaLonde, 2002, Poulain, 2004).

Other papers suggest that methylation takes place within the snowpack. Scott (2001) reports that snowpacks have a higher percentage of bioavailable mercury (bioHg) than other watershed inputs: ~44% bioHg of THg in snow, 5% in rain, 2% in throughfall (precipitation that falls through the tree canopy and interacts with the vegetation), and 3% in runoff.

St. Louis (2005) connects the amount of mercury re-emitted to the atmosphere to the amount of mercury available for methylation: the longer the residence time in the snowpack, the more mercury available for methylation. St. Louis (2005) measured low concentrations of THg but with high percentages of MeHg at snowmelt. This finding is intriguing because it suggests that elevated total concentrations of mercury in snowpacks may not correspond to elevated concentrations of bioavailable mercury. St. Louis also found that methylation is actually occurring within the snowpack. It may, in fact, be the ratio of MeHg to THg that is important when trying to discover the sources of elevated mercury in fish at the end of the bioaccumulation chain.

## Effect of halides and other solutes on redox transformations

The presence of halides or other solutes in the snowpack has been shown to alter the redox transformations of mercury in snow. Mercury bound with solutes is less likely to photo-oxidize into GEM and be re-emitted to the atmosphere. Therefore, snowpacks with higher concentrations of halides (e.g. sea salts in the Arctic) retain more of the deposited mercury throughout the season than snowpacks with

lower concentrations of solutes (such as temperate, inland sites in Idaho). These mechanisms have been observed and measured in the environment as well as experimentally (LaLonde, 2003). This process partly explains the higher concentrations of mercury in the spring meltwater pulses in the Arctic.

## Retention of mercury in snow

One of the major conclusions to be drawn from this discussion is that Arctic snowpacks are likely to *accumulate* and *retain* more mercury than snowpacks in temperate, inland regions, such as Idaho. Snowpacks in southern Idaho, however, might be expected to retain similar amounts of mercury to one another, and, if mercury concentrations at one site were found to be significantly higher than mercury concentrations at another site, it could be hypothesized that a variation in mercury input (i.e. atmospheric deposition) could be deduced. This idea forms the basis of the current study: by comparing the mercury *retained* in two regional southern Idaho snowpacks, any significant difference might be attributed to variation in local atmospheric sources.

Yet the best sampling strategy to detect the mercury retained in snowpacks remains open to debate:

LaLonde (2003) suggests that composite samples of the entire snowpack or samples from the lower strata are more appropriate than surface samples for studies using the snowpack as a medium through which THg travels from atmosphere to watershed. Vertical profiles of mercury concentration in snowpacks are reported to have an inverse relationship with depth (Amyot, 2003, LaLonde, 2003, St. Louis, 2005), with the highest concentrations found at the snow/air interface and lowest at the snow/ground interface (or snow/ice interface if measured on sea ice.)

This inverse relationship of concentration and depth is not true, however, for vertical profiles of MeHg concentrations. St. Louis (2005) found that MeHg concentrations remained fairly constant throughout the snowpack profile, causing the ratio of MeHg to THg to increase with depth. They conclude that RGM is more likely to be photoreduced and evacuated from the snowpack, while MeHg remains methylated within the snowpack. So the lower strata, which LaLonde (2003) suggests are more appropriately representative of THg retained in the snowpack and released to snowmelt, may actually

contain the same concentrations of bioavailable mercury as the higher strata, except the signal is confused if one looks exclusively at THg.

## Limitations of current sampling strategy

It is important to note that the concentrations measured in the current study represent the accumulated, retained portion of mercury in the snowpack and do not necessarily represent the concentrations at the time of deposition nor the concentrations that will eventually enter the meltwater in the spring. Depending on the time of day when the sample was taken, the date of sampling, the location within the snowpack sampled, and the lag from the time of snow deposition until sampling, the concentrations of mercury may differ and might not represent either total mercury deposition or the concentrations that will eventually be released in snowmelt.

With these factors to consider, it is difficult to reach conclusions about relative mercury concentrations in snowpacks, even when care is taken to consider the gains and losses likely over time. However, by comparing the measured concentrations at different sites and looking at both composite and stratified values, the amount of mercury contained in the snowpack at one site relative to another might be constructed. By taking into account the snowpack structure, meteorological conditions, time and date of sampling, and storm trajectories, significant differences in concentrations might be apportioned and attributed to possible sources.

# Methods

The following sections describe the methods used to gather mercury samples in snow, the laboratory procedures used to determine the chemical concentrations in the samples, and the data quality assessment.

## Field Procedures

In March 2006, mercury samples were collected from snowpacks at a site within the SFCR watershed (Pomerelle) and at a background site in the Boise Mountains (Pilot Peak). Locations of the sampling sites are shown in Figure 1.

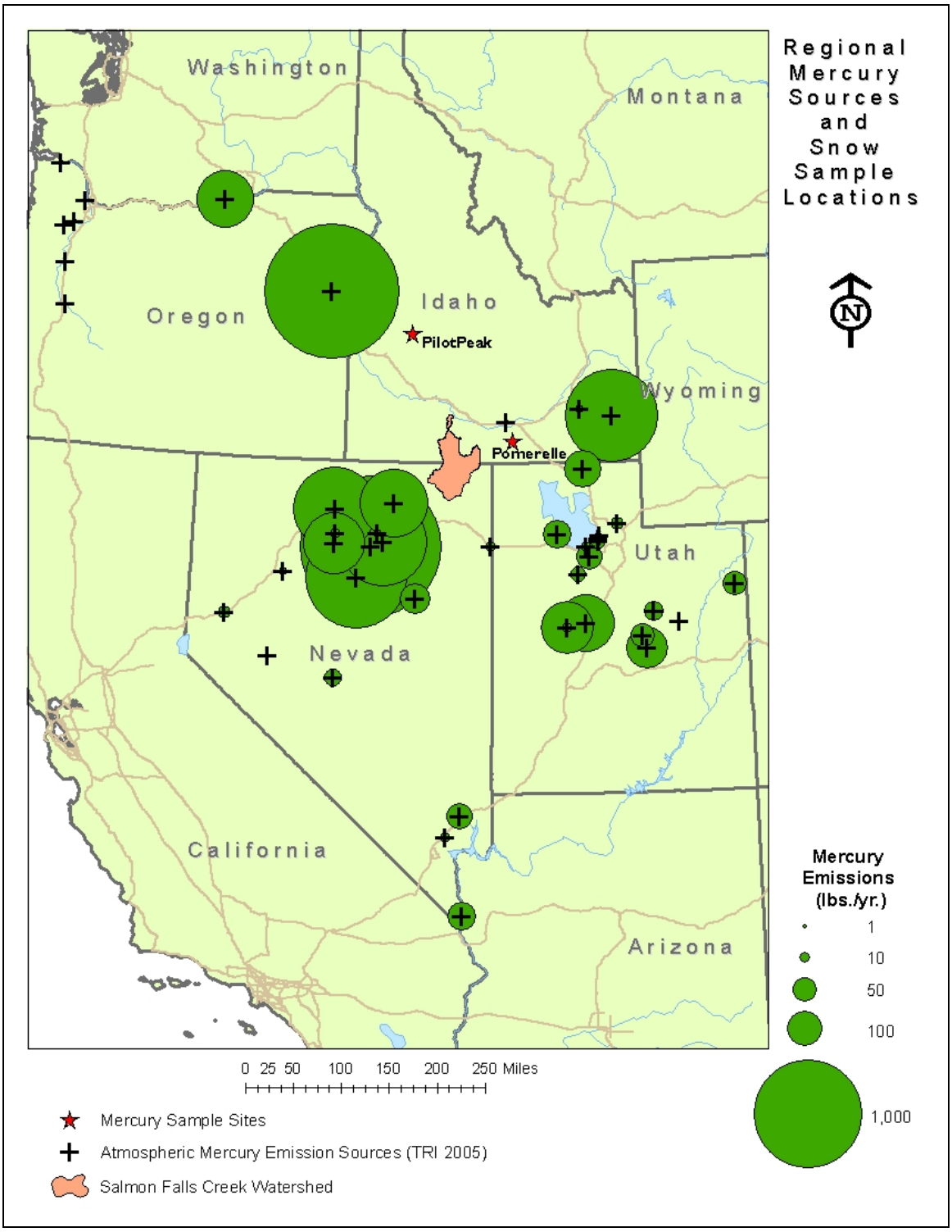



**Figure 1. Location of snow sample sites, Salmon Falls Creek watershed, and regional atmospheric mercury sources.**

The Pomerelle site was sampled on March 11 and Pilot Peak on March 15. Sites were selected and snow pits excavated, taking care to avoid contamination from human activity and vegetation. Snow was excavated to the ground, and the stratigraphy and physical character of the snowpacks were observed according to customary techniques (Colbeck, 1990).

The physical properties of the snowpack at each sample site were examined to determine the following:

1. The height of the snow above the ground surface was measured with a metric tape.
2. Individual layers in the snowpack were identified by running a gloved finger down the face of the pit wall and noting changes in density, hardness, or texture; visual signs of stratification were also taken into account.
3. The break between each layer was measured and recorded as height above ground level.
4. Temperatures at ten-centimeter (10-cm) intervals throughout the profile were recorded with a calibrated thermistor.
5. Additional temperature measurements were taken within specific layers, as necessary.
6. Each layer in the profile was examined for hardness, moisture content, density, and grain type and size, as follows:
    - Layer hardness was examined using the *hand resistance test* (Colbeck, 1990). This is a qualitative test designed to produce a relative value of hardness. Starting with a fist, objects of progressively smaller area are thrust into the snow with a penetration force of about 50 Newtons (N). The value assigned specifies the first object that does not penetrate the layer: fist, four fingers, one finger, pencil, or knife (i.e., “F”, “4F”, “1F”, “P”, or “K”, respectively).
    - *Moisture content* was determined using the *squeeze test* (Cline, 2001, Colbeck, 1990). A fistful of snow from each layer is extracted and squeezed briefly with one gloved hand. The resulting adherence of the snow and the presence or absence of liquid water is then assessed and classified. A layer is determined to be *dry* when little or no adherence is observed. Snow is considered *moist* when the snow sticks together, but liquid water is not visible with a hand lens. Snow is *wet* when the squeeze test creates a perfect

snowball and liquid water is visible between grains with a hand lens. Snow is *very wet* when water can be squeezed out with moderate pressure.

- The *density* of the snow was assessed by inserting a plastic cylinder of known weight and volume into each layer, filling it with snow, and recording the weight on a simple spring scale. Density was then calculated by subtracting the weight of the empty cylinder from the total weight and dividing by cylinder volume.
- *Snow grain size* and *shape* were classified with a hand lens and laminated black card printed with a millimeter grid. Crystals were collected from each layer by scraping the wall with the card. After examination with the hand lens, grains were assigned a basic shape of *rounded*, *faceted*, or *mixed* (Cline, 2001). Size was assigned by measuring a number of grains and determining an average diameter against the measurement grid.

Results of the snow profiles describing strata, crystal type and size, moisture content, hardness, and density are shown in Figure 2. Temperature profiles are reported in Figure 3.

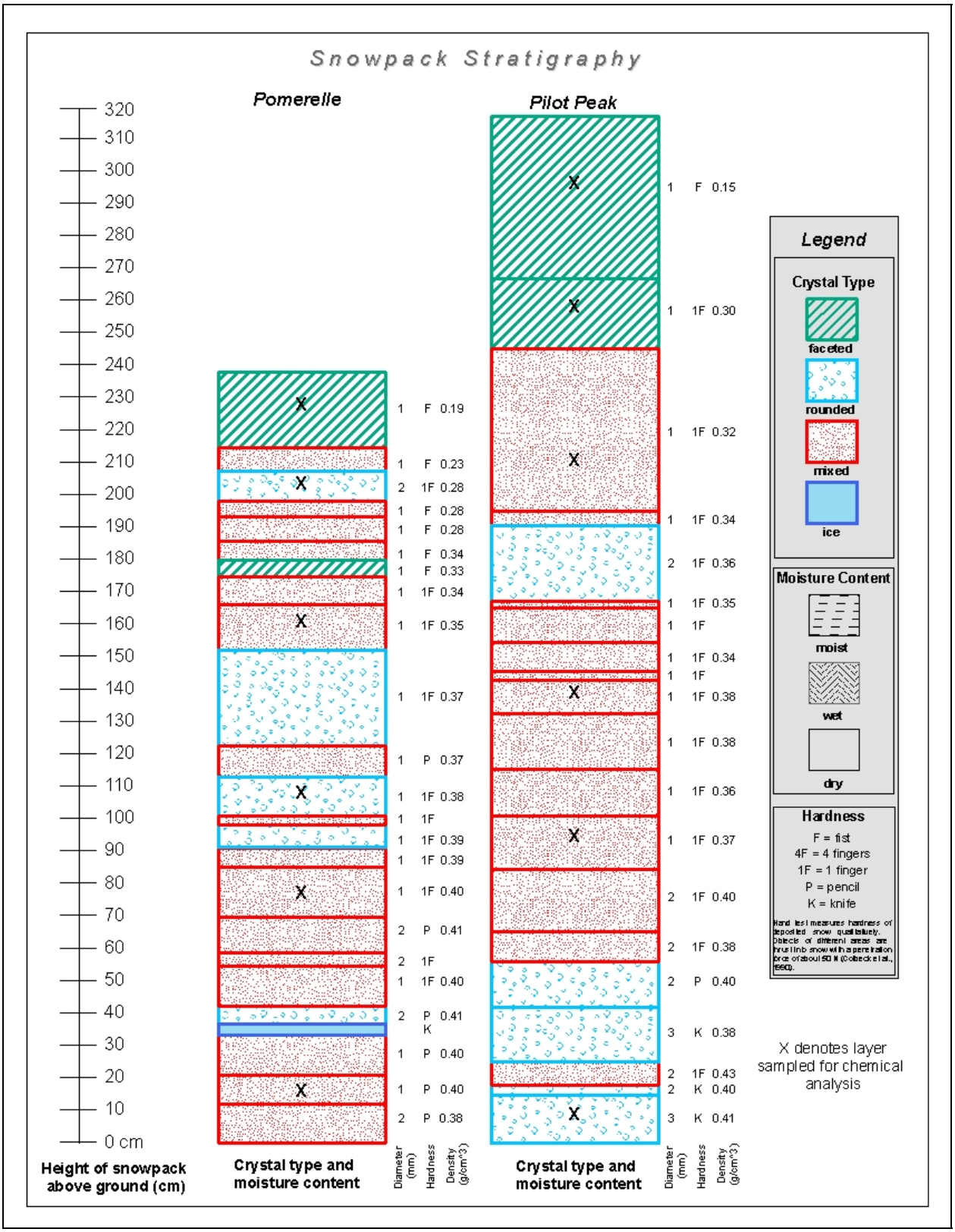



**Figure 2. Stratigraphy and physical characteristics of Pomerelle and Pilot Peak snowpacks.**

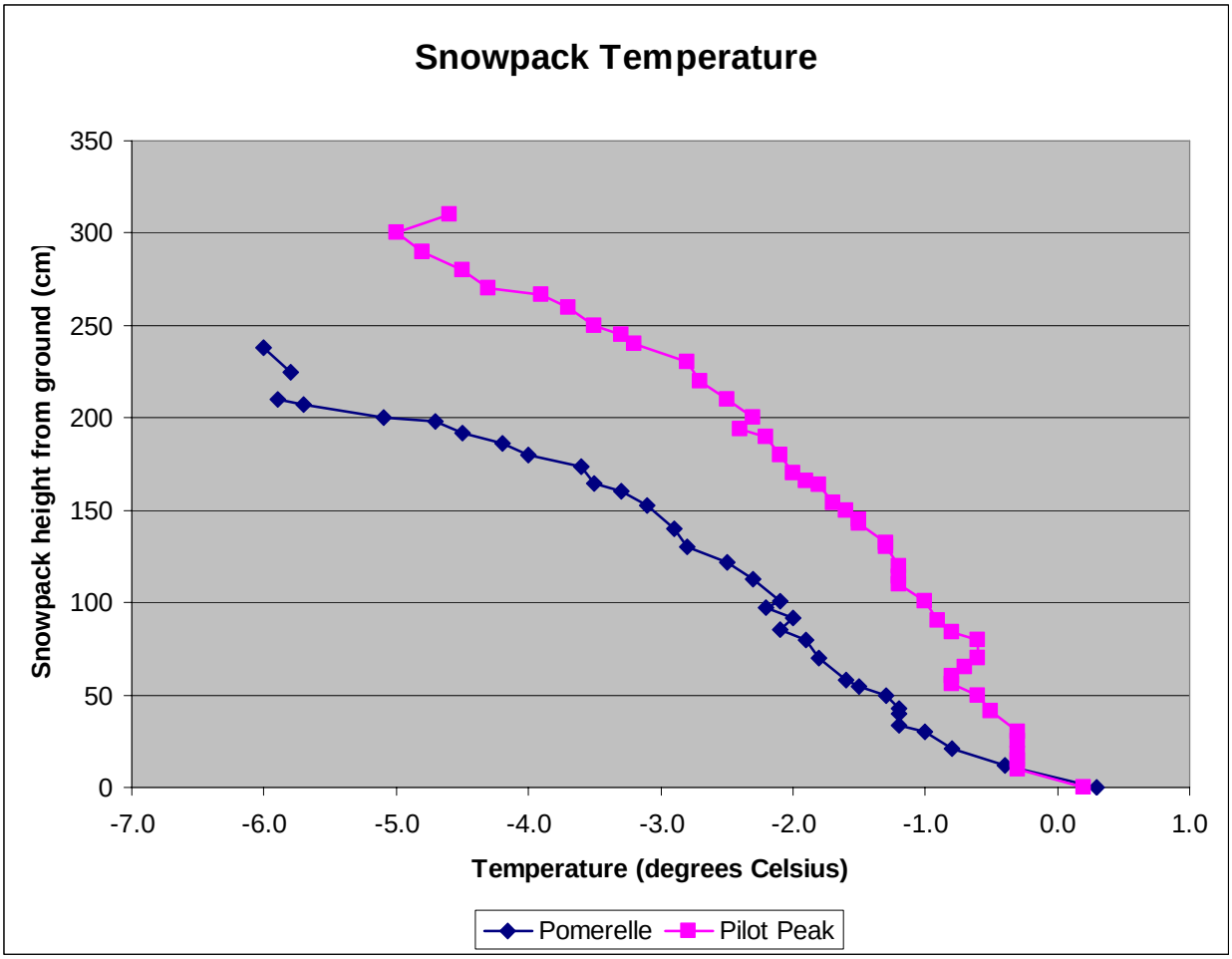



**Figure 3. Measured temperature gradient in Pomerelle and Pilot Peak snowpacks.**

After the snow was characterized, chemical samples were taken according to the "clean hands/dirty hands" technique (Snyder-Conn, 1997). Samples for mercury analysis were collected from six strata at each site, with one duplicate taken for each sample. Samples for nitrate ($NO_3$), sulfate ($SO_4$), and chloride (Cl) were collected from the same six strata with no duplicates taken. Two composite samples for all species, with duplicates, were taken of the entire snowpack at Pomerelle, and one composite sample for all species, with duplicate, was taken at Pilot Peak.

Samples collected for chemical analysis are listed in Table 1, and the strata (snow height) from which they were taken are noted in Figure 2.

**Table 1. Samples collected for chemical analysis from Pomerelle and Pilot Peak snow pits.**

| ***Pomerelle*** | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Snow height from ground (cm) | Sample Name | Hg (ng/L) * | CL (mg/L) ** | $NO_3$ (mg/L) | $SO_4$ (mg/L) | Duplicate Sample Name | Hg (ng/L) | CL (mg/L) | $NO_3$ (mg/L) | $SO_4$ (mg/L) |
| 15 | PM1 | 4.190 | 0.304 | 0.028 | 0.200 | PMA | 3.430 | | | |
| 76 | PM2 | 2.910 | 0.200 | 0.016 | 0.200 | PMB | 1.590 | | | |
| 107 | PM3 | 4.870 | 0.200 | 0.044 | 0.200 | PMC | 5.040 | | | |
| 152 | PM4 | 2.400 | 0.200 | 0.022 | 0.200 | PMD | 2.720 | | | |
| 198 | PM5 | 1.600 | 0.200 | 0.056 | 0.200 | PME | 3.840 | | | |
| 224 | PM6 | 4.700 | 0.200 | 0.039 | 0.200 | PMF | 3.250 | | | |
| composite | PM7 | 6.650 | 0.767 | 0.051 | 0.432 | PMG | 6.310 | 2.610 | 0.060 | 0.414 |
| | PM8 | 6.130 | | | | PMH | 5.800 | | | |
| Note: all 0.200 values are <0.200 | | | | | | | | | | |
| | | | | | | | | | | |
| | | | | | | | | | | |
| ***Pilot Peak*** | | | | | | | | | | |
| Snow height from ground (cm) | Sample Name | Hg (ng/L) | CL (mg/L) | $NO_3$ (mg/L) | $SO_4$ (mg/L) | Duplicate Sample Name | Hg (ng/L) | CL (mg/L) | $NO_3$ (mg/L) | $SO_4$ (mg/L) |
| 10 | PP1 | 3.090 | 0.200 | 0.040 | 0.200 | PPA | 3.280 | | | |
| 94 | PP2 | 1.020 | 0.200 | 0.020 | 0.200 | PPB | 0.870 | | | |
| 140 | PP3 | 0.920 | 0.200 | 0.020 | 0.200 | PPC | 1.370 | | | |
| 206 | PP4 | 1.030 | 0.200 | 0.040 | 0.200 | PPD | 0.830 | | | |
| 254 | PP5 | 1.200 | 0.200 | 0.030 | 0.200 | PPE | 1.920 | | | |
| 284 | PP6 | 5.170 | 0.200 | 0.040 | 0.200 | PPF | 4.190 | | | |
| composite | PP7 | 3.010 | 0.200 | 0.040 | 0.200 | PPG | 2.180 | 0.200 | 0.050 | 0.200 |
| Note: all 0.200 values are <0.200 (0.200 mg/L is the method detection limit.) | | | | | | | | | | |

* ng/L = nanograms per liter

** mg/L = milligrams per liter

A detailed description of collection techniques summarized here can be found in the 2006 field report (IDEQ, 2006) and in the final report for the 2005 snow sampling event (IDEQ, 2005b).

## Laboratory Procedures

For Pomerelle, sixteen snow samples, one field blank, and one trip blank were prepared and analyzed in accordance with USEPA Method 1631E (USEPA, 1996). For Pilot Peak, fourteen snow samples, one field blank, and one trip blank were prepared and analyzed.

Mercury concentrations in the snow samples were determined by Brooks Rand, LLC. The snow was thawed, and the resulting water samples were oxidized with bromine monochloride (BrCl.) Each sample was then analyzed using stannous chloride ($SnCl_2$) reduction, single-trap gold amalgamation, and cold vapor atomic fluorescence spectrometry. Appendix A, page 39, contains the Quality Assurance Summary provided by the laboratory.

Trip blank results for both sites were below the *method detection limit*[1] (MDL). Mercury concentrations in the field blanks were above the MDL (0.19 nanograms per liter [ng/L] for Pomerelle and 0.17 ng/L for Pilot Peak) but below the *practical quantitation limit*[2] (PQL). These detectable concentrations are below the *method-defined control limit*[3] of 0.5 ng/L and less than one-fifth of the sample results. The field blank concentrations are therefore insignificant compared to the sample concentrations.

Concentrations of $NO_3$, $SO_4$, and Cl in the snow samples were determined by the Idaho Department of Health and Welfare Laboratory using USEPA Methods 300.0 and 353.2 (USEPA, 1993). Appendix B, page 43 contains the Quality Control Package provided by the laboratory for nitrate analysis; Appendix C, page 47 contains the Quality Control Report Sheet for the chloride and sulfate analysis.

[1] The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero (Bauer, R., Baylor, K., Jackson, E., Ngo, E., AND Saracino, R. *RCRA Corrective Action Program: Data Review Guidance Manual*. IN IX, R. (Ed.), USEPA.

[2] The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The PQL is 5 to 10 times the MDL (Ibid.)

[3] Range of acceptable results for each type of quality control measurement. They may be set up on a project-specific basis, or they may be derived internally at a laboratory from historic QC performance data (Ibid.)

## Data Quality Assessment

The Data Quality Objectives (DQO) for this study are outlined in the Quality Assurance Project Plan (QAPP) (IDEQ, 2005a). Table 2 contains the requirements for Data Precision, Accuracy, and Measurement Range.

**Note:** The minimum detection limit (MDL) for total mercury (0.01 ng/L) reported in the QAPP is incorrect and should be given as 0.10 ng/L. The MDL reported by Brooks Rand is 0.10 ng/L (See Appendix A.)

### *Mercury*

The accuracy (or recovery) for the Pilot Peak mercury samples is 93-105%. One of the calibration verification analyses for the Pomerelle samples yielded a 68% recovery, which the lab ascribed to a pipetting error. The standard was reanalyzed twice, yielding recoveries of 97% and 102%. The other standards produced recoveries of 85% and 83%, which conform to the criteria range.

**Table 2. Data quality assessment requirements for precision, accuracy, and measurement range.**

| Parameter | Criteria | | |
|---|---|---|---|
| | Minimum Detection Limits | Accuracy (Acceptable Range of Recovery %) | Precision (Acceptable Range %) |
| Total Mercury | 0.01 ng/L | 80-110 | 10-30 |
| Sulfates | 0.1 µeq/L | 80-110 | 10-30 |
| Nitrates | 0.1 µeq/L | 80-110 | 10-30 |
| Arsenic | 0.25 µg/L | 80-110 | 10-30 |
| Chloride | no requirement | no requirement | no requirement |

### *Nitrate, Sulfate, and Chloride*

The Quality Control Package provided by the laboratory for the nitrate analysis (Appendix B: page 43) seems to indicate that the accuracy criteria were met, with recovery values of 100.4% and 99.6% for Pomerelle and Pilot Peak, respectively. The precision criteria were met as well, with values of 117.4% for Pomerelle and 105% for Pilot Peak. No MDL was reported by the laboratory.

The $SO_4$ samples met the accuracy DQO with recovery values of 100.4% for Pomerelle and 81.5% for Pilot Peak (Appendix C, page 47). Values of 100% and 94.5%, for Pomerelle and Pilot Peak, respectively, satisfied the precision criteria. No MDL was reported by the laboratory.

The Cl samples met the accuracy DQO with recovery values of 102% for Pomerelle and 85% for Pilot Peak (Appendix C, page 47). Values of 96% and 102%, for Pomerelle and Pilot Peak, respectively, satisfied the precision criteria. No MDL was reported by the laboratory.

### *Data Representativeness*

All sampling procedures were performed in accordance with the requirements outlined in the Snowpack Sampling and Analysis Plan (IDEQ, 2005a), which satisfies the DQO for Data Representativeness.

To fulfill the Data Comparability objective, the QAPP states that "snowpack sample data will be compared to the multi-year USGS snowpack database" (IDEQ, 2005a). This comparison and others are made in the Results and Discussion section of this report.

Although the requirements for the Data Completeness quality objective are recorded as TBD, or *to be determined*, in the QAPP, seven samples each of total mercury, sulfates, and nitrates were planned for the 2005 collection event. The 2006 event collected more than double this number, as well as samples for chloride concentration analysis.

All the required DQOs have been satisfied as described, and the data are judged to be unbiased, representative, precise, and accurate, and, therefore, fit for analysis.

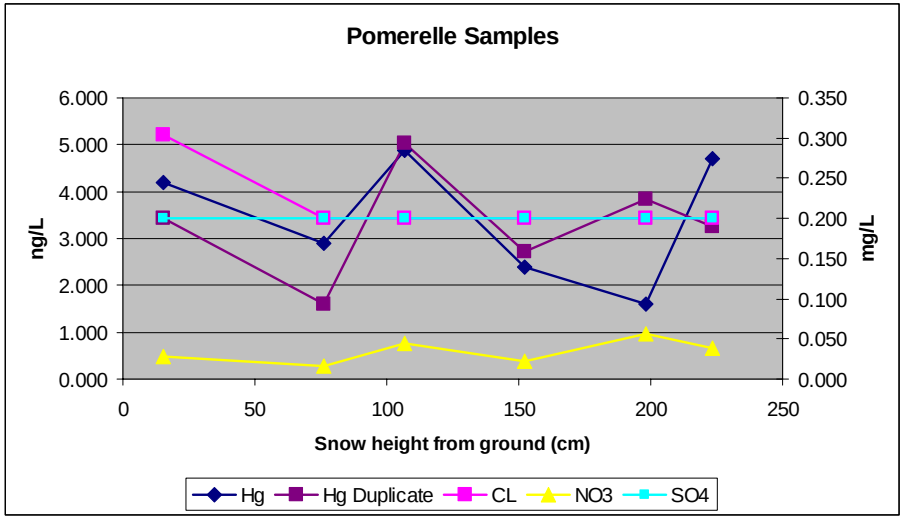
# Results and Discussion

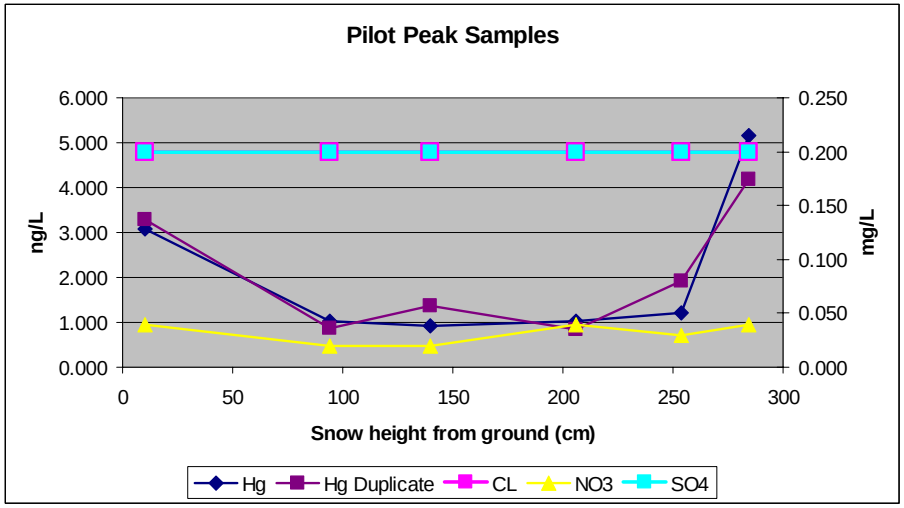
The following section describes the results of the snowpack sampling, including chemical analyses, statistical analyses, and snowpack stratigraphy. The results are then compared to concentrations found in the literature.

A trajectory analysis was undertaken to reveal any spatial trends in storm paths. The findings of this analysis are presented as well.

## Analytical Results

Concentrations of total mercury, sulfate, nitrate, and chloride in snow at each of the sample sites are listed in Table 1 and shown in Figure 4. Correlation coefficient matrices for each sample set, as compared to their duplicates, are also shown in Figure 4. Values shown in red indicate positive correlations and are discussed in the following.




Pomerelle Correlation Coefficient with composite

| | Hg (ng/L) | CL (mg/L) | $NO_3$ (mg/L) | $SO_4$ (mg/L) | Hg dup (ng/L) |
|---|---|---|---|---|---|
| Hg (ng/L) | 1 | | | | |
| CL (mg/L) | 0.727927 | 1 | | | |
| $NO_3$ (mg/L) | 0.282878 | 0.38244 | 1 | | |
| $SO_4$ (mg/L) | 0.704345 | 0.983039 | 0.4232653 | 1 | |
| Hg dup (ng/L) | 0.766436 | 0.727806 | 0.7844565 | 0.73396908 | 1 |

Pilot Peak Correlation Coefficient with composite

| | Hg (ng/L) | CL (mg/L) | $NO_3$ (mg/L) | $SO_4$ (mg/L) | Hg dup (ng/L) |
|---|---|---|---|---|---|
| Hg (ng/L) | 1 | | | | |
| CL (mg/L) | 8.48E-17 | 1 | | | |
| $NO_3$ (mg/L) | 0.644993 | 2.25E-16 | 1 | | |
| $SO_4$ (mg/L) | 8.48E-17 | 1 | 2.251E-16 | 1 | |
| Hg dup (ng/L) | 0.934381 | -1.1E-16 | 0.5662258 | -1.092E-16 | 1 |

**Figure 4. Concentrations of total mercury, sulfate, nitrate, and chloride contained in snow samples at Pomerelle and Pilot Peak. Corresponding correlation coefficient matrices for each sample set are included. Values highlighted in red indicate positive correlations and are discussed in the following.**

The Pilot Peak mercury data are highly correlated with their duplicates at 0.934, while the Pomerelle mercury data are less so (0.766), mainly due to the divergence of concentrations in the two highest strata. $NO_3$ shows a weak positive correlation (0.566 and 0.645) with THg at the Pilot Peak site. One set of Pomerelle Hg samples are strongly correlated with $NO_3$ (0.784), but not so with the Hg duplicate (0.283). When compared with the mean values of Hg and the duplicate, the correlation with $NO_3$ is 0.668. The other species should not be considered for correlation with THg, because all samples were below minimum detection levels, except one.

The solutes ($SO_4$, Cl, and $NO_3$) measured are thought to have potential for use as tracer species:

- $SO_4$ has been used as a proxy for industrial sources of solutes in snowpacks (St. Louis, 2005) because sulfate is a by-product of coal-powered utility and industrial boilers as well as ore roasters processing ores high in sulfides. The presence of $SO_4$ in snowpacks also increases the production of MeHg: sulfate-reducing bacteria contribute to mercury methylation (Snyder-Conn, 1997).
- Cl is a halide, and halides have been shown to enhance the oxidation of GEM in snowpacks (Ariya, 2004, Douglas, 2005, Poulain, 2004, Snyder-Conn, 1997, St. Louis, 2005). Cl and pH may affect the volatility and methylation of RGM and MeHg in snowpacks (St. Louis, 2005).
- $NO_3$, which is also a byproduct of combustion processes, created through atmospheric oxidation of nitrogen dioxide ($NO_2$) and nitric oxide (NO), is also thought to have potential as a proxy for THg.

However, the low levels of solute concentration reported here and the lack of strong correlation with THg suggest high $SO_4$ sources may not be related to mercury deposition. The lack of chloride, especially, signifies that oxidation of GEM may not be enhanced within the snowpack and the gaseous mercury may be lost to the atmosphere more readily (Ariya, 2004). The slight correlation with $NO_3$ hints at a relationship between the atmospheric mercury deposition at these sites and an emitter that employs combustion processes.

## Snowpack Stratigraphy

The physical characteristics of the Pomerelle and Pilot Peak snowpacks, as shown in Figure 2 and Figure 3, are summarized and discussed here. The snow profiles reveal strong temperature gradients, signifying that diffusion and chemical transformation of mercury likely has occurred in the snowpacks. The unmatched stratigraphy suggests that each site receives snow deposits from some different storms and, thus, mercury from different sources.

Both sites have similar temperature regimes: slightly above freezing at the snow/ground interface and steadily decreasing to the snow surface. The Pilot Peak surface layer exhibits a slightly warmer temperature than the layer below. These cold temperatures and the strong gradient from ground to surface show that melting has not occurred within the snowpacks and, therefore, mercury most likely has not been washed out of the snowpacks. The temperature gradients do imply, however, that crystal metamorphosis has taken place, and moisture transfer has occurred, even though both snowpacks are very dry. These processes would affect the chemical transformation and diffusion of mercury between layers.

Pilot Peak had the deepest snow, and both snowpacks had recently received fresh deposits. However, the pattern of layers in each profile do not clearly match, revealing that the two sites do not receive snow deposits from all the same storms and implying that the mercury deposited at these sites may originate from disparate sources.

Pomerelle was the only site to contain an ice layer in its profile, buried deep within the pack. This ice layer may have been the result of a rain-on-snow event or a period of warmth during which the surface melted and refroze before being buried. This ice layer, with its lack of interstitial air, would form a barrier to the transfer of moisture or gaseous mercury.

## Vertical Profiles of Mercury Concentration in Snowpacks

Figure 5 compares the mercury concentrations from the two sample sites. Concentrations in the Pomerelle sample set, as a whole, are statistically significantly higher than those in the Pilot Peak sample set (Student's t-test). Each sample set also has one value from individual strata that is statistically

significantly higher than the rest of the sample set: at Pomerelle, the middle stratum, and at Pilot Peak, the top stratum.

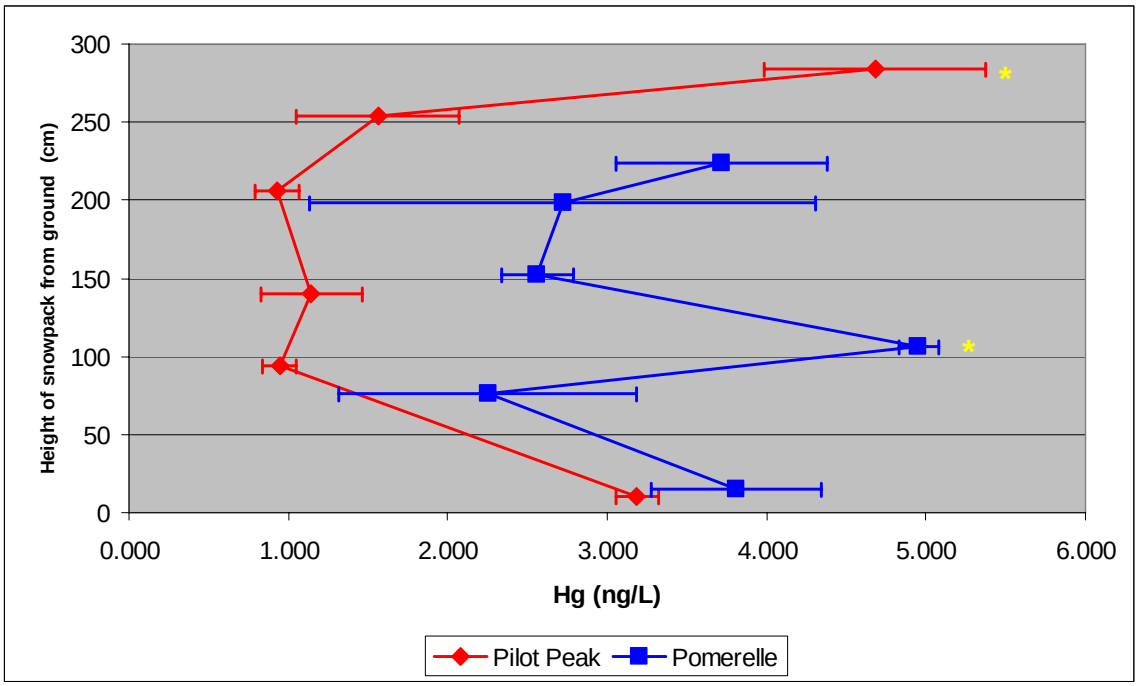



**Figure 5. Comparison of total mercury concentrations at Pomerelle and Pilot Peak sample sites. Each data point is the mean of one sample and a duplicate. Error bars represent one standard deviation. Yellow stars indicate samples with statistically significantly higher values than the remainder of the sample set (Student's t-test). Concentrations in the Pomerelle sample set, as a whole, are statistically significantly higher than those in the Pilot Peak sample set.**

The vertical profiles of concentrations from each of the sites show a similar signal, with higher concentrations in the upper and lower strata and lower concentrations in the middle strata. The exception to this pattern is the one high value that stands out in the middle stratum of the Pomerelle profile.

Vertical snowpack profiles reported in the literature are variable. St. Louis (2005) reports that average concentrations of THg decreased from the surface to the bottom of the snowpack but offers no explanation; instead, the authors point to the ratio of MeHg to THg in the vertical profile as the metric of interest.

Susong (2003) describes two different vertical profiles from two snowpacks in southeast Idaho: one where average concentrations increase at the base of the snowpack and one where average concentrations increase at the surface of the snowpack. The explanation given by Susong points to either

re-emission from soil or higher concentrations of mercury in the snow at deposition as factors that may increase concentrations at the base of the snowpack.

Dommergue (2003a) shows profiles of snowpits excavated at the same site before and after a melt episode. The results are striking, revealing a distinct change in the vertical profile. Before melt, mercury concentrations were lowest at the base, increasing towards the top and decreasing at the surface. After melt, the concentrations were highest at the surface, lowest in the middle, and slightly higher at the base. During the time lapse, the mercury balance in the snowpack was transformed. Evidence like this makes it difficult to build a case for using the elevated mercury concentration of a single stratum to infer that the source of the air parcel that deposited the mercury in that stratum is the cause of the elevated concentration. Mercury, which is subject to the influence of temperature, sunlight, wind, pressure, and the physical metamorphosis of snow crystals in snow, is too volatile to be captured and maintained without change throughout the season.

## Comparison of Mercury Concentrations with Previously Published Results

Figure 6 compares the concentrations measured in the current study with those reported in the literature. The values for the current study compare favorably with other values reported from Idaho (Abbott, 2002, Susong, 2003, IDEQ, 2005b). Mercury concentrations in the Arctic tend to be higher than concentrations in the mid-latitudes or in ice core samples because they include values elevated by springtime Mercury Depletion Events (MDEs) (Amyot, 2003, LaLonde, 2003). Coastal Arctic sites also retain more mercury in snow because these snowpacks contain sea-salts (or halides) which promote the re-oxidation of GEM (Poulain, 2004, Amyot, 2003, Ariya, 2004).

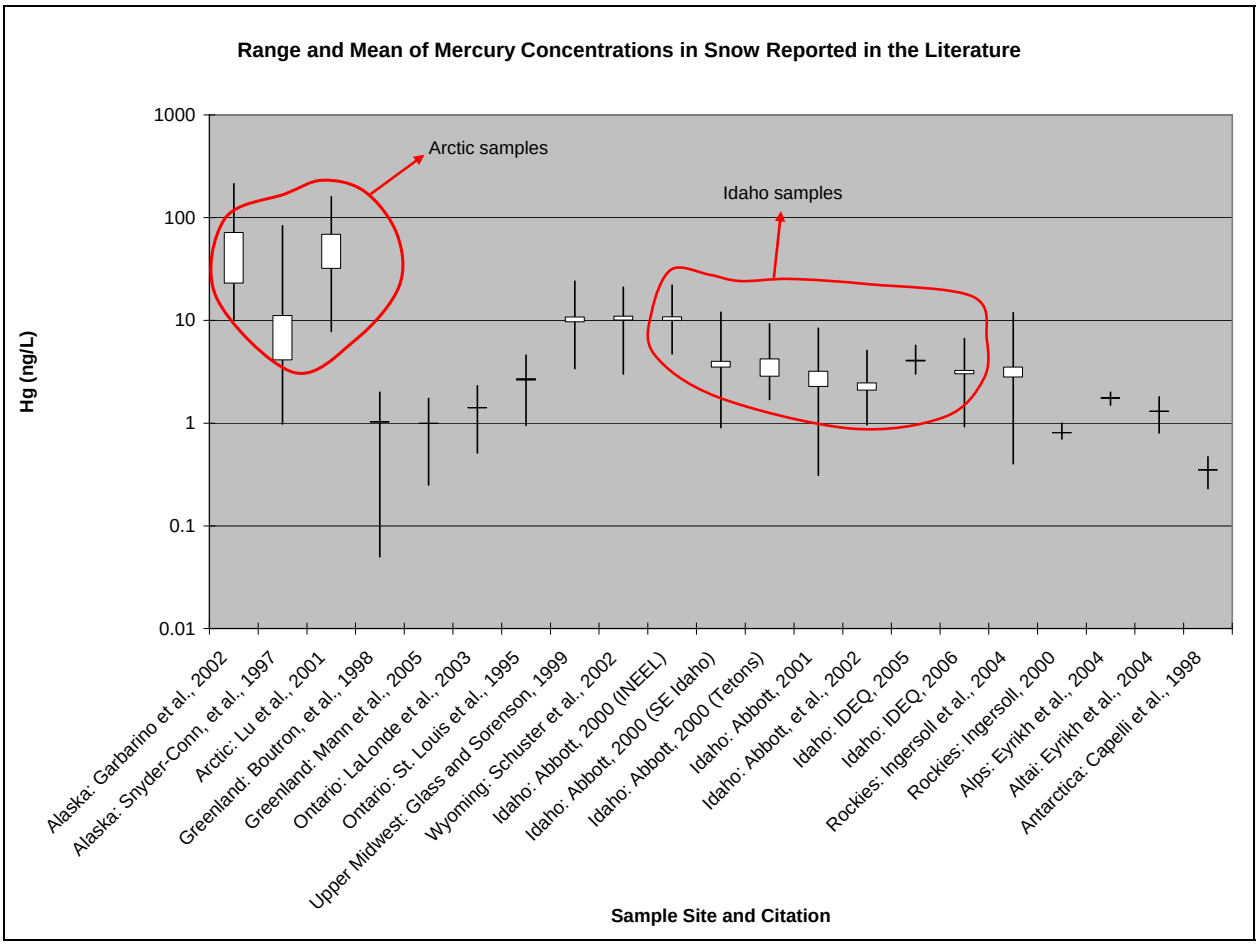



**Figure 6. Values of total mercury measured in studies reported in the literature compared to this study. Box-whisker plot represents the mean, median, and range (minimum and maximum) of values reported.**

It can be concluded from the data that the mercury concentrations measured in this study are comparable to mercury values reported by other studies performed in the region. However, the concentrations resulting from this study cannot be considered elevated when compared with other values reported in the literature.

On the other hand, the concentrations measured in the SFCR watershed are, statistically speaking, significantly higher than those concentrations measured at the background site. Can this relative difference be attributed to a particular atmospheric source? Can the high values at each site be connected to a group of possible storms and subsequently attributed to a source region?

A storm trajectory analysis was undertaken to examine these questions.

## Trajectory Analysis

Meteorological analyses using trajectories calculated with the NOAA HYSPLIT model (Draxler, 2003, Rolph, 2003) have been performed by other researchers to attribute mercury source contributions from specific emissions sources to snowpacks (Hall, 2005, Abbott, 2006). This study employed a similar method to determine possible sources of atmospheric mercury deposition.

Trajectories were run, using the ETA Data Assimilation System (EDAS40) dataset with a 40 km grid cell resolution (NOAA, 2004). Backward trajectories were calculated, starting at midnight on each day of the snow accumulation season for which there was a recorded snowfall at the SNOTEL station nearest the sample site. Parameters used for the trajectory analysis included a 48-hour modeling period and receptor heights of 0 m, 100 m, and 500 m above ground level.

The resulting trajectory files were downloaded, in shapefile format, and a sector analysis was performed in ArcGIS. Each set of trajectories (three heights for each storm) was assigned a direction based on the path traveled to the point of origin (N, S, E, W, NW, SW, NE, SE). The directional distribution was calculated for the trajectories, and the average direction was chosen from the resulting rotation of the standard deviational ellipse. (A standard deviational ellipse represents the standard deviation of the x and y coordinates from the mean center. The directional distribution indicated by the long axis describes the directional trend.)

Figure 7 illustrates the trajectory analysis process, and Figure 8 displays the results of the analysis.

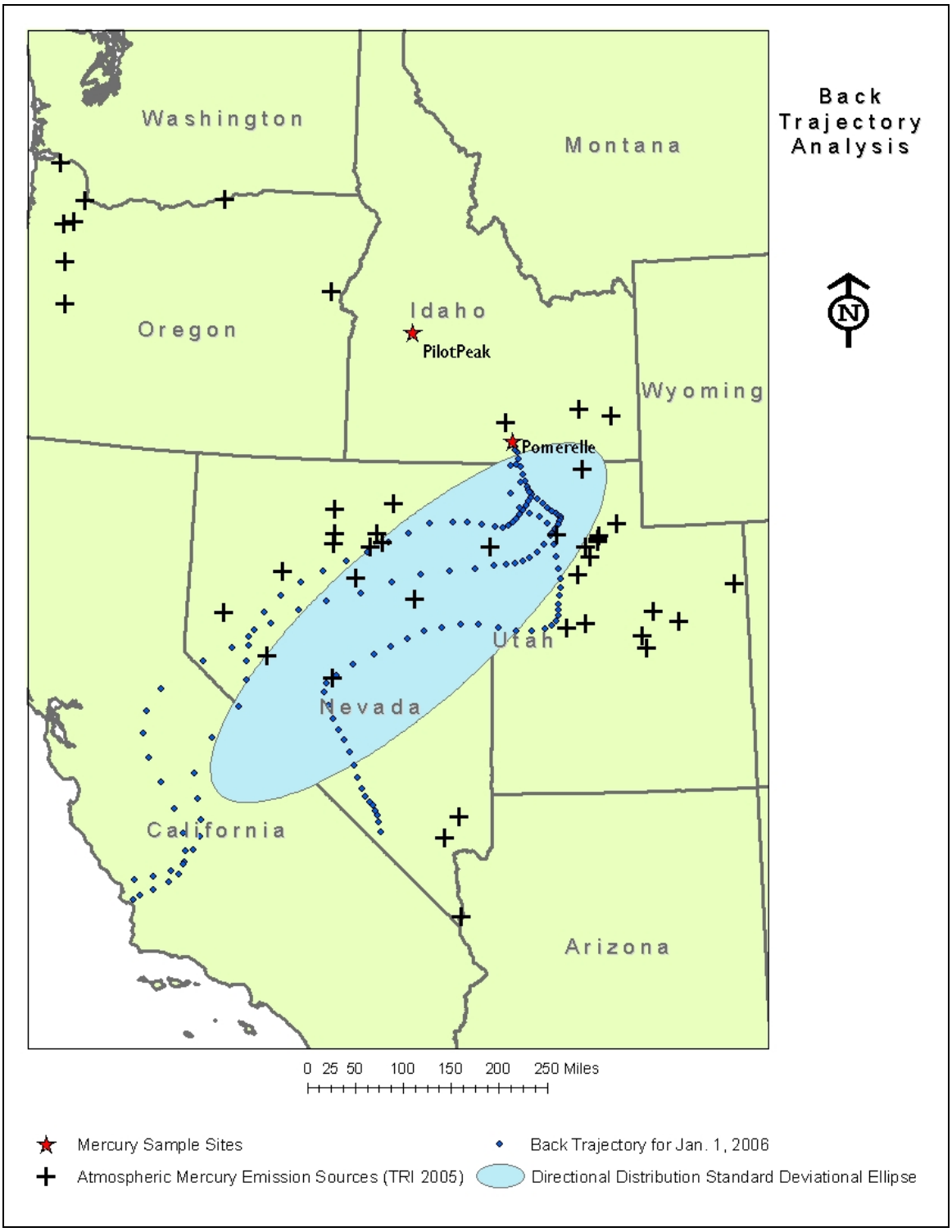



**Figure 7. Example back trajectory analysis for January 1, 2006. Scattered blue dots show the paths taken by air parcels ending at 0, 100, and 500 meters above ground level at Pomerelle. Model time is 48 hours. The standard deviational ellipse calculated for the trajectories shows the standard deviation of the x and y coordinates from the mean center. The directional distribution indicated by the long axis describes the directional trend. This trajectory was assigned to the southwest sector.**

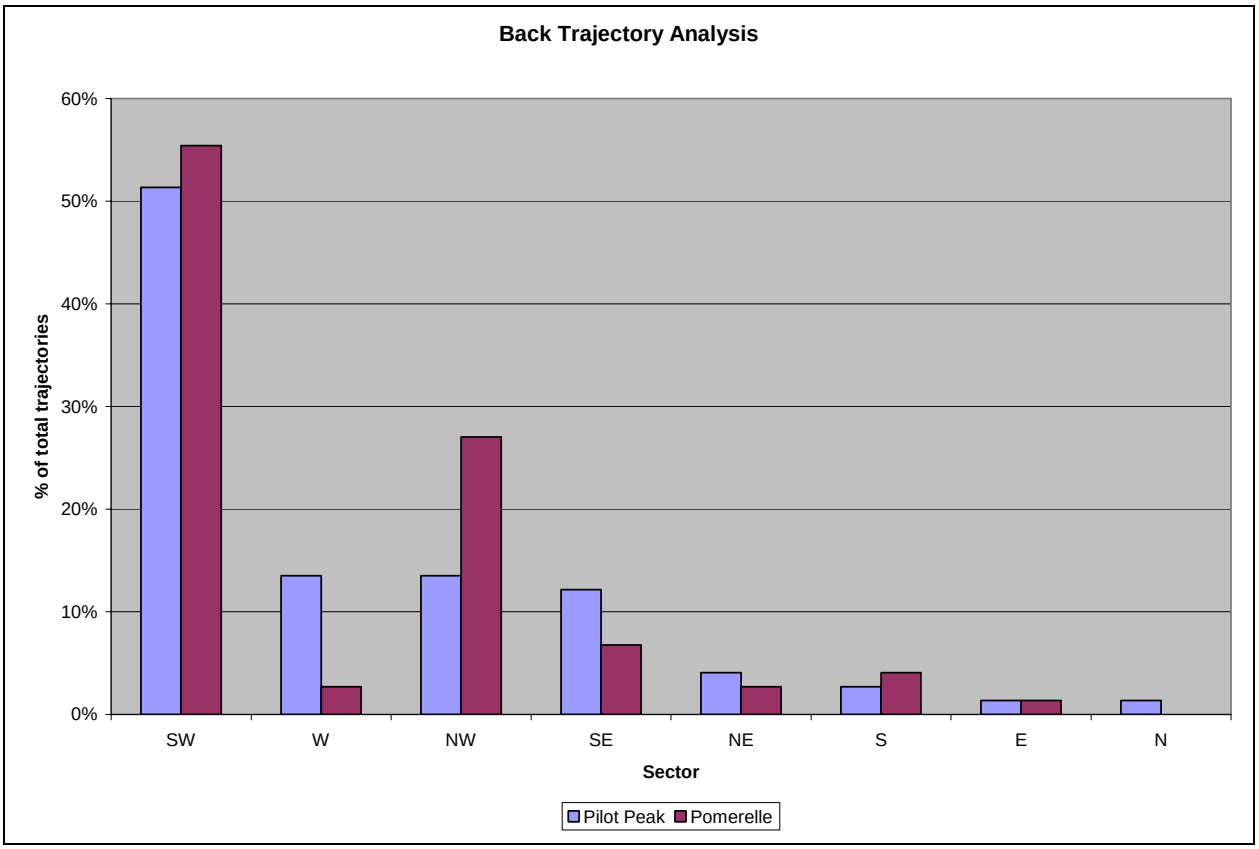



**Figure 8. Summary of back trajectory analysis for sample sites. Each group of trajectories for a particular date was assigned a directional sector based on the orientation of the long axis of the standard deviational ellipse.**

More than half of the storms depositing precipitation in the form of snow at each study site originate from the southwest. More storms from the northwest reach Pomerelle than reach Pilot Peak, while westerly and southeasterly storms are more likely to affect Pilot Peak.

## Intersection of Trajectories and Regional Mercury Sources

GIS analysis was utilized to determine which storm trajectories followed pathways across major regional mercury sources. These mercury sources were plotted (see Figure 1 for locations and 2005 TRI-reported mercury emissions) and intersected with the back trajectories, which were buffered by 40 km to represent better the 40 km resolution of the HYSPLIT model results. The results of the intersections between trajectories and sources are given in Figure 9, Figure 10, and Figure 11.

Back trajectories ending at the Pilot Peak site (Figure 9) intersect the Amalgamated Sugar (Paul), Newmont Twin Creeks Mine (NV), and Ash Grove Cement (Durkee, OR) facilities most often. These facilities are located in three disparate directions from Pilot Peak (southeast, south, and northwest,

respectively); thus, no pattern is evident. No facilities are intersected by more than 20% of the total Pilot Peak trajectories.

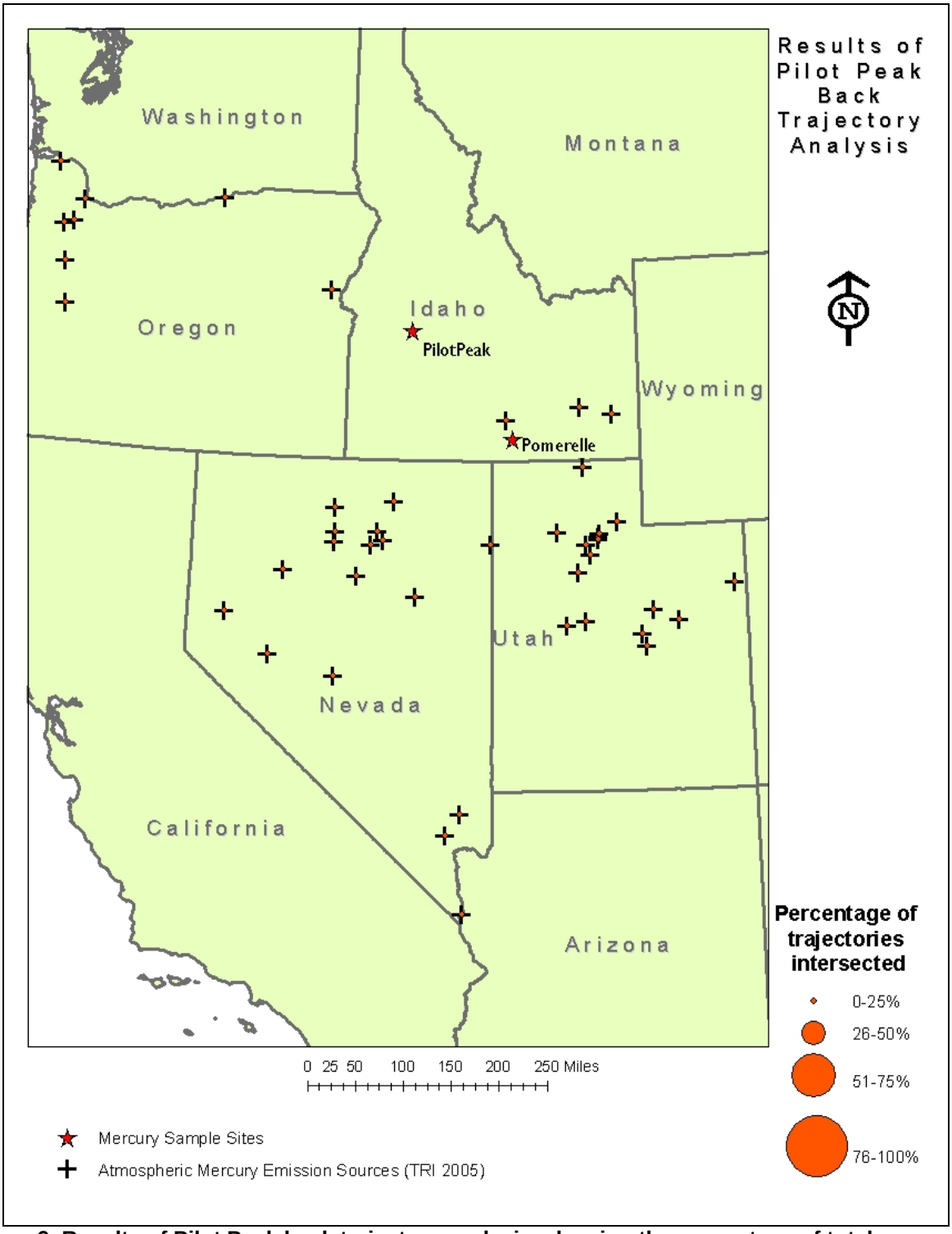



**Figure 9. Results of Pilot Peak back trajectory analysis, showing the percentage of total trajectories that intersected regional mercury emitters.**

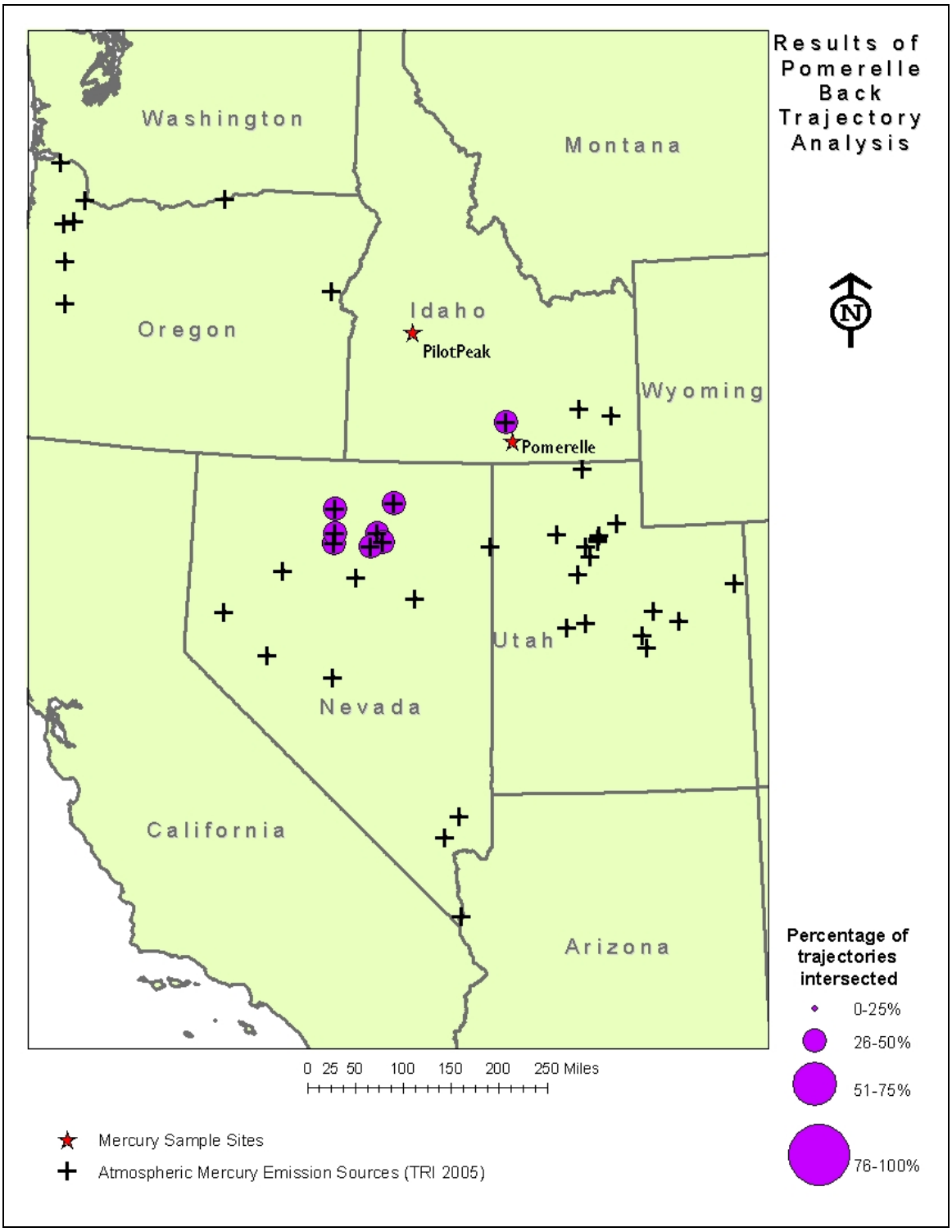



**Figure 10. Results of Pomerelle back trajectory analysis, showing the percentage of total trajectories that intersected regional mercury emitters.**

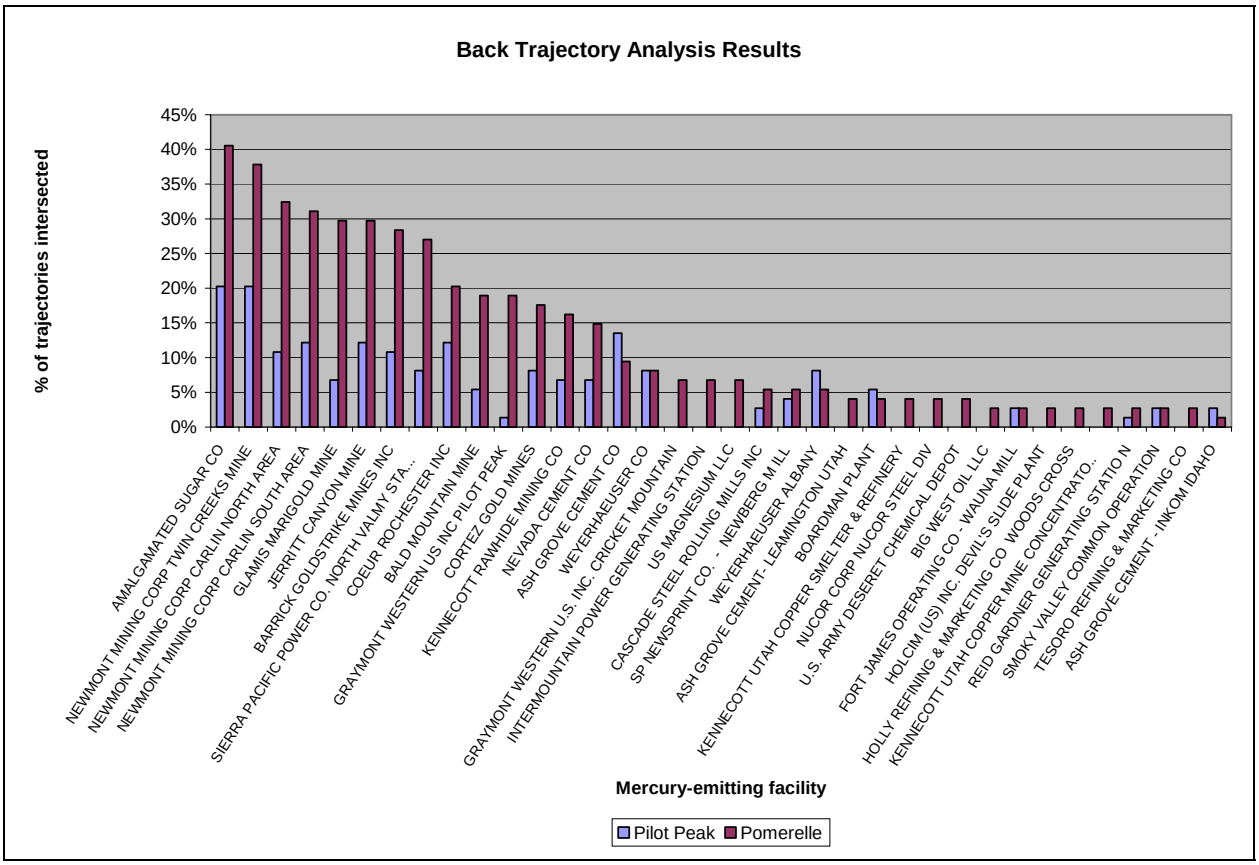



**Figure 11. Back trajectory analysis results showing percentage of total trajectories at each site that intersected a mercury-emitting facility.**

Back trajectories ending at the Pomerelle site (Figure 10) intersect the Amalgamated Sugar (Paul), Newmont Twin Creeks Mine, Newmont Carlin North, Newmont Carlin South, Glamis Marigold Mine, Jerritt Canyon Mine, Barrick Goldstrike Mine, and Sierra Pacific Power (North Valmy Station) facilities most often. Each of these facilities was intersected by more than 25% of the total Pomerelle back trajectories.

All of the trajectories intersected with the Amalgamated Sugar Paul facility, but this result is an artifact of the 40 km buffer used to represent the HYSPLIT model resolution, as the Paul facility is within 40 km of the Pomerelle study site. If the directions of the storms passing by the Paul facility are taken into account, then the number of intersections is significantly reduced: the Paul facility falls within the 40 km buffer of 41% of the storm trajectories that arrive at Pomerelle from the west, north, or northwest, the direction in which lies the Amalgamated Sugar facility. This 41% is the value shown in Figure 10 and Figure 11.

The cluster of facilities in northern Nevada that are in the path of more than a quarter of the storms that eventually deposit snow at the Pomerelle site may influence or contribute to the amount or character of the mercury deposited. The proximity of the Amalgamated Sugar plant to the study site indicates that this facility may have an effect on mercury deposition at the Pomerelle site as well.

## Mercury Deposition by Storm Event

The statistically significant high values in the snowpacks at each of the study sites may be bracketed by a group of storms by their position within the snowpack. There were 74 storms that deposited snow at the SNOTEL sites adjacent to the study sites, and there were 24 snow layers identified in the Pomerelle snowpack—20 in the Pilot Peak snowpack. Due to the metamorphosis of the snow throughout the season, not every snow deposition event has a corresponding stratum in the snowpack, but a reasonable estimate of the date of deposition can be made by comparing the stratigraphy with the meteorological record.

Pilot Peak's snow stratum having the highest mercury concentration is the uppermost layer, in which the sample was retrieved at 284 cm, 34 cm below the snow surface. Assuming that this snow arrived within the two weeks preceding collection (March 1-15), there were nine storms that could have deposited the snow. The majority of these storms originated from the southwest (44%) or west (22%).

Pomerelle's highest-concentration stratum is located in the middle of the snowpack, corresponding to the approximate midpoint of the season (late December through early January) between first snowfall (October 30) and the sample date (March 11). Of the 12 storms that occurred during the final week in December and the first week of January, 75% arrived from the southwest.

Figure 12 and Figure 13 map the facilities intersected by the high storm trajectories for each study site, and Figure 14 shows the corresponding outcome for the facilities of interest. The Amalgamated Sugar facility results are again adjusted for the buffer artifact by accounting for storm directions approaching Pomerelle.

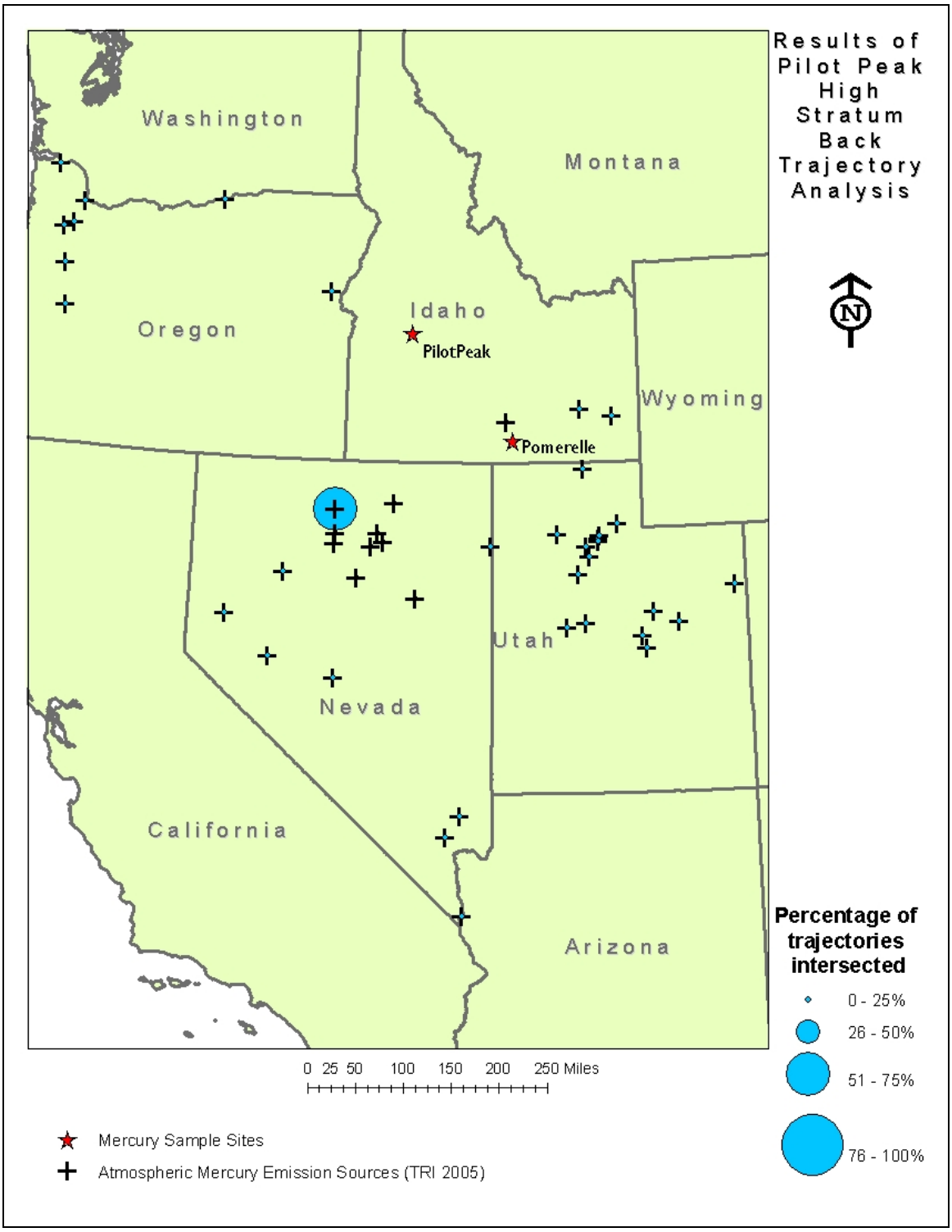



**Figure 12. Results of Pilot Peak high concentration stratum back trajectory analysis showing the percentage of total trajectories that intersected regional mercury emitters.**

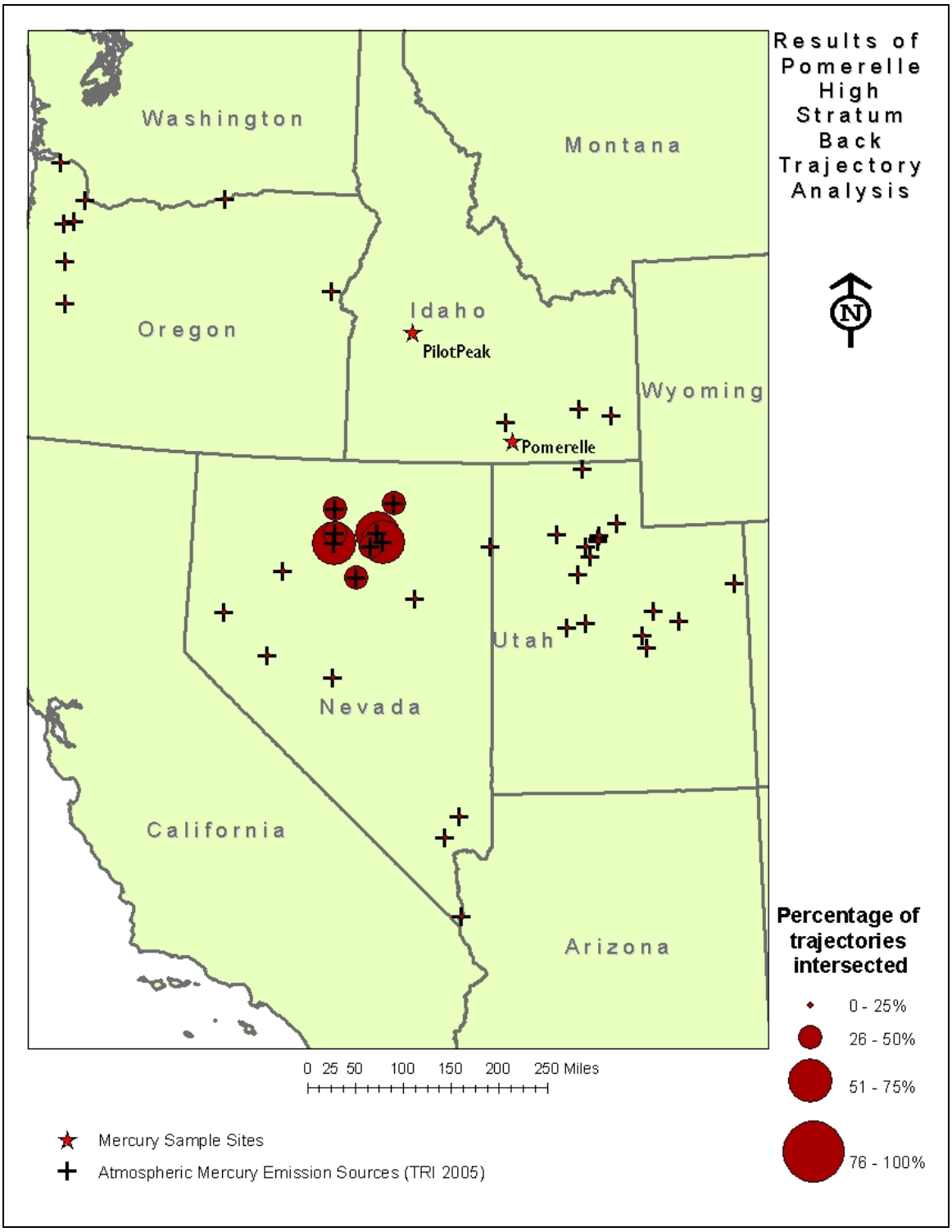



**Figure 13. Results of Pomerelle high concentration stratum back trajectory analysis showing the percentage of total trajectories that intersected regional mercury emitters.**

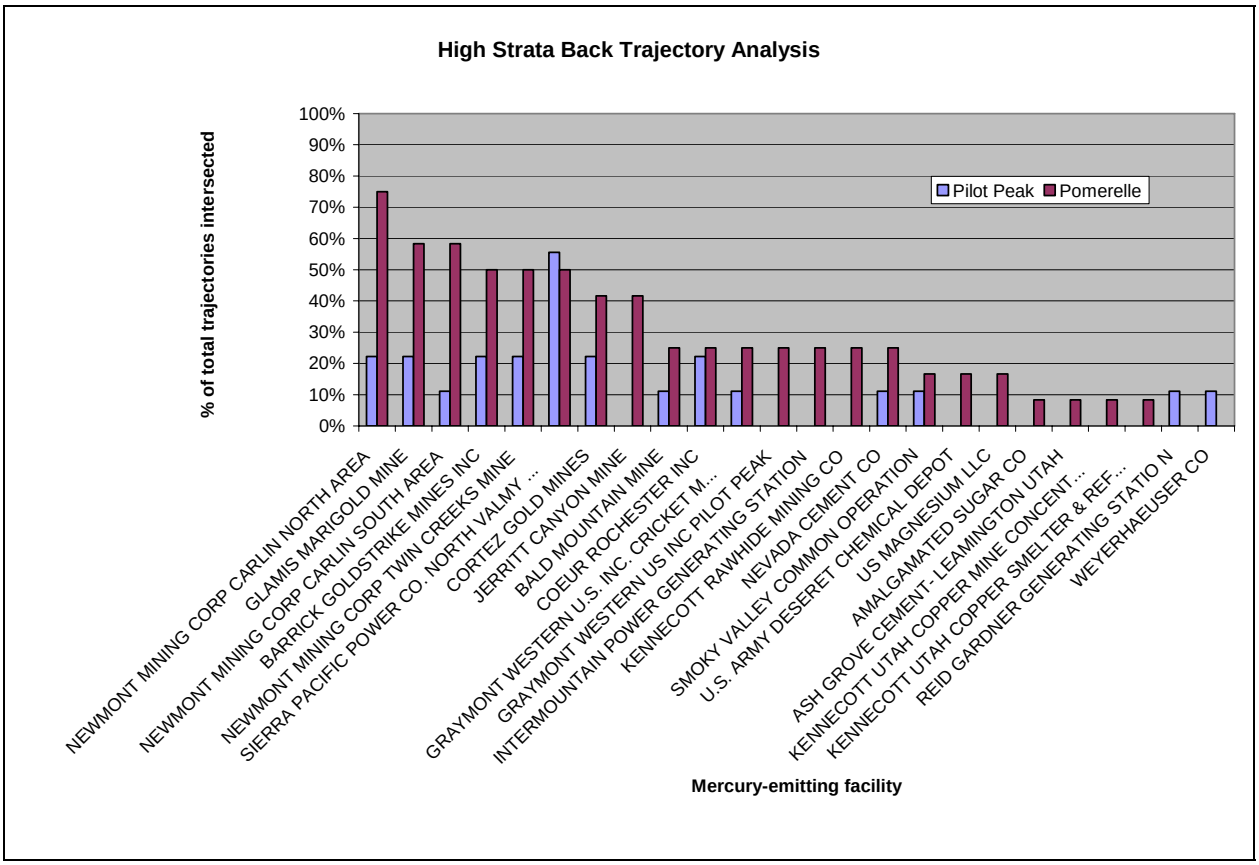



**Figure 14. Back trajectory analysis results showing percentage of total high strata trajectories that intersected a mercury-emitting facility.**

The results show that more than half the high storm trajectories heading to Pilot Peak passed over one facility in northern Nevada (Sierra Pacific Power, North Valmy Station).

The Pomerelle analysis reveals the contributions of one facility (Newmont Carlin North) to 75% of the high storm trajectories, two facilities to 58%, three facilities to 50%, and two more to 42%. All the facilities intersecting greater than 25% of the Pomerelle high trajectories are clustered in northern Nevada. The analysis suggests that a possible source region for the statistically significant higher mercury values in the Pomerelle snowpack is in northern Nevada. However, in spite of this implication, the possibility remains that the high strata in the Pilot Peak and Pomerelle snowpacks are the result of chemical reactions occurring within the snowpack after the mercury-laden snow was deposited.

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# Conclusions and Recommendations

The 2006 Mercury Snowpack Study was undertaken as part of a multi-media sampling strategy designed to identify the source(s) of mercury contamination in Salmon Falls Creek Reservoir. The investigation measured mercury concentrations in two snowpacks in southern Idaho and researched the behavior of mercury in snow. Mercury concentrations in the two snowpacks were found to be comparable to other regional concentrations reported in the literature, but these concentrations could not be considered elevated.

Total mercury concentrations at the sampling site nearest Salmon Falls Creek Reservoir were statistically significantly higher than at the background site. Both sites exhibited individual snowpack strata having statistically significantly higher concentrations of mercury than the remainder of the strata.

Back trajectory analysis revealed that a cluster of mercury-emitting facilities in northern Nevada, as well as the nearby Amalgamated Sugar plant in Paul, intersected greater than 25% of the storm trajectories that deposited mercury in snow at the Pomerelle site. No such pattern was evident at the Pilot Peak site. Trajectory analysis for the high strata exposed a similar spatial pattern for both sites: more than half the storms that bracketed the high layers passed over facilities in northern Nevada. These relationships are an unavoidable result of typical weather patterns in the region.

Although the storm trajectory analysis suggests that mercury emitted from these facilities may make its way into Salmon Falls Creek Reservoir through snow deposition, current scientific knowledge of the behavior of mercury in snow makes this connection difficult to reach conclusively. Mercury is volatile in snow, and the high concentrations of total mercury in individual layers could be a result of chemical transformations and diffusion of mercury that occurred within the snowpack after deposition and not the result of snow containing high concentrations of mercury at the time of deposition.

Three changes to the sampling strategy could be made to determine which of these processes (deposition of snow having high mercury concentration or transformation of mercury within the snowpack) are the main contributors to higher mercury concentrations:

- To relate a mercury concentration in a specific snowpack stratum to a specific storm, it would be important to more accurately pin down the stratigraphy. By monitoring the snowpack and the meteorology regularly throughout the season (perhaps at one- or two-week intervals), the concentrations in a particular layer could be tied to one storm and could also be followed throughout the season. As the layer is buried deeper and deeper within the snowpack, repeated measurements of the mercury content would reveal the fluctuations in concentration, if any. If the concentrations remained high relative to other layers throughout the season, then the high values could be attributed to the source of the storm. If the concentrations rose (or fell) subsequent to deposition, then it would be clear that the values are the result of interactions within the snowpack.
- To improve understanding of the chemical mechanisms taking place at the study sites methylmercury should be measured in addition to total mercury. Methylmercury seems to be more stable in snowpacks than total mercury, and it is the form that does the damage in the watershed.
- Sampling should be performed in, not near, the Salmon Falls Creek Reservoir watershed. It is the mercury that collects in this basin that eventually ends up in the fish and poses health risks to humans.

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# Appendix A: Quality Assurance Summaries for Mercury Analysis

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# QUALITY ASSURANCE SUMMARY

BROOKSRAND
TRACE METALS ANALYSIS & PRODUCTS

3958 6th Avenue NW
Seattle, WA 98107
Voice: 206-632-6206
Fax: 206-632-6017

***Batch #:*** **06-0207** ***Method #:*** **EPA 1631.E**

***Analyte:*** **Hg** ***Matrix:*** **Water**

**BIAS** *Criteria: Recovery = 77-123%*
**Continuing Calibration Verification (CCV)**

| *QCS ID* | *Certified Value ng/L* | *Measured Value ng/L* | *Recovery %* |
|---|---|---|---|
| CCV1 | 5.00 | 4.25 | 85% |
| CCV2 | 5.00 | 3.40 | 68% |
| CCV3 | 5.00 | 4.83 | 97% |
| CCV4 | 5.00 | 5.11 | 102% |
| CCV5 | 5.00 | 4.14 | 83% |

**BIAS** *Criteria: Recovery = 85-115%*
**Independent Calibration Verification (ICV)**

| *QCS ID* | *Certified Value ng/L* | *Measured Value ng/L* | *Recovery %* |
|---|---|---|---|
| ICV* | 16.01 | 15.67 | 98% |

* Preparation of the CRM NIST 1641d.

**BIAS** *Criteria: Recovery = 71-125%, RPD<24%*
**Matrix Spikes/Matrix Spike Duplicates (MS/MSD)**

| | | *Matrix Spike* | | | *Matrix Spike Duplicate* | | | |
|---|---|---|---|---|---|---|---|---|
| *Sample ID* | *Sample Value ng/L* | *Spiked Value ng/L* | *Measured Value ng/L* | *MS Recovery %* | *Spiked Value ng/L* | *Measured Value ng/L* | *MSD Recovery %* | *Duplicate RPD* |
| 06BR0378-02 | 3.43 | 9.99 | 15.39 | 120% | 9.90 | 15.35 | 120% | 0% |
| 06BR0378-09 | 1.60 | 4.92 | 7.37 | 117% | 4.96 | 6.88 | 106% | 7% |

**1.0% BrCl Method Blanks (MB)** *Criterion: MB < 0.5 ng/L*

| *MB1 ng/L* | *MB2 ng/L* | *MB3 ng/L* | *Average ng/L* | *StDev ng/L* |
|---|---|---|---|---|
| 0.04 | 0.12 | 0.07 | 0.08 | 0.04 |

**1.0% BrCl Method Blanks (MB)** *Criterion: MB < 0.5 ng/L*

| *MB5 ng/L* | *MB6 ng/L* | *MB7 ng/L* | *Average ng/L* | *StDev ng/L* |
|---|---|---|---|---|
| 0.06 | 0.14 | 0.09 | 0.10 | 0.04 |

1.0% BrCl MB prepared in triplicate.
Average MB result multiplied by appropriate factor to produce correction factor for each sample preservation BrCl level.

| **Detection Limits** | |
|---|---|
| *MDL ng/L* | *PQL ng/L* |
| 0.10 | 0.25 |

04/06/06
*Quality Assurance Officer*

*Project Manager*

*4/6/2006* *Page 1 of 1*

**Figure 15. Quality Assurance Summary for mercury analysis of Pomerelle samples.**

# QUALITY ASSURANCE SUMMARY

BROOKSRAND
TRACE METALS ANALYSIS & PRODUCTS

3958 6th Avenue NW
Seattle, WA 98107
Voice: 206-632-6206
Fax: 206-632-6017

***Batch #:*** **06-0211** ***Method #:*** **EPA 1631.E**

***Analyte:*** **Hg** ***Matrix:*** **Water**

**BIAS** *Criteria: Recovery = 77-123%*
**Continuing Calibration Verification (CCV)**

| *QCS ID* | *Certified Value ng/L* | *Measured Value ng/L* | *Recovery %* |
|---|---|---|---|
| CCV1 | 5.00 | 4.64 | 93% |
| CCV2 | 5.00 | 5.10 | 102% |
| CCV3 | 5.00 | 5.23 | 105% |

**BIAS** *Criteria: Recovery = 85-115%*
**Independent Calibration Verification (ICV)**

| *QCS ID* | *Certified Value ng/L* | *Measured Value ng/L* | *Recovery %* |
|---|---|---|---|
| ICV* | 16.01 | 15.68 | 98% |

* Preparation of the CRM NIST 1641d.

**BIAS** *Criteria: Recovery = 71-125%, RPD<24%*
**Matrix Spikes/Matrix Spike Duplicates (MS/MSD)**

| | | *Matrix Spike* | | | *Matrix Spike Duplicate* | | | |
|---|---|---|---|---|---|---|---|---|
| *Sample ID* | *Sample Value ng/L* | *Spiked Value ng/L* | *Measured Value ng/L* | *MS Recovery %* | *Spiked Value ng/L* | *Measured Value ng/L* | *MSD Recovery %* | *Duplicate RPD* |
| 06BR0397-01 | 3.09 | 9.95 | 13.98 | 109% | 9.99 | 14.11 | 110% | 1% |
| 06BR0397-10 | 1.92 | 4.95 | 7.28 | 108% | 4.96 | 7.63 | 115% | 5% |

**1.0% BrCl Method Blanks (MB)** *Criterion: MB < 0.5 ng/L*

| *MB1 ng/L* | *MB2 ng/L* | *MB3 ng/L* | *Average ng/L* | *StDev ng/L* |
|---|---|---|---|---|
| 0.07 | 0.09 | 0.06 | 0.07 | 0.02 |

1.0% BrCl MB prepared in triplicate.
Average MB result multiplied by appropriate factor to produce correction factor for each sample preservation BrCl level.

| **Detection Limits** | |
|---|---|
| *MDL ng/L* | *PQL ng/L* |
| 0.10 | 0.25 |

4/6/06
*Quality Assurance Officer*

*Project Manager*

*4/6/2006* *Page 1 of 1*

**Figure 16. Quality Assurance Summary for mercury analysis of Pilot Peak samples.**

# Appendix B: Quality Assurance Summary for Nitrate Analysis

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# QUALITY CONTROL PACKAGE

| | |
|---|---|
| Customer Sample # PM 1-7, PM-G | PP 1-7, PP-G |
| Lab Sample # 0603 0314 – 0603 0321 | 0603 0352 – 0359 |
| Analytical Date 3/21/06 | 3/30/06 |
| Analyst: Beth Orde | |
| MRL 117.4% (+/- 30%) | MRL 105%(+/- 30%) |
| CB <MRL | CB <MRL |
| LFB 100.4% (90-110%) | LFB 99.6% |
| LRB <MRL | LRB <MRL |
| Blank Spike 93.2% (90-110%) | BS 95.6% |
| Column Efficiency Ck (CEC) 99.0% (>92%) | CEC 98.0% |
| Auto Dilutor Ck.(ADC) 94.4% (90-110%) | ADC 96.3% |
| IPC 99.3% ; 99.4% (90-110%) | IPC 99.7%;101%;102% |
| CCB <MRL | CCB <MRL |
| Dups/Reps 0% RPD (<20%) | 1.4% RPD; 2.0% RPD |
| LFM 91.9%R (90-110%) | 90.6%R ; 95.6%R |

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# Appendix C: Quality Assurance Summary for Sulfate and Chloride Analysis

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QUALITY CONTROL REPORT SHEET

ANALYST Fleana Elder

DATE 3/15/2006

| LAB TRACKING NUMBERS | CUSTOMER SAMPLE IDs |
|---|---|
| 0603 314 | PM-1 |
| 315 | PM-2 |
| 316 | PM-3 |
| 317 | PM-4 |
| 318 | PM-5 |
| 319 | PM-6 |
| 320 | PM-7 |
| 321 | PM-6 |

| | SPIKE, ppm | RECOVERED, ppm | %RECOVERY | Acceptance Criteria |
|---|---|---|---|---|
| FLUORIDE | 0 | | | |
| CHLORIDE | 20.0 | 20.309 | 102% | Nondrinking water |
| SULFATE | 20.0 | 20.083 | 100.4% | 75-125% |

QC ✓

Duplicates

| | RPD% | LD1 | LD2 |
|---|---|---|---|
| Cl | 13.5% | 0.767 | 0.670 |
| SO4 | 1.40% | 0.432 | 0.426 |

Acceptance Criteria <20%

MRL check 0.200 mg/L

| | Rec% | Recovered |
|---|---|---|
| Cl | 96.0% | 0.192 |
| SO4 | 100% | 0.200 |

QUALITY CONTROL REPORT SHEET

ANALYST Ileana Elder

DATE 4/6/2006

| LAB TRACKING NUMBERS | CUSTOMER SAMPLE IDs |
|---|---|
| 0603 352 | PP-1 |
| 353 | PP-2 |
| 354 | PP-3 |
| 355 | PP-4 |
| 356 | PP-5 |
| 357 | PP-6 |
| 358 | PP-7 |
| 359 | PP-6 |

| | SPIKE, ppm | RECOVERED, ppm | %RECOVERY | Acceptance Criteria |
|---|---|---|---|---|
| FLUORIDE | 0 | | | non-drinking water |
| CHLORIDE | 0.200 | 0.170 | 85.0% | 75-125% |
| SULFATE | 0.200 | 0.163 | 81.5% | |

QC ✓

| Spiked Duplicates | RPD% | LD1 | LD2 |
|---|---|---|---|
| Cl | 0.873% | 0.228 | 0.230 |
| SO4 | 6.13% | 0.336 | 0.316 |

Acceptance Criteria <20%

| MRL check 0.200 mg/L | Rec % | Recovered |
|---|---|---|
| Cl | 102% | 0.205 |
| SO4 | 94.5% | 0.189 |

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