Rio Tinto Alcan

# KMP $SO_2$ EEM Program – Technical Memo P01

# **Atmospheric Sulphur Dioxide**
# Passive Diffusive Sampler Network: 2011–2012

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# 1 Overview

A passive diffusive sampler is a device for measuring the gaseous atmospheric concentration of an analyte by diffusion through a static air layer onto an adsorbent membrane. They require no electricity, no pumps, have no moving parts, they are compact and portable, inexpensive, and simple to use.

Passive samplers should ideally provide reliable, cost-effective measurements of air concentrations at multiple locations to evaluate 'hotspots' or determine long-term trends. Observations represent time-integrated 'average' concentrations for the exposure period, typically one week to one month.

# 2 Kitimat Passive Diffusive Sampler Network

During 2011 and 2012, Rio Tinto Alcan operated a passive sampler network to provide empirical observations of atmospheric sulphur dioxide ($SO_2$) concentrations.

A comprehensive network review was carried out during 2012, with the goal to move towards a low maintenance, cost-effective reliable network of $SO_2$ passive samplers providing scientifically defensible data to support the Environmental Effects Monitoring Program.

This technical memo describes the monitoring results for the 2011 and 2012, and recommendations from the network review.

# 3 Network Overview

The network was established during 2011 with 19 sites, and expanded in 2012 with the addition of two sites (n = 21). The majority of the monitoring sites were located in and around Kitimat (see Figure 1 and Table 1). During 2011, the network was operated for 11 weeks (04 August–20 October), and 21 weeks during 2012 (17 May–18 October).

Passive samplers were deployed weekly at each site (one sampler per site), using Radellio samplers coated with triethanolamine (TEA). Weekly exposures are recommended (by the manufacturer) in regions where relative humidity is > 70%.

The limit of quantification for Radellio TEA samplers is 1 ppb (7 days). The analysis of sampler membranes was carried out by Maxxam Analytics.

To evaluate the performance of the passive samplers, they were co-located with four (five during 2011) continuous stations (see Figure 2).

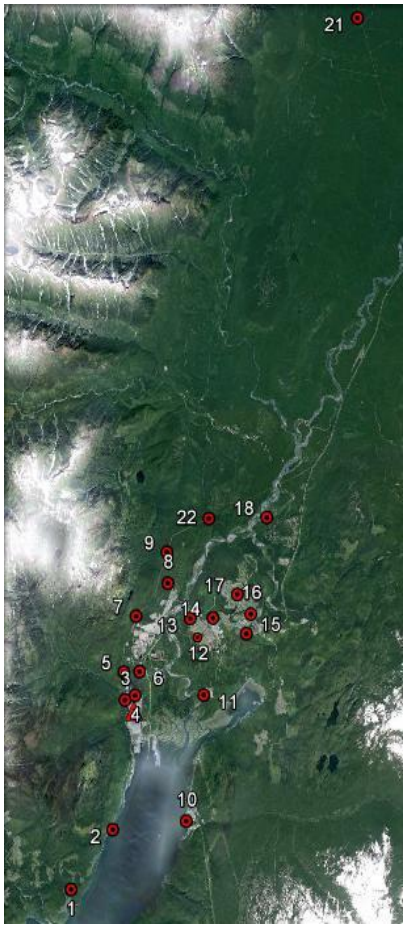



Table 1. ID, name and location (latitude and longitude) of monitoring sites in the Kitimat Passive Diffusive Sampler Network. Note: Only the first 19 stations were operated during 2011.

| ID | Site Name | Latitude | Longitude |
|---|---|---|---|
| 1 | Bish Road Lookout | 53.9380 | -128.727 |
| 2 | Bish Site | 53.9647 | -128.704 |
| 3 | Rifle Range | 54.0170 | -128.709 |
| 4 | KMP | 54.0195 | -128.703 |
| 5 | Bend | 54.0282 | -128.713 |
| 6 | Haul Road | 54.0293 | -128.702 |
| 7 | Sand Hill | 54.0514 | -128.710 |
| 8 | PNG Station | 54.0664 | -128.691 |
| 9 | Claque Mountain | 54.0787 | -128.695 |
| 10 | Kitamaat Village | 53.9734 | -128.651 |
| 11 | Low Spot | 54.0246 | -128.652 |
| 12 | Low Channel | 54.0469 | -128.664 |
| 13 | Kitimat Riverlodge | 54.0540 | -128.671 |
| 14 | Kitimat City Centre MAML | 54.0559 | -128.654 |
| 15 | Colghlin Park | 54.0521 | -128.628 |
| 16 | High School | 54.0602 | -128.627 |
| 17 | Whitesail | 54.0669 | -128.639 |
| 18 | Cablecar | 54.0996 | -128.626 |
| 19 | Williams Creek* | 54.4276 | -128.447 |
| 21 | Power Line Corridor | 54.0950 | -128.668 |
| 22 | Onion Lake Ski Trail | 54.3035 | -128.616 |

* Site 19 is located north of Kitimat close to Terrace Airport. Site 20 was not established.

Figure 1. Location of monitoring sites in the Kitimat Passive Diffusive Sampler Network. Note: the network was composed of 19 sites in 2011, and expanded to 21 during 2012. The site name and co-ordinates are given in Table 1.


Figure 2. Location of continuous sulphur dioxide monitoring stations (red and yellow squares) where passive diffusive samplers were co-deployment during 2011 and 2012.

# 4 Kitimat Passive $SO_2$ Network: 2011

During 2011, more than 60% of exposed samplers were reported by Maxxam as less than the MDL (method detection limit0, i.e., they were recorded as non-valid observations.

This prompted questions on the appropriate period of sample exposure (1 week, 2 week, etc), sampler limit of detection, site locations, quality of analytical procedures, suitability of samplers under (regionally) high humidity, etc.

# 5 Kitimat Passive $SO_2$ Network: 2012

To address the issues identified during 2011, a comprehensive network review was carried out. The review included the following tasks:

1. Laboratory analytical procedures were reviewed and revised (method update);
2. The 2011 raw data were recaptured;
3. Site criteria were evaluated and sites relocated (where required);
4. The network was expanded (2 new sites);
5. Rotating triplicate sample exposure were implemented (replaced rotating duplicate);
6. A database was established for 2011 and 2012 results;
7. Data quality objectives were establised to evaluate data, i.e., comparison to continuous stations, variability between replicate exposures;
8. A focused co-exposure trial was carried out.

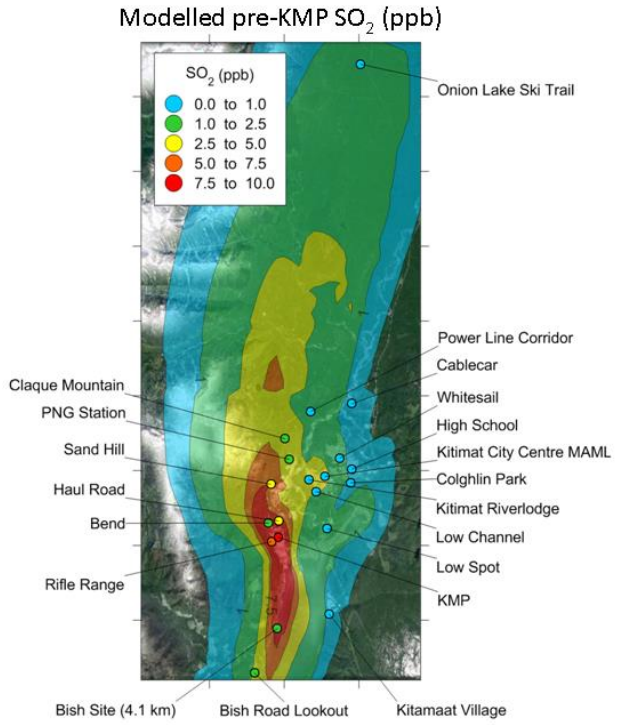
During 2012, ~100% of exposures were greater than the analytical detection limit (compared with < 40% during 2011). There were several potential reasons for the increase in data:

1. Changes in meteorology and / or emissions during 2012 compared with 2011;
2. Changes (updates) to sites and field procedures;
3. Upgrades to analytical equipment (Maxxam);
4. Changes in laboratory methods (Maxxam);
5. Ongoing external review of Maxxam results

As a result, the 2012 monitoring season provided data to: [i] assess spatial variability of atmospheric $SO_2$, [ii] evaluate variation between replicate exposures, and [iii] assess performance against continuous samplers.

[i] Spatial variability in atmospheric $SO_2$: The data showed a strong gradient in atmospheric $SO_2$ across stations during 2012 based on the median of weekly observations during the period 07 June–11 October 2012 (n = 14–18; observations blank corrected).

Higher concentrations were observed along the 'plume' broadly consistent with modelled data (see Figure 3).




| Atmospheric $SO_2$ (ppb) | |
|---|---|
| KMP | 9.94 |
| Rifle Range | 5.51 |
| Haul Road | 3.84 |
| Sand Hill | 2.69 |
| Bend | 2.33 |
| Bish Site (4.1 km) | 2.03 |
| Claque Mountain | 1.43 |
| Bish Road Lookout | 1.41 |
| PNG Station | 1.25 |
| Onion Lake Ski Trail | 0.86 |
| Power Line Corridor | 0.60 |
| Kitimat Riverlodge | 0.19 |
| Low Channel | 0.11 |
| Whitesail | 0.06 |
| Cablecar | 0.05 |
| City Centre MAML | 0.03 |
| Kitamaat Village | 0.02 |
| Low Spot | 0.02 |
| Williams Creek | 0.00 |
| Colghlin Park | 0.00 |
| High School | 0.00 |

Figure 3. Median atmospheric sulphur dioxide ($SO_2$) concentrations observed during 2012 (07 June–11 October) at passive diffusive sampler monitoring sites. Modelled (pre-KMP) atmospheric $SO_2$ concentrations are also shown (left). Note: Onion Lake Ski Trail and Power Line Corridor are greyed as these sites were not in operation during the entire 2012 monitoring period.

[ii] Variability in replicate exposures: During 2012, there were 29 triplicate exposures (encompassing 7, 14 and 28 day exposures); the variability between replicates was evaluated using the coefficient of variation (COV, i.e., standard deviation / mean × 100).

The average COV between replicate samplers (n = 3) was 39.0%, the median was 31.6%. In general, high COV may be caused by low atmospheric concentrations. Limiting the analysis to sites with observations > 1 ppb (n = 7), the average COV between replicate samplers (n = 3) was similarly 38.6%, and the median COV was 30.6%.

**The high variability between replicate exposures is a concern.**

[iii] Comparison with continuous samplers: During 2012, there were 46 one-week and 23 two-week exposures co-located with continuous $SO_2$ samplers; the correspondence between passive and continuous was assessed using linear regression ($R^2$).

The coefficient of determination between continuous and passive atmospheric concentrations for one week exposures was $R^2 = 0.449$ (n = 46), and for two week exposures was $R^2 = 0.590$ (n = 23).

Limiting analysis to sites with observations > 1 ppb; the relationship between continuous and passive atmospheric concentrations for one week exposures was $R^2 = 0.021$ (n = 12), and for two week exposures was $R^2 = 0.440$ (n = 4).

**The limited correspondence with continuous data is a concern.**

# 6 Co-Exposure Study

During 2012, triplicate passive samplers for Ormantine tubes, Willems badges and Radiello were co-exposured at three sites with continuous $SO_2$ samplers (Haul road, Riverlodge and Kitamaat village; see Figure 2), for exposure periods of 1, 2 and 4 weeks during the period 16 August–27 September (7 exposures). Further two sets of Radiello were exposed and analysed at Illinois University (ILL) and Maxxam Analytics (MAX).

The objective of the study was to evaluate [A] variability in triplicate samplers, [B] the performance of Radiello compared with other samplers and continuous samplers, the influence of exposure length, and [C] Maxxam analytical procedures.

[A] Variability in triplicate exposures: The variability (COV) was evaluated as the average across all stations and all exposures, the average for the high conentration site, and with increasing exposure length.

Average Variability in triplicate samplers across all sites and exposures:
- Ormantine tubes: Not evaluated as > 59% returned < DL.
- Willems badges: 7.2% (range 1.0–15.5%).
- Radiello (ILL): Not presented as three exposures were 'lost'.
- Radiello (MAX): 31.3% (range 5.8–93.7%).

Variability in triplicate samplers at the high concentration site (Haul road):
- Willems badges: 6.0% (range 2.7–9.6%)
- Radiello (MAX): 35.3% (range 5.8–93.7%)

Variability in triplicate samplers with exposure length (1, 2 and 4 weeks):
- Willems badges: 6.3%, 8.2% and 6.4%
- Radiello (MAX): 44.3%, 31.9% and 26.3%

[B] Passive against continuous $SO_2$ data: The amount measured on the passive membrane was compared (using linear regression) against cumulative $SO_2$ measured at the co-located continuous stations (see Figure 4). Note: continuous data for Haul road were not included as data were unavailable owing to equipment error. The loss of data for the high concentration site severely limited the assessment.

[C] Inter-laboratory comparison: Co-exposed sets of triplicate Radiello samplers were sent to Illinois and Maxxam (3 sites × 4 exposures). In addition, WMO standard QC solutions were supplied to both laboratories.

Comparison of measured concentrations between laboratories was good ($R^2 = 0.95$) owing to the gradient in atmospheric concentration; however, there was considerable scatter in the

data at lower concentrations. Further, maxxam had higher absolute difference for target WMO solutions compared with Illinois (9.0% compared with 0.6%).

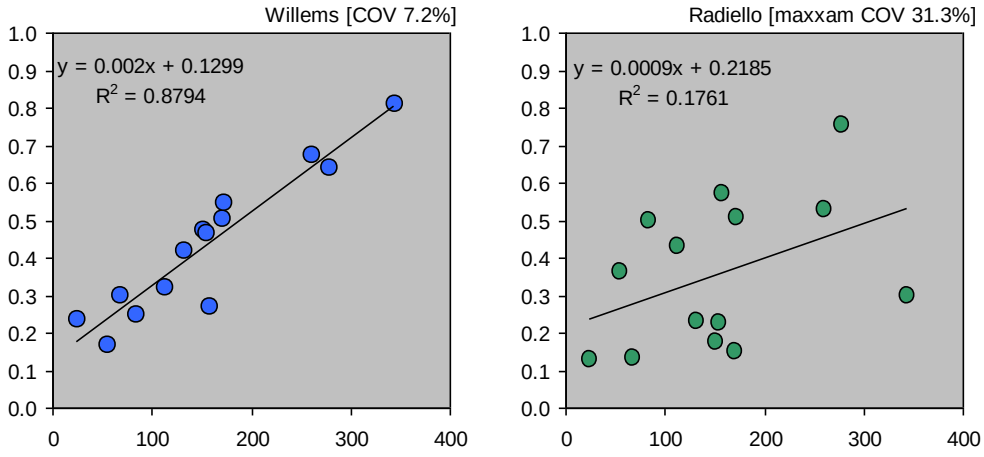



Figure 4. Comparison of cumulative continuous $SO_2$ (ppb [x-axis]) against amount on passive samplers (mg $L^{-1}$) for Willems badge and Radiello samplers.

# 7 Conclusions

There was a significant improvement in the number of data observations during 2012 (virtually no data flagged as <DL by Maxxam); however, variability in replicate exposures and the limited correspondence with continuous measurement is a concern (may be related to field and / or laboratory procedures, or regional suitability of TEA-based samplers).

Nonetheless, the data showed a consistent gradient in air concentrations associated with the plume, i.e., the 2012 summary statistics provides a 'reasonable' spatial ranking of atmospheric $SO_2$.

# 8 Recommendations

1. The network was heavily weighted to low concentration regions (related to previous human health focus); it is recommend that many of the 'urban' sites be moved to regions predicted to experience increases in air concentration (consistent with modelled plume);

2. Two week exposures show no loss in measurement accuracy; it is recommended that exposure duration is increased to two weeks (or greater), and replication is increased at sites;

3. Supplemental sampler exposure evaluation should be carried out to evaluate variability and sampler performance at high air concentrations;

4. As per manufacturer specifications, TEA-based Radiello samplers appear to be sensitive to high humidity and have a detection limit of < 1 ppb (weekly exposure). An alternative

(commercial) sampler is recommended for future monitoring, e.g., potassium or sodium carbonate (e.g., IVL or AGAT PAQS) or possibly Nylasorb based (e.g., Willems) samplers.