RioTinto

KMP SO_2 EEM Program – Technical Memo P03

Atmospheric Sulphur Dioxide
Passive Diffusive Sampler Network: 2015 Pilot Study Results

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Submitted September 2016

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1 Overview

A pilot study to evaluate the performance of passive sulphur dioxide (SO_2) samplers against active (continuous) SO_2 monitors was proposed under the Environmental Effects Monitoring (EEM) program prior to re-establishment of a passive sampler network (see Technical Memo P02: Passive Diffusive Sampler Network: Pilot Study, March 2015).

Passive samplers will be deemed effective, i.e., reliable for network deployment, if they exhibit: (a) a high correlation with continuous SO_2 monitors (e.g., $r \geq 0.8$), and (b) low variability between replicate exposures.

Passive samplers were co-deployed across three monitoring stations (reflecting a gradient in SO_2 air concentrations) during summer 2015. This memo briefly describes the results of the pilot study.

2 Study Design

The objective of the pilot study was to evaluate the performance of passive diffusive SO_2 samplers against continuous SO_2 monitors across a gradient in air concentrations. Specifically, the pilot study evaluated the performance of two commercial samplers (with carbonate-based membrane coatings; see Technical Memo P02) and the variability in replicate exposures.

Passive samplers can be used to provide empirical observations of atmospheric SO_2 concentrations to (a) assess spatial and temporal changes, (b) evaluate modelled concentration fields, and (c) estimate dry deposition of SO_2 (see Technical Memo P01 and P02).

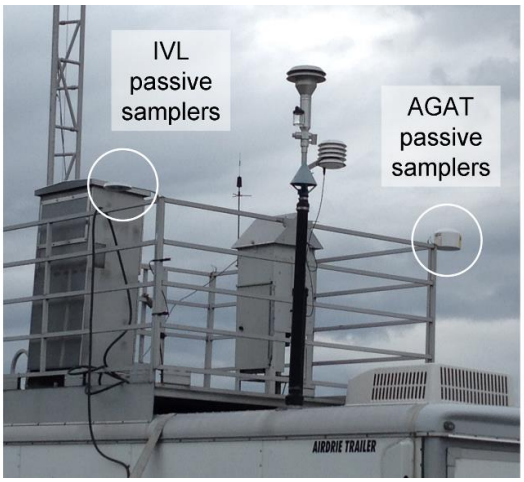

Figure 1. Deployment of passive diffusive samplers (obtained from IVL and AGAT) at continuous sulphur dioxide monitoring station. For further details on passive samplers see: IVL: www.diffusivesampling.ivl.se, and AGAT Laboratories: www.agatlabs.com/energy/air-quality-monitoring/passive-monitoring.cfm.

The pilot study was carried out between 24 July and 16 October 2015 (12 weeks). Two commercial samplers with carbonate-based membrane coatings (IVL and AGAT) were co-located with continuous samplers (Figure 1) at three monitoring stations (Figure 2) spanning a gradient in

atmospheric SO_2 (Kitimat Smeltersite [KMP], Haul Road and Riverlodge [highest to lowest SO_2]). Passive samplers were deployed in duplicate at each station for two-week and four-week exposures to evaluate the effect of exposure length on sampler performance. The pilot study included six two-week and three four-week deployments (see Table 1). The study period covered two seasons, summer and autumn, reflecting a range in temperature (Table 1). While temperature (as a surrogate of photochemical activity) plays a dominant role in the atmospheric chemistry of SO_2, given the proximity of the emissions source, aluminium production is the dominant driver of variability in atmospheric SO_2 in the region.

The deployment and collection of passive samplers was carried out by WSP (Jim Young). Following deployment all samplers were returned to their respective manufacturer (or supplier) for analysis.

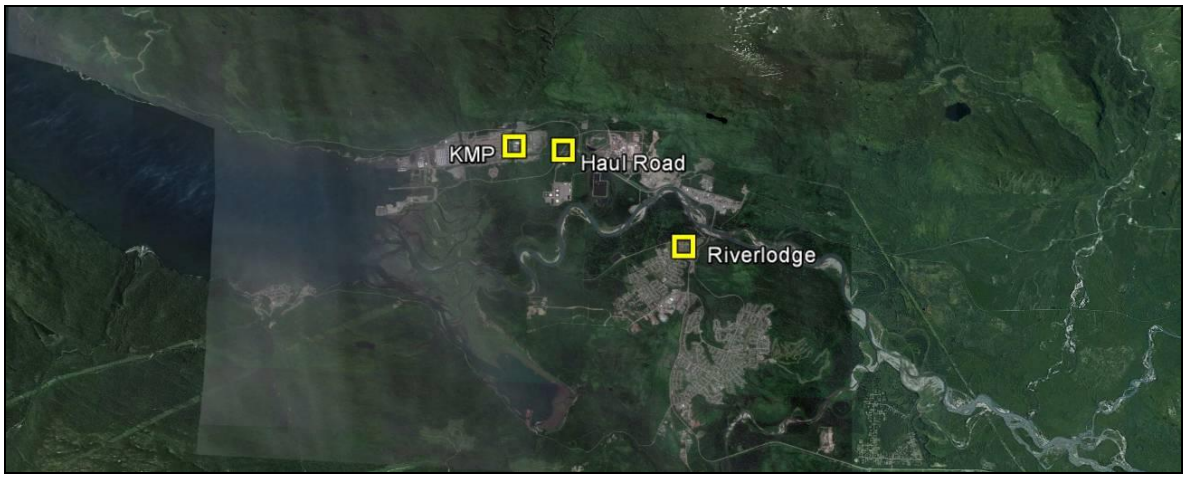

Figure 2. Location of continuous sulphur dioxide monitoring stations with co-deployment of passive samplers during the 2015 pilot study. Kitimat Smeltersite [KMP] (latitude: 54.01951, longitude: –128.70257, elevation: 2), Haul Road (latitude: 54.02919, longitude: –128.70269, elevation: 11) and Riverlodge (latitude: 54.05389, longitude: –128.67144, elevation: 18).

Table 1. Deployment number and date for the two-week and four-week passive sampler exposures. The average air temperature at the Kitimat Smeltersite and Riverlodge stations is also shown.

Exposure	Deployment #	Deployment date (dd/mm/yyyy)	Temperature (°C)	
			Kitimat Smeltersite	Riverlodge
Two-week	1	24/07/2015	15.9	15.2
	2	07/08/2015	17.2	16.5
	3	21/08/2015	13.4	12.7
	4	08/09/2015	12.3	11.1
	5	18/09/2015	10.5	8.8
	6	02/10/2015	10.1	7.9
Four-week	1	24/07/2015	16.5	15.8
	2	21/08/2015	12.8	11.9
	3	18/09/2015	10.3	8.4

3 Results

Average SO_2 concentrations during the study period (24 July–16 October) measured by the active monitors ranged from 0.3 ppb (Riverlodge) to 3.1 ppb (Smeltersite), with ambient concentrations approximately five times higher at Haul Road compared with Riverlodge, and eight times higher at Smeltersite compared to Riverlodge (Tables 2 and 3). In general, concentrations were higher during the summer months (July and August), with higher temperatures (Figure 1, Tables 1 and 2).

Average SO_2 estimated by the passive samplers (IVL and AGAT) during the study period showed a similar range in air concentrations ranging from 0.2 [0.2] ppb (AGAT [IVL] Riverlodge) to 2.8 [3.1] ppb (AGAT [IVL] Smeltersite). Moreover, average SO_2 estimated by the passive samplers showed a strong linear relationship with the active data during both two-week (IVL R^2 = 0.99; AGAT R^2 = 0.98) and four-week (IVL R^2 = 0.99; AGAT R^2 = 0.98) exposures (Figure 4).

While IVL and AGAT passive samplers showed a strong linear relationship to the active data, the difference between replicate samplers was lower for IVL, notably lower for the four-week exposures (see Tables 2 and 3). In addition, the majority of observations at Riverlodge were at the limit detection (0.2 ppb) or below detection for the AGAT samplers (5 of 9 observations were returned as < 0.2 ppb; Table 2 and 3). Overall the two-week and four-week exposures showed a similar relationship to the active data but four-week exposures had a lower difference between replicates and lower difference (%) between active and passive air concentrations (for Smeltersite and Haul Road).

The pilot study was carried out during a period of very low (aluminium production and) emissions under the Kitimat modernisation project. The low emissions resulted in low atmospheric SO_2 concentrations, which was a challenge for the passive samplers. In concert, the proportional (%) variability between replicate samplers under low atmospheric SO_2 concentrations was high, despite their very low absolute difference. However, as SO_2 emissions increase post-modernisation, the level of detection and variation between replicates will improve (for both samplers).

4 Conclusion

Passive samplers showed a strong linear relationship with the active data for ambient SO_2. However, the IVL samplers showed a slightly better relationship, with a lower variation between replicates and lower difference between passive and active observations compared with AGAT samplers (more so for four-week exposures). More importantly, the majority of observations at Riverlodge were below detection for the AGAT samplers. However, the low atmospheric concentrations (< 0.5 ppb) at Riverlodge were also a challenge for the IVL samplers.

It should be noted that the pilot study was carried out during a period of low SO_2 emissions; as emissions (and atmospheric concentrations of SO_2) increase the performance of passive samplers will improve (as evidence by passive sampler performance across the atmospheric concentration gradient in the pilot study). Similarly, under the plume (with elevated atmospheric SO_2 concentrations), the performance of samplers will improve, allowing for the delineation of the areas more likely to influenced by SO_2 emissions. As aluminium production and emissions increase post-modernisation, passive diffusive samplers will provide reliable empirical observations of atmospheric SO_2 concentrations to (a) assess spatial and temporal changes, (b) evaluate modelled concentration fields, and (c) estimate dry deposition of SO_2.

5 Recommendations

It is recommend that the passive SO_2 network use the IVL samplers with an exposure period of one month (noting that regions with atmospheric concentrations < 0.5 SO_2 ppb will show greater variability between replicates, and higher uncertainty against active measurements).

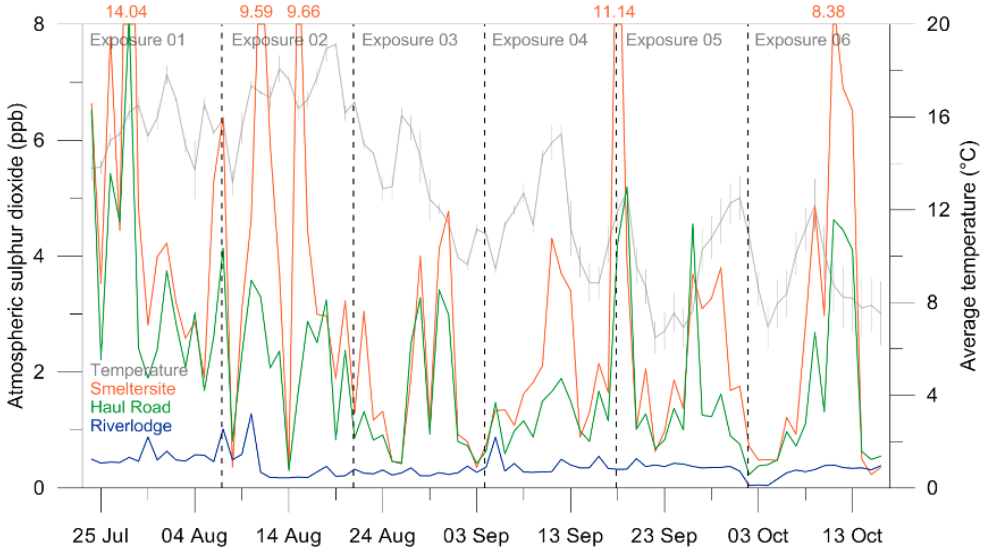

Figure 3. Daily ambient atmospheric sulphur dioxide (ppb) measured at Kitimat Smeltersite (orange), Haul Road (green) and Riverlodge (blue) during the period 24 July–16 October 2015. The average air temperature at Kitimat Smeltersite and Riverlodge is also shown (grey) with daily variation between the stations indicated by the vertical lines.

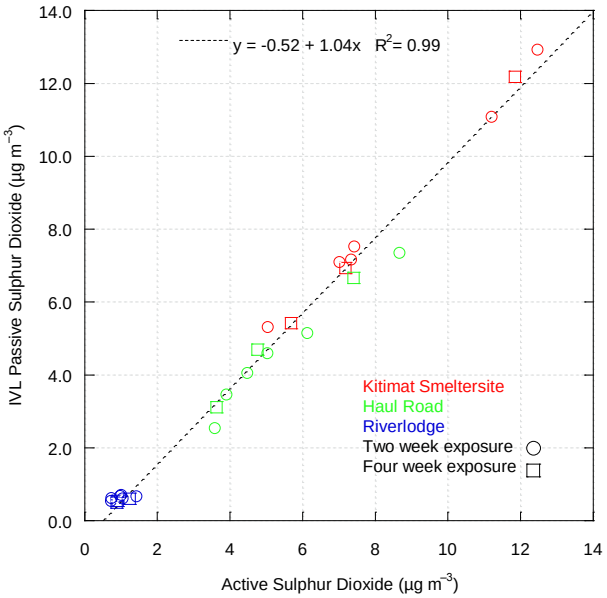

Figure 4. Comparison of IVL passive diffusive samplers for sulphur dioxide against continuous measurements at Kitimat Smeltersite (red), Haul Road (green) and Riverlodge (blue) during 24 July–16 October 2015. Passive samplers were deployed in duplicate at each stations for two-week (open circle) and four-week (open square) exposures.

Table 2. Average ambient sulphur dioxide (ppb) during two-week exposures for active (ACT) and passive (IVL and AGAT) samplers co-deployed at three stations (Kitimat Smeltersite, Haul Road and Riverlodge). See Table 1 for deployment dates. The difference (%) in replicate (n = 2) passive samplers and the difference (%) between active and passive samplers is also given.

Station	Deployment	Sulphur dioxide (ppb)			Replicates (%)		Active (%)	
		ACT	IVL	AGAT	IVL	AGAT	IVL	AGAT
Smeltersite	1	4.62	4.73	4.65	5.5	10.8	2.4	0.7
	2	4.17	4.10	3.75	0.5	2.7	1.8	10.1
	3	1.85	1.96	1.75	3.9	17.1	5.6	5.5
	4	2.72	2.72	2.20	3.1	9.1	0.0	19.0
	5	2.55	2.58	2.15	3.2	14.0	1.1	15.7
	6	2.66	2.62	2.00	2.6	0.0	1.7	24.9
Haul Road	1	3.21	2.69	2.60	17.0	30.8	16.1	18.9
	2	2.28	1.90	1.85	11.6	5.4	16.7	18.9
	3	1.43	1.27	1.10	9.2	18.2	11.3	23.3
	4	1.31	0.92	0.70	13.4	0.0	30.2	46.6
	5	1.82	1.66	1.30	12.4	15.4	8.8	28.7
	6	1.62	1.47	1.20	4.7	0.0	9.2	26.0
Riverlodge	1	0.53	0.24	0.20	0.0	0.0	54.0	62.0
	2	0.39	0.22	0.30	20.9	0.0	42.3	22.8
	3	0.27	0.23	0.20	3.2	0.0	16.5	26.0
	4	0.36	0.24	<0.2	35.4	–	32.2	–
	5	0.37	0.25	<0.2	13.7	–	31.5	–
	6	0.26	0.20	<0.2	0.0	–	26.0	–

Table 3. Average ambient sulphur dioxide (ppb) during four-week exposures for active (ACT) and passive (IVL and AGAT) samplers co-deployed at three stations (Kitimat Smeltersite, Haul Road and Riverlodge). See Table 1 for deployment dates. The difference (%) in replicate (n = 2) passive samplers and the difference (%) between active and passive samplers is also given.

Station	Deployment	Sulphur dioxide (ppb)			Replicates (%)		Active (%)	
		ACT	IVL	AGAT	IVL	AGAT	IVL	AGAT
Smeltersite	1	4.40	4.50	4.35	6.2	6.9	2.3	0.5
	2	2.08	1.97	1.90	8.5	10.5	5.3	4.5
	3	2.61	2.49	2.40	2.9	8.3	4.6	4.1
Haul Road	1	2.74	2.46	2.40	0.3	33.3	10.4	6.7
	2	1.33	1.13	0.95	3.9	10.5	15.2	16.6
	3	1.72	1.68	1.40	4.8	14.3	2.6	10.3
Riverlodge	1	0.46	0.22	0.20	6.1	0.0	51.4	39.2
	2	0.33	0.20	<0.2	5.1	–	40.6	–
	3	0.32	0.18	<0.2	5.9	–	44.3	–