RioTinto

KMP SO_2 EEM Program – Technical Memo F01

Atmospheric Sulphur

Filter Pack Measurements of Particulate Sulphate

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1 Overview

The total deposition of atmospheric sulphur is an essential informative indictor under the Environmental Effects Monitoring (EEM) program (ESSA et al., 2014).

Total deposition refers to the deposition of both wet and dry atmospheric sulphur species. Dry deposition is derived from empirical observations of gaseous and particulate sulphur, i.e., sulphur dioxide (SO_2) and particulate sulphate (pSO_4^{2-}), respectively. Under the EEM, SO_2 and pSO_4^{2-} will be measured using a two-stage filter pack during several discrete campaigns throughout the Kitimat valley. These observations will be used to asses the dominance of pSO_4^{2-} in the region.

This technical memo briefly describes the measurement of pSO_4^{2-} in the Kitimat valley under the EEM during 2017.

2 Study Design

Measurements of particulate and gaseous sulphur can be made using a filter pack system, i.e., a filter holder with successive stages of filters connected to an air flow system (Figure 1). A two-stage filter pack consists of a membrane filter and a hydroxide impregnated filter; particulates are collected on the first filter, and gaseous pollutants on the second. The filter pack is protected from rain by a shelter (Figure 1). Filter pack systems are widely used as they provide reliable measurements of pSO_4^{2-} and SO_2, and are less demanding that alternative methods (NILU, 2001).

The two-stage filter holders were developed by the Norwegian Institute for Air Research (URL: www.innovationnilu.com). The first stage holds a 47 mm Teflon (PTFE) filter to capture particulates, and the second stage holds a 47 mm cellulose filter impregnated with potassium hydroxide to capture SO_2. The holder is connected to a diaphragm pump with a recommend flow rate of 15 L min^{-1} for daily sampling. The filter system, filter preparation, extraction and analysis are described in detail in the 'EMEP Manual for Sampling and Chemical Analysis' (NILU, 2001).

During June and October 2017, filter packs were deployed at Haul Road, Riverlodge, Whitesail and Lakelse Lake monitoring stations to measure daily concentrations of pSO_4^{2-} and SO_2. Site selection was limited to locations with access to power; during 10–20 June, one filter pack was rotated between three locations (Haul Road, Riverlodge, and Lakelse Lake). However, during 21–27 October 2017, four filter packs were operated in parallel across the four stations (using pumps provided by WSP).

3 Results

A total of 29 filter pack measurements were carried during 2017; 9 measurements were carried out between 10–20 June, and 20 measurements between 21–27 October (see Appendix A Table A1). The PTFE filter (first stage) was analysed for range of particulate species including sulphate (SO_4^{2-}) and trace elements (aluminium [Al], lithium [Li], nickel [Ni]

and vanadium [V]), and the impregnated filter (second stage) was analysed for major anions including SO_4^{2-} (as a measure of atmospheric SO_2).

Average SO_2 ranged from 0.5 to 10.6 µg m^{-3}, and pSO_4^{2-} ranged from 0.06 to 0.20 µg m^{-3} (Table 1). Atmospheric sulphur species (SO_2 and pSO_4^{2-}) showed the same gradient across the measurement locations; the highest average concentrations were observed at Haul Road and lowest at Lakelse Lake (measurements at Whitesail were carried out only during October, which was heavily influenced high rainfall volumes). To evaluate the performance (reliability) of the filter packs, daily measurements SO_2 (filter pack) were compared with continuous hourly measurements (average to daily observations) at the active monitoring stations (Figure 2). In general, there was good correspondence between filter pack and active daily measurements of SO_2 ($R^2 = 0.93$).

The oxidation of SO_2 to pSO_4^{2-}, which is a secondary pollutant, determines the lifetime of sulphur in the atmosphere. The relative mass ratio of pSO_4^{2-} to total atmospheric sulphur may be used as an indicator of the rate of conversion, e.g., sulphur conversion ratio (see Equation 1). The average sulphur conversion ratio (F_s) showed an opposite gradient to concentration; at Haul Road F_s = 2%, compared with 9% at Riverlodge and Whitesail, and 14% at Lakelse Lake (Table 1), which indicates that pSO_4^{2-} has a longer atmospheric lifetime than SO_2.

$$Sulphur\ conversion\ ratio\ (F_s) = \frac{pSO_4^{2-}}{SO_2 + pSO_4^{2-}} \qquad \text{(Equation 1)}$$

Average SO_2 and pSO_4^{2-} were strongly correlated (r = 0.92), similarly pSO_4^{2-} was strongly correlated to trace elements, e.g., Al (r = 0.91), Li (r = 0.97) and V (r = 0.92). The strong correlations suggest similar emission sources (Table 1).

Table 1. Average gaseous sulphur dioxide (SO_2), particulate sulphate (pSO_4^{2-}), sulphate conversion ratio (Fs), and particulate trace elements (aluminium [Al], lithium [Li], nickel [Ni] and vanadium [V]) during June and October 2017.

Site	n	SO_2	pSO_4^{2-}	F_s	Al	Li	Ni	V€
		µg m^{-3}		%	ng m^{-3}			
Haul Road	6	10.607	0.199	1.8	18.703	0.029	0.189	1.203
Riverlodge	9	1.178	0.120	9.2	3.794	0.019	0.083	0.079
Whitesail$	6	0.535	0.055	9.3	3.057	0.012	0.145	0.002
Lakelse Lake	8	0.586	0.092	13.6	2.853	0.012	0.089	0.099

$ Whitesail only has October observations; € During October 2017 all observations of V were below detection at Lakelse Lake, and all but one were below detection at Whitesail (<DL set to 0.0005 ng m^{-3}).

4 Conclusion

Gaseous SO_2 and pSO_4^{2-} displayed a similar gradient across the measurement stations; the highest concentrations were observed at Haul Road and lowest at Lakelse Lake. However, sulphur conversion ratios (%) show an inverse relationship. ranging from 2% at Haul Road to 14% at Lakelse Lake indicating a longer atmospheric lifetime for pSO_4^{2-} compared to SO_2.

The 2017 results demonstrate the ability of the filter pack samplers to provide reliable measurements of particulate and gaseous air pollutants. Further measurement campaigns are

planned for February and June 2018; portable filter packs will be utilised during June 2018 to expand the measurements to seven sites across the Kitimat valley, with the objective to assess the sulphur conversion ratio along the plume path.

5 Literature Cited

ESSA Technologies, J. Laurence, Limnotek, Risk Sciences International, Trent University, and Trinity Consultants. 2014. Sulphur Dioxide Environmental Effects Monitoring Program for the Kitimat Modernization Project. Program Plan for 2013 to 2018. Prepared for Rio Tinto BC Works, Kitimat, BC. 99 pp.

NILU 2001. EMEP manual for sampling and chemical analysis. Norwegian Institute for Air Research, EMEP/CCC-Report 1/95 (Revision: November 2001).

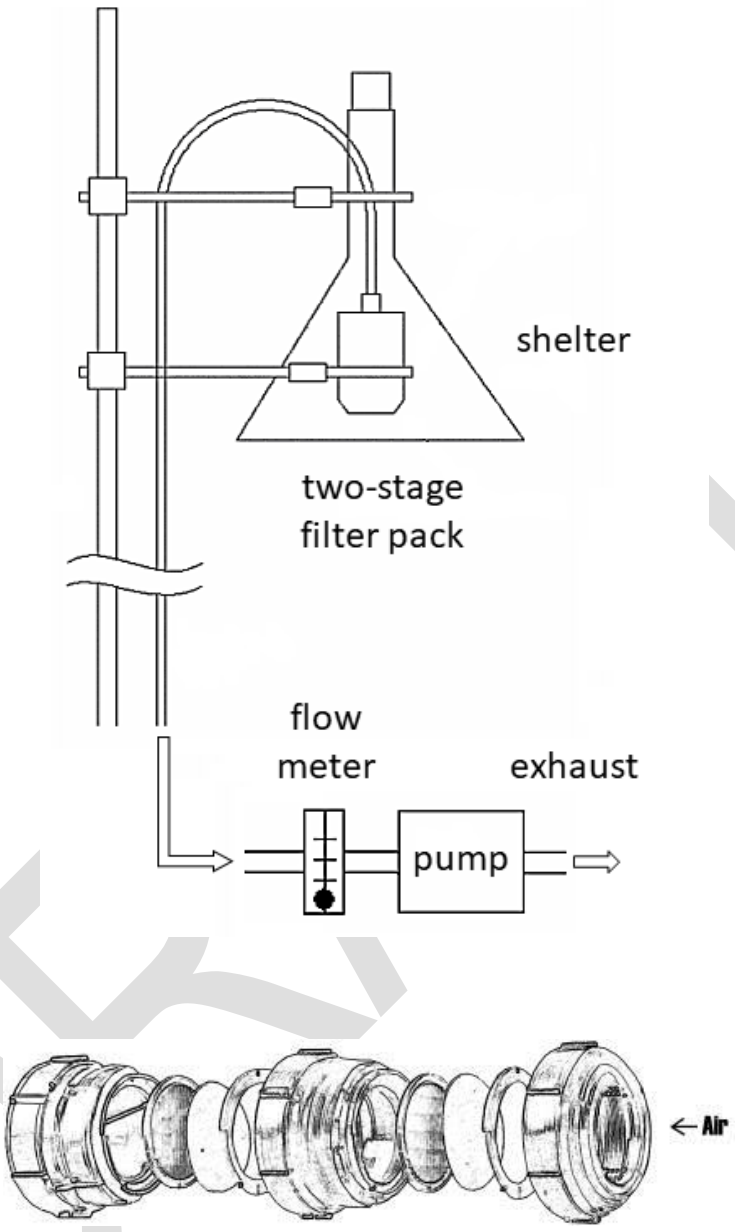

Figure 1. Upper panel: Filter pack sampling system, with NILU filter holder, shelter, inline flow meter and pump. Lower panel: Two-stage NILU filter holder showing an exploded view of the individual components (see Appendix A Figure A1 for details on holder components).

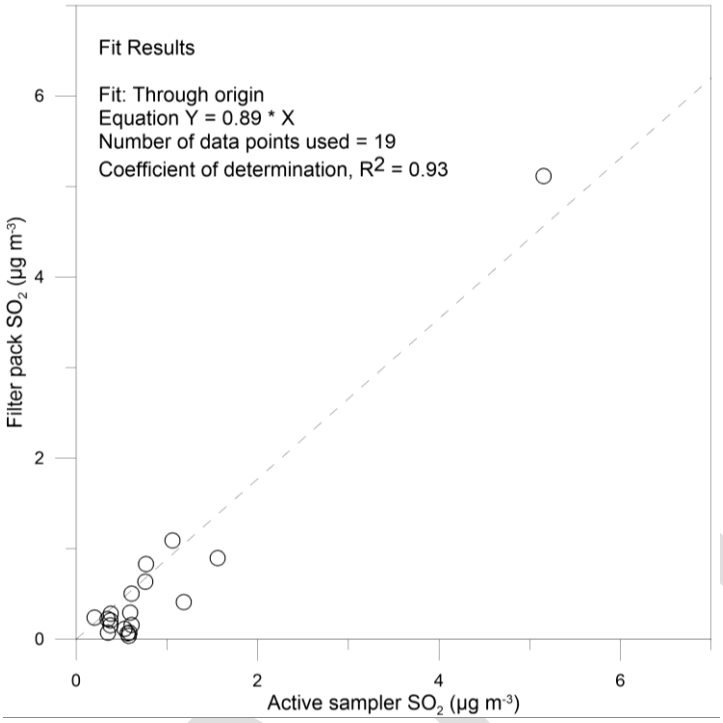

Figure 2. Comparison of active sulphur dioxide (SO_2) against filter pack measurements (µg m^{-3}) at Haul Road, Riverlodge and Whitesail during June and October 2017. Filter pack samplers were exposed at each station for one day (see Appendix A Table A1 for exposure dates). The scatter plot includes a linear regression of active against filter pack (R^2 = 0.93).

Appendix A.

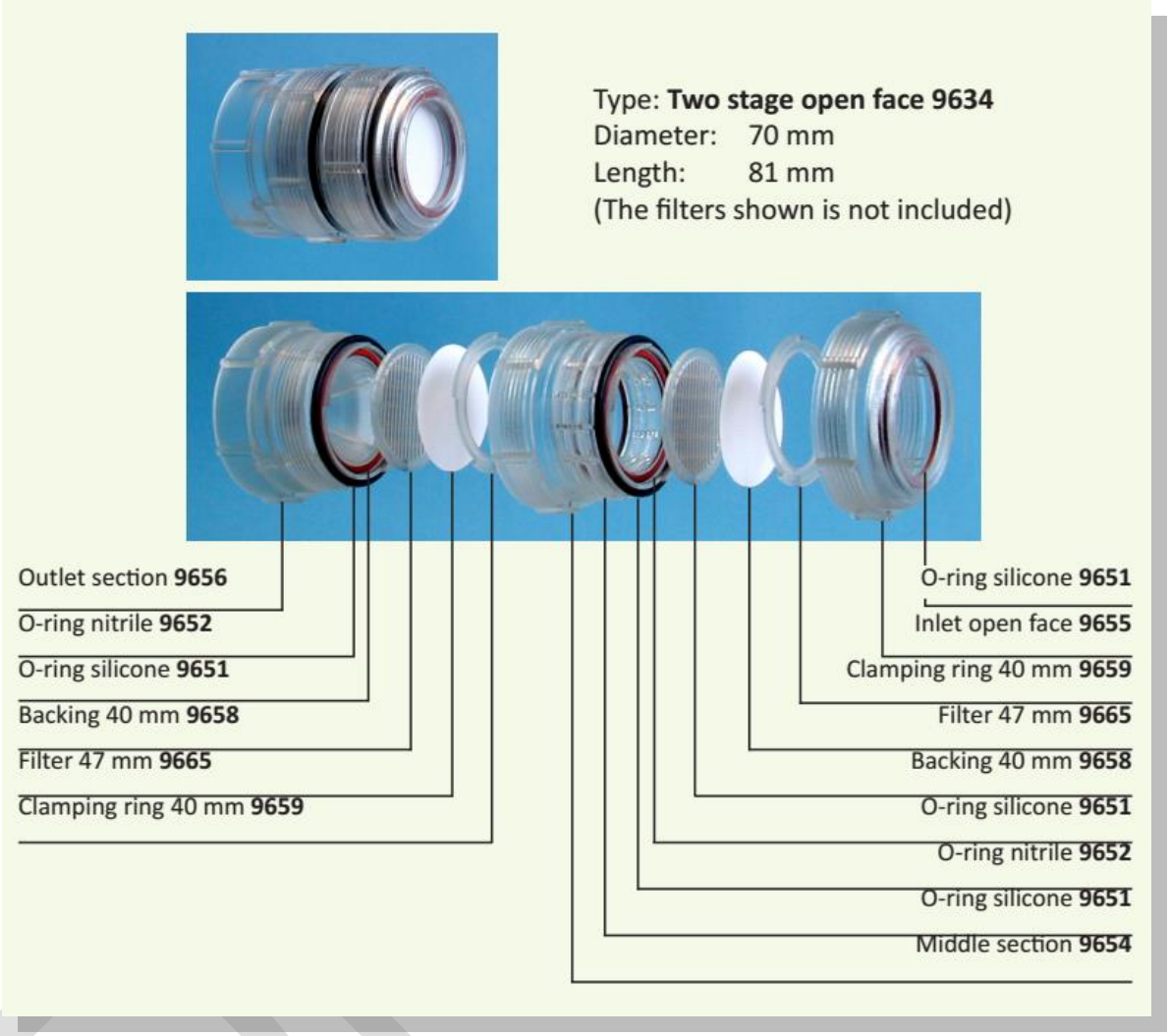

Figure A1. Two-stage open face NILU filter holder system (URL: www.innovationnilu.com).

Table A1. Daily concentrations (µg m^{-3}) of particulate sulphate (pSO_4^{2-}), gaseous sulphur dioxide (SO_2), and the sulphate conversion ratio (F_s) from filter pack measurements during June (n = 3) and October (n = 3–6) 2017.

Site	Start Date yyyy-mm-dd	pSO_4^{2-} µg m^{-3}	SO_2 µg m^{-3}	F_s ratio
Haul Road	2017-06-12	0.319	23.069	0.01
Haul Road	2017-06-13	0.254	14.431	0.02
Haul Road	2017-06-14	0.180	2.534	0.07
Haul Road	2017-10-24	0.230	22.119	0.01
Haul Road	2017-10-25	0.079	1.162	0.06
Haul Road	2017-10-26	0.130	0.327	0.28
Lakelse Lake	2017-06-10	0.134	0.958	0.12
Lakelse Lake	2017-06-18	0.285	1.164	0.20
Lakelse Lake	2017-06-19	0.237	1.112	0.18
Lakelse Lake	2017-10-21	.	0.248	.
Lakelse Lake	2017-10-22	0.059	0.253	0.19
Lakelse Lake	2017-10-23	0.008	0.451	0.02
Lakelse Lake	2017-10-24	.	0.339	.
Lakelse Lake	2017-10-25	.	0.159	.
Riverlodge	2017-06-15	0.116	0.686	0.14
Riverlodge	2017-06-16	0.221	0.801	0.22
Riverlodge	2017-06-17	0.256	3.080	0.08
Riverlodge	2017-10-21	0.050	0.637	0.07
Riverlodge	2017-10-22	0.190	0.591	0.24
Riverlodge	2017-10-23	0.094	0.439	0.18
Riverlodge	2017-10-24	0.036	1.800	0.02
Riverlodge	2017-10-25	0.114	2.353	0.05
Riverlodge	2017-10-26	.	0.215	.
Whitesail	2017-10-21	0.030	0.208	0.13
Whitesail	2017-10-22	0.136	0.833	0.14
Whitesail	2017-10-23	.	0.453	.
Whitesail	2017-10-24	0.012	0.183	0.06
Whitesail	2017-10-25	0.134	1.424	0.09
Whitesail	2017-10-26	0.014	0.106	0.11