

Effects of process changes on concentrations of individual malodorous sulphur compounds in ambient air near a Kraft pulp plant in Thunder Bay, Ontario, Canada

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Abstract

Ambient air samples were collected at several locations in the community around a major Canadian pulp and paper plant over a period of several months, before and after major process changes. These changes, which occurred in the spring of 2006, included the closure of one of two Kraft pulp mills on site and the shutting down of a chemical recovery boiler and associated black liquor oxidation systems. The facility currently operates one Kraft mill producing both hardwood and softwood market pulp and a two machine paper mill with thermomechanical and deinking pulp mills. All ambient air samples were collected downwind from the plant in Teflon bags and analyzed for volatile reduced sulphur compounds using a gas chromatograph equipped with a pulsed flame photometric detector and a cryogenic trapping system. The frequency distributions of the concentrations of hydrogen sulphide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulphide (DMS), and dimethyl disulphide (DMDS) were compared before and after the process changes. DMS was found to be the most abundant reduced sulphur compound in ambient air before the changes with an average concentration of 1.49 ppbv. After the changes, the average concentrations of CH_3SH , DMS, and DMDS decreased by 28, 70, and 58%, respectively. The concentration of H_2S was below its detection limit of 0.90 ppbv in most of the samples collected both before and after the process changes.

Keywords: reduced sulphur compounds, Kraft pulp mill, odour, pulsed flame photometric detector, gas chromatography, cryogenic trap, hydrogen sulphide, methyl mercaptan, dimethyl sulphide, dimethyl disulphide.



1 Introduction

The Bowater plant located in Thunder Bay, Ontario, Canada includes both newsprint and Kraft pulp manufacturing facilities. Before 3 May 2006, two Kraft pulp mills ("A" mill and "B" mill) produced a combination of hardwood and softwood elemental chlorine free bleached market pulp. The chemical recovery process utilized two recovery boilers ("B" and "C") and two lime kilns ("A" and "B"). On 3 May 2006, the "A" Kraft mill, which included the "B" recovery boiler and the "A" lime kiln, was shut down.

Since 1994, the plant has invested in several air improvement initiatives to reduce total reduced sulphur (TRS) and particulate emissions, including:

- i. installation of scrubbers and electrostatic precipitators on the bark boilers (1994/1996),
- ii. improvements to the "B" Recovery Boiler (1995/99/02),
- iii. upgrades to the bleach and chemical plant scrubbers (2001/03),
- iv. removal of the old "A" recovery boiler (2001),
- v. construction of new low odour "C" recovery boiler utilizing 3 levels of combustion air to ensure complete combustion of the black liquor and a non-contact evaporation system to evaporate water from the liquor prior to burning (2001),
- vi. discontinuation of weak black liquor oxidation system (2003) and replacement with a total heat recovery (THR) system where pure oxygen is used to more efficiently converting the sulfide in black liquor to thiosulfate and thus raise the heating value of the black liquor prior to burning in the recovery boiler,
- vii. replacement of wet scrubbers on the "A" and "B" lime kilns with electrostatic precipitators (2004), and
- viii. installation of a dilute non-condensable gas (DNCG) system to collect, concentrate, and incinerate reduced sulfur gases emitted from roof top tank vents and chip bin exhausts (2004).

Four reduced sulfur compounds, i.e. hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS) emitted from kraft pulp mills are mainly responsible for odour problems. These compounds are collectively designated as Total Reduced Sulphur (TRS). The odour threshold for TRS compounds are very low: 0.41 ppbv for H_2S , 0.07 ppbv for CH_3SH , 3.0 ppbv for DMS, and 2.2 ppbv for DMDS, where ppbv refers to parts per billion on a volume basis [1].

The TRS concentration is defined as the sum of the sulphur contributions from the four individual TRS compounds:

$$C_{TRS} = C_{H_2S} + C_{CH_3SH} + C_{DMS} + 2C_{DMDS} \quad (1)$$

where C refers to concentration on a volume or molar basis. Under the ambient air quality criteria (AAQC) in Ontario, the limit on 1-hour average TRS concentration is 40 mg/m³ as H_2S [2], which corresponds to a TRS volume concentration of 27 ppbv. TRS compounds normally present no health hazard to humans, except at very high concentrations.



The determination of reduced sulphur compounds is complicated by their high reactivity, which can result in severe losses during sampling and analysis. The materials that come in contact with the samples must be inert toward sulphur compounds to minimize these losses.

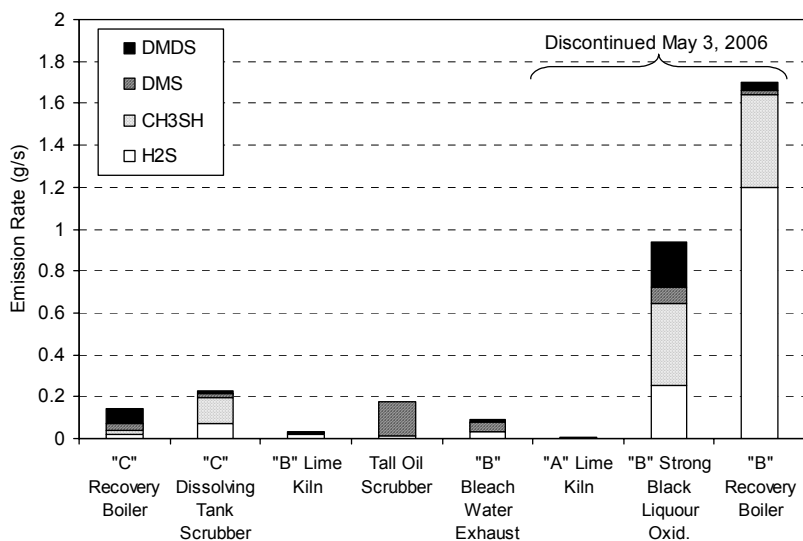


Figure 1: Summary of main TRS sources for Bowater facilities [3].

Table 1: Annual emissions of TRS compounds for the entire Bowater plant.

	H ₂ S	CH ₃ SH	DMS	DMDS
Emissions (kg/yr)				
- Before 3 May 2006	47,939	29,478	6,262	10,999
- After 3 May 2006	4,351	4,422	3,359	3,039
Percent Reduction	91%	85 %	46%	72%

1.1 TRS emissions inventory

Figure 1 shows the emission rates of TRS compounds in g/s from the major individual point sources at the Bowater plant measured in September 2005 [3]. All sources operate between 94 and 98% of the time, except for the tall oil scrubber, which only emits 8% of the time. The "B" Recovery Boiler and the B Strong Black Liquor oxidation unit were by far the largest sources of TRS compounds before 3 May 2006. However, these sources were discontinued with

the shut-down of the "A" Kraft mill on 3 May 2006. Annual emissions of TRS compounds in kg/year for the entire plant before and after 3 May 2006 are reported in Table 1. The operating times of each source were taken into account to calculate annual emissions. The emissions of H_2S and CH_3SH were the most affected by the closure of the "A" Kraft mill, with reductions of 90.9% and 85%, respectively. Emissions of DMS and DMDS were also reduced by 46.4 and 72.4%, respectively.

1.2 Objectives

This paper reports the results of analysis of TRS compounds in ambient air samples collected before and after 3 May 2006 downwind of the plant main stack. The effects of the "A" Kraft mill shutdown on the concentrations of individual TRS compounds in ambient air are quantified. The changes in ambient air concentrations are then compared with changes in TRS emission rates from the plant.

2 Methods

2.1 Air sampling methods

Ambient air samples were collected in the community surrounding the Bowater plant outside the plant boundaries from 5 April to 14 September 2006. Before the shutdown of the "A" Kraft mill, a total of 18 samples were collected on 9 different days between 5 April and 2 May 2006. After the shutdown of the "A" Kraft mill, 39 samples were collected on 21 different days between 23 May and 14 September 2006. On each sampling date, the sampling location was selected to be downwind from the plant main stack. All the sampling was done within a 2-km radius from the plant. Figure 2 shows a map of the 10 sampling locations that were used around the Bowater plant.

A schematic of the air sampling apparatus is shown in Figure 3. Ambient air is drawn through a 1/4-in OD Teflon sampling tube whose inlet is held at 2 m above the ground by pole mounted on a tripod. The Teflon tube is connected to one side of a Teflon port inserted through the wall of a 1450 Pelican case (Pelican Products, Torrance, California) having interior dimensions of 37.1 x 25.8 x 15.2 cm. The other side of the Teflon port is connected to a 2 L (23 cm x 23 cm) Teflon bag (Chromatographic Specialties, Brockville, Ontario) held inside the Pelican case. A second port on the Pelican case allows for connection to an SKC 224-44XR air-sampling pump (SKC Inc., Eighty Four, Pennsylvania) via Tygon tubing. Because the Pelican case is airtight, drawing air from the interior of the pelican case with the air sampling pump causes the Teflon bag to fill with ambient air drawn through the Teflon sampling tube. This set-up ensures that the sampled air only comes in contact with Teflon, which is inert towards reduced sulphur compounds. Each air sample was collected within a period of 4 min at a rate of 450 mL/min.



Figure 2: Aerial photograph of the Bowater plant and sampling locations.

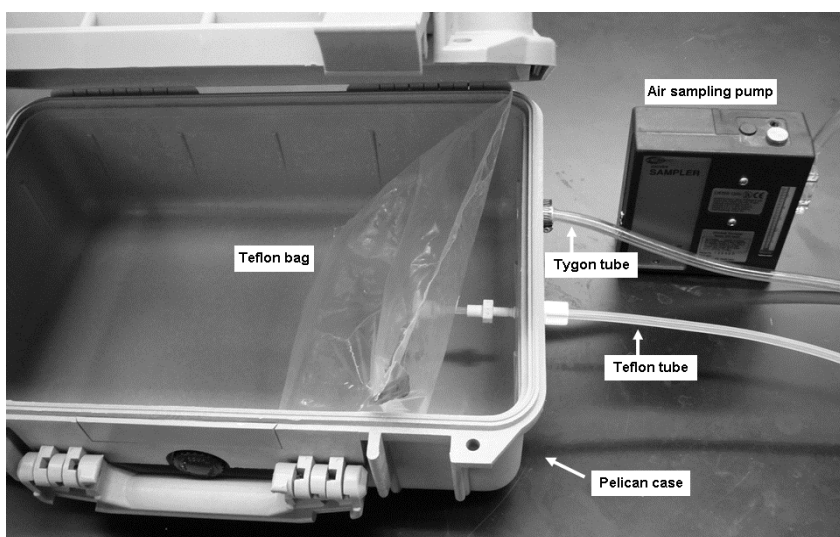


Figure 3: Schematic of air sampling apparatus.

During sampling, a portable meteorological station (Signal Weather Services, Dryden, Ontario) was used to monitor the wind speed, wind direction, temperature, and relative humidity at 1-minute intervals. Once an ambient air sample is collected, the Pelican case is opened, the valve of the Teflon sampling bag is closed, the bag is removed, and a new bag is installed for collecting the next air sample. After collection, the air samples were stored in an insulated cooler bag with cold packs for transportation to the laboratory. Upon arrival in the laboratory, the samples were transferred to a fridge and analyzed within 2 to 3 hours after collection. To minimize sampling costs, Teflon bags were re-used after flushing at least three times with ultra-high purity nitrogen gas. Tests were carried out to ensure that re-used bags did not introduce contamination in the new samples.

2.2 Analytical methods

The ambient air samples were analyzed by a trace level sulphur analyzer consisting of a gas chromatograph (Varian CP 3800, Palo Alto, California) equipped with a pulsed flame photometric detector (PFPD) and interfaced with a cryogenic trap (Lotus Consulting, Long Beach, California) for pre-concentration of ambient samples. Air samples were introduced in the Lotus preconcentrator by connecting the valve of the Teflon bag to the inlet port of the preconcentrator with a Teflon fitting. A mass flow controller located downstream of the cryogenic trap controlled the flow rate at which air was removed from the bag. For each analysis, a total volume of 210 mL of ambient air flowed through the trap. All the tubing that comes into contact with the air sample in the analytical equipment is treated with a silcosteel™ coating (Restek Corporation, Bellefonte, Pennsylvania) to prevent adsorption of active sulphur compounds. Details of the analytical system and calibration procedures can be found in Catalan [4]. The calibration was repeated every two weeks to ensure accuracy of the analytical results. The absolute instrument sensitivity (AIS) was determined to be 0.90 ppbv for H₂S, 0.51 ppbv for CH₃SH, 0.092 ppbv for DMS, and 0.009 ppbv for DMDS. The AIS is a reliable and conservative measure of detection limit for volatile sulphur compounds by GC-PFPD [5].

The stability of reduced sulphur compounds in the Teflon sampling bags was assessed by introducing a gas mixture containing 2.1 ppbv H₂S, 4.7 ppbv CH₃SH, 1.5 ppbv DMS, and 1.0 ppbv DMDS in a clean Teflon bag and then periodically withdrawing aliquots which were analyzed to monitor the changes in concentration with time. These initial concentrations were representative of concentrations measured in actual ambient air samples. Figure 4 shows the composition of the gas mixture as a function of time. Any change from the initial concentration is due to decomposition of TRS compounds in the gas phase or adsorption on the bag walls. The concentrations of all the TRS compounds remained within 10% of the initial concentrations for at least 3 hours after the Teflon bag was filled. CH₃SH exhibited the largest losses (-7% after 2.7 hours and -20% after 3.8 hours). By contrast, the concentration of DMDS was found to remain constant for more than 7 hours. Similar results were obtained when the initial concentrations were doubled. These results indicate that no significant



losses of TRS compounds from ambient air samples can be expected during the time that separated sample collection from analysis (< 3 hours).

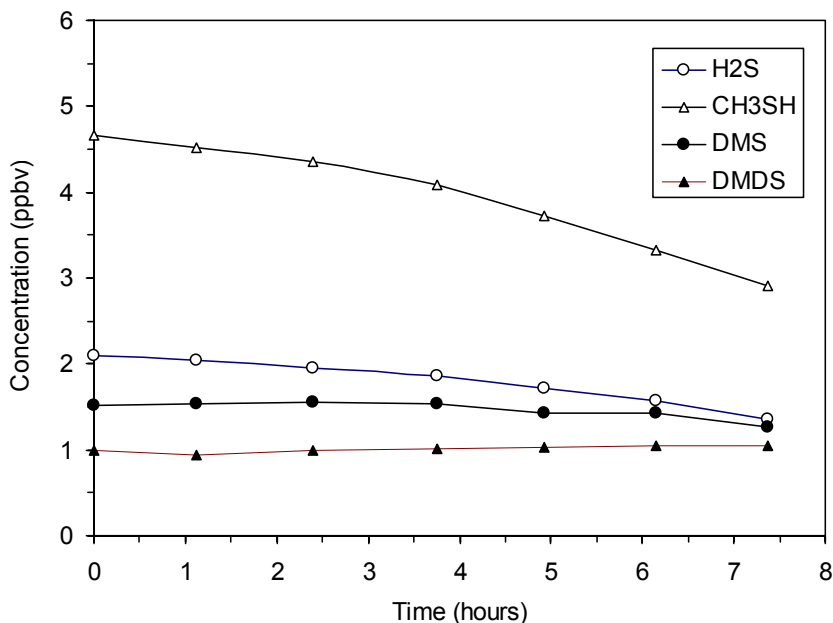


Figure 4: Stability of TRS compounds in Teflon sampling bag.

3 Results and discussion

Figures 5(a)–(d) show the frequency distributions of the concentrations of DMDS, DMS, CH₃SH, and H₂S, respectively. For each compound, two distributions corresponding to the data taken respectively before and after 3 May 2006 are shown. The *x*-axis represents the frequency of ambient air samples having a concentration greater than the stated values. For example, Figure 5(b) shows that 59% of the samples collected before 3 May 2006 had a DMS concentration greater than 1 ppbv, whereas only 12% of the samples collected after that date had a DMS concentration greater than 1 ppbv. Frequency distributions for DMS and DMDS concentrations consistently shifted toward lower concentrations after 3 May 2006 (Figures 5(a) and 5(b)), thus demonstrating the beneficial effect of the “A” Kraft mill shutdown on concentrations of DMS and DMDS in ambient air.

The frequency distributions for CH₃SH concentrations (Figure 5(c)) contain much fewer data points than those for DMS and DMDS. This is because CH₃SH was below the detection limit in most of the ambient air samples. Before 3 May 2006, CH₃SH was detected in only 35% of the samples. After that date, CH₃SH was detected in only one sample out of 39 samples. On the single occasion when

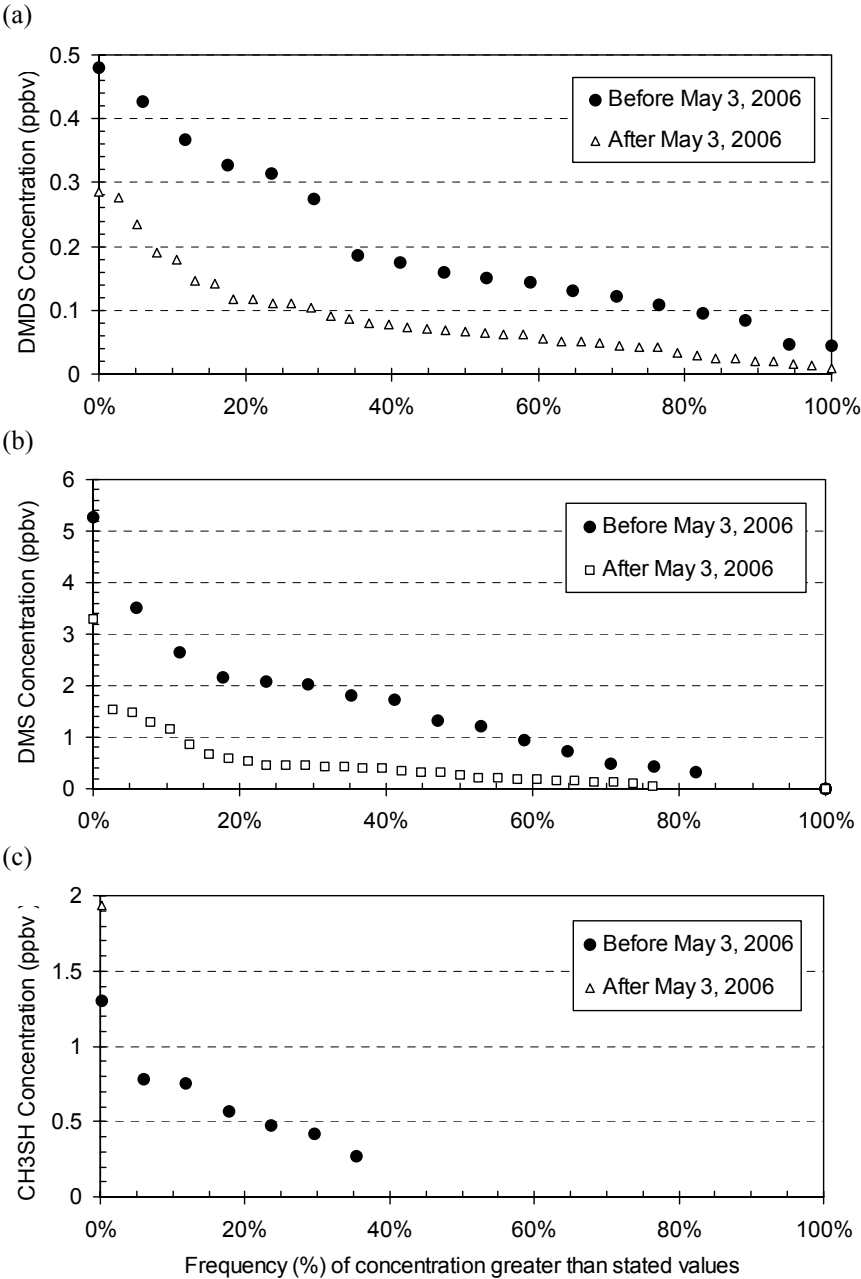


Figure 5: Frequency distributions of (a) DMDS, (b) DMS and (c) CH₃SH concentrations in ambient air samples.



(d)

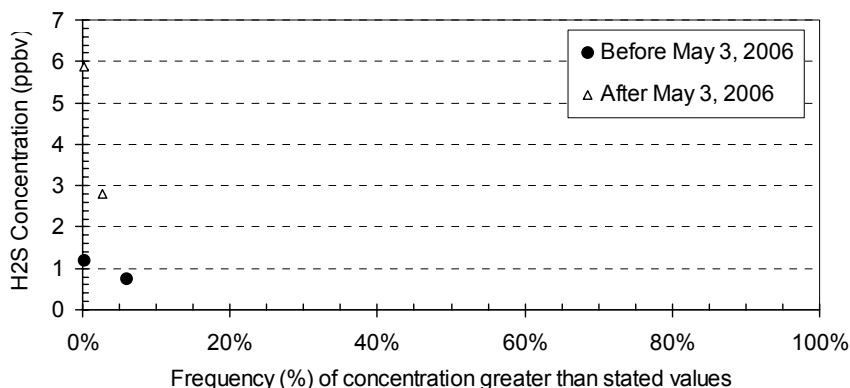


Figure 5 (cont'd): Frequency distributions of (d) H₂S concentrations in ambient air samples.

CH₃SH was detected (30 August at 2:21pm), its concentration was the highest that was recorded in the entire sampling campaign (1.94 ppbv). Overall, the “A” Kraft mill shutdown resulted in a large decrease in the frequency of detectable CH₃SH concentrations in ambient air samples. It is worth noting that on three occasions before 3 May 2006, CH₃SH was detected and quantified at levels below the reported absolute instrument sensitivity of 0.51 ppbv. This is because the AIS is calculated using an average root mean square (rms) noise evaluated over several chromatograms [5], whereas the actual rms noise for a particular chromatogram can be lower than the average rms noise, thus allowing measurement of the analyte below the reported AIS.

The frequency distributions for H₂S concentrations indicate that H₂S was only detected in two samples before and after 3 May 2006 (Figure 5(d)). On the two occasions when H₂S was detected after 3 May 2006, the H₂S concentrations (2.8 and 5.9 ppbv on 20 June at 3:52pm and 30 August at 2:21pm, respectively) were higher than concentrations detected before 3 May 2006. Therefore, the data for H₂S do not reveal a beneficial effect of the “A” Kraft mill shutdown on H₂S concentrations in ambient air. However, because more than 90% of the samples had undetectable H₂S concentrations, both before and after 3 May 2006, no reliable conclusion can be made about trends in H₂S concentrations.

For each TRS compound, Table 2 presents the average concentration before and after 3 May 2006, the percent change in average concentration resulting from the “A” kraft mill shutdown, and the confidence level that the difference in average concentrations is statistically different, as determined from a Student's *t*-test. Concentrations below the detection limit were arbitrarily assumed to be equal to half the AIS (i.e., 0.45 ppbv for H₂S, 0.25 ppbv for CH₃SH, and 0.046 ppbv for DMS) for the purpose of calculating average concentrations. This assumption greatly affected the average concentrations of H₂S and CH₃SH but had almost no effect on the average DMS and DMDS concentrations because

DMS was rarely below the detection limit and DMDS was always above the detection limit.

Table 2: Average concentrations of TRS compounds in ambient air before and after the shutdown of the “A” Kraft mill.

	H ₂ S	CH ₃ SH	DMS	DMDS
Before 3 May 2006	0.51	0.41	1.49	0.202
After 3 May 2006	0.65	0.29	0.45	0.086
Percent of Change	+27%	-28%	-70%	-58%
Confidence level (<i>t</i> -test)	62%	83%	99.4%	99.8%

DMS was the most abundant TRS compound before 3 May 2006 with an average concentration of 1.49 ppbv. The average DMS and DMDS concentrations in ambient air dropped respectively by 70% and 58% after the shutdown of the “A” Kraft mill. These drops are comparable to the declines in the emissions of these compounds from the plant (46% for DMS and 72% for DMDS, see Table 1). Moreover, the results of the Student’s *t*-test indicate that the shutdown of the “A” Kraft reduced the average concentrations of DMS and DMDS in ambient air with a confidence level larger than 99%. The difference in numerical values between changes in emissions and changes in ambient air concentrations could be due to the fact that emissions fluctuate as a function of time. For example, the tall oil plant, which is a major contributor to DMS emissions (see Figure 1), only runs intermittently. Hence, the DMS concentration measured in ambient air is dependent on whether the tall oil plant is operating at the time of sampling. By contrast, the change in DMS emission rate is calculated on a yearly basis and accounts for the number of operating hours of each source.

The results of the Student’s *t*-test for CH₃SH indicate that the average concentration of this compound decreased after the shutdown of the “A” Kraft mill with a confidence level of 83%. The average concentration of CH₃SH decreased by 28%, which is much less than the 85% decrease in CH₃SH emissions from the plant (Table 1). However, because CH₃SH was below the detection limit of 0.51 ppbv in most of the ambient air samples collected after 3 May 2006, the actual decrease of the average CH₃SH concentration may be underestimated. For example, if samples with undetectable CH₃SH were assumed to contain no CH₃SH rather than a concentration equal to half the AIS, the calculated reduction in the average CH₃SH concentration would be 80%, which is very close to the change in CH₃SH emissions.

At first glance, the data for H₂S appears to indicate that the average concentration of this compound increased after the shutdown of the “A” kraft mill. However, the *t*-test shows that this would not be a valid conclusion since the confidence level for a change in the average H₂S concentration is only 62%. This low confidence level reflects the fact that most of the H₂S concentrations were below the detection limit of 0.90 ppbv both before and after 3 May 2006.



It is important to point out that the data do not rule out that the average H₂S concentration may have actually decreased after the shutdown of the “A” kraft mill (as could be logically expected given that the H₂S emissions from the Bowater Plant decreased by 91%), but the detection limit for H₂S is too high to demonstrate this effect.

4 Conclusions

On 3 May 2006, the Bowater pulp and paper plant located in Thunder Bay shut down one of its two Kraft mills, thus reducing its overall air emissions of H₂S, CH₃SH, DMS, and DMDS by 91, 85, 46, and 72%, respectively. Analyses of ambient air samples collected in the community surrounding the plant between 5 April and 14 September 2006 have shown that the concentrations of CH₃SH, DMS, and DMDS decreased by 28, 70, and 58%, respectively after the shutdown date. The effect of the shutdown on H₂S concentrations in ambient air could not be ascertained because most of the samples had H₂S concentrations below the detection limit of 0.90 ppbv, both before and after the shutdown.

Acknowledgement

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