TRS inventories and air dispersion modeling for odor reduction at a kraft mill with an activated sludge treatment plant

BRIAN O'CONNOR AND CHRISTIAN LEDOUX

ABSTRACT: Detailed knowledge of a mill's atmospheric total reduced sulfur (TRS) emissions, coupled with air dispersion modeling, can be an effective way to plan odor reduction strategies. For the kraft mill in question, the results from the air dispersion model indicated that the emissions from the treatment system were having the greatest and most frequent impact on ambient TRS in the surrounding community. Different modeling scenarios demonstrated that a small innocuous vent from the sludge dewatering building (mix tank vent) was a major contributor to ambient TRS in the area surrounding the mill. The model also indicated that eliminating the TRS from this single simple source would significantly reduce the contribution of odors from the treatment system.

Application: Detailed knowledge of a mill's atmospheric TRS emissions, coupled with air dispersion modeling, can be an effective way to plan odor reduction strategies.

The release of odorous emissions from the kraft pulping process, mainly in the form of total reduced sulfur (TRS) compounds, continues to be a concern to mill personnel and the surrounding community. The TRS gases, comprised of hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide all possess very low odor thresholds in the low parts per billion range. Although exposure to current ambient air levels of these TRS gases, within kraft mills or the surrounding communities, is unlikely to cause adverse health effects [1], their presence can be unpleasant and a nuisance.

The odors from kraft pulping are generated and released from a number of different locations at a mill. Some of the TRS sources are directly related to the production of pulp, such as the recovery furnace stack and brownstock washer vents, while other sources are related to the effluent treatment plant, such as emissions from the primary clarifier. Given the complexity of a kraft mill, it is not always straightforward to determine the impact that changes to a particular area might have on the concentration of ambient TRS in the community. In order to answer this question, the best tool available is air dispersion modeling. Coupled with comprehensive TRS emission inventories, air dispersion models can offer considerable input into the decision-making process at a mill.

The Industrial Source Complex Short-Term Version 3 (ISCST3) air dispersion model, developed by the U.S. Environmental Protection Agency (EPA) [2], is one of the more frequently used algorithms for this type of application. The model is based upon the assumption of a Gaussian-shaped gas plume and can be used to assess pollutant concentrations from a variety of sources associated with an industrial facility. The model is fairly sophisticated in that it allows for actual source locations to be identified and can handle multiple sources, including point (e.g., stack), volume (e.g., ditches), area (e.g., clarifiers or lagoons) or open pit types. The model also calculates the effect of local disturbances, such as building downwash, on point sources. It can use meteorological data from the surrounding region to account for the atmospheric conditions that affect the distribution of air pollution on the modeling area.

The intent of this study was to use recent mill source emission results for TRS, in combination with an air dispersion model, to estimate the ambient TRS concentrations that can be expected along the mill's property and in the surrounding area. We also ran modeling scenarios for individual sources or groups of sources in order to determine the contributions of different areas of the mill to odors. This would ensure that any areas targeted for future TRS reduction would provide the most benefit towards minimizing ambient odor in the community.

MATERIALS AND METHODS

Sampling of process vents for stack gas velocity and TRS

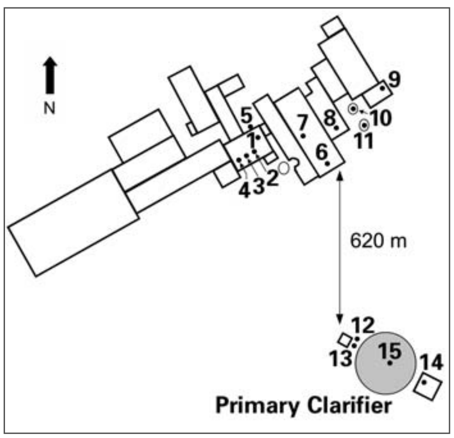
At each of the individual stacks or vents, we calculated the stack gas velocity and collected a sample of gas for TRS analysis. We calculated the velocity of the gas for each stack from a variety of different measurements obtained during the run. These included static and barometric pressure, moisture content, pressure differential, temperature profile, and molecular weight of the stack gas. We conducted these measurements according to standard Environment Canada protocols [3]. For the collection of the gas sample, a quarter inch Teflon® tube was placed in the vent. The gas first passed through an impinger containing phosphoric acid for moisture removal. It was then collected and stored in a 10 liter (L) Tedlar® bag using an integrated bag sampler (Model 1062 Supelco, Canada), as per Environment Canada Protocol for TRS sampling [4].

Analysis of the Tedlar® bag for TRS components using gas chromatography (GC)

The Tedlar® bags were analyzed for the four TRS components (i.e., hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide) using a portable

STACKS	SITE LOCATION	STACK HEIGHT, m	GAS EXIT VELOCITY, m/s	TRS EMISSION RATE, mg/s AS H_2S
Mill stacks				
Brownstock washer	1	21	15.6	167
Brownstock washer	2	21	15.6	26.7
Brownstock washer	3	21	15.2	2.8
Brownstock washer	4	19.5	12.8	3.0
Foam breaker	5	19.5	10.3	123
Recovery furnace	6	59.9	11.2	181
Smelt dissolving tank	7	52.9	4.6	176
Combined recovery furnace/ smelt dissolving tank	8	59.9	23.3	187
Lime kiln	9	29.8	10.9	80
Green liquor clarifier	10 - 11	14.3	12	22
Treatment system sources				
Misc. vent off grit chamber	12	4.6	3.3	93
Misc. vent off grit chamber	13	4.0	3.3	22
Sludge mix tank	14	5.5	1.5	244
Primary clarifier	15	1	-	55.5

I. TRS emission data for the Kraft mill stacks and treatment system area sources.



1. Schematic of the mill buildings with the location of the TRS emission points identified according to Table I.

gas chromatograph (Voyager model from PE Photovac) equipped with a photoionization detector (PID). We analyzed a 1 mL sample of the gas collected in the Tedlar® bag using the preloaded columns, specific for TRS analysis, in the Voyager GC at an oven temperature of 80°C. A gas cylinder containing hydrogen sulfide [19.0 parts per million (ppm)], methyl mercaptan (24.1 ppm), dimethyl sulfide (22.9 ppm) and dimethyl disulfide (20.7 ppm), purchased from Matheson Tri-Gas, Inc., was used as the calibration standard for the gas chromatograph.

Air dispersion modeling

The ISCST3 air dispersion model was used in this study to predict odor affects in the community. The model accepts hourly meteorological data records to define the conditions of transport and diffusion. For each scenario, we ran the model in urban mode for simple and complex terrain using regulatory defaults for wind profiles and no hourly concentrations for calm winds. We loaded the TRS information for the various stack and area sources into the model, along with detailed building dimensions and stack information (i.e., height, gas temperature and exit velocity), property boundaries, and five years of meteorological data encompassing both surface and upper air mixing height data. The surface and upper air data were obtained from Environment Canada monitoring stations located within approximately 50 kilometers (km) of the mill site.

Sampling for TRS emissions from the primary clarifier using a flux chamber

Emissions of TRS from the surface of the primary clarifier were measured using an EPA designed flux chamber [5]. The flux chamber is a practical means of quantifying chemical emissions from large surface areas. The procedure involves floating the flux chamber on the aqueous surface and sweeping the chamber with a constant rate (5 L/min) of clean air supplied from a gas cylinder. After allowing the chamber to equilibrate for a period sufficient to replace the volume three times (approximately 20 min), a gas sample is typically withdrawn using a 10 L bag sampler. The bag is then analyzed for individual TRS components using a portable gas chromatograph. We sampled the primary clarifier on two separate occasions, taking 12 samples at different locations each time. The average TRS emission rate from the primary clarifier, reported as hydrogen sulfide, was determined to be 55.5 milligrams per second (mg/s) (0.0145 mg/s/m^2 for the clarifier area of 3826 m^2).

RESULTS AND DISCUSSION

Inventory of mill TRS emission sources

We produced a complete inventory of the potential sources contributing to TRS at the mill using Environment Canada protocols. The stack gases were characterized for all of the parameters that are required as input into the air dispersion model (i.e., velocity, temperature, TRS emission rate). We used an EPA flux chamber to obtain TRS emissions from the primary clarifier. A total of 26 TRS emission sources were examined in the study. **Table I** lists sources that were found to have TRS emission rates greater than 2 mg/s (as H_2S). Several of the sources sampled (i.e., causticizing vents, white liquor clarifiers, slaker and green liquor reservoir) exhibited only minor TRS emissions—less than 1 mg/s as hydrogen sulfide (H_2S)—and hence were not included in the air dispersion calculations. Interestingly, one of the top TRS emission sources from the mill was associated with the sludge dewatering operations. TRS emissions of 244 mg/s (as H_2S)

were measured from a small vent located on top of the sludge mix tank, presumably due to the buildup of anaerobic by-products in the sludge mixing chamber. The top five emission sources of TRS at the mill were the following:

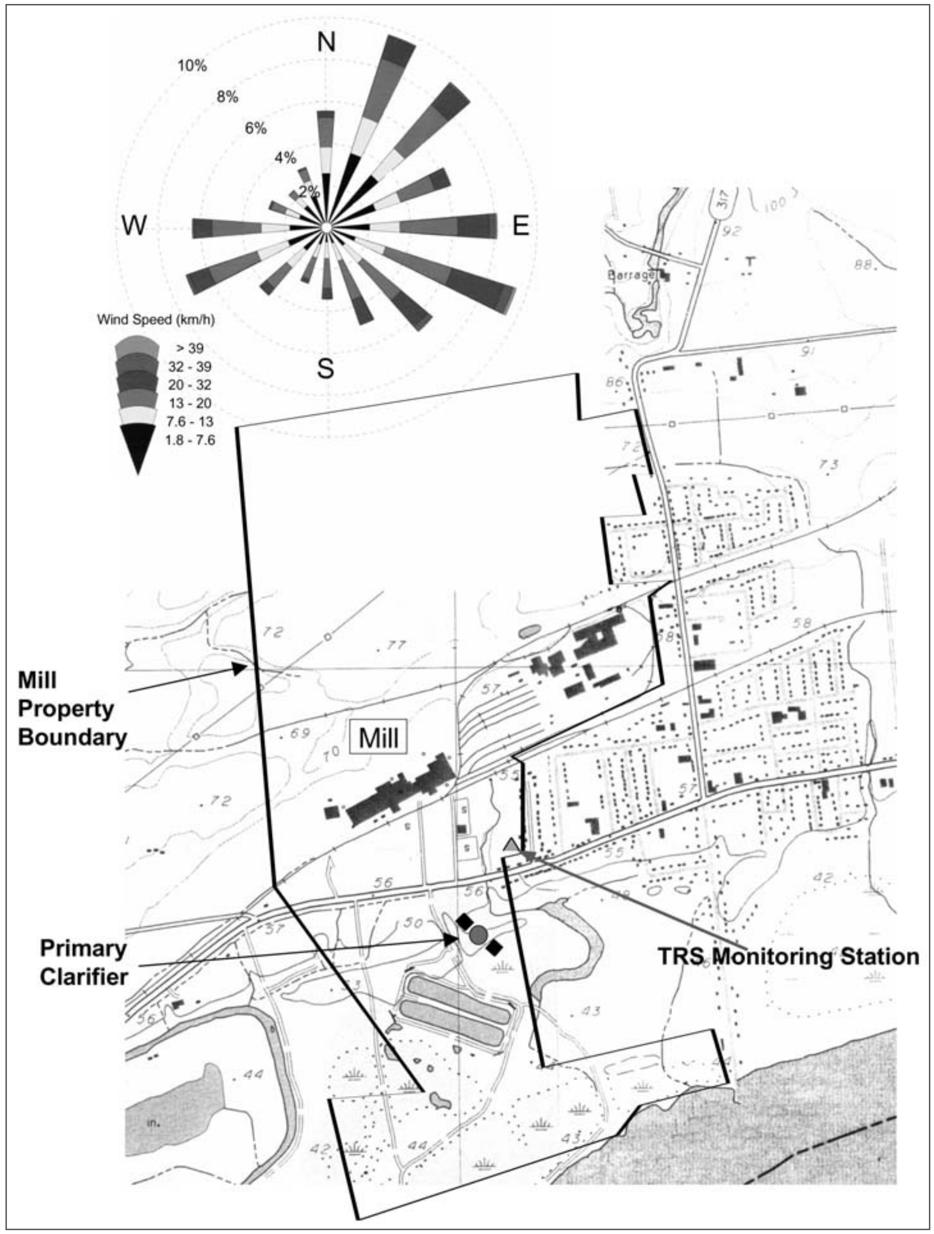
- the sludge mix tank vent (site location #14),
- the combined recovery furnace/smelt dissolving tank stack (site location #8),
- the recovery furnace stack (site location #6),
- the smelt dissolving tank stack (site location #7)
- a brownstock washer vent (site location #1).

A schematic of the mill buildings, with the locations of the individual stacks, listed in Table I, is presented in **Fig. 1**.

Meteorological data

The model used five years of hourly surface and upper air meteorological data. Information on the wind speed and wind direction, averaged over a five year period (referred to as a wind rose plot), along with the location of the mill and its property boundaries in relation to the town, is presented in **Fig. 2**. Figure 2 also identifies the mill's TRS ambient air monitoring station (triangle).

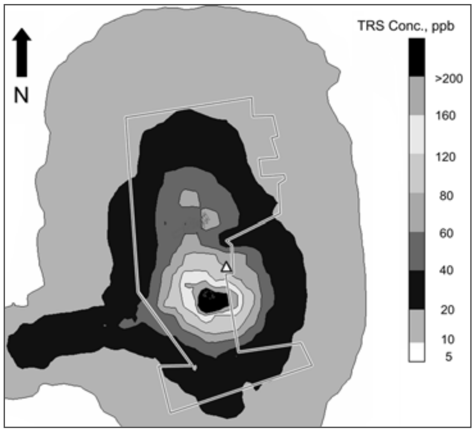
The wind rose plot is an efficient and convenient means of presenting the variations in the wind conditions at the mill site. The arms represent the wind direction, the length of the radial arm gives the total percent frequency of winds blowing in that direction while the different sections of the arms represent the frequency of the different wind speeds. For example, the wind rose in Fig. 2 indicates that winds blowing towards the northeast occurred approximately 9% of the time, with wind speeds of less than 7.6 kilometers per hour (km/h) accounting for a little over 3% of the total. The average wind speed at the site was 12.7 km/h with calm winds (i.e., < 0.5 m/s) prevailing 7.6% of the time. The wind rose data in Fig. 2 shows that the winds tend to be blowing predominantly towards the northeast and southeast. Winds blowing to the northwest were relatively rare. Given that the town is situated to the east of the mill (Fig. 2), the prevailing winds would tend to blow the mill's TRS emissions towards the town. When the wind is blowing towards the northeast the emissions from the treatment system would be expected to have the greatest impact on odors in the town, while southeast winds would involve emissions from the mill stacks.



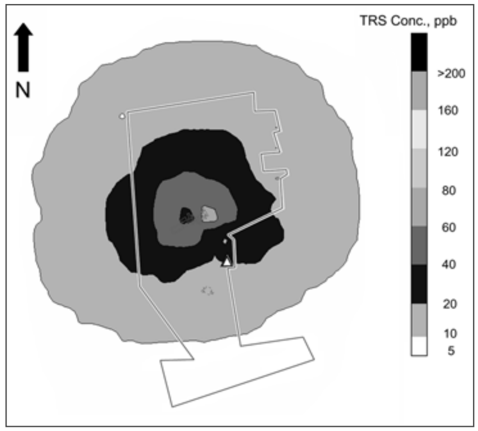
2. Information on the wind flow patterns and the mill property boundary in relation to the town. The radial arms indicate the direction the wind is blowing towards.

Air dispersion modeling Results

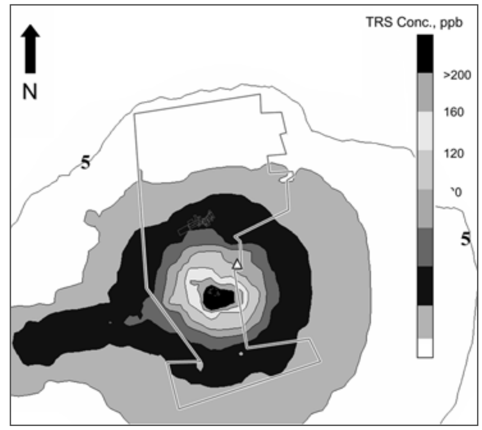
When working with air dispersion models, it is important to note that the contours that are generated illustrate the **maximum values** (i.e., worst-case estimates) that are expected to occur over the averaging period that is being investigated. The contour plots, as such, do not provide any information concerning the length of time that these levels would persist at any given location. They are not meant to predict day-to-day variations that occur in the areas surrounding the mill. However, the air dispersion models can calculate the number of hours that a given point would be expected to exceed a certain TRS level. For example, if a guideline required compliance with a



3. Worst-case estimates of the 1-h ambient TRS concentrations for all of the mill sources. The line represents the mill property and the triangle the ambient TRS monitoring station.



4. Worst-case estimates of the 1-h ambient TRS concentrations for the mill production sources (#1-11). The line represents the mill property and the triangle the ambient TRS monitoring station.



5. Worst-case estimates of the 1-h ambient TRS concentrations for the treatment system sources (#12-15). The line represents the mill property and the triangle the ambient TRS monitoring station.

1 hour average of 40 parts per billion (ppb) TRS at the property line, the air dispersion model could calculate the percent of time that this value would be exceeded.

The entire mill TRS emissions were modeled together in order to estimate the maximum 1 hour ambient TRS concentrations, at ground level, that could be expected at the mill's property boundary and in a defined grid surrounding the mill site. For this study a 5-km by 5-km rectangular grid was set up with receptors located at 200-m intervals over the entire area. The terrain elevations over the grid were included in the modeling calculations. All building dimensions were entered into the model to allow consideration of building downwash effects. In addition to this, we ran several different modeling scenarios, with individual sources or groups of sources, in order to identify the area that might be having the largest impact on ambient TRS concentrations.

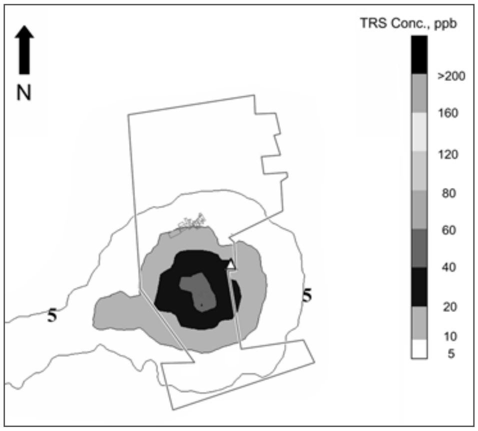
Contour plots of ambient TRS concentrations

The contour plot in **Fig. 3** shows the worst-case estimates for the maximum 1-h ambient TRS concentrations, in ppb, for the entire mill. In general, the contour plot for all of the mill sources indicates that the maximum 1-h average concentration of TRS in the town would be expected to range between 5–99 ppb. The maximum 1-h TRS concentration expected at the air monitoring station, located on the property boundary, determined through the modeling, was estimated to be 99 ppb. The actual maximum 1-h ambient TRS concentration measured at the monitoring station, over the course of one year, was found to be 92 ppb. Therefore, it appears that the air dispersion model is providing a realistic estimate of the ambient TRS concentrations in the area surrounding the mill.

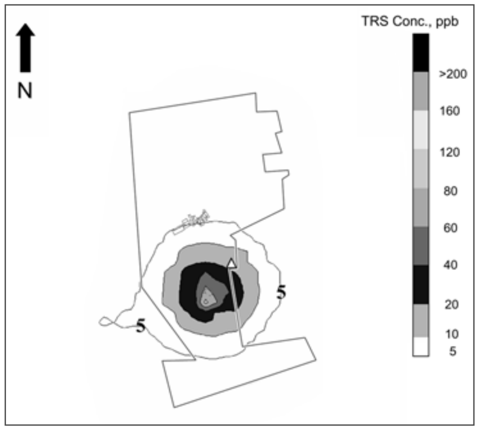
In order to identify the impact of the various areas on ambient TRS, models were run using only the stacks associated with pulp production (Sites #1–11) in one scenario (**Fig. 4**), and using emissions associated with the treatment system (Sites #12–15) in another scenario (**Fig. 5**). Comparing the contour plots in Figs. 3–5 suggests that a significant fraction of the TRS at the monitoring station arises from the mill's treatment system. The mill's ambient TRS monitoring station happens to be situated relatively close to the treatment system and hence, when the wind is blowing in a northeasterly direction, the monitoring station would be expected to detect elevated levels of TRS.

At the mill, the main TRS sources from the production line are the stacks associated with combustion processes (i.e., recovery furnace, smelt dissolving tank and lime kiln). Because these stacks are relatively high, their emissions would tend to be well dispersed and may not have a great impact on any given area adjacent to the mill. The highest concentration of TRS along the mill property line from these sources would be approximately 15–30 ppb (Fig. 4). We would expect the highest concentration of TRS in the town from these emission sources to be between 5–30 ppb. The estimated concentration of ambient TRS at the monitoring station was calculated to be 23 ppb. In comparison to the contour for the entire mill in Fig. 3, it is obvious that the production area of the mill is not the cause of the elevated level of 99 ppb of TRS at the ambient air monitoring station. When the wind is blowing in a southeasterly direction, the maximum contribution from the mill is expected to be only 23 ppb. In contrast, the contour for the treatment system (Fig. 5) demonstrates that under the right wind conditions (northeast direction), it is the TRS emissions from this source that are responsible for the high level of 99 ppb TRS at the air monitoring station. The emissions from the treatment system would contribute to ambient TRS concentrations in town of between 5-99 ppb.

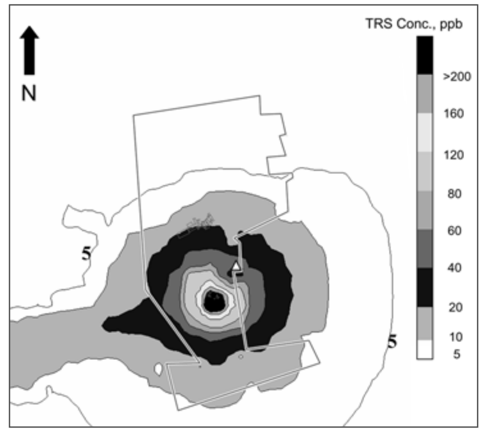
In the town, wind direction will determine the ambient TRS concentrations. Given the location of the mill buildings and stacks and the treatment system, the air dispersion modeling indicates that only one area will be significantly affecting odors in the town at any given



6. Worst-case estimates of the 1 hour ambient TRS concentrations for emissions from the grit chamber vents (#12-13). The line represents the mill property and the triangle the ambient TRS monitoring station.



7. Worst-case estimates for the 1 hour ambient TRS concentrations for emissions from the primary clarifier (#15). The line represents the mill property and the triangle the ambient TRS monitoring station.



8. Worst-case estimates for the 1 hour ambient TRS concentrations for emissions from the sludge mix tank (#14). The line represents the mill property and the triangle the ambient TRS monitoring station.

time. When the wind is blowing towards the northeast, emissions from the treatment system will affect the town most significantly. If the wind is blowing towards the east or southeast, then the emissions from the mill stacks are more important. The effect on the TRS concentrations at the ambient air monitoring station appears to be approximately four times greater when the wind is blowing the treatment system emissions in that direction, as compared to when emissions from the mill stacks are blown towards the town.

In order to delineate the influence of the different areas of the treatment system on ambient TRS, we ran separate air dispersion models for the TRS emissions from the grit chamber vents (sites #12 and #13), the primary clarifier (site #15), and the sludge mix tank vent (site #14). The contour plots for these three scenarios are presented in **Figs. 6–8**, respectively. In terms of influence on the ambient TRS monitoring station, the figures indicate that the mix tank vent has the largest impact on ambient TRS, followed by the grit chamber vents and the emissions from the primary clarifier. **Table II** shows the maximum calculated TRS concentrations from these sources at the TRS monitoring station. Note that the values in Table II refer to the maximum calculated concentrations expected to occur at the various sites. Since the maximum concentrations may occur on different days, it is not possible to calculate the exact contribution of each source to ambient TRS in this manner. In order to understand the contribution of the various sources, we ran the model for the date that corresponded to the maximum contribution from the entire treatment system at the air monitoring station (i.e., 99 ppb), which was predicted to occur on August 13th at 10 p.m. For this worst-case estimate, the contributions of the different areas of the treatment system towards ambient TRS at the monitoring station were calculated to be as follows: mix tank (70%), grit chamber vents (19%) and the primary clarifier (11%). Clearly, the sludge mix tank vent was the key area from the treatment system that was having the largest affect on ambient TRS in the vicinity of the monitoring station.

SITE	MAXIMUM AMBIENT TRS CONCENTRATION, ppb	DATE MAXIMUM OCCURRED
Grit chamber vent	25	August 10th, 2 a.m.
Primary clarifier	15	August 15th, 10 p.m.
Mix tank vent	70	July 19th, 10 p.m.

II. Calculated maximum ambient TRS concentration from various treatment system sources.

Using air dispersion modeling results for decision making

The goal of the air dispersion modeling was to understand the impact of the mill's various sources on ambient TRS in the surrounding community. This information is essential in order to ensure that future improvements at the mill will be at the proper sources and provide the most benefit towards minimizing ambient odor. The contour plots generated for this report, indicate that the treatment system, specifically the sludge mix tank vent, is one source where TRS reduction initiatives would be beneficial in reducing the ambient TRS concentrations in the surrounding community.

In an attempt to minimize the impact of the mill on odors in the community, the mill tries to keep the ambient concentration of TRS at the monitoring station below a certain target level. In order to demonstrate the influence of the mix tank emissions on this target, and the benefits of reducing this particular emission point as opposed to others, we ran air dispersion models and calculated the number of hours the target TRS level would be exceeded (**Table III**). Taking into account all of the sources (i.e., #1–15) that were modeled, the results indicate that approximately 7.1% of the time the mill would

SITES	MAXIMUM CALCULATED TRS AT MONITORING STATION, ppb	TIME THAT TARGET TRS VALUE IS EXCEEDED AT MONITORING STATION
All sources (#1 - 15)	99	7.1%
Treatment system (#12 - 15)	99	6.6%
Production sources (#1 - 11)	23	0.5%
Mix tank (#14)	70	3.9%
All sources without the mix tank	38	3.2%

III. Calculated time that the ambient TRS at the monitoring station exceeds the mill's internal target value.

be above its TRS target value at the ambient monitoring station. As shown by the contour plots, it is the emissions from the treatment system that have the largest impact on the TRS monitoring station, accounting for 93% of the time that the target value is exceeded. In contrast, the contribution from the mill production stacks (i.e., #1–11) indicated that these emissions would account for only 7% of the time that the mill's TRS target is exceeded. The treatment system's mix tank vent, alone, accounts for 55% of the time that the target value is expected to be exceeded. Therefore, if the TRS emissions from the mix tank were eliminated, the time that the mill would exceed its target TRS value at the ambient monitoring station would be significantly improved (i.e., from 7.1% to 3.2%). Examination of the actual ambient TRS concentrations at the monitoring station indicated that from 1998–2000, the mill exceeded its target TRS value 6%–10% of the time. Therefore the estimated exceedence of 7%, calculated by the model, is very close to the measured value.

At first glance, the mix tank vent seems innocuous as it is comprised of a small 11-in diameter fiberglass pipe extruding from the side of the solids dewatering building. Without a detailed knowledge of the workings of the treatment system and the sludge dewatering facilities, it would be very easy to miss this particular area. Luckily, having been identified as a significant source of TRS, it is also one of the easiest areas where a minimum capital investment has the potential to make a significant impact on odor reduction. A number of different products on the market have the ability to control anaerobic activity from sludge. In fact, the mill recently ran a short trial and found that it could easily and consistently reduce the TRS emissions from this source to near zero.

CONCLUSIONS

Detailed knowledge of a mill's atmospheric TRS emissions, coupled with air dispersion modeling, can be an effective way to plan odor reduction strategies. For this kraft mill, the results from the air dispersion model indicated that the emissions from the treatment system were having the greatest, and most frequent, impact on ambient TRS in the surrounding community. Different modeling scenarios demonstrated that a small innocuous vent from the sludge dewatering building (mix tank vent) was a major contributor to ambient TRS in the area surrounding the mill. The model also indicated that eliminating the TRS from this simple source would significantly reduce the contribution of odors from the treatment system. **TJ**

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O'Connor

Ledoux

Brian O'Connor is group leader, environmental, Paprican, 570 Boulevard St-Jean, Pointe-Claire, Quebec H9R 3J9 Canada, Email: boconnor@paprican.ca; Christian Ledoux, steam plant technical assistant, Fraser Papers Inc., 284 Elizabeth, Thurso, Quebec J0X 3B0 Canada.