

HEALTH RISK ASSESSMENT OF ENVIRONMENTAL EXPOSURE TO MALODOROUS SULFUR COMPOUNDS IN CENTRAL SLOVAKIA (RUŽOMBEROK AREA)

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Abstract. Ambient air quality in and around the city of Ružomberok, located in northern Slovakia is influenced by a variety of malodorous reduced sulfur compounds in emissions from the pulp mill factory, which uses the kraft process. Reduced sulfur compounds are a group of inorganic and organic chemicals containing sulfur atoms in their lowest oxidation state (S^{2-}), including hydrogen sulfide, mercaptans, dimethyl sulfide, dimethyl disulfide and other sulfur compounds. We present results from a screening level human health exposure and risk assessment of these malodorous compounds in the Ružomberok area. Analyses are based on ambient air quality monitoring data collected by the pulp mill factory and the Slovak Ministry of the Environment Hydrometeorological Institute (HI). Pulp mill factory data include measurements of total reduced sulfur compounds (TRS) and hydrogen sulfide from the year 2002. HI provided continuous monitoring of ambient TRS in one station located in this area. Samples were collected at nine sites chosen based on evaluation of geographic, climatic and demographic factors, and screening level exposure and risk assessments were performed for five exposure localities. Screening level analyses include calculation of hazard indices for each locality based on average daily dose. In addition, recommendations for health risk management at the governmental, private, and municipal level are presented.

Key words: total reduced sulfur (TRS); hydrogen sulfide, environmental exposure, hazard quotient (HQ).

1. INTRODUCTION

Ružomberok, located in northern Slovakia is a historically industrialized city. Until recently local industry has been dominated by a large textile company and a pulp and paper mill. The textile manufacturer went out of business in 2006. The pulp mill employs the kraft pulping process, and as a result has a considerable influence on ambient air quality in and around the city. Specifically, the kraft process results in the release of malodorous emissions due in part to the use of sodium sulfide in combination with sodium hydroxide for the digestion of wood chips. The combined effect of these two compounds allows for rapid delignification of wood while allowing the cellulose fibers to keep their strength. However, this process results in the release of reduced sulfur compounds. These compounds, measured together in this study

as total reduced sulfides (TRS), include hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), and methylsulfides ($((CH_3)_2S$ and $(CH_3)_2S_2$) (Young 2005). Of these, methyl mercaptan and hydrogen sulfide are the predominant components of emissions and all are malodorous at low concentrations.

Hydrogen sulfide is a colorless, flammable gas with an odor of rotten eggs. The odor threshold is within the range of 0.03-0.05 mg/m^3 . Approximately 95 percent of H_2S present in the atmosphere is produced naturally from volcanic eruptions, sulfur springs and biological decomposition (Alberta Environment 2004). Methyl mercaptan is a colorless, flammable gas with a characteristic odor reminiscent of decayed cabbage. The odor threshold is 0.04 $mg \cdot m^{-3}$. CH_3SH is evolved naturally from mineral deposits, natural gas, petroleum, and biological decomposition. It is also an essential

flavor component of several vegetables such as onion, garlic, and nut (Young 2005). Dimethyl sulfide is a colorless, flammable, slightly water-soluble liquid with a characteristic odor of decayed vegetables. The odor threshold is in the range of 0.0025 mg.m^{-3} to 0.16 mg.m^{-3} (Alberta Environment, 2004). $(\text{CH}_3)_2\text{S}$ has the unique capability of enhancing and intensifying other odors. Due to this property it is used in warning odorants and odor masking agents (Alberta Environment, 2004). Dimethyl disulfide is a colorless, flammable liquid with a characteristic odor of decayed fish (Alberta Environment 2004). The odor threshold is in the range of $0.0003 - 0.014 \text{ mg.m}^{-3}$ (Alberta Environment, 2004).

Primary anthropogenic sources of TRS include oil and gas processing facilities, kraft pulp mills, food processing plants, livestock feedlots and chemical manufacturing plants. For this analysis the primary route of exposure to ambient TRS is assumed to be through inhalation. Health effects associated with inhalation exposure to TRS are diverse and compound-specific, but include difficulty breathing, headache, and nausea. Exposure to elevated concentrations of TRS may result in eye and respiratory tract irritation. TRS are rapidly metabolized and do not accumulate in the body. Long-term exposure of 1 ppm or less results in no adverse effects to the eyes, skin or lungs (Alberta Environment, 2004). Some of TRS compounds (hydrogen sulfide) can cause acute psychosis with cognitive function damage (Drimalova, 2003). There are no indications of other adverse health effects such as cancer, reproductive, or developmental effects attributable to TRS (Young 2005, Alberta Environment, 2004).

2. EXPERIMENTAL PROCEDURES

2.1. Study design

This analysis was conducted as part of a special Slovak Ministry of Health project entitled "Health impact of organic sulfur compounds arising from Kraft pulp production in Ružomberok area". The project was conducted in three stages over the course of 44 months beginning in May, 2001. These stages included: (1) design of the human health risk assessment, (2) effects assessment (hazard identification and dose-response assessment), and (3) exposure assessment and risk characterization. This paper focuses on the second and third steps of the project. The effects assessment included a review of available information related to the physical-chemical properties and acute, sub-acute,

sub-chronic and chronic toxicity effects. The exposure assessment focused on the selection of homogenous exposure areas in and around the Ružomberok area and the quantification of exposure concentrations of TRS within these areas. Risk characterization included both a qualitative assessment of the risks of TRS exposure as well as a quantitative assessment of exposure concentration. The quantitative assessment focused on the calculation of hazard quotients (HQ) for exposure to hydrogen sulfide for each of the exposure areas identified in the exposure assessment. In this case, HQs, defined as the ratio of the exposure concentration to a reference concentration for specific pollutant, were calculated based on the U.S. Environmental Protection Agency Reference Concentration (RfC) for hydrogen sulfide. A hazard quotient less than or equal to 1 indicates that no adverse health effects are expected as a result of exposure; a hazard quotient greater than 1 indicates the possibility of adverse health effects.

The Regional Authority of Public Health Banská Bystrica (Slovak republic) was an expert guarantor of the project.

2.2. Study areas and sampling sites

Exposure to TRS was assessed for five groups of inhabitants in and around of the town of Ružomberok, and for one cohort of individuals in Liptovská Lúžná, who were considered exposed to background concentrations of these chemicals. The exposure groups, shown in table 1, were selected based on following criteria:

a) Geographic and demographic factors (topography, population density, etc.). The exposure relevant diagnoses have been considered also. They were especially cardiovascular diseases, respiratory diseases (e.g. asthma) and some cancer diagnosis (lung cancer).

The research locality includes territory at west part of Liptov hollow basin on the junction of rivers Váh, Likavka and Revúca. The Veľká Fatra Mountains creates west border of the basin, Chočské vrchy hills are at the north side and Low Tatras Mountains at the south part of the basin.

b) Climate factors (specifically, dominant wind direction). River basin of the Váh river and surrounding are classified as light-warm, moistly area with cold winter, rest of territory is classified as cold area with average temperature 7.1°C . The climate condition are characterized with high frequency of days with temperature inversion (127-148 days per year), this determinant is very significant (considering to air dispersion condition).

Table 1 Description and Number of Inhabitants in Each Exposure Group.

Exposure Group (Total No. of Inhabitants)	Measurement Station (Code)	Town/Village Name	No. of inhabitants
A (2178)	Ivachnová (7)	Ivachnová	475
		Liptovská Teplá	885
		Bešeňová	398
		Liptovský Michal	261
		Madočany	159
B (2546)	Martinček (4)	Martinček	425
	Lisková (5)	Lisková	2,121
C (8,207)	Černová (1a) Hrboltová (1b)	Černová	1,430
		Hrboltová	676
		Rybárpole	1,516
		settlement Kľačno	4,585
D (22,000)	Riadok (2) Supra (3)	Ružomberok-central part	6,500
		Biely Potok	1,700
		other settlements	8,000
		settlement Juh	5,700
E (2,336)	Štiavnička (6)	Štiavnička	539
		Liptovská Štiavnica	847
		Ludrová	950
Background (2,933)	Liptovská Lúžná	Liptovská Lúžná	2933

The periods with whole day temperature inversion, few days one after another are characteristic for winter season. The dominant wind direction is from the west, with average speed 1.6m.s^{-1} . Ružomberok is locality with highest rainfall amount in Liptov hollow basin, rest of area is in rainfall shadow induced by Low Tatras Mountains (Čeman, 2007).

c) Outputs of emissions dispersion study which rendered paper mill factory as main emissions producer.

2.3. Measurements methods

Ambient air concentrations of H_2S and TRS (measured as total sum of organic sulfur compound) were measured at a total of nine automatic gauging stations for various years from 1999 through 2005. One fixed automatic gauging station equipped with a TRS analyzer (TEI 43 C) is located near the personal gate-house of the SUPRA division and the intersection of Interstate Highway 18 Žilina – Poprad and Interstate Highway 59 Banská Bystrica. Measurements were made at this location from 1999 through 2005. Mobile automatic gauging stations – (TRS analyzer API 101A, which measured H_2S and TRS), were used in the localities of Černová, Lisková, Martinček, Štiavnička and Ivachnová on monthly intervals from 2002 through 2005.

TRS Analyzers used in this study measure H_2S and/or TRS continuously by pulsed fluorescence technology. Prior to measurement all SO_2 in the air sample is scrubbed out to prevent interference with the measured H_2S concentration. H_2S in the sample is then converted to SO_2 . The sample is then drawn through a sample chamber where it is irradiated with pulses of ultra-violet light. Any SO_2 in the sample is excited to a higher energy level and upon returning to its original state, light or fluorescence is released. The amount of fluorescence measured is proportional to the SO_2 (converted from H_2S or TRS) concentration. The TRS analyzer worked on exactly the same principle as the H_2S analyzer. The only difference was that the conversion of sulfur compounds to SO_2 occurs at a much higher temperature. Therefore there is a more complete conversion of sulfur compounds to SO_2 .

2.4. Data analysis and interpretation

Standard methods for data analyses were used. For each measurement station simple summary statistics used to characterize exposure were calculated (arithmetic mean, maximum and minimum value, and 75th and 95th percentile). The 95th percentile of the concentration distribution is applied for the worst-case exposure scenario and the 75th percentile for the reasonable likely exposure scenario. The overall exposure concentrations of

total reduced sulfur and hydrogen sulfide for each exposure group (A, B, C, D, E) were calculated by averaging the 75th or 95th percentile exposure concentrations from each sampling station determined to contribute to that group's exposure.

3. RESULTS

3.1. Total reduced sulfur and hydrogen sulfide concentrations

Ambient air quality results are presented in tables 2 and 3. Measurements using mobile stations started in 2002 at five measurement sites, which were supplemented with another four monitoring

sites in 2005 (including a background station).

Annual averages fluctuated at particular locations; however the Supra sampling location experienced relatively stable TRS concentrations during the period 1995-2005. Annual TRS concentrations visually decreased slightly over time. In the years 2002 and 2003, the highest annual concentrations were measured at the Černová stations. Maximum concentrations across all stations have been measured at the Martinček station since 2004. The lowest concentrations of TRS were measured at the Štiavnička station throughout the measurement period. Concentrations of hydrogen sulfide show similar trends as TRS (Tab. 3).

Table 2 Measurements of Total Reduced Sulfur (TRS) at Individual Measurement Sites $\mu\text{g}\cdot\text{m}^{-3}$

locality	year	mean	max	min	95 perc.	75 perc.	No.of samples
Ružomberok Supra	1999	8.4	68.0	0.5	28.0	11.4	350
	2000	4.4	15.4	0.0	9.3	5.6	360
	2001	4.2	13.6	0.0	8.9	5.4	365
	2002	3.8	16.3	0.0	7.6	4.5	344
	2003	5.3	19.7	0.9	10.1	6.7	363
	2004	4.3	18.7	0.1	9.3	4.7	361
	2005	9.0	59.6	0.2	21.5	10.8	364
Ružomberok Riadok	2003	5.7	30.4	0.1	15.0	7.7	180
	2004	4.4	20.0	0.3	8.8	5.3	365
	2005	5.0	14.2	0.9	8.4	5.8	365
Černová	2002	13.7	44.2	6.4	22.9	16.0	61
	2003	20.0	51.0	5.7	42.2	23.3	56
	2004	4.7	14.4	0.5	8.2	5.6	148
	2005	7.5	48.9	0.5	21.9	9.0	364
Ivachnova	2002	6.1	11.2	3.7	8.0	6.9	30
	2003	5.1	8.0	1.0	7.7	6.4	60
	2004	3.6	8.0	2.2	4.8	3.7	42
	2005	2.4	5.3	1.0	3.6	2.8	72
Lisková	2002	6.9	9.3	4.5	9.1	7.7	30
	2003	8.6	16.3	3.7	13.6	9.6	90
	2004	4.3	14.2	1.5	7.8	5.9	117
	2005	4.1	34.8	0.6	13.6	4.2	365
Martinček	2002	10.1	19.5	5.6	14.2	11.5	30
	2003	12.7	26.6	7.8	19.8	13.7	59
	2004	7.9	24.2	1.7	17.7	9.3	89
	2005	6.6	12.1	4.2	10.6	7.8	90
Štiavnička	2002	1.5	14.7	0.0	3.0	1.9	31
	2003	3.9	7.2	1.0	6.4	5.3	57
	2004	2.9	5.3	1.2	4.9	4.1	59
	2005	4.3	6.0	1.9	5.8	4.8	40
Hrboltová	2004	7.6	12.1	4.0	11.0	8.7	31
	2005	4.6	9.5	1.5	8.1	5.7	66
Background	2005	3.8	8.4	0.7	8.0	7.4	19

These ambient measurements were used as direct estimates of exposure concentration throughout the Ružomberok area. No adjustments were made for time-activity patterns. Two separate exposure scenarios were evaluated: a worst-case scenario using the 95th percentile values and the reasonable likely exposure scenario using the 75th percentile of the concentration distributions. Tables 4 and 5 show calculated exposure concentrations.

The differences of exposure between the worst-case and the reasonable likely exposure scenarios are evident. The aim of the worst-case scenario modeling is to cover situations that are not very probable, but under certain conditions may

occur. The reasonable likely exposure scenario is meant to represent normal exposure situations yet be protective of potentially sensitive population groups (e.g., children and the elderly).

Differences between individual exposures groups were tested statistically using standard linear regression analysis. In the case of TRS exposure, only Exposure Group C was found to be statistically significantly different from background (+4.01, $p < 0.001$) at a significance level of 0.05. In the case of hydrogen sulfide, two exposure groups were found to be statistically significant from background at the 0.05 level of significance: Exposure Groups A (+0.97, $p = 0.012$) and C (+0.93, $p = 0.016$).

Table 3. Measurements of Hydrogen Sulfide (H_2S) at Individual Measurement Sites in $\mu\text{g.m}^{-3}$

locality	year	mean	max	min	95 perc.	75 perc.	No.of samples
Černová	2002	3.4	9.8	1.0	6.1	4.4	61
	2003	5.8	21.1	1.1	14.1	7.0	56
	2004	1.6	2.5	0.8	2.1	1.9	59
Ivachnova	2002	1.2	1.8	0.4	1.8	1.5	30
	2003	1.2	2.4	0.2	1.9	1.4	60
	2004	1.4	3.6	0.7	1.9	1.6	42
	2005	0.8	2.4	0.2	1.3	0.9	72
Lisková	2002	0.9	2.6	0.1	1.9	1.3	30
	2003	2.1	5.1	0.6	3.6	2.7	90
	2004	1.9	2.8	1.2	2.6	2.2	29
Martinček	2002	1.6	2.4	0.9	2.3	1.8	30
	2003	1.9	5.7	0.4	3.4	2.8	59
	2004	2.5	8.2	0.3	5.8	3.0	89
	2005	2.1	5.1	1.4	4.4	2.3	90
Štiavnička	2002	0.5	2.3	0.0	1.1	0.7	31
	2003	0.6	1.6	0.0	1.3	0.9	57
	2004	1.1	2.5	0.0	2.0	1.4	90
	2005	1.6	4.8	0.0	4.3	1.9	71
Hrboltová	2004	2.1	4.2	1.5	3.8	3.2	31
	2005	1.6	4.0	0.2	3.5	2.1	66
Background	2005	1.7	4.0	0.2	3.7	3.6	19

Table 4. Exposure Concentrations for the Worst Case Exposure Scenario

Exposure group	Relevant stations ^a	Statistical function	H_2S $\mu\text{g.m}^{-3}$	TRS $\mu\text{g.m}^{-3}$
A	7	mean calculated using 95 perc. in 2002-2005	1.7	6
B	4, 5	mean calculated using 95 perc. in 2002-2005	3.4	13.3
C	1a,1b	mean calculated using 95 perc. in 2002-2005	5.9	19
D ^b	2, 3	mean calculated using 95 perc. in 2002-2005	-	12.7
E	6	mean calculated using 95 perc. in 2002-2005	2.2	5
Backgr.	8	95 percentile in the year 2005	3.7	8

^a The stations codes see in table 1.

^b Hydrogen Sulfide measurements were not made for this exposure group.

Table 5 Exposure Concentrations for Reasonable Likely Exposure Scenario

Exposure group	Relevant stations ^a	Statistical function	H ₂ S μg.m ⁻³	TRS μg.m ⁻³
A	7	mean calculated using 75 perc. in 2002-2005	1.4	5
B	4, 5	mean calculated using 75 perc. in 2002-2005	2.3	8.7
C	1a,1b	mean calculated using 75 perc. in 2002-2005	3.7	11.4
D ^b	2, 3	mean calculated using 75 perc. in 2002-2005	-	6.8
E	6	mean calculated using 75 perc. in 2002-2005	1.2	4
Backgr.	8	75 percentile in the year 2005	3.6	7.4

^a The stations codes see in table 1. ^b Hydrogen sulfide measurements were not made for this exposure group.

Statistically significant decreases in ambient concentrations were found for both TRS (-0.58/year, $p < 0.001$) and H₂S (-0.25/year, $p < 0.001$) over time.

3.2. Hazard quotient calculation

Hazard Quotients (HQ) were calculated based on the reference concentration (RfC) for hydrogen sulfide (0.002 mg.m⁻³), and were calculated for both the Worst Case and Reasonably Likely emission scenarios. The HQ is calculated as ratio of the exposure concentration to the RfC (Equation 1)

$$HQ = \text{Exposure Concentration} / \text{RfC}$$

If the hazard quotient is calculated to be less than or equal to 1, then no adverse health effects are expected to occur as a result of exposure. If the hazard quotient is greater than 1, then adverse health effects are possible. Following figures (1 and 2) show the HQ values for individual exposure groups.

HQs exceed a value of 1 for Exposure Group C in the Reasonable Likely exposure scenario throughout the measurement period. In addition, HQs were calculated to exceed a value of 1 for Exposure Group B for the years 2003 and 2004.

Results from the Worst Case scenario show overall increased HQ values as compared to the Reasonable Likely exposure scenario. HQs are greater than 1 for Exposure Groups B and C for all years of the analysis and for Exposure Group E in 2005.

4. DISCUSSION

This is the first study to analyze results of malodorous sulfur measurements in ambient air in Slovakia. This is of great importance for the Environmental Health sector. Results from this study can be viewed in the context of similar studies detailed in peer-reviewed literature and reports from other countries. A considerable amount of data and information are available from Canadian and other sources. Results from this study are discussed in the context of such information sources below.

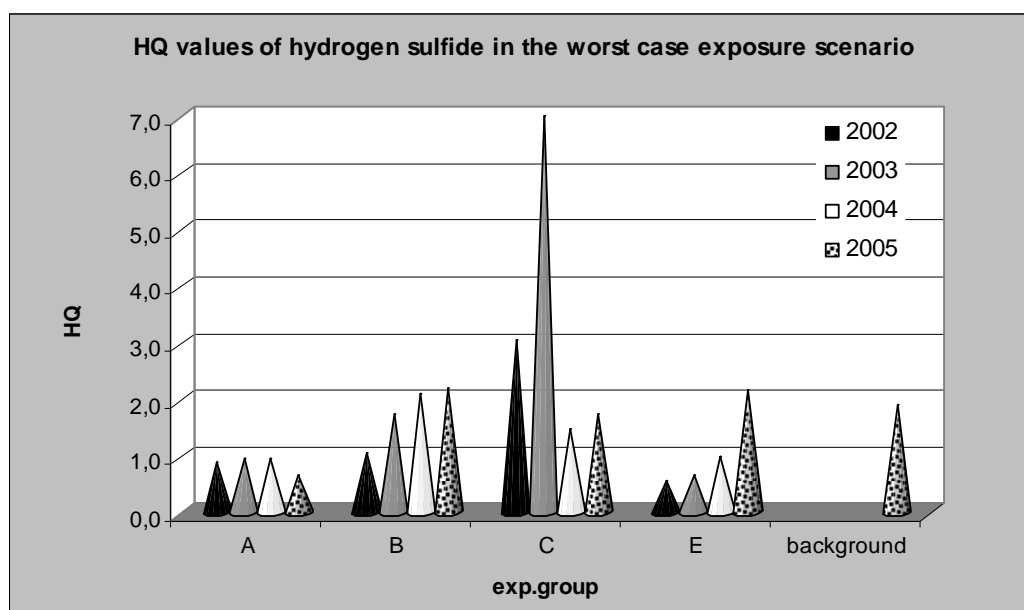


Figure 1. HQ values for the Worst Case exposure scenario

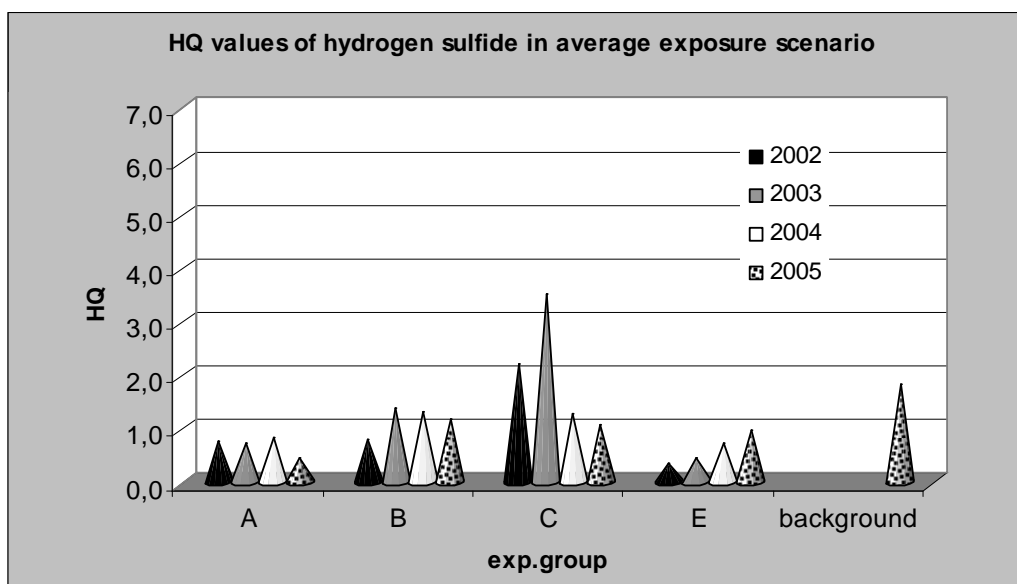


Figure 2 HQ values for Reasonable Likely exposure scenario

4.1. Hydrogen sulfide concentrations

Ambient air concentrations of H_2S have been analyzed at 80 monitoring stations operating for the past three years in Alberta. These stations are located in areas affected by oil and gas exploration and production facilities such as sour gas wells, gas and crude oil batteries, gas and oil processing plants, oil refineries, and tar sands mining and processing plants. Monthly monitoring results for the January 1999 to November 2001 period made by Alberta Environment (AENV) contain 1,653 entries of peak H_2S concentrations (1-hour averaging time). Excluding the highest three concentrations in this data set, the average concentration of peak H_2S (1-hour average) from anthropogenic sources in Alberta is 0.00602 ppm (equivalent to 6.02 ppb or $8.5 \mu\text{g.m}^{-3}$) based on a three year monitoring period (Alberta Environment 2004).

4.2. Total reduced sulfur concentrations

In the year 2000, monitoring for TRS compounds was performed at 10 ambient locations in Ontario, Canada. The highest annual TRS mean ($1.5 \mu\text{g.m}^{-3}$) was recorded in Oakville. Elevated TRS levels are mainly attributed to the pulp and paper industry (Jaakkola, 1990).

Continuous monitoring of TRS compounds in Alberta, Canada has been performed at five permanent stations located near Kraft process pulp mills, except one station, which is located in the vicinity of an oil sands mining and processing operation. The total annual average of 24-hour

monthly concentrations for all stations was $1.6 \mu\text{g.m}^{-3}$ (Alberta Environment 2004).

4.3. Health effects

As part of the South Karelia Air Pollution Study in Finland, residents in the vicinity of paper mills were studied for respiratory and other symptoms. Highly polluted areas had concentrations of hydrogen sulfide (annual mean of $8 \mu\text{g.m}^{-3}$ and maximum daily average of $100 \mu\text{g.m}^{-3}$). In addition to these hydrogen sulfide measures, concentrations of methyl mercaptan were also measured. Numbers of complaints by residents in the severely polluted areas were compared with those from moderately polluted and non polluted areas. Dose-related increases in eye and nasal symptoms cough during the previous 12 months were observed in the severely polluted areas, compared with the control group (Jaakkola, 1990).

Marttila et al. (1995) evaluated the health effects of long-term exposure to malodorous sulfur compounds of pulp mill origin, including respiratory symptoms and headaches in children. In the severely polluted area in Finland, the annual mean concentrations of hydrogen sulfide and methyl mercaptan were estimated to be 6 ppb (8 mg.m^{-3}) and 1.0 - 2.5 ppm ($2 - 5 \text{ mg.m}^{-3}$), respectively. The highest daily average concentrations measured were 71 ppm (100 mg.m^{-3}) and 25 ppm (50 mg.m^{-3}), respectively. The incidence of nasal symptoms, cough, eye symptoms, and headache were increased in the severely polluted community, but were not statistically significant. The authors concluded that

exposure to malodorous sulfur compounds may affect the health of children.

5. CONCLUSIONS

The results of this study will be used to inform health policy decision-making. Health management recommendations have been formulated, which include a recommendation of continued monitoring of reduced sulfur compounds and increased public outreach. Specifically, health risk communication has been identified as one of the priority areas.

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