



Trends in Passively-Measured Ozone, Nitrogen Dioxide and Sulfur Dioxide Concentrations in the Athabasca Oil Sands Region of Alberta, Canada

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ABSTRACT

The Athabasca Oil Sands Region (AOSR) in northeastern Alberta, Canada has attracted much international attention in recent years due to the increased level of oil sands operations. A passive sampling program was initiated in 1999 to monitor ozone (O₃), nitrogen dioxide (NO₂) and sulfur dioxide (SO₂) in the AOSR for the estimation of the exposure of the forest monitoring sites and the characterization of temporal trends. Since 1999, highest concentrations of O₃ and NO₂ occurred in April and winter, respectively. The observed spring O₃ maximum is common in the northern hemisphere. The higher winter-time NO₂ concentrations were due to low atmospheric mixing height, stable atmosphere, and higher emissions during winter.

Sen-Theil trend analysis, a non-parametric analysis for temporal trending, determined that O₃ concentrations from 2000 to 2009 did not change. NO₂ concentrations increased slightly at three sites, and significantly increased at two sites closer to stationary and mobile sources. SO₂ concentration was increasing at JP107 and was decreasing at JP101. SO₂ concentrations did not increase at 4 other sites close to the major emissions. This suggests that SO₂ emissions were likely stable.

Spatial analysis was conducted to characterize the concentration distribution in the region. The O₃ concentrations were low near the emission sources (9.4 km) likely due to local O₃ titration. Highest NO₂ and SO₂ concentrations were measured near the main source area. Generally, passively measured monthly average concentrations of O₃, NO₂ and SO₂ stabilized at 20, 48 and 48 km from the main source area suggesting NO₂ and SO₂ emission influences were limited to < 50 km away from the major sources. However, one site (JP107) located near the Athabasca River Valley, 94 km north of the main source area, had higher SO₂ and NO₂ concentrations. This could be attributed to influence of valley flow, and/or to additional sources added in the region since 2007.

Keywords: Trend; Athabasca oil sands region; Passive sampler; Ozone; Sulfur dioxide; Nitrogen dioxide.

INTRODUCTION

Oil sands are a mixture of clay, sand, water and bitumen. Oil sands deposits occur in the Athabasca, Peace River and Cold Lake regions of Alberta, Canada. Canada's Oil Sands deposits cover some 140,200 km² reported by Alberta Energy (2011). The AOSR in northeastern Alberta is the largest deposit, and it has attracted global attention due to environmental concerns over the rapid pace of industrial expansion related to bitumen extraction. The AOSR resource is estimated to contain some 170 billion barrels of recoverable oil. As of January 2011, Canada is third to Venezuela and Saudi Arabia in terms of global oil reserves (CAPP, 2011). In the AOSR, approximately 20% of the resource is situated close enough to the surface to be mined with shovels and

trucks. The remainder of the bitumen lies deep below the surface and can only be recovered at this time by in-situ extraction methods such as Steam Assisted Gravity Drainage (SAGD). Oil production in 2010 was 1.5 million b/d (barrels of oil per day) with production expected to reach 3.5 million b/d by 2025 (CAPP, 2010).

In the AOSR there are varied emission sources including natural (e.g., forest fires and vegetation), oil sands operations (i.e., fixed, mobile, fugitive), and urban/transportation. Nitrogen dioxide (NO₂) and sulfur dioxide (SO₂) are the major criteria air contaminants emitted from the oil sands operation processes. According to the Canadian National Pollutant Release Inventory (NPRI), 2009 emissions from main stacks were 1.6, 79 and 307 tones/d for NH₃, NO_x (NO and NO₂, expressed as NO₂) and SO₂, respectively (<http://www.ec.gc.ca/inrp-npri/>). Facility reporting indicates stacks (flue-gas desulfurization) as the major SO₂ sources with NO_x emission sources being split between stacks and area sources (i.e., mine-fleets) at ratios dependent upon process used.

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www.wbea.org) is a multistakeholder, not-for-profit organization created in 1997 and has been responsible for monitoring air quality in the AOSR since its inception. Continuous, time-integrated, and passive methods are used for assessing ambient air quality. Time-integrated methods include filter-based 24-hour PM_{2.5} and PM₁₀ measurements for mass, ionic and metal species. The continuous monitors (84 analyzers at 15 stations) provide real time data but require ease of access and power. Outside of the Athabasca River Valley in the boreal forest, WBEA has used passive sampling techniques since 1999 to measure ambient concentrations of selected air pollutants. The advantages of passive samplers are low cost, no power requirement, and ease of maintenance. The disadvantages are low sensitivity, inability to resolve peak concentrations, possible interference from other species and significant influence of wind speed, temperature and relative humidity on passive sampler performance (Krupa and Legge, 2000). Passive samplers have been successfully used for monitoring large-scale, long term trends of air pollutants in remote areas (Krupa and Legge, 2000; Cox, 2003; Seethapathy *et al.*, 2008; Bytnerowicz *et al.*, 2010).

The principle of passive samplers is that gas molecules are collected by diffusion using a collection medium coated with a chemical having specific affinity to the substance of interest. The sampling flow-rate of passive samplers is mainly controlled by pore size of the diffusion barrier, relative humidity, wind speed, and temperature. Many passive samplers have been developed for the pollutants of interest, including inorganic and organic compounds (Krupa and Legge, 2000; Cox, 2003; Namiesnik *et al.*, 2005; Kot-Wasik *et al.*, 2007; Levy *et al.*, 2007; Seethapathy *et al.*, 2008; Campos *et al.*, 2010). The data collected by passive samplers can be used to estimate spatial distribution and temporal trends of the pollutants being measured to link with effects on forest health indicators and to estimate the deposition of atmospheric species of interest (Krupa *et al.*, 2001; Ray, 2001; Cape *et al.*, 2004; Delgado-Saborit and Esteve-Cano, 2008; Sicard *et al.*, 2011).

To characterize SO₂, NO₂ and O₃ concentrations for further analyses of sulfur/nitrogen deposition and photochemistry in the AOSR, passive sampling methodology has been applied to monitor these three species at remote forested sampling locations up to 150 km from oil sands processing facilities (upgrading facilities). The objectives of this study were (1) to characterize seasonal variation in concentrations and (2) to describe the temporal trend of ambient NO₂, SO₂, and O₃ concentrations in the AOSR.

METHODS

Sampling Sites

The passive sampling program was initiated at remote boreal forest sites in 1999. The remote boreal forest sites are accessible only by helicopter. The 10 remote sampling sites and the major industrial operations are shown in Fig. 1. Data from six remote sites (JP107, AH3, AH7, JP101, JP104, and JP102) were used in the 10 year (2000–2009) trending. Data from ten sites (JP107, AH3, AH7, JP101,

JP104, JP102, JP205, JP210, JP212, and JP213) were used for spatial analysis of concentrations in 2008 and 2009. Sites JP104, JP212, JP102, AH3, and AH7 are within 50 km to industrial activities. The remaining sites JP107, JP101, JP205, JP213, and JP210 are > 50 km away from industrial activities.

The coordinates of a reference point (AMS 2), three community stations, and 10 remote sites with the corresponding distances to the reference point are listed in Table 1. AMS 2 is designated as industrial site and located in the middle of the industrial activities. AMS 1, AMS 6 and AMS 8 are located in residential areas of Fort McKay, Fort McMurray and Fort Chipewyan, respectively (Fig. 1). The populations of Fort McKay, Fort McMurray and Fort Chipewyan were 562, 61,374, and 847 persons (respectively) in Canadian 2011 Census (<http://www.statcan.gc.ca>). AMS 1 is in close proximity to oil sands operations, and AMS 6 and AMS 8 are 34 km south and 186 km north from the reference point, respectively. Data from four of the 15 WBEA air monitoring stations (AMS 1, AMS 2, AMS 6, and AMS 8) with continuous monitors were used in this study.

AMS 2 was set as a reference point to characterize the relationship between concentrations of three species and distance since AMS 2 is in the geographic center of the two largest stationary emission sources. Passive samplers were collocated with continuous monitors at two community stations, AMS 1 and AMS 6, to evaluate the accuracy and precision of passive samplers for O₃, NO₂ and SO₂. AMS 8, a community station, was set as a background station for the O₃ concentration comparison from the continuous monitor.

Sampling and Analysis

The sampling period was monthly from April to September, and bimonthly from October to March. Due to lower concentrations, and due to access challenges, a bimonthly sampling schedule was adopted during the winter. This schedule resulted in nine sets of samples being collected each year at remote sites. Bimonthly concentrations were applied to each month directly. Duplicate samples were acquired at each remote site. The passive samplers were situated 2 m above the forest canopy on 18 m towers. To prevent the gravitational deposition of aerosols, the passive samplers were placed facedown under a shelter.

The all-season SO₂ passive sampling system (SPSS) (Tang *et al.*, 1997), all-season NO₂ passive sampling system (NPSS) (Tang *et al.*, 1999) and O₃ passive sampling system (OPSS) (Tang and Lau, 2000) were used to measure SO₂, NO₂ and O₃. As shown in Fig. 2, the OPSS comprises two parts: a Teflon film as a diffusion barrier and a filter coated with sodium nitrite as an O₃ collection medium, separated by an air gap as the diffusion area. NPSS and SPSS were similar to the OPSS, but used Teflon film as the diffusion barrier, and CHEMIXTM as the collection medium for NO₂, and a sodium carbonate coated filter for SO₂. SO₂, O₃ and NO₂ samples were extracted and analyzed by ion chromatography (DX-120, Dionex Corp., US) for sulfate, nitrate and nitrite concentrations. Following collection, the passive sampler was stored in a sealed container delivered to a commercial laboratory and analyzed within 30 days.

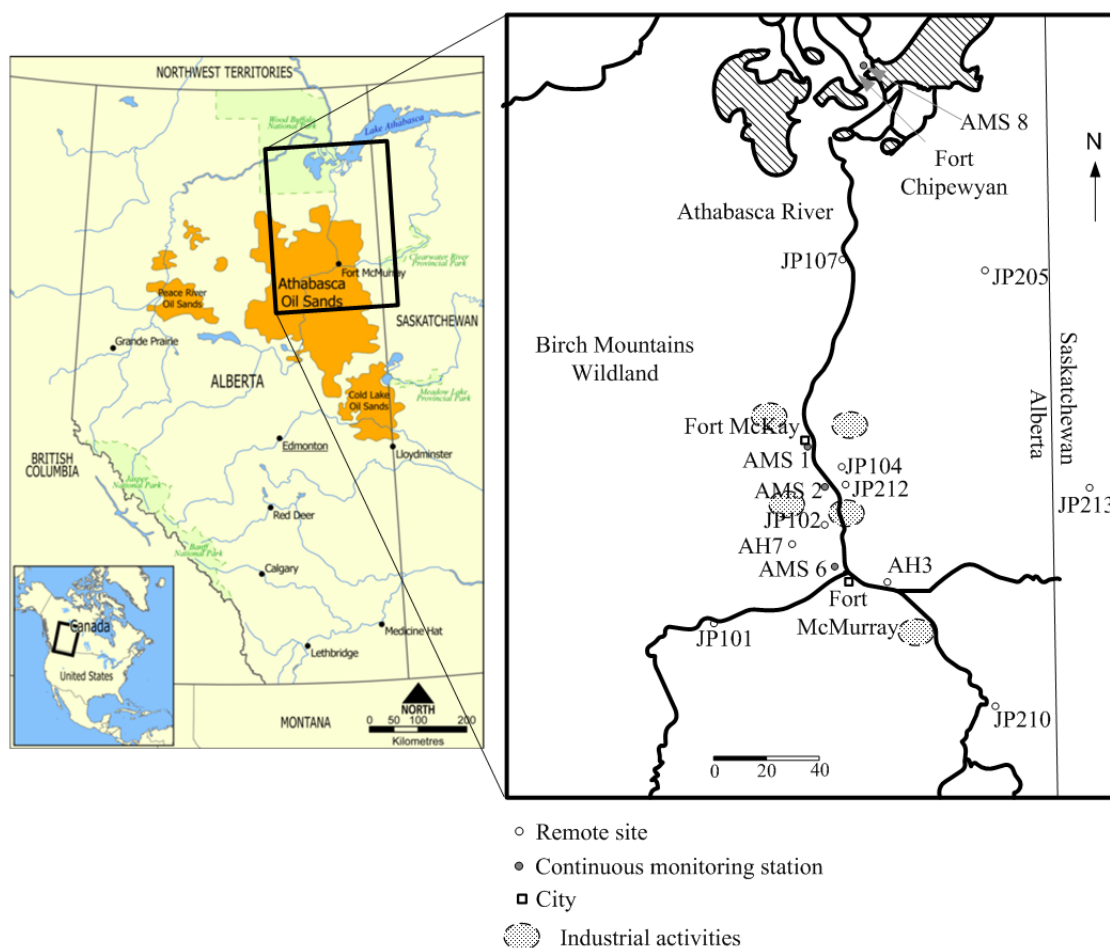


Fig. 1. Map of sampling locations in Alberta, Canada (http://en.wikipedia.org/wiki/File:Athabasca_Oil_Sands_map.png).

Table 1. Coordinates of 14 sampling sites.

Site	Description	Latitude	Longitude	Distance ^a (km)
AMS 1	Community station (Fort McKay)	N 57°11.367	W 111°38.427	16.2
AMS 6	Community station (Fort McMurray)	N 56°45.081	W 111°28.582	33.7
AMS 8	Community/Background station (Fort Chipewyan)	N 58°42.504	W 111°10.584	186.2
JP101	Remote site	N 56°32.375	W 112°16.529	71.6
JP107	Remote site	N 57°53.415	W 111°26.113	93.9
JP102	Remote site	N 56°54.577	W 111°32.443	15.7
JP104	Remote site	N 57°07.169	W 111°25.460	11.5
AH3	Remote site	N 56°41.785	W 111°07.337	47.7
AH7	Remote site	N 56°49.789	W 111°46.070	27.5
JP205	Remote site	N 57°50.528	W 110°26.872	110.8
JP210	Remote site	N 56°16.307	W 110°26.776	110.5
JP212	Remote site	N 57°03.236	W 111°24.532	9.4
JP213	Remote site	N 57°02.717	W 109°45.071	110.0
AMS 2	Reference point (Industrial station)	N 57°02.987	W 111°33.829	0

Distance^a: the distance from the site to the reference point, AMS 2.

Sampling flow rates of SO₂, NO₂ and O₃ passive samplers are calculated by Eqs. (1–3).

$$R_s = 12.769 T^{0.5} - 0.540 RH + 0.276 WSP - 135 \text{ for SO}_2 \quad (1)$$

$$R_s = 25.960 T^{0.5} - 0.175 RH + 0.180 WSP - 388 \text{ for NO}_2 \quad (2)$$

$$R_s = 14.8 T^{0.5} + 0.259 RH + 0.275 WSP - 197 \text{ for O}_3 \quad (3)$$

R_s = Sampling flow rate (mL/min)

T = Temperature (K)

RH = Relative humidity (%). If RH > 80, then RH = 80.

WSP = Wind speed (cm/s). If WSP > 130, then WSP = 130.

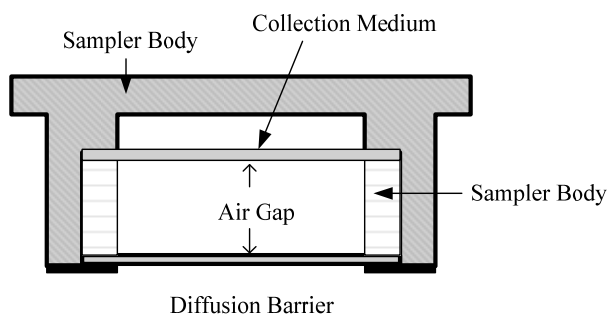


Fig. 2. Passive sampler (Tang *et al.*, 2000).

A SO₂ monitor (43A, Thermo Electron Instruments Inc), NO₂ monitor (42C, Thermo Environmental Instruments Inc), and O₃ monitor (49C, Thermo Environmental Instruments Inc) were employed to monitor real time SO₂, NO₂ and O₃ concentrations at AMS 1 and AMS 6 for the evaluation of the passive samplers. The passive samplers at these stations were installed 1 m above the station roof, near the inlet for the gas analyzers. Triplicate passive samples of SO₂, NO₂ and O₃ were collected monthly at the stations. Twelve sets of samples were collected each year from 2003 to 2008.

The method detection limits of SO₂, NO₂ and O₃ passive samplers were 0.1, 0.1, and 0.1 ppb and laboratory blanks for identifying laboratory contamination were < 0.1 ppb. The mean of relative standard deviation (RSD, %) were 8% (n = 136) for SO₂, 10% (n = 136) for NO₂ and 7% (n = 137) for O₃.

Data Analysis

Two models were used in the O₃, NO₂ and SO₂ trending analyses: (1) simple linear regression (parametric method) for a preliminary trending analysis; and (2) Sen-Theil trend analysis (non-parametric method) for an advanced trending analysis.

Simple Linear Regression

The simple linear regression, as shown in Eqs. (4–6) (Weisberg, 2005), was used in the preliminary Exploratory Data Analysis (EDA).

$$Y_t = \alpha + \beta t + \varepsilon \tag{4}$$

where Y_t is the value of the measured variable Y at time t , α and β are the regression intercept and slope respectively (ε represents the error term). Their estimators are computed as follows (bars represent corresponding means):

$$\hat{\beta} = \frac{\sum_{t=1}^n (t - \bar{t})(Y_t - \bar{Y})}{\sum_{t=1}^n (t - \bar{t})^2} \tag{5}$$

$$\hat{\alpha} = \bar{Y} - \hat{\beta}\bar{t} \tag{6}$$

n is the number of observations ($n = 120$).

Sen-Theil Trend Analysis

Sen-Theil trend analysis of time series was applied for advanced trending analysis. Sen-Theil trend analysis of time series does not assume any parametric properties, which are required for the standard simple linear regression trend analysis. It is based on a nonparametric concept calculating slopes between any pair of observed data. Considering a time series of observations $x_1, x_2, x_3, \dots, x_n$ ($n = 120$ in this study), the Sen-Theil algorithm computes all slopes of the form

$$S_{ij} = \frac{x_i - x_j}{i - j} \tag{7}$$

where x_i is the pollutant concentration at time $i = 1, 2, 3, \dots, 120$, $i = 1$ representing January 2000, and $i = 120$ representing December 2009. There are altogether $N = \binom{n}{2} = \frac{n(n-1)}{2}$ such pairs. The corresponding slopes are ordered according to their magnitude as follows:

$$S^{(1)} \leq S^{(2)} \leq S^{(3)} \leq \dots \leq S^{(N)} \tag{8}$$

Then if N is odd, $N = 2 \times k + 1$ then

$$S = \text{Sen slope} = \text{Median}(S^{(i)}) = S^{(k+1)} \tag{9}$$

If N is even, $N = 2 \times k$, then

$$S = \text{Sen slope} = (S^{(k)} + S^{(k+1)})/2 \tag{10}$$

In order to get the lower limit S_{low} and the upper limit S_{high} of the corresponding $(1 - \alpha) \times 100\%$ confidence interval for Sen slope, we calculate

$$C_\alpha \approx z_{\alpha/2} \left\{ \frac{n(n-1)(2n+5)}{18} \right\}^{1/2} \tag{11}$$

where $z_{\alpha/2}$ is the corresponding critical point of the of the Gaussian distribution. Then we set $M_1 = (N - C_\alpha)/2$ and $M_2 = (N + C_\alpha)/2$. The corresponding Sen-Theil $(1 - \alpha) \times 100\%$ confidence interval limits are

$$S_{low} = S^{(M_1)} \text{ and } S_{high} = S^{(M_2+1)} \tag{12}$$

RESULTS AND DISCUSSION

Monthly Variation in Ambient Concentrations

O₃ Concentration

Monthly O₃ concentrations at six remote sites are illustrated in Fig. 3. All sites clearly showed an annual cycle. The highest O₃ concentrations occurred in April, a spring maximum, with a small increase visible in November. The spring O₃ maximum is a common phenomenon at the northern hemisphere. Several hypotheses for the spring O₃ maximum are: (1) stratospheric intrusion (Levy *et al.*, 1985; Logan, 1985; Dickerson *et al.*, 1995; Moody *et al.*, 1995;

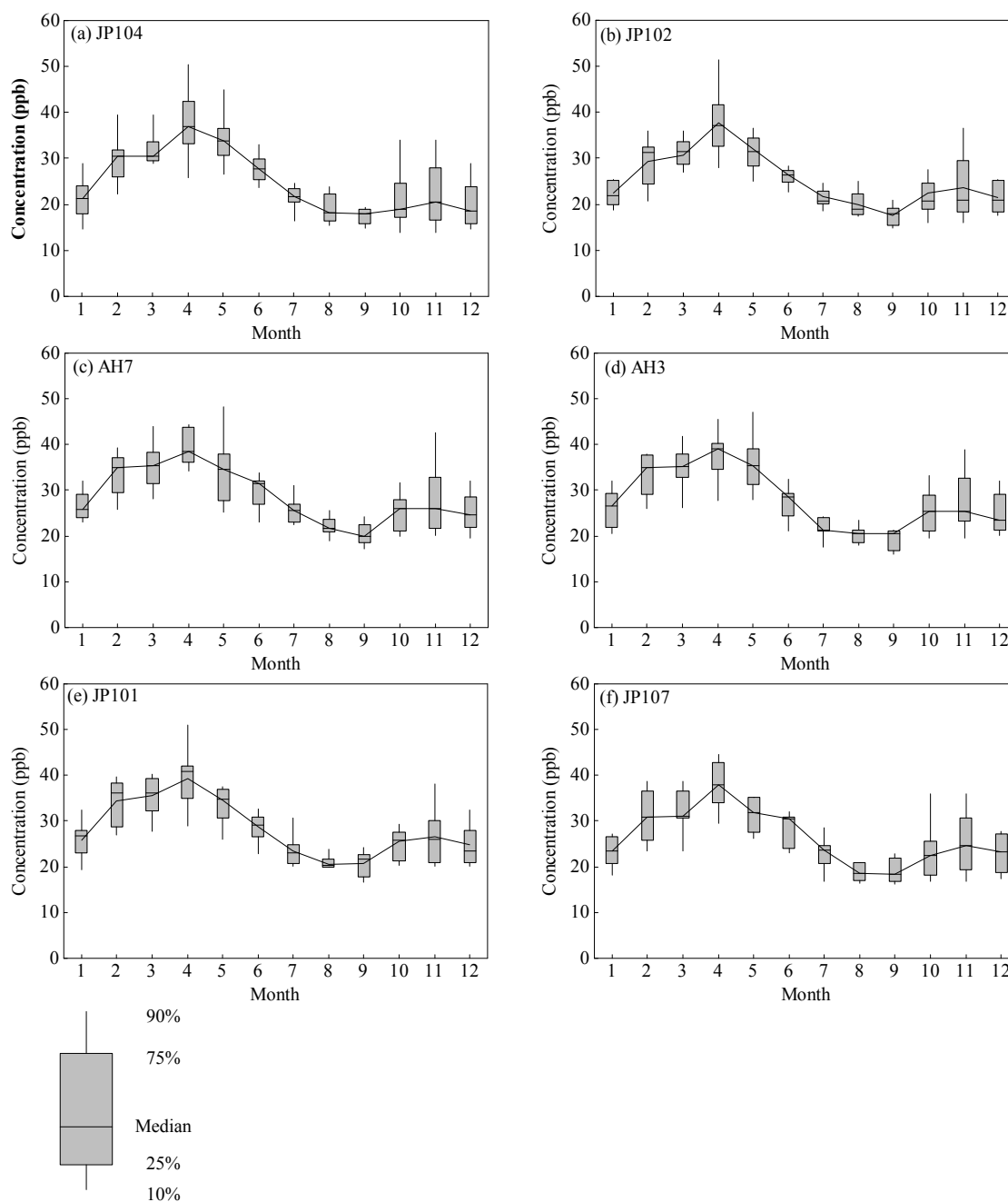


Fig. 3. Monthly variation in passively measured O₃ concentrations from 2000 to 2009, (a) JP104, (b) JP102, (c) AH7, (d) AH3, (e) JP101, and (f) JP107.

Oltmans *et al.*, 2004); (2) wintertime accumulation of ozone at high latitudes (Liu *et al.*, 1987; Honrath *et al.*, 1996); and (3) phase overlap between stratospheric injection and tropospheric ozone production (Wang *et al.*, 1998; Yienger *et al.*, 1999). However, it should be noted that maximum 1-hr O₃ concentration was observed by the O₃ continuous monitor in summer, likely due to photochemical reaction.

Interestingly, the small increase observed in November has apparently become less pronounced in recent years. Angle and Sandhu (1986) also reported on O₃ concentrations in Birch Mountains and at Bitumount from 1977 to 1980, when only two oil sands operations were in production. They

found that monthly O₃ concentrations exhibited a bimodal distribution in the Birch Mountains, approximately 100 km NE of Fort McMurray, but not in Bitumount closer to the oil sands development near the Athabasca River Valley. It is unlikely the oil sands activities caused the observed secondary November O₃ peak.

NO₂ Concentration

We measured higher NO₂ concentrations in the winter months (Fig. 4) due to a stable atmosphere, lower mixing height, slower photochemical reactions, and higher emissions. The examples resulting in higher NO_x emissions in the

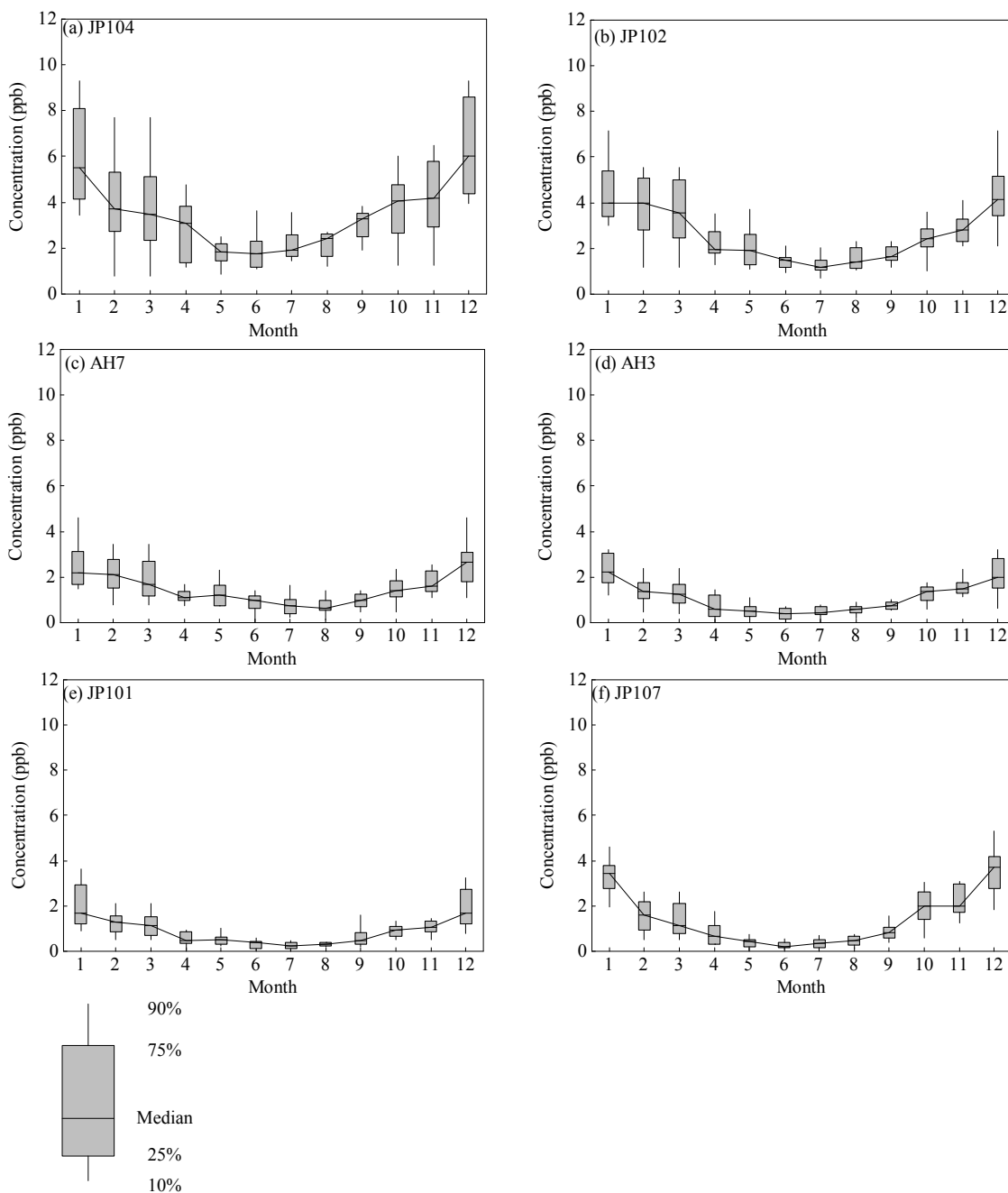


Fig. 4. Monthly variation in passively measured NO₂ concentrations from 2000 to 2009, (a) JP104, (b) JP102, (c) AH7, (d) AH3, (e) JP101, and (f) JP107.

winter include: (1) more NO_x emit to atmosphere from both on-road and non-road vehicles at both idling (USEPA, 1998) and cold-start conditions; and (2) residential heating in the winter. At 57 degrees N latitude, day length is very short (circa 7 hours minimum), and temperature is extremely low in the winter months, and these factors necessarily result in slow photochemical reaction rates.

Protelli (1977) and Davison *et al.* (1981) have estimated the mixing heights for Fort Smith, Stony Plain, and around the Mildred Lake area (near AMS 2). The mixing heights calculated by Davison *et al.* (1981) were based on the seasonal analysis of minisonde measurements, and the mean

maximum afternoon mixing heights from Protelli (1977) were based on the analysis of radiosonde measurement. The mixing heights ranged from very low (208–270 m in January) to high (1,499–2,396 m in May and June) for Protelli’s study, and 1,000 m in summer for Davison *et al.* (1981). In general, the mixing heights are well established to vary significantly from winter to summer.

Among the six sites, NO₂ concentrations were highest in the winter months at JP104 (median 6 ppb) and JP102 (median 4.13 ppb) as these sites are closer to two main emission sources. The NO₂ concentrations at AH7, AH3 and JP101 had a similar pattern, and concentrations ranged

from 0.25 to 2.65 ppb. However, JP107, 94 km north of oil sands operations, but in the Athabasca Valley influence, also had higher NO_2 concentrations during winter months.

SO_2 Concentration

Monthly SO_2 concentrations are shown in Fig. 5. Interestingly, three types of SO_2 concentration patterns were found. At JP104 and JP102, no clear trend was observed. The SO_2 concentrations at these two sites might be influenced by the emissions directly. At AH3, JP101 and JP107, SO_2 concentrations had a seasonal pattern which was low in summer and high in winter. The lower mixing height and

stable atmosphere are the major reasons for high SO_2 concentrations in the winter months. In summer, the SO_2 reactions including dry deposition and heterogeneous reaction with aerosols to form sulfate (Seinfeld and Pandis, 2006) are usually faster due to more water surface area, higher concentrations of oxidants and higher temperature. The distance (or time) between the emissions and these three sites allowed SO_2 to undergo direct deposition, heterogeneous reaction, and within plume dilution. AH7 behaved as a transitional site between these two groups, sometimes impacted by emissions directly (i.e., May, Fig. 5(c)).

Overall, O_3 , and NO_2 monthly concentrations demonstrated

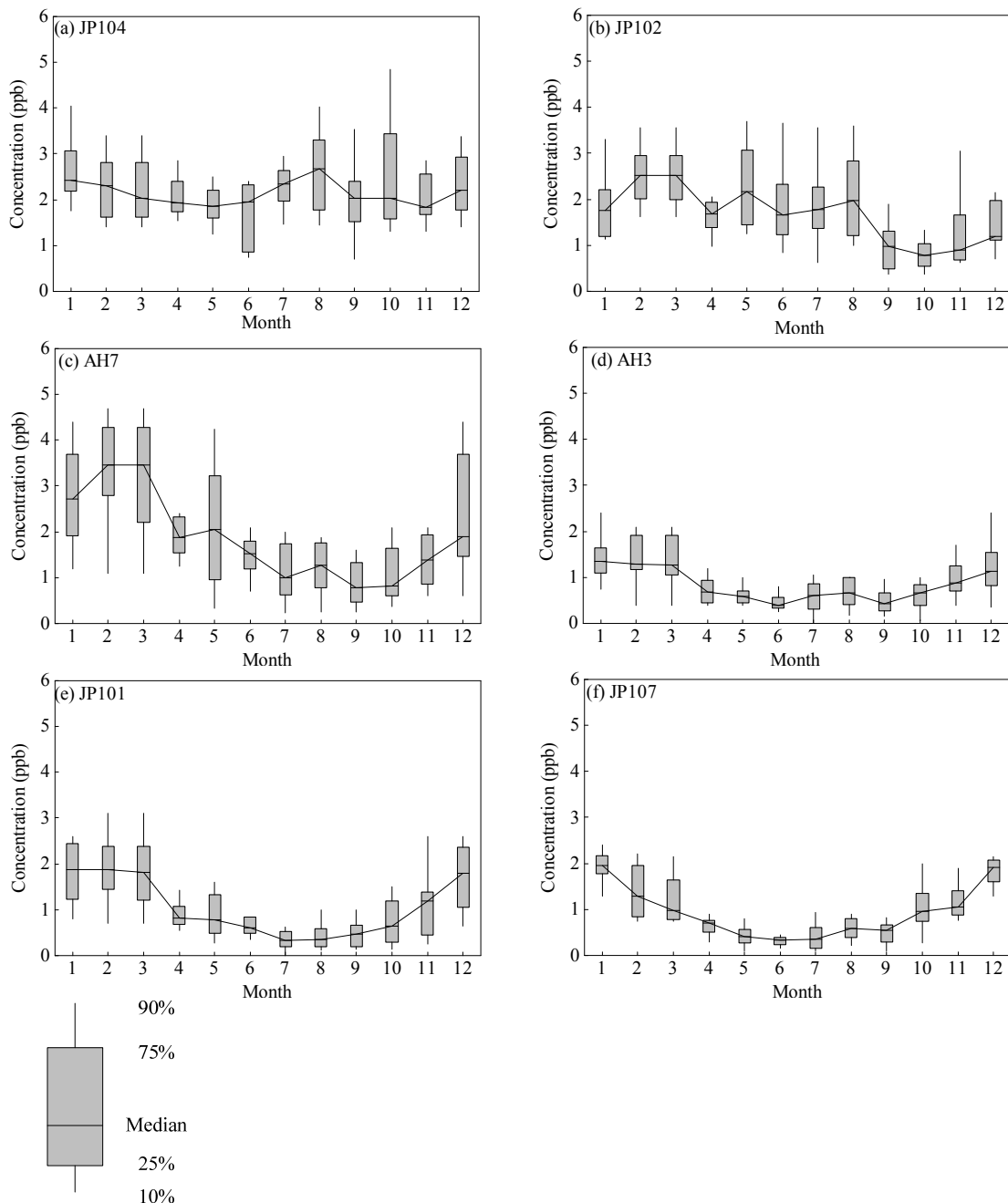


Fig. 5. Monthly variation in passively measured SO_2 concentrations from 2000 to 2009, (a) JP104, (b) JP102, (c) AH7, (d) AH3, (e) JP101, and (f) JP107.

the annual cycles in which O₃ and NO₂ concentrations reached their maximums in April and winter, respectively. SO₂ concentrations at sites (i.e., JP104 and JP102) close to emissions did not exhibit any seasonal patterns but the SO₂ concentration seasonal pattern was clear at sites (AH3, JP101 and JP107) 48 km away from the reference point.

10 Year Trend Analysis

The passive dataset comprises a monthly time series covering the time period from January 2000 to December 2009. It consists of 2,160 data points, including a few missing values due to sample loss in the field. Both simple linear regression model and Sen-Thiel trend analysis of time series were used for the 10 year trend analysis of O₃, NO₂ and SO₂ data from JP104, JP102, AH7, AH3, JP101 and JP107.

Simple Linear Regression Model

The simple linear regression model used annual average concentrations of O₃, NO₂ and SO₂ to examine the 10-year trend. During 2000 to 2009, all p-values for O₃ trend analyses (Fig. 6) at 6 sites were > 0.47 (Table 2) indicating no statistically significant change in O₃ during the period of this study. The highest O₃ concentrations occurred at all six sites in 2004 (Fig. 6). As displayed in Fig. 7, the peak annual average concentration was also observed by the O₃ continuous monitor at our background continuous monitoring station (AMS 8, located in Fort Chipewyan, Alberta) which is 180 km north from the reference point. Hence, the peak concentrations in 2004 might be influenced by the regional O₃ background concentration. Overall, the O₃ concentrations at JP104, JP102 and JP107 were lower than the concentrations at AH7, AH3 and JP101 (Fig. 6). JP104 and JP102 are close to large industrial NO_x emissions.

The concentrations of NO₂ at four of the six sites increased slightly from 2000 to 2009 (Fig. 8). These sites were JP104 (p

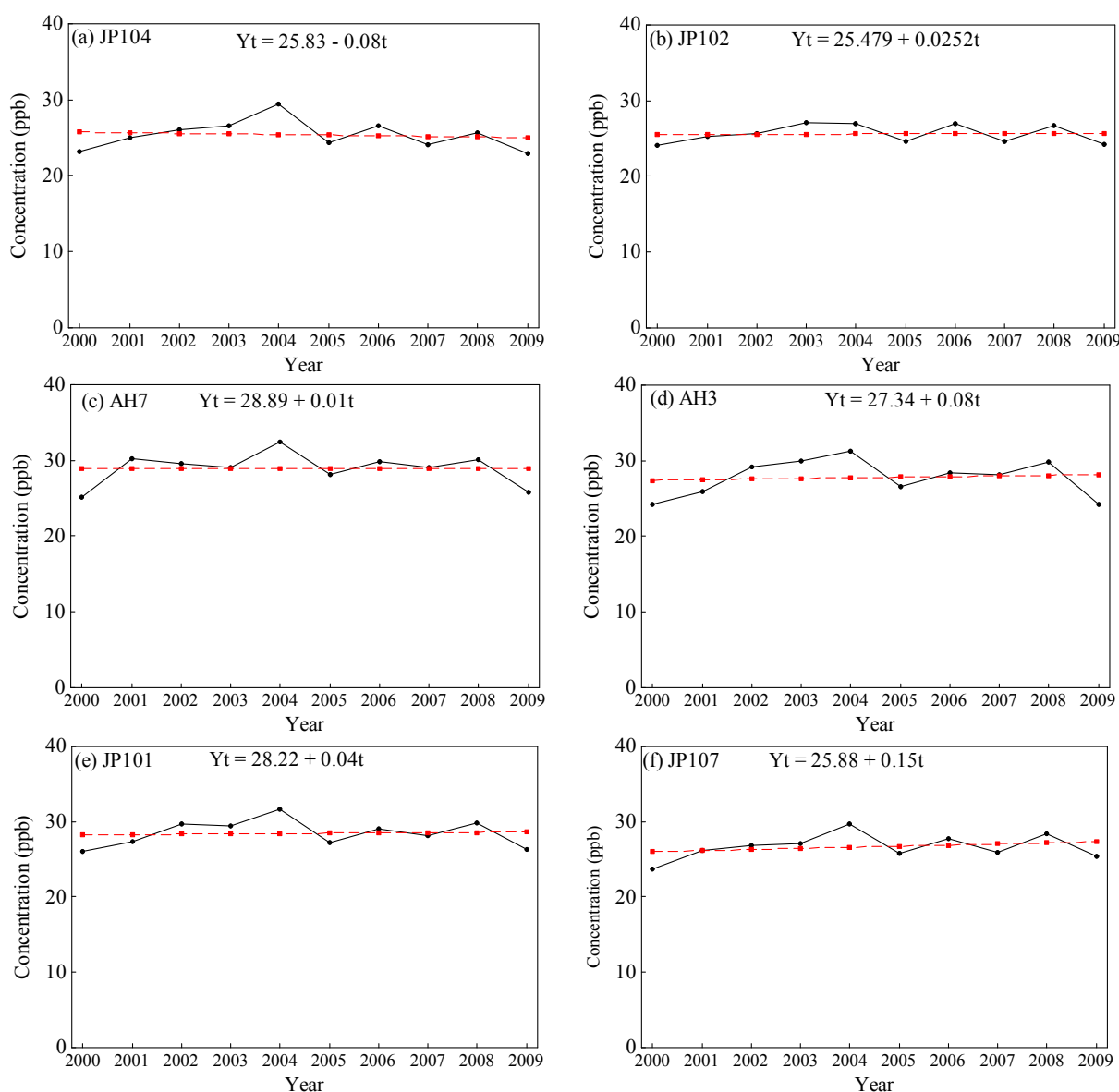


Fig. 6. Ten year O₃ trend analysis, (a) JP104, (b) JP102, (c) AH7, (d) AH3, (e) JP101, and (f) JP107.

Table 2. Simple linear regression analysis results for O₃, NO₂ and SO₂ passive concentrations.

Site	Model	R ²	p value	Trend
O₃				
JP104	Yt = -0.08t + 25.83	1.6 × 10 ⁻²	0.73	No significant change
JP102	Yt = 0.03t + 25.48	3.8 × 10 ⁻³	0.86	No significant change
AH7	Yt = 0.01t + 28.89	8.7 × 10 ⁻⁵	0.98	No significant change
AH3	Yt = 0.08t + 27.34	1.0 × 10 ⁻²	0.78	No significant change
JP101	Yt = 0.04t + 28.22	5.2 × 10 ⁻³	0.84	No significant change
JP107	Yt = 0.15t + 25.88	6.8 × 10 ⁻²	0.47	No significant change
NO₂				
JP104	Yt = 0.349t + 1.554	7.7 × 10 ⁻¹	< 0.01	Increasing
JP102	Yt = 0.131t + 1.809	5.5 × 10 ⁻¹	0.01	Increasing
AH7	Yt = 0.064t + 1.154	2.9 × 10 ⁻¹	0.11	No significant change
AH3	Yt = 0.064t + 0.733	4.7 × 10 ⁻¹	0.03	Increasing
JP101	Yt = -0.008t + 0.923	1.6 × 10 ⁻²	0.73	No significant change
JP107	Yt = 0.099t + 0.797	5.5 × 10 ⁻¹	0.01	Increasing
SO₂				
JP104	Yt = -0.007t + 2.226	1.4 × 10 ⁻²	0.74	No significant change
JP102	Yt = -0.012t + 1.915	4.3 × 10 ⁻²	0.56	No significant change
AH7	Yt = -0.010t + 2.120	5.2 × 10 ⁻³	0.84	No significant change
AH3	Yt = 0.002t + 0.892	1.7 × 10 ⁻³	0.91	No significant change
JP101	Yt = -0.016t + 1.206	6.5 × 10 ⁻²	0.48	No significant change
JP107	Yt = 0.025t + 0.834	2.4 × 10 ⁻¹	0.15	No significant change

*: t = 0 for year 2000.

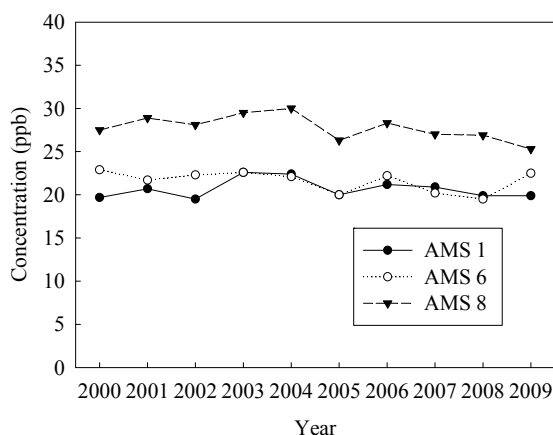


Fig. 7. Ten year O₃ mean annual concentrations (from hourly concentration) at 3 continuous monitoring stations.

< 0.01), JP102 (p = 0.01), AH3 (p = 0.03) and JP107 (p = 0.01) (Table 2). JP104 and JP102 are 11.5 and 15.7 km away respectively from the reference point. Increased NO₂ concentrations may be related to increased oil sands activities over the past 10 years. The NO₂ concentrations at AH7 (p = 0.11) and JP101 (p = 0.73) exhibited no significant change over 10 years.

For the 10-year SO₂ trend analyses at the six sites (Fig. 9 and Table 2), the low R-square values (< 2.4 × 10⁻¹) with p-values (> 0.15) demonstrated no significant change in SO₂ concentrations during the past 10 years, as bitumen production increased. The intercepts (> 1.915), however, indicated that SO₂ concentrations at sites near the main industrial area (JP104, JP102 and AH7) were higher than those at other remote sites. SO₂ is generated from bitumen

processing, notably combustion and/or coking processes as a part of the conversion of bitumen to synthetic crude oil. Sulfur reduction systems have been adopted to control sulfur emission from stacks. The use of sulfur reduction systems could be the key factor for no increase in SO₂ concentration level.

Sen-Thiel Trend Analysis of Time Series

The missing value pattern analysis revealed that the missing data patterns are conducive to imputation of missing data using standard statistical algorithms. The imputation method used fully conditional specification and predictive mean matching with regression model when required. There are no missing data after the imputation.

As shown in Figs. 3 to 5, the seasonal variations indicating strong periodicity can be clearly identified. In general, time series with a periodic component $M(t)$ which has periodicity d , given by a monthly periodic/seasonal nature is expressed as a linear combination of *sine* and *cosine* functions, which is called as harmonic regression function (HRF) (Bloomfield, 2000).

$$M(t) = a_0 + \sum_{j=1}^k (a_j \cos(\lambda_j t) + b_j \sin(\lambda_j t)) \quad (13)$$

where a_j and b_j are unknown parameters and λ_j are fixed frequencies, each being an integer multiple of $2\pi/d$, and a_0 is a constant.

Fig. 10 are the same time series (observed data) with the fitted harmonic regression function which captures seasonal periodicity for O₃, NO₂ and SO₂ at JP107 and the corresponding harmonic trend functions (seasonality) are Eq. (14), Eq. (15) and Eq. (16). The periodicity is very

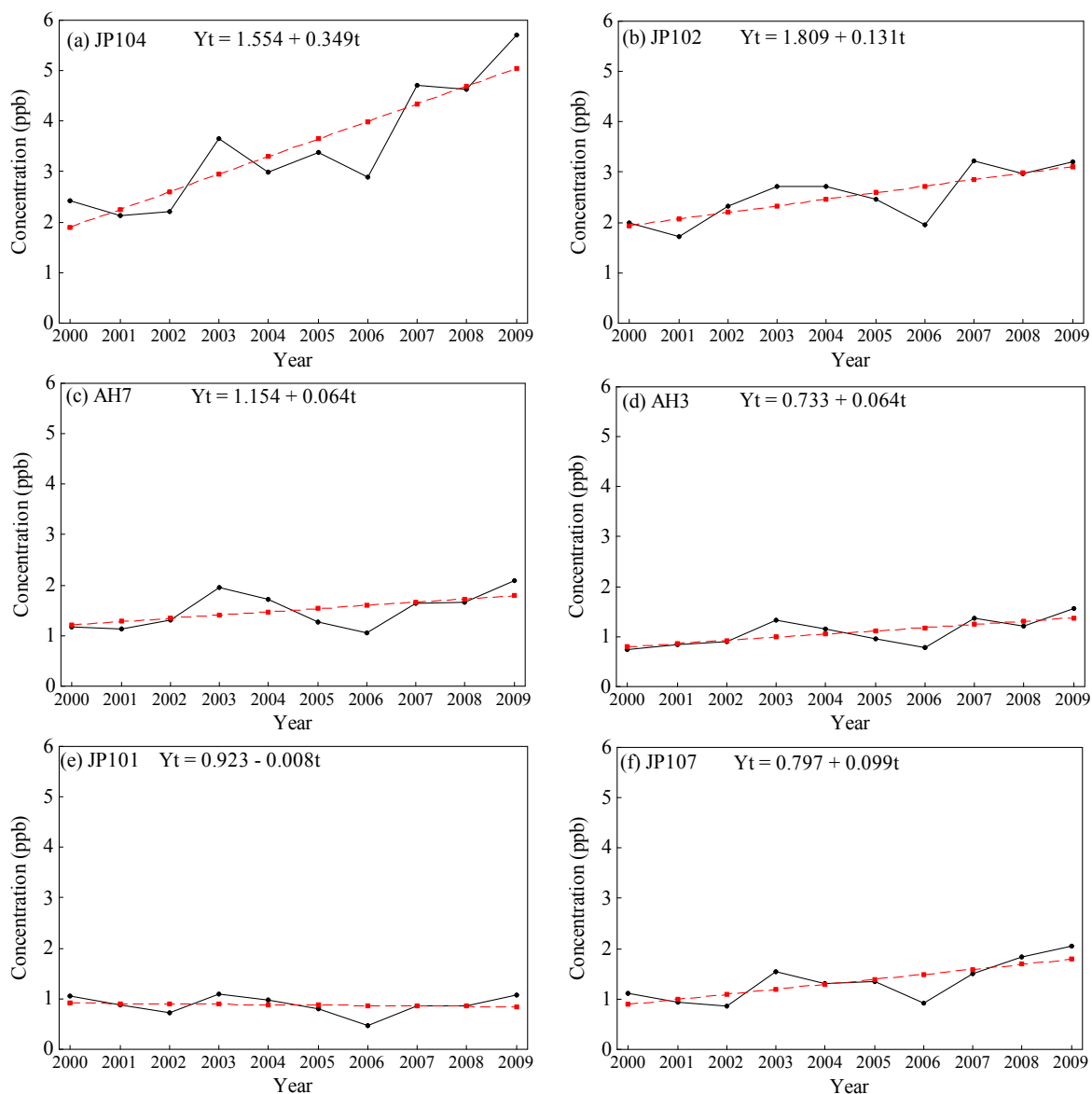


Fig. 8. Ten year NO₂ trend analysis, (a) JP104, (b) JP102, (c) AH7, (d) AH3, (e) JP101, and (f) JP107.

significant. We can clearly see the 12-months seasonal periodicity of O₃, NO₂ and SO₂ at JP107 and also very significantly high autocorrelations.

$$O_3(t) = 26.890000 - 1.7188727 \times \cos(20 \pi t/N) + 6.9198216 \times \sin(20 \pi t/N) - 0.44416667 \times \cos(40 \pi t/N) - 2.7323101 \times \sin(40 \pi t/N) - 0.29666667 \times \cos(60 \pi t/N) - 0.6200000 \times \sin(60 \pi t/N) \text{ (ppb)} \quad (14)$$

$$NO_2(t) = 1.3783333 + 1.3119753 \times \cos(20 \pi t/N) + 0.14639958 \times \sin(20 \pi t/N) + 0.31583333 \times \cos(40 \pi t/N) + 0.047631397 \times \sin(40 \pi t/N) + 0.16833333 \times \cos(60 \pi t/N) + 0.061666667 \times \sin(60 \pi t/N) \text{ (ppb)} \quad (15)$$

$$SO_2(t) = 0.97416667 + 0.67148602 \times \cos(20 \pi t/N) + 0.24135148 \times \sin(20 \pi t/N) + 0.10500000 \times \cos(40 \pi t/N) + 0.13279056 \times \sin(40 \pi t/N) + 0.035000000 \times \cos(60 \pi t/N) + 0.0066666667 \times \sin(60 \pi t/N) \text{ (ppb)} \quad (16)$$

where $t = 1$ representing January 2000, and $t = 120$ representing December 2009 and $N = 120$.

Gilbert (1987) states that a standard regression test in such cases can be misleading if seasonal cycles are present, data are not normally distributed, and/or the data are serially correlated. Furthermore, Gilbert (1987) states that the slope computed using the simple linear regression model based on least squares can deviate greatly from the true slope if there are gross errors or outliers in the data. Hence, calculating Sen nonparametric slope and performing Sen-Theil test of trend significance (Sen, 1968; Hollander and Wolfe, 1973) are required to determine and verify the trending. Table 3 has listed the computation values: Sen slope (Sen) and the corresponding Sen-Theil 95% confidence interval (S_{low} , S_{high}). Based on values of Sen , S_{low} , and S_{high} , SLOPE was determined and it states the result of the test of significance for the slope (existence of a trend).

It is quite interesting to compare results of the Sen-Theil

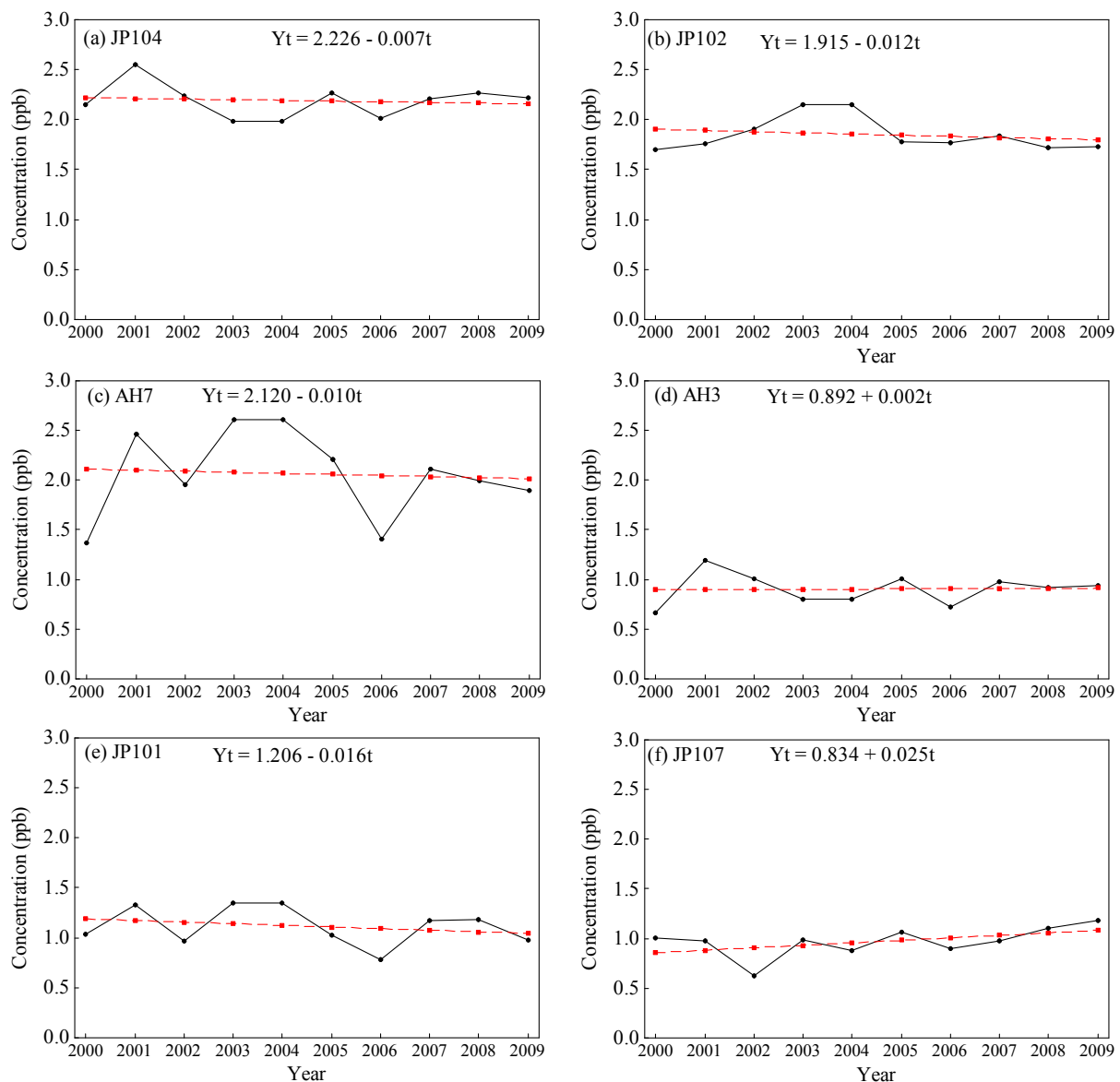


Fig. 9. Ten year SO₂ trend analysis, (a) JP104, (b) JP102, (c) AH7, (d) AH3, (e) JP101, and (f) JP107.

tests with the linear regression results. There is a complete agreement in O₃ case indicating O₃ concentrations had no statistically significant differences in the 10 years. In case of NO₂, there is a full agreement at JP107, JP104, JP101, and AH3 at which NO₂ concentrations were increasing at JP107, JP104 and AH3. In case of JP102, the linear regression model concludes that trend was increasing while Sen-Theil test concludes perhaps increasing. In case of AH7, linear regression analysis concludes that there is no trend while Sen-Theil test concludes perhaps there might be trend. In case of SO₂, linear regression concludes that there is no trend in all cases agreeing with Sen-Theil test conclusions except at JP107 where Sen-Theil test concludes that perhaps there might be an increase and at JP101 where Sen-Theil test concludes that there perhaps might be a decrease. Thus Sen-Theil analysis is in a very good agreement with the linear regression conclusions. However, while using linear regression may be questionable on the groups of theoretical

assumptions, Sen-Theil analysis is in every respect fully statistically justified. Furthermore, Sen-Theil analysis yields slightly more refined conclusions indicating that linear regression analysis conclusions might be tenuous.

From 2000 to 2009, the O₃ and SO₂ concentrations did not exhibit any significant changes (increasing or decreasing). The NO₂ concentrations at sites, i.e., JP104, JP102, and AH3, near the major emission sources, have increased during the past 10 years.

Concentrations of SO₂, NO₂ and O₃ in the AOSR

In 2005, three sites (JP205, JP201, and JP213) were added to the passive sampling network. In 2007, site JP212 was established to further characterize NO₂, O₃ and SO₂ concentrations in air near the major facilities. The annual average concentrations at six sites from 2001 to 2003, and at 10 sites from 2008 to 2009 were used to evaluate concentration changes over time.

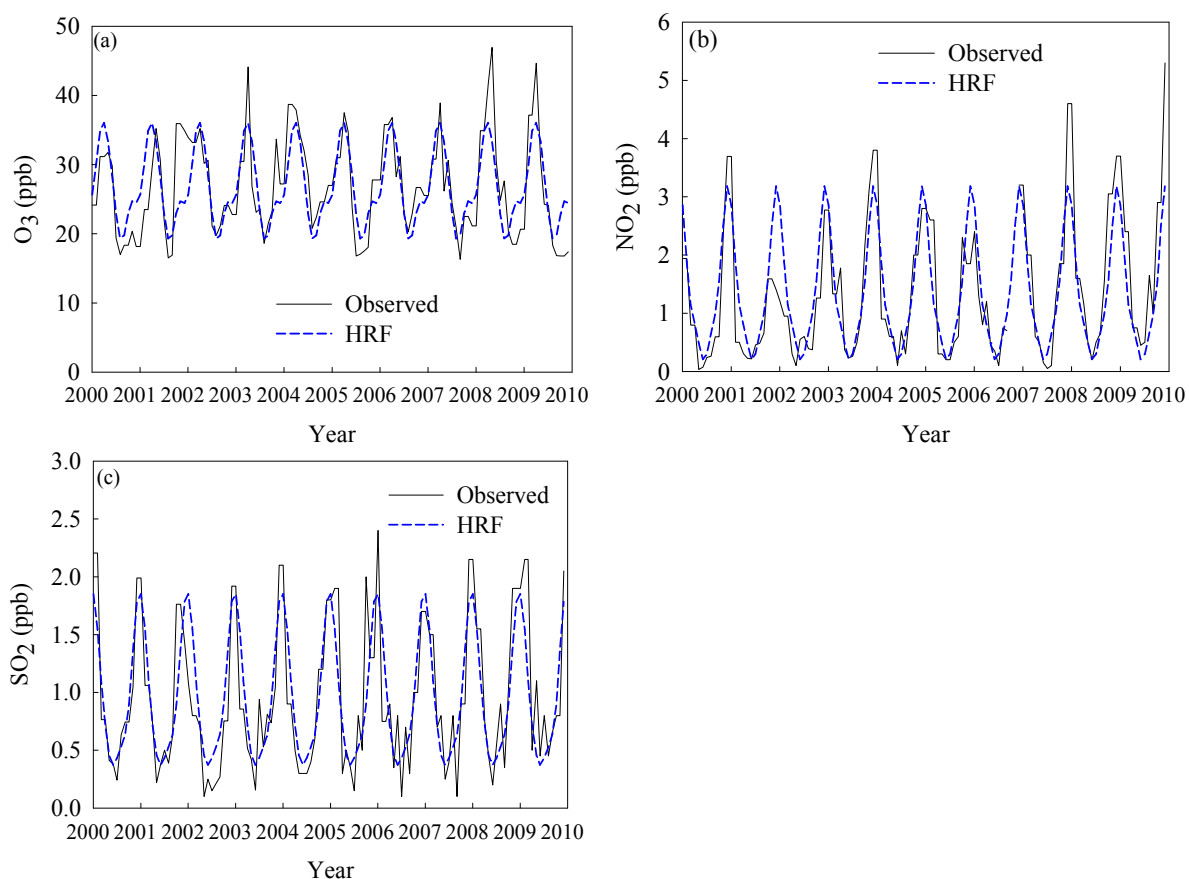


Fig. 10. Harmonic regression function (HRF) for (a) O₃, (b) NO₂ and (c) SO₂ at JP107.

Table 3. Sen-Theil test of slope significance.

	S_{low}	Sen	S_{high}	SLOPE*
O₃				
JP104	-0.065	-0.030	0.004	No
JP102	-0.047	-0.016	0.017	No
AH7	-0.051	-0.013	0.023	No
AH3	-0.036	0.000	0.036	No
JP101	-0.051	-0.015	0.021	No
JP107	-0.047	-0.006	0.030	No
NO₂				
JP104	0.015	0.023	0.033	Yes
JP102	0.000	0.005	0.012	Perhaps
AH7	0.000	0.004	0.008	Perhaps
AH3	0.001	0.004	0.008	Yes
JP101	-0.002	0.000	0.004	No
JP107	0.001	0.006	0.012	Yes
SO₂				
JP104	-0.005	-0.001	0.002	No
JP102	-0.005	0.000	0.004	No
AH7	-0.007	0.000	0.005	No
AH3	-0.002	0.000	0.003	No
JP101	-0.006	-0.003	0.000	Perhaps decrease
JP107	0.000	0.002	0.004	Perhaps

SLOPE *

No: no statistically significant slope (trend) at 95% confidence level.

Yes: statistically significant positive slope (trend) at 95% confidence level.

Perhaps: statistically non-significant slope (trend) at 95% confidence level.

O₃ Concentration

The spatial variation of O₃ concentrations is shown in Fig. 11(a). The multi-year O₃ concentrations were relatively low (17.4–21.5 ppb) at 9 km from AMS 2. The likely explanation is localized O₃ titration. Higher NO concentrations occur near major emission sources, and oxidation of NO by O₃ to form NO₂ would be expected. The O₃ concentration was stable at around 20 km, at 25 ppb in 2009.

Three sites, JP205, JP210 and JP213, are situated in northeast, southeast and east of the oil sands operations, and are all around 100 km away from the reference point. The lowest O₃ concentration was observed at JP205.

The highest O₃ concentrations were observed at site JP213 located in Saskatchewan. Most of the time, the monthly O₃ concentrations at JP213 were higher than those at other sites. Monthly concentrations were highly correlated at sites JP213 and JP205 ($R = 0.957$) and sites JP213 and JP210 ($R = 0.956$).

NO₂ Concentration

The NO₂ concentrations were lower and less variable at a distance of 48 km (Fig. 11(b)). The NO₂ concentrations from 2008 to 2009 were higher than those from 2001 to 2003. The NO₂ concentration decreased significantly within 30 km of the reference point. The highest NO₂ concentration (5.7 ppb) was at JP104, 2.7 times the concentration at 30 km in 2009. The NO₂ concentrations (4.16 ppb) at 9.4 km, site JP212, were lower than those (5.70 ppb) at 11.5 km, JP104. Site JP212 is close to the major emission sources of NO_x and NO is the major form of NO_x emitted. The O₃ titration results in elevated NO₂ concentration and lower O₃ concentrations. In addition, there was another industrial NO_x emission source close to JP104 site which might cause the elevated NO₂ concentration. However, higher NO₂ concentration and lower O₃ concentration were observed at JP107, 94 km from the reference point, for both 2008 and 2009.

SO₂ Concentration

The monthly average SO₂ concentrations (> 1.7 ppb) were higher within 28 km of the reference point. The SO₂ concentrations became quite stable and were low at a distance of 48 km. Lower SO₂ concentrations could result from emissions dilution, deposition and atmospheric chemical reactions of SO₂. The highest SO₂ concentration (2.6 ppb in 2003 and 2.2 ppb in 2009) was at 11.5 km (JP104).

In 2009, JP107 had slightly higher SO₂ concentration than in 2001 to 2003. As shown in Fig. 5(f), SO₂ concentrations were low in summer and the emissions from forest fire might not be the reason to explain the elevated SO₂ concentration. Besides, the occurrence of fires in 2008 and 2009 was low. In general, the SO₂ concentrations in the past 10 years at all sites were very similar year to year.

In summary, O₃ concentrations were low near the emission sources, while SO₂ and NO₂ concentrations were higher near the reference point. The highest NO₂ concentration was observed at 11.5 km, JP104. Elevated NO₂ and SO₂ concentrations were observed at JP107 in 2008 and 2009. The possible explanations are the influence of the Athabasca

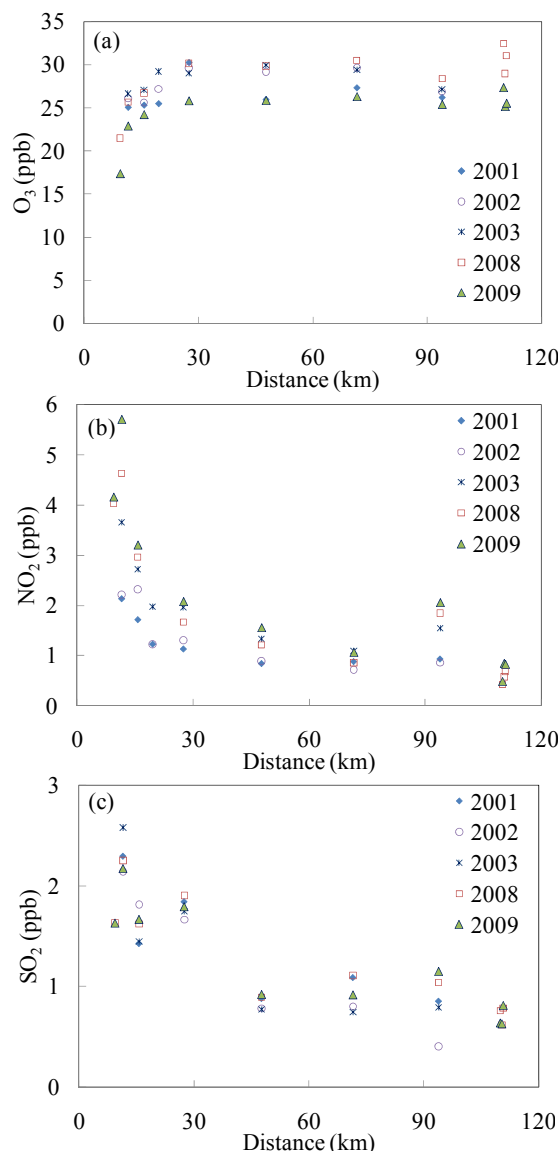


Fig. 11. Variation of concentrations with distance from AOSR reference point for (a) O₃, (b) NO₂, and (c) SO₂.

Valley flow and the new industrial emission near JP107. Further investigation should be conducted to verify the main source.

Comparison of Passive and Active Measurements

Collocated passive and active measurements were obtained at AMS 1 and AMS 6 ($n = 138$ for O₃, $n = 139$ for NO₂, and $n = 142$ for SO₂).

O₃ Measurement

The O₃ concentrations from the OPSS and the continuous monitor are shown in Fig. 12(a). The O₃ monthly average concentrations from the OPSS ranged from 10.0 to 43.3 ppb, and hourly concentrations from the continuous monitor ranged from 9.6 to 36.9 ppb. Most data points are within the $\pm 30\%$ range of O₃ concentrations from continuous monitor.

Descriptive statistics are listed in Table 4. The median of O₃ concentrations from the OPSS, 22.0 ppb, was slightly

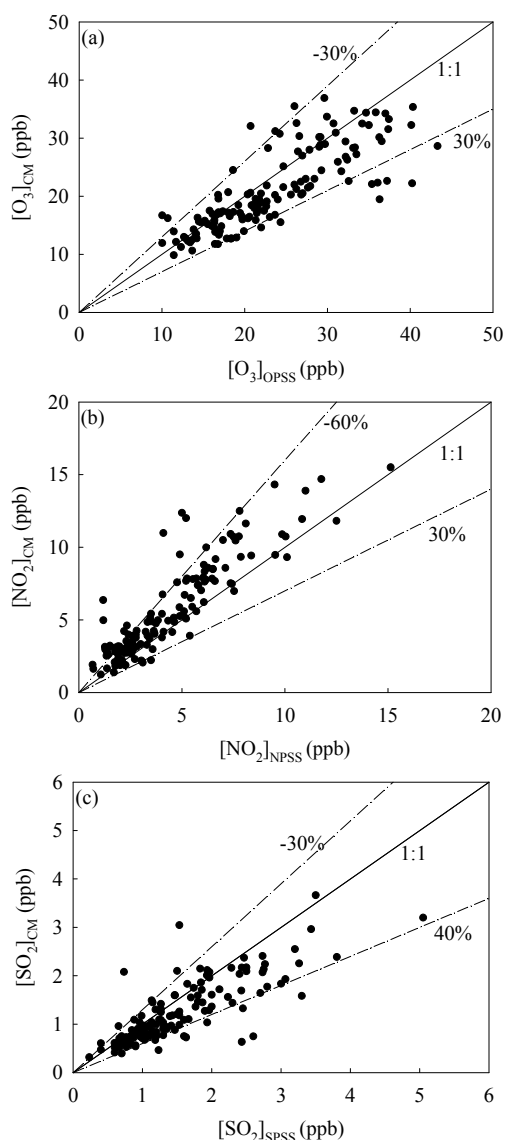


Fig. 12. (a) O_3 , (b) NO_2 , and (c) SO_2 concentration comparison between continuous and passive measurements.

higher than that from the continuous monitor, 19.5 ppb. The Pearson correlation coefficient was 0.81 which implies the O_3 concentrations from two measurements were correlated. However, the p-value was < 0.01 indicating the O_3 concentrations from two measurements were significantly different.

NO₂ Measurement

Monthly average NO_2 collocated concentrations exhibited a wider range from 1.23 to 15.50 ppb. The NO_2 concentrations from the NPSS were lower than those from the continuous monitors as shown in Fig. 12(b). Most data points from the NPSS were between -60% and 30% of NO_2 concentrations from the continuous monitor. The deviation increased when NO_2 concentrations were higher.

The median NO_2 concentration from the NPSS, 3.67 ppb, was lower than hourly concentration from the NO_2 continuous monitor, 4.85 ppb. The Pearson correlation

coefficient was 0.90 and the p-value was < 0.01 which indicates that the means between two measurements were statistically significantly different.

SO₂ Measurement

The monthly average SO_2 concentrations were generally low and the concentrations ranged from 0.32 to 3.66 ppb. The SO_2 concentrations from the SPSS were generally higher than those from the continuous monitors within the range of -30% to 40% as displayed in Fig. 12(c).

The median SO_2 concentration from the SPSS, 1.27 ppb, was slightly higher than the mean hourly concentration from the SO_2 continuous monitor. The Pearson correlation coefficient is 0.76 and the p-value of t-Test is lower than 0.01 indicating the mean SO_2 concentrations from two measurements were statistically significantly different.

In general, the NPSS underestimated the NO_2 concentration and the OPSS and SPSS overestimated the O_3 and SO_2 concentrations slightly. Significant difference between continuous measurement and passive measurement is likely due to inability of passive samplers to react to short-exposures, and higher concentrations (Krupa and Legge, 2000). In other words, the concentrations from the passive samplers cannot be applied as the concentrations from the continuous measurement. However, high correlation coefficients between two measurements still demonstrate the passive measurement can be effectively used to determine the long-term trend.

CONCLUSIONS

The monthly O_3 concentrations showed the expected spring O_3 maximum which is a common phenomenon at the northern hemisphere. The NO_2 concentrations were high in the winter months due to the stable atmosphere, lower mixing height, and higher emissions. The SO_2 concentrations did not have a clear seasonal pattern near the major emission sources and the SO_2 concentrations had a similar seasonal pattern with NO_2 concentrations at distant sites (50 km away from the reference point).

Trending analysis using linear regression and non-parametric Sen-Theil testing agreed very well and both analyses showed no significant change for O_3 concentrations during the past 10 years at all six sites. Sen-Theil analysis concluded that NO_2 concentrations at the locations near the major emission sources were increasing.

The concentrations of O_3 , NO_2 and SO_2 became less variable at 20, 48 and 48 km, respectively from the reference point (AMS 2). The highest concentrations of NO_2 and SO_2 were at 11.5 km from the reference point and they were 5.7 ppb for NO_2 and 2.2 ppb for SO_2 in 2009. JP107 may have received contributions from the influence of valley flow, new industrial or natural emission sources since 2007 resulting in higher NO_2 and SO_2 concentrations and lower O_3 concentration.

Continuous and passive measurement techniques have different purposes and uses. The data from passive measurement can be compared for general trending, but should not be compared on an absolute basis.

Table 4. Descriptive statistics for O₃, NO₂ and SO₂ concentrations (ppb) from passive samplers and continuous monitors.

	O ₃		NO ₂		SO ₂	
	CM ¹	OPSS	CM	NPSS	CM	SPSS
Mean	21.1	23.4	5.70	4.43	1.22	1.50
Median	19.5	22.0	4.85	3.67	1.00	1.27
Stdev ²	7.0	7.8	11.06	7.38	0.62	0.81
Minimum	9.6	10.0	1.23	0.67	0.32	0.23
Maximum	36.9	43.3	15.50	15.13	3.66	5.05
Sample number	138	138	139	139	142	142
Pearson Correlation	0.81		0.90		0.76	
p (T ≤ t) two-tail	< 0.01		< 0.01		< 0.01	

CM¹: Continuous Monitor.

Stdev²: standard deviation.

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