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Contribution of emissions from the oil sands activities in Alberta, Canada to atmospheric concentration and deposition of nitrogen and sulfur species at a downwind site

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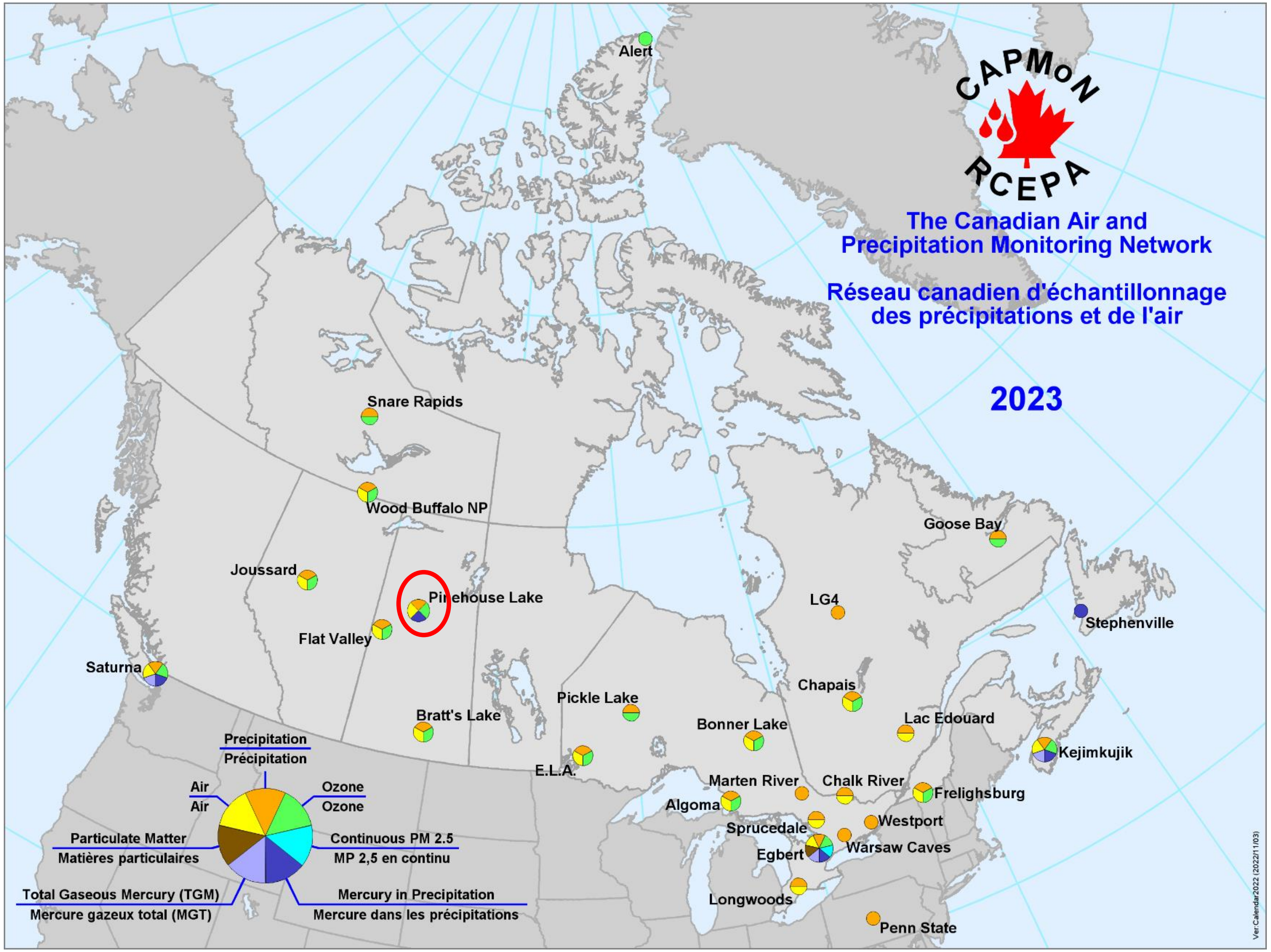
INTRODUCTION

- Atmospheric sulfate (SO_4^{2-}) and most nitrogen (N) compounds from anthropogenic NO_x and SO_2 emissions are acidifying pollutants, the deposition of which can harm sensitive ecosystem.
- Deposition of N compounds to ecosystem can also lead to eutrophication and threaten biodiversity.
- The facilities and operations in the Athabasca oil sands region (AOSR) are large sources of NO_x and SO_2 emissions. Most previous studies on N and S depositions focused on regions within 50 km from the center of the oil sands facilities. A few studies covered distances up to 135 km.
- Lack of studies downwind (350 km) at sensitive ecosystems.

[Blake & Goulding (2002); MacKenzie & Dietrich (2020); Behera et al. (2013); Zhang et al. (2018); McLinden et al. (2020); Fenn et al. (2015); Hsu et al. (2016); Watmough et al. (2014); Makar et al. (2018)]



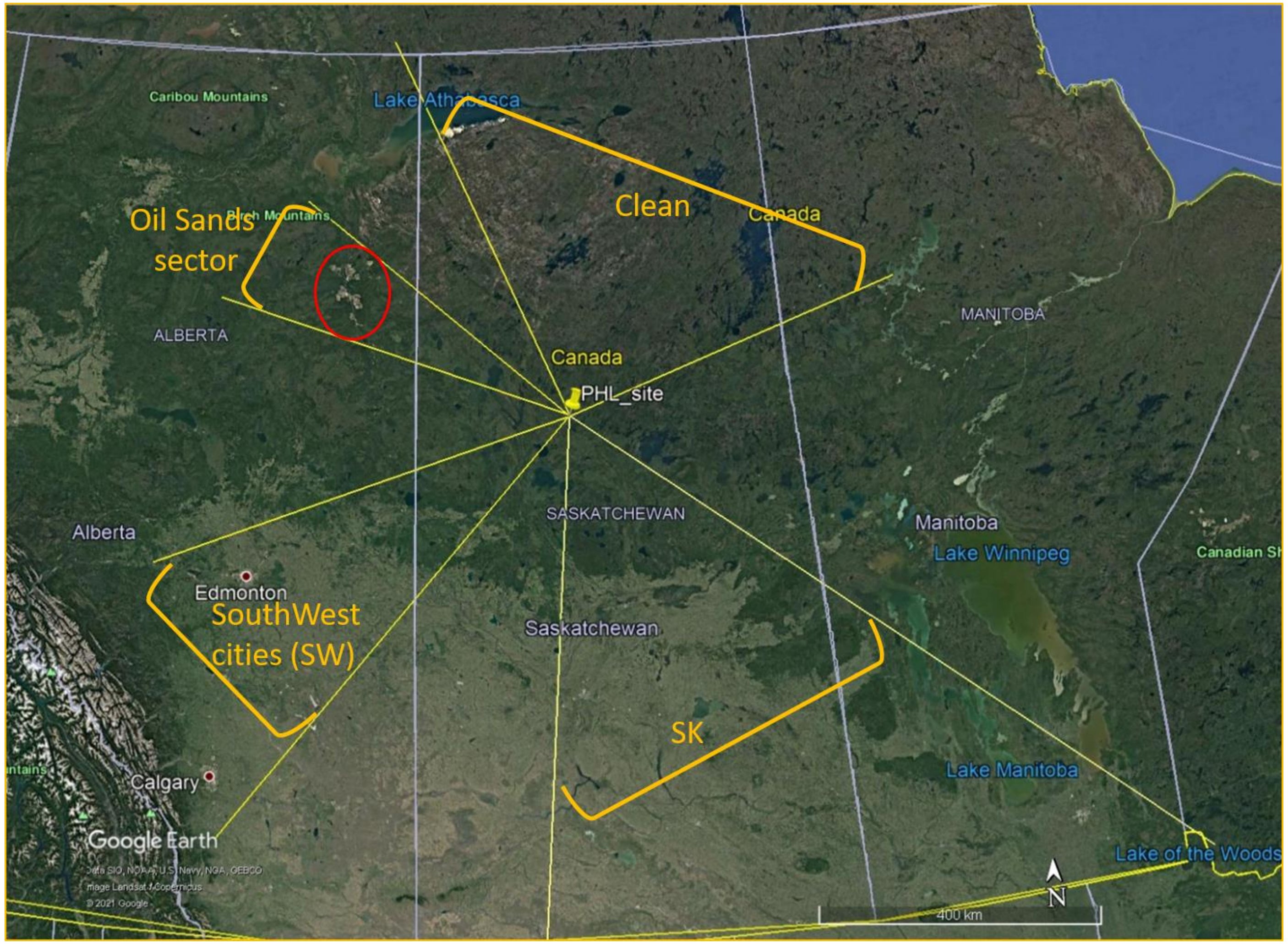
Canadian Air and Precipitation Monitoring Network (CAPMoN)

- ❑ Results at Pinehouse Lake site (2015-2019), located in the boreal forests of Saskatchewan.
- ❑ Region of water bodies in northern Saskatchewan has been considered as acid-sensitive.
- ❑ This study investigated the atmospheric concentration and deposition of N and S species about 350 km downwind of the Athabasca oil sands facilities to understand the long-range impact of NO_x and SO_2 emissions.

- CAPMoN air filter pack concentration (daily): HNO_3, SO_2, pSO_4^{2-}, pNO_3^-, pNH_4^+, Na^+, Mg^{2+}, Ca^{2+}, K^+, and Cl^-
- CAPMoN precipitation depth and concentration (daily): SO_4^{2-}, NO_3^-, NH_4^+, Na^+, Mg^{2+}, Ca^{2+}, K^+, Cl^-, and pH
- Ambient continuous concentration (5-min average): NO_y, NO, NO_2, NH_3, and SO_2

[Jeffries et al. (2010); Cathcart et al. (2016)]

METHODOLOGY - TRAJECTORY SECTOR ANALYSIS



HYSPLIT air mass back trajectories (3-day backward):

- For dry deposition: Trajectories start at ½ boundary layer height, starting at every hour every day
- For wet deposition: Trajectories start at 1 km above ground level, starting at every three hours (0, 3, 6,…, 21 h UTC) for days with precipitation
- "Clean" sector was included to estimate the anthropogenic (%) when calculating oil sands emission contribution from the Oil Sands (OS) sector.
- SW and SK sectors were included for sectoral contributions to compare to the OS sector.
- Sector assignment of sampling days
- 39 days were analyzed separately as the Fire influenced days, to minimize the influence of wildfire emissions.

[Google Earth Pro. 2021-09-10; HYSPLIT - Stein et al. (2015)]

METHODOLOGY – DEPOSITION CALCULATION

- Concentration of unidentified $NO_y = NO_y - HNO_3 - pNO_3^- - NO_2 - NO$
- Dry deposition: the inferential method:

$$F_{dry} = V_d \times C_{air}$$

V_d is dry deposition velocity calculated for

  - Gases: HNO_3, NO_2, NH_3, SO_2 [Zhang et al. (2003)]
  - V_d (unidentified NO_y) = 0.05 × V_d (HNO_3) + 0.3 × V_d (pNO_3^-) + 0.65 × V_d (PAN) [Zhang et al. (2009)]
  - Fine and coarse particles for pNO_3^-, pSO_4^{2-}, pNH_4^+, base cations and Cl^- [Zhang and He (2014)]

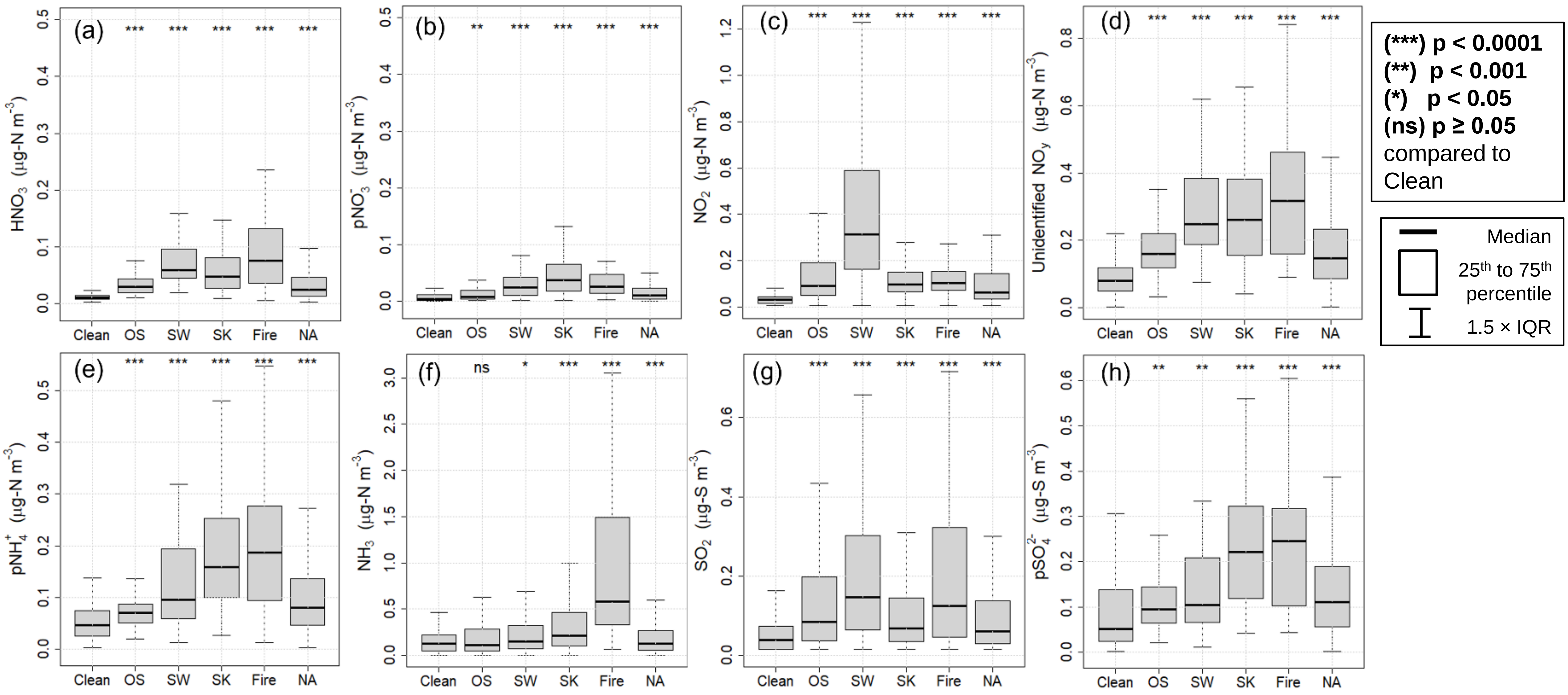
- Wet deposition (daily)

$$F_{wet} = concentration\ (daily) \times precipitation\ depth\ (daily)$$

NO_3^-, SO_4^{2-}, NH_4^+, base cations and Cl^-

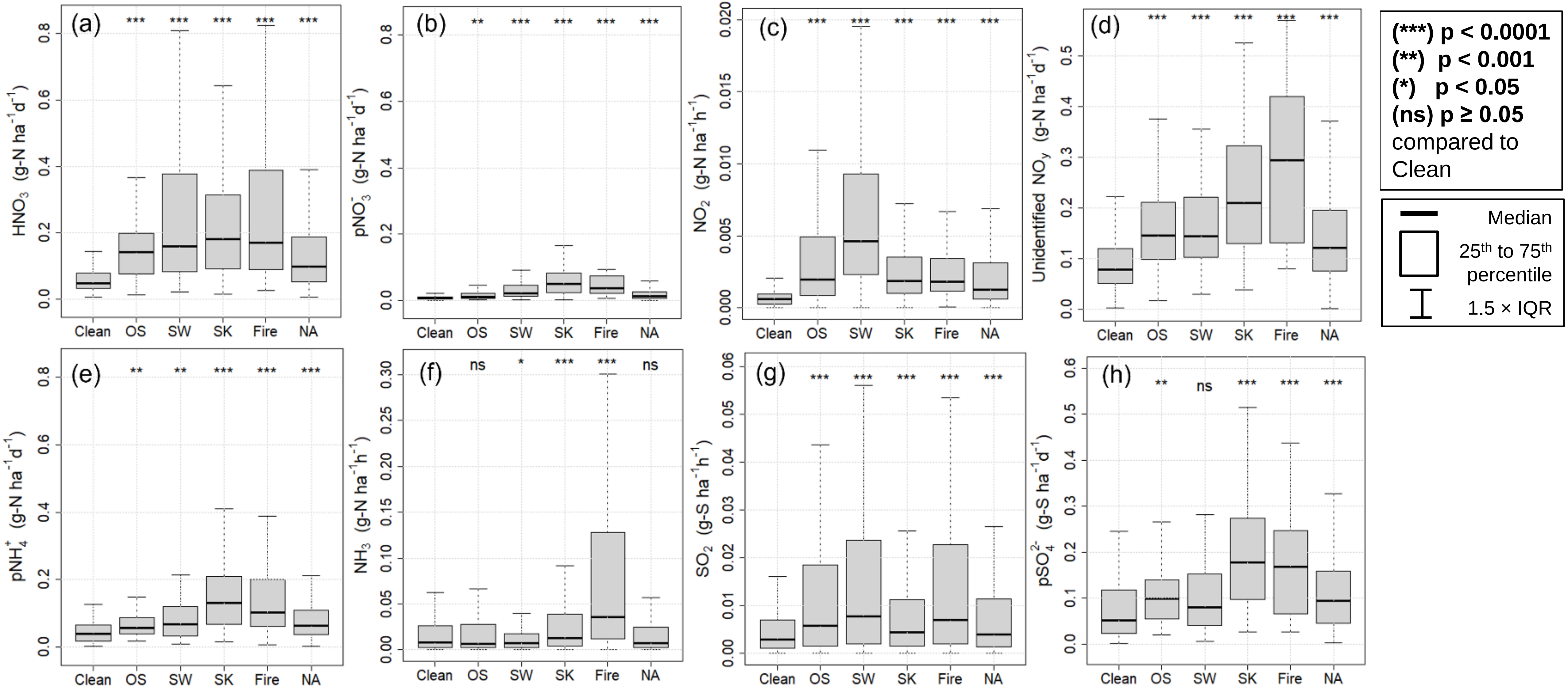
[Zhang, L., Brook, J. R., & Vet, R. (2003). ACP, 3(6), 2067–2082; Zhang, L., Vet, R., O'Brien, J. M., Mihele, C., Liang, L., and Wiebe, A. (2009), JGR, D02301; Zhang, L., & He, Z. (2014). ACP, 14(7), 3729–3737.]

RESULTS - AIR CONCENTRATION



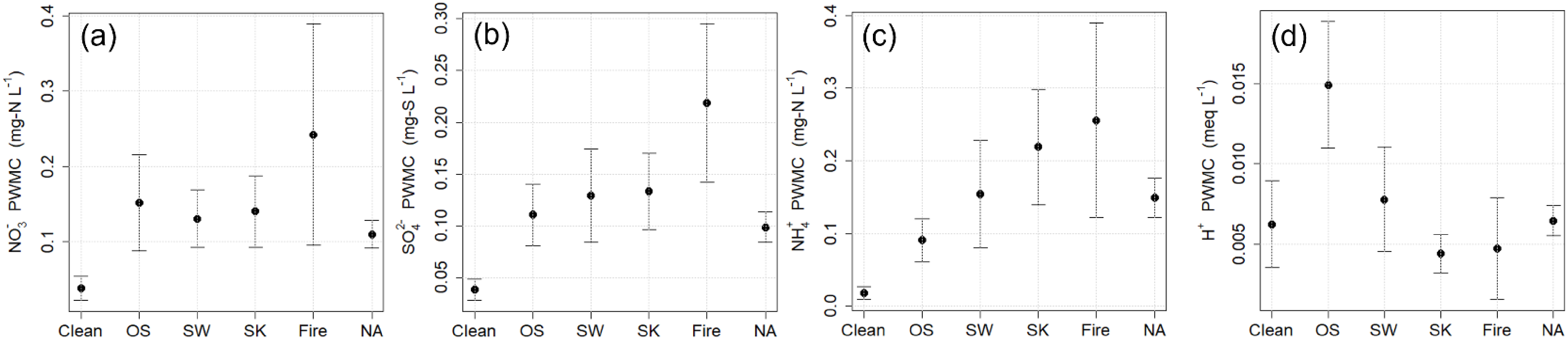
- Statistically significant differences between the OS and the Clean sector were observed for all the species, except for NH_3.
- NH_3 concentration on fire-influenced days were significantly higher. SK sector was the second highest sector.
- Results suggest that a significant portion of emitted SO_2 was transported downwind before being oxidized to pSO_4^{2-}.

RESULTS - DRY DEPOSITION



- Results of dry deposition fluxes from different sectors are very similar to the concentration results.
- Important contributions from SW and SK sectors.

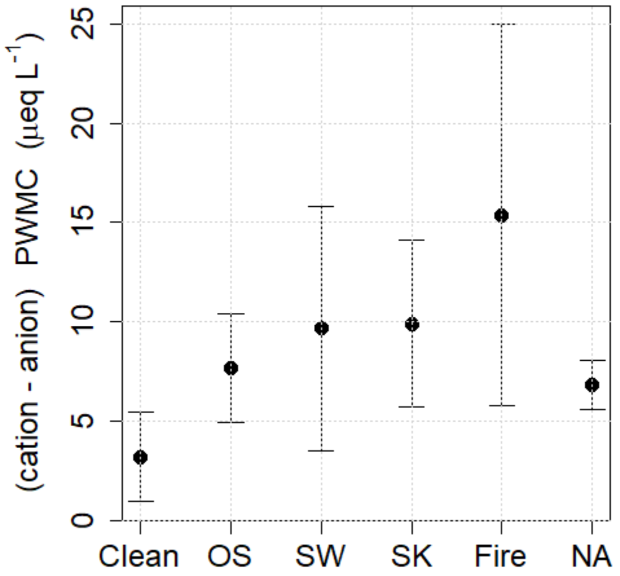
RESULTS – PRECIPITATION-WEIGHTED MEAN CONCENTRATION (PWMC)



pH	5.21	4.83	5.11	5.36	5.33	5.19

- For NO_3^-, SO_4^{2-} and NH_4^+, the differences of PWMC between the OS and Clean sectors were 76 ± 54 %, 65 ± 33 %, and 81 ± 44 %, respectively.
- The pH from the OS sector was the lowest.

- Excess cation concentration was calculated to estimate organic acids concentrations. Concentrations from OS sector were greater than the Clean Sector.



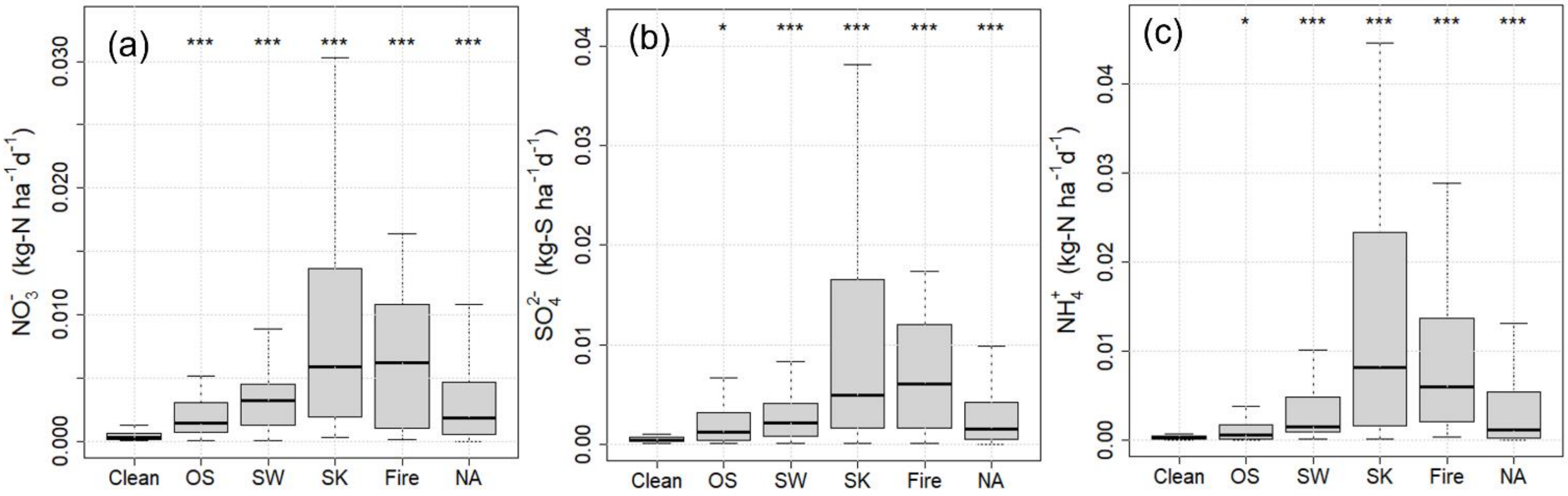
precipitation-**w**eighted **m**ean **c**oncentration (PWMC):

$$\overline{C_w} = \sum_{i=1}^{n} C_i P_i \Big/ \sum_{i=1}^{n} P_i$$

Excess cations (μeq L^{-1}) = measured cations + H^+ – (measured anions + HCO_3^-)

* The error bars of the PWMC are the 95% confidence intervals, by Cochran (1977).

RESULTS - DAILY WET DEPOSITION



(***) p < 0.0001
(**) p < 0.001
(*) p < 0.05
(ns) p ≥ 0.05
compared to Clean

Median
25th to 75th percentile
1.5 × IQR

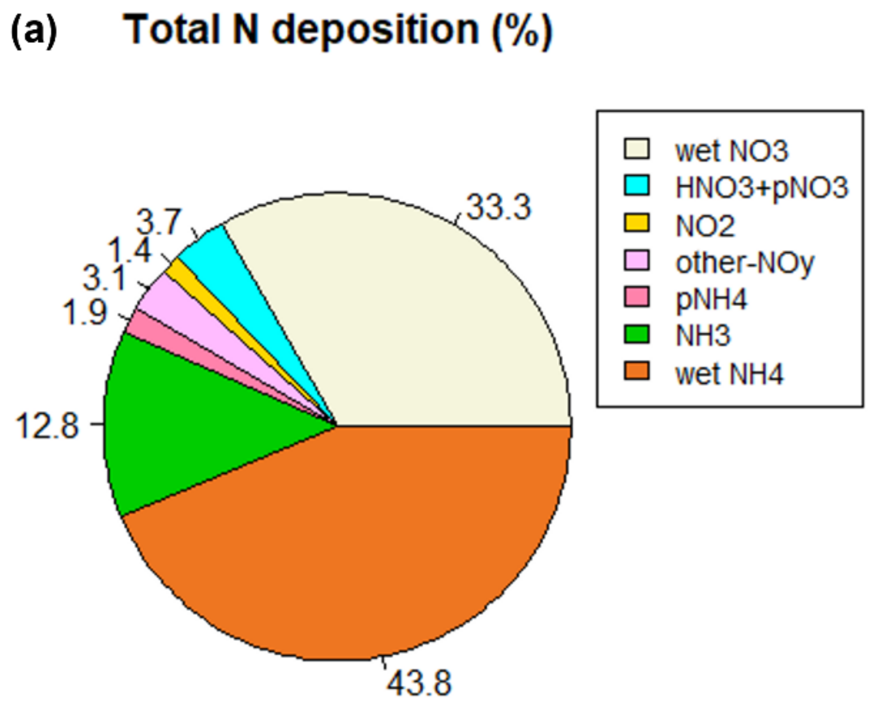
- The wet deposition fluxes of NO_3^-, SO_4^{2-}, and NH_4^+ in samples assigned to the OS and the Clean sector were also significantly different, respectively.
- Wet deposition fluxes from the SW and SK sectors were significant.

CONTRIBUTION OF OIL SANDS EMISSIONS (PHL)

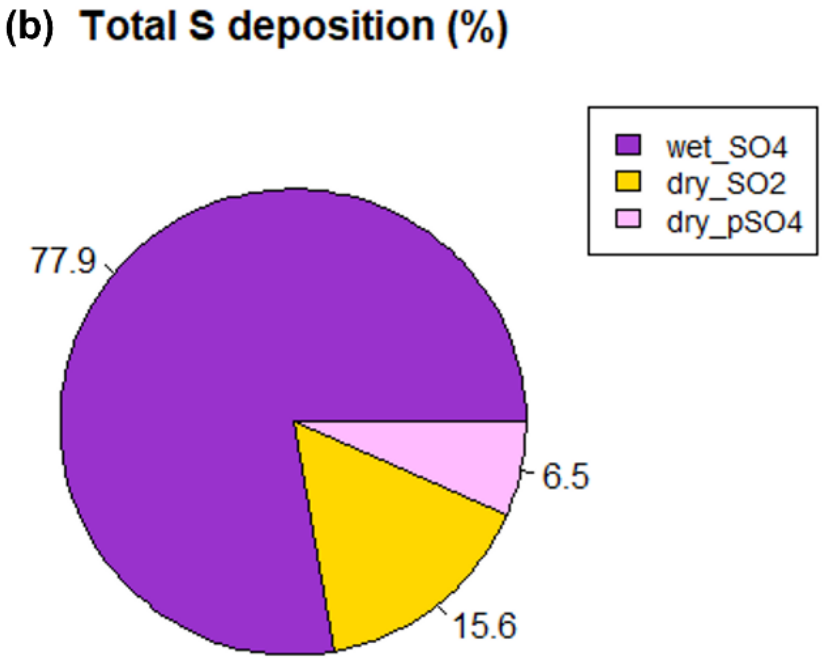
		Contribution of the OS sector (%)	Anthropogenic (%)	Contribution of oil sands emissions (%)
Dry deposition	HNO_3	15.2	64 ± 18	9.7 ± 2.7
	pNO_3^-	8.9	51 ± 29	4.5 ± 2.6
	pNH_4^+	11.3	34 ± 15	3.8 ± 1.7
	pSO_4^{2-}	12.1	45 ± 19	5.4 ± 2.3
	SO_2	18.9	55 ± 7.1	10.4 ± 1.3
	NO_2	19.6	67 ± 5.9	13.1 ± 1.2
	NH_3	-	-	Not significant
	Unidentified NO_y	14.9	51 ± 16	7.6 ± 2.3
Wet deposition	NO_3^-	16.5	76 ± 54	12.5 ± 8.9
	NH_4^+	7.5	81 ± 44	6.0 ± 3.3
	SO_4^{2-}	13.7	65 ± 33	8.7 ± 4.4
Total deposition	$HNO_3 + pNO_3^- + NO_2$ + unidentified NO_y			11.9 ± 7.4
	$NH_3 + pNH_4^+$			5.0 ± 2.7
	All N species			8.0 ± 3.5
	S species ($SO_2 + pSO_4^{2-}$)			8.7 ± 3.6

- The oil sands emissions in AOSR contributed the most to the dry deposition of NO_2, followed by SO_2 and HNO_3, consistent with expectation since SO_2 and NO_2 are the most abundant primary pollutants in the plumes from the oil sands region.
- The oil sands emissions contributed to 13%, 9% and 6% of the wet depositions of NO_3^-, SO_4^{2-}, and NH_4^+, respectively.
- The oil sands emissions contributed to 8% and 9% of the total N and S deposition fluxes at this site during 2015-2019.
- Other sectors had significant contributions to the deposition.

CONTRIBUTIONS OF SPECIES TO TOTAL DEPOSITION



1.9 kg-N ha $^{-1}$ y^{-1}



0.7 kg-S ha $^{-1}$ y^{-1}

Study period:
2015 – 2019

- Wet deposition dominated (77% and 78%) the total deposition of N and S.
- The observed total S deposition (about 44 eq ha^{-1} y^{-1}) at the Pinehouse Lake site exceeded the critical loads (CLs) of acidity of 2 out of 5430 lake catchments within 100 km.
- Reduced N contributed more than oxidized N. The observed total N deposition is comparable to the medians of calculated $CL_{nut}N$ of the two ecoregions around the site.
- Given the uncertainty in total N deposition and variability in $CL_{nut}N$ results for ecoregions, it is important to keep monitoring the deposition of N species at sensitive regions in northern Saskatchewan.

[Cathcart et al. (2016); Murray et al. (2017); Wu et al. (2018)]

Thank you!

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