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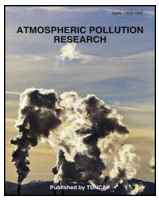

Analysis of atmospheric ammonia concentration from four sites in Quebec City region over 2010–2013

A.D. Larios[a,d], F. Chebana[a,*], S. Godbout[b], S.K. Brar[a], F. Valera[d], J.H. Palacios[b], A. Avalos Ramirez[a,c], F. Saldoval-Salas[a,d], J.P. Larouche[b], D. Medina-Hernández[d], L. Potvin[b]

[a] Institut National de la Recherche Scientifique (INRS), Centre Eau, Terre & Environnement, 490, rue de la Couronne, Québec, QC, G1K 9A9, Canada
[b] Institut de Recherche et de Développement en Agroenvironnement (IRDA), 2700 rue Einstein, Québec, QC, GIP 3W8, Canada
[c] Centre National en Électrochimie et en Technologies Environnementales (CNETE), 2263, av. du Collège, Shawinigan, QC, G9N 6V8, Canada
[d] Instituto Tecnológico Superior de Perote, Km 2.5. Carretera Perote- México, Perote, Ver, 91270, Mexico

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ABSTRACT

This study presents an analysis of atmospheric ammonia (NH_3) concentration from four different sites located in the Portneuf municipality and Quebec City over 2010–2013 years. The determination of NH_3 concentration was performed using passive samplers. Seasonal Mann-Kendall test at 5% significance level was used to analyse the trend in each of the sites. Results showed slight increases and decreases in NH_3 concentration, but the trend was not significant ($\alpha = 0.05$) from 2010 to 2013 in all the evaluated sites. The annual average concentration of the evaluated sites fluctuated from 0.35 to 17.51 μg/m^3. Thus, due to that the annual average concentration of NH_3 in sites 1 to 3 was higher than 1 μg/m^3, which is considered as the critical value for protecting of sensible vegetation close to emission source of NH_3. It is suggested to extend the measurements for a longer period and increase the number of sites in order to follow the trends of atmospheric NH_3 concentration at local and regional scale and have information about the NH_3 concentration trend in Quebec.

1. Introduction

The concentration of ammonia (NH_3) in the atmosphere presents significant spatial and temporal variations depending on the type of land use, anthropogenic activities, seasonal changes associated with the variation of air temperature, wind patterns, radiation, humidity, pH and roughness of the surface receptors. In rural areas, these variations are also linked with agricultural practices, such as manure spreading operation and changes in population size of animals (Bittman et al., 2015; Thöni et al., 2004).

Agriculture, including animal feedlot operations, is considered as the largest emission source of NH_3 with 80.6% of the global anthropogenic emissions followed by 11% from biomass burning and 8.3% from the energy sector, including industries and traffic (Behera et al., 2013). In Canada, NH_3 emissions in 2014 were 22% higher than in 1990 (Canada, 2017a). In 2014, agriculture was the main emission source accounting 93% of the total NH_3 emissions followed by industrial activities and transport, representing 3% and 2% respectively. Alberta, Saskatchewan, Ontario, and Quebec emitted the highest amounts of NH_3 in Canada in 2014, contributing 30%, 20%, 18% and 14% of emissions respectively. For all provinces, the increase of NH_3 emissions was mainly attributed to agricultural fertilizer use and larger livestock populations (Canada, 2017a). In urban areas, NH_3 concentration is associated with the local traffic, urban industries, waste containers, sewerage systems or air mass arriving from agricultural sources (Krupa, 2003). It is known that the chemical reaction of NH_3 with nitrogen oxides (NO_x) and sulfur dioxide (SO_2) in the atmosphere results in ammonium nitrate and ammonium sulphate formation which causes visibility degradation. Due to these problems, the inventory of NH_3 emissions and concentration in air of urban areas is highly recommended (Jansen et al., 2014; Wang et al., 2015).

In the case of forest areas, they can play the role of emission sources or sinks of atmospheric NH_3. This role depends on the gradient of NH_3 concentration between the canopy and the atmosphere (Hansen et al., 2013; Massad et al., 2010). NH_3 emissions are issued from forest areas during forest clearing; organic matter decomposition from soil or when the atmospheric concentration of NH_3 is lower than the canopy compensation point. Conversely, forest areas assimilate NH_3 when the atmospheric concentration is higher than the canopy compensation point. Canopy compensation point is the concentration which the plants

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* Corresponding author.
E-mail address: Fateh.Chebana@ete.inrs.ca (F. Chebana).

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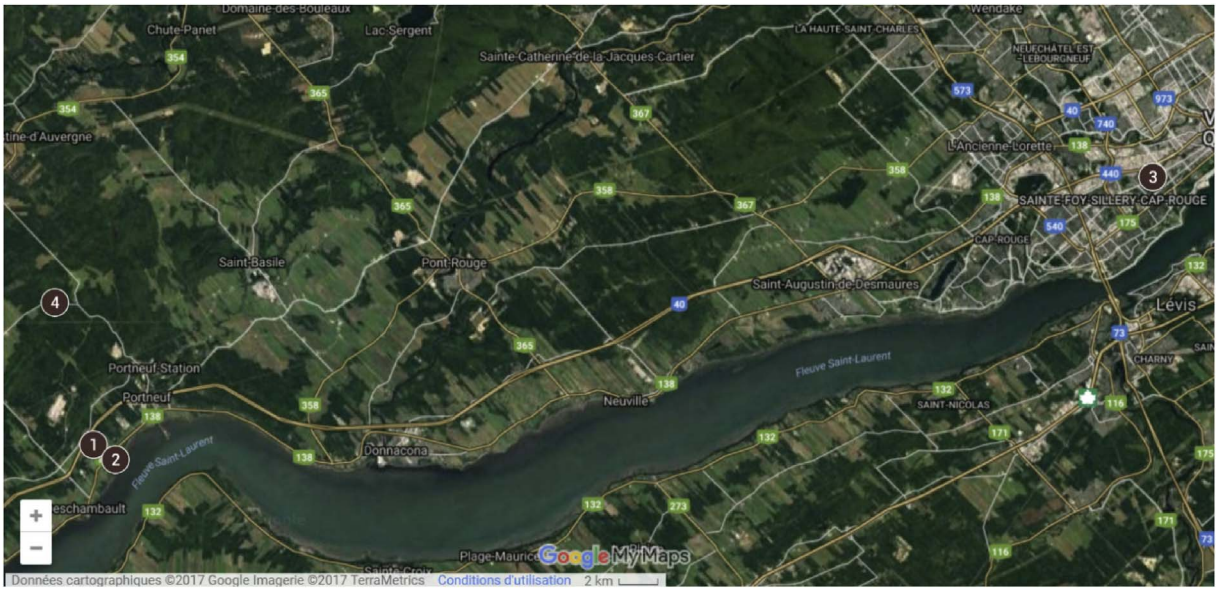

Fig. 1. Geographical location of sampling sites (1 = Site 1; 2 = Site 2; 3 = Site 3; 4 = Site 4).

neither gain nor lose NH_3 (Behera et al., 2013).

Although, advanced satellite instruments in orbit are used to measure NH_3 concentration. It is considered that the integration of satellite measurements with ground-based measurements will enable better assessments and understanding of local to global atmospheric NH_3 and information on its spatial distribution through the long-term trend analysis (Van Damme et al., 2014; Yao and Zhang, 2013). Seasonal Mann-Kendall trend test (SMK), as extension of the Mann-Kendall test, is widely used to analyse climatologic, hydrologic and atmospheric trends on a time series when seasonal cycles are present in the data. It is a non-parametric test to detect time-serial trends without requiring a normal data distribution. Furthermore, SMK test may even be used although there are missing or tied values (Gilbert, 1987; McLeod et al., 1991). In this context, the Research and Development Institute for the Agri-environment (IRDA, Quebec City) created a database of NH_3 concentration over the years 2010–2013 from four different sites located in the Portneuf municipality and Quebec City. This work presents the results of the measurement and the analysis of atmospheric NH_3 concentration trends in order to evaluate the temporal behavior of NH_3 concentration from January 2010 to December 2013.

2. Materials and methods

The concentration was monitored monthly for four years using passive samplers (PS). The PS were 12 mm long with an internal diameter of 20 mm. The ensemble of samplers and the measurement method was similar to that reported by Martin and Rodhe (1997) and Dammgen (2007). Fluoropore membrane filters (PTFE) (Millipore, Fisher Scientific, Quebec, QC) of 25 mm diameter and pores of 1 μm; regenerated cellulose membrane filters type 184 (Sartorius Stedim, Fisher Scientific, Quebec, QC) of 25 mm diameter and pores of 0.45 μm were used to construct the samplers. The cellulose filters were impregnated with 50 μL of citric acid solution (2%) and placed in the desiccator with its top cover assembly for 15 min. In each sampler, a PTFE membrane was placed between the two stainless steel grids in front of the filter to protect the cellulose filter, to damp the effects of the swirling air and to promote molecular diffusion (Dammgen, 2007). Before and after sampling, the passive samplers were transported in polypropylene tubes (four passive samplers per tube). A filter paper soaked with the solution of citric acid was placed inside each tube as a preventive measure to a possible absorption of ammonia during the transport. Four passive samplers were inserted in a support connected to a holder at 2 m above the ground. At the end of the sampling period (1 month), the samplers were recovered and placed in the same tube used for transport. The sample size for each site comprised 48 measurements. In the laboratory, the cellulose filters were removed from the samplers and eluted with 5 ml of distilled water followed by continuous shaking for 60 min. Afterwards, the extracted solution was filtered by microfiltration (0.45 μm) and the ammonium nitrogen ($N\text{-}NH_4^+$) content was analysed in a flow injection analyser (QuikChem FIA+, ATS scientific INC, Burlington, ON., Canada). Later, the atmospheric NH_3 concentration was calculated according to Dammgen (2007). Two cellulose filters impregnated with 25 μL and 50 μL of standard solution $N\text{-}NH_4^+$ (100 ppm) were used as positive controls. Also, two cellulose filters without standard solution of $N\text{-}NH_4^+$ were used as negative controls during $N\text{-}NH_4^+$ analysis. The detection and quantification limit of the analyser was around 0.012 and 0.041 mg/L, respectively. Detection and quantification limits correspond to 0.06 and 0.22 $\mu g/m^3$ of NH_3 that can be detected and determined with an acceptable level of repeatability precision and trueness ($\alpha \leq 0.05$). These values were lower than the average of NH_3 concentration measured in the filters blanks which were around 0.82 $\mu g/m^3$. Thus, taking into account these values, the performance of the instrument and measuring method was considered as acceptable. To calculate the monthly NH_3 concentration in each one of the evaluated sites, the concentration detected in the filters blanks was subtracted to the concentration measured in each one of the samples. After subtraction of the blank value, all the negative values were not considered for data analysis. Thus, the values presented in this study were considered as NH_3 concentration representatives of each evaluated site.

Site 1, 2 and 4 were located in the Portneuf municipality to the southwest of Quebec City (Fig. 1). Site 1 was placed in a prairie of the municipality of Deschambault close to crops and grazing fields at 46.6784° of latitude north (N) and −71.9240° of longitude west (W). Site 2 was also located in Deschambault close to animal housings and grassland at 46.6713°N and −71.9104W. Site 3 was located in the urban zone of Quebec City at 46.7928°N and −71.2608W. Site 4 was placed in the middle of a private forest in St-Gilbert at 46.7388°N and −71.9483 W.

For the analysis of the database of the measured monthly NH_3 concentrations and of a database of fine particles ≤ 2.5 μm in aerodynamic diameter (PM_{25}) from the National Air Pollution Surveillance Program (NAPS) (Canada, 2017c), locally weighted scatterplot smoothing (lowess) curves were made to summarize the relationship of