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SNOW SAMPLING AS A METHOD FOR VALIDATING THE DEPOSITION PATHWAY IN AIR QUALITY MODELS: HISTORICAL OVERVIEW AND MAIN RECENT FINDINGS IN ESTONIA

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Abstract: Stable snow cover is a natural collector of ingredients deposited from the air. Samples taken in late winter through entire snow cover accumulated over a few months give us a chance to quantify the winter-time deposition rates with relatively low cost. In Estonia the snow samples, with deposition quantification purpose, were taken and chemically analysed since 1985. Depending on stability of snow cover and availability of resources for research, high-quality data were produced for nearly 1/3 of years during almost four-decade period. Basic anions and cations were measured in all studies. Suspended matter, trace metals and elemental carbon were analysed occasionally, on availability of resources. Historically, the focus of research has been on an industrial area in north-eastern part of the country, where *kukersite* oil shale is mined, combusted in thermoelectric power plants and used to produce the shale oil. The emissions from *kukersite* oil shale combustion contain alkaline, calcium-rich fly ash together with sulphur dioxide. Since 1990´s the snow-based deposition fluxes have been applied to validate the deposition pathway of local-to-regional Gaussian model AEROPOL, as quantification of deposition is important to understand the damage to ecosystems. In 2002 – 2003 an effort in cooperation with Finnish Meteorological Institute was taken for testing the HILATAR atmospheric chemistry-transport model. In recent years, after dramatic decrease of industrial emissions due to smaller use of oil shale and more effective purification of smoke gases, the new focus of snow-based deposition research is on small towns and settlemets, where dominating emission source is residential firewood heating.

Key words: *snow, deposition, air pollution, air quality modelling, kukersite, residential heating,*

INTRODUCTION

Stable snow cover is a natural collector of ingredients deposited from the air. Samples taken in late winter through entire snow cover accumulated over a few months give us a chance to quantify the winter-time deposition rates with relatively low cost. Moreover, layer-wise snow sampling can give a reconstruction of time series of deposition flux, assuming that the accumulation dates of layers can be identified, based on accumulated precipitation amounts and ice crusts formed during short thawing episodes.

In Estonia the snow samples, with deposition quantification purpose, were taken and chemically analysed since 1985. Depending on stability of snow cover and availability of resources for research, high-quality data sets were produced for nearly 1/3 of years during almost four-decade period. Basic anions and cations were measured in all the studies. Chemical composition of solid deposit, trace metals (Kaasik et al., 2000), black carbon and even fly ash particles of specific shape (Kaasik et al., 2005) were analysed occasionally, on availability of resources.

Historically, the focus of research has been on an industrial area in north-east of the country, where *kukersite* oil shale is mined, combusted in thermoelectric power plants and used to produce the shale oil. In recent years the usefulness of snow samples to quantify the deposition fluxes from residential heating in small towns and rural areas is in focus of our research.

SNOW-BASED QUANTIFICATION OF DEPOSITION FLUXES

The basic idea of snow-based quantification of deposition flux is simple: taking a sample through the snow cover with a tube sampler of known cross-section area. Then, knowing the time interval of snow accumulation, we can calculate the average deposition fluxes of analysed ingredients. Assuming that the snow has accumulated long enough, we can compare not only the fluxes at different sites in the same year, but also in different years.

Industrial pollution, an historical overview

In Estonia the *kukersite* oil shale, a solid fossil fuel of unique composition is mined, combusted to produce electric energy and used to produce the shale oil, neaerly equivalent to heavy fuel oil, in retorting process. *Kukersite* is an extremely calcium-rich fuel due to its limestone-like mineral part, which makes its fly ash strongly alkaline, just opposite to the acidic ash of coal. A remarkable consequence of fly ash influx is alkalization of naturally acidic soils, like peat and podzol, and excess of nutrients that makes the mineral land species to grow on the bog, changing the natural ecosystem dramatically and conditionng decomposition of accumulated peat (Karofeld 1996).

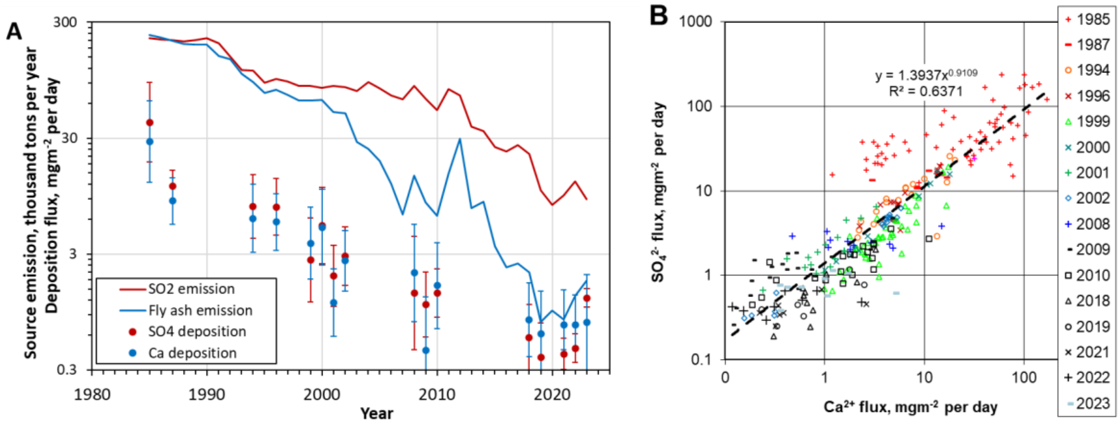

Figure 1. Snow-based deposition fluxes of sulphate and calcium ions (geometric means and standard deviations) compared to emissions of sulphur dioxide and fly ash (A) and site-wise comparison of measured sulphate and calcium deposition fluxes (B) through years in Estonian oil-shale mining and processing area.

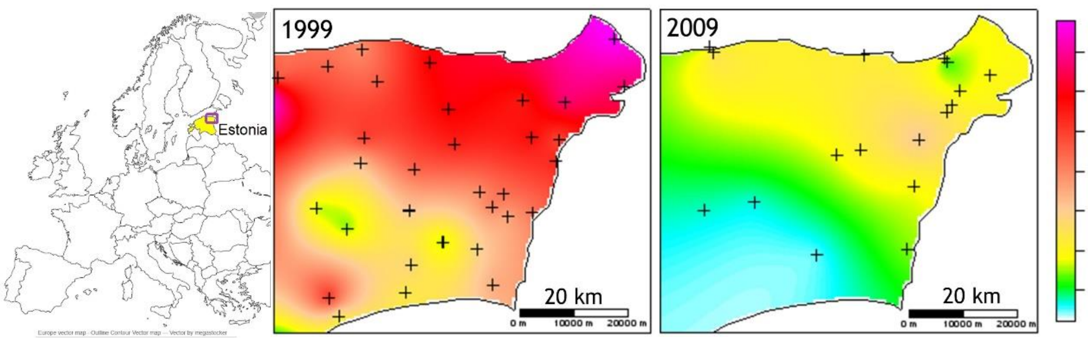

Figure 2. De-alkalization of winter-time precipiations during the decade of most dramatic fall of fly ash emission: map of pH of snow water collected in 1999 and 2009. Black crosses indicate snow sampling sites. Research area is shown in the map of Europe as a violet rectagle. Color scale at right shows pH values.

The earliest (before 1990) snow-based deposition studies in this area were made by Institute of Ecology and Marine Research of Estonian Academy of Sciences and published in Estonian language only (Voll, 1989). Later on the research was carried out in Tartu Observatory and (since 2002) in University of Tartu, led by Marko Kaasik. An historical overview of emissions of fly ash and sulphur dioxide, and snow-based average deposition fluxes of calcium and sulphate ions is provided in Figure 1. Domination of alkaline fly ash over acidic oxides in past has led to strongly alkaline precipitation, which has turned to closer to normal with decrease of emissions (Figure 2).

Model validation efforts

The first comparison of air pollution transport and deposition model AEROPOL, developed then in Tartu Observatory, was carried out in 1990´s and based on extensive snow sampling campaign in 1985, during the high of emissions from energy production in oil-shale-fired thermal power plants (Kaasik et al., 1999). Backed with achieved fair agreement between model and measurement on calcium and sulphate deposition for 1985, the AEROPOL model was applied for retrospective quantification of deposition fluxes since beginning of extensive oil shale use in 1960´s. Next year a snow-based model validation data set was presented in the framework of HARMO initiative (Kaasik, 2000).

Snow-based deposition data in North-Eastern Estonia were used to validate the HILATAR model developed in Finnish Meteorological Institute (Sofiev et al., 2003). Slight underestimation and rather high linear correlation (0.67) between modelled and measured fly ash deposition was found.

Deposition in rural areas

Along with decrease of industrial pollution, pollution caused by local sources, residential firewood heating in first order, is gradually drawing attention of authorities. In Estonia, there are no air quality monitoring stations in small towns or villages besides urban stations and rural background stations. Thus, snow-based measurements constitute an option to estimate the relative pollution level in these rather extensive areas.

However, these measurements can give good indication only if the snow cover is stable enough, preferably lasting more than 30 days. Therefore, during recent unstable winters the area for reasonable measurements was limited with eastren part of the country. One of the good areas is the north-eastern part of the country (described in two previous subsections), which is rather far away from the warm influence of Atlantic ocean and Baltic Sea Proper. Another snowy area is located in South-Eastern part of Estonia. Due to remakable height, 100 – 300 meters above sea level, average temperature is slightly lower than at lowlands. Although the temperature difference due to height is in order of 1 °C only, it is a remarkable factor in typical wintertime cyclonal weather, when temperature variates narrowly above and below the freezing point.

Snow samples were taken within and around town of Otepää (2200 inhabitants) in 2022, 2023 and 2024 at 8 sampling sites located 110 – 180 m above sea level. Otepää, often called ”the winter capital” of Estonia, is the most prominent ski resort in Baltic countries, which has hosted some world cup competitions in cross-country skiing. Permanent snow cover before taking the samples lasted 79 days in 2022, 41 days in 2023 and 53 days in 2024. Anions and cations analyzed in all these years were: NH_4^+, Cl^-, NO_3^-, SO_4^{2-}, Na^+, Ca^{2+}, K^+ and Mg^{2+}. In 2022 the organic carbon and elemental carbon (nearly same as black carbon) were measured in snow samples, following the EUSAAR 2 protocol. Detail description of method is given by Meinander at al. (2020).

In Figure 3 are shown summary deposition fluxes of analyzed ions (average of 2022, 2023 and 2024) and deposition fluxes of elemental carbon (2022) in maps of surroundings of Otepää. Four samples were taken within the densely inhabited area of Otepää town, two samples in its southern outskirts (sports and leisure areas) and two in remote areas about 10 km south-west and north of the town. Deposition of both ions and elemental carbon (assumed mostly from residential fiewood heating in this area) tends to be higher within the town, but variations are rather high both in densely populated area and out of it. Deposition of ions (dominated by Cl^- and Na^+) was found highest near the main crossing where a few thousand vehilces pass daily. Deposition of elemental carbon was found highest in southern part of the town, near the secondary school of Otepää.

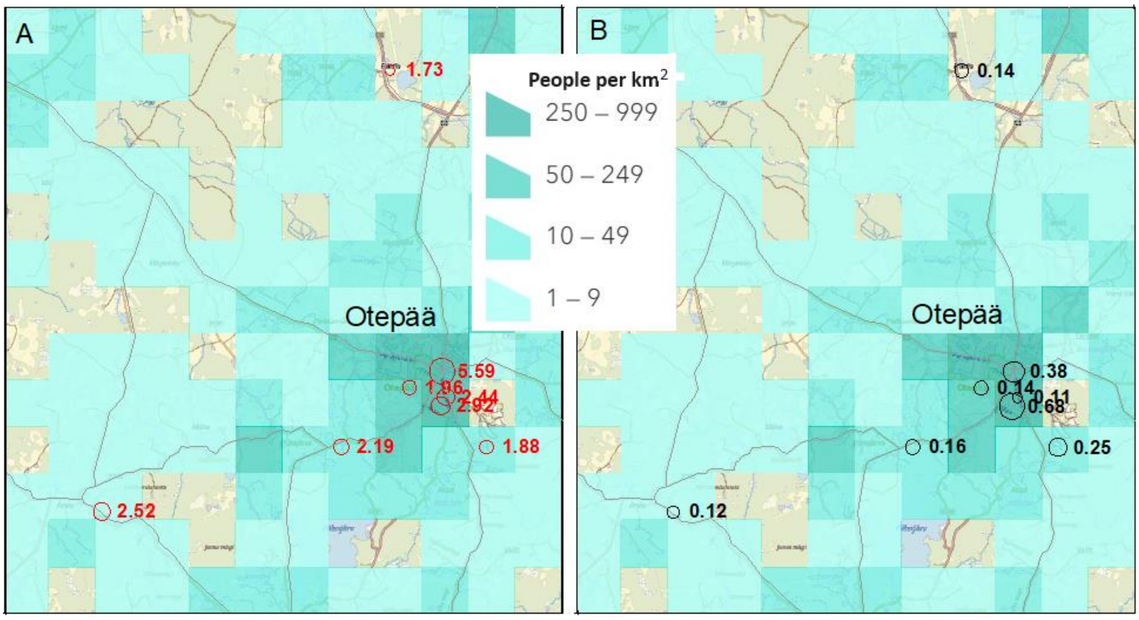

Figure 3. Snow-based deposition fluxes of sum of anions and cations (A, average 2022, 2023 and 2024) and elemental carbon (B, 2022) in Otepää area (South-East Estonia). Population density in one kilometre squares (population census, 2021) is shown as gradation of green color. Flux in each measurement site is marked with size of circle as marker and numerical value (mgm^{-2} per day).

CONCLUSIONS

Four-decade time series of snow-based air pollution deposition measurements in North-East Estonian industrial area reveals the continuous and prominent decreasing trend in air pollution due to decrease of *kukersite* oil shale mining and smoke gas purification measures. These data have been successfully used for validation of atmospheric chemistry-transport models. Recent two decades have added new data that can be used for the same purpose. Efforts in tracing the pollution of residential, mostly firewood-based heating in a rural area with a small town consitute a promising example for low-cost estimation of air pollution in areas, where no premanent air quality monitoring stations are located.

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