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## 10.4. ANALYSIS OF PARTICULATE MATTER AND SMALL ION CONCENTRATION IN THE INDOOR ENVIRONMENT BASED ON A BALANCE EQUATION

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### ABSTRACT

The purpose of this work was to explore the relationship between particulate matter (PM) and small ion (SI) concentration in a typical indoor environment. Changes in SI concentration are due to several factors. Firstly, SI are constantly created in pairs by ionizing radiation that exists in the environment. They are also continually destroyed in a process of recombination. Additionally, SI can attach to PM. Because of this, a change in PM concentration directly results in a change in SI concentration. The SI balance equation can be used to quantitatively describe the above-mentioned processes. We will interpret the results obtained from measuring a wide range of relevant air quality parameters in a typical indoor environment, occupied on workdays, within the framework of balance equation.

### INTRODUCTION

The importance of indoor air quality cannot be overstated, especially due to the fact that most people spend large part of their day indoors (in industrialized countries this may exceed 90%). For some age groups, such as the elderly population, this can even easily amount to 100 percent. Concerns about possible health effects are illustrated by the fact that, regardless of indoor or outdoor setting, elevated exposure risks can exist even at relatively low concentrations. Furthermore, while indoor and outdoor conditions are certainly linked (e.g. via a simple ventilation process), some air pollutants are more prominent outdoors (e.g. gaseous pollutants, sulphur dioxide or ozone) while some are typically more prominent indoors (e.g. formaldehyde, carbon monoxide or nitrogen oxides and radon) [1]. In addition to gaseous pollutants, the concentration of airborne particulate matter also raises concerns since, in many European cities according to the European environment agency reports [2], it is two to three times higher (outdoors) than that recommended by the World Health Organization (WHO). This can easily be worse in an indoor environment, especially in view of serious health effects that may result from long-term exposure to an elevated concentration of particulate matter [3].

In this paper we focus on a smaller subset of air pollution phenomena which includes concentrations of radon, small ions (SI) and particulate matter (PM). It is important to note, that while the health effects of radon [4] and particulate matter [3] are well known, the health effects (some authors even state possible benefits, or at least perceived benefits) of small ions are less obvious, see for example [5]. Nevertheless, since all three quantities are linked via the balance equation, even though the health effects are only firmly established for radon and PM, it is justified to consider all three simultaneously.

Let us briefly consider the physical processes that are involved in changes in SI concentration. Firstly, SI are constantly created, in pairs, by ionizing radiation that exists in the environment. There are several natural sources of ionizing radiation that are responsible for air-ion production in the lower troposphere, cosmic rays, radon and terrestrial gamma radiation. Ionization from cosmic rays comprises approximately 20% of the total surface ionization rate. Remaining 80% arises from natural  $\alpha$  and  $\beta$  emitters in the air and soil, although air-ion pair generation near the ground varies mostly with the concentration of  $^{222}\text{Rn}$  and its progenies. The half-life of  $^{222}\text{Rn}$  is 3.82 days and the decay product is an alpha particle with energy 5.49 MeV. The decay of  $^{222}\text{Rn}$  generates a large number of nitrogen and oxygen molecular ions (order of magnitude  $\sim 10^5$ ) per each  $\alpha$ -particle. As a consequence, the near-ground ionization rate caused by background ionization, is about 10 ion pairs/cm<sup>3</sup>s in continental areas. Within microseconds of the ionization process, primary ions evolve through the process of hydration to form small cluster ions, also known as small air ions or nano-air ions. This class of air ions can survive much longer, up to 100s, depending predominantly on air pollution and air density [6].

To summarize, small air ions are electrically charged clusters consisting of several molecules in which ordinarily neutral atmospheric molecules/atoms have gained or lost electrons. While particulate matter can also be charged, it is composed of a much larger number of molecules and is thus up to several orders of magnitude larger in diameter compared to small ion clusters.

SI are also continually being destroyed in a process of recombination, producing neutral molecular clusters. In addition to the process of recombination, SI can attach to PM. Because of this, a change in PM concentration directly results in a change in SI concentration. A significant portion of PM in the urban environment is a result of human activities, where smaller particles are typically associated with the process of combustion occurring in vehicles, industrial activities, biomass burning, and similar, while larger particles are typically due to construction and demolition activities, entrainment of outdoor dust and similar. The SI balance equation can be used to quantitatively describe the above-mentioned processes.

The outline of this paper is as follows. First, we provide a detailed explanation of the small ion balance equation and derive the link between small ion concentration, volumetric production rate and particulate matter concentration. Then we describe the method that was used in the indoor measuring campaign, in which all relevant parameters appearing in the balance equation are measured either directly or via an important proxy. We will show that under a quasi-steady state approximation, it makes sense to use the linear regression model to describe the interdependence between concentrations of larger aerosol particles of various diameters and small ion concentrations. Finally, conclusions about several linear models that were derived are given along with directions of future work.

## BALANCE EQUATION AND QUASI STEADY STATE

The small air ion concentration ( $n_{\pm}$ ) is determined by the following balance equation

$$\frac{dn_{\pm}}{dt} = q - \alpha n_{\pm} n_{\mp} - n_{\pm} \beta Z \quad (1)$$

where  $q$  is the volumetric production rate,  $Z$  is the aerosol number concentration,  $\alpha$  coefficient accounts for the losses of ion-to-ion recombination and  $\beta$  represents an effective ion-aerosol attachment coefficient, which is the integral over the size distribution of aerosol particles. The balance equation can include additional terms. If electrostatic deposition (occurring mainly in indoor air) is included in a model, there is an additional right-hand side term  $-\delta^{\pm} n^{\pm}$ , where  $\delta$  is an electrostatic deposition rate coefficient of the air ions.

If we assume  $n_{+} \approx n_{-}$  (note that in reality  $n_{+} \approx 1.12n_{-}$  which is due to the different mobility of positive and negative small ions, but that constant can be absorbed into  $\alpha$  coefficient), the balance equation reduces to:

$$\frac{dn_{-}}{dt} = q - \alpha n_{-}^2 - n_{-} \beta Z. \quad (2)$$

In a quasi-steady state, the differential equation reduces to quadratic equation:

$$\alpha n_{-}^2 + n_{-} \beta Z - q = 0. \quad (3)$$

Since concentration of small ions must be positive, only the positive branch is the solution:

$$n_{-} = \frac{\beta Z \left( \sqrt{1 + \frac{4\alpha q}{\beta^2 Z^2}} - 1 \right)}{2\alpha} \quad (4)$$

If we use the Taylor expand term in parenthesis, under the assumption that  $\alpha$  is very small, and we obtain:

$$n_{-} \approx \frac{q}{\beta Z}. \quad (5)$$

Since  $\beta$  represents an effective ion-aerosol attachment coefficient, which is the integral over the size distribution of aerosol particles, we can expand the above term as:

$$n_- \approx \frac{q}{\sum \beta_i Z_i}. \quad (6)$$

This result can also be more readily derived starting from the balance equation if we neglect the quadratic term present in (1). Since our campaign was situated indoors, the electrostatic deposition rate coefficient could also be included, and the balance equation now reads (under the assumption of a quasi-steady state):

$$\frac{dn_-}{dt} \approx 0 \approx q - n_- (\beta Z + \delta^-) \quad (7)$$

and after expanding  $\beta Z$  term we obtain:

$$n^- \approx \frac{q}{\sum \beta_i Z_i + \delta^-} \quad (8)$$

or more conveniently

$$\sum \beta_i Z_i + \delta^- \approx \frac{q}{n^-}. \quad (9)$$

The form of the above equation suggests linear regression is a justified modeling approach if we want to model the interdependence between the concentration of larger aerosol particles of various diameter and small ion concentration. The physical meaning of the coefficients in linear regression ( $\beta_i$ ) are an ion-aerosol attachment coefficient and the intercept term corresponds to the electrostatic deposition rate coefficient of the air ions ( $\delta^-$ ). Note however, that in a non-laboratory type of campaign, one cannot precisely control the aerosol distribution and there may be a significant correlation between individual channels corresponding to different particle sizes, which makes calculation (and interpretation) of the regression coefficients as attachment coefficients largely approximate.

A few notes about the physical nature of the ion-aerosol attachment coefficient are relevant. Ions attach differently to neutral and charged particles. In the case of neutral particles, the attachment of small ions can be described using diffusion theory

$$\beta_{\text{diffusion}} = 4\pi r_{\text{particle}} kT (B_e / e). \quad (10)$$

where  $B_e$  is electrical mobility,  $r_{\text{particle}}$  is radius of the particle,  $T$  absolute temperature,  $e$  is elementary charge, and  $k$  is the Boltzmann constant. In the case of charged particles, diffusion is still a factor, but an additional term is needed to account for the movement of ions due to the electrostatic field of a particle

$$\beta_{\text{charged}} = \beta_{\text{diffusion}} + (eB_e / \epsilon_0). \quad (11)$$

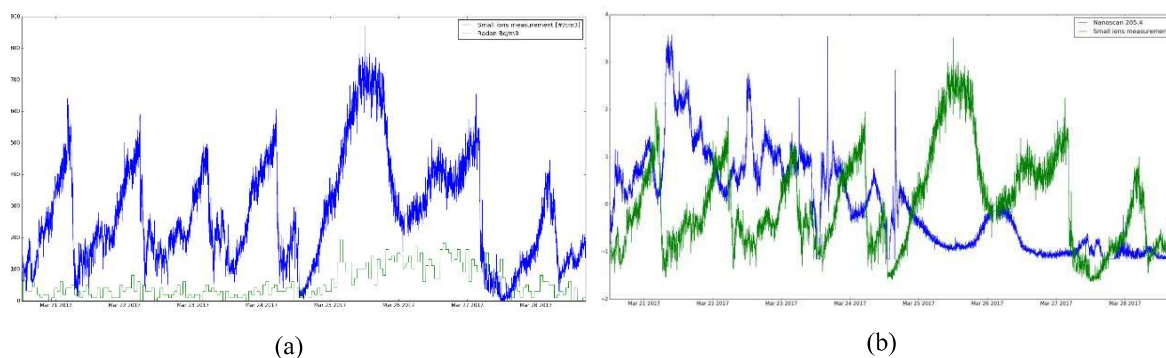
As a result, the approximate physical picture of the attachment process is not simple, and can further depart from real physical processes since during experiments we will certainly encounter multiply charged particles, a non-steady state regarding charge distribution of large aerosols etc. The (simplified) theory also suggests that the attachment coefficient would be larger for particles of a larger diameter.

## METHOD AND RESULTS

A wide range of relevant air quality parameters were measured in the indoor environment, occupied on workdays, in March 2017. The measurements included SI measurements using a Gerdien-type air ion detector (Kolarz, 2012), PM concentrations in a 10nm to 10um diameter range using TSI NanoScan SMPS Model 3910 and TSI Optical particle sizer 3330, gravimetric measurements of particles in 3 fractions, and local temperature, pressure and humidity. In addition, the radon concentration level was measured hourly using a Radon Scout. The collected data describes all relevant processes: 2 minute SI concentration measurements describe a steady state, radon

concentration gives insight into the rate of volumetric ion pair generation and 1 minute PM measurements give insight into main loss mechanism for SI.

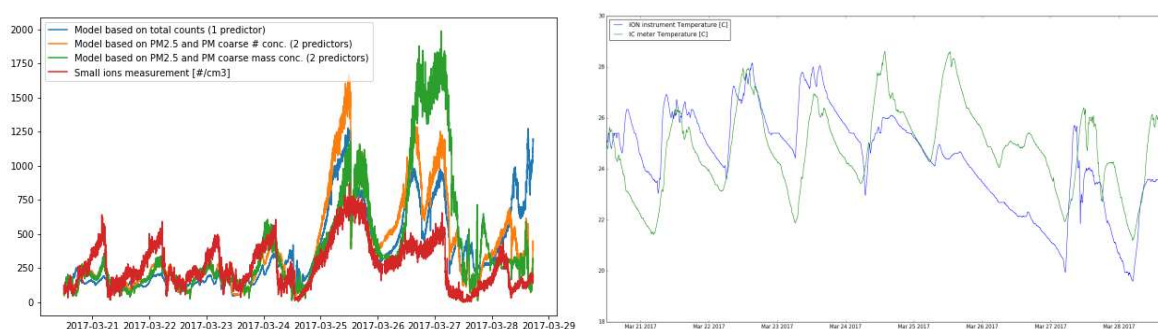
Initial exploratory data analysis shows that there is a correspondence between the increase in radon concentration and the increase in ion concentration, shown in Fig. 1a.



**Figure 1.** Initial exploratory data analysis a) Radon concentration vs. small ion concentration b) Normalized TSI NanoScan data from 205.4nm channel vs. normalized small ion concentration

We opted not to use radon data as a proxy for the volumetric production rate, due to a large temporal resolution of radon data and since the rolling average would introduce a lag presenting an adverse effect on the calculation of correlations of other variables with radon data. Instead we assumed that the volumetric production rate is constant and that the change in SI concentrations is mainly due to a variation of PM concentrations. Justification for such simplification can be found in Figure. 1b, where normalized TSI NanoScan data from 205.4nm channel vs. normalized small ion concentration is shown. As can be seen from Figure. 1b, roughly speaking, increases in PM concentration are matched with decreases in SI concentration, and vice versa. It is worth mentioning that this effect is most clearly seen for the channel shown in Figure. 1b, despite the fact that theoretical considerations regarding the attachment coefficients given in previous section suggest an increase in the attachment of ions to particles with an increase in particle diameter. However, this effect could be also due to non-controlled PM size distribution which is expected in non-laboratory conditions.

The relationship between SI concentration and PM concentrations was derived using a quasi-steady-state approximation of the SI balance equation. As stated earlier, the form of this relationship suggests that the use of linear regression in modelling is a sound and well-justified approach, and that the regression coefficients can be interpreted as ion-particle attachment coefficients. Since there was a large number of individual channels (13 NanoScan and 16 OPS channels), with a significant cross correlation, the ordinary least squares approach was not a reliable method, producing unphysical results. To ensure the regression coefficients had physical meaning we used a non-negative least squares solver [7], and aggregation of channels into total counts and typical PM fractions. Results are shown in Figure. 2a.



**Figure 2.** a) Comparison of small ion measurements and 3 models based on total counts and PM fractions b) Additional temperature measurements from IC meter and a Gerdien-type air ion detector

## CONCLUSION

All models show daily variations of small ion concentration; however, it seems that models are prone to overestimation, occurring in periods of low particle counts. An additional possibility for larger discrepancies could be temperature variation as seen in Figure. 2b, which is not accounted for in the model. Future work may incorporate additional parameters into modelling, such as temperature, and also introduce more complex models, based on the machine learning approach, where a choice of predictors would be based on the underlying physics. Also, more complex models would not require neglect of the quadratic term, thus potentially, improving the results. However, direct physical interpretation of model parameters in this case could be lost. In the case of a model based on total counts, the attachment coefficient is estimated to be  $8.45e-06 \text{ cm}^3 \text{ s}^{-1}$ . Note, however, that interpretation of the regression coefficients as attachment constants is somewhat approximate since there is a significant correlation between individual channels, corresponding to different particle diameter.

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## REFERENCES

1. Höpfe, Peter, and Ivo Martinac. "Indoor climate and air quality." *International journal of biometeorology* 42, no. 1 (1998): 1-7.
2. *Air quality in Europe - 2018 report*, ISBN 978-92-9213-990-2, European Environment Agency, Denmark, 2018.
3. Kim, Ki-Hyun, Ehsanul Kabir, and Shamin Kabir. "A review on the human health impact of airborne particulate matter." *Environment international* 74 (2015): 136-143.
4. National Research Council. *Health effects of exposure to radon: BEIR VI*. Vol. 6. National Academies Press, 1999.
5. Charry, Jonathan M. *Air ions: physical and biological aspects*. CRC press, 2018. (reprint, originally published in 1987)
6. Kolarž, P., Miljković, B., & Čurguz, Z. (2012). Air-ion counter and mobility spectrometer. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 279, 219-222.
7. Lawson, Charles L., and Richard J. Hanson. *Solving least squares problems*. Society for Industrial and Applied Mathematics, 1995.