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Atmospheric electricity as a proxy for air quality: Relationship between potential gradient and pollutant gases in an urban environment

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ABSTRACT

A relationship between Trace Gases (TG), NO_x, SO_2, O_3, and the Atmospheric Electric Potential Gradient (PG), through Ion/Particulate Matter (PM) interaction, is established in the urban environment of the city of Lisbon (Portugal). Analysis was restricted to 1988–1990, when simultaneous measurements of PG and TG were taken. Reasonable linear relationships between PG and TG concentrations have been found. A formulation relating PG with TG concentrations allows the estimation of constants of proportionally between TG-PM to be ~50 cm^{-3} ppb^{-1}; which are similar to the values found in direct TG-PM measurements in UK cities, validating the present results.

1. Introduction

Air pollution can be defined as the presence of pollutants, such as nitrogen oxides (NO_x), sulphur dioxide (SO_2), ozone (O_3), carbon monoxide (CO) and particulate matter (PM) in the air, which can cause negative effects on human health and vegetation [8]. Emissions of these pollutants can lead to a complex series of physical and chemical transformations in urban and regional areas [26]. The main source of NO_x in an urban environment is fossil fuel combustion originating from both stationary sources (i.e. power generation) and mobile sources (i.e. transport), while minor natural sources can include bacteria, volcanic action and lightning and non-combustion anthropogenic processes (e.g. HNO_3 manufacture, welding processes and the use of explosives). The annual mean concentrations of NO_2 (the major component of NO_x) in urban areas are generally found to be between 20 and 90 μgm^{-3} (~10–48 ppb), with peaks occurring twice a day as a consequence of rush hour traffic [27]. In urban areas, SO_2 is emitted predominantly from fossil fuel combustion at power plants, residential activities (e.g. heating), traffic, and other industrial facilities, as well as from shipping near ports and coastal or inland shipping routes [7]. Other minor sources of SO_2 include smelting, manufacturing of sulphuric acid, conversion of wood pulp to paper, incineration of refuse and extraction of elemental sulphur from ore. The annual urban mean concentrations of SO_2 in Europe and the US oscillated between 10 and 30 μgm^{-3} (~3–12 ppb) [25]. O_3 is an important photo-oxidant that is produced from NO_x catalysed photochemistry throughout the troposphere (e.g. Ref. [19]. Other photochemical reactions can produce a number of oxidants including peroxyacetyl nitrate as well as aldehydes, formic acid, and an array of short-lived radicals, which can produce and build up O_3 downwind of urban areas. The maximum level of O_3 observed in urban areas is well above 100 ppb (e.g. Ref. [16]). PM in urban areas is mainly composed of metals, organic compounds, materials of biological origin and elemental carbon (e.g. Ref. [39]. Particulates can be classified as either primary or secondary, according to their origin. Primary particulates are those emitted directly to the atmosphere, while secondary particulates are those formed by reactions involving other pollutants. In the urban context, most secondary PM occur as sulphates and nitrates formed from reactions involving SO_2 and NO_x, with typical annual mean values between 10 and 40 $\mu g\ m^{-3}$ (black smoke method) or 50–150 $\mu g\ m^{-3}$ (gravimetric method) [33]. At the sub-

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micron fraction (PM_1), there is often a significant contribution from secondary organic aerosol (SOA) as highlighted by Ref. [22].

In atmospheric electricity, a global electrical circuit is evidenced by a measurable atmospheric electric potential gradient at the Earth's surface, usually referred to as Potential Gradient (PG[1]). Global thunderstorm activity transfers charge to the ionosphere, which returns to the ground by means of an air-Earth current through air; weakly ionised due to the presence of cluster-ions produced by solar and cosmic rays and ground based radiation. PG typically has a magnitude between 100 and 200 V m^{-1} in fair weather, but can be affected by sources of space charge, such as charged clouds or local sources of ions [14]. The effect of air pollutants, specifically particulate matter (PM), on the atmospheric PG is one of the most successful and largely explored applications of atmospheric electricity. Recent publications by the authors review this in detail; the interested reader is referred to these publications [35–37]. The basic physics of this process is summarized as follows: an increase in PM concentration depletes ions in the atmosphere, reducing the air conductivity and hence (according to Ohm's law) increasing PG. Of particular interest has been the ability to use historical records of PG since the industrial revolution [2] to retrieve pollution dynamics and smoke estimates [15]. More recently, attention has been given to the possibility of assessing smoke plume dynamics by combining PG measurements with HYSPLIT particle trajectory modelling [6].

To date, much less attention has been given to the relationship between Trace Gases (TG) and PG. In the literature the most prominent publications on this subject are those by Guo and co-authors, [9,10]. In these papers, those authors state that PG can be simultaneously a proxy of both PM and TG; the argument given to justify this is that both TG and PM influence the PG, but according to different mechanisms. The linear relationship between PG and PM is well established and has been described earlier. In the case of TG, the linear influence on PG is justified as TG contribute to the increase of the ion recombination rate, α [9,10]. This results in a net reduction of ion production, that consequently reduces the air conductivity and therefore increases PG; explaining the PG-TG relationship. A detailed discussion of ion recombination is beyond the scope of the present work, but the interested reader is referred to seminal works on atmospheric ions available in the literature, e.g. Ref. [1]. Furthermore, this mechanism has been intensively debated as ion recombination is considered to be a key aspect in particle formation (e.g. the CLOUD experiments at CERN [20], and references therein) but it is the current view that there is no direct relationship between TG concentration and PG. The observed statistical correlation for PG and TG found in the work of Guo and co-authors [9,10] is considered to result from an indirect relation; TG are proportional to PM and as PM influences PG a relation appears to hold between PG and TG. Proportionality of TG and PM concentrations has been shown in a number of different studies undertaken in urban environments. Among which [23], analysed data from Manchester, Birmingham and Edinburgh (UK) and found reasonable values of proportionality, ~50 cm^{-3} ppb^{-1}, for PM and TG concentrations. Therefore, empirical evidence justifies the assumption of a linear relationship between TG concentrations and atmospheric PG measured at ground level.

The present work aims to clarify the linear relationship between PG and TG concentration, mediated by PM, as observed by Refs. [9,10]. A linear proportionality is assumed between PM and TG, following observations by Ref. [23]; and the formulation derived by Ref. [15]; is adapted to describe the linear relationship between PG and PM. With these assumptions a simple formula is derived relating PG-TG; which is shown to be linear. This formula is tested against observations in Lisbon, Portugal (1988–1990) and reasonable results are found which are supportive of the indirect PG-TG relation, clarifying this long-standing issue.

2. Theoretical background and formulation

The theoretical framework for the approach used here follows a similar method outlined in previous work by the authors [36]. Atmospheric small ions (clusters of molecules around a central ion) are produced by ionisation of air molecules, mainly by cosmic rays or radioactive decay [13]. A steady-state equation for ion formation and loss in the presence of PM was derived by Ref. [18] and is expressed as:

$$q - \alpha n^2 - \beta_a Z_a n = 0. \tag{1}$$

Where n is the mean ion concentration, q is the ion production rate (this is assumed to be q~10 $cm^{-3}s^{-1}$), α is the ion recombination rate, β_a is the effective ion-PM attachment coefficient for the PM size distribution in question, and Z_a is PM number concentration. Eq. (1) neglects the positive to negative ion imbalance, as it is assumed a quasi-equilibrium state perturbed by the presence of PM. To relate urban PG measurements with TG, it is considered that most of the atmospheric ion loss is caused by ion-PM attachment and not by ion recombination; this assumption is validated by the work of [38]. The solution to this equation is straightforward:

$$n = \frac{1}{2\alpha}\left[\sqrt{(\beta_a Z_a)^2 + 4\alpha q} - \beta_a Z_a\right]. \tag{2}$$

For cases with relatively high PM concentration (~3000 cm^{-3}), such as would be expected in urban environments, Eq. (2) can be expanded in a Taylor series to yield a simple relationship between ion number concentration and PM number concentration:

$$n \approx \frac{q}{\beta_a Z_a}. \tag{3}$$

Details of this derivation can be found in Ref. [36]. With Eq. (3) the atmospheric electric conductivity can be written as:

$$\sigma_t = 2\mu_m e n \approx \frac{2\mu_m e q}{\beta_a Z_a}, \tag{4}$$

where μ_m is the mean electric mobility (the factor 2 is justified by the contribution of both positive and negative ions having similar mobilities) and$e$ is the electron charge. The influence of charged PM on atmospheric electric conductivity is neglected due to their relatively low mobility [42]. Using (quasi-static) Ohm's law, it is possible to relate PG with σ_t by:

$$PG = \frac{J_z}{\sigma_t} \approx \frac{J_z}{2\mu_m e q}\beta_a Z_a, \tag{5}$$

whereJ_z is the air-Earth density current (usually considered to be ~2 pAm^{-2}). Eq. (5) relates PG and Z_a linearly and is similar to relationships found by Refs. [15,36] and [12]. Finally, supported by experimental observations by Ref. [23]; an empirical linear relation is used to relate Z_a and TG concentration, $[X]$, of the type:

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[1] PG is defined as the vertical component of the surface atmospheric electric field, E_z, by definition this field is negative in fair-weather days (field vector directed downwards). The convention used for PG, in order to have positive values for fair-weather days, is to define PG = -E_z. This definition has been used from the beginning of atmospheric electricity and details can be found at [5].