ASSESSMENT OF THE ACCEPTABLE CONCENTRATIONS OF SULPHUR DIOXIDE IN THE AIR OVER BULGARIA ACCORDING TO THE DETERIORATION OF SOME TECHNOLOGICAL MATERIALS

H. Chervenkov

National Institute of Meteorology and Hydrology - branch Plovdiv, "Ruski" 139, Plovdiv 4000, Bulgaria, e-mail: hristo.tchervenkov@meteo.bg

Abstract: Air pollution effects on materials have been known for a long time. The original aim of the International Co-operative Programme for Materials (ICP-Materials) was to perform a quantitative evaluation of the effect of sulphur pollutants in combination with nitrogen oxides and other pollutants as well as climatic parameters on the atmospheric corrosion of important materials. The dose/response functions constitute the main results of the programme and are of outmost importance. In this study they are used to solve the reciprocal task – to find the degree of the pollution with sulphur dioxide that by fixed other parameters ensure that the rate of materials corrosion is in certain, "acceptable" limits. The calculated results are comprised with the actual pollution levels. This is as possible way to assess and map quantitatively the acceptable concentrations of sulphur dioxide in the air over Bulgaria according to the deterioration of seven wide used technological materials.

Key words: Acceptable Levels, Air Pollution, Dose/response functions, Material deterioration, Sulphur Dioxide

Introduction

Atmospheric pollution is an important factor in material deterioration including degradation of systems used for material protection. Due to pollution, the lifetime of technological products is shortened. Buildings, other structures, as well as objects of cultural heritage exposed to the atmosphere deteriorate more rapidly. The resulting physico-chemical and economic damage can be significant - not to mention the loss of unique parts of our cultural heritage and hazards due to endangered reliability of complicated technological devices. Also, as the result of weathering due to especially acidifying pollutants, a significant part of the metals used in constructions and products are emitted to the biosphere with a potential hazard to the environment. Laboratory exposures demonstrated already in the 1930's the corrosive effect of sulphur dioxide (SO_2), which was later confirmed by several exposure programmes as by International Co-operative Programme on Effects on Materials, including Historic and Cultural Monuments (ICP Materials). The main aim of this programme is to perform a quantitative evaluation of the effects of multi-pollutants such as sulphur and nitrogen compounds, ozone and particles as well as climate parameters on the atmospheric corrosion of important materials, including materials used in objects of cultural heritage (Tidblad et al., 1998). There are many other parameters that can influence the damage to materials; it is an interplay between chemical, physical and biological parameters. ICP Materials focus on effects of acidifying pollutants, and their interplay with natural climatic factors. Corrosion is, however, a process that occurs even in the absence of pollutants and the aim is to quantify to which extent pollutants accelerates the ”natural” or background corrosion of materials.

Dose-response functions and goal of the study

An extensive statistical analysis not only confirm the corrosive effect of SO_2 but also enable quantification of the effects of other environmental parameters for a wide range of materials. A dose-response function links the dose of pollution, measured in ambient concentration and/or deposition, to the rate of material corrosion (Tidblad et al., 1998). The dose-response functions, which separate the effect of dry and wet deposition, constitute the main result of the programme. They can be used for mapping areas of increased risk of corrosion and for calculation of corrosion costs (Kuchera, 2004). The results of ICP Materials not only confirm the corrosive effect of SO_2 in combination with other pollutants but also enable quantification for a wide range of materials. The deterioration of some materials in Bulgaria owing to air pollution was estimated in (Chervenkov, 2007). In this study however, the dose-response functions for seven different materials (weathering steel, zinc, aluminum, copper, bronze, limestone and sandstone) are used to solve the reciprocal task – to find the degree of the pollution that by fixed other parameters ensure that the rate of materials corrosion is in certain, “acceptable” limits. Traditionally and with right, SO_2 has been regarded as the most important corrosion stimulator. Because despite the abatement in the last decades, the sulphur pollution in Bulgaria remains relatively high (Lovblad et al. 2004; Chervenkov 2006) this study is focused on this pollutant.

Definition of Acceptable levels

Atmospheric corrosion and deterioration of materials is a cumulative, irreversible process, which proceeds even in the absence of pollutants. The critical loads/level approach used for ecosystems has to be modified in relation to degradation of materials as even the lowest concentration of pollutants causes an increase in the deterioration rate. This leads to the concepts of acceptable corrosion rates and pollution levels. The acceptable corrosion rate (Ka) must be determined by technical and economic considerations based on the specific application of a material. For model calculations, however, and for the purpose of comparing different materials with respect to their pollution sensitivity, different levels of acceptance can be defined by relating the corrosion rate to corrosion rates in areas with ‘background’ pollution (Kb), by multiplying with a factor n. Ka = n × Kb. Acceptable pollution levels for different n-values can be calculated using the dose-respons functions. for individual materials. According the ICP-Materials recommendations and the previous study (Chervenkov, 2007) n is fixed to 1,5. The background (according (Kuchera, 2004)) and acceptable corrosion rates expressed for a 1-year exposure period are shown in Table 1

Table 1. Background and acceptable *(n = 1,5)* corrosion rates for a 1-year exposure period

Material	1-year background corr. rate, Kb	1-year acceptable corr. rate, Ka
Weathering steel	72 g m^{-2}	108 g m^{-2}
Zinc	3.3 g m^{-2}	5.0 g m^{-2}
Aluminium	0.09 g m^{-2}	0.14 g m^{-2}
Copper	3.0 g m^{-2}	4.5 g m^{-2}
Bronze	2.1 g m^{-2}	3.2 g m^{-2}
Limestone	3.2 μm	4.8 μm
Sandstone	2.8 μm	4.2 μm

Computational domain, initial data and performed calculations

Because only Bulgarian climate data are available, the computational domain is limited over the territory of Bulgaria. The domain is part from the standard EMEP-domain with a gridcell 50×50 km horizontal resolution and consist from 11×13 gridcells (Figure 1). The actual climatic data for the medium annual temperature, relative humidity and for the precipitation amount from 19 synoptical stations are taken from the NIMH – BAS database. The meteorological dataset is prepared after interpolation of these data over the domain. As additional information for the further comparison the newest (i.e. for the year 2004) datasets for the concentrations of the main pollutants are taken from the EMEP (European Monitoring and Evaluation Programme) database. This is free available web-based service for scientific use. The ICP-materials empirical formula, connecting the NO_2 and the O_3 concentration is used, because no mass-concentration data for the ozone are available. According the dose-response functions the acceptable concentrations of the sulphur dioxide in the surface air for each gridcell and material are calculated.

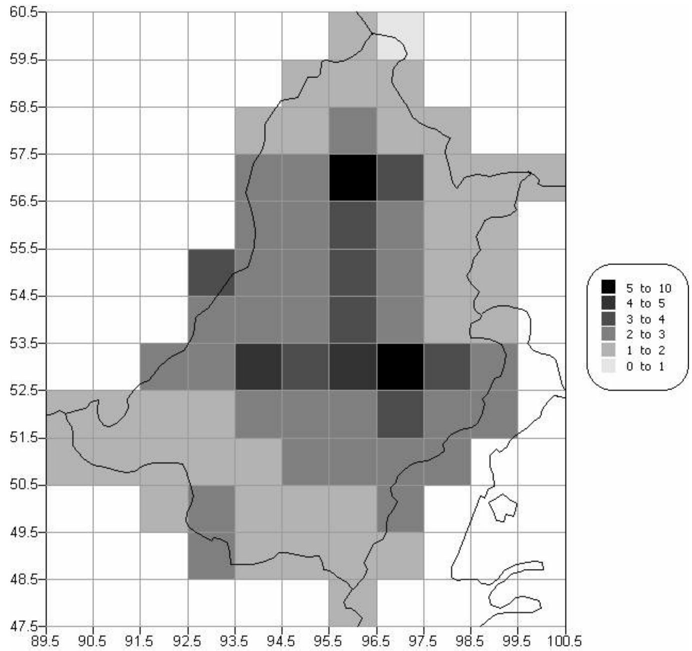

Fig. 1. Mean annual concentration in the surface air (unit: μg(S)/m^3, year: 2004) of sulphur dioxide according the EMEP database.

Treatment of acceptable levels as air quality standard

The primary goal of every international or national air quality standard is to set limits for pollutants considered harmful to public health and the environment. Usually this limit is a single value, a threshold for the chosen pollutant and averaging time. The output from the above described calculation consists from a set of seven different acceptable levels - by one for each material for every griddcell (Akij; where i =1,11, j = 1,13 are the coordinates of the current gridcell, and k = 1,7 is the index for the material) . Highest sensitivity shows the weathering steel and the stone materials and lowest the aluminum. It is convenient from practical point of view to define a common ("unified") for all materials acceptable level of air pollution Aij. They are many reasonable ways to do this. The most logical choice for this limit is simply to select the minimal value (for all gridcells this is the value for the weathering steel) Aij = Aminij. This definition ensures that all materials are protected reliably. The comparison with real concentrations sows (Figure 2) that this standard produces significant smaller, hard achievable limits. That's why the author recommendation is to choice the average value as threshold Aij = Aaverij. Figure 3 shows the ratio between the real concentration and the concentration according this criterion. Can be seen that even in the case of this definition the real concentrations are still significant greater. Of course the results from the previous chapter allow many other definitions and considerations, depending from the specific conditions.

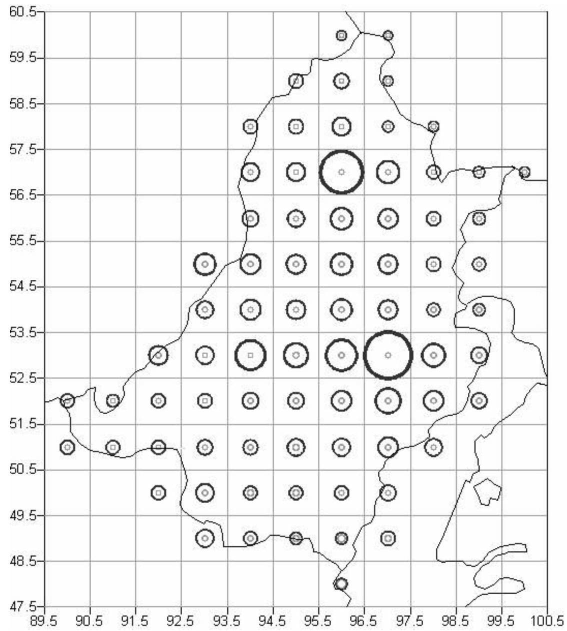

Fig. 2. Comparison between the real concentrations (EMEP data, black circles) and the calculated acceptable concentration for the weathering steel (grey circles). The radius of every circle is proportional to the corresponding value.

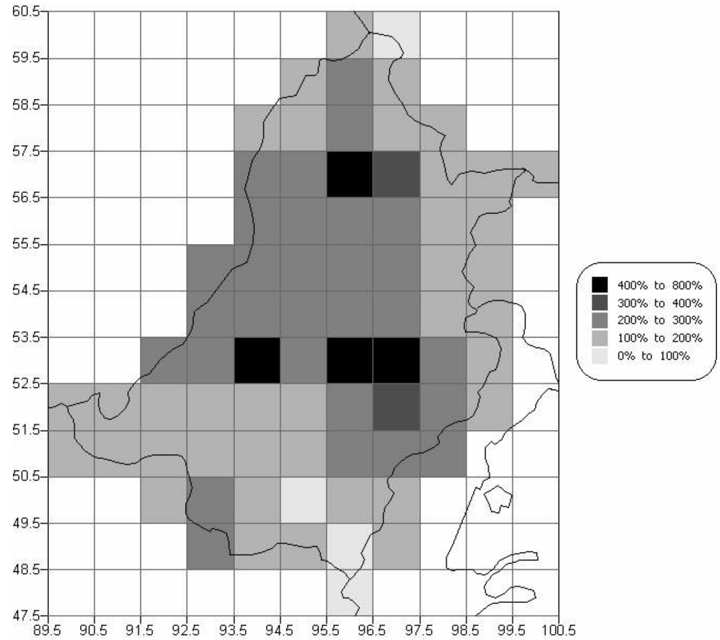

Fig. 3. Ratio between threshold concentrations ("unified" acceptable level) and the real concentration in each gridcell.

Conclusion

The dose-response functions are proper physico-mathematical way to estimate the acceptable levels of the pollution with a chosen pollutant by a certain climate. These levels can be treated as long-term permissible limits of the air pollution. The performed calculations shows that even concentrations far below from these considered harmful to human health caused significant corrosion for a long periods of exposure. That's why more attention has to be paid of this phenomenon in the next editions of the air quality standards. Such studies can be used also for assessment of the ecochemical and "ecoclimatological" situation in given areas, for technical and economical studies and so on. The comparison between the obtained results and the real concentrations is a clear evidence of the need of further significant abatement of the pollution of Bulgaria with sulphur dioxide.

References

Chervenkov, H. (2006) Transboundary atmospheric exchange and pollution of Southeast Europe with oxydized sulphur. Ph.D. thesis 115 pp, National Institute of Meteorology and Hydrology, Bulgaria.

Chervenkov, H. (2007) 'Assessment of material deterioration in Bulgaria owing to air pollution', Int. J. Environment and Pollution, Vol. 31, Nos. 3/4, pp.385–393.

Kuchera, V. (ed.) Mapping Manual 2004 – 4 Mapping of Effects on Materials, Retrieved March 2006 from http://www.icpmapping.org/pub/manual_2004/mapman_4.pdf

Lovblad, G., Tarasson L., Torseth, K., Dutchak, S., (2004) EMEP Assessment. Part I – European Perspective, Chapter2: Sulphur pp. 42 - 44

Tidblad J, Kucera V, Mikhailov A. A. (1998) Statistical analysis of 8-year materials exposure and acceptable deterioration and pollution levels. (Report № 30 UNECE International Co-operative Programme on Effects on Materials Including Historic and Cultural Monuments, Swedish Corrosion Institute, Stockholm, Sweden).

Определяне на приемливите концентрации на серния диоксид във въздуха над България в зависимост от ерозията на някои технологични материали

Х. Червенков

Резюме: Влиянието на замърсяването на въздуха върху материалите е известно отдавна. Основната задача на Международната Кооперативна Програма за Материалите (ICP-Materials) бе да намери количествена експертна оценка на ефекта на серносъдържащите замърсители и азотните оксиди както и на другите реагенти във взаимодействие с климатичните параметри върху атмосферната корозия на някои значими материали. Т. нар. функции "доза/ефект" са основен резултат от работата на

Програмата и имат голямо практическо значение. В това изследване те са са използвани за решаване на обратната задача – намиране на пределната концентрация на серния диоксид при фиксирани други параметри, за която ерозията не превишава определени, “приемливи” граници. Получените резултати са сравнени с актуалните нива на замърсяване. Показано е, че това е и възможен начин за оценка и картиране на пределно допустимите концентрации на серен диоксид във въздушния басейн над България.