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# DEPENDENCE OF $SO_2$ OF IMMISSIONS MEASUREMENT METHODS FOR SELECTED AREAS POWER PLANT VOJANY

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The results of imperfect knowledge of the natural environment's basic laws show that the negative effects of our actions are manifested in most cases only belatedly, in forms such as: the loss of arable land, the extinction of rare species of plants and animals, the depletion of the ozone layer, the climate change, the deterioration of air quality, the acid rain, the worsening quality of surface and ground water, the surface loss of rainforests and many other negative aspects of our thoughtless actions. For the measurement of sulphur concentration, we chose locality surrounding the power plant Vojany, where we identified two locations for mounting our stands. The first place was the village Tušice, and the second one the area of AMS Leles. This is where we planted in alkaline strips in stands used for this purpose and by the sorption – cumulative method we evaluated concentrations of sulphur amount collected on the strips. In the period 2012–2014, we conducted experiments in regular 30-day intervals; we performed 104 analyses of filter plates using the sorption-cumulative method. The current position of some habitats infestation causes damage to various parts of environment. Therefore, we consider it relevant to continue in monitoring this affliction and quantifying the extent of its negative effects. The proposed procedure with the possibility of a retrospective determination of concentrations of $SO_2$ using mathematical modelling can also be used for the determination of old burdens.

**Keywords:** pollutants concentration, pollution, methods for measuring pollution

The basic condition for the existence of life on Earth in any form is good environment. Air pollution is a problem that continues to this day and is linked to the industrial revolution and overall development of society. Manifestations of degradation of air, even the smallest, eventually disappear, but their effects remain. There are also talks about the deterioration of the situation in accordance with the diagnosis of new pollutants, identifying hidden consequences, but also about raising standards for classification of air pollution (Báreková et al., 2011).

Air, as one of the fundamental components of the environment, has a special position in relation to the other two – soil and water. The pollution of soil and water is minimal, but with the help of water, soil is getting cleaned (Fuska et al., 2013).

Dry and wet deposit contaminants from air have negative effects and cause damage to materials, soil, water, fauna and flora (Benson, 1979).

The current level of air pollution compared to the peak reached in the 80s of the 20$^{th}$ century is on the other hand better, but the consequences of the current situation still require attention and monitoring (Húska, Jurík and Tátošová, 2005).

Air quality significantly affects the state of the environment, human health, as well as individual ecosystems. Air protection legislation in force until 31 August 2002 was based primarily on the emission principle, i.e. it regulated the behaviour of operators of the air pollution sources by limiting the release of pollutants into the atmosphere. Although air quality has been identified by pollution limits, air pollution was not a priority in terms of the management of air protection. A similar practice was used by other European countries. Therefore, an EU framework directive obliges Member States to create conditions and to implement measures to ensure that air quality is maintained where it is good and in other cases needs to improve (Article 1 of the Framework Directive). The air protection is thus placed in the first place, especially the emphasis on achieving a quality of air, which, based on current scientific knowledge does not endanger neither human health nor the environment (Grešová et al., 2012).

To minimize the adverse impact of emissions and air pollution exposure to heavily indebted habitat, it is necessary to maintain regular monitoring and measurement. The methods that determine the concentrations of pollutants in the atmosphere can be divided into indirect and direct. The direct methods are directed to manual analytical procedures with active air pumping through a suitable absorbent. This includes sorption-cumulative method-West Gaeko method, colorimetric method I and II. etc. (Cryer et al., 2001).

Indirect methods determine the concentrations of pollutants using mathematical models of dissemination of transmission and transformation of pollutants in the air and provide a whole range of functions. Except for substitution of direct measurements, these methods identify current emission situation in areas without measurements as

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a forecasting routine of expected conditions (maximum and average), the impact of the introduction of new resources in the range and simulation of conditions "ex post" in documenting ongoing emission situations in the past. A very important component of this approach is the selection of adequate model for the required purpose and pollutant and a high degree of representativeness inputs. The choice of support programs and algorithms (Schnelle, 2002) is also linked to this.

The situation is more complicated in the case of annual (seasonal, to a lesser extent multi-annual) crops whose substrate is permanently influenced by agrotechnical interventions and the introduction of land drainage materials and agrochemicals. Current concentrations of contaminants in the atmosphere are either isolated or synergistic, and are below the threshold values for damaging agricultural crops, and the issues of critical loads for non-forest vegetation are not being solved at all (Halászová and Kliment, 2013).

## Material and methods

### Characteristics of monitored sites

For monitoring concentrations of sulphur in the air we determined the Vojany location. Automated measuring station (AMS) Leles (operated by ENVITECH, authorized by SHMÚ Bratislava, the results verified the appropriate District Environmental Office) was built in the imission area, as the measure of the total concentration of the pollutant. The second area where the stand was placed to capture air pollution by sulphur sorption – cumulative method is located within Tušice.

The Vojany Power Plant (SE – EVO) is located in eastern Slovakia in the Michalovce district, 7 km to west of Veľké Kapušany.

The plant consists of two energy production plants:

- Vojany power plant I (6 × 110 MW). EVO I operation consists of 6 blocks, burning coal, natural gas and mazut. Turbo-generators have a capacity 6 × 110 MW, and after five years of construction they were put into operation in 1966.
- Vojany power plant II (6 × 110 MW). EVO II consists of just 6 units with a capacity of 6 × 110 MW. The operation plant was built between 1968 and 1974 and boilers burn natural gas and heavy fuel oil.

The total installed capacity of 1,320 MW means the SE – EVO is the largest thermal power plant in Slovakia. The main mission of Vojany power plant is to provide transmission support services to Slovak power system with the highest quality, safety and reliability and the lowest impact on the environment.

### Methodological approach

**Direct methods: sorption-cumulative method**

To determine the load by sulphur on the affected area, we chose the sorption-cumulative method which is ranked among the direct measurement methods by CSN 03 8211 (a method developed by SVÚDM – Prague Běchovice). This method is designed for long-term measurements of concentrations of $SO_2$ and its compounds in places where the


**Figure 1** Weather stations with the filter plate – Leles and AMS

**Figure 2** Weather station with the filter plate Tušice

aggression of atmosphere is measured. The resulting value of sorbed amount of $SO_2$ (including sorbed particles $SO_3$, $H_2SO_4$ and soluble sulphates) per unit area of the surface strongly basifies filter plates (filters) and describes immediate aggressive effect on the atmosphere.

The filter plates that capture sulphur compounds are placed on a rack, which are made according to the parameters specified in CSN 03 8110. Height recess of filter plates is set at 2.2 meters above the ground by the CSN. The first stand with weather stations installed in the area of automated monitoring stations (AMS) Leles, shows Figure 1 and the other in the village Tušice, Figure 2, which is located 30 km from the power plant Vojany. Dimensions of the filter plates are 0.15 × 0.31 × 0.003 meters, mounted on metal meteorological booth. Exposure time was set at 30 days and time for exchange was set to 5 pm.

After 30 days of exposure, the filter plates, which are saturated in $Na_2CO_3$ solution, have been analytically processed.

The collected compound from the filters is mechanically processed and leached 24 hours in distilled water. $H_2O_2$ oxidized sulphur compounds are added to $SO_4^{-2}$. The solution is filtered and then the filtrate is topped up in a volumetric flask to 500 $cm^3$. Self determination is carried out by pipetting 10 $cm^3$ and sample is acidified to a solution of chloroacetic acid to pH 2–3. Then, the sample is completed by 20 $cm^3$ of ethanol. Anions $SO_4^{-2}$ are determined by using ethanol solution of Ba $(ClO_4)^2$ in the mixed indicator Thorin-methylene blue from green to pink colour. Surface fallout is determined by the ratios set out in STN 03 8211, 03 8203 (Lazor, 2010).

The preparation of filter plates and determination of $SO_2$ were carried out by titration of the Department of Chemistry Slovak University of Agriculture.

### Direct measurement of air-conditioned containers LU 3000 (AMS Leles)

AMS LELES (Figure 1) measures the amount of $SO_2$ analyzer using Thermo Electron Corporation, model 43C, which operates using ultraviolet fluorescence method, based on the emission of radiation of $SO_2$ molecule excited by UV radiation for passing the base energy state. Before entering the fluorescence sample analyzer the air passes through the filter to exclude interferences due to contamination of solid particles. The sample is then passed by air through the hydrocarbon separator to remove the interference due to the possible presence of an aromatic hydrocarbon. The air sample then enters the fluorescence reaction chamber where the sample is irradiated with UV radiation pulsing.

The transition to a lower energy emits level for UV radiation of $SO_2$ molecule and their intensity is proportional to the concentration of $SO_2$ in the sample. The emitted radiation passes through a band-pass filter which passes only the photomultiplier to radiation having a wave length emitted by the excited $SO_2$ molecules. Photomultiplier detects

**Table 1** The measured concentrations of $SO_2$ in $\mu g.m^{-3}$ in the area of Leles and Tušice

| Measuring period | Concentrations $SO_2$ in $\mu g\ m^{-3}$ S-C method Leles | Concentrations $SO_2$ in $\mu g\ m^{-3}$ AMS Leles | Concentrations $SO_2$ in $\mu g\ m^{-3}$ S-C method Tušice |
|---|---|---|---|
| **29. 2. 12–30. 3. 12** | 25.8 | 2.7 | – |
| **30. 3. 12–29. 4. 12** | 16.06 | 1.7 | – |
| **29. 4. 12–30. 5. 12** | 16.81 | 1.2 | – |
| **30. 5. 12–29. 6. 12** | 33.94 | 0.6 | – |
| **29. 6. 12–29. 7. 12** | 56.28 | 1.9 | – |
| **29. 7. 12–28. 8. 12** | 51.12 | 3.6 | – |
| **28. 8. 12–27. 9. 12** | 45.04 | 3 | – |
| **27. 9. 12–27. 10. 12** | 57.02 | 2.2 | – |
| **27. 10. 12–26. 11. 12** | 32.45 | 2.8 | – |
| **26. 11. 12–25. 12. 12** | 42.87 | 5.5 | – |
| **25. 12. 12–24. 1. 13** | 44.36 | 3 | 54.79 |
| **24. 1. 13–23. 2. 13** | 40.63 | 3.7 | 45.35 |
| **23. 2. 13–25. 3. 13** | 48.83 | 4.3 | 45.59 |
| **25. 3. 13–24. 4. 13** | 31.18 | 3.7 | 48.83 |
| **24. 4. 13–23. 5. 13** | 47.25 | 2.5 | 35.43 |
| **23. 5. 13–21. 6. 13** | 61.15 | 3.6 | 39.89 |
| **21. 6. 13–20. 7. 13** | 14.29 | 3.3 | 37.66 |
| **20. 7. 13–18. 8. 13** | 35.43 | 1.7 | 50.32 |
| **18. 8. 13–16. 9. 13** | 22.03 | 1.9 | 39.89 |
| **16. 9. 13–15. 10. 13** | 25.01 | 1.4 | 16.81 |
| **15. 10. 13–13. 11. 13** | 28.73 | 2.4 | 9.36 |
| **13. 11. 13–12. 12. 13** | 39.15 | 3.1 | 10.11 |
| **12. 12. 13–10. 1. 14** | 36.92 | 1.9 | 11.6 |
| **10. 1. 14–08. 2. 14** | 30.96 | 2.8 | 7.87 |
| **8. 2. 14–9. 3. 14** | 19.7 | 2.2 | 12.34 |
| **9. 3. 14–6. 4. 14** | 15.6 | 2.1 | 16.7 |
| **6. 4. 14–5. 5. 14** | 14.7 | 2.1 | 14.8 |
| **5. 5. 14–3. 6. 14** | 12.5 | 1.6 | 13.2 |
| **3. 6. 14–2. 7. 14** | 17.1 | 2.2 | 22.77 |
| **2. 7. 14–31. 7. 14** | 12 | 1.5 | 20.78 |

emission of UV radiation $SO_2$ molecules migrating to lower energy states.

The photodetector, in the rear of the fluorescent chamber continuously monitors the UV source and the pulsing is connected to a circuit that compensates for variations in UV light. UV photomultiplier converts the fluorescence into an electric signal. The sample is then passed through the air flow sensor capillary constant flow, providing over a shell-side trap hydrocarbons. Suction internal sample pump is placed at the output of the analyzer. The analyzer compensates deviations of the output signal caused by the device's internal temperature fluctuations and compensates for pressure changes in the fluorescent chamber.

The intensity of the fluorescence emission is proportional to the number of molecules in the detection volume of $SO_2$ and thus the concentration of $SO_2$. The concentration of sulphur dioxide is directly measured in units of volume fraction if the analyzer is calibrated using a standard with a concentration expressed as volume fraction. Results are expressed in μg $m^{-3}$ after conversion in the evaluation system of standard conversion rates (Ochodnická, 2012).

The data measured by automated monitoring station were provided to us by ENVITECH Trenčín (operator) with the written consent of the Vojany Power Plant (investor) and the said company which manages the given monitoring station.

## Results and discussion

### Sorption-cumulative method

Principle of this long-term method for measurement of concentrations of sulphur dioxide is the capturing of acidic sulphur compounds on the surface of alkaline surface and determination by sulphur titration. In our project, we consider this the most appropriate method.

During the entire period of measurement from 29. 2. 2012 to 31. 7. 2014 in Leles area, 60 filter plates were used. The highest measured value of the sorbed sulphur compounds was 61.15 μg $m^{-3}$, in contrast to the lowest value, 12 μg $m^{-3}$. The average value amounted to 32.50 μg $m^{-3}$.

Measurement of air-conditioned containers LU 3000 (AMS Leles)

As with sorption cumulative method, we measured the concentrations of sulphur oxides in the same 30-day intervals through the analyzer Thermo Electron Corporation, operating with ultraviolet fluorescence method.

Measurements took place from 2012 to 2014, namely from 29. 2. 2012 to 31. 7. 2014 in Leles area where the automated monitoring station is installed. Since the second study site Tušice is not considered hazardous, it is not in the program EMEP and neither has it monitoring concentrations of $SO_2$ data, so we cannot perform comparison of two monitoring stations in different locations. The measured values for the whole period from the two methods are given in Table 1.

Similar to the S-C method, we can see an increase in concentration of $SO_2$ in summer (29. 7.–27. 9. 2012), as well as the value of an upward and downward trend, which is repeated regularly. We are attributing it to relatively stable changes in dispersion conditions in Slovakia during the year. The highest value of UV fluorescence reached 5.5 μg $m^{-3}$ in 2012, while the lowest was 0.6 μg $m^{-3}$.

Sulphur dioxide concentrations measured by UV fluorescence method for 2014. The volume of $SO_2$ does not exceed 3 μg $m^{-3}$. The highest concentrations ranging from 2.8 to 2.9 μg $m^{-3}$. Which, compared with 2012 is 1.89 times less than in 2014. Minimum seized was 1.5 μg $m^{-3}$ sulphur dioxide.

As we can see, the data measured by UV-fluorescence are significantly lower than the EN method, which justifies that the filter pads adsorb other sulphur compounds as well ($SO_3$, $SO_4$, $H_2SO_4$, $H_2SO_3$) and not only $SO_2$, whereas the UV fluorescence method measures Sulphur dioxide only.

Sulphur dioxide emissions has had a steady downward trend since 1990, due to energy consumption and decline in major energy sources, such as power stations Vojany (Torseth et al., 2012).

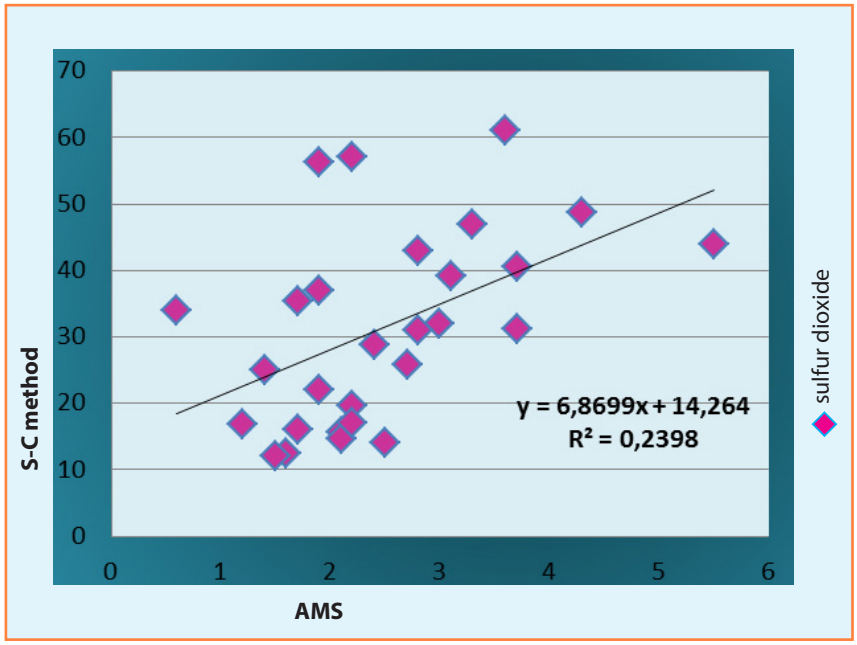


**Figure 3** Linear regression of S-C and UV-F method

### Conclusions

Automated monitoring systems are not effective enough to cover territories that are exposed to short-term pollution. Quantitative methods used for registration of short-term extremes are technically demanding and linked to energy facilities. Summation methods are not accurate enough and are not detecting any extreme situations destroying the concentrations system limits and critical ecosystems capacities.

We compared the UV-florescence method and the S-C method using linear regression test (Figure 3) in locality Leles using information recorded throughout the whole research time. Determination

coefficient was identified as $R_2$ = 0.2398, which does not prove the most effective correlation. However, we are taking in consideration that S-C method is aimed on the concentration of sulphur in the atmosphere in general.

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## References

BÁREKOVÁ, A. – SKLENÁR, Š. – TÁTOŠOVÁ, L. 2011. Metodika nakladania s tuhým komunálnym odpadom v podmienkach vidieckej zástavby. Prvé vydanie, Nitra : SPU, 2011, 115 s. ISBN 978-80-552-0539-7.

BENSON, P. E. 1979. Wersatile Dispersion Model for Predicting Air Pollutants Leveles Near Highmays and Arterial Strets, Interin Report, Federal Higway Administration, Wasshington, D. C. 1979.

CRYER, S. A. – WESENBEECK, I. J. 2001. Predicted 1,3 dichlorpropene air contentrations resulting from tree and vine applicatons in California. In Journal of Environmental Quality, vol. 6, 2001, pp. 1887–1895.

FUSKA, J. et al. 2013. Assessment of the actual water basin capacity with the use of GIS = Ocena rzeczywistej pojemność zbiornika wodnego z wykorzystaniem GIS. In Acta scientiarum Polonorum, vol. 12, 2013, no. 3, pp. 3–10. ISSN 1644-0765.

GREŠOVÁ, L. et al. 2012. Methods of soil roughness estimation for wind erosion equation. In Acta horticulturae et regiotecturae, vol. 15, 2012, special number, pp. 15–19. ISSN 1335-2563.

HALÁSZOVÁ, K. – KLIMENT, M. 2005. Legislative access to botton deposits applications of small water reservoir in Kolinany. In Acta horticulturae et regiotecturae, vol. 8, 2005, pp. 194–197. ISSN 1335-2563.

HÚSKA, D. – JURÍK, Ľ. – TÁTOŠOVÁ, L. 2005. Forest as important part of healthy landscape. V rámci časopisu zborník „International Scientific Symposium: Anti-erosive and water-protective role of the forest and methods its preservation and improvement. In Šumarski list, vol. 13, 2005, pp. 5244–5245. ISSN 0373-1332.

LAZOR, P. et al. Load on selected agroecosystems by nitrogene and sulphur in the region Krompachy. In Acta horticulturae et regiotecturae, vol. 8, 2005, pp. 240–244. ISSN 1335-2563.

OCHODNICKÝ, M. 2012. AMS na meranie kvality ovzdušia [e-mail]. Message for: Róbert Lenárt. 2012-04-18 [quoted: 2012-11-02].

SCHNELLE, K. B. 2002. Air Pollution Control Technology Handbook. CSC Press LLC, Florida. 389 p. ISBN 0-8493-9588-7.

TORSETH, K. et al. 2012. Introduction to the European Monitoring and Evaluation Programme (EMEP) and observed atmospheric composition change during 1972–2009. In Atmospheric Chemistry and Physics, vol.12, 2012, pp. 5447–5481.