Monitoring Ambient Air Quality in the Carpathian Region of Ukraine

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Abstract: Ivano-Frankivsk oblast is located in the south-western part of Ukraine, close to the geographical center of Europe at the junction of the two major geographic units, the East European Plain and the Eastern Carpathians (the Carpathian region of Ukraine). Between September 2013 and September 2015, the expert group of the Department of Organic and Analytical Chemistry of Vasyl Stefanyk Precarpathian National University conducted the mobile monitoring of air cleanliness in Ivano-Frankivsk region; the authors monitored the level of air contamination with seven gases: carbon monoxide and dioxide, sulfur dioxide, nitrogen dioxide, hydrogen sulfide, ammonia, formaldehyde, beta-particles, and gamma radiation. For this purpose, there were used six automatic analyzers "Dozor-C-P", the formaldehyde Gas Analyzer "MIC-98170", and the radiometer "TERRA". The monitoring resulted in the making of three maps of Ivano-Frankivsk region, on which the average levels of concentration of three particular gases (CO₂, SO₂, and CH₂O) throughout all the districts of the oblast were marked. There was registered the excess of CH₂O limits—the consequences of the presence of the chipboard and wood-fiber production, for which formaldehyde is used as a raw material. Also there was observed the excess of SO₂ in the air caused by gas fumes from vehicles and thermal power stations.

Key words: Monitoring, precarpathian, air quality, concentration, radiation, air pollution, MC (maximum concentration).

1. Introduction

The project on testing ambient air quality in the transboundary region of Ukraine-Romania (Clean Air Management in the Romania-Ukraine Transboundary Area (CLAMROUA), HUSKROUA/1101/127, was approved by the Joint Monitoring Committee of the Joint Operational Programme Hungary-Slovakia-Romania-Ukraine European Neighborhood and Partnership Instrument Cross-border Cooperation Programme 2013-2015 [1].

Ivano-Frankivsk (Precarpathian) region is situated between 47°30' south latitude and 23°31' east longitude. Its area is 13.9 thousand κm^2 . The population is 1,381 thousand people. Ivano-Frankivsk oblast is also located close the geographical center of Europe, in the south-western part of Ukraine, at the junction of two major natural geographic units-the East European Plain and the Eastern Carpathians, in the Carpathian region of Ukraine [2].

From September 2013 to September 2015, the expert group of Department of Organic and Analytical Chemistry from Vasyl Stefanyk Precarpathian National University tested ambient air quality in Ivano-Frankivsk region in terms of 7 gases: carbon monoxide and dioxide, sulfur dioxide, nitrogen dioxide, hydrogen sulfide, ammonia, formaldehyde and beta-particles, and gamma radiation contamination.

2. Methodology

For this study, the authors used six automatic analyzers "Dozor-C-P" individually for each of the aforementioned gases (produced and certified by the company NPP "Orion" in Kharkiv, Ukraine), automatic



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analyzers of the formaldehyde "MIC-98170" (produced and certified by the company "MIC METER INDUSTRIAL COMPANY" Taiwan), and radiometer MKS-05 "TERRA" (produced and certified by the company "Ecotest" Ukraine). The automatic analyzers "Dozor-C-P" apply an electrochemical or infrared rapid method for automatic quantification of each of these seven gases individually in a natural atmosphere [3]. The application of the radiometer MKS-05 "TERRA" detector of γ -radiation and β -particles is based on Geiger-Muller SBM-20-1. It converts radiation into the sequence of voltage pulses, which number per unit time in proportion to the intensity of radiation detected [4].

3. Results and Discussion

The authors investigated the air quality along more than 16 road routes in the Ivano-Frankivsk region, with the total length of about 2,000 km, in more than 200 towns, villages, and cities in the region. Overall, the authors did not find significant violations of norms in terms of exceeding MC (maximum concentration) for seven toxic gases (CO, CO₂, SO₂, NO₂, H₂S, NH₃, and CH₂O) in the ambient air in most towns (Fig. 1). However, the authors did detect significant excess of the MC formaldehyde (0.035 mg/m³ in Fig. 2) in the village of Broshniv, Rozhniativ district, Ukraine. Formaldehyde belongs to a group of chemical carcinogens with a general toxic effect of 0.012 mg/m^3 and allergenic effect of 0.011 mg/m^3 [5]. Low concentrations of formaldehyde (10 ppm) lead to an increase in malignant proliferation of melanoma cells, while not affecting normal keratinocytes [6]. MC of formaldehyde is 0.05 mg/L in the water and 0.05 mg/m³ in the air of the working area (Kurta Sergei et al. 2015). The average air MC in the towns and villages are 0.003 mg/m³ [7, 8]. It is crucial to detect the pollution of ambient air by formaldehyde as shown in such studies as "Measurements of formaldehvde at the US-Mexico border during the Cal-Mex 2010 air quality study" [9] and "Impact of formaldehyde and VOCs from waste treatment plants upon the ambient air nearby an urban area (Spain)" [10]. Nevertheless, there are no data on formaldehyde in the Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe [11].

Overall, there are no concerns about air pollution and radiation in Ivano-Frankivsk region. However, it still could be improved if the authors take a number of researches. The ambient air pollution by 7 gasses when compared to MC in Ivano-Frankivsk region can be seen in Fig. 1 [12]. It is obvious that SO_2 concentration in the ambient air is close to MC.



Fig. 1 Average gas content (mg/m³) in the air, Ivano-Frankivsk region (Monitoring results between September 2013 to September 2015). Number 1-experimental data, number 2-maximum concentrations (MC) allowed in Ukraine [7].



Fig. 2 Ivano-Frankivsk region map with the indicated concentrations of formaldehyde content (mg/m³) in ambient air (Results of monitoring from September 2013 to September 2015). MC (maximum concentrations) of formaldehyde in ambient air of towns and villages is 0.03 mg/m³.



Fig. 3 Ivano-Frankivsk region map with the indicated concentrations of sulphur dioxide content (mg/m³) in the air (Results of monitoring from September 2013 to September 2015). MC of sulfur dioxide in the air of towns and villages is 0.5 mg/m³.

The authors drew two maps (Figs. 2 and 3) to show the average concentration of two gases (SO₂, and CH₂O) in the ambient air in all Ivano-Frankivsk region districts. The higher intensity of color indicates the increase in the concentration of a gas in various districts of Ivano-Frankivsk region. Notably, the authors did not find any violations or results that would signify any problems with the concentration of CO, CO₂, NH₃ and NO₂ in the ambient air of Ivano-Frankivsk oblast; therefore, the authors did not draw any maps for these gasses.

In 2013-2015, the main air pollutants in Ivano-Frankivsk region were chemical plants and enterprises producing and distributing electricity, gas and water, and railroad transportation. Recently, there has been a tendency to reduce emissions of pollutants

into the atmosphere in the Carpathian region of Ukraine. Specifically, the main polluters of the air are:

(1) Burshtyn TES coal-fired power station, Burshtyn', Galytskyj district (max. SO₂ emissions);

(2) "SWISS KRONO" company, Broshniv-Osada, Rozhniativskyj district (CH₂O emissions);

(3) LLC Karpatnaftochim, which belongs to Lukoil company (Russia) and 7 private chemical companies, Kalush district (CO, CO₂, NO₂, H₂S, NH₃, and chlorinated hydrocarbons emissions);

(4) JSC "Neftekhimik Carpathians" and LLC "LC Interplyt Nadvirna", Nadvirna (CO, CO₂, and CH₂O emissions);

(5) Main pipeline division "Prykarpattransgas" and utility enterprise "Ivano-Frankivsk-vodoekotehprom", Ivano-Frankivsk (CO and CO₂ emissions);



Fig. 4 Histogram of the average background radiation in Ivano-Frankivsk region (Results of monitoring from September 2013 to September 2015). 1: rates of γ -radiation, μ Sv/h, 2: β -particles, $10^3/(\text{cm}^2 \cdot \text{min})$. MC dose of background radiation for rates of γ -radiation = 0.5 μ Sv/h, and for β -particles = 0.005 × $10^3/(\text{cm}^2 \cdot \text{min})$.

(6) JSC "Ivano-Frankivskcement" and JSC firm "Barva", Yamnytsia, Tysmenytsia district (CO, CO₂, and chlorinated hydrocarbons emissions);

(7) Cars, trucks, and special road transport (more than 2.6 million) (CO, CO₂, SO₂, NO₂ emissions).

Of crucial importance is the presence of high concentrations of sulfur dioxide (SO₂) in the atmosphere (Fig. 3) reaches MC in some districts. This can be explained by the scattering of harmful emissions through the tall pipe of Burshtyn TES throughout the Ivano-Frankivsk region, and under certain weather conditions over the entire Carpathians. This can cause the presence of sulfur dioxide, even in the most environmentally friendly mountainous Verkhovyna, Kosiv, and Rozhniativ districts. It is also reinforced by burning low quality automotive fuel, gasoline and diesel in cars, the number of which has increased to 2.6 million [13].

Formaldehyde, which can also be classified as one of the dangerous emissions, is concentrated and reaches MC in the areas of production of chipboard and wood-fiber (SWISS KRONO company in Broshniv-Osada (0.035 mg/m³), Rozhniativ district, LK Interplit in Nadvirna, TOV SORBES in Nadvirna, Uniplyt LLC in Vygoda, Dolina district) (Fig. 2). This phenomenon can be explained by the fact that these companies use 45 thousand tons of urea-formaldehyde and melamine-formaldehyde resin which contain toxic formaldehyde for the production of 450 thousand m³ of the chipboard and wood-fiber plates.

The results of background radiation analysis, such as rate of x-radiation and β - particles, showed that the level of background radiation is much lower than MC value in Ukraine (Fig. 4) [14, 15].

4. Conclusions

(1) The results show that the concentration of pollutants (carbon monoxide and nitrogen dioxide) in the ambient air in Ivano-Frankivsk region is less than MC accordingly to Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe [11]. The content of SO₂ compared to MC (Directive

2008/50/EC) is four times higher (0.4957 mg/m³; MC is 0.125 mg/m³).

(2) It is necessary to optimize environmental management, biodiversity. reforestation and afforestation conservation, land structure optimization, reduction of anthropogenic impact (emissions and discharges of hazardous substances into the environment) by the greening of all industries to improve the environmental situation of Ivano-Frankivsk region.

(3) There is a need to replace and install new electrostatic and other systems on Blocks №1-8 of Burshtyn TES and inculcate desulphurization technology to capture and deactivate sulfur dioxide, nitrogen oxides, and carbon oxides. It is necessary to optimize combustion regime in boilers by sealing the combustion chambers and to install the gas-cleaning unit after waste utilization rotary kiln Burshtyn TES.

(4) Reducing greenhouse gas emissions is possible by the construction of the line processing sewage sludge on Utility Enterprise "Ivano-Frankivsk-vodoekotehprom" and on 3 pig farms Ltd. "Danosha" due to the synthesis and use of biogas for heat and electricity.

(5) Can reduce formaldehyde emissions for manufactures chipboard and wood-fiber plates enterprises "SWISS KRONO" town Broshniv-Osada Rozhniativ District, LK Interplit Nadvirna TOV SORBES town Nadvirna, Uniplyt LLC v.Vygoda Dolina District Ivano-Frankivsk (Precarpathian) region of Ukraine by installation of water absorption devices by clearing and capture gaseous formaldehyde and its recycling and processing.

(6) Must install an additional quality control of motor fuels (petrol and diesel) to sulfur content, octane and cetane number, by an independent not state examination and analysis of all types of fuel.

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References

[1] Michnea, A. M., and Kurta, S. 2013. Clean Air Management in the Romania-Ukraine Transboundary Area (CLAMROUA), registration number: 1101/127 "the Action" approved by the Joint Monitoring Committee (hereinafter referred to as JMC) of the Joint Operational Programme Hungary-Slovakia-Romania-Ukraine European Neighbourhood and Partnership Instrument Cross-border Cooperation Programme, 98 p. https:// www.researchgate.

net/publication/295875551_Part_II_Ukraine_Ua.

- [2] Kurta, S. A., Voronych, O. L., Matkivskyi, M. P., and Dzhura, U. Ya. 2015. Monitoring at the Ukraine-Romania Cross-Border Region in Teaching Methods of Environmental Sciences. Physics and Technology of Thin Films and Nanosystems. Materials XV INTERNATIONAL CONFERENCE//Pod Society. Ed. Honored Scientist of Ukraine, d.h.n Prof. D. Freik-Ivano-Frankivsk-400p.
- [3] Manual Alarm Gas Analyzer "Dozor-C-P." Developed LLC NPP "Orion"/Vykon.S.Yu. Sokolov. M. Kharkiv Ukraine—with 13.
- [4] Operating Manual ER VIST.412129.006-06 Dosimeter-Radiometer MKS-05 "TERRA".
- [5] Kurta, S. 2014. Environmental Protection Issues in the Ivano-Frankivsk Region, Ukraine//The Conference of the project: "Clean Air Management in the Romania-Ukraine Transboundary Area (CLAMROUA)" –HUSKROUA 1101/127. 19-20/11. Hotel Rivulus in Baia Mare. http://firtka.if.ua/?action=show&id=63539.
- [6] Rizzi, M., Cravello, B., Tonello, S., and Renò, F. 2016. "Formaldehyde Solutions in Simulated Sweat Increase Human Melanoma but Not Normal Human Keratinocyte Cells Proliferation." *Toxicology in Vitro* 37: 106-12.
- [7] State Sanitary Rules of Air Protection of Settlements (from Contamination by Chemical and Biological Agents). 2007. Ministry of Health of Ukraine. The Text of the Legal Act as at Mar. 27, N 201 of 09.07.97. s. Kiev.
- [8] Agency for Toxic Substances and Disease Registry (ATSDR). 1999. Toxicological Profile for Formaldehyde (Draft). Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA. https://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=220&tid

=39.

- [9] Zheng, J., Zhang, R., Garzón, J. P., María, E., Huertas, L. M., Ma, Y., Torres-Jardón, R., Ruiz-Suárez, L. G., Russell, L., Takahama, S., Tan, H., Li, G., and Molina, L. T. 2013. "Measurements of Formaldehyde at the U.S.-Mexico Border during the Cal-Mex 2010 Air Quality Study." *Atmospheric Environment* 70: 513-20.
- [10] Gallego, E., Roca, F. J., Perales, J. F., Guardino, X., Gadea, E., and Garrote, P. 2016. "Impact of Formaldehyde and VOCs from Waste Treatment Plants upon the Ambient Air nearby an Urban Area (Spain)." *Science of the Total Environment* 568: 369-80.
- [11] Gemmer, M., and Xiao, B. 2013. "Air Quality Legislation and Standards in the European Union: Background, Status and Public Participation." *Advances in Climate Change Research* 4 (1): 50-9.
- [12] Kurta, S., Voronych, A., and Fedorchenko, S. 2015. "Environmental Technologies Deactivation, Utilization and Recycling of Solid and Liquid Waste Production Wallpapers//VI Międzynarodowe Sympozjum Naukowe dla Doktorantów, Studentów i Młodych Naukowców Uczelni Rolniczych pt. Inno-wacyjne Badania w rolnictwie i na rzecz rozwoju obszarów wiejskich." Bydgoszcz Ciechocinek Polska (17-19): 81-2.
- [13] Kurta, S. 2015. Environmental Protection Issues in the Ivano-Frankivsk Region, Ukraine//The Conference of the project: "Clean Air Management in the Romania-Ukraine

Transboundary Area (CLAMROUA)." HUSKROUA 1101/127. 03-05/06. Hotel Rivulus in Baia Mare. http://www.pu.if.ua/uk/konkursy-i-hranty/2064-mizhnaro dnyi-proekt-menedzhment-chystoho-povitria-u-rumunsko -ukrainskomu-transkordonnomu-rehioni-clamroua.

[14] Kurta, S. 2014. Environmental Protection Issues in the County of Ivano-Frankivsk, Ukraine//The Conference of the Project: "Clean Air Management in the Romania-Ukraine Transboundary Area (CLAMROUA)" HUSKROUA 1101/127.10-11 April. Ivano-Frankivsk. Ukraine.

http://www.pu.if.ua/uk/novyny/875-prezentatsiia-mizhnar odnoho-proektu-kontrol-za-chystotoiu-povitria-u-transkor donnomu-rehioni-ukraina-rumuniia.

[15] Kurta, S. 2015. Results of Air Quality in the Ukraine-Romania transboundary area, Ivano-Frankivsk region, Ukraine in 2014-2015//The Conference of the project: Clean Air Management in the Romania-Ukraine Transboundary Area (CLAMROUA) HUSKROUA 1101/127. 16-17/06. Ivano-Frankivsk. http://www.pu.if.ua/uk/novyny/3363-vidbulosia-zakliuch ne-zasidannia-mizhnarodnoi-ukrainsko-rumunskoi-konfer entsii-clamroua-kontrol-za-chystotoiu-povitria-v-transkor donnomu-rehioni-ukraina-rumuniia.