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ENVIRONMENT AND POLLUTION MANAGEMENT OF POLLUTION VOLATILE ORGANIC COMPOUNDS IN CLUJ-NAPOCA

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Key words: pollution, degradation, volatile organic compounds, auto traffic.

Abstract. Pollution negative influences the environmental, human health, buildings and increase the production of waste. We are currently witnessing pollution and degradation in some cases irreversible, of the environment. Environmental issues are extremely complex and cover all sectors. Worldwide, industrial pollution strategies necessary to reduce emissions to the atmosphere hydrocarbons, volatile organic compounds (VOCs) and other polluants in urban areas. The highest concentrations of volatile organic compounds of more than 80 mg/m^3 occur in densely populated areas. The latest data reported in the residential area of Cluj-Napoca values did not exceed 20 m /m^3. However peaks reported VOC concentrations, depending on the season, exceeding the upper limit that according to Law. 104/2011 is 75 μ/m^3. It was identified due to increase annual mean concentration of VOCs as, in particular, road traffic exceeding sanitary standards on the main traffic routes within the city. In this paper the results obtained after carrying out an analysis of the average VOC concentration recorded in the city Cluj-Napoca as a result of car traffic. They were pursued average concentrations of VOCs resulting from the combustion of liquid fuels, petrol and diesel type. Analyzing the results obtained are proposed solutions for reducing VOC emissions. The rule under which these solutions have been proposed to reduce the concentration of VOCs took into account the possibility implementation and maintenance costs thereof.

Introduction

At global level there are numerous reports on the disastrous effects of increasing urban pollution (by Miranda et al. 2012, Diaconu et al. 1997). This pollution, mainly the accumulation of solids in air, s one of the causes increased morbidity and mortality due to cardiovascular and respiratory diseases. Urban pollution is generally caused by fine particulate solide, fine powders of heavy

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metals, noxious gases, VOCs (by Manescu and Manole 1994, Leung 2015, Breen et al. 2015).

Cluj-Napoca enviromental characterization: Relief Cluj-Napoca, which is located in the city assembly, summarizing particularities of the three major physical-geographical units, within which lies the Apuseni Mountains, of Someş

Climate data for Cluj-Napoca

Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
Record high °C (°F)	14.0 (57.2)	19.3 (66.7)	26.6 (79.9)	30.2 (86.4)	32.8 (91)	34.8 (94.6)	37.0 (98.6)	38.0 (100.4)	33.7 (92.7)	32.5 (90.5)	26.8 (80.8)	18.7 (65.7)	38.0 (100.4)
Average high °C (°F)	0.3 (32.5)	3.2 (37.8)	9.5 (49.1)	15.9 (60)	20.7 (69.3)	23.6 (74.5)	24.5 (76.1)	24.3 (75.7)	20.7 (69.3)	14.6 (58.3)	6.3 (43.3)	1.8 (35.2)	13.6 (56.5)
Daily mean °C (°F)	−3.4 (25.9)	−1.2 (29.8)	4.1 (39.4)	9.8 (49.6)	14.2 (57.6)	16.6 (61.9)	18.2 (64.8)	17.8 (64)	14.1 (57.4)	8.5 (47.3)	2.4 (36.3)	−1.5 (29.3)	8.2 (46.8)
Average low °C (°F)	−6.5 (20.3)	−4.7 (23.5)	−0.6 (30.9)	3.9 (39)	8.6 (47.5)	11.3 (52.3)	12.7 (54.9)	12.2 (54)	8.9 (48)	3.8 (38.8)	−0.7 (30.7)	−4.2 (24.4)	3.7 (38.7)
Record low °C (°F)	−34.2 (−29.6)	−32.5 (−26.5)	−22.8 (−9.0)	−8.4 (16.9)	−3.5 (25.7)	0.4 (32.7)	5.2 (41.4)	3.5 (38.3)	−3.8 (25.2)	−8.8 (16.2)	−20.3 (−4.5)	−37.8 (−36.0)	−34.2 (−29.6)
Average precipitation mm (inches)	24 (0.94)	20 (0.79)	22 (0.87)	48 (1.89)	69 (2.72)	95 (3.74)	81 (3.19)	60 (2.36)	36 (1.42)	31 (1.22)	30 (1.18)	32 (1.26)	548 (21.57)
Average snowfall cm (inches)	6.8 (2.68)	11.5 (4.53)	5.8 (2.28)	1.3 (0.51)	0.0 (0)	0.0 (0)	0.0 (0)	0.0 (0)	0.0 (0)	0.5 (0.2)	2.6 (1.02)	5.8 (2.28)	33.5 (13.19)
Average precipitation days (≥ 1.0 mm)	6	5	5	9	11	11	10	8	6	6	7	7	91
Mean monthly sunshine hours	70.5	98.8	165.2	174.7	230.8	238.6	273.8	261.6	204.0	148.2	73.5	54.2	2,065
Source #1: NOAA[30]													
Source #2: Romanian National Statistic Institute (a-themes 1961–2000)[31]													

Fig. 1. The geographical position, topography and climate information from ClujNapoca (https://en.wikipedia.org/wiki/Cluj-Napoca)

Plateau and Transylvania Depression. The complexity of lithological substrate, as various manifestations of external agents, determined the formation of a very different relief. The town's great variety are due to geological structure formed of

clay, marl, limestone and sand, prezerved in the area Cetatuia (by Mac and Floca 1997, Zamfir 1979). Recent sedimentary formations can be notice if we take a closer look to the existing pastures and terraces alog Somes Mic river.

The town's city name comes from the Latin word "Clusium", meaning enclosed place". The city's geographical position, in a valley surrounded by hills, is a major factor in the occurrence of fog. Between pilots landing at airport Someşeni, Cluj is being as "the town with one hundred sunny days".

The urban area, influenced by physical-geographical, social, historical and economical factors, has been in a continuously developed in the terms of size, structure and position. Nowadays Cluj-Napoca covers a surface of 170 km^2 from East to North-East. Cluj-Napoca's quite various, causing a series of microclimate differences; they are influenced by alttitude Fig. 1, landforms structure and orientation, by geological stucture, the mountains' angle of inclination and exposion to solar radiation and also by the movement of air currents steam of air. (by Mac and Floca 1997, Zamfir 1979).

Groundwather from river meadows and inferior terraces are like continuous flows. They are made by the wather comes from the nearby rivers, by the infiltration which come from the mountain in the driets periods.It is well known that water show up a certain kind of natural agressivity against the concrete with sulfat ions, the infiltration from the mea lakes, like that from Someseni (aprox. 6000 mg/l) have the most distructive impact. Near the industrial sites the groundwather agressivity in even greater due to the presence of some acid substances, industrial waste, polluated rain falls and leanage at different tehnological installations.

1. The current situation

1.1. Air pollution represents one of the main factor which negatively influences people's healthy and life's quality (Fig. 2). The disconfort caused by dust smells, poor visibility, the acid rainfalls, dust and corrosive gases are only some of the major problems faced by the people who live in Cluj-Napoca. Pollution spreads especially through the air, affecting directly and indirectly, not only human but also all the other elements of the natural or artificial environment. (by Breen et al. 2015, Charlesworth and Lees 1999).

Due to the presence of lead in gasoline, the areas with heavy traffic have a certain amount of lead in the air. Most of the gas pollutans have acid composition, wich affects not only the air quality but also all the other components of the natural or articial environment. Because of the water from the air, some of the primary polluants may be cause the apperence of very agressive secondary polluants like photochemical oxidants, sulfuric acid nitric. (by Breen et al. 2015, Ponticiello et al. 2015).

Urban polluants agressivity from Cluj-Napoca has native effects not only upon people's states of healty (raise of mortality and morbidity rate), but also upon the industrial and civil buildings. So the solid and liquid aerosol combined with the acid gases highly oxidant cause a raise of corrosion and degradation of degree of concrete, wood, glass, rubber and paint.

Figure 2. Pollution in Cluj-Napoca

In comparison, traffic in Bucharest is about 70% and is the main source of pollution. In this regard they are tracked different categories of pollutants like NO_x, SO_2, CO, NO, powders (total suspended particles with aerodynamic diameter less than 10 micrometres and 2.5 micrometres black smoke) components of the powder (elemental carbon, PAHs, lead), volatile organic compounds (benzene, butadiene). Complete combustion of the fuel in the engines of motor vehicles into the atmosphere removes water vapor (13%), carbon dioxide (13%), nitrogen (74%) (Ardelean 2010).

1.2. Water pollution sources and causes Cluj-Napoca surface natural water contain amont of gasses dissolved from the atmosphere mineral salts, coloidal substances and different organic impuritiers. Heavy rains cause a severe contamination of the rivers, because of a destroing combination of some factors sewage and industrial water leakage, drainage. The negative effects refer to high polluant level such as: heavy metals, bacteria, hydrocarbons, mineral oils, detergents, pesticide and terrains' degradation meaning the loss of their aesthetic value.

Polution sources (Mac and Floca 1997, Zamfir 1979) can be various and can be located at the surface, underground or beyond the level of underground water. The toxic effects of the chemical substances upon people's healt are not entirely known; the lead has the highest negative impact upon the environment.

- ***Pb*** is a toxic substance without any physiological function. People are expose to the lead's negative effects especially by inhalating the resulted gases from the combustible burning $Pb(C_2H_5)_4$. Human body inhalates a quantity wich range between 100-400 μg Pb/day. The main anthropogenic source is reprezented by the biomass burning used at fuel manufacturing. Volatile organic compunds represent the primary polluants caused by stationary and mobile sources.
- The term *"**volatile organic compounds**"* (COV) is generally used for any organic compound wich has a steam pressure smaller than 0.1 mm in standard conditions (of 20 ^{0}C). COV's pollution effects are: toxicity and unpleasant smell, photochemical oxidant presented in the troposphere, destruction of the ozone layer and the greenhouse effect.
- ***The oil products*** are complex substances which may include many kinds of oraganic compounds made of C, H, N, O, S and some metals like vanadium and nichel. Because of their toxic characteristics, the oil products inhibit the microbial activity.
- ***Special conditions wich cause polluants dispersions***. Used sewage represents 0,8% of the total internal and town's sewage water. The average flow is of 38,71% mc/day and the maximum one of 2,584 mc/day. The estimate quantity and concentration of polluants release in the environment, can be estibilished by calculatind the sewage pollutind indicators. (Table 1).

In Cluj-Napoca city, according to the regulations, the evacuated wastewater doesn't exceed the levels stipulated in the NTPA-002.

a) Suspensions may be found in concentrations of up to 224.13 mg/l and density of 520 g /day.

b)The organic watters represented by CBO_5 in a concentration of 186,2 mg/l and a density of 432 g/day.

c) The oil products that result from the accidental loss at the improper manipulation, maximum 100g/mc fuel.

Gas stations function according to NP-004-05 Normative, and because the underground water is at -2,5 m dept, with the possibility of raising the level up to 1,5 m, it is absolutely necesary to store the fuel in special warehouses endowed wish ventilation systems, level indicators devices, fittings, lightiningcapture devices, vapour capture systems.

In case of fuel sorage from Cluj-Napoca, the main pollution source are the wastewaters from the social-administrative groups and the rainwater from the industrial station. So there is a leakage of oil products directly in the drainage system or in the main collecting storehouse. In Cluj-Napoca the gas stations, storehouse and auto-services do not have the obligativity of being equipped wish installations that separate the oil products. The polluants concentrations and wastewater massflow collected from the platform, are represented by the resulted

petroleum substances after the volatile substances evaporate when the cars are fueled at gas stations. The maximum fuel loss represents 1,4 kg for each distributed m^3.the concentration of petroleum eter from the platform waters collected is 3,468 m^3/day, and the substances mass of debit of 104,98g /zi, concentration of polluants in the effluents from of wastewater treatment platforms are shown Table 2.

Table 1. The sewage quality indicators evacuated in the town's drainage or wastewater treatment station (NTPA-002: 2002).

Quality Indicator	**U.M.**	**Normal values**
Temperature	^0C	40
pH	unit pH	6,5-8,5
Material in suspension (MS)	mg/dm^3	350
Oxigene biochemical consume at every 5 days (CBO_5)	mg O_2/dm^3	300
Oxigene chemical consume -Potassium dichromate method (CCO(Cr))	mg O_2/dm^3	500
Ammonia nitrogen (NH_4^+)	mg/dm^3	30
Total phosphorus (P)	mg/dm^3	5,0
Biodegradabil sintetic detergents	mg/dm^3	25,0
Rezidual clor (Cl_2)	mg/dm^3	0,5

In the fuel depots in Cluj-Napoca are the main sources of pollution of wastewater from the social group-administration officer and the storm water parks fuel tanks and concrete platforms. Thus there is oil leaking directly into the main collector sewer or very rarely accidental. In Cluj-Napoca there is not yet imposed a requirement that all stations, warehouses, car service and car wash sites must carry oil separators. Pollutant concentrations and mass flows of wastewater collected from the oil platform, are the substances resulting from the evaporation of volatile substances from loss of fuel during refueling of motor vehicles. Maximum loss of fuel supply is about 1.4 kg per m3 distributed. The concentration of substances extractable with petroleum in waters collected from the platform is 3468 m_3/day, and the mass flow of substances is 104,98g/day, the concentration of pollutants in the effluents from sewage treatment plants platforms are presented in Table. 2.

Table 2. Polluant concentration in waters discharged

Indicator	**Concentration at evacuation**	
	Calculated mg/l	**Admitted mg/l**
Suspensions	190,87	350
CBO_5	158,0	300
Extratible	1,51	20

1.3. Air pollution: Causes and sources: The surces of air pollution, in the case of gas stations, are: the way in wich the fuel is stored, poor handling at the tanks' filling and the powered cars at gas stations. The polluants characteristic to these sources are volatile organic compounds, respectively hydrocarbons (heptan) (By Manescu and Manole 1994).

The emision factors used by MAPPM with which you can calculate the mass flow of VOCs discharged into the atmosphere due to evaporation losses are:

- filling of the gas station tanks 0,88 kg/m^3;
- fuel storage 0,12 kg/m^3/day;
- gas pump loss 1,40 kg/m^3.

Not only COV gets into the atmosfere, but also a certain amount of lead (it is contained by anyfuel). Considering that Premium gasoline has a COV concentration of 3%, and that 60 % of it is lead, the result is 0.0315 g/h, at storage is 0.1296 g/h and 0.036g/h at tanks filling.

The storage tehnological flow of the pertoleum products takes place in the open air; this are represntes the working place for many people. The environmental factor is influenced by emissions of volatile oarganic compounds found in the gasoline and lead tetraetil. Reagarding the gasoline concentration level found in air, it has been notice a 83.3% concentation below the normal limit, from which 57.5% (<100 mg/m^3) and 33,5% (>100mg/m^3). Only 16,7% from the total number of samples exceed the normal limits. The level of gasoline found at the working palces has the concentration value of 100 mg/m^3, so below the normal limit; the measurements were made at below zero temperature.

The relative humidity is between 95% and 60% and it is closely limited by the presence of clouds. The estabilished concentrations of hydrocarbons display an average value of 100mg/m^3 in total accordance wish the sanitary rules and the Ministry of Enviroment norms, below 150 mg/ m^3.

The heavy rood traffic, so specific to the great cities like Cluj-Napoca, represents autohel major source of air pollution. It is responsabile for some secondary polluants, modifications of the ozone layer and weather conditions, poor visibility, presence and persistence of fog. Car pollution represents 64% of the total of carbon monoxide emissions, wich come from the internal combustion engines which use gasoline instead of disel (gasoline does not produce so much carbon monoxide).

Considering the number of cars powered by diesel or gasoline, the mileage, the cars' fuel consumation, thea amount of polluants from the air can be easily calculated. This is shown in the following Figure 2.

Residential space heating Romania currently use boilers that run on methane gas. By burning methane gas from thermal power plants are resulting flue gases containing CO, NOx, SOx and particulates. Based on use of gas, emission factors,

data resulting from the calculation burning mass flow of polluants and polluant emission concentrations. Their variation is a function of flame temperature, gas concentration, and residence time S.A. (Vasilache M, 2008).

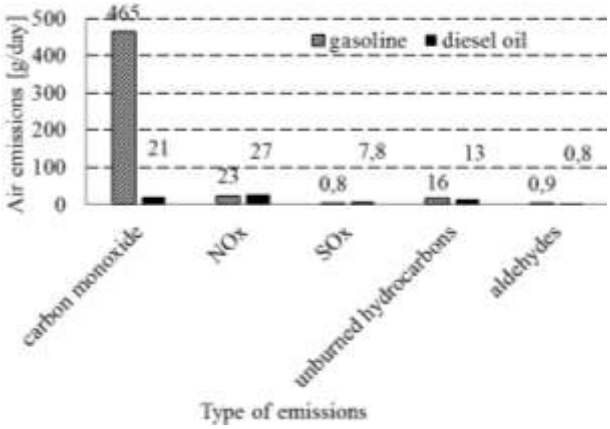

Figure 2. Atmospheric emissions, depending on the type of fuel

2. Reducing pollution at the source

Pollution source at gas stations cannot be controlled. There is a vapours collect as much as possibile of the quantity of vapours resulted from the fuel evaporation. Almost 50% are condensed and transformed in fuel again; they get in tanks, reducing the loss especially in worm season. Unfortunatelly not all the gas stations from Cluj-Napoca have such an equipment, COV pollution still remaining a major problem for the city.

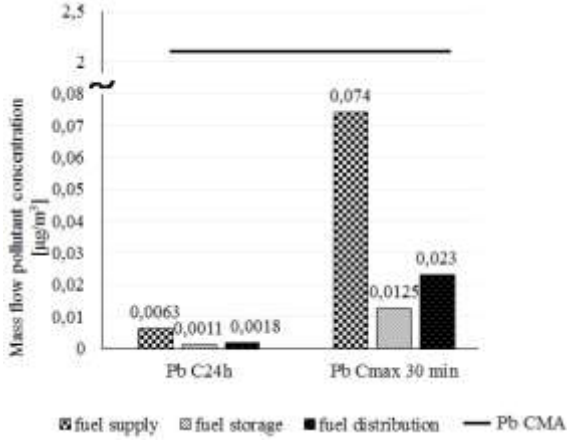

Figure 3. The value of mass flow rates polluant concentrations

In the case of fuel depots, the volatile organic compunds are evacuated in the atmosfere through ventilation valves. They are used especially where the tanks are filled or drained, the so called "big breaths" and when there is daily of variations temperature the so called "small breaths". The evaluation of the pollution source can be made considering the impact the atmosphere (emissions of polluants).

The mass flow values of the polluant concentration, such lead, compared to the normal owes, are show in the Fig. 3.

The mass flow values of polluant concentrations such as COV, compared to the normalowes, are shown in the Fig. 4.

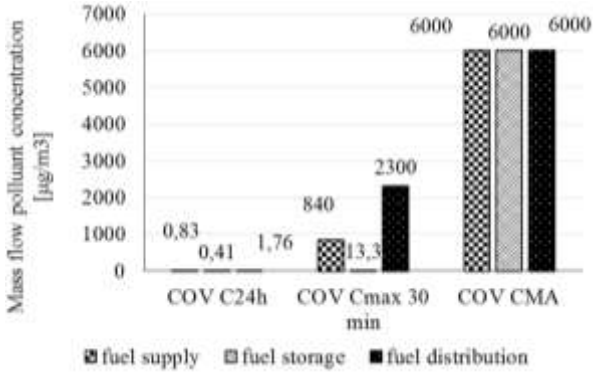

Figure 4. The value of mass flow rates of polluants like VOCs concentrations

Conclusions

A good knowledge of the pollution sources, of the mass flow, eradication of the uncontrolled or accidental emisions, the proper use of production facilities, implementation of air quality monitoring system, are fundamental aspects of the strtegies of enviroment protection.

The tehnical measures referto the use of high quality fuel, meaning without lead, sulfur or benzene, standard carbon emission and COV. COV reduction may be also reached by planting trees along the main roads and streets, by using a tipe of asphalt that reduces noise, by building bridges and tunnels meant to avoid high traffic areas.

Internal combustion engines represent the main cause of air pollution. There are a lot of solutions controling the polluants such as: modification of the internal combustion engines, the producing of some less polluting substitutes, the finding of some less polluting power sources instead of the internal cobustion engine.

The solution means to find source tehnologies able to reduce SO_2 si NO_x emissions, this can be done by a direct and indirect reduction of sulphur quantity.

According to the present research, it can be sai that:

- Due to the geographical position, of close type in Cluj-napoca the average annual humidity is high and steam of air takes place heavly.
- Because of the improper traffic conditions both for pedestrians and vehicles realised through a series of projects regarding the development of pedestrian bicycle traffic. hese projects should take into account costs as low as possible throughout the expected life and the possibility of fast implementation and easy maintenance.
- Use and upgrading devices to reduce emissions and VOC vapor recovery from fuel depots and loading points.
- Install systems in high traffic areas that accumulate air pollution depollution and purified it.
- Promote an effective system for checking the the exhaust gases of vehicles

Implementation of education programs / development of the population, starting from the very early age and encourage the use of public transportation or means of transport cleaner.

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Hotărâre nr. 1856/2005 privind plafoanele naţionale de emisie pentru anumiţi poluanţi atmosferici

Hotărâre nr. 568/2001 privind stabilirea cerințelor tehnice pentru limitarea emisiilor de compuși organici volatili rezultați din depozitarea, încărcarea, descărcarea şi distribuţia benzinei la terminale şi la staţiile de benzină

NTPA-002 Normativ din 28 februarie 2002 privind conditiile de evacuare a apelor uzate in retelele de canalizare ale localitatilor si direct in statiile de epurare.

NP 004-05 Normativ pentru proiectarea, executarea, exploatarea, dezafectarea si postutilizarea statiilor de distributie carburanti la autovehicule.

Ordin de Ministru nr. 859/2005 privind aprobarea unor ghiduri necesare punerii in aplicare a H.G. nr. 699/2003 privind stabilirea unor măsuri pentru reducerea emisiilor de compuşi organici volatili datorate utilizării solvenţilor organici în anumite activităţi şi instalaţii

Ordin nr. 3299/2012 pentru aprobarea metodologiei de realizare şi raportare a inventarelor privind emisiile de poluanţi în atmosferă

STAS 11369/1-88. Road vehicules noxious emissions determination. Admissible limits and test methods for vehicles with wight up to 3500 kg

*** https://en.wikipedia.org/wiki/Cluj-Napoca