Comparing Carbonyls Levels in Indoor Air in two Offices - Green and Old Building

RALUCA DIODIU[1,2,*], TOMA GALAON[1]

[1]National Research and Development Institute for Industrial Ecology ECOIND, 71-73 Drumul Podu Dambovitei Street, 060652, Bucharest, Romania

[2]Babes-Bolyai University, Faculty of Environmental Science and Engineering, 30 Fantanele Str., 400294, Cluj Napoca, Romania

The concentrations of 17 carbonyl compounds were investigated in indoor air of two offices - one located in a green building and the other in an old building, both from Bucharest. Indoor air samples were collected during normal activities of the working staff on passive samplers. Two analytical techniques were used: Ion Chromatography for carboxylic acids and High Performance Liquid Chromatography for aldehydes and ketones. A questionnaire was administrated in order to collect information about buildings characteristics, indoor furniture, decorating materials and electronical devices used during the sampling. Formaldehyde, acroleine+acetone, acetaldehyde, hexaldehyde and carboxylic acids were the most abundant compounds that accounted for more than 50% of the total carbonyls. The majority of the aldehydes showed higher concentrations in the old building office compared to the concentrations found in the green building office. Regarding the carboxylic acids: the concentration of formic acid was slightly higher in the old building office versus the green building office; in the case of acetic acid, the concentration found in the old building office was around two times higher comparing to the green building office.

Keywords: carbonyls, indoor air, aldehydes, formaldehyde, formic acid, acetic acid

The quality of air, as our environment, is an important factor that can influence our day to day activities, our health and the quality of our lives overall.

A lot of studies were done on air quality worldwide. In Romania, studies regarding air pollution varied from a simple method validation to a more complex ones including air quality characterization based on dry atmospheric deposition [1], particulate matter chemical composition [2], and on urban noise levels [3, 4].

Many of these studies determined the presence of carbonyls in air samples with the tendency of accumulating in indoor air. The predominant carbonyls in indoor environments are aldehydes, mainly formaldehyde and acetaldehyde, accompanied by acetic and formic acids. These carbonyls were studied in homes [5], offices [6], churches [7], kindergartens and schools [8].

The interest in this type of air pollutants is due to their effects on human health and other mammals. Formaldehyde is classified in Group 1 as being human carcinogen by the International Agency for Research on Cancer [9] and probable human carcinogen by US EPA [10]. Acetaldehyde is classified in Group 2B being a possible carcinogenic in humans [11-13]. Regarding formic and acetic acids, studies showed that long term exposure can cause allergies [14, 15].

Main sources of carbonyls indoor are furniture and building materials emissions, like: particleboard, plywood and fiberboard furniture, sealing and flooring [16, 17].

The aim of this study was to determine and compare the concentration of 17 carbonyls compounds in indoor air of an office situated in a green building and an office situated in an old building from Bucharest, Romania. The carbonyls compounds included: acetaldehyde, acetic acid, acetone, acrolein, benzaldehyde, butyraldehyde, crotonaldehyde, 2,5-dimethylbenzaldehyde, formaldehyde, formic acid, hexaldehyde, isovaleraldehyde, propionaldehyde, *o*-tolualdehyde, *m*-tolualdehyde, *p*-tolualdehyde and valeraldehyde.

Experimental part

Sampling was done in a period of 10 days in two offices located within the city of Bucharest. One of the offices was located in an old building on a crowded city road (Regina Elisabeta Boulevard) at ground level with the windows facing an interior courtyard. The other office was located in an office building in Pipera and built with materials as an ecological building.

All the indoor air samples were collected during normal activities of the working staff on passive samplers in order to not disturb the work conditions. For sampling aldehydes DSD-DNPH cartridges from Sigma-Aldrich were bought and used as sampling devices. This type of cartridges contains DNPH (2,4-dinitrophenilhydrazine) which reacts with aldehydes from air forming hydrazones derivatives, whom are a more stable compounds then aldehydes, and can be retained in the sampling devices. After sampling, aldehydes were extracted into a volumetric flask with a known volume by acetonitrile and then analyzed by HPLC.

Formic and acetic acids were sampled using passive radial diffusive sampler from Radiello composed of: RAD166 adsorbing cartridges, RAD1201 blue diffusive body with attaching supporting plate. After sampling, acetic and formic acids were extracted in water using an automatic stirrer; each sampler was stirred 5 min, followed by 1 h pause and another 5 min of stirring.

For the quantification of aldehydes, a calibration standard TO11/IP-6A Aldehyde/Ketone-DNPH Mix certified reference material from Sigma-Aldrich with 15µg/mL concentrations of each hydrazone derivatives of the targeted aldehyde in acetonitrile. For the quantification of formic acid and acetic acid, as formate and acetate, standars of 1000µg/mL in water were purchased from LGC Standards.

Aldehydes were determined using a high performance liquid chromatograph model Agilent 1200, coupled with a UV detector. Analytical conditions included two Acclaim Carbonyl C18 columns (250 mm * 4.6 mm, 5µm,) coupled

* email: raluca_dio@yahoo.com

in series, a diode array detector (DAD) set at 365 nm wavelength, 2 mL/min flow rate, 25µL injection volume, 25°C column temperature and a gradient mobile phase of acetonitrile / water as seen in table 1 [18].

Table 1
GRADIENT USED IN THE HPLC ELUTION OF THE ALDEHYDES

Time (minutes)	*ACN (%)*	*Water (%)*
0.0	60	40
30.0	75	25
50.0	100	0
55.0	100	0
55.1	60	40
70.0	60	40

An ion chromatography system model Dionex ICS-5000+ Integrated Reagent Free, equipped with a conductivity detector and an Anion Self-Regenerating Suppressor (Dionex AERS 500 2mm) was used for formic and acetic acids quantifications. Separation was done on an IC Dionex IonPac AS 18 column with guard. The analytical conditions included an isocratic elution, with 10mM KOH eluent for 20 min, column temperature of 20°C and 5 µL injection volume [19].

Results and discussions

Carbonyls concentrations were quantified by external standard calibration. The calibration curves covered the range of interest and showed good linearity, all presenting r^2 >0.999.

The TO-11A EPA method with DNPH, used in this study for aldehydes is recommended for the determination of formaldehyde and can be used for other aldehydes but cannot complete separateacrolein from acetone as proven in literature [20]; in this study concentrations of acrolein and acetone will be referred as acrolein + acetone.

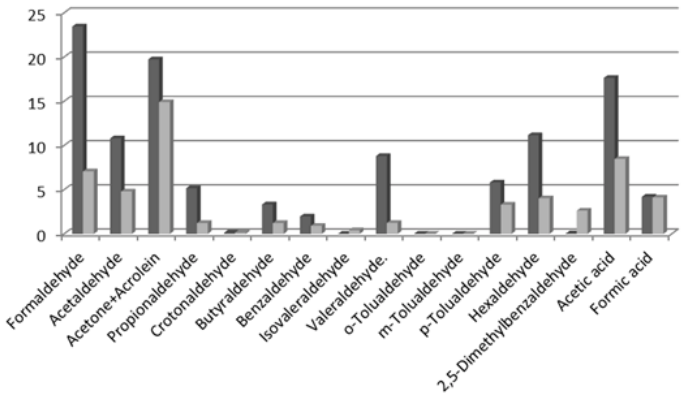

Fig.1. Mean concentrations (µg/m^3) of the aldehydes from all the indoor air samples.

The mean concentrations of the targeted pollutants from all the air samplers from the two offices are showed in figure 1. With dark grey are represented the carbonyls concentrations of the office from the old building. The carbonyls concentrations of the office from the green building are represented using light grey. The majority of the aldehydes showed higher concentrations in the old building office compared to the concentrations found in the green building office; with 2,5-dimethylbenzaldehyde being the exception. Concentrations of formic acid were slightly higher in the old building office versus the green building office. Acetic acid, concentrations found in the old building office were around two times higher comparing to the ones from green building office.

Figure 2 and figure 3 presents the most abundant carbonyls as a percentage in the total carbonyls concentration (Σ carbonyls) for each office. In both offices the percentage of formaldehyde, acroleine+acetone, acetaldehyde, hexaldehyde and carboxylic acids were the most abundant compounds that accounted for more than 50% of the total carbonyls.

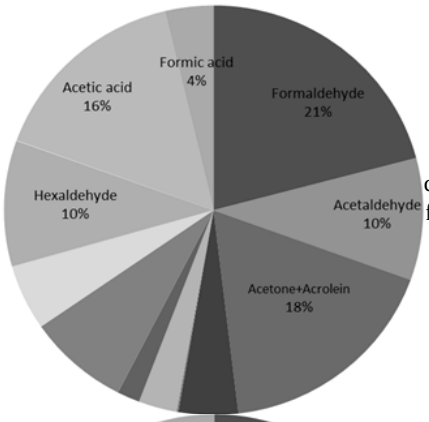

Fig.2. Percentage of the most abundant carbonyls in the office from the old building.

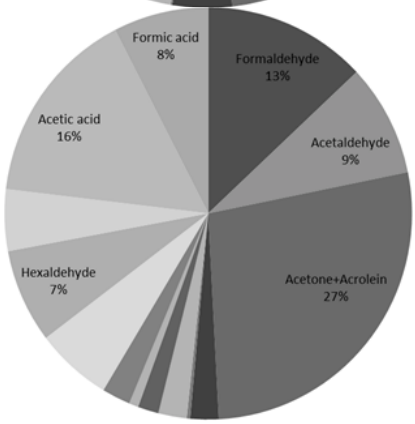

Fig.3. Percentage of the most abundant carbonyls in the office from the green building.

Total carbonyls concentration determined for the office from the old building was 112.23 µg/m^3. The office from the green building had a total carbonyls concentration of 54.43 µg/m^3; making it two times lower than the total carbonyls concentration obtained for the office from the old building.

In the office of the old building, concentration of the targeted aldehydes followed the next pattern: formaldehyde > acrolein+acetone > acetic acid> hexaldehyde > acetaldehyde > valeraldehyde > *p*-tolualdehyde >propionaldehyde >formic acid> butyraldehyde> benzaldehyde > crotonaldehyde and 2,5-dimethylbenzaldehyde.

Concentration of the targeted aldehydes in the office of the green building followed the pattern:

acrolein+acetone> acetic acid>formaldehyde> acetaldehyde > formic acid> hexaldehyde > *p*-tolualdehyde >2,5-dimethylbenzaldehyde> valeraldehyde > butyraldehyde> propionaldehyde> benzaldehyde >crotonaldehyde and isovaleraldehyde.

Comparing the concentrations of the indoor air samplers found in this study with outdoor air concentrations of carbonyls from other studies realized in Bucharest [6], it can be said that indoor sources of carbonyls exist in both studied offices. Analyzing the questionnaire, the potential indoor carbonyls sources included the furniture, building materials, floor and sealing type of the two offices.

Conclusions

From the total of seventeen carbonyls (aldehydes, acetone and carboxylic acids) fourteen were found in quantifying quantities in all the samplers. The most

abundant aldehydes were: formaldehyde, acroleine +acetone, acetaldehyde, hexaldehyde and carboxylic acids.

The highest concentrations of carbonyls were found in indoor air samples from the office of the old building in comparison to the concentration found in the office from the green building. Based on the results found, both offices have indoor sources of carbonyls.

Acknowledgements: The tests have been done inside the Program Nucleu (PN 16 25 01 15) financed by the Ministry of Education and Research of Romania whom we thank with this opportunity for all the support.

References

1. PETRESCU, M., BUCUR, E., VASILE, A., DIODIU, R., VASILE, G.G., DANCIULESCU, V., BRATU, M., TANASE, G., International Symposium The Environment and the Industry, 2016, p. 376.
2. PACURARIU, L., MATEESCU, M., SZCZEPANSKI, P., DANCIULESCU, V., NECHIFOR, A. C., Rev. Chim. (Bucharest), **64**, no. 7, 2013, p. 680.
3. BRATU, M., DANCIULESCU, V., BUCUR, E., VASILE, A., International Symposium The Environment and the Industry, 2015, p. 201.
4. DANCIULESCU, V., BUCUR, E., PASCU, L. F., VASILE, A., BRATU, M., J. Environ. Prot. Ecol., **16**, no.3, 2015, p.815.
5. DIODIU, R., GALAON, T., BUCUR, E., PASCU, L. F., Rev. Chim. (Bucharest), **67**, no. 8, 2016, p. 1466.
6. DIODIU, R., GALAON, T., BUCUR, E., STEFAN, D. S., PASCU, L. F., Rev. Chim. (Bucharest), **67**, no.12, 2016, p. 2396.
7. BUCUR, E., DANET, A. F., LEHR, C. B., LEHR, E., NITA-LAZAR, M., Rev. Chim. (Bucharest), **67**, no. 8, 2016, p. 1421.
8. ROBA, C., ROSU, C., NEAMTIU, I., GURZAU, E., Universitatis Babes-Bolyai, seria Ambientum, **56**, no. 2, 2011, p. 85.
9. IARC. Formaldehyde, 2-butoxyethanol and 1-tertbutoxypropanol-2-ol., Monographs on the evaluation of carcinogenic risks to humans. Lyon: World Health Organization, 2006, p. 325.
10. US EPA. Integrated Risk Information System (IRIS) on Formaldehyde. National Center for Environmental Assessment, Office of Research and Development, Washington, D.C. 1999.
11. US EPA. Integrated Risk Information System (IRIS) on Acetaldehyde. National Center for Environmental Assessment, Office of Research and Development, Washington, D.C. 1999.
12. IARC. IARC monographs on the evaluation of carcinogenic risks to human. Reevaluation of some organic chemicals, hydrazine and hydrogen peroxide: acetaldehyde. IARC, Lyon, France, 1999, 71.
13. WHO, Acetaldehyde. Environmental Health Criteria, No. 167, World Health Organization, Geneva, 1995.
14. US EPA. Formic acid – fact sheet. Retrieved from http://cfpub.epa.gov. Accessed on November 2016.
15. US EPA. Acetic acid – fact sheet. Retrieved from http://cfpub.epa.gov. Accessed on November 2016.
16. SALTHAMMER, T., MENTESE, S., MARUTZKY, R., Chem. Rev., **110**, 2010, p. 2536.
17. BAUMANN, M.G.D., LORENZ, L.F., BATTERMAN, S.A., ZHANG, G.Z., Forest Prod. J., **50**, 2000, p. 75.
18. United States Environmental Protection Agency (US EPA): Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) (EPA-625/R-96/010b), Compendium Method TO-11A; Centre for Environmental Research Information, Cincinnati, OH, USA, 1997.
19. DIODIU, R., BUCUR, E, International Symposium The Environment and the Industry, 2016, p. 207.
20. JIANG, C., ZHANG, P., Front. Environ. Sci. Engin., **6**, no. 2, 2012, p. 184.

Manuscript received: 15.01.2017