**BABEŞ-BOLYAI UNIVERSITY**

**Faculty of Environmental Science and Engineering**
**Environmental Science Doctoral School**

# Contributions to the study of aldehydes and organic acids in homes and offices

# - Doctoral Thesis Summary -

**PhD student: Raluca Diodiu**

**PhD professors:** **Prof. Dr. Constantin Cosma**
**Prof. Dr. Hab. Lucian Copolovici**

*CLUJ-NAPOCA*
*2017*

# Content

# Key words

- indoor air,
- aldehydes,
- fornaldehyde,
- acetaldehyde,
- carbonyls,
- organic acids,
- passive sampling,
- active sampling

# 1. Introduction

## 1.1. Issues addressed

If we quantify working hours at the office, sleep, performing different household activities, we realize that we spend most of the time indoors. It has been estimated that the time spent inside can reach up to 90% of our time. The United States Environmental Protection Agency (US EPA) estimates that a person receives about 75% of the exposure to chemicals at home, which means that the places most people find the safest place, is the one that expose them to the highest quantities of dangerous pollutants.

Epidemiological studies have suggested an association between the degree of indoor air pollution and the health of the human respiratory system. The latter is constantly subjected to the action of pollutants present in air, the epithelium of the breathing paths representing the first contact and at the same time the first barrier of the organism against pollutants present in the air.

## 1.2. Objectives of the thesis

This doctoral thesis aimed to make an assessment of indoor air quality regarding the presence of carbonyl compounds in dwellings and offices located in Bucharest - Romania. Case studies of this doctoral thesis were conducted in twenty dwellings and three office buildings (six offices) along several sampling campaigns that took place during 2015.

The carbonyl compounds monitored in this work in indoor air and ambient air samples are acetaldehyde, acetic acid, acetone, acroleine, benzaldehyde, butyraldehyde, crotonaldehyde, 2,5-dimethylbenzaldehyde, formaldehyde, formic acid, hexaldehyde, isovaleraldehyde, *o*-tolualdehyde, *m*-tolualdehyde, *p*-tolualdehyde and valeraldehyde.

Each interior space is to a great extent different from another interior space, therefore, within the thesis, each interior space where the sampling will be carried out will be characterized in terms of furniture, ceiling composition, floor type, room volume, technical equipment present and other potential sources of carbonyl compounds. For homes, residents will complete a questionnaire to include this issue, and in the case of offices, the information will be taken from the administrative service of the firms operating in those premises. All of this will help us to characterize each sampling space in terms of carbonyl compound concentrations.

In order to have a complete picture of indoor air quality, they will be determined, along with the concentrations of carbonyl compounds of interest inside, their concentrations in ambient air. Thus, a comparison can be made between the concentrations determined in case studies in indoor air in both dwellings and offices and the concentrations obtained for the same compounds of interest for ambient air.

By comparing the concentrations obtained in indoor air with ambient air, I/O Ratio (indoor/outdoor) will be realized which will provide us information about the location of the sources of the compounds determined.

In the thesis, both passive and active air sampling will be carried out. Several sampling points will be selected in which both sampling will be performed in the same time. By comparing the results from both methods, the correlation between the two sampling methods can be assessed.

Concentrations of the carbonyl compounds determined will be statistically analyzed and we will see what correlation exists between each carbonyl compound.

After the determination of carbonyl compounds concentrations for a particular dwelling or office, the degree of exposure to the persons living or working in the housing and offices where the sampling was carried out shall be estimated.

All this will give us an insight into the quality of indoor air regarding the carbonyl compounds in the homes and offices where case studies will be conducted.

## 2. History of Literature

### 2.1. Sources in the indoor air of compounds of interest

Carbonyl compounds are omnipresent in the environment, with both natural and anthropogenic sources. In the atmosphere, carbonyl compounds are often formed by the oxidation reaction of hydrocarbons. Sources of aldehydes in homes include: building materials, laminate flooring, adhesives, paints and solvents, household products, furniture made of chipboard, plywood and plywood with resin adhesive made with formaldehyde, smoking and fire open stoves. Organic acids can appear directly in the indoor air or can be emitted directly into the indoor air of various materials.

## 2.2. The health effects of compounds of interest

Recent studies that looked at the effects of exposure of humans and animals to carbonyl compounds have shown negative effects on the respiratory system.

Of the carbonyl compounds, those that have had obvious negative effects on health are formaldehyde and acetaldehyde. IARC integrates formaldehyde into Group 1, meaning it is carcinogen to humans and acetaldehyde in Group 2B, meaning human carcinogen. US EPA integrates formaldehyde into group B1 as being probably human carcinogen, based on limited evidence in human subjects. Acetaldehyde is classified by US EPA in group B2, meaning: probably human carcinogen with sufficient evidence of carcinogenicity in humans.

## 2.3. Proposed limit concentrations for compounds of interest

Of the carbonyl compounds of interest for this thesis, only in the case of formaldehyde was attempted to establish limits of concentration in the indoor air in the form of recommendations, as followed:

- WHO sets the value of 100 μg/$m^3$ for a 30-minute exposure period;
- US EPA recommends 55 μg/$m^3$ for one hour exposure and 8 μg/m3 for exposure for 8 hours;
- The European Commission, through the INDEX Project, proposes in 2005 the concentration of 30 μg/$m^3$ for a 30-minute exposure period and a concentration of 1μg/$m^3$ for one hour exposure.

## 2.4. Previous investigations of indoor air quality

### 2.4.1 Situation in Europe on indoor air quality

Several indoor air quality projects have been carried out in Europe over the past twenty years with the following acronyms: INDEX (2002-2004), AIRMEX (2003-2008), EnVIE (2004-2008), BUMA (2006-2009) SEARCH (2006-2009 and 2010-2013), HealthVent (2010-2012), EPHECT (2010-2013), OFFICAIR (2010-2013), and SINPHONIE (2010-2012)

### 2.4.2. The current state of knowledge regarding the concentration of compounds of interest

Table 2 shows the concentrations of carbonyls of interest in indoor air determined in various air quality monitoring studies. The table includes the results of

42 articles and studies in which concentrations of different carbonyl compounds in indoor air were determined by different sampling and analysis methods. It provides an overview of everything that has been determined about carbonyl compounds in indoor air, summing up location, year, author, type of indoor space and determined concentrations that were published and accessed from the last seventeen years.

# 3. Materials and Methods

## 3.1. Analytical techniques used in the thesis

In the present thesis the following analytical techniques were used: high performance liquid chromatography and ion chromatography.

High Performance Liquid Chromatography has been used to develop the analytical method for aldehydes and acetone determination.

Ion chromatography was used in the thesis to develop the organic acids method determination.

## 3.2. Sampling of air samples

### 3.2.1. Method of extraction of aldehydes

Determination of aldehydes by liquid chromatography implies their derivatization to a more stable form using derivatizing agents. Subsequently, the derivatization compounds were eluted and analyzed on the chromatograph.

#### 3.2.1.1. Active method for the extraction of aldehydes

In the case of the studies realized in offices, along with passive sampling, an active sampling was also carried out. This was accomplished using silicagel and DNPH model ORBO 555 (6mm × 110mm), purchased from Sigma Aldrich. To remove potential interference from ozone in air, a LpDNPH Ozone Scrubber 1.5g potassium iodide scrubber, purchased from Sigma Aldrich.

After sampling, extraction is carried out in acetonitrile.

#### 3.2.1.2. Passive aldehyde sampling method

For the case studies realized by passive sampling, Passive Sampling Devices DSD-DNPH Diffusive Sampling Devices were purchased from Supelco, catalog number 28221-U with related accessories.

The elution is carried out using a solid phase cartridge extractor equipped with a vacuum manifold. Acetonitrile is used for elution.

### 3.2.2. Method of sampling organic acids

#### 3.2.2.1. Active method for the sampling of organic acids

ORBO 52 Small Activated Silica Gel Absorbent Tubes contain two silicon parts separated by glass wool for gas and vapor sampling. The first part contains 150mg and the second part 75mg.

For active silica gel absorbent tubes, the extraction is performed by mechanically agitating the beads with 5 ml of water for 10 minutes, and then allowed to stand for 10 minutes.

#### 3.2.2.2. Passive method for the sampling of organic acids

In the case studies of this paper, the passive sampling of organic acids was accomplished using passive devices from Radiello purchased from Sigma Aldrich, composed of: RAD 166 (triethanolamine cartridge), RAD 1201 (blue body), and RAD 121 (Triangular plate for support with pliers for workplace sampling).

Extraction of analytes from silica gel tubes and passive triethanolamine (TEA) cartridges is performed in water with a conductivity of <10 μS / cm, similar to the procedure presented in (NIOSH, 1994).

## 3.3. Analytical methods for the determination of aldehydes and organic acids

### 3.3.1. Analytical method for the determination of aldehydes

A high performance liquid chromatograph model Agilent 1200, coupled with a UV detector was used for the determination of aldehydes and ketones. Analytical conditions included two Acclaim Carbonyl C18 columns (250 mm * 4.6 mm, 5 μm,) coupled in series, a diode array detector (DAD) set at 365 nm wavelength, 2 mL/min flow rate, 25 μL injection volume, 25°C column temperature and a gradient mobile phase of acetonitrile / water.

The elution gradient was as follows: upon sample injection, linear gradient from 60 to 75% acetonitrile/40 to 25% water in 30 min, linear gradient from 75 to 100% acetonitrile/25 to 0% water in 20 min, hold at 100% acetonitrile for 5 min, reverse gradient to 60% acetonitrile/40% water in 1 min, and maintain isocratic at 60% acetonitrile/40% water for 15 min.

A calibration standard: TO11/IP 6A Aldehyde/Ketone- DNPH Mix certified reference material, with 15 µg/mL concentration of aldehydes and ketones, was purchased from Sigma-Aldrich. The calibration standard contains the hydrazone derivatives of the fifteen targeted aldehydes and ketones.

### 3.3.2. Analytical method for determination of formic and acetic acids

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.

For the determination of formic acid and acetic acid, as formate and acetate, standards of 1000 µg/mL for each in water were purchased from LGC Standards.

## 4. Results and discussions

### 4.1. Location of Sampling Points

Case studies within this thesis were conducted in Bucharest.

### 4.2. Case study 1 - Assessment of the concentration of compounds of interest in ambient air

Concentrations ranged from 0.01-2.22 µg/m³, their sum being 5.83 µg/m³. The concentrations for the carbonyl compounds in descending order were: acetic acid, acrolein + acetone, formic acid, formaldehyde, acetaldehyde and butylaldehyde, o-tolualdehyde, p-tolualdehyde, hexaldehyde, propionaldehyde, benzaldehyde, isovaleraldehyde, valeraldehyde, 5 dimethylbenzaldehyde and crotonaldehyde.

### 4.3. Case Study 2 - Assessing the concentration of compounds of interest in indoor air

In this case study, concentrations of carbonyl compounds of interest in twenty dwellings in the city of Bucharest were determined. Organic acids and aldehydes were taken simultaneously (see Annex 1) and passive sampling for both aldehydes and organic acids was chosen in order not to disturb the day-to-day activities of the occupants. Sampling took place in dormitory for half of the dwellings and for the other half was carried out in the living room. The sampling period was approximately 10 days in October and November 2015.

The inhabitants filled in a questionnaire that provided us with data about the material from which the furniture was made, the age of the furniture, if there were recent renovations, the ceiling material, the floor, the windows, the existence of the animals in the dwelling, the number of inhabitants, and the location of the dwelling windows against the traffic arteries.

No open fire heaters or air conditioners have been used throughout the sampling period; The exchange of air with the outside was done by opening the windows.

The highest concentration was found in the case of acroleine+acetone. The most compact values were obtained for formaldehyde; and the highest variation in the concentartion determined was found for acrolein+acetone.

Concentration of the targeted carbonyls tend to fallow the following pattern: formaldehyde > acrolein+acetone > acetic acid > acetaldehyde > hexaldehyde > formic acid > valeraldehyde > benzaldehyde > butyraldehyde > propionaldehyde > ptolualdehyde >2,5-dimethylbenzaldehyde > o-tolualdehyde > isovaleraldehyde > crotonaldehyde and *m*-tolualdehyde.

### 4.4. Case study 3 - Correlation of concentrations of compounds of interest with the age of furniture in dwellings

In this case study a correlation of the determined concentrations within the thesis was carried out in dwellings with the age of the furniture in the sampling room. Figures 58, 59, 60, 61 are graphically represented by the concentrations of the carbonyl compounds in the houses and the age of the furniture. In order to make the correlation more visible, an average of the concentrations of the carbonyl compound was also achieved.

The highest concentration of carbonyl compounds was obtained in indoor air samples from rooms with new furniture, but not all homes participating in this study followed this pattern. The highest concentrations of carbonyl compounds were found in indoor air samples in new furniture rooms (under one year).

Concentration decreases with increasing furniture age for the following carbonyl compounds: formaldehyde, acetaldehyde, acrolein + acetone, crotonaldehyde, benzaldehyde, benzaldehyde, valeraldehyde, o-tolualdehyde and hexaldehyde, formic acid and acetic acid.

For the following carbonyl compounds, no correlation could be highlighted between the concentrations determined in homes and age of furniture: propionaldehyde, butylaldehyde, m-tolualdehyde, p-tolualdehyde and 2,5-dimethylbenzaldehyde.

**4.5. Case Study 4 - Sources of Compounds of Interest in Housing**

In this case study we compared the values obtained for the carbonyl compounds in the 19 dwellings with the values obtained in the ambient air. This is how the indoor / outdoor report was established. The results are presented in Table 8.

Values obtained for the indoor / outdoor ratio were greater than 1 for most dwellings for most carbonyl compounds. This demonstrates the existence of interior sources that have a much greater weight than outdoor sources in the ambient air.

The results obtained by analyzing the values of the determined concentrations within the dwellings can be seen in Table 9. Within this table we can see the degree of correlation between the concentrations of each carbonyl compound with the other carbonyl compounds determined in dwellings in the study.

The highest degree of correlation was achieved between the ubiquitous carbonyl compounds: formaldehyde and butylaldehyde, formaldehyde and benzaldehyde, propionaldehyde and m -tolualdehyde, butylaldehyde and benzaldehyde, butylaldehyde and valeraldehyde, butylaldehyde and hexaldehyde, benzaldehyde and valeraldehyde, benzaldehyde and hexaldehyde, valeraldehyde and hexaldehyde , Acetic acid and formic acid.

**4.6. Case Study 5 - Assessment of the concentration of interest-bearing compounds in offices**

In this case study, concentrations of interest compounds were determined in six offices located in three buildings in Bucharest. Offices B1, B2, B3 and B4 are located in the building marked on the sampling map with the number 1 blue. The B5 office is located in the building marked on the sampling map with the number 2 blue and the office B6 is located in the 3 blue bulgarian building.

At all sampling sites, organic acids and aldehydes were sampled concurrently. The temperature and humidity parameters were recorded in the offices during the sampling period using thermo-hygrometers.

Concentration values ranged from 54.43 to 128.68 μg/m$^3$. The highest concentrations were found in B2, the sum of the concentrations of interest compounds of 128.68 μg/m$^3$. B5 had the sum of concentrations very close to B2, which is 121.23 μg/m$^3$. In descending order of total concentrations of commonweights of interest, B1 (99.29 μg/m$^3$), B3 (89.76 μg/m$^3$), B4 (76.18 μg/m$^3$) and B6 (54.43 μg/m$^3$). The highest concentrations were found in formaldehyde, acetaldehyde, acrolein + acetone, hexaldehyde and acetic acid.

### 4.7. Case study 6 - Comparison of two sampling methods used to determine the concentration of compounds of interest in indoor air

In this case study, a comparison was made between the concentrations obtained for the aldehydes and ketones of the carbonyl compounds of interest by passive sampling and by active sampling. The sampling was carried out in 4 offices in the same office building between March 2-11, 2015.

The active levy in order to avoid disrupting the persons working in the laboratories was done after the 16 to 16 hour program at 7 am. The passive sampling was carried out at the same sampling points as the active sampling.

In order to compare the two sampling methods, the values obtained were used to make Bland-Altman diagrams. These are shown in Figure 74. Figure 74 is composed of Bland-Altman diagrams made from the concentrations obtained by active sampling and the concentrations obtained by passive sampling. On an ordinate, the difference between the passive sampling concentration and the active sampling concentration is plotted. The abscissa is the mean of the two concentrations.

All diagrams show the existence of a good correlation between the two methods. Thus, the two methods can be used interchangeably to determine the carbonyl compounds of interest within the offices.

### 4.8. Case Study 7 - Sources of Office Interests

In this case study we compared the values obtained for the carbonyl compounds in the 6 offices with the values obtained in the ambient air. Thus, the indoor / outdoor ratio for office concentrations can be established. This was calculated by dividing the concentrations obtained in each office by the values obtained for ambient air.

The existence of indoor sources is also indicated in all offices for most carbonyl compounds. The ratio of concentrations in ambient air to indoor air is overhead for most of the compounds of interest.

Table 11 shows the Spearman coefficient of the correlation of the difference of the ranges for the values of the office concentrations.

The highest degree of correlation was achieved between the ubiquitous carbonyl compounds: formaldehyde and o-tolualdehyde, formaldehyde and m - tolualdehyde, formaldehyde and formic acid, acrolein + acetone and p-tolualdehyde, propionaldehyde and butylaldehyde, propionaldehyde and valeraldehyde, butylaldehyde and valeraldehyde, o-tolualdehyde and p-tolualdehyde, o-tolualdehyde and formic acid.

### 4.9. Case Study 8 - Health Risks Given by Concentrations of Compounds of Interest in Dwellings and Offices

This case study has attempted to estimate the degree of health risk to which people living in the dwelling or operating in offices where the determinations of compounds of interest in this thesis have been exposed.

Table 12 shows the average, minimum and maximum exposure levels for homes and offices calculated for formaldehyde, acetaldehyde, acrolein + acetone, propionaldehyde, crotonaldehyde, benzaldehyde, valeraldehyde, hexaldehyde, formic acid and acetic acid. In assessing exposure levels for compounds of interest in dwellings, the highest risk was found in acrolein + acetone. Similarly to the present situation in the dwellings of this thesis, in offices the highest risk was determined for acrolein + acetone.

When comparing the present situation in the dwelling with that of the office in terms of health risk based on exposure to the maximum concentration, there is a single carbonyl compound at high risk for health in the dwelling, while there are no compounds of interest in the offices high risk; in terms of low risk, in dwellings there are eight compounds to six in the case of offices. With regard to compounds of interest that do not pose a health risk concern, only one carbonyl compound in the dwellings falls into this category; in comparison with dwellings, in the offices were identified four carbonyls which are in this category.

### 4.10. Case Study 9 - Comparison of Compound Interest Results in Dwellings and Offices with the Results of the Literature

In this case study, an average of the values obtained in the dwellings and offices was compared and compared with the values obtained in the literature in articles that were taken in similar locations.

The values in this thesis lie somewhere in the middle of the range of concentrations determined in dwellings, being close to the values determined by Bari et al., 2015 and Duan et al., 2014. In the case of acetaldehyde, comparing the average of the study with other values from the specialized literature in dwellings, it is found that the average value within the present thesis is close to the average of the values obtained for all the values determined in the studies. Comparing the average result obtained in the thesis for hexcaldehyde with other values from the specialized literature determined in dwellings, it is found that the values determined in the thesis were half the average for all the concentrations in the studied studies. Regarding propionaldehyde, the mean of the values determined in dwellings within the thesis is lower than the average values presented in the previous literature studies. Similarly, lower values were obtained for: acrolein + acetone, crotonaldehyde, butylaldehyde, benzaldehyde, and isovaleraldehyde. In the case of valeraldehyde, the mean value determined in the thesis is higher than the values determined in the other studies. Compared with the values determined in other studies, the average for the three compounds (o-tolualdehyde, m-tolualdehyde and p-tolualdehyde) in dwellings showed the highest value. 2,5-dimethylbenzaldehyde showed the closest approximation to the mean value of the concentrations compared to the mean obtained from the values determined in the other studies.

The mean value of formaldehyde determined in the offices was very similar to the average of the concentrations determined in the studies in the literature. The mean value determined in the thesis for acetaldehyde was very close to the mean values determined in the other studies in the literature, being 10% lower. The mean of the values determined in the thesis had the lowest value of studies that determined acrolein + acetone in offices.

# 5. Conclusions and future research

## 5.1. Final conclusions

This doctoral thesis determined the concentrations of 17 carbonyl compounds in the air inside 20 homes and 6 offices. The concentrations of the compounds of interest in ambient air were also determined. Thus indoor air quality has been evaluated, providing information about the possible concentrations we are exposed to in our everyday life both at work and in our own home.

In addition to the conclusions reached by this thesis, after analyzing the data obtained, the novelty elements are also the novelty of this type of study in Romania. From our knowledge, there were no scientific papers other than the one that were of the author of this thesis that would address the characterization of the 17 carbonyls of interest in the air inside the dwellings and offices or in the ambient air for the given location or Romania.

With regard to aldehydes and acetone determined in the thesis both in dwellings and offices, depending on the values of the determined concentrations, they can be divided into two groups. The first group consists of aldehydes with a concentration value higher, with average values ranging from 9.97 μg/m$^3$ to 30.64 μg/m$^3$. This group included: formaldehyde, acetaldehyde, acrolein + acetone and hexaldehyde. Formaldehyde had the highest concentration average in offices and dwellings, and acrolein + acetone had the highest concentration value determined.

The second group had average values ranging from 0.08 μg/m$^3$ to 3.68 μg/m$^3$. This group included propionaldehyde, crotonaldehyde, butylaldehyde, benzaldehyde, isovaleraldehyde, valeraldehyde, *o*-tolualdehyde, *m*-tolualdehyde, *p*-tolualdehyde, hexaldehyde, and 2,5-dimethylbenzaldehyde. In most dwellings and offices the smallest concentrations of carbonyl compounds were obtained for crotonaldehyde and *m*-tolualdehyde.

It was not possible to establish a correlation between the value of the concentrations of carbonyl compounds in dwellings and offices with the value of temperature and humidity. This was due to the fact that these parameters did not vary greatly in the sampling areas.

Within homes, a connection between the age of the furniture and the concentration of formaldehyde, acetaldehyde, acrolein + acetone and hexaldehyde could be observed. The newer the furniture in the sampling room was, the higher the concentrations were compared with the average concentration values for that carbonyl compound.

The same trend was also observed for the following carbonyl compounds: crotonaldehyde, benzaldehyde, isovaleraldehyde, valeraldehyde and o-tolualdehyde. However, due to the fact that the concentration values are small and do not vary greatly, we consider that more in-depth studies are required to be able to state whether their concentration values correlate with the age of the furniture.

No correlation could be highlighted between the concentrations determined in dwellings and the age of furniture for the following carbonyl compounds: propionaldehyde, butylaldehyde, m-tolualdehyde, p-tolualdehyde and 2,5-dimethylbenzaldehyde.

As for organic acids, acetic acid showed higher values than formic acid in all dwellings, with acetic acid concentrations averaging more than 6 times the concentrations of formic acid.

It was observed that formaldehyde concentrations were lower than the average in dwellings where the concentration of acrolein + acetone was 2-5 times higher than the average.

Parallel measurements in B1, B2, B3 and B4 offices in Building 1 both by active and passive methods showed that the values determined by the two sampling methods have values that varied very little to nothing between them.

Concerning the sources of carbonyl compounds, the comparison of the concentration values determined in the indoor air with the ambient air by the Indoor/Outdoor Ratio and the Spearman Test showed the presence of indoor sources both in the dwellings and in the offices for all carbonyl compounds in almost all sampling locations.

In terms of exposure, indoor air quality poses a higher health risk than office air quality in which concentrations of carbonyl compounds of interest have been determined. The highest risk for health after exposure was highlighted for acrolein + acetone in both homes and offices.

Even if the concentration of each carbonyl compound in the indoor air is low and it does not appear to pose a health risk, many of these pollutants are found together in the indoor air, thus creating a health risk of cumulative exposure to all pollutants.

## 5.2. Future research directions

By addressing a field where there is still a need to deepen existing knowledge, this PhD thesis presents many possibilities to be continued in the future.

With regard to studied carbonyl compounds, the thesis can continue with their study in wider campaigns that include more homes and/or office buildings. Moreover, indoor air quality studies on these compounds may be extended to other indoor areas not covered in the thesis or other works in Romania.

In addition to the carbonyl compounds discussed in the thesis, other compounds can be investigated in indoor air or one can try to reveal the presence of other new compounds. All this will lead to a more complete characterization of indoor air.

The link between pollutants present in indoor air and human health must be seen from the perspective of a combined risk from the risks of several pollutants. All this can improve human health by raising awareness and taking action to reduce pollution sources.

There is a need for further research on human health guides or control measures for pollutants at sources based on chemical families or on classes of pollutants that have the same health effects. Doing so will reduce the risks to human health.

Thus, this thesis can continue with new studies that provide a more complete picture of the indoor environment in which modern man spends much of his life.

# Selective Bibliography

AIRAKSINEN, L. K., TUOMI, T. O., TUPPURAINEN, M. O., LAUERMA, A. I. & TOSKALA, E. M. 2008. Inhalation challenge test in the diagnosis of occupational rhinitis. Am J Rhinol, 22, 38-46.

AO, C. H., LEE, S. C., YU, J. Z. & XU, J. H. 2004. Photodegradation of formaldehyde by photocatalyst TiO2: effects on the presences of NO, SO2 and VOCs. Applied Catalysis B: Environmental, 54, 41-50.

ARTS, J. H., RENNEN, M. A. & DE HEER, C. 2006. Inhaled formaldehyde: evaluation of sensory irritation in relation to carcinogenicity. Regul Toxicol Pharmacol, 44, 144-60.

ARTS, J. H. E., MUIJSER, H., KUPER, C. F. & WOUTERSEN, R. A. 2008. Setting an indoor air exposure limit for formaldehyde: Factors of concern. Regulatory Toxicology and Pharmacology, 52, 189-194.

BACHAND, A. M., MUNDT, K. A., MUNDT, D. J. & MONTGOMERY, R. R. 2010. Epidemiological studies of formaldehyde exposure and risk of leukemia and nasopharyngeal cancer: a meta-analysis. Crit Rev Toxicol, 40, 85-100.

BARRO, R., REGUEIRO, J., LLOMPART, M. & GARCIA-JARES, C. 2009. Analysis of industrial contaminants in indoor air: part 1. Volatile organic compounds, carbonyl compounds, polycyclic aromatic hydrocarbons and polychlorinated biphenyls. J Chromatogr A, 1216, 540-66.

BAUMANN MGD, LORENZ LF, BATTERMAN SA & (), Z. G.-Z. 2000. Aldehyde emissions from particleboard and medium density fiberboard products. Forest Prod J, 50.

BURGAZ, S., ERDEM, O., CAKMAK, G., ERDEM, N., KARAKAYA, A. & KARAKAYA, A. E. 2002. Cytogenetic analysis of buccal cells from shoe-workers and pathology and anatomy laboratory workers exposed to n-hexane, toluene, methyl ethyl ketone and formaldehyde. Biomarkers, 7, 151-61.

CHEUNG, H., TANKE, R. S. & TORRENCE, G. P. 2000. Acetic Acid. Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH Verlag GmbH & Co. KGaA.

**DIODIU, R.,** BUCUR, E., GALAON, T. & PASCU, L. F. 2015. Indoor air exposure to aldehydes and ketones in rooms with new and old furniture of a new office building. Journal of Environmental Protection and Ecology, 16, 832-838.

**DIODIU, R.** & DOGEANU, A. 2016. Development and validation of an analytical method for quantitative determination of carboxylic acids in air samplers. Energy Procedia, 85, 201 - 205.

**DIODIU, R.** & GALAON, T. 2017. Comparing Carbonyls Levels in Indoor Air in two Offices – Green and Old Building. In press Rev.Chim.(Bucharest).

**DIODIU, R.,** GALAON, T., BUCUR, E. & PASCU, L. F. 2016a. Aldehydes and Acetone in Indoor Air of 19 Houses from Bucharest. Rev.Chim.(Bucharest), 67, 1466-1468.

**DIODIU, R**., GALAON, T., BUCUR, E., STEFAN, D. S. & PASCU, L. F. 2016b. Aldehydes, Acetone, Formic and Acetic Acids in Indoor Air of an Office Building. Rev.Chim.(Bucharest), 67, 2396-2399.

DUONG, A., STEINMAUS, C., MCHALE, C. M., VAUGHAN, C. P. & ZHANG, L. 2011. Reproductive and developmental toxicity of formaldehyde: a systematic review. Mutat Res, 728, 118-38.

FREY, S. E. 2014. Indoor Air Quality Investigations on Particulate Matter, Carbonyls, and Tobacco Specific Nitrosamines.

HE, Z., ZHANG, Y. & WEI, W. 2012. Formaldehyde and VOC emissions at different manufacturing stages of wood-based panels. Building and Environment, 47, 197-204.

HIETALA, J., VUORI, A., JOHNSSON, P., POLLARI, I., REUTEMANN, W. & KIECZKA, H. 2000. Formic Acid. Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH Verlag GmbH & Co. KGaA.

KADEN DA, MANDIN C, NIELSEN GD & WOLKOFF P. 2010. Formaldehyde. In: WHO Guidelines for Indoor Air Quality: Selected Pollutants. Geneva: World Health Organization [Online]. Available: https://www.ncbi.nlm.nih.gov/books/NBK138711/.

KOTZIAS, D., KOISTINEN, K., KEPHALOPOULOS, S., CARRER , P., MARONI, M., SCHLITT, C., JANTUNEN, M., COCHET, C., KIRCHNER , S., LINDVALL, T., MCLAUGHLIN, J. & MOLHAVE, L. 2005. INDEX EUR 21590 EN report. EUR - Scientific and Technical Research Reports, 334.

KRIEBEL, D., MYERS, D., CHENG, M., WOSKIE, S. & COCANOUR, B. 2001. Short-term effects of formaldehyde on peak expiratory flow and irritant symptoms. Arch Environ Health, 56, 11-8.

LANG, I., BRUCKNER, T. & TRIEBIG, G. 2008. Formaldehyde and chemosensory irritation in humans: a controlled human exposure study. Regul Toxicol Pharmacol, 50, 23-36.

LAZARIDIS, M. 2011. Indoor Air Pollution. First Principles of Meteorology and Air Pollution. Dordrecht: Springer Netherlands.

LE BERRE, C., SERP, P., KALCK, P. & TORRENCE, G. P. 2000. Acetic Acid. Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH Verlag GmbH & Co. KGaA.

LINO DOS SANTOS FRANCO, A., DOMINGOS, H. V., DAMAZO, A. S., BREITHAUPT-FALOPPA, A. C., DE OLIVEIRA, A. P., COSTA, S. K., OLIANI, S. M., OLIVEIRA-FILHO, R. M., VARGAFTIG, B. B. & TAVARES-DE-LIMA, W. 2009. Reduced allergic lung inflammation in rats following formaldehyde exposure: long-term effects on multiple effector systems. Toxicology, 256, 157-63.

LOUPA, G., CHARPANTIDOU, E., KARAGEORGOS, E. & RAPSOMANIKIS, S. 2007. The chemistry of gaseous acids in medieval churches in Cyprus. Atmospheric Environment, 41, 9018-9029.

LOUPA, G. & RAPSOMANIKIS, S. 2008. Air pollutant emission rates and concentrations in medieval churches. Journal of Atmospheric Chemistry, 60, 169-187.

MAYNARD, R. 2000. Environmental toxicants: human exposures and their health effects. Occup Environ Med, 57, 503-4.

MCGREGOR, D., BOLT, H., COGLIANO, V. & RICHTER-REICHHELM, H. B. 2006. Formaldehyde and glutaraldehyde and nasal cytotoxicity: case study within the context of the 2006 IPCS Human Framework for the Analysis of a cancer mode of action for humans. Crit Rev Toxicol, 36, 821-35.

NIELSEN, G. D., HANSEN, L. F., ANDERSEN, B., POULSEN, N. & OTTO, M. 1998. Indoor Air Guideline Levels for Formic, Acetic, Propionic and Butyric Acid. Indoor Air, 8, 8-24.

NIELSEN, G. D., LARSEN, S. T. & WOLKOFF, P. 2013. Recent trend in risk assessment of formaldehyde exposures from indoor air. Arch Toxicol, 87, 73-98.

NIELSEN, G. D. & WOLKOFF, P. 2010. Cancer effects of formaldehyde: a proposal for an indoor air guideline value. Arch Toxicol, 84, 423-46.

NIOSH 1994. Method 2011 Manual of Analytical Methods (NMAM),Fourth Edition, 8, 15.

O'BRIEN, P. J., SIRAKI, A. G. & SHANGARI, N. 2005. Aldehyde sources, metabolism, molecular toxicity mechanisms, and possible effects on human health. Crit Rev Toxicol, 35, 609-62.

ROWELL, R. M. 2012. Handbook of Wood Chemistry and Wood Composites, Second Edition CRC Press.

SALTHAMMER, T., MENTESE, S. & MARUTZKY, R. 2010. Formaldehyde in the Indoor Environment. Chem Rev, 110, 2536-72.

SCHWIER, A. N., SAREEN, N., MITROO, D., SHAPIRO, E. L. & MCNEILL, V. F. 2010. Glyoxal-Methylglyoxal Cross-Reactions in Secondary Organic Aerosol Formation. Environmental Science & Technology, 44, 6174-6182.

THETKATHUEK, A., YINGRATANASUK, T. & EKBURANAWAT, W. 2016. Respiratory Symptoms due to Occupational Exposure to Formaldehyde and MDF Dust in a MDF Furniture Factory in Eastern Thailand. Advances in Preventive Medicine, 2016, 11.

WOLKOFF, P. & NIELSEN, G. D. 2010. Non-cancer effects of formaldehyde and relevance for setting an indoor air guideline. Environ Int, 36, 788-99.

ZHANG, J., LIOY, P. J. & HE, Q. 1994a. Characteristics of aldehydes: concentrations, sources, and exposures for indoor and outdoor residential microenvironments. Environmental Science & Technology, 28, 146-152.

ZHANG, J., WILSON, W. E. & LIOY, P. J. 1994b. Sources of organic acids in indoor air: a field study. J Expo Anal Environ Epidemiol, 4, 25.