Chapter 3

Aldehyde Measurements in Indoor and Outdoor Environments in Central-Southern Spain

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1. Introduction

Aldehydes are indoor and outdoor chemical pollutants of particular interest due to their potential adverse health effects on humans and to their important role in atmospheric chemistry. In fact, carbonyls are of critical importance since they are the most stable intermediate species in the oxidation of volatile organic compounds. Even in the indoor environments, aldehydes can be released from ozone reactions with unsaturated VOCs [1]. The most important global source of formaldehyde and acetaldehyde in the atmosphere is of secondary origin, and it is the oxidation of natural and anthropogenic hydrocarbons. However, motor vehicle exhausts represent the primary emission source of these pollutants in urban areas [2].

In occupational and residential indoor environments, predominant carbonyls are aldehydes, mainly formaldehyde and acetaldehyde. Formaldehyde, usually the most abundant aldehyde in air, is classified in Group 1 (human carcinogen) by the International Agency for Research on Cancer [3] and acetaldehyde is classified in Group 2B as a possible carcinogenic in humans [4, 5]. Also, benzaldehyde and acrolein are suspected carcinogens and mutagens, as well as other low-molecular-mass aldehydes, which reactivity and possible mutagenicity are similar to those of acetaldehyde [6-8].

Generally speaking, exposure to carbonyls is higher indoors than outdoors. Indoor aldehyde concentrations are usually 2-10 times higher than the outdoor ones [9, 10], indicating the presence of significant indoor sources such as direct emissions and indoor chemical formation although these higher values are also due to the low air exchange rates in the indoor environment [11]. Particularly, formaldehyde is widely used not only in construction (wood processing, furniture, textiles, and carpeting) but also in various industries [12, 13]. It is also a by-product of certain anthropogenic activities (e.g., smoking tobacco, burning automotive (and other) fuels, and residential wood burning) [12]. Formaldehyde is even a component of many consumable household products such as antiseptics, medicines, cosmetics, dish-washing liquids, fabric softeners, shoe-care agents, carpet cleaners, glues and adhesives, lacquers, etc. [14, 15]. Formaldehyde is also employed as food preservative [16, 17]. For these reasons, formaldehyde is generally found in higher concentrations indoors than outdoors.

Because aldehydes may contribute to different diseases and are mainly found in indoor environment, their measurements are of particular interest, especially when it is known that most people in developed countries spend up to 90% of their time indoors [18]. The objective of this study is to measure and analyze the levels of formaldehyde and acetaldehyde and even other carbonyls in indoor and outdoor air in this region from central-southern Spain. The measurements have been carried out in different sampling periods from 2010 to 2014. Very few studies have been carried out in the indoor air in Spain with the aim of determining different air pollutants [19-27] and most of which have been focused on particulate matter [20, 23-26]. In this paper, the levels of carbonyls in different indoor environments in our country are presented for first time. It consists of new field campaigns together with the results obtained from our previous studies [21, 29].

2. Experimental section

2.1. Sampling sites and their characteristics

Ciudad Real is an urban area with around 65,000 inhabitants and is located in the heart of La Mancha region in central-southern Spain (38.59°N, 3.55°W, at approximately 628 m above sea level) in a fairly flat area, 200 km south of Madrid. With a low presence of industry, traffic is the most important source of air pollution in this city [28]. Puertollano (38° 42''N 04° 07''W, at approximately 700 m above sea level) is a very important industrial area with almost 52,000 inhabitants located at 40 km to the southwest of Ciudad Real. The existent industries situated about 5-6 km southeast from the town center include an oil refinery, a petrochemical industry, a nitrogen fertilizer factory, two power plants, and a coal mine, which means an important source of air pollution in this city. Field measurements in the ecological area were conducted on the southwestern border of the park at about 6 km east of the village of Horcajo de los Montes (39.2°N, 04.4°W, 617 m above sea level) (see Fig. 1). Meteorologically, this zone is characterized by very hot and dry summer period with high insulation (Fig. 1).

The first series of field measurements was conducted in Ciudad Real from September 2008 to April 2009 and were focused on different places of the Faculty of Chemistry: two research laboratories, a laboratory used by practical classes, an office, and the bar of the campus. In addition, an outdoor sampling point was selected to measure levels of the aldehydes. Also, indoor and outdoor measurements were carried out in two private homes, one with smokers (home 1) [19]. Indoor measurements were carried out in two points of the homes, the kitchen and the living room.

Figure 1. Situation map of Ciudad Real, Puertollano, and the sampling point in Cabañeros National Park.

In a second series of measurements, aldehydes (formaldehyde, acetaldehyde, acrolein, acetone, propanal, crotonaldehyde, butanal, benzaldehyde, pentanal, tolualdehydes, and hexanal) were measured in six reading rooms of the campus library and also different common rooms of another building of the Faculty of Chemistry. The third series of field measurements was conducted in two classrooms of one school in Ciudad Real and Puertollano and in two homes (living rooms) in Puertollano. All these measurements were carried out in 2012 and 2013. Finally, during August-November 2010 and February-August 2011, carbonyl compounds were measured in the ecological area of Cabañeros National Park [29].

The first series of field measurements was carried out using Analyst® passive samplers, while Radiello® passive samplers were used in the other campaigns. The Analyst® passive sampler was used for assessment only for formaldehyde and acetaldehyde; for this reason and because both aldehydes produce adverse health effect and formaldehyde is the most abundant aldehyde, this study focuses especially on formaldehyde and acetaldehyde, although in some places other carbonyls have also been measured such as the campus library, some places in the Faculty of Chemistry, or Cabañeros National Park.

2.2. Sampling and analytical methods

Radiello® (Fondazione Salvatore Maugeri, Padova, Italy) and Analyst® (Marbaglass, Palombara Sabina, Rome, Italy) passive samplers were used for monitoring carbonyl compounds. The Radiello® passive samplers for carbonyls consist of a stainless steel cartridge filled with

2,4-dinitrophenylhydrazine-coated Florisil® inside a diffusive body, while Analyst® sampler consists of three parts: a polyethylene cylinder, an antiturbulence net (made of silver for outdoor sampling or stainless steel for indoor sampling), and a 2,4-DNPH-coated adsorbent bed (Florisil or silica gel). Analyst® passive samplers were prepared in the laboratory. A detailed description of both passive samplers is given elsewhere [19].

Indoor devices were positioned at a height of 1.5-2.0 m above the floor, in the middle of the room when possible. Outdoor samples were taken simultaneously in the windows or balconies and protected from bad weather conditions by a mountable polypropylene shelter (for Radiello) or stainless steel shelter (for Analyst).

The sampling duration of the Analyst® samplers was 14-20 days, while Radiello® was 7 days. After exposure, the Radiello® cartridges were introduced in their sealed glass tubes, and the Analyst® was cap and stored in the dark and refrigerated until the analysis. Field blanks were transported together with samplers to the sampling point.

The extraction of the hydrazones and the analytical conditions have been described in previous works [19, 29]. Briefly, both Analyst® and Radiello® passive samplers were extracted with 2 ml of acetonitrile (HPLC grade), and the extract was filtered (PTFE 0.45 mm) and analyzed by HPLC (Varian prostar, CA, USA) coupled to a photodiode array detector. For this, 20 µl of the solution obtained after extraction was injected by a sampling loop into a reversed-phase column C-18 (a Varian Microsorb MV 100-5, 25 cm length × 4.6 mm i.d. and a Supelcosil™LC-18 25 cm × 4.6 mm × 5 µm for the Analyst® and for Radiello®, respectively) and detected at a wavelength of 365 nm, according to the literature. The program of the mobile phase was as follows: 0-7 min, 60% acetonitrile (HPLC grade), and 40% water (from a Milli-Q system); 7-20 min, a gradient up to 100% acetonitrile. The flow was 1 ml min^{-1}.

A series of standards (TO11/IP-6A Aldehyde/Ketone-DNPH Mix, Supelco, Bellefonte, USA) containing formaldehyde, acetaldehyde, acrolein, acetone, propanal, crotonaldehyde, butanal, benzaldehyde, isopentanal, pentanal, o-tolualdehyde, m-tolualdehyde, p-tolualdehyde, hexanal, and 2,5-dimethylbenzaldehyde in acetonitrile were used to obtain a five-point calibration curve for each compound in concentration ranges similar to the tested samples (0.2-4 µg ml^{-1}). There were very good linear relationships between concentration and instrumental response for all carbonyls measured ($R^2 > 0.99$).

2.3. Quality assurance

Blank samples, limits of detection (LOD), and reproducibility of the Analyst® and Radiello® passive samplers were assessed for quality assurance. Method detection limits (MDLs) were defined as three times the standard deviation of the blanks. The aldehyde amount in the Analyst® blank samples ranged from 0.06 to 0.11 µg for formaldehyde (estimated air concentration, 0.19-0.35 µg m^{-3}) and from 0.04 to 0.31 µg for acetaldehyde (estimated air concentration, 0.17-1.32 µg m^{-3}). LOD values for blank samples were 0.39 µg for formaldehyde and 0.09 µg for acetaldehyde, corresponding to a concentration of 1.2 and 0.4 µg m^{-3}, respectively, calculated for a period of 14 days. The coefficients of variation in the reproducibility test ($n = 5$) were 5.8% for formaldehyde and 4.5% for acetaldehyde, while for the Radiello® passive samplers

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ranged from 0.5% (acetaldehyde) to 4.5% (m/p-tolualdehyde) for carbonyl compounds except for acetone, which was 10%. Method detection limits calculated for a sampling period of 7 ranged from 0.01 μg m^{-3} for 2,5-dimethylbenzaldehyde and isopentanal to 0.26 μg m^{-3} for acetaldehyde.

3. Results and discussion

Table 1 shows a summary of the formaldehyde and acetaldehyde concentrations in all sampling sites investigated in Ciudad Real and Puertollano.

3.1. Levels of carbonyls in indoor environments

3.1.1. Faculty of chemistry

The Faculty of Chemistry consists of several buildings, and the laboratories sampled are in a different building to the rest of common areas listed in Table 1. These common areas in the case of Inorganic and Organic Chemistry Departments are halls where offices and laboratories are around or near them.

In the laboratories sampled, the formaldehyde levels varied between 4 and 23.5 μg m^{-3} depending on the laboratory, while those of acetaldehyde varied from 1.3 to 13.2 μg m^{-3}. The class practical laboratory showed the highest formaldehyde and acetaldehyde concentrations, while the lowest concentrations were found in Research Laboratory 1. The difference between Research Laboratory 1 and the other two laboratories (Research Laboratory 2 and class practical lab) was the ventilation, a fact that could explain the differences in the concentrations of the two aldehydes [19]. Although literature information is hardly available for carbonyl compounds measured in laboratories, these measurements are in the range of those determined in research laboratories and class practical laboratories in an academic institute in Fortaleza, Brazil [30], and are lower than those determined in Rio Grande University in Brazil [31] for a research laboratory and class practical laboratories as shown in Table 2 for comparison.

Sampling site	*n*	Formaldehyde			Acetaldehyde			
		Average ± SD	Min	Max	Average ± SD	Min	Max	Reference
Ciudad Real (urban area) *Research Laboratory 1*								[19]
Indoor	11	7.7 ± 3.0	4.0	11.6	5.3 ± 2.1	1.3	7.6	
Outdoor	10	1.5 ± 0.4	0.9	2.3	1.7 ± 0.6	0.8	3.1	
Research Laboratory 2	2	18.8 ± 4.0	16.0	21.6	5.5 ± 0.8	4.9	6.0	[19]
Class practical lab	2	19.6 ± 5.6	15.6	23.5	1.2 ± 1.4	11.2	13.2	[19]

Sampling site	*n*	Formaldehyde			Acetaldehyde			
		Average ± SD	Min	Max	Average ± SD	Min	Max	Reference
Office	4	11.3 ± 2.0	8.5	13.3	5.7 ± 1.3	5.0	7.7	[19]
Common areas *Faculty Chemistry*								This study
Inorganic chemistry (2nd floor)	2	9.2 ± 0.6	8.8	9.7	2.0 ± 0.2	1.9	2.1	
Organic chemistry (2nd floor)	2	17.8 ± 0.6	17.4	18.2	2.9 ± 0.2	2.7	3.0	
Library (2nd floor)	2	12.7 ± 0.9	12.1	13.3	2.4 ± 0.07	2.3	2.4	
Reception (1st floor)	2	11.5 ± 0.3	11.2	11.7	2.3 ± 0.006	2.3	2.3	
Hall (1st floor)	2	6.0 ± 0.3	5.7	6.2	1.5 ± 0.03	1.5	1.5	
Coffee area (1st floor)	2	6.1 ± 0.3	5.9	6.2	1.6 ± 0.2	1.4	1.7	
Outdoor	2	1.7 ± 0.4	1.4	2.0	1.8 ± 1.7	0.6	3.0	
Bar	1	13.4	-	-	26.0	-	-	[19]
University library								This study
Ground floor	8	11 ± 1.9	8.4	14.1	5.2 ± 0.9	4.2	6.8	
First floor	8	10.6 ± 1.6	8.6	14.2	5.05 ± 0.8	4.0	5.9	
Second floor	8	11.1 ± 1.4	8.4	15.0	5.1 ± 0.7	4.2	6.1	
Outdoor	4	2.1 ± 0.4	1.6	2.6	2.2 ± 0.5	1.6	2.9	
Home 1								[19]
Living room	1	75	-	-	19.2	-	-	
Kitchen	2	43.7 ± 2.2	42.1	45.2	21.5 ± 4.4	18.4	24.6	
Outdoor	6	2.2 ± 0.5	1.3	2.7	2.4 ± 1.1	0.82	3.55	
Home 2								[19]
Living room	4	46.0 ± 5.6	41.6	53.3	57.4 ± 8.5	43.3	62.2	
Kitchen	2	38.2 ± 3.3	35.8	40.5	69.2 ± 8.2	63.4	75.0	
Outdoor	6	3.1 ± 0.8	1.9	4.2	3.8 ± 2.0	1.2	6.5	
School								This study
Indoor	4	18.9 ± 4.7	14.7	23.1	5.2 ± 1.8	3.6	6.7	
Outdoor	2	1.8 ± 0.8	1.2	2.3	2.1 ± 2.1	0.6	3.6	
Puertollano (industrial area)								
School								This study
Indoor	4	35.4 ± 14.6	21.5	49.2	8.5 ± 5.4	3.7	13	
Outdoor	2	2.0 ± 1.6	0.9	3.1	0.4 ± 0.1	0.3	0.5	

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Sampling site	n	Formaldehyde			Acetaldehyde			
		Average ± SD	Min	Max	Average ± SD	Min	Max	Reference
Home 1								This study
Indoor	8	24.1 ± 7.5	17.4	37.1	15.2 ± 5.0	9.3	21.4	
Outdoor	8	3.1 ± 0.6	2.4	3.8	2.4 ± 0.9	1.5	3.9	
Home 2								This study
Indoor	8	74.8 ± 27.3	37.9	107.5	23.6 ± 10.7	9.6	36.3	
Outdoor	8	3.2 ± 0.7	2.2	4.3	2.4 ± 0.9	1.2	3.5	
Cabañeros (ecological area)								
Outdoor	46	0.96 ±0.54	b.d.l	2.56	0.79 ± 0.49	0.13	1.89	[29]

Table 1. Formaldehyde and acetaldehyde concentrations (μg m^{-3}) in indoor and outdoor environments

In the office, the levels of formaldehyde and acetaldehyde were 11.3 and 5.7 μg m^{-3}, respectively. Formaldehyde and acetaldehyde concentrations were quite similar to those obtained for the offices with no smokers of a public building in Rome [19] and were lower than the levels found in the offices of Rio Grande University [31]. The values for formaldehyde are also in the range of those measured in offices from different countries from Europe [32].

Regarding common areas, formaldehyde and acetaldehyde concentrations ranged from 5.7 to 18.2 μg m^{-3} and from 1.4 to 3.0 μg m^{-3}, respectively. The lowest levels for both aldehydes were found on the first floor (hall and coffee area). The coffee area is located on the right side of the hall, and it is not separated from this by any wall. The hall has an extension of approximately 350 m^2, and there is not any furniture; there are some tables and chairs and two vending machines in the coffee area only. Because of this, it seems reasonable that the low levels of both aldehydes are found here. The highest levels were registered on the second floor especially in the Organic Chemistry Department, where the levels were similar to those obtained in the research laboratory 2 and the class practical laboratory placed in another building. This fact could be due to the reactions between the variety of organic solvents employed and ozone, but ozone levels are low usually in indoor environments, and they have not been measured in this study. Therefore, care must be taken when assuring this. The library is located beside the Organic Chemistry Department, which could influence the levels of formaldehyde found here. The reception is located on the first floor and presents levels of formaldehyde and acetaldehyde higher than those found on the other two sampling points of the first floor, maybe due to the presence of a big copying machine in the room and the emission of ozone with the consequent reaction with the unsaturated VOCs in the air (such as cleaning products) [1].

Not only formaldehyde and acetaldehyde have been measured in these common areas of the Faculty of Chemistry but also other carbonyls have been identified and quantified and are shown in Table 3. These are acrolein-acetone, crotonaldehyde, benzaldehyde, pentanal, p-tolualdehyde, and hexanal. The most abundant carbonyl was acrolein-acetone (both

Site	Formaldehyde (μg m^{-3})	Acetaldehyde (μg m^{-3})	Activity	Reference
Rio Grande University, Brazil	32.3-41.0	18.3-26.2	Office	[31]
Rome	8.9-9.4	4.2-4.7	Office	[19]
Europe	3-33	-	Offices	[32]
Fortaleza, Brazil	0.32-81.6	1.2-4.43	Research laboratories	[30]
Rio Grande University, Brazil	96.5	79.4	Research laboratory	[31]
Fortaleza, Brazil	3.78-60.75	1.4-3.18	Class practical laboratories	[30]
Rio Grande University, Brazil	56.5-161.5	38.1-91.2	Class practical laboratories	[31]
Modena, Italy	1.7-67.8	-	Libraries	[36]
Strasbourg, France	8.6-94.5	3.7-25.9	Libraries	[37]
Helsinki, Finland	8.1-77.8	3.7-41.5	Living room	[45]
Strasbourg, France	6-93	0-66	Living room	[44]
10 European cities	14.4 ± 4.9-30.7 ± 17.8	9.6 ± 2.3-15.8 ± 5.4	Homes	[43]
Bari, Italy	3.2-49	1.3-23.5	Kitchen	[46]
Paris, France	21.7±1.9	10.1±1.8	Kitchen	[39]
Lisbon, Portugal	6.3-23.8	-	Schools	[49]
11 European cities	5.6-49.7	1.4-29.1	Schools and kindergarten	[32]

Table 2. Formaldehyde and acetaldehyde concentrations measured in different indoor environments in previous studies

appear together in the chromatogram) with a range of concentration between 14.2 and 58.3 μg m^{-3}. The rest of carbonyls present concentrations between 0.2 μg m^{-3} for benzaldehyde and 4.1 μg m^{-3} for hexanal (without taking into account formaldehyde and acetaldehyde explained above).

The indoor/outdoor ratio is generally used to infer penetration to indoor environments and indoor sources. An I/O ratio lower and close to one indicates more outdoor sources [33]. In all sites, air concentrations for formaldehyde inside the buildings were between 5 and 13 times higher than outside, which appears to indicate that strong indoor sources exit, clearly determining indoor air concentrations. The same conclusion can be obtained for the pair acrolein-acetone or p-tolualdehyde (I/O = 8-20) and hexanal (I/O = 13-34), but the indoor levels of these two last carbonyls are low in all sampling sites. For the rest of compounds, the main source could be from outdoor even acetaldehyde with a ratio of 2.4-4.4.

Carbonyl	Inorganic hall	Organic hall	Library	Reception	Hall first floor	Coffee area	Outdoor
Formaldehyde	10.1	19.5	13.9	12.6	6.5	6.6	1.5
Acetaldehyde	2.1	3.1	2.5	2.4	1.6	1.7	0.7
Acrolein-acetone	58.3	16.4	14.2	40.1	30.4	22.4	<LOD
Propanal	1.4	0.3	0.2	<LOD	0.9	0.2	<LOD
Butanal	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Croton-aldehyde	0.5	1.3	0.7	0.9	0.6	0.4	0.4
Benzaldehyde	0.3	0.3	0.2	-	0.2	0.2	<LOD
Pentanal	1.0	0.7	0.8	2.1	0.4	0.4	0.2
p-tolualdehyde	0.8	1.0	0.6	0.5	0.7	0.4	0.05
hexanal	1.6	3.4	2.8	4.1	1.8	1.6	<LOD

Table 3. Carbonyls measured and their concentrations (in μg m^{-3}) in the common areas of Faculty of Chemistry

3.1.2. Bar

In the bar of the campus (about 200 m^2), the concentration of acetaldehyde was much higher than that of formaldehyde. The higher acetaldehyde value could be due to the cigarette smoke and combustion processes such as those carried out in the kitchen of the bar, although acetaldehyde is also present in many foods and alcoholic drinks [3, 5]. These levels of carbonyls are lower than expected. Hodgson et al. [34] estimated that cigarette smoking contributed from 57% to 84% to the total formaldehyde levels in the smoking areas of cafeterias where the formaldehyde concentrations varied between 5 and 42 μg m^{-3} when 20-100 cigarettes were being smoked. The combustion of 5-10 cigarettes in a room of 30 m^2 increases the formaldehyde concentrations from 240 to 600 μg m^{-3} [35]. However, formaldehyde levels measured in the bar were low and similar to those found in the teacher's office and in Research Laboratory 1 probably due to mechanical ventilation and the great surface of more than 200 m^2 of the bar.

3.1.3. University campus library

Carbonyl concentrations were also measured in the University Campus Library since paper can emit large amounts of formaldehyde [36]. Six reading rooms of the library and a sampling point outdoor were monitored during four consecutive weeks from February 6 to March 5, 2011. Two passive samplers were placed in two reading rooms on the ground floor and the same on the first and the second floor. The total samples were 28 between indoor and outdoor sampling.

The carbonyl compounds identified in the library were formaldehyde, acetaldehyde, acetone-acrolein, propanal, crotonaldehyde, butanal, benzaldehyde, pentanal, p-tolualdehyde, and hexanal, and their average concentrations were as follows (in μg m^{-3}): 10.9 ± 1.3, 5.1 ± 0.2, 12.4 ± 2.4, 2.5 ± 0.1, 0.4 ± 0.1, 15.4 ± 1.3, 0.55 ± 0.05, 2.9 ± 0.4, 0.8 ± 0.2, and 6.6 ± 1.1, respectively (quoted errors correspond to the standard deviation). Butanal appeared overlapped with an interference (no carbonyl compound) in the samples. Their high levels obtained with respect to the rest of carbonyls together with the UV spectrum indicate that butanal appears overlapped with other carbonyl compound may be 2-butanone. Both compounds appear together in the chromatogram when a standard is introduced under the analytical conditions. Therefore, butanal has not been considered for the discussion. The most abundant carbonyls were acetone-acrolein and formaldehyde. Their concentrations in the individual samples varied from 8.6 to 17.3 μg m^{-3} and from 8.4 to 15 μg m^{-3}, respectively.

Carbonyl	Ground floor	First floor	Second floor	Outdoor
Formaldehyde	11.0 ± 1.9	10.6 ± 1.9	11.1 ± 2.2	2.1 ± 0.4
Acetaldehyde	5.2 ± 0.9	5.1 ± 0.8	5.1 ± 0.7	2.0 ± 0.5
Acrolein-acetone	15.0 ± 1.9	11.1 ± 1.7	11.2 ±1.8	3.8 ± 0.8
Propanal	2.4 ± 0.3	2.6 ± 0.5	2.6 ± 0.4	1.0 ± 0.1
Crotonaldehyde	0.4 ± 0.1	0.5 ± 0.3	0.4 ± 0.3	0.7 ± 0.1
Benzaldehyde	0.5 ± 0.1	0.6 ± 0.1	0.6 ± 0.1	0.3 ± 0.06
Pentanal	3.3 ± 1.0	2.6 ± 0.4	2.7 ± 0.6	1.0 ± 0.1
p-tolualdehyde	0.9 ± 0.5	0.7 ± 0.1	0.8 ± 0.3	0.7 ± 0.3
hexanal	7.7 ± 2.0	5.9 ± 0.9	6.1 ± 0.9	1.7 ± 0.07

Table 4. Levels of carbonyls (in μg m^{-3}) measured in the Campus University Library together with standard deviations

Generally, the concentrations of the carbonyl compounds found in the different reading rooms of the library were low. These values are in the range of those obtained in 20 university libraries in Strasbourg (France) [37], where the levels found ranged from 8.6 to 94.5 for formaldehyde, from 3.7 to 25.9 μg m^{-3} for acetaldehyde, from 2.1 to 58.8 μg m^{-3} for hexanal, from 0.2 to 5.3 μg m^{-3} for benzaldehyde, and from 0.7 to 16.3 μg m^{-3} for propanal. Our measurement values for formaldehyde are also in the range of those reported by Fantuzzi et al. [36] for 16 libraries of the university of Modena (Italy), which ranged from 1.7 to 67.8 μg m^{-3} with an average value of 32.7 ± 23.9 μg m^{-3} (see Table 2). However, the average concentrations for formaldehyde calculated in this study are lower than the studies mentioned above. Formaldehyde, acetaldehyde, propanal, benzaldehyde, and hexanal have usually been detected in libraries [37].

Table 4 shows the concentrations of all carbonyls measured on the different floors of the library. There are not differences between the concentrations measured of the carbonyl compounds in the different reading rooms of the different floors of the library. The indoor/outdoor ratios vary from 0.65 crotonaldehyde, which indicates mainly outdoor sources to 5.1 for formaldehyde indicating mainly indoor sources. Other I/O ratios that could suggest indoor sources but are not strong are 3.3 for acetone and 3.8 for hexanal.

3.1.4. Private houses

Formaldehyde and acetaldehyde measurements were performed simultaneously in the living room and outdoor in Ciudad Real and Puertollano; aldehydes in the kitchens were also measured only in Ciudad Real (see Table 1). Homes were ventilated as usual by opening the windows during the sampling. Two samples were collected at the same time in Ciudad Real, while the samples were collected during 8 consecutive weeks in Puertollano. All houses were located in an area of moderated traffic. Approximate home ages are between 1 and 8 years old in Ciudad Real and Puertollano; only home 2 in Ciudad Real is more than 10 years. This information is important since building materials can emit formaldehyde, but these emissions generally decrease with the age of the house. Smoking people are present in one house of each town.

Formaldehyde indoor air concentration was in average 24.5 and 15.3 times higher than the concentration outdoor in Ciudad Real and Puertollano, respectively, while acetaldehyde was 11.5 and 7.9 times higher in Ciudad Real and Puertollano, respectively. These ratios are similar to those found by Geiss et al. [32] for a new manufacturer house (20.2 for formaldehyde and 9.2 for acetaldehyde); however, the homes in Ciudad Real are more than five years old and between 1 and 8 in Puertollano. This fact indicates that strong indoor sources existed, clearly determining indoor air concentrations and denoted that indoor sources were dominant for these compounds. Indoor materials such as consumer products, furniture, and decorations are important indoor sources [38-41]. Carbonyls such as acetaldehyde are generated from smoking [42]. A smoker person lives in home 2 (Ciudad Real) and presented the highest acetaldehyde levels in both kitchen and living room. Home 1 (Puertollano) is also the home of one smoker, but the frequency of smoking is low; in this case, the levels of acetaldehyde are even lower than the levels obtained in the homes of nonsmokers. Except for home 2 from Ciudad Real, formaldehyde levels were higher than the acetaldehyde ones. Bruinen de Bruin et al. [43] measured formaldehyde and acetaldehyde concentrations in residential environments in ten European cities, demonstrating mean levels in the range of 14.4 ± 4.9 μg m^{-3} (Dublin) to 30.7 ± 17.8 μg m^{-3} (Arnhem) for formaldehyde and from 9.6 ± 2.3 to 15.8 ± 5.4 μg m^{-3} (Budapest) for acetaldehyde, thus confirming low concentrations of aldehydes in European homes. Another recent study measured formaldehyde and acetaldehyde inside the homes of Strasbourg (France) [44]. The indoor levels were in the range of 6 to 93 μg m^{-3} for formaldehyde and from 0 to 66 μg m^{-3} for acetaldehyde. Therefore, the mean concentration of formaldehyde in the indoor air in the present work is in the range of those found in other European cities such as Strasbourg or Helsinki (8.1-77.8 μg m^{-3}) [45] (see Table 2). Indoor acetaldehyde had also a mean concentration similar to that obtained in other European cities (see Table 2), except for home 2 in Ciudad Real wherein concentration is the highest with an average of 57.4 μg m^{-3}. This concentration is in agreement with some living rooms in Strasbourg [44], where the range of concentrations was from 0 to 66 μg m^{-3} for acetaldehyde.

In the case of concentrations of aldehydes measured in the kitchens of Ciudad Real, formaldehyde presents practically the same level for both homes. Our mean value is approximately 40% higher than that reported in previous studies [39] and is in the range of that reported in reference [46] for a study performed in Bari (Italy). For acetaldehyde, the mean concentration registered in the kitchen home 2 is higher than those reported in other European cities.

According to the World Health Organization, the lowest formaldehyde concentration that has been associated with nose and throat irritation after short-term exposure is 100 $\mu g\ m^{-3}$ [47]. Therefore, it represents the recommended maximal value. In our study, there is no such place with formaldehyde values exceeding this level. Despite that, it is important to note that the sampling period was 14 days for the Analyst® passive sampler (homes in Ciudad Real) and 7 days for Radiello® (homes in Puertollano). Thus, our results express an average concentration over a long period and do not provide information about exposure peaks, which must be higher than the average concentration measured. However, other recommended values exist, which were exceeded in our study. For example, the indoor formaldehyde concentrations in the homes monitored exceeded the guideline value of 30 $\mu g\ m^{-3}$ proposed for the prevention of irritant effects [48] referred to a period of 30 min.

Hence, it is necessary to carry out an exhaustive research with more homes monitored in order to assess the health risk. In addition, taking into account the low outdoor pollution levels observed, an adequate airing of the rooms could reduce the indoor pollution by formaldehyde and acetaldehyde. Nevertheless, this study only presents preliminary results of the private homes in Ciudad Real and Puertollano due to the low number of samples. Measurements in Ciudad Real were performed only to check the viability of the Analyst® passive sampler in the indoor environment [19]. Regarding homes in Puertollano, this study presents the preliminary results of a further research. There are not clear differences between the levels of formaldehyde and acetaldehyde registered in the urban and industrial area.

3.1.5. Schools

Two schools were sampling for the present study, one in Ciudad Real and one in Puertollano located in the same area as the homes sampled. Samples were simultaneously collected in two classrooms from each school and outside the building. Every classroom has an area of about 50 m^2, and there are between 20 and 27 children. The school in Puertollano is more than 20 years old, and the classrooms have not been renovated recently, while in Ciudad Real, the school is also old but the classrooms were renovated 7 years ago. The ventilation in both schools is natural by opening the windows during 15 min per day.

The concentration of formaldehyde and acetaldehyde was slightly higher for the industrial area 35.4 ± 14.6 and 8.5 ± 5.4 $\mu g\ m^{-3}$, respectively, versus 24.3 ± 4.7 and 6.2 ± 1.8 $\mu g\ m^{-3}$, respectively, for the urban area. The concentrations of formaldehyde were more abundant than the acetaldehyde ones. In both schools, the air concentrations for both aldehydes inside the buildings were higher than outside. The indoor/outdoor ratios for formaldehyde and acetaldehyde in Ciudad Real were 13.5 and 2.9, respectively, and were higher for both aldehyde in the school from the industrial area 17.7 and 21 for formaldehyde and acetaldehyde, respectively. Except acetaldehyde in the school from Ciudad Real, formaldehyde and acetaldehyde are mainly indoor pollutants derived from indoor sources.

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Our data for formaldehyde are similar or a bit higher than the levels registered in fourteen schools in Lisbon (Portugal) [49]. The levels of both aldehydes are in agreement with the concentrations registered in eleven European cities [32] (see Table 2).

The levels of formaldehyde exceeded the guideline value of 30 μg m^{-3} proposed for the prevention of irritant effects [48] in the industrial area. High levels of formaldehyde are likely associated with the age of building and renovating activities of old buildings. However, both schools are more than 10 years old, and they did not have recent renovation therefore, these levels are due to other sources.

3.2. Levels of carbonyls in outdoor environments

In all sampling sites, formaldehyde and acetaldehyde were present in both indoor and outdoor air. Generally, in all sites, air concentrations for these aldehydes inside the buildings were higher than outside. Mean values for formaldehyde in Ciudad Real varied between 1.5 and 3.1 μg m^{-3}, while acetaldehyde varied between 1.7 and 3.8 μg m^{-3} for the sampling period of December-February. Outdoor acetaldehyde concentrations were similar to those of formaldehyde. In the case of the industrial area, formaldehyde varied in the range of 2 (in March) and 3.2 μg m^{-3} (May-June) and acetaldehyde varied between 0.4 (in March) and 2.4 μg m^{-3} (May-June), being formaldehyde levels slightly higher than the acetaldehyde ones. Similar values were found in samplings conducted in rural and semirural areas [50-52].

Formaldehyde/acetaldehyde ratio has been proposed as an indicator of the biogenic source of formaldehyde [53] and can vary between 1 (urban area) and 10 (deciduous forest). This ratio for Ciudad Real and Puertollano is between 0.9 and 1.3 reflecting typical values for urban air. The formaldehyde/acetaldehyde ratio for the sample taken in the school in Puertollano gave a value of 5, which could imply a biogenic contribution in the early spring.

A study about levels of carbonyls was carried out in the ecological area of Cabañeros National Park [29]. Twelve compounds were identified and quantified: formaldehyde, acetaldehyde, acetone-acrolein, propanal, crotonaldehyde, butanal, benzaldehyde, isopentanal, pentanal, o-tolualdehyde, m/p-tolualdehyde, and hexanal (the sum of m/p-tolualdehyde and acetone-acrolein was reported because they could not be well separated by the analytical method). The most abundant carbonyls were hexanal, acetone-acrolein, formaldehyde, and acetaldehyde.

Because of the study covered all seasons, August 2010 was the most carbonyl-polluted month followed by July 2011 and September 2010. October and November 2010 were the months with lower concentration of carbonyl compounds showing an apparent seasonal variation with maximum values observed in summer months. The concentrations of the carbonyls were as follows: acetone-acrolein mixing ratios ranged from 0.35 in February to 4.52 μg m^{-3} in June 2011, with an average of 1.78 μg m^{-3}, while ambient levels of hexanal varied from 0.67 μg m^{-3} in October to 1.72 μg m^{-3} in April; the average concentration during the sampling period was 1.06 μg m^{-3}. Formaldehyde was in the range of values below detection limit and 2.56 μg m^{-3} in October and June, respectively, with an average concentration of 0.96 μg m^{-3} and acetaldehyde varied from levels below detection limits in February, March, and April to 1.89 μg m^{-3} in June. The concentrations of other carbonyls ranged from non-detected to 1.18 μg m^{-3}.

The seasonal cycles obtained for formaldehyde, acetaldehyde, and acetone-acrolein with respect to the other carbonyls suggest different formation mechanism and sinks compared to the others. This could be due to photochemical processes (oxidation of biogenic and even anthropogenic hydrocarbons that arrive to the area under determined meteorological conditions) and also the direct emission from vegetation. For example, two Mediterranean tree species such as *Quercus ilex* (holm oak), one of the most abundant oak in the study area, and *Pinus pea* (Italian stone pine) emit formaldehyde and acetaldehyde [54, 55].

The formaldehyde and acetaldehyde concentrations measured at Cabañeros National Park are in the same range or lower than the levels reported in other forests or rural areas (Germany [56] and Brazil [57]). Our data are similar to those reported in the small village of Covelo in Portugal, considered as a rural/forest site [58].

On the other hand, the levels found in the ecological area during the months of February and March for formaldehyde (0.51 and 0.59 μg m^{-3}) and acetaldehyde (0.33 and 0.29 μg m^{-3}) are lower than those registered in the urban (outdoor samples collected at the same time as common areas of Faculty of Chemistry or University Library) and industrial area (outdoor samples collected in the school) during the same period. Also, the levels of both aldehydes during the months of May and June were lower (1.15-1.37 μg m^{-3} for formaldehyde and 0.70-1.09 μg m^{-3} for acetaldehyde) than the levels registered in the industrial area during the same months in the outdoor samples collected in the homes.

3.3. Health risk evaluation

Formaldehyde is classified in Group 1 by IARC. It was based on inhalation causing squamous cell carcinoma in rats and nasopharyngeal cancer in humans [3]. Recently, the classification has been expanded with formaldehyde causing leukemia and limited evidence of sinonasal cancer in humans [59]. The lowest concentration reported to cause sensory irritation of the eyes in humans is 0.38 mg m^{-3} for 4 h. Increases in eye blink frequency and conjunctival redness appear at 0.6 mg m^{-3}, which is considered equal to the no-observed-adverse-effect level (NOAEL). There is no indication of accumulation of effects over time with prolonged exposure, and there is no evidence indicating an increased sensitivity to sensory irritation to formaldehyde among people often regarded as susceptible (asthmatics, children, and older people) [60].

The formaldehyde exposure-response relationship is highly nonlinear and biphasic, supporting a NOAEL that allows setting a guideline value [60]. This means that it cannot be assumed a low-dose linear relationship for the carcinogenic effects, and therefore, the calculation of the incremental lifetime risk of cancer for formaldehyde, assuming a low-dose linear relationship, would give a value highly overestimated and it would be meaningless.

As commented above, WHO established a guideline value for formaldehyde of 100 μg m^{-3} that should not be exceeded for any 30-min period of the day [47]. This short-term guideline will also prevent effects on lung function as well as long-term health effects, including nasopharyngeal cancer and myeloid leukemia [60].

We can compare our data with the short-term guideline value of 100 μg m^{-3}. In our study, the maximum values registered in the different environments were below 100 μg m^{-3}, except for home 2 in the industrial area that registered a maximum value of 108 μg m^{-3} during one of the 8 weeks sampled. The average concentrations for formaldehyde found in this study ranged from 6 to 75 μg m^{-3} in indoor environments, while outdoor concentrations were considerably lower. These values are below the guideline value considered preventive of carcinogenic effects; however, our results represent an average value during 1 or 2 weeks of exposition, and this guideline value is referred to a period of 30 min. Nevertheless, as long as formaldehyde concentrations are below 100 μg m^{-3}, there should be no chance of developing cancer.

On the other hand, the most important way to control the indoor formaldehyde concentration is the air exchange rate and the use of low-emitting materials and products. Environmental tobacco smoke and ozone-initiated reactions of alkene compounds may contribute to temporary peak levels [60]

4. Conclusion

This paper presents an overview of the concentrations of priority aldehydes observed in indoor and outdoor air in an urban and an industrial area of central-southern Spain. Very few studies have been carried out in the indoor air of Spain. Therefore, we have tried to gather the data previously published about formaldehyde and acetaldehyde in this region and other new data to obtain a general view of the levels in different outdoor and indoor environments.

From the results, we can conclude that the highest concentrations of formaldehyde and acetaldehyde are found inside the homes and schools. The levels of formaldehyde in laboratories or in rooms near laboratories, where many kinds of solvents are used, are much lower. Overall indoor and outdoor concentrations of formaldehyde and acetaldehyde in all sites sampled were below the threshold limit of 100 μg m^{-3} proposed by WHO [47] associated with nose and throat irritation and also to prevent all types of cancer. Therefore, it represents the recommended maximal value. In our study, there is no such place with formaldehyde values exceeding this level. Despite that, it is important to note that the sampling period was 14 and 7 days for Analyst® and Radiello®, respectively. Thus our results express an average concentration over a long period and do not provide information about exposure peaks, which must be much higher than the average concentration measured. On the other hand, the indoor formaldehyde concentrations in the homes and one school monitored exceeded the recommended guideline value of 30 μg m^{-3} proposed by Kotzias et al. [48] for the prevention of irritant effects. Also this value is referred to a period of 30 min.

Therefore, although the indoor sources are dominant for all sites sampled, the most important to be studied are at homes and schools. This is only a preliminary study about the levels of formaldehyde and acetaldehyde in homes and schools due to the low number of samples, and an exhaustive research is necessary in order to better characterize the chemical composition of the air that people breathe daily and to assess the health risk.

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