Investigation of indoor air volatile organic compounds concentration levels in dental settings and some related methodological issues

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Summary. The assessment of indoor air volatile organic compounds (VOCs) concentration levels in dental settings has a big health relevance for the potentially massive occupational exposure to a lot of diverse contaminants. The comparison of the VOCs profile relative to indoor conditions and to the corresponding outdoor concentrations, as well as the discovery of possible correlations between specific dental activities and VOCs concentration variations are of utmost importance for offering a reliable characterization of risk for dentists and dental staff health. In this study we review the most relevant environmental studies addressing the VOCs contamination level in dental settings. We analyze the methodological problems this kind of study must face and we report preliminary results of an indoor air investigation, carried out at dental hospital in Italy, the "Ospedale odontoiatrico George Eastman" of Rome, in which general lines for the analysis of dental settings in environmental terms are sketched. The aim of this work is to identify the kind of problems a typical enclosed (non-industrial) environment indoor air investigation has to cope with by means of the analysis of a case study.

Key words: dental setting, volatile organic compounds, indoor/outdoor air, methyl-methacrylate, aldehydes, dental setting, dental emergency unit, total volatile organic compounds.

Riassunto (*Indagine dei livelli di concentrazione dei composti organi volatili (COV) nel presidio odontoiatrico ed alcune relative problematiche metodologiche*). La valutazione dei livelli di concentrazione dei COV nel presidio odontoiatrico ha una grande rilevanza per la potenziale elevata esposizione professionale a molti e diversi contaminanti. Il confronto tra i livelli di concentrazione dei COV nell'*indoor* e nell'*outdoor* della struttura odontoiatrica, come pure l'indagine di possibili correlazioni tra specifiche procedure odontoiatriche e relative variazioni di concentrazioni dei COV, sono di grande importanza ai fini di una attendibile caratterizzazione del rischio per la salute degli odontoiatri e staff odontoiatrico. In questo lavoro vengono analizzati gli studi più rilevanti dal punto di vista ambientale effettuati nel settore dei COV in strutture odontoiatriche descrivendo le problematiche metodologiche che questo tipo di indagine comporta. Vengono inoltre riportati i risultati preliminari di un'indagine, effettuata presso l'Ospedale odontoiatrico George Eastman di Roma, nella quale sono schematizzate le linee generali per l'analisi degli ambienti interni (*indoor*) dei presidi odontoiatrici. Lo scopo di questo lavoro è quello di individuare le principali problematiche che possono porsi nella progettazione di una tipica indagine dell'aria *indoor* di un ambiente confinato (non-industriale), per mezzo dell'analisi di un caso di studio.

Parole chiave: presidio odontoiatrico, composti organi volatili, aria interna/esterna, metil-metacrilato, aldeidi, pronto soccorso odontoiatrico, composti organi volatili totali.

INTRODUCTION

The most important environmental threat in indoor areas was widely recognized in the volatile organic compounds (VOCs) concentration levels that could in principle greatly surpass the baseline outdoor levels [1-9].

VOCs are of great concern because of their adverse health effects [10]. The health effects of exposure to VOCs in the non-industrial indoor environment range from sensory irritation at low/medium levels of exposure to toxic effects at high exposure levels [11]. Moreover VOCs have been implicated as causative agents in asthma and building-related illness [12].

In the case of dental settings, both substances (such as acrylate compounds, organic solvents, disinfectants, etc.) and dental materials routinely used in the course of dental procedures can spread into

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air within the dental working environment and affect the related indoor air quality possibly giving rise to dermatological and respiratory effects [13].

Only few airborne volatile organic compounds during dental procedures have been thoroughly investigated. For example, Henriks-Eckermann *et al.* [14] investigated the exposure levels of dental personnel to airborne methacrylates during the placing of composite resin restorations in six dental clinics in Finland. Both area and personal sampling were performed, but special attention was paid to the measurement of short-term emissions from the patient's mouth.

A recent study [15] investigated the exposure levels of methyl methacrylate (MMA) and 2-hydroxyethylmethacrylate (2-HEMA) in dental clinics.

More recently a questionnaire based study [16] concerning the exposure of dentists and dental staff to the total burden of contaminants from material, solvents and disinfectants used in dentistry has also been reported. The exposure of dental workers to acrylate compounds, mercury amalgam, solvents or disinfectants was investigated with a special emphasis to the risk of miscarriage. Exposure to acrylate compounds, disinfectants and solvents was assessed on the basis of data on occupation, working tasks and occupational exposure during the first trimester of pregnancy obtained by means of the administration of questionnaires. The questionnaire included questions on the frequency of placing and removing amalgam and composite resin fillings and the trade names of the used products, the frequency of using disinfectants.

Even though the questionnaires are very detailed, they may be affected by many possible biases that cast doubts on the general validity of the study [17], due to the possible over- and under-reporting of exposure .

From our point of view, in order to design a novel, and possibly as much as possible unbiased, investigation of VOCs concentration levels related to dentistry settings, the only two really relevant studies to take into consideration are those by Godwin *et al.* [18] and by Helmis CG, *et al.* [19].

Helmis CG, *et al.* assessed the burden of volatile organic compounds in a dental clinic in terms of the aggregate measure "Total Volatile Organic Compounds" (TVOC) [20] rather than explicitly taking into account the concentrations of all analysed VOCs individually. On the basis of the technical definition of TVOC proposed by an European Collaborative Action (ECA-IAQ 1997) [11], the TVOC parameter only represents a narrow chromatographic window of organic compounds that are volatile. In other words, TVOC comes from the summation of VOC concentrations (in mg/m^3) within a specific chromatographic window leaving outside other potentially relevant pollutants.

Godwin *et al.* in their study on a dental setting, beside the assessment of total volatile organic compounds (TVOC), investigated individual volatile compounds and quantified the most abundant (methanol, methyl-acrylate (MA), methyl-methacrylate (MMA) and Iso-methyl metacrylate).

What is lacking in both the studies, that in turn motivates our specific study, is a specific attention to the boundary conditions of the chemical measurements that could affect the specific outcomes of the study and thus not allowing to give a reliable estimation of the effective concentration level of VOCs. Of utmost importance in this view is, in our opinion, the sketching of correlations between specific dental activities and VOCs concentration variations.

The dental setting is a complex environment in which a lot of diverse operations take place and in which different patterns of exchange with outdoor do exist.

A lot of boundary conditions like the crowding of working stations (dental chair partitioning), the ventilation design, the style of work of different professionals, the time course of subsequent dental procedures and the related routine measures for the control of infections can deeply affect the obtained results.

In this paper we examine the only two available studies on the indoor air quality of dental settings in order to derive some hints, both on the positive (what to do) and negative (what to avoid) sides, for our specific investigation. We analyze some methodological issues this kind of study must face and we report a pilot study of indoor air VOCs investigation, carried out at the biggest dental hospital in Italy, the "Ospedale odontoiatrico George Eastman" of Rome, in which the general lines for the analysis of dental settings are sketched, and the preliminary results of some VOCs (BTEX, MMA and few aldehydes) concentrations are given.

INDOOR AIR QUALITY (IAQ) INVESTIGATION IN RESIDENTIAL AND NON-INDUSTRIAL BUILDINGS: VOCS AND TVOC MEASUREMENTS

The specific VOCs that can be detected in indoor air, vary depending on the methods used for measurements. The VOCs detectable in a single building may consist of hundreds of different organic compounds which makes analysis and risk assessment (including combined effects) for these compounds an exceptionally difficult task [20].

Because of the complexity of measuring airborne concentrations of large numbers of individual VOCs, measurement methods that indicate the total concentration of a broad range of indoor airborne VOCs, are sometimes employed. Thus, in these cases, the term "total volatile organic compound" or "TVOC" concentration is used and it refers to the resulting concentration of multiple aisborne VOCs.

In this regard, it is worth to note that an European Collaborative Action (ECA-IAQ 1992) [20] for deriving indoor air quality guidelines for VOCs (excluding formaldehyde and carcinogenic VOCs), proposed two practical approaches. Both approaches use the term TVOC but adopting different definitions.

One approach takes into consideration, for the total VOC (TVOC) concentration, four exposure ranges of increasing concern (measured by gas chromatography (GC) techniques and a flame ionisation detector calibrated against toluene) as follows: a comfort range (< 0.2 mg/m^3), a multifactorial exposure range (0.2-3 mg/m^3), a discomfort range (3-25 mg/m^3), and a toxic range (> 25 mg/m^3).

The other approach establishes that TVOC concentration should not exceed the value of 300 µg/m^3. Such TVOC concentration was apportioned to different chemical classes, as follows:

1. Alkanes: 100 µg/m^3;
2. Aromatic hydrocarbons: 50 µg/m^3;
3. Terpenes: 30 µg/m^3;
4. Halocarbons: 30 µg/m^3;
5. Esters: 20 µg/m^3;
6. Aldehydes and ketones (excluding formaldehyde): 20 µg/m^3;
7. Other: 50 µg/m^3.

Furthermore, no individual compound should exceed 50% of the average value of its class or exceed 10% of the measured TVOC value.

Another European Collaborative Action (ECA-IAQ 1997) [11] recommended a definition of TVOC and a method for sampling and analysis. Beside specific recommendations of analytical kind, what is important to stress here are the following two main principles informing the above mentioned guidelines.

1. For detecting insufficient or poor ventilation of an enclosed environment, TVOC concentration measured by means of a direct reading instrument may be used. In this case the TVOC entity may be considered as an indicator of insufficient or poorly designed ventilation.
2. For identifying high polluting activities of an enclosed environment, TVOC concentration measured by means of a direct reading instrument with sufficiently high time resolution, may be used. This is done by measuring the concentrations at different positions in a space and comparing the relative variations in concentrations with that expected from the type of ventilation in use in the investigating space. In this case the TVOC entity may be considered as an indicator of the presence of high polluting activities in an indoor environment.

The above principles clearly point to the crucial importance of boundary conditions, such as ventilation, heterogeneity of space, time course, as the main modulators of the outcome of environmental analyses. As a matter of fact, if high TVOC concentrations occur in a building, this may either indicate that there are strong indoor or outdoor sources or, if this is not the case, that general or local ventilation is inadequate.

AN EXAMINATION OF THE TWO AVAILABLE STUDIES ON INDOOR AIR QUALITY IN DENTAL SETTING

Both Godwin *et al.* [18] and Helmis CG, *et al.* [19], addressed the problem of VOCs in dental setting mainly in terms of TVOC measurements.

In the study of Godwin *et al.* [18], the investigated dental setting has an area of 2400 ft^2 ($\cong$ 240 m^2) and consists of the following separate areas:

- 5 dental operatories room (with a dental chair);
- reception/waiting area/office administration;
- laboratory room;
- sterilization room;
- darkroom;
- staff and patients restrooms.

The analysed dental setting operates in one shift (08:00 a.m-05:00 p.m) and it is mechanically ventilated.

Simultaneous indoor and outdoor air TVOC real-time monitoring 24 hours/day for a 1-week period, were carried out at three sites of the dental setting, as follows:

1. at a dental chair partitioning, around 1 m behind the dental chair and 1.5 m above the floor;
2. at the laboratory, under the bench containing the model trimmer and sink;
3. at an outdoor window of the investigated dental setting.

TVOC concentrations were measured using photoionization detectors (ModuRae model) calibrated with 4 ppm toluene.

As a result, during a 24 hours/day, the trend of continuous indoor air TVOC concentration, at the dental chair partitioning, reported in a scale 0-4 ppm, showed TVOC concentration values never reaching the value of 1 ppm (expressed as toluene equivalent) and sometimes not detected ($\cong$ 0 ppm) by the used instrument. However, the TVOC concentration trend showed no net difference between the working and non-working hours.

Beside the TVOC monitoring, individual volatile organic compounds were also measured by collecting air samples in evacuated stainless steel passivated SUMMA canisters, over 2-4 hour periods and during the same week and the normal work hours (8 a.m-5 p.m). The collected samples were analyzed for 77 compounds using gas chromatography/mass spectroscopy (GC/MS). The most abundant individual volatile organic compounds quantified were methanol, methyl-acrylate, methyl-methacrylate (MMA) and isobutyl-methacrylate. Such individual quantified VOCs concentrations at the three locations did not highlight any clear difference between the monitored locations in which different dental activities took place. However, concerning the outdoor concentrations of such individual VOCs, as stated by Godwin *et al.*, the outdoor site sampling was somewhat affected by indoor sources contaminants due to the location of the window.

All in all, the Goldwin *et al.* study gives us an indication of a negligible indoor air VOCs pollution in their investigated dental setting.

Helmis CG, *et al.* [19], measured only the TVOC parameter, over a period of three months, during both working days and weekends, in a selected dental clinic containing a room equipped with 38 dental chairs (as deduced from the figures and tables in their study). The dental clinic has an area of 290 m^2 and operates in two shifts (08:00-12:30 and 13:00-17:00) with 70-100 occupants in every shift and it is naturally ventilated.

TVOC concentrations were measured using two photo-ionization detectors (FIDs) (IAQRAE and ppbRAE of RAE systems, resolution: 10 ppb and 1 ppb respectively, accuracy: 10%) calibrated with isobutylene.

Indoor air TVOC real-time monitoring 24 hours/day for a 3-month period, were carried out in the dental working.

During the working hours, indoor air displayed an average TVOC concentration value of 1900 μg/m^3, with maximum concentration values, varying between 2000-5500 μg/m^3. During the non-working hours, including also the night and weekends, it was found an average TVOC concentration value of 950 μg/m^3.

From these data we can appreciate the huge difference between the Goldwin *et al.* [18] and Helmis CG, *et al.* [19] outcomes, probably due to the different layout and ventilation of the studied dental settings, as well as to the different types of dental working activities that take place in each dental setting.

The difference between TVOC concentration in working hours and non-working hours observed by Helmis *et al.* is an interesting, albeit rough, preliminary indication of a correlation between working activity and pollution. Helmis *et al.* attributed the extremely high observed TVOC concentrations to the nature of the materials and substances used for the dental procedures, which were mainly acrylic, while in the same time they stressed the crucial role played by the ventilation conditions.

The maximum values observed, varying between 2000-5500 μg/m^3, were associated with the use of detergent products for cleaning and disinfecting the surfaces of the working posts at the beginning and the end of each shift. It is important to note that Helmis *et al.* found background concentrations (950 μg/m^3) much higher than the outdoor concentrations of TVOC (of 140 μg/m^3, as derived from spot outdoor measurements with the portable instrumentation). This was attributed to: a) the cleaning of all surfaces at the end of working day and to the clinic kept closed during the non-working hours and weekends; b) the possibility that during the working hours the walls absorb TVOC and re-emit them during the non-working hours.

Other intensive measurements of TVOC, at two different positions of the same investigated room (dental area), confirmed the presence of high TVOC concentrations.

At one position, that within an area of the room in which some machines for grinding, smoothing and polishing acrylic materials were present, the obtained TVOC concentrations were twice as high as those of the other position. Such difference in concentration level was attributed to the presence and work of machines for grinding, smoothing and polishing acrylic materials that acted as additional TVOC sources.

In this regard, it is worth noting that it is much more convenient, for increasing the generalization power of a study, to identify all the possible sources of "wild variation" *before* and not *after* the completion of the study. This will limit the risk of *post hoc* explanation that dramatically lower the relevance of a study. By definition a *post hoc* explanation can be attached to any piece of evidence. Clearly we are aware that *post hoc* explanations, in a complex field like environmental science is, cannot be wholly avoided.

If we consider the methodology used in the study of Helmis *et al.* for the TVOC investigation, under the TVOC parameter definition and the indications for its use proposed by the European Collaborative Action [11, 20], the obtained results indicate both an insufficient or poorly designed ventilation of the investigated dental setting and the presence of high polluting activities (*e.g.,* grinding, smoothing and polishing acrylic materials).

In fact, they measured the TVOC concentration in a space and compared concentrations with that expected from an hypothetical ventilation design that would allow TVOC concentrations not exceeding the limit of 300 μg/m-3 [11, 20].

Furthermore, the measurements of TVOC concentrations carried out, by means of an instrument with high time resolution, at two different locations of the dental space, allowed the identification of high polluting activities (grinding, smoothing and polishing acrylic materials), by comparing concentration variations with the activity pattern.

While Helmis CG, *et al.* [19] attributed the observed TVOC level to specific acrylic substances used as dental material in the investigated area, Godwin *et al.* [18] did not find any consistent association between the dental material used and the concentration levels of some MA compounds.

From these two studies we may draw the following considerations:

- the different layouts and ventilation designs of the investigated dental settings together with the different dental activities that take place do not allow any comparison between the two situations;
- dental settings become more complicated to compare each other if we consider that they are located in different urban areas, where additional pollution sources including traffic can affect the indoor air quality;
- while the data coming from each investigated setting may be representative of many other dental settings, extrapolation to the general case is not practically feasible, as also stated by Godwin *et al.* [18] since variation among dental settings layout, dental procedures and protocols in force can significantly affect the outcome;
- possible relevant contamination concentration modifiers are the existent partitioned dental chairs, layout ant ventilation design, the types and number of den-

tal procedures carried out, work shift, dental materials and substances used in the dental procedures and the procedures for the control of infections (such as cleaning, disinfecting, chemical sterilization etc.).

We drew on the lack of consistent indications, as for the VOCs sources linked to dental activities, to think of a strategy, potentially overcoming the above sketched methodological limitations, by both taking explicitly into consideration the effect of potentially modifiers factors as covariates, and adopting a correlative attitude in which the VOCs concentrations are correlated with external varying parameters, such as the number of dental procedures that take place and the outdoor air VOCs concentrations.

PLANNING THE INDOOR AIR STUDY OF DENTAL SETTING: A CASE STUDY

The first step of the planning of an indoor air VOCs study of dental settings concerns the selection of a suitable sample that would be representative of both current dental settings (as they stand with current dental area layout, spaces and apparatus) and dentistry settings (namely current dental care and work protocols, materials and substances in use in dentistry).

This issue, as we stressed above, has to deal with a lot of ancillary considerations ranging from ventilation, crowding, size, seasonality and in general all the boundary conditions affecting the core problem. This predominance of the boundary conditions over the apparent main problem (VOCs concentration) is common to all environmental studies that, by definition, dealing with "environment" have the multiplicity of the aspects collapsing in the word "environment" as object of study.

Thus, in planning the indoor air study of dental setting, the two most basic questions are:

- which type of dental setting(s) (dental clinic, dental hospital or private dental office, dental partitioning etc.) and size (in terms of number of patients treated per day, of number of dental chair partitioning etc.) do we take as samples;
- which main local features of the specific setting do we take as potential effect modifiers.

Basically, the size of a dental work area can range from single dental chair to a large area of dozen of dental chairs. For example, in the case of the study of Helmis that investigated a common space divided by panels into 19 compartments (each containing two dental chairs). While the dental setting investigated by Godwin included, among others, 5 dental operatory room, specifically 5 separate dental chairs partitioning each with a single dental chair.

Selection of a dental and dentistry setting sample

The dental hospital "Ospedale odontoiatrico George Eastman" of Rome was selected and the related dental emergency ward was chosen for the investigation; being the only dental facility that operates 24 hours a day, treats about 38 000 patients per year. This allows for a fairly constant level of possible pollution (seasonal effect ruled out) and of a quite standard use of dental materials and substances.

The patients referring to the emergency ward are quite numerous and heterogeneous in terms of administered dental procedures. Both factors – patient volume and related dental status – may constitute an interesting sample, that could be large enough to investigate correlations among the dental activities carried out, the number of patients and the possible contamination of the ward. In fact as shown in *Table 1*, that reports the types and number of dental procedures carried out during the last six years, the trend of the dental activity performed is, with a good approximation, quite constant (in terms of number and types of dental procedures per year carried out, quantity and type of materials and substances used per year etc.).

The dental hospital "Ospedale odontoiatrico George Eastman" of Rome consists of an individual three-floor building. The dental hospital is located in a densely populated urban area of the city of Rome, with heavy traffic streets due the nearby university, medicine departments, ambulatories, clinics etc. The hospital building construction dates back to the 1950s, and has been refurbished in the last years. Refurbishment

Table 1 | [(a)] *Trends of types of dental pathologies in patients referred to dental emergency ward in the last six years*

Year	Total dental procedures carried out	Pulpitis No. dental procedures	Pulpitis %	Periodontitis acute No. dental procedures	Periodontitis acute %	Periodontitis chronic No. dental procedures	Periodontitis chronic %	Abscess No. dental procedures	Abscess %
1	15934	4719	29.62	5193	32.59	2778	17.43	3244	20.36
2	16838	5293	31.43	5352	31.78	2750	16.33	3443	20.45
3	16400	4665	28.44	5671	34.58	2609	15.91	3455	21.07
4	15338	4061	26.48	5235	34.13	2682	17.50	3360	21.91
5	14953	3783	25.30	5054	33.80	2957	19.77	3159	21.13
6	13698	2918	21.30	4501	32.86	3251	23.73	3028	22.10

[(a)] *The listed dental pathologies entail the following dental procedures:*
- *procedures necessary to relieve pain, or eliminate acute infection –* e.g., *starting root canal treatment on infected teeth, draining abscesses and infected areas;*
- *procedures involving application of medications, temporary fillings for fractured teeth.*

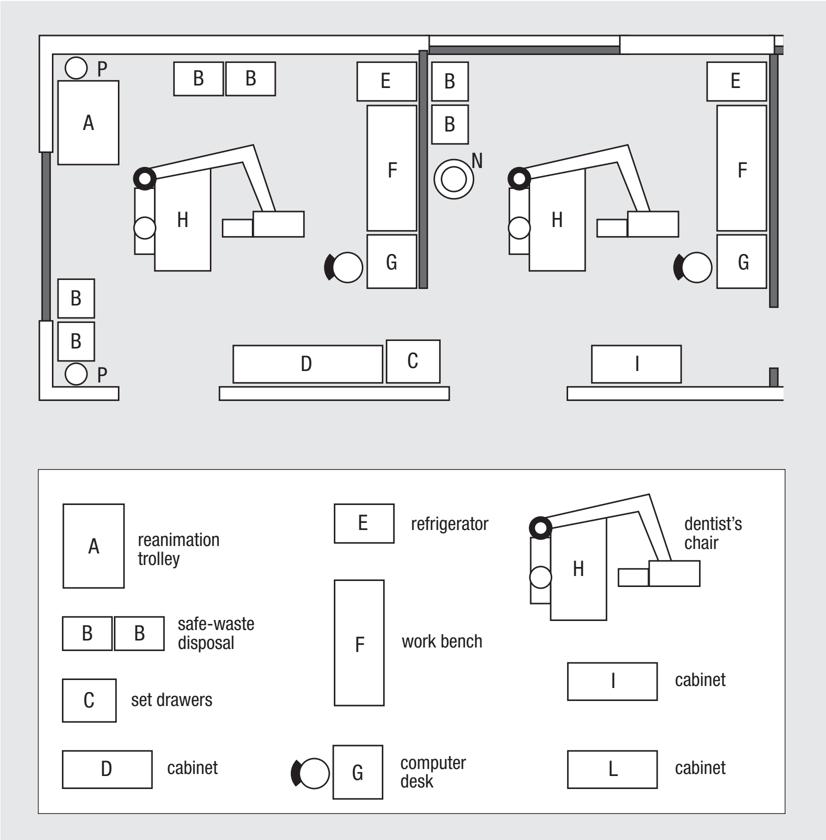

Fig. 1 | *Layout of the dental working area monitored.*

comprises of the installation of new furniture, renewal of wards internal layout, wall painting, lying of new insulation.

The investigated emergency unit of the hospital is placed on the ground floor of the three-floor hospital building. Several services (such as hall, waiting room and the reception of the hospital) are on the ground floor as well, in the vicinity of the emergency unit. The floor of the dental emergency ward is covered with a PVC flooring. All working area is naturally vented by windows.

The above sketched features make the chosen site almost ideal for controlling the relative importance of different environmental factors on the observed pollution levels.

Layout of the monitored working area

For testing, an area of the emergency unit divided by panels into two compartments (dental chairs partitioning) was chosen.

As shown in *Figure 1*, that reports the layout of the monitored working area, the workstation has two entrance doors, both communicating with the reception area. Its layout of design includes two dental chairs partitioning. Each dental chair partitioning has approximately an area of 15 m^2. In each dental chair partitioning it is present the necessary for the visit, the basic diagnostics and first aid treatments.

The total space appears as a common environment since these two dental chairs partitioning are just separated, only for the privacy of the patients, by melamine panels which are 1.40 m high.

Common cabinets or set drawers, containing tools or chemicals, are also available for a common use. The patient is introduced into one of the dental chair partitioning and invited to seat in order to undergo the preliminary visit and treatment. Two patients, one per each dental chair, can be cured at the same time.

Dental procedures carried out in the monitored working area

Table 2 reports the types and number of dental procedures carried out during the three monitored periods. By protocol, only such procedures are allowed in the emergency ward.

As reported in *Table 2*, a small percentage of procedures concerned the removal of mercury amalgam and composite fillings. By protocol at the emergency ward, only temporaries fillings that do not involve neither mercury amalgam nor composite filling materials are allowed.

The materials and chemical agents used during the course of the dental procedures carried out in the monitored periods are:

- eugenol (temporary cement);
- carbocaine;
- m-cresol, formalin and glutaraldehyde are ingredients of substances sometimes used as root canal antiseptics;
- chlorhexidine.

The intermediate level dental work surface disinfectants contain, as active ingredients o-phenylphenol, benzoyl-p-chlorophenol and n-alkyl-n-benzyl-n,n-dimethylammonium chloride.

Indoor/outdoor air sampling method

For gaining an immediate information on the presence of volatile organic compounds in indoor/outdoor air of dental setting, an attempt is made in performing a fast and easy-to-use method of air sampling, as the emergency unit is operating 24 hours-a day and crowded every time by out-patients. Passive samplers were used for indoor and outdoor air sampling.

Sampling indoor air quality can be accomplished using several methods. For sampling indoor air quality in indoor areas (*e.g.,* office building, school, hospitals, and non industrial building) with expected low concentrations (with respect to industrial workplaces) of organic chemicals, passive sampling is more appropriate than active pumped sampling. Moreover it is a method less intrusive for the dental staff and more appropriate when the aim of investigation is the evaluation of the extent of a time-weighted average (TWA) human exposure to VOCs by inhalation route [21, 22].

VOCs measurements: BTEX, MMA, Aldehydes

Among the large number of possible VOCs, we selected the following compounds: benzene, toluene, ethylbenzene, and m-o-p-xylenes (BTEX), methyl methacrylate (MMA), and six aldehydes (formaldeh yde, acetaldehyde, propionaldehyde, benzaldehyde, n-butyraldehyde and lutaraldehyde).

This choice stems from the fact that BTEX are often used as markers for the exposure to VOCs [23], and benzene has been classified by IARC as carcinogenic to humans *(Group 1)*.

Methyl methacrylate (MMA) is a monomer of acrylic resin and widely used in dental procedures. Methyl methacrylate is a strong sensitizer and occupational respiratory diseases such as asthma caused by methacrylates in dental technicians were reported [24, 25].

Aldehydes are indoor and outdoor chemical pollutants of particular interest due to their potential impact on asthma and allergic symptoms [26]. Among the aldehydes, formaldehyde has been classified by IARC as carcinogenic to humans *(Group 1)*. In dental practice, formaldehyde may be present as an ingredient of root canal antiseptics.

Glutaraldehyde is a chemical that is used as a cold sterilant to disinfect and clean heat-sensitive medical, surgical and dental equipment. Routine exposure to glutaraldehyde is known to cause adverse health effects. Glutaraldehyde usage is declining in dental setting and it is not used as such in the investigated dental setting. However, it may be present as an ingredient of root canal antiseptics.

Acetaldehyde has been classified by IARC as possibly carcinogenic to humans *(Group 2B)*. Propionaldehyde, benzaldehyde, and butyraldehyde were also quantified in order to have eventually other terms of comparison with other indoor areas in which they have been widely studied.

Indoor and outdoor air VOCs (BTEX, MMA and aldehydes) sampling points and duration

Simultaneous samplings of indoor and outdoor air over a week of three different months (July, August, and September) were carried out at the dental ward and at the outdoor window of a separate room of the ward. Clearly this was simply a pilot study to check the reliability of the obtained measures, given the concentration of measurements in the summer period could bias the obtained results.

For sampling, the Radiello passive simpler (code No.165) for aldehydes [3-5] and the Radiello passive sampler (code No.130) for BTEX and MMA were used [1-2].

Four passive samplers were simultaneously placed as follows:

1. two samplers, one for BTEX and MMA and the other for aldehydes, set aside at about 1.70 m height in the breathing zone and about 1.5 m distant from each dental chair;
2. two samplers, one for BTEX and MMA and the other for aldehydes, set aside at the outdoor window of a separate room.

The samplers were left for a consecutive 7-days period during which time occupants (dental staff, dentists etc.) were asked to ignore the existence of the samplers.

Table 2 | [(a)] *Types and number of dental procedures carried out in each monitored week of July, August and September*

month	Total No.dental procedures carried out	pulpitis	periodontitis acute	periodontitis chronic	abscess	tooth filling	amalgam removal	composite removal	medication
July	232	60	28	17	11	97	10	5	4
August	332	79	38	33	16	128	9	20	9
September	150	32	11	25	7	65	4	1	5

[(a)] *The listed dental pathologies entail the following dental procedures:*
- *procedures necessary to relieve pain, or eliminate acute infection –* e.g., *starting root canal treatment on infected teeth, draining abscesses and infected areas;*
- *procedures involving application of medications, temporary fillings for fractured teeth.*

The in-field sampler preparation took place by installing the collection cartridge, that is housed in a sealed glass tube before sampling, into the diffusive body that was screwed into the supporting plate. The sampling samplers were taken off after 7 days exposure time.

The cartridge of each sampler was removed and housed again immediately in the sealed glass tube, transported to laboratory and kept at 4 °C until VOCs analyses.

The identification and determination of BTEX and MMA were based on retention times and confirmed by gas chromatography-mass spectrometry (GC6890 HP-MS 5973 HP) analyses.

The identification and determination of individual aldehydes were performed by reverse phase HPLC.

BTEX and MMA analyses

After sampling, BTEX collected onto the adsorbent cartridge of each sampler were desorbed. Two milliliters carbon disulfide (CS_2) were directly introduced into the Radiello (code 130) glass tube, without drawing out the cartridge, and stirred from time to time for 30 min. The extracts were analyzed by gas chromatograph equipped with flame ionization detector (FID) for BTEX and analyzed by gas chromatograph with single ion monitoring (SIM) for MMA. The whole procedure used in our previous studies [1-2] was entirely applied in this work

BTEX instrumental analysis

For the identification and determination of volatile organic compounds (VOCs), a gas chromatograph (GC 6890 HP) with flame ionization detector (FID) was used.

Conditions of the GC/FID analyses:
- Rtx-5MS capillary column, 60 m length, 0.25 mm diameter, 0.1 µm film thickness;
- injector temperature: 280 °C;
- gas carrier flow (helium):1.6 ml/min;
- temperature programme: 35 °C (isothermal for 4 min), 4 °C/min to 120 °C. (isothermal for 2 min) 5 °C /min to 200 °C. (isothermal for 5 min);
- detector temperature: 250 °C.

The identification and determination of VOCs were based on retention times and confirmed by gas chromatography-mass spectrometry (GC6890 HP-MS 5973 HP) analyses.

For the quantitative determination of benzene, toluene, ethylbenzene, xylenes, the instrument was calibrated using five standard concentrations covering the concentration of interest for indoor/outdoor ambient air [1, 2]. The detection limit of the analytical procedure was based on a signal/noise ratio = 3. To asses the precision of the analytical procedure, each sample was injected three times on the capillary chromatographic column and a standard deviation ranging from 2 to 3% was obtained [1, 2].

Methyl Methacrylate (MMA) analyses

After sampling, MMA collected onto the adsorbent cartridge of each sampler were desorbed. Two milliliters carbon disulfide (CS_2) were directly introduced into the Radiello glass tube, without drawing out the cartridge, and stirred from time to time for 30 min. The extracts were analyzed by means of gas chromatograph with single ion monitoring (SIM). The whole procedure used in our previous studies [1-2] was entirely applied in this work

Methyl Methacrylate (MMA) instrumental analysis

The identification and determination of methylmetacrylate was based on retention time and confirmed by a gas chromatography-mass spectrometry (GC6890 Agilent Technologies -MS 5973 Agilent Technologies) with single ion monitoring (SIM).

Conditions of the GC/MS (SIM) analyses:
- Rtx-5MS capillary column, 60 m length, 0.25 mm diameter, 1.0 µm film thickness;
- injector temperature: 280 °C;
- gas carrier flow (helium): 2.0 ml/min;
- temperature programme: 35 °C (isothermal for 2 min), 1 °C/min to 45 °C (isothermal for 1 min), 5 °C /min to 75 °C (isothermal for 3 min), 10 °C /min to 175 °C (isothermal for 3 min), 15 °C to 250 °C (isothermal for 3 min);
- detector temperature: 250 °C.

The detection limit of the chemical method for MMA was 0.01 µg/m^3.

Aldehydes analyses

The investigated aldehydes were formaldehyde, acetaldehyde, propionaldeyde, benzaldehyde, n-butyraldehyde, and glutaraldehyde.

After sampling, aldehydes collected onto the adsorbent cartridge of the sampler (Radiello, code 165) coated with 2,4dinitrophenylhydrazine, of each sampler were desorbed. Two millilitres acetonitrile (Riedel-de Haen) were directly introduced into the cartridge container recapped and stirred from time to time for 30 min. The resulting solution was filtered (micropore filter membrane, porosity 0.45 mm) and kept capped at 4 °C until analysis.

Aldehydes instrumental analysis

Aldehydes analyses were performed by reverse phase HPLC. A HPLC-(Agilent Technologies 1100 series) equipped with Restek Ultra C18 HPLC column, length 150 mm, 4.6 mm diameter, 5 µm packing particle size, and UV detection.

Calibration was made by means of a direct injection of standards, at known concentration,

of hydrazones in acetonitrile (Supelco).

Aldehydes were detected by UV 365 nm detector.

Each sample solution of 20 mm^3 was injected and eluted as follows:
- eluents used: acetonitrile and water;
- eluent flow rate: 1.9 cm^3/min;
- isocratic elution with acetonitrile/water 38:62 v/v for 5 min, then with a gradient of elution for 19 min with acetonitrile 100% v/v.

Identification and quantification of carbonyl compounds were based on retention times and peak areas of the corresponding calibration standards, respectively. The instrument was calibrated using five standard concentrations covering the concentration of interest for indoor/outdoor ambient air. The detection limit of the chemical method for MMA was 0.01 μg/m^3

Determination of aldehydes sampling precision was based on laboratory triplicate measurements (n = 3) collected in the laboratory along with the sample from the sampler. To asses the precision of the analytical procedure, each sample was injected three times on the capillary chromatographic column and a standard deviation expressed as relative standard deviation (RSD%) ranging from 3 to 6% was obtained.

The whole procedure used in our previous studies [3-5] was entirely applied in this work.

RESULTS AND DISCUSSION

BTEX
(benzene, toluene, ethylbenzene, m-o-p-xylenes)

Table 3 lists the obtained indoor and outdoor air mean concentrations of BTEX (benzene, toluene, ethylbenzene, m-o-p-xylenes) and the number of dental procedures carried out, at the investigated dental work area, in each of the monitored weeks in July, August and September.

The obtained concentrations, for each of the individual compounds, were below occupational exposure limits set by relevant institution such as the National Institute for Occupational Safety and Health (NIOSH), the Occupational Safety and Health Administration (OSHA), American Conference of Industrial Hygienists (ACGIH), etc.

The obtained dental indoor and outdoor concentrations quoted as ratios (I/O) were higher than unity for benzene, pointing to higher concentration of such compound in indoor air than in outdoor. The dental indoor and outdoor concentrations of toluene quoted as ratios (I/O) were about equal 1 and similar to some of the indoor/outdoor ratios (I/O) found in certain homes in the city of Rome [1]. The dental indoor and outdoor concentrations of xylenes quoted as ratios (I/O) were higher than the unity, with the exception of the week of July in which the ratios (I/O) were lower than the unity. Also for xylenes, the ratios (I/O) are similar to some indoor/outdoor ratios (I/O) found in some homes of the city of Rome [1].

However, a systematic survey involving a much greater number of samples is needed to draw any realistic conclusion on the actual level of BTEX in the studied dental setting.

Methyl Methacrylate (MMA)

As reported in *Table 3*, the obtained indoor air mean concentrations of MMA were far below occupational standards, *e.g,* the 8-hour threshold limit value time-weighted average (TLV-TWA) occupational standard for MMA is 100 ppm; 410 000 μg/m^3 (OSHA and ACGIH).

The dental indoor and outdoor concentrations of MMA quoted as ratios were much higher than unity (Indoor $_{MMA}$ /Outdoor $_{MMA}$ >>>1) pointing to a specific dental indoor contamination source.

However, as shown in *Table 3*, the weeks in which there were more cases of composite removal, the MMA concentration was lower than the other weeks. Thus, MMA levels cannot be associated to specific dental activities (such as dental procedures entailing the removal of composite fillings) that were expected to emit some emissions; *e.g.,* on the week with MMA generating potential (more cases of composite removal). This observation agrees with that made by Goldwin *et al.* that attributed the possible cause of the presence of MMA to the mechanical ventilation not effective for avoiding the mixing of contaminated air from areas (laboratories) in which the MMA compound was used.

Generally, in dental settings, the handling of composite materials, resulting in airborne methacrylates, may happen mainly at two sites: at the nurse's desk where the dosage and mixing of the material is done and at the patient's mouth during the application procedure and the drilling of the composite material. However, protocol adopted by the investigated dental emergency ward only provides for removal of the composite mate-

Table 3 | *Dental indoor and outdoor air mean concentrations (a) (μg/m3) of BTEX and MMA and number of dental procedures carried out in each monitored week of July, August and September*

Month	Total no. dental procedures carried out	In benz	Out benz	In toluen	Out toluen	In ethylben	Out ethylben	(b) in m-p xylene	In O-xylene	(c) Tot in xylenes	Outm-p-xylene	Outo-xylene	(d) Tot out xylenes	In metacr	Out metacr
July	232	3.9	1.5	5	4.6	n.d	n.d.	1.45	2.05	3.5	1.5	3.3	4.8	1.8	0.1
August	332	4.4	0.5	5.6	4.9	n.d	n.d.	1.7	3.15	4.85	1.6	3.1	4.7	2.9	0.2
September	150	2.6	0.5	5.9	5.1	n.d	n.d.	1.8	2.8	4.6	1.7	1.9	3.6	9.1	0.1

(a) Standard deviation expressed as relative standard deviation (RSD%) ranged 2-3%
(b) M-xylene and p-xylene isomers were not separated by the used analytical method
(c) TOT IN XYLENES is the sum of isomers of xylene (INm-pXylene and INo-Xylene)
(d) TOT OUT XYLENES is the sum of isomers of xylene (OUT m-pXylene and OUT o-Xylene).
n.d. = not detected.

Table 4 | *Dental indoor and outdoor air mean concentrations (a) (µg/m³) of each measured aldehyde and number of dental procedures carried out in each monitored week of July, August and September*

Month	No. dental procedures carried out	In form	Out form	In acetal	Out acetal	In prop	Out prop	In butyr	Out butyr	In benzal	Out benzal	In glutaral	Out glutaral
July	232	3.6	2.2	10.7	3.6	2.6	2.5	12.8	11.9	0.3	0.3	n.d.(B)	n.d.(B)
August	332	4.2	2.7	8.7	3.1	2.5	0.9	11.8	9.5	0.3	n.d.(B)	n.d.(B)	n.d.(B)
September	150	3.7	2.2	4.7	1.9	1.8	1.2	8.75	6.4	0.2	n.d.(B)	n.d.(B)	n.d.(B)

(a) *Standard deviation expressed as relative standard deviation (RSD%) ranged 3-6%.*
(b) *n.d. = not detected for a detection limit of 0.01 µg/m³*

rial. Thus, in our case the presence of MMA may be attributed to the movement of contaminated air from one ward to another through opening doors.

The hospital is dominated by natural ventilation and it is difficult to keep under control the movement of contaminated air from one area to another.

Central atrium, various halls and openings for example, could draw air from other wards into the volume of the atrium, hall and corridor distributing contaminated air into any areas on these levels.

However, a systematic survey involving a much greater number of samples is needed to draw realistic conclusions on the actual level of MMA in the studied dental setting.

Aldehydes

Table 4 lists the obtained indoor/outdoor air mean concentrations of aldehydes. Glutaraldehyde was never detected in all monitored weeks. In this regard, there is to note that the detection limit of the used sampler system and sampling duration (a 7-day exposure) is 0.1 µg/m³. In this regard, it is worth to note that even though the detection limit of the used sampler is 10 times higher than the detection limit of the used analytical method (that is 0.01 µg/m³), it is far below the occupational exposure standard, set by NIOSH, that for glutaraldehyde is 0.2 ppm (0.8 mg/m³) (expressed as ceiling value – at no time should this exposure limit be exceeded).

The obtained concentrations of formaldehyde were below the occupational standards, *e.g.,* the occupational standards for formaldehyde are 0.016 ppm (Conversion 1 ppm = 1.23 mg/m³) (NIOSH) and 0.75 ppm (OSHA PEL).

The literature reports that levels of formaldehyde in outdoor air are generally below 0.02 mg/m³ (20 µg/m³) in urban settings, and typically 0.02-0.06 mg/m³ (20-60 µg/m³) in the indoor air of houses [27]. Although the obtained concentrations were below (5-15 times) these values, a systematic survey involving a much greater number of samples is needed to draw any realistic conclusion on the actual level of formaldehyde in the studied dental setting.

Acetaldehyde concentrations were also below occupational exposure limit set by OSHA PEL that is 200 ppm (360 mg/m³).

Propionaldehyde concentrations were also below the occupational exposure limit set by by ACGIH in 2003 that is 20 ppm. While for benzaldehyde and butyraldehyde no occupational exposure limit has been set.

The indoor and outdoor aldehydes concentrations, for each detected aldehyde, quoted as ratios (I/O) resulted higher than1, pointing to higher concentration of such compounds in dental indoor air than in outdoor.

VOCs: BTEX +MMA+Aldehydes

Table 5 reports the total indoor and outdoor air mean concentrations of measured VOCs (BTEX +MMA+aldehydes concentrations) along with the types and number of dental procedures carried out , in each monitored week of July, August and September.

As reported in *(Table 5)*, the total indoor air pollution due only to BTEX and MMA (TOT IN(BTEX +MMA), increases over time. Conversely, the total indoor pollution due only to aldehydes (TOT IN(ALDEHYDES)), decreases.

Thus, both TOT IN(BTEX +MMA) and TOT IN(ALDEHYDES) seems to depend on the specific month (season effect) rather than on the number of dental procedures carried out. However, the total indoor pollution (TOTAL IN (BTEX +MMA+ ALDEHYDES) due to both TOT IN(BTEX +MMA) and TOT IN(ALDEHYDES) is somewhat linked to the number of dental procedures, thus pointing to an indoor source of BTEX, MMA and aldehydes.

Again we must state this is a pilot and not a definitive study, but the fact the pollution correlates with the amount of activity is an indication of a possible causative effect of dental activity on the observed VOCs profile.

Again, a systematic survey involving a by far greater number of samples is needed for proving such conclusions. Here, given the methodological nature of the work, it is sufficient to state the general philosophy adopted privileging the search for correlation between the amount of activity and the observed chemical measurements over the simple check of concentrations.

Furthermore, we need to increase the data on indoor air contaminants in dental settings and investi-

Table 5 | *Total[(a)] indoor and outdoor air mean concentrations of measured VOCs[(a)] (μg/m³) and types and number of dental procedures carried out in each monitored week of July, August and September*

Month	Pulpitis	Periodontitis acute	Periodontitis chronic	Abscess	Tooth filling	Amalgam removal	Composite removal	Medication
July	60	28	17	11	97	10	5	4
August	79	38	33	16	128	9	20	9
September	32	11	25	7	65	4	1	5

Month	No. Dental procedures	Tot in (BTEX +MMA)	Tot In (Aldehydes)	Tot out (BTEX +MMA)	Tot Out (aldehydes)	Total in (BTEX+MMA + aldehydes)	Total out (BTEX+MMA + aldehydes)
July	232	14.2	29.1	11.0	20.6	43.3	31.6
August	332	17.9	27.5	10.3	16.2	45.4	26.5
September	150	22.2	19.2	9.3	11.7	41.4	21.0

[(a)] *Measured VOCs = BTEX (benzene +toluene+ethylbenzene+xylenes) +MMA+aldehydes (formaldehyde + acetaldehyde + propionaldeyde + benzaldehyde + n-butyraldehyde + glutaraldehyde).*

gate the outdoor air quality since outdoor air quality represents a factor for the removal, dilution or both, of indoor contaminants that must be considered as a priority. We still lack the indoor/outdoor concentrations data that would allow assessing where the observed link between activity and indoor air quality is a signal of an effective dental activity induced pollution or an outcome of the exchange between indoor and outdoor air pollution.

Our results, in terms of actual measured concentrations, are not comparable with those from Goldwin because their results concern a dental settings that operates about 7-8 hours per day and does not work in the weekend, while the dental emergency unit we investigated operates 24 hours a-day. Moreover, Goldwin *et al.* used, for the estimation of individual VOCs, a sampling duration of 2-4 hours, while in our case a consecutive 7-day sampling was used.

Of course, our investigation is not comparable with that carried out by Helmis *et al.* because they use a detection system based on direct-reading instrument which does not separate the mixture of VOCs into its individual volatile organic compounds, whereas in our study we quantified the investigated individual VOCs.

CONCLUSION

Currently calculated concentrations cannot be stipulated in representing VOCs concentration levels in dental settings. A systematic survey involving a great number of samples is needed for proving any conclusion. We can in any case affirm that the above sketched general lines for the analysis of dental settings in environmental terms allows for an unbiased estimate of VOCs concentration especially for the possibility to compare indoor and outdoor concentrations and to sketch correlations with on-going activity of the hospital.

The location of the dental hospital into a very polluted area forces us to imagine a strict paired samples comparison of outdoor/indoor VOCs concentrations. This paired comparison transforms an apparent background contaminants concentration of the location (the outdoor pollution covers possibly relevant indoor concentrations) into a strength, allowing many of these contaminants to reach a measurable quantity (in terms of concentration) that in (their) turn can be immediately allocated to an outdoor or specific source thanks to the paired sampling. Moreover it is well known that indoor and outdoor environments are in close contact and undergo significant exchanges [5], and the presence of external sources (and sinks) is crucially important for detecting fluxes.

As shown in *Figure 1*, the presence of different working areas linked by various degrees of shared space (different work posts with different activity inside the same space) allows estimation of the degree of diffusion of the possible contaminants by the analysis of the spatial dependence of the between pollutants correlations in function of the mutual spatial distance.

The types and the number of dental procedures that are taken into consideration allows for a potential correlation between the relative frequency of different dental procedures and the concentration of contaminants. Last but not least the kind of materials and substances used drive the attention of the environmental chemist to the type of analytical measurements most suited for the specific site.

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