CONTROLLED HUMAN REACTIONS TO BUILDING MATERIALS IN CLIMATIC CHAMBERS. PART II: VOC MEASUREMENTS, MICE BIOASSAY, AND DECIPOL EVALUATION[1]

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During monitoring human reactions to the emission of volatile organic compounds (VOC) from four commonly used building materials in climatic chambers, subjective votes of IAQ, judgement of the IAQ in the decipol scale by a trained panel, and simultaneous VOC measurements were performed. The irritating potency of the materials was measured by mice bioassay. All these parameters are compared. The VOC measurements showed several malodorants and irritants which were suitable for substitution. Some abundant VOC identified in the headspace analyses were absent in the chamber air. A high formaldehyde concentration (743 μgm^3) was measured for a particle board coated with an acid-curing paint which was not reflected by a significant increase in decipols though a long lasting irritating potency was observed in the mice bioassay. A rubber floor covering and a nylon carpet exhibited a marked increase in decipols compatible with a number of odorous VOC identified in the air. A degreasing effect of lipophilic VOC dissolving the lipid multilayer of the tear film is proposed as a mechanism involved in eye irritation.

PURPOSE

The general scope of this study was to expose asthmatic persons with non-specific hyperreactive airways and non-asthmatics to four different building materials in climate chambers. The results of the clinical investigations thereof are reported elsewhere (1). This paper deals with measurements of volatile organic compounds (VOC) in the chambers with and without persons present, headspace analyses of the emission of VOC from the building materials, measurements and evaluation of the irritating potency of the materials by use of mice bioassay, and subjective perception of the air and judgement of the air quality in the decipol scale by use of a trained panel.

MATERIALS and METHODS

The building materials were selected based on criteria shown in Table 1. Materials 2-4 were used as received. Material 1 was a composite one consisting of a gypsum board which has been hung with wall paper followed by painting using a waterborne based paint. The total area of the materials was 70-74 m^2. The materials were inserted in the climate chambers as outlined below.

Twin climate chambers each 3.6·2.5 m^2 constructed of stainless steel (2) were adjusted to 22.0 ± 0.2° C, 45 ± 2 % rh, and an air exchange rate set to 0.5 h^{-1}. The materials were inserted into the chambers 65 hours prior to exposure of subjects. The subjects exposed for 6 hours each time, voted 9 times a day on the subjective perception of the atmospheric climate. The perception of the air quality was also judged 6-8 times on the decipol scale (3) by a trained panel (4). The empty chambers were also judged (placebo). The results are shown in Table 2.

VOC were measured in triplicate on Tenax tubes for Perkin-Elmer ATD-50 as described elsewhere (5). Sampling time was 30 min and sampling flow was 100.0 ml min^{-1} (± 3%) using Dupont Alpha-1 pumps. Calibration was performed by injection onto the Tenax tube with methanol solutions of weighed samples at three different concentrations in triplicate. The relative standard (RSD) was deviation from 1.2-3.8 % for VOC except for acetone and toluene when subjects were present. Total VOC was determined by pooling the measured VOC with toluene equivalents of the unidentified integration area. The RSD for TVOC was 2.2-9.2 %. Formaldehyde was sampled in water in duplicate and analysed using Hantzsch reagent and fluorescence spectroscopy. The RSD was 0.9-6.3 %. Headspace analyses of the materials was performed as described previously (6).

The mice bioassay was performed as follows. Each building material was inserted into a 200 l stainless steel tank which was then closed for one hour. The tank air was circulated in a closed system which was obtained by connecting a glass exposure chamber (3.3 l), the tank and a metal bellows pump by teflon tubings. Mice were exposed head-only (7-9). The respiratory rate and the tidal volume were obtained from the pressure changes monitored by plethysmography. The exposure was carried out for 10 min. then the system was disconnected and the tank was ventilated (50 % rh, air exchange rate of 0.5 h^{-1}) until the next experiment at ambient temperature. The respective loadings of the tank were 1/3, 1, 3, and 9 plates of material 4. The loading was 3 and 9 plates, respectively, for the other materials. The plate dimension was 0.45·0.66 m^2

Table 1. Criteria for selection of four building materials, their approximate age (months) at the time of experiments, and the total area (m^2) exposed in the chamber.

Material	Age/Area		Criteria
1. Waterborne painted wall paper on gypsum board	0.5	74	They are in general use They are an integral part of various types of buildings
2. Rubber floor covering	8	70	They are in direct contact with the indoor air
3. Nylon carpet with rubber mat	8	72	They are expected to cause indoor air problems
4. Acid-curing coated particle board	1	72	They are finished products Emission is constant during the experiment

RESULTS

The results of the VOC measurements are shown in Tables 3-4. Table 3 shows the qualitative identification and six most abundant VOC found in the headspace analysis. Table 4 shows the quantitative VOC measurements in the chambers with building materials and subjects present in experiments 1 and 4. The dominant VOC from material 1 were the propandiol, 2-butoxyethanol and Texanol[R] the origin of which is the waterborne paint (10). These VOC, however, were neglible in the headspace analysis. Limonene originates from humans and their activities. The large RSD observed for acetone and toluene reflects their human origin. The dominant VOC from material 2 were styrene and methylstyrene, diisopropylbenzenes, and isododecene; indene and 4-vinyl-1-cyclohexene including 4-phenylcyclohexene were found in minor amounts. Both the styrenes and vinylcyclohexene originate from the production of the ABS polymer. The presence of isododecene has been observed in an increasing number of materials (6,11); its origin, however, is uncertain because it may be used as a solvent or it may be a butadiene trimer. Toluene and acetone were the two most abundant VOC with nylon carpet. This is partly due to the presence of humans (vide supra). Other VOC were diisopropylbenzenes and isododecene; the siloxanes [72-73], however, were found in much lower relative concentration as opposed to the headspace analysis. The major VOC from material 4 were butanol and formaldehyde.

The emission of formaldehyde from the acid curing paint gave rise to a marked decrease of the respiratory rate in the mice bioassay. The experiments showed that for the two highest loadings the decrease of the respiratory rate was long lasting. A statistical significant decrease of the respiratory rate (> 10 %) was not observed for the other three materials.

The results of the decipol evaluations of the air quality for the four materials are shown in Table 2 together with the result of an empty chamber.

Table 2. Air quality votes (visual scaling), decipol evaluation, TVOC and formaldehyde in $\mu g*m^{-3}$, irritation found in mice bioassay, and tear film quality index[□] from 4 building materials.

Material	Votes	Decipol	TVOC	CH2O	Mice	Eye
1. Painted gypsum board	4.0	9.3	1,230	86	no	-2
2. Rubber floor	6.4	24.1	1,923	11	no	-4
3. Nylon carpet	5.8	20.8	1,406	26	no	-3
4. Particle board	5.4	16.4	1,109	743	yes	-1
Empty chamber	2.3	8.5	63	12		0

□) -4 = worst.

Table 3. VOC identified by static headspace analyses of 4 building materials (1-4).

Alkanes:
1. Pentane 1*,3,4,6
2. 2-Methylbutane 3
3. Hexane 2,3,6*
4. 2-Methylhexane 2,3
5. 3-Methylhexane 2,3
6. Heptane 1,3,4
7. Octane 3
8. 2-Methyloctane 2
9. 3-Methyloctane 2,4
10. Nonane 2,4
11. Decane 2*,4
12. 4-Methyldecane
13. Undecane 2,3*
14. Dodecane

Alkenes/Cycloalkanes:
15. Heptene 2
16. Methylcyclohexane 2,3
17. Methylcycloheptane 2
18. Ethylcyclohexane 2
19. 4-Vinyl-1-cyclohexene 2*
20. α-Pinene 1*,4*,6*
21. ß-Pinene 4,6
22. 3-Carene 4,6*
23. Limonene 4
24. 1-Methyl-4-(methylethyl)-cyclohexane, c/t 2
25. Isododecene 2,3*,6*

Aromatics:
26. Benzene 2,3
27. Toluene 1,2,3*,4
28. Ethylbenzene 2,3
29. Xylenes 3,4*
30. 2-Ethyltoluene 2*,4
31. 3-Ethyltoluene 4
32. Propylbenzene 4
33. Styrene 2*,3
34. α-Methylstyrene 2*
35. Methyl propylbenzene 2
36. Indene 2
37. 1,3-Diisopropyl-benzene 2*,3*
38. 1,4-Diisopropyl-benzene 2*,3*
39. 1,2,3-Trimethylbenzene 4
40. 1,2,4-trimethylbenzene 4
41. Triisopropylbenzene
42. 4-Phenyl-1-cyclohexene 3

Alcohols/Diols:
43. 2-Propanol 4
44. Propanol 4
45. Isobutanol 1*,4
46. Butanol 1*,3,4*
47. 1,2-Propandiol 1
48. 2-Metoxyethanol 4
49. 2-Butoxyethanol 1

Esters:
50. Methyl acetate 4
51. Ethyl acetate 4
52. Isobutyl acetate
53. Butyl acetate 4D*
54. Texanol 6

Aldehydes/Ketones:
55. Formaldehyde
56. Acetaldehyde 3,4
57. Propanal 1*,4
58. 2-Methylpropanal 4
59. Butenal 4
60. Butanal 1*,4
61. Pentanal
62. Hexanal 1*,4*,6*
63. Heptanal 4
64. Acetone 1*,3*,4*,6*
65. 3-Methyl-2-butanone1
66. 2-Methyl-3-pentanone1
67. Acetophenone 2

Miscellaneous:
68. Carbondisulfide 3
69. Acetonitrile 3
70. 2-Methylfuran 1
71. 2-Ethylfuran 1
72. Hexamethyl-cyclotrisiloxane 3*
73. Octamethyl-cyclotetrasiloxane 3
74. Unknown 3*

*) Among 6 most abundant VOC.

Table 4. Concentrations ($\mu g \cdot m^{-3}$)* and emission factors ($\mu g \cdot ^{-2} \cdot h^{-1}$) of VOC and formaldehyde emitted from 4 building materials (1-4) and empty chamber.

Material/VOC	Conc.	Emission Factor	Odor	Irritant	Action
1. Waterborne painted wallpaper on gypsum wall:[□]					
Acetone	62[#]	13			
Hexanal	24	5			
Toluene	50[#]	11			
1,2-Propandiol	676	145			
2-Butoxyethanol	129	28			
Limonene	65	14	yes		
Texanol[R]	158	34			
Unidentified[£]	115	25			
Total VOC	1,230	264			
Formaldehyde	86	18		yes	
2. Rubber floor covering:					
Acetone	8	1.7			
Acetophenone	62	13	yes		yes
Undecane	32	7			
Toluene	9	1.9			
Styrene	191	41	yes		yes
α-Methylstyrene	404	87	yes		yes
Indene	69	15	yes		yes
1,3-Diisopropylbenzene	195	42	yes		yes
1,4-Diisopropylbenzene	102	22	yes	yes	yes
4-Vinyl-1-cyclohexene	15	3	yes	yes	yes
Isododecene	108	23			
Unidentified[£]	779	167			
Total VOC	1,923	412			
Formaldehyde	11	2.4			
3. Nylon carpet with rubber mat:[□]					
Undecane	57	12			
Acetone	141	30			
Hexanal	16	3.4	yes		
Toluene	515	110			
1,3-Diisopropylbenzene	112	24			
1,4-Diisopropylbenzene	42	9	yes	yes	yes
Limonene	57	12	yes		
Isododecene	43	9			
Unidentified[£]	297	64			
Total VOC	1,406	301			
Formaldehyde	26[$]	5.6			
4. Acid-curing painted particle board:					
Acetone	31	6.6			
Toluene	19	4.1			
Butanol	846	181	yes		yes
Unidentified[£]	214	46			
Total VOC	1,109	238			
Formaldehyde	743 (min)[&]	159		yes	yes

*) All VOC measurements were triplicate with a relative SD < 4 %, except if otherwise stated. Formaldehyde measurements were duplicate with a RSD ≤ 1.5 %, except otherwise stated. #) Relative SD = 10-15 %. $) Relative SD = 6.4 %. £) Toluene equivivalents. □) Subjects present. &) More than 25 % recovered in back-up.

DISCUSSION

The VOC measurements in the chambers showed that it is possible to perform short term (30 min) air sampling with a relative standard deviation of the order of 2-4 % (n=3). There appeared to be a fair agreement between VOC found in the headspace analyses and in chambers, except for the painted gypsum wall and the nylon carpet. The relative proportion of siloxanes [72-73] were found neglible in the chamber air as opposed to the headspace analysis. A rationale for this may either be a low air exchange efficiency at the fleece surface of the carpet or adsorption (sink) on chamber walls and personel clothing. The reason for the difference between headspace and chamber air analysis of material 1 may be that the emission is strongly ventilation dependent.

Several VOC identified in the headspace analyses were malodourants and irritants requiring some action (see Table 3). These may be substituted with other odorless and harmless organic compounds or removed during the manufacturing process to produce healthy building materials (6,12). This yields especially for the rubber floor covering and the nylon carpet. The emission of formaldehyde from the acid-curing painted particle board was more than a factor of 5 higher than the Danish building code.

Neither air quality votes nor decipol evaluation appear to correlate with TVOC showing its limited use as an marker of IAQ.

Irritation in eyes and upper respiratory tract (sensory irritation) may be quantified by a mice bioassay which allows a prediction of the irritating effect in humans (9). The concentration threshold giving rise to a decrease of the respiratory rate (RD-0) will when multiplied by 0.2 provide an estimate of the maximum level accepted in the industrial environment (TLV) (9). A decrease greater than 10 % will therefore correspond to a very irritating concentration. Materials 1-3 did not show a statistical significant decrease of the respiratory rate as similarly found for the lung functions (1).

The materials were ventilated with an air exchange rate of 0.5 h^{-1} which is an average rate found in many modern buildings (13). The use of a closed system for the mouse bioassay is realistic because of a low ventilation efficiency in many houses (13).

Comparison of the decipol evaluation of the particle board coated with an acid curing paint with the formaldehyde concentration showed that the decipol concept is not sensitive to a strong irritant like formaldehyde. The reason for this is that the reaction time for perception and evaluation in decipol units is too short for formaldehyde to be effective and the odor perception of butanol instead takes place (14). The high concentration of formaldehyde resulted also in both eye and throat irritation (1) in accord with (15).

The relative standard deviations of the evaluated decipol values has been estimated to about 8 % of the quoted values. The differences observed are therefore due to the emission from the materials. The high decipol value for material 2 is compatible with its relative high emissions of odors (olfactory active components) (see Tables 3-4). Material 1 with a low decipol value has similarly a low content of odors. More detailed studies are required for these relations.

The high abundance of lipophilic VOC like aromatics and isododecene is compatible with the highest tear film quality index for materials 2 and 3 (see Table 2) because they would have a degreasing effect of the lipid multilayer of the tear fluid (16) producing a perforated tear film. Irritants may then penetrate and dissolve in the tear fluid. Both materials 1 and 4 emit primarily hydrophilic VOC thus corresponding to a lower degreasing capacity.

CONCLUSION

The headspace analyses of the materials showed that several VOC emitting from the materials were either malodorants or irritants and they should be removed and substituted with harmless compounds. The biological tests suggest that complaints would be anticipated from use of the particle board which has been coated with an acid curing paint compatible with the heavy emission of formaldehyde. The other materials although exhibiting a higher

TVOC, malodorants and irritants did not respond to the bioassay. It was demonstrated that the decipol concept apparently is not significantly susceptible to an irritant like formaldehyde even at high concentration. A high decipol response appears to relate to a high number of odorous VOC while TVOC appears not to be a useful marker of IAQ. A new hypothesis about the eye irritation mechanism is proposed based upon a degreasing effect of the lipid multilayer of the tear film.

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