Quaternary Ammonium Compounds – case studies and sampling methods

Carmen Kroczek[1] and Jörg Thumulla[1]

[1]anbus analytik GmbH, Fürth, Germany

[*]*Corresponding email: ck@anbus-analytik.de*

SUMMARY
The use of quaternary ammonium compounds (QUATS or alternatively named QAC, QAV or Quat) within indoor mold remediations often leads to lawsuits due to the possible health risk. Some of these lawsuits were expert monitored by us. In this study we report about indoor contaminations resulting from QUATS-containing disinfectant applications in homes. The results of chemical QUATS analyses display the range of indoor QUATS concentrations after typical mold remediations. In respect to the reported biological health impact, the handling of these persistent biocide chemicals should be reconsidered. The use of QUATS is not necessary for professional mold remediation according to the state of art.

IMPLICATIONS
In addition to previous data of background contamination with QUATS in house dust, the results depicted here give for the first time an overview of the resulting indoor contamination after the use of QUATS-containing disinfectants e.g. on materials and treated surfaces. Taken together, the results demonstrate the importance of using residue-free disinfectants, e.g. isopropanol, within the mold remediations.

KEYWORDS: *QUATS, mold remediation, dialkyldimethyl-ammonium compounds (DDAC), benzylalkyl-dimethylammonium compounds (BAC), cationic surfactants*

INTRODUCTION
The German Federal Environment Agency (Umweltbundesamt, UBA) advises in the guideline for mold remediation against the usage of persistent biocides for decontamination due to the release of chemical substances during and after the application which can be health hazards for the occupants and user (UBA, 2005). For inevitable use of disinfectants the application of residue-free disinfectants like isopropanol or hydrogen peroxide is demanded in the guideline. Despite this guideline cleaning and remediation companies often use persistent disinfectants like quaternary ammonium compounds (QUATS) as fungicidal active agent. QUATS belong to the cationic surfactants group. Surfactants are enriched in adipose cell membranes of living organisms and can consequently impair the normal functions of cell membranes. It is this property in particular which enable QUATS to act as biocide agents. Indoor cationic surfactants can be adsorbed to house dust and reach ambient air as POM (organic compounds associated with particulate matters) by airborne fine dust particles.

QUATS are widely used as disinfectant chemicals in hospitals and work effective against bacteria. The toxic activity against mold is less effective and less quantitative. Although QUATS are considered as non-toxic to humans, a known amplifying and prolonging effect on substances like alcohol or aldehydes exists (Bode-Chemie, 2007). This is because of an increasing permeability of membranes compared to other organic substances due to the damage of the protective water lipid membranes of the outer skin. Consequently, this has a drastic effect on the absorption level of toxic substances. Hence, this amplifying effect has also to be assumed for mycotoxins, beta-glucanes or enzymes being released within microbial

contaminations. This is especially relevant in the case of mold remediatons where the mold affected materials were removed but the removal of secondary contaminations by precision cleaning is missing. BAC e.g. are also known as eye irritants. BAC reduce the stability of the tear film and exposure to BAC can result in dry eye symptoms. BAC can damage the cornea - even in deeper layers (Kuppens, E.V et al. 1995; Herreras, J.M. et al., 1992)

METHODS

Quaternary ammonium compounds (QUATS) were analysed by HPLC-MS/MS as previously described by Thumulla and Friedle (2007). QUATS house dust sample reference values were already published in this study. The samples for the dust reference values came from the widest possible representative selection from the pool of house dust samples taken for the German Environmental Survey for Children 2003/06. Within this study Friedle, Thumulla and Snepvangers (Indoor Air 2008, Kopenhagen) have shown an overview of common house dust QUATS concentrations in german homes. In respect to this, a significant estimation of an indoor QUATS exposure on the basis of approved measuring methods was allowed.

RESULTS

Case study 1: Large-scale application of a QUATS-containing disinfectant within the mold remediation in a single family home

The following case study describes the large-scale application of a QUATS-containing disinfectant within a mold remediation in a single family home (Aachen, Germany). The samples were taken in the year 2007 after the occupants could not move back into their home because of health problems.

Table 1. Results case study 1

	Results EFH Aachen this study			**Statistical comparative data (percentile value)** *[Thumulla J und Friedle A (2007)]*		
	S1 top floor	**S2 2nd floor**	**S3 1st floor**	**P-50**	**P-90**	**P-95**
BAC-10				0,1	0,7	0,9
BAC-12	45	51	76	8,4	24,3	53,3
BAC-14	27	26	42	3,4	8,3	26,4
BAC-16	5,4	7,2	13	1	3,2	7,2
Σ BAC	**77,4**	**84,2**	**131**	**13,3**	**29,5**	**88,7**
DDAC	**960**	**97**	**54**	**2,8**	**10**	**12,2**
Σ QUATS	**1115**	**265**	**316**	**17,6**	**44,3**	**105,7**

- BAC-10 (Benzalkoniumchloride mit R=C_{10})
- BAC-12 (Benzalkoniumchloride mit R=C_{12})
- BAC-14 (Benzalkoniumchloride mit R=C_{14})
- BAC-16 (Benzalkoniumchloride mit R=C_{16})
- DDAC (Didecyldimethyl-ammoniumchloride)

The results show that the sum of the persisting QUATS in the remediated building exceeds the 95. percentile of representative comparative flats 2.5 to 10 times. The indoor normal value (median, 50. percentile) is exceeded by the factor 20 to 60. Therefore, a considerable contamination with biocides belonging to the class of quaternary ammonium compounds was determined. (Remark: Until now the building is still not inhabited!)

Case study 2: Small-area application of a QUATS-containing disinfectant

A further example (from Mannheim, Germany) illustrates the small-area application of a QUATS-containing disinfectant in an apartement within a mold remediation (directly sprayed on approx. 0,5 m^2 of the wall paper in the master bedroom). Because the tenant was afraid of a relevant contamination of the apartement and the inventory the subsequent dispute resulted

in a lawsuit. For determination of possible contaminations material samples of treated and untreated areas as well as samples from untreated surfaces and the inventory were taken.
The comparison of the analysis results with the reference values of house dust samples clearly showed that the detected QUATS concentrations on untreated wall surfaces and inventory (stored in the flat and in the garage) are in a range with the background contaminations ubiquitary present in german apartments. For that reason no relevant contamination was assessed. Moreover, the comparison of the percentage ratio of the single Benzylalkoniumchlorides (BAC) show an evident distinction between the percentage composition of the identified BAC on the untreated surfaces/materials and the treated surfaces/materials. Hence, the detected BAC concentrations on the untreated surfaces/materials can be traced back to another source than the used QUATS-containing disinfectant.

Table 2. Results case study 2

Sample	**Benzylalkoniumchloride**								
	BAC-C10		BAC-C12		BAC-C14		BAC-C16		Σ BAC
	mg/kg		mg/kg		mg/kg		mg/kg		mg/kg
Disinfection product (Treatment)	3	0,1%	1500	68%	700	32%	10	0,5%	2200
Master bedroom									
Wall paper, treated area	**1,8**	0,3%	**490**	69%	**220**	31%	**1,7**	0,2%	**714**
Plaster below wall paper, treated area	**0,8**	0,2%	**270**	66%	**140**	34%	0,8	0,2%	**412**
Wall paper, untreated area	**0,15**	0,8%	**9,9**	51%	**8,4**	43%	0,9	4,6%	**19,4**
Dust	0,04	0,3%	**10**	71%	**4**	28%	0,09	0,6%	**14,1**
Hall									
Wall paper	0,09	1,2%	5,4	70%	2,2	28%	0,03	0,4%	7,72
Living room									
Wall paper	0,03	3,6%	0,48	57%	0,29	35%	0,04	4,8%	0,84
Dust	0,02	0,4%	3,2	71%	1	22%	0,26	5,8%	4,48
Chair cushion	<		0,09	47%	0,07	37%	0,03	15,8%	0,19
Garage									
Stored objects	**0,23**	0,7%	20	63%	11	35%	0,32	1,0%	**31,6**
Children's room									
Dust	0,01	0,6%	1,1	65%	0,53	31%	0,05	3,0%	1,69
Comparative data house dust Thumulla and Friedle (2007)									
P - 50	0,1	0,8%	8,4	63%	3,4	26%	1	8%	13,3
P - 90	0,7	2,4%	24,3	82%	8,3	28%	3,2	11%	29,5
P - 95	0,9	1,0%	53,3	60%	26,4	30%	7,2	8%	88,7

Case study 3: Large-scale application of a QUATS-containing disinfectant in a condominium

The last study case deals with the lawsuit resulted from a mold remediation in a condominium in Garmisch-Partenkirchen, Germany which was carried out in 2006. In the focus of the conflict between owner and renovation company was the concern that the mold remediation was not carried out properly, not as ordered, uncompleted and non-professional.
Part of the ordered and scheduled remediation was the large-scale surface disinfection with residue-free disinfectants, e.g. isopropanol. However the documents showed the usage of a QUATS-containing disinfectant. Even three years after the mold remediation was performed, the identification of untreated and treated surfaces was possible. For assessment and distinction if the carried out work was not as ordered, uncompleted and non-professional we took wipe samples (result table: "wipe") and material samples ("mat"). For this purpose

surface samples were taken by wiping defined surface areas and whole material samples were analysed so the surface content could be specified analog the wipe samples.
Table 3 summarizes the samples and the corresponding QUATS surface contaminations.

Table 3. Results case study 3

Sample		**Area**	**BAC-C10**	**BAC-C12**	**BAC-C14**	**BAC-C16**	**Sum BAC**	**DDAC**
Unit		m²	µg/m²	µg/m²	µg/m²	µg/m²	µg/m²	µg/m²
Cellar I: plaster surface	mat.	0,0121	33	1.000	360	170	1.560	3.100
Cellar I: wall (up)	mat.	0,081	1.900	61.000	26.000	13.000	102.000	100.000
Cellar I: ceiling	mat.	0,01	1.400	47.000	19.000	8.900	76.300	79.000
Cellar II: plaster surface	mat.	0,0121	33	1.200	400	170	1.800	4.900
Cellar II: wall (up)	mat.	0,011	1.800	53.000	25.000	12.000	91.800	94.000
basement Hall: timber stair (down)	wipe	0,2	-	14	6	2	22	24
Kitchen: chipboard on fridge glossy coated	wipe	0,3465	16	670	200	75	961	840
Kitchen: wood	wipe	0,875	0,5	39	15	6,9	61,4	73
Kitchen: stainless steel hood	wipe	0,508	17	660	180	62	919	720
Living room: wooden cupboard	mat.	0,0005	-	120	40	-	160	160
Bedroom: wardrobe, chipped wood	mat.	0,002	20	1.300	570	300	2.190	2.700
Slatted frame	wipe	0,22	11	710	300	150	1.170	1.100
Headboard	wipe	0,44	1,9	110	41	17	170	150

The results demonstrate that QUATS are detectable on every surface differing in their concentration by the factor 5.000. A typical background contamination of BAC as source for the detected concentration can be excluded because the identified QUATS always showed a characteristic correlating ratio between the class of BAC and DDAC. This characteristic ratio 1:1 of these substances is also described in the safety data sheet for the ingredients of the used disinfectant. Thumulla and Friedle (2007) discovered that within background contaminations the sum concentration of BAC and the concentration of DDAC do not correlate together (R^2 of 0,0046). This means that QUATS (BAC and DDAC) normally found indoors are independently of each other. In the case of the detected QUATS concentrations in the analysed apartment there is a strong correlation (R^2 of 0,9987) between sum concentration of BAC and the concentration of DDAC. Therefore these detected QUATS could be clearly identified as residues of the used disinfectant.

DISCUSSION

Since there has been comparatively little field-based research on these classes of cationic surfactants given the levels of QUATS observed after mold remediation, the presented case studies give for the first time an overview about the resulting indoor contamination concentrations of QUATS on materials, house dust and treated surfaces in addition to previous house dust studies. A quantitative measure of uncertainty was not readily determined, but we estimate that results are within 20% of the true values. Nevertheless the study reveals a strong relevant indoor contamination problem even years after the use of QUATS-containing disinfectants. Although QUATS are not considered as acute toxic to humans and despite their minor volatility a potential health risk cannot be excluded. Interestingly, in accordance with that a new biocide product guideline concerning this class of cationic surfactants is on its way. Furthermore, the study presented here can help to get a first

impression of relevant indoor contaminations and therefore could be a good assessment tool within lawsuits.

CONCLUSIONS

The performed analyses show that the usage of quaternary ammonium compounds (QUATS) as disinfectant leads to long-lasting persistent indoor contaminations. In accordance with the current state of knowledge occupants cannot be aware of a potential health risk caused by disinfectant residues as QUATS. Some case studies reveal that inhalative uptake of particle-bound QUATS advance the development of allergic respiratory diseases or even act as a trigger factor for asthma (Nielsen et al., 2007). Furthermore, it is known that QUATS in particular BAC can cause contact dermatitis (Houtappel et al., 2008). In principle, the usage of QUATS-containing disinfectants has to be regarded as critical as there is not only the potential health risk but also the risk for users to be liable for extensive decontamination measures and to be sued for damages. Hence, the handling and use of disinfectants should be reconsidered because the use of long-lasting biocides as QUATS is no longer state of art for professional mold remediation.

ACKNOWLEDGEMENT

We thank Albrecht Friedle for the support of the QUATS study and Dr. Thomas Haumann for helpful comments.

REFERENCES

Friedle A, Thumulla J, Snepvangers K (2008). QUATsernary ammonium compounds (QUATS) in house dust", in: Indoor Air 2008, Kopenhagen

Houtappel M, Bruijnzeel-Koomen CA, Röckmann H (2008) Immediate-type allergy by occupational exposure to didecyl dimethyl ammonium chloride. Contact Dermatitis. 2008 Aug; 59(2):116-7.

Nielsen GD, Larsen ST, Olsen O, Løvik M, Poulsen LK, Glue C, Wolkoff P.(2007). Do indoor chemicals promote development of airway allergy? Indoor Air. 2007Jun; 17(3): 236-55. Review.

Thumulla J und Friedle A (2007). Quartäre Ammoniumverbindungen (QAV) im Hausstaub, in Umwelt, Gebäude & Gesundheit – Innenraumschadstoffe, Fogging und Gerüche, Hrsg. Arbeitsgemeinschaft ökologischer Forschungsinstitute (AGÖF), Springe-Eldagsen 2007

Bode-Chemie. (2007). Hintergrundwissen Desinfektionswirkstoffe, Oberflächenaktive Verbindungen (QAV). http://www.bode-chemie.de/science/hintergrundwissen/ desinfektionswirkstoffe_oberflaechenaktive_verbindungen.php

UBA 2005: Innenraumlufthygiene-Kommission des Umweltbundesamtes (German Federal Environment Agency), Hrsg. (2005): Leitfaden zur Ursachensuche und Sanierung bei Schimmelpilz-wachstum in Innenräumen („Schimmelpilz-Sanierungsleitfaden“)

Kuppens, E.V., de Jong, C.A., Stolwijk, T.R., de Keizer, R.J., van Best, J.A. (1995), "Effect of timolol with and without preservative on the basal tear turnover in glaucoma" , Br. J. Ophthalmol. *79, 339-342 (1995)*

Herreras, J.M., Pastor, J.C., Calonge, M., Asensio, V.M. (1992), "Ocular surface alteration after long-term treatment with an antiglaucomatous drug" , Ophthalmology *99, 1082-1088 (1992)*