New and less recognized risks with building materials: volatile organic compounds, replacement chemicals, and nanoparticles

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Emina Kristina Petrović
Victoria University of Wellington, Wellington, New Zealand

8.1 Introduction

Following the discussions in Chapter 6 and Chapter 7, this chapter looks into the Stage 1 or with the early recognition of health risks associated with a particular substance, when early indications of plausible or likely adverse health effects are articulated, this being the point of reasonable "suspicion" that a particular substance could be harmful. Based on such "suspicion" more research is then undertaken to prove or disprove it, which leads to more articulation of health effects, and potentially triggers recognition and progression towards Stages 2 and 3. The key question of this section is whether it is possible to observe any indications in current practices that substances "suspected" of being hazardous are held back from introduction into everyday use. In this section, two types of "suspected" hazards are reviewed: substances that have been "suspected" for a while, and newly developed substances.

8.2 On-going suspicion—volatile organic compounds from carpets

While the risks associated with formaldehyde, phthalates, and PVC, discussed in Chapter 7, are reasonably well established, much more confusion surrounds volatile organic compounds (VOCs) from carpets. During the 1980s, when sick building syndrome was most discussed, carpets were often seen as a contributing factor. In fact, in 1999, one study evaluated the direct impact on workers' productivity of exposure to fumes from a 1980s' carpet sample 20 years later, showing the adverse effect still held strong (Wargocki et al., 1999). One relevant observation from that experiment was that the sample did not present elevated total VOCs (TVOCs), but rather elevated levels of certain individual VOCs, in this case acetone, acetic acid and aldehydes, ketones, and organic acids (Wargocki et al., 1999). Some literature has since concluded that because the irritant potential and toxicity of individual VOCs vary widely, evaluation of VOCs through a

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combined measure of TOVCs can no longer be supported (ASHRAE, 2009, section 10.10). However, in contemporary carpet-related regulations TVOCs are still reported in some sources, some are expressed in relation to individual VOCs, and some combine both approaches, jointly suggesting poor regulative protocols.

Table 8.1 compares leading European voluntary labeling schemes for how they define TVOC levels (Katsoyiannis et al., 2008). In addition to varying levels, these schemes also use different testing chambers, test durations, and report results in different units. To evaluate the importance of such differences, one study tested four carpet samples using various testing chambers and periods, concluding that differences of as much as 75% were possible (Katsoyiannis et al., 2008). They concluded that establishing a clearer pan-European regulating protocol for carpets would be simpler for the users and those conducting tests and could even prove more cost-effective for manufacturers (Katsoyiannis et al., 2008).

There are similar issues in New Zealand, where two voluntary schemes currently operate: one through the Carpet Institute of Australia (2013) and one through Environmental Choice New Zealand (2011 and 2012), with numerous differences between them. Table 8.2 compares levels of individual VOCs listed by these schemes with the official classification of the same chemicals for their impact on human health. One observable feature is that some of the VOCs listed are recognized as substances of very high concern (e.g., benzene and formaldehyde), many have different lower levels of recognition, while some do not appear on any lists (e.g., 4-phenylcyclohexene and 2-ethylhexonoic acid). Therefore, there is great variety around the wide range of chemicals used in carpets in their recognized impact on human health, representing different stages of recognition.

For the purpose of discussion of Stage 1 substances, 4-phenylcyclohexene (4PCH) is a good example of the complexities encountered when evaluating the health impact of less recognized chemicals. Already in the early 1990s, research on emissions from carpets established that 4PCH was one of the VOCs emitted from new carpets, "responsible for new carpet odour" (ASHRAE, 2009, section 11.9), and differences were observed between different technologies used for backing and presence or level of 4PCH emissions (Beekman et al., 1996; Singhvi et al., 1990). Generally, 4PCH is a byproduct of the polymerization process between styrene and butadiene, which are the main components of styrene-butadiene rubber (SBR) (SBR is discussed in more detail in Chapter 9). ASHRAE recommends that it should only be tested for in carpets and fabrics with SBR backing (ASHRAE Standard 189.1-2011). However, 4PCH is found in carpets with SBR backing and laminated fabric backing (Katsoyiannis et al., 2008). Recent studies have found only a small proportion, up to 30%, of carpet samples with no 4PCH and no clear relationship could be observed between different carpet and backing materials and the presence of 4PCH (Katsoyiannis et al., 2008; Wilke et al., 2004). This, together with evaluations of 4PCH in some paper printing technologies (Landy et al., 2004), seems to indicate that the use of 4PCH has expanded from just being related to SBR backing.

Table 8.2 shows the results of a search through official organizations on VOCs from carpets. However, these sources provide very little information on 4PCH (Table 8.2). A PubMed database search returned only a small number of articles which related to animal tests of 4PCH for acute toxicity, and which made no conclusive observations (Beekman

Table 8.1 Emissions requirements (or test chamber concentrations) of leading European voluntary labeling schemes for carpet materials

	Leading European voluntary labeling schemes for carpet materials								
	AgBB	**CESATF**	**M1**	**LQAI**	**Nature Plus**	**Blue Angel**		**GUT**	**Emicode EC1**
	Germany	**Rance**	**Finland**	**Portugal**	**Europe**	**Germany/ Europe**	**Austrian Ecolabel**	**Germany/ Europe**	**Europe**
TVOC after 3 days	10,000 μg/m^3	5000 μg/m^3		5000 μg/m^2/h		1200 μg/m^3		300 μg/m^3	(10 days) 500 μg/m^3
TVOC after 28 days	1000 μg/m^3	200 μg/m^3	200 μg/m^2/h	200 μg/m^2/h	200−300 μg/m^3	360 μg/m^3	380 μg/m^2/h		
Formaldehyde (HCHO)	28 days: 120 μg/m^3	28 days: 10 μg/m^3	28 days: 50 μg/m^3	28 days: 10 μg/m^3	28 days: 36 μg/m^3	28 days: 60 μg/m^3	–	10 μg/m^3	1 days: 50 μg/m^3

Source: Katsoyiannis et al. (2009).

Table 8.2 Comparison between regulated levels of VOCs in carpets in New Zealand, and the classification of the same chemicals for impact on human health

Substance description	AU ACCS Max emiss. (24 h) μg/h/m^2	NZ Env. Choice for syn. carpet μg/m^3	US Green label plus Max emiss. (24 h) μg/h/m^2	Classification by: • ECHA • IARC • CAL/OSHA	Health effects	General use
Benzene C_6H_6	55	30	55	• 1 ECHA 2008 • 1 IARC 2012 • Cal classified	Benzene is carcinogenic (IARC 1982). Prolonged exposure at levels below 1 ppm (3.2 mg/m^3) can lead to mutagenicity and carcinogenicity. Concerns for fertility also mentioned	Available in petrol, normal traffic pollution and close to petrol stations. Also in some paints, car interior accessories, and perfumes
Formaldehyde CH_2O	10	16	16	• 1 ECHA 2012 • 1 IARC 2012 • Cal classified	Carcinogenic	Numerous uses in building materials, mainly as part of gluing agents, and chemical treatments. In carpets used as biocide/antimicrobial
Toluene $C_6H_5-CH_3$	280	150	280	• 2 ECHA 2004 • 3 IARC 1999 • Cal classified	Possible acute, system and specific organ toxicity due to inhalation or dermal exposure, neurological and cardiovascular toxicity, concerns for fertility and developmental effects, and spontaneous abortions due to inhalation	In high-octane blending petrol, as solvent for paints and coating, gums, resins, oils, rubber, and adhesives, as an intermediate in the preparation of many chemicals, dyes, pharmaceuticals, detergents, and explosives, for printing and manual cleaning
Styrene C_8H_8	410	220	410	• Not classified • 2B IARC 2002 • Cal classified	Harmful by inhalation, sensitizer; toxic for nervous system, liver, and eyes; conclusively observed to be toxic to fertility and toxic to reproductive development, some strong relations to carcinogenesis	Used in plastics, latex paints and coatings, synthetic rubbers, polyesters, and styrene-alkyd coatings. In construction in pipes, fittings, lighting fixtures, synthetic marble, flooring, carpet backing, molded furnishing

Acetaldehyde C_2H_4O	20	4.5	130	• Not classified • 2B IARC 1999 • Cal classified	Could be respiratory sensitizer, and carcinogenic for oral and bronchial tumors, possible skin sensitization, aspiration hazard and possible reproductive toxin Other: Probable carcinogen (Carpet Institute of Australia) Endocrine-disrupting chemical, carcinogen, teratogen, and causes allergic airway inflammation (Kawano et al., 2012)	Natural product of combustion and photo-oxidation of hydrocarbons, industrial use as intermediate, used in silvering of mirrors, leather tanning, denaturant for alcohol, fuel mixtures, hardener for gelatine fibers, as flavoring agent, in cosmetics, in glue and casein products, preservative for fish and fruit, in paper industry, in carpets used as biocide/ antimicrobial
Vinyl Acetate $C_4H_6O_2$	400	100	190	• Not classified • 2B IARC 1995 • Cal classified	Acute toxicity oral and dermal; skin irritation, respiratory sensitization, reproductive toxicity, suspected carcinogenesis for oral exposure	Used to make polyvinyl acetate adhesives for paper, wood, glass, metals, and porcelain, also in latex water paints, coatings for paper, textile, and leather, base for inks and lacquers, in cosmetics, pharmaceuticals, food additives, and pesticides
Naphthalene $C_{10}H_8$	20	4.5	8.2	• Not classified • 2B IARC 2002 • Cal classified	Limited evidence of adverse health effects, mainly lungs for inhalation	Used in manufacture of phthalic anhydride which is used as intermediate in the production of phthalate plasticizers, resins, dyes, pharmaceuticals, insect repellents, also used in baby oils
Caprolactam $C_6H_{11}NO$	120	100	130	• Not classified • 4 IARC 1999 • Cal classified	No carcinogenic effect observed, possible skin sensitization, aspiration hazard and possible reproductive toxin, more concerns regarding toxicity than carcinogenesis (IRIS)	Primarily used in manufacture of synthetic fibers and resins (nylon 6), bristles, film, coating, synthetic leather, plasticizers, paint vehicles, cross-linking agent for polyurethanes
1-Methyl-2-Pyrrolidone C_5H_9NO	300	160	300	• Not classified • NA • Cal classified	Respiratory and skin sensitization, aspiration hazard, concern that it may damage fertility or the unborn child due to oral exposure	Used as a solvent for resins and acetylene, as paint stripper
Nonanal $C_9H_{18}O$	24	13	24	• Not classified • NA • NA	Skin and eye irritation, possible skin sensitization, reproductive toxicity, and germ cell mutagenicity	Used in flavors and perfume production
Octanal $C_8H_{16}O$	24	7.2	13	• Not classified • NA • NA	Skin and eye irritation	Used as flavoring, in perfumery, in preparation of synthetic citrus oils

(*Continued*)

Table 8.2 (Continued)

Substance description	AU ACCS Max emiss. (24 h) μg/h/m^2	NZ Env. Choice for syn. carpet μg/m^3	US Green label plus Max emiss. (24 h) μg/h/m^2	Classification by: • ECHA • IARC • CAL/OSHA	Health effects	General use
2-Ethylhexonoic Acid $C_8H_{16}O$	46	25	46	• NA • NA • NA	Some indications of oral toxicity (PubChem Compound)	Chemical intermediate in manufacture of resins for baking enamels, lubricants, detergents, flotation aids, and corrosion inhibitors; catalyst for polyurethane foaming
4-Phenylcyclohexene $C_{12}H_{14}$	50	2.5	50	• NA • NA • NA		

The Australian Carpet Classification Scheme (ACCS) follows ISO 10580:2010, and all ECS Level carpets have to comply with this; Environmental Choice New Zealand for synthetic carpets (document for wool does not set VOC levels); US Green Label Plus, the Carpet and Rug Institute. The AU and US scales provide a 24-h emission VOC emissions rate immediately after carpet manufacture in μg/h/m^2, while the NZ scale has a loose definition.
IARC evaluates only carcinogenesis to humans (group 1—carcinogenic; group 2A—probably carcinogenic; group 2B—possibly carcinogenic; group 3—not classifiable; group 4—probably not carcinogenic); ECHA and CAL/OSHA classify priority substances due to toxicology and/or carcinogenesis, thus "no classification" means that at this point substance is not recognized as needing classification. Substances that could not be found for either organization were noted as NA (not available).
Source: Carpet Institute of Australia, 2013. Australian carpet classification scheme incorporating the environmental certification scheme: technical guidelines. http://www.carpetinstitute.com.au/environment/index.htm (retrieved August 2013.); Environmental Choice New Zealand (2011 and 2012); Carpet and Rug Institute (US), 2013. Available from: www.carpet-rug.org (accessed August 2013.) (Carpet and Rug Institute (US), 2013); ECHA (2013); International Agency for Research on Cancer (IARC), 2013. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Available from: http://monographs.iarc.fr/ENG/Classification/index.php (accessed January-August 2013.) (IARC, 2013); CAL/OCHA 2013; Integrated Risk Information System (IRIS), 2013. Available from: http://www.epa.gov/iris/index.html (accessed August 2013.) (IRIS, 2013); PubChem Compound, 2013. Available from: http://www.ncbi.nlm.nih.gov/pccompound (accessed August 2013.); Agency for Toxic Substances and Disease Registry (US) (ATSDR), 2013. Available from: <www.atsdr.cdc.gov> (accessed August 2013.) (ATSDR, 2013).

et al., 1996). However, search of the PubChem Compound database under the BioActivity summary returned six "inactive" items, which indicate that 4PCH is genotoxic in human embryonic kidney cells (PubChem Compound, 2013). In addition, Toxnet: toxicology data network indicated that reports were produced in the early 2000s evaluating acute toxicity of 4PCH in animals, but these could not be accessed. Therefore, currently it seems unlikely that the 4PCH impact mechanisms on human health are understood. However, the absence of clear adverse effects does not mean that 4PCH should be considered safe, simply because there are only a small number of studies and no clear adverse effects. Furthermore, the available information indicates an adverse health effect is possible, and more research is needed to explain this. Nevertheless, recently 4PCH has been introduced into the food packaging industry (Landy et al., 2004) and therefore exposure of the general population to it is likely to increase.

This treatment of 4PCH is very characteristic of many substances currently in use. While chemicals that produce acute toxicity at relatively low levels are increasingly becoming recognized as unhealthy, with subsequent regulation of these, currently there are no good mechanisms for evaluating the health effects of chemicals that are less aggressively adverse to human health. This means that the lessons from phthalates are still not absorbed, because absence of very clear acute toxicity does not mean the absence of adverse effects. Indications of in utero toxicity for kidney tissue clearly belong to this type of less obvious impact. Therefore, VOCs that are commonly used in carpet production but not found in lists of high-risk chemicals should generally still be approached with caution.

Similar patterns can be observed with a number of other everyday chemicals. For example, water-based paints and varnishes are generally considered safer than their solvent-based equivalents. However, there is an increasing body of research recognizing the toxicity of common solvents used in water-based products, even at very low levels (Lin et al., 2013; Spee et al., 2012). 2-Butoxyethanol, also known as ethylene glycol monobutyl ether ($BuOC_2H_4OH$) is an organic solvent used in some water-based paints and surface-coating products (ASHRAE, 2009, section 11.9). It is listed in California Occupational Safety and Health Regulations as a hazardous substance (CAL/OSHA, 2013), although in 2004 the EPA removed it from its list of hazardous air pollutants (EPA, 2004). Others have observed that 2-butoxyethanol has been related to poor indoor air quality complaints (Rella et al., 2012). Jointly these observations indicate that for the last 10 years, 2-butoxyethanol has been on the point of Stage 1 recognition as risk, while still present in many products. (For a more detailed discussion on paints and varnishes see Chapter 9).

The problem is that most research efforts are focused on more recognized hazards and providing sufficient knowledge to lead to effective removal of these, while borderline hazardous substances receive marginal research attention. Unfortunately, that does not mean that they are safe, but rather that they are not well understood.

8.3 Replacement and new substances

One important area of new development is substances that replace those phased out as hazardous. More recently, replacements for formaldehyde, phthalate plasticizers,

and fire-retardants have been developed. For phthalates and fire-retardants early observations show that regulations against one set of such chemicals produced an increase in use of other chemicals from the same family. For phthalates the change was from shorter-chain phthalates (such as DEHP) to longer-chain phthalates (such as DINP) (Holmgren et al., 2012), and to a number of nonphthalate plasticizers (see Chapter 7). For fire-retardants the change was from a polybrominated diphenyl ether (PBDE) fire-retardant mixture PendaBDE to more prolific use of tris(1,3-dichloroisopropyl) phosphate (TDCPP), a suspected human carcinogen (Stapleton et al., 2012). Unfortunately, in both cases the replacement chemicals are simply less researched and less well understood for their health effects (Holmgren et al., 2012; Stapleton et al., 2012). The issue here is the interpretation of the wording: "suspected of adverse health effects." If using the precautionary principle, "suspected" could be seen as meaning "probably" if not "likely," while the manufacturers seem to be interpreting it as "ready to use." This is especially the case with TDCPP which is at least in the early Stage 2 of recognition. This implies that many substances which are introduced as replacements for eliminated risks could also be seen as being in the entry stages of the same process of recognition of health risks. Fig. 8.1 illustrates this almost cyclic process.

Similarly, although many formaldehyde-free products are increasingly available, PubMed currently reports only a very small number of studies on their health impact, indicating replacements are introduced without much evaluation of their health effect. However, there are some exceptions. For example, one study explored the health impact of the change from a phenol-formaldehyde bonding agent in fiberglass insulation to a carbohydrate-carboxylic acid binder, observing that in vitro this binder did not impact the biosolubility of glass wool insulation, but also noted that droplet sizes had an impact (Potter and Olang, 2013). Droplet size of the bonding agent, which

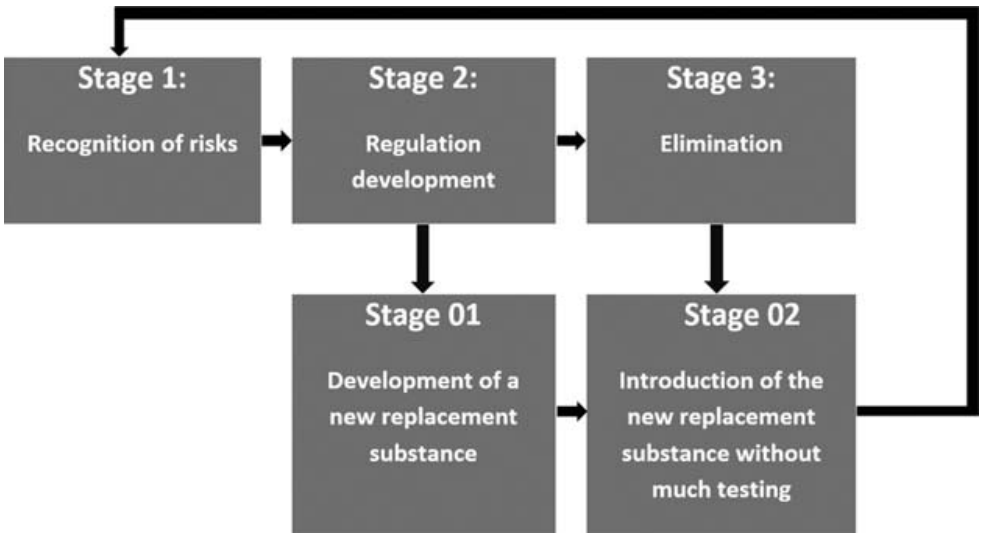

Figure 8.1 Cycle of introduction of replacement substances into testing for adverse impact on human health.

greatly varied in the samples studied, seems controllable by careful manufacturing. This indicates that much more sophisticated research is needed in these early stages of development of new materials, if they are to be reliably safe.

One area of recent development is materials that use nanoparticles. With the technology that enables design at scales unprecedented in the past, a range of completely new material characteristics is becoming available for the first time. Unfortunately, there are already warnings about nanoparticles. Researchers have remarked that nanoparticles are likely to impact the human body similarly to microparticles, the best known of these being the asbestos family (Donaldson and Poland, 2012; Sanchez et al., 2009; Pacheco-Blandino et al., 2012). If learning from the experiences with asbestos, the problem would seem to be the shape and size of particles and their biopersistency within the human body. For asbestos it was the long, thin shape and very long biopersistency that produced inflammation and subsequent onset of disease after a long latency. Because this knowledge is available, it seems reasonable to use it when developing new materials with similar features. However, texts that deal with design and the exciting opportunities nanotechnology offers fail to mention risks associated with such particles (Yeadon, 2011), indicating the same mistakes could be repeated.

8.4 Discussion on Stage 1 and conclusion

Although Chapter 7, recorded some acceleration in the way substances now in Stage 2 of recognition are progressing towards elimination, the overall impression is that this progress is generally still slow. The experience with lead and asbestos showed that it can take a long time before the total impact is fully understood. The experiences with formaldehyde and phthalates could unfortunately be just "the very tip of the iceberg" because they are only the most recognized risks from the great array of chemicals introduced into everyday use since the mid-20th century. The actions observed with Stage 1 substances indicate that potentially very limited learning from past mistakes has occurred. Substances that are "suspected" to be harmful are readily used, and their use often increases while the recognition of risks also increases.

Unfortunately, the scientific understanding of these risks is still partial, and if proof of harmful affect is needed prior to any action, such proofs do not exist for many of the substances. One aspect of concern is the very limited understanding of effects these substances create when people are exposed to their various combinations. One estimate suggests that if only three chemical combinations were to be comprehensively evaluated, it would need 166 million tests, and take 11,000 years, assuming 15,000 tests per year (Armstrong et al., 2007, p. 61). Evaluating 11 chemical combinations would take a million times longer than the universe has existed (Armstrong et al., 2007, p. 61). Therefore, currently assuming there is sufficient scientific knowledge on the health risks associated with building and furnishing

materials is unrealistic, and all professional activities have to develop work strategies that acknowledge this limitation.

The solution to this problem is the precautionary principle, and the literature sources that adopt this idea are the popular works related to building biology or those based on their authors direct personal experiences (Baker-Laporte et al., 2008; Thompson, 2004; Hobbs, 2003; Bower, 1989, 2000). In fact, these can act as "whistle blowers" for Stage 1 of recognition, because they do not have to adhere to academic nor regulative protocols, provide the most comprehensive lists of potential risks, and offer useful practical advice on their avoidance. Their only problem is that precisely because of their character, they might not be taken seriously by many. If the predominant logic is that "suspicion" is not enough, but rather a proof is needed prior to any change, these works fail to provide such proofs.

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