Overview on the existing knowledge on leaching of biocides from building materials

Sammenstilling af eksisterende viden vedr. udvaskning af biocider fra byggematerialer

Scientific briefing from DCE – Danish Centre for Environment and Energy Date: 11 Marts 2022 | **23**

Kai Bester, Institute for Environmental Science, Aarhus University

AARHUS UNIVERSITY
DCE – DANISH CENTRE FOR ENVIRONMENT AND ENERGY

Data sheet

Scientific briefing from DCE – Danish Centre for Environment and Energy

Category:	Scientific briefing
Title:	Overview on the existing knowledge on leaching of biocides from building materials
Author:	Kai Bester
Institution:	Aarhus University, Institute for Environmental Science, DCE - Danish Centre for Environment and Energy
Referee:	Pia Lassen
Quality assurance, DCE:	Susanne Boutrup
Linguistic QA:	Pia Lassen
External comment:	Danish Ministry of Environment. The comments can be found here: http://dce2.au.dk/pub/komm/N2022_23_komm.pdf
Claimant:	Danish Ministry of Environment
Please cite as:	Kai Bester. 2022. Overview on the existing knowledge on leaching of biocides from building materials, Aarhus University, DCE - Danish Centre for Environment and Energy, 13 s. – Scientific briefing no. 2022|23 https://dce.au.dk/fileadmin/dce.au.dk/Udgivelser/Notater_2022/N2022_23.pdf
	Reproduction permitted provided the source is explicitly acknowledged
Front page photo:	Kai Bester/Ulla Bollmann
Number of pages:	13

Contents

1 Biocides in construction materials – relevant compounds and usages 4

Objectives of this report 4

2 Mechanisms for leaching 6

Dependency of emissions to rain, windspeed and –direction 6

Pseudo-persistence in soil 7

Relevant transformation processes in the equipped materials 8

3 Suggestions of compounds to be included in the monitoring 10

4 Other open questions 12

Metabolites and transformation products 12

Undeclared biocides 12

Waste/reuse strategies 12

5 References 13

1 Biocides in construction materials – relevant compounds and usages

Objectives of this report

This reports intents to i) give an overview on, which biocidal compounds can be found in building materials for exterior use - including which building materials are relevant. ii) assessing which compounds and which applications within the building materials are most prone for leaching of biocides. The basis of this report are compound properties, use in the building industry and earlier findings in environmental samples. The focus is on compounds that are currently in use, and need (or have) approval under the biocidal products regulation (BPR, EU, 2012) as well as other compounds that are relevant to this field.

The project is a task within the agreement between Aarhus University and the Ministry of Environment of Denmark (MIM) and the Ministry of Food, Agriculture and Fisheries of Denmark (FVM) on research-based public sector consultancy.

Biocides are used for various purposes in building materials[1,2]:

1. As film preservatives (Product type (PT)7) (typically in paint) to prevent growth of algae (diuron, terbutryn, cybutryn[3]), fungi (carbendazim) and bacterial films (isothiazolionenes) that cause a priori aesthetical problems but in the long run also trigger problems for the paint integrity.

2. As wood preservatives (PT8) - this is typically paint used on wood equipped with especially fungicides (propiconazole, tebuconazole, carbendazim[4], iodocarb (IPBC), to enhance the lifetime of the wooden structures.

3. To protect fiber, leather, rubber, and polymerized materials (PT9) – especially the polymerized materials are getting increasing relevant for the building industry.

4. Construction materials (PT10) - this is including all other construction materials, such as masonry products like renders, sealants etc. using similar compounds as mentioned under 1.

5. Bitumous/polymeric roof sealants: especially mecoprop is heavily used in this application[5] to protect these relative soft materials against the growth

[1] In this briefing "building materials" is including all materials that are relevant for the building industry and is thus not synonymous with the terminus technicus "construction materials" of the Biocidal Products Regulation (BPR) (EU 2012)
[2] This briefing is not including insecticides for indoor usage or urban pesticides
[3] Cybutryn has been very relevant as antifouling compound, but has been outphased in what is now PT7 for a long time
[4] Carbendazime is no longer registered in PT8 but is still used as film preservative on wood (PT7 and PT10)
[5] MCPP (and its precursors are heavily used in this field, even though there is not registration of the compound in the BPR

of larger plants on top of flat roofs, leading to roots growing through the material, leading to untight materials.

6. Preservation under storage (PT6) - most construction materials (paints, renders, sealants) are distributed as aqueous suspensions, often via do-it-yourself markets. The designers of these systems thus have to consider considerable shelf storage (3-24 months) and have to enhance shelf life with biocides thus the product is not infested with microorganisms at the moment of application. The products are thus regularly equipped with in-can preservatives. It is well known that isothiazolinones (methylisothiazolinone (MI), chloro methyliosothiazolinone (CMI) as well as benzisothiazolinone (BIT) and octylisothiazolinone (OIT) are heavily used for this purpose. Probably, also other PT6 compounds are used in construction materials as well, though there is little data on that.

Balancing sustainability and environmental contamination

Generally, the use of biocides in building materials is due on the one hand to increased sustainability by increasing service life especially on surface layers of buildings as well as increasing demands on insulation. On the other hand usage of biocides lead to enhanced emissions of these compounds especially into surface waters and urban soils. There are a lot of measures to decrease the need for biocides such as:

Change designs of buildings by:

a) Using more overhanging roofs to prevent rain reaching walls

b) Using surfaces that do not need protection (stones, glass)

Or change delivery and shelf life situations:

c) Solvent based or dry systems need les in-can preservatives.

2 Mechanisms for leaching

Dependency of emissions to rain, windspeed and –direction

It is common of all construction material related biocides, that they are *a priori* mobilized (leached) during rainfall and that inputs into the environments during dry weather are very low. Dependent on the placement of the equipped structure the emissions are dependent on rain amount (horizontal structures like roofs) or driving rain, which is the product of rain amount and windforce (vertical structure such as walls) (figure 1). – Obviously, rain just falling from above hardly reaches walls, while rain in combination with wind strongly reaches walls on the wind exposed sides of the building. – The emissions into the environment are thus dependent on rain, windspeed and –direction (figure 2) (Bester et al., 2014). Interestingly, only very weak first flush effects can be seen, thus it can be assumed the emissions occur from the materials and not from dust on top of the materials (figure 3).The strong link to rainfall has severe consequences for monitoring programs: The main inputs (and thus concentrations) into surface waters are to be expected with the supposedly clean rain runoff water that is only occurring under rainfall. Monitoring programs that do not take this into account will produce erratic and very difficult to interpret data (Bester et al., 2014). To assess emissions it is helpful to sample as close to source as possible and under as defined rain and wind conditions as possible. To assess surface water data, it will be necessary to link to urbanized areas, rain and wind data as well as expected time of appearance (flowpath and length) of the runoff water in the respective surface water (Bester et al., 2014).

An additional challenge is included in the contaminated runoff rain water: This is usually considered as a very clean resource of water that is often supposed to be used either directly as drinking water or after infiltration (groundwater recharge).

Figure 1. Wind driven rain (from Bester et al., 2014).

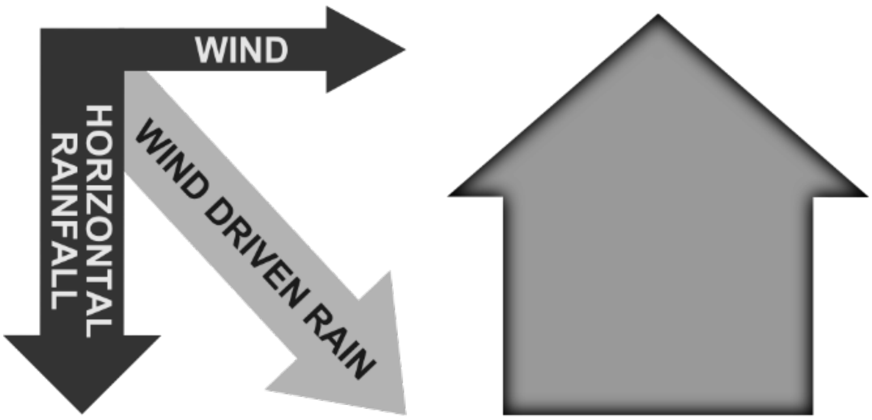
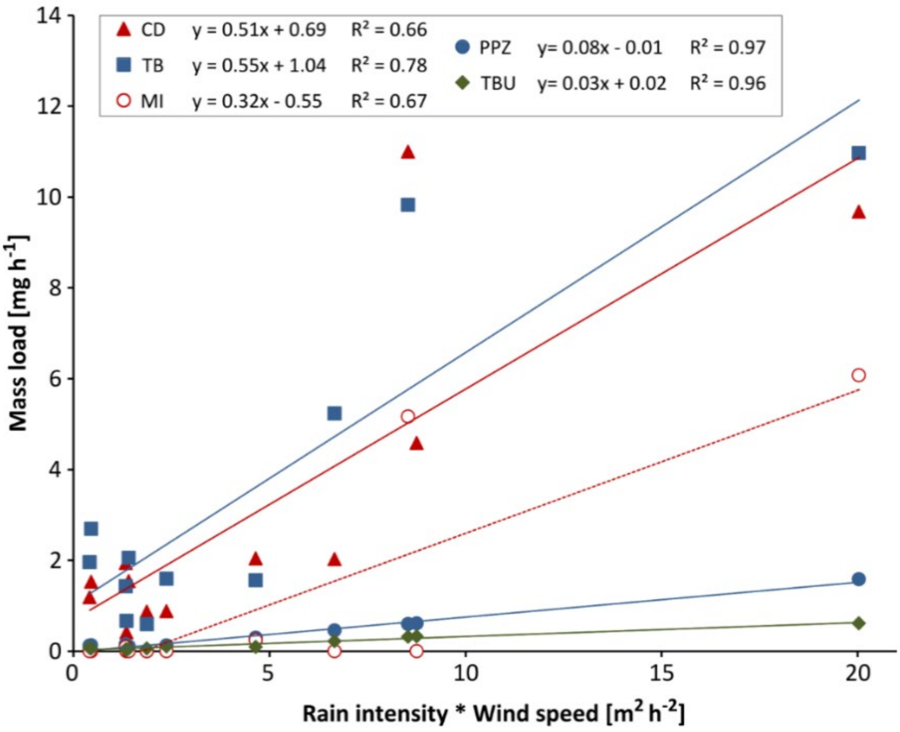


Figure 2. Mass loads of biocides (M_{WDR}) in relation to rain intensity (I_{Rain}) times wind speed (U) in the Silkeborg stormwater catchment (Shown are all compounds with R^2 > 0.48; Abbreviations: CD: Carbendazim, TB: Terbutryn, MI: Methylisothiazolinone, PPZ: Propiconazole, TBU: Tebuconazole; one peak event for terbutryn is excluded) (from Bester et al., 2014).



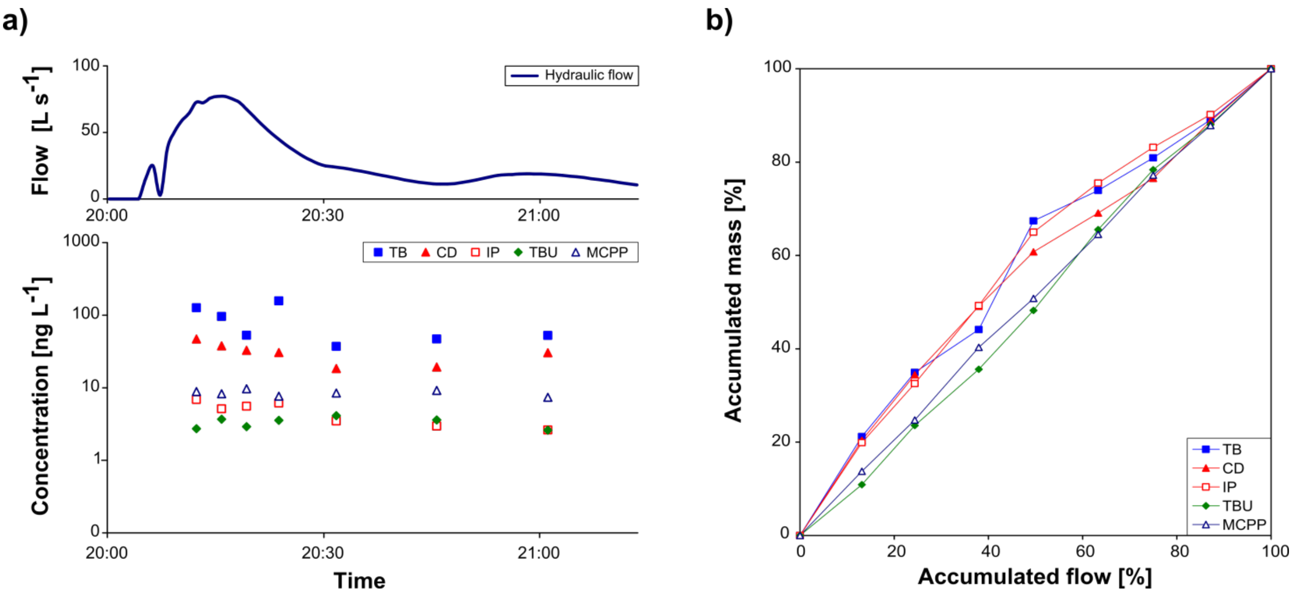
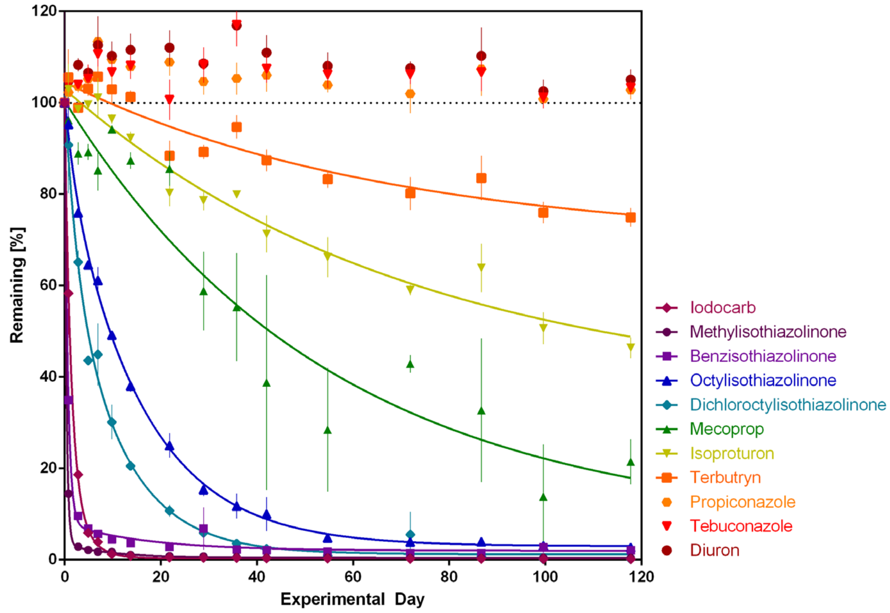


Figure 3. a) Common biocide concentration dynamics during a rain event and b) Evaluation of first flush dynamics in a common rain event. Abbreviations: TB: Terbutryn, CD: Carbendazim, IP: Isoproturon, TBU: Tebuconazole, MCPP: Mecoprop (from Bester et al., 2014).

Pseudo-persistence in soil

When relating to receiving environmental compartments such as the soil, one major difference to, e.g., pesticides should be noted: while pesticides would be used infrequently (at least ideally only once every few years), degradation speed in the soil to a large extent controls the concentrations of the active ingredients in the soil. Biocides are contained in construction materials and will be released with every rain event, thus even compounds that are degraded relatively rapidly (within days and weeks) will have continuous inputs and thus relative constant concentrations in the receiving soils (figure 4; Bollmann et al., 2017b). – This has dear consequences for urban drinking water resources, e.g. the high frequency of detection of DMS (*N,N* Dimethyl sulfamide) in ground and drinking water in the urban regions are most probably rather related to biocidal use (wood protection) of dichlofluanid and toylfluanid in construction materials related than pesticidal use.

Figure 4. Degradation kinetics of building material relevant biocides in soil in a laboratory experiment with one time dosing. In reality, there would be fresh mobilisation from the building materials with new rainfall approaximately every week (and thus weekly new input), it is obvious, that even those compounds that degrade rapidly, will have constantly high levels in those soils that receive runoff from building parts that are equipped with biocides (from Bollmann et al., 2017b).



Relevant transformation processes in the equipped materials

It has been demonstrated that biocides in paints are photodegraded (figure 5) to a relevant fraction as photodegradation products can be found both in the leachate water and in the polymeric material itself (figure 6). Whether the photodegradation occurs a) in an aqueous layer on top of the material, b) on the top layer of the polymer and the degradation product diffuses back into deeper layers of the polymeric material or c) photodegradation reaches deep layers of the polymeric materials is not verified at this moment. Most probable at the current state of knowledge seems to be a combination of a) and b) (Bollmann et al., 2016, 2017a, 2018).

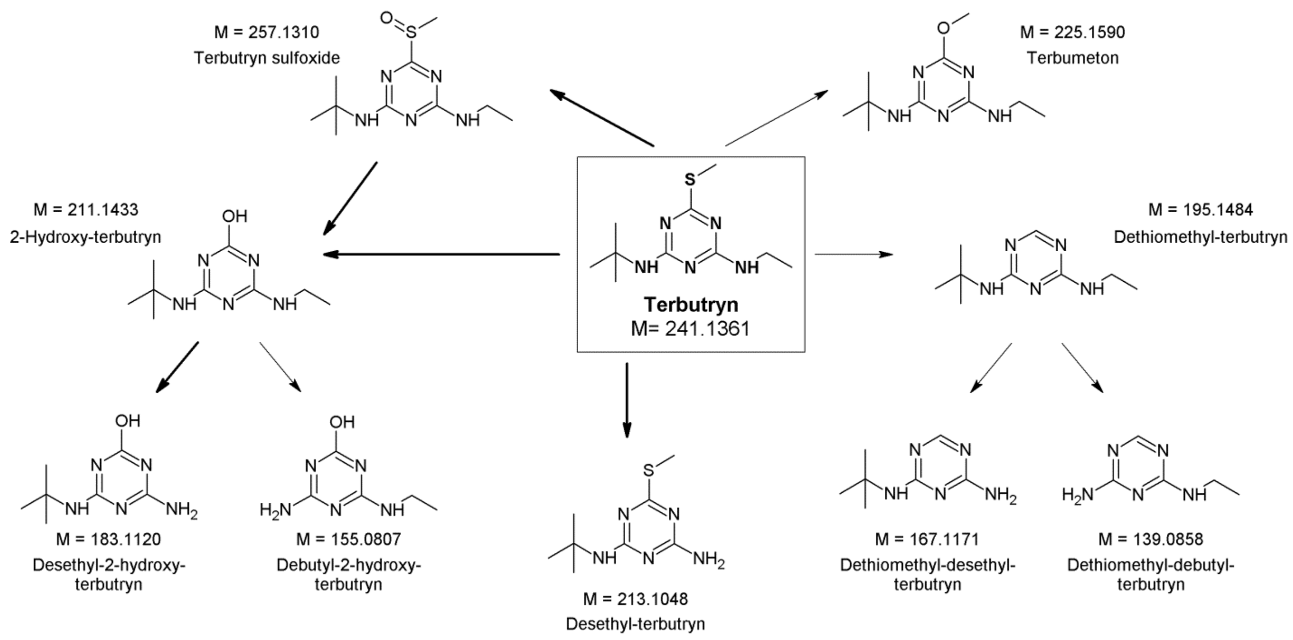
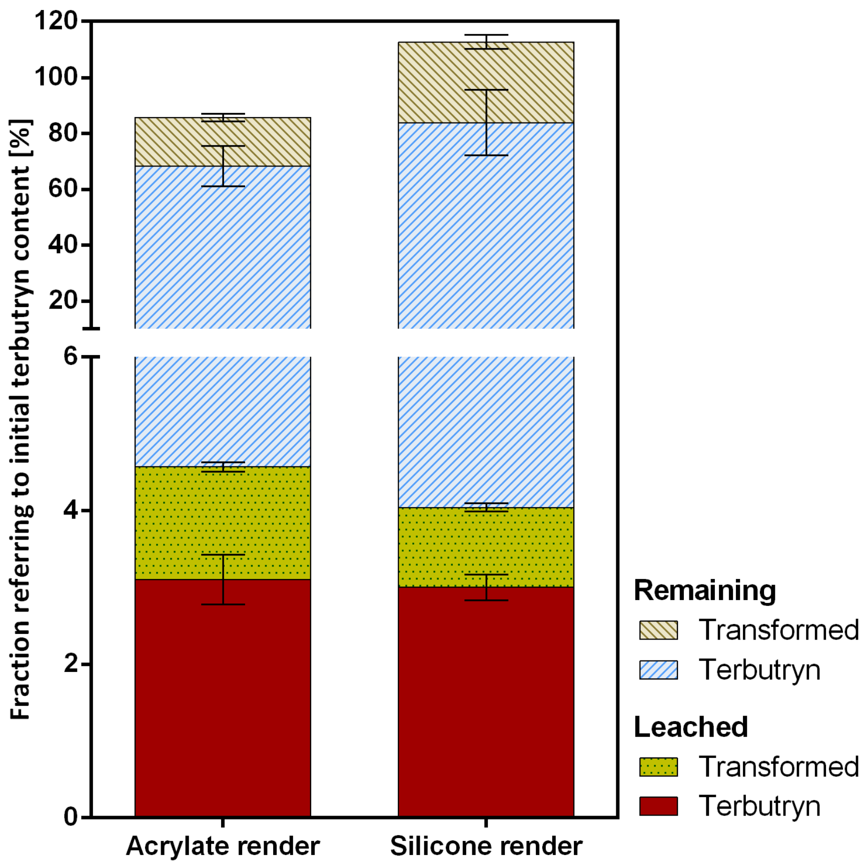


Figure 5. Photodegradation of terbutryn on a paint/render system (from Bollmann et al., 2016).

Figure 6 Mass balance of terbutryn: leached terbutryn - terbutryn detected in run-off water (average from 3 panels), leached transformed - sum of transformation products detected in run-off (average from 3 panels), remaining terbutryn - terbutryn in render after 19 month exposure (average of 10 extracts from one panel), remaining transformed - sum of transformation products in render after 19 month exposure (average of 10 extracts from one panel); error bars: standard error of mean (from Bollmann et al., 2016).



).

).

3 Suggestions of compounds to be included in the monitoring

77

Table 1. Compounds with known issues.

Compound	Function	Reasoning
Triazines		
Terbutryn	Algicide, paints	8-55 ng/L in wastewater (Bester et al., 2014), 10-20 ng/L in detention ponds (Vollertsen et al., 2017). Metabolite M1 should be included.
Isothiazolinones		
Octylisothiazolinone (OIT)	Fungicide, bactericide, in can preservative, film preservative, paints, silicone	0-34 ng/L in wastewater (Bester et al., 2014), Pseudo persistent, found in stormwater 10-30 ng/L in detention ponds (Vollertsen et al., 2017). Transformation product should be included.
Benzyl isothiazolinone (BIT)	Bactericide, in can preservative, paints, silicone	1-50 ng/L in stormwater (Bester et al., 2014)
Methylisothiazolione (MI)	Bactericide, in can preservative	0-191 ng/L in waste- (Bester et al., 2014), 1-300 ng/L in stormwater (Bester et al., 2014), 10-30 ng/L in detention ponds (Vollertsen et al., 2017).
Dichloro octyl isothiazolinone, (DCOIT)	Bactericide	0-230 ng/L in wastewater (Bester et al., 2014).
Carbamates		
Iodocarb (IPBC)	Fungicide	10-100 ng/L found in stormwater (Bester et al., 2014); 10-50 ng/L in detention ponds (Vollertsen et al., 2017).
Carbendazime	Fungicide, wood, paints	Persistent compound, 20-63 ng/L in wastewater, 10-900 ng/L in stormwater; 0-10 ng/L in urban surface waters (Bester et al., 2014), detention ponds (10-80 ng/L; Vollertsen et al., 2017).
Azoles		
Propiconazole	Fungicide, wood, paints	Persistent compound, endocrine activity. 0-4540 ng/L in wastewater, 0-30 ng/L in stormwater; Bester et al., 2014
Tebuconazole	Fungicide, wood, paints	Persistent compound, endocrine activity.. 0-78 ng/L in wastewater 1-100 ng/L in stormwater, 0-20 ng/L urban surface waters (Bester et al., 2014) 10-30 ng/L in detention ponds (Vollertsen et al., 2017). Metabolites (hydroxy tebuconazoles) should be considered
Phenoxy acetic acids		
Mecoprop	Plant regulator, rooftops	9-150 ng/L in wastewater under rain conditions, 1-50 ng/L in stormwater, 0-200 urban surface waters (Bester et al., 2014).
Quaternary ammonium compounds		
Benzalkoniumchloride (BAK 10, 12, 14, 16)	Roof and terrasse "cleaners"	0.03-30 µg/L in surface and stormwater (Bester et al., 2022).

Table 2. Compounds that would merit a suspect screening in context with building materials.

Biocide	Product type	Relevance for construction materials
Dichloro-N-[(dimethylamino)sulphonyl] fluoro-N-(ptolyl)methanesulphenamide (Tolylfluanid)	7, 8, 21	Film preservative (paints), wood preservative, Metabolite DMS should be included, registration in PT8 expired
Diuron	7, 10,	Film preservative (paints), construction materials (renders), metabolites DCPMU and DCPU should be included
Fludioxonil	7, 9, 10,	Film preservative (paints), Polymerised materials, construction materials preservative
2-Methyl-1,2-benzothiazol-3(2*H*)-one; (MBIT)	6, 13	Preservative (in-can preservative), not approved in PT 13
2,2′-Dithiobis[N-methylbenzamide] (DTBMA)	6	Preservative (in-can preservative)
2,2′,2″-(Hexahydro-1,3,5-triazine-1,3,5- triyl)triethanol (HHT)	6	Preservative (in-can preservative)
N,N′-Methylenebismorpholine (MBM)	6, 13	Preservative (in-can preservative)
N-(trichloromethylthio)phthalimide (Folpet)	6, 7, 9	Preservative (in-can preservative), film preservative (paints), polymeric materials preservative
p-[(Diiodomethyl)sulphonyl]toluene	7	Film preservative (paints)
Penflufen	8	Wood preservative
Pyrithione zinc (Zinc pyrithione)	2, 6, 7, 9, 10, 21	Film preservative (paints) - Currently one of the most used biocides[7].
Sodium dimethyldithiocarbamate	9, 11, 12	Preservative for polymeric materials,
2-Thiazol-4-yl-1H-benzoimidazole (Thiabendazole)	7, 8, 9, 10	Film preservative (paints), wood preservative, polymeric materials, construction materials (renders)[6]. Registration in PT8 expired.
(Benzothiazol-2-ylthio)methyl thiocyanate (TCMTB)	9, 12	Polymeric materials preservative
Thiacloprid	8	Wood preservative, registration is expired
Thiamethoxam	8, 18	Wood preservative, registration in PT8 expired
Thiram	9	Polymerised materials[7]
(Benzyloxy)methanol	6, 13	Preservative (in-can preservative)
1,3-Bis(hydroxymethyl)-5,5-dimethylimidazolidine-2,4-dione (DMDMH)	6, 13	Preservative (in-can preservative)
2,2-Dibromo-2-cyanoacetamide	2,4,6,11,12,13	Algaecide, Preservative (in-can preservative)
2,2'-Dithiobis[N-methylbenzamide]	6	Preservative (in-can preservative)
2-Bromo-2-(bromomethyl)pentanedinitrile (DBDCB)	6	Preservative (in-can preservative)
2-Butyl-benzo[d]isothiazol-3-one (BBIT)	6, 7, 9, 10, 13	Preservative (in-can preservative), film preservative (paints), polymerized materials, construction materials (renders)
2-Phenoxyethanol	1, 2, 3, 4, 6, 13	Algaecide, preservative (in-can preservative), not approved in PT 13
Azoxystrobin	7, 9, 10	Film preservative (paints), polymerized materials, construction materials (renders)
Biphenyl-2-ol	1,2,3,4,6,7,9, 10, 13	Preservative (in-can preservative), film preservative (paints), polymerized materials, construction materials (renders)

[6] The compound is also wastewater relevant due to its high usage as post harvest pesticide for citrus fruit.

[7] This compound will probably need analyzing via its hydrolysis products.

4 Other open questions

Metabolites and transformation products

Opposite to the pesticide regulations, the BPR (EU2012) is primarily assessing the parent compounds as such and only a general identification is suggested. - An in depth identification, by e.g., following the mass balance of a ^{14}C marked compound and conducting high resolution mass spectrometry is not required[8]. – While some dossiers provide good knowledge on metabolites, others are very scarce about it and independent research needs to point out towards undescribed transformation products that in reality are relevant for the environment (Bollmann et al., 2016, 2017b 2018).

Undeclared biocides

Currently there seems to be an evolving dispute on whether the biocidal products regulation's main objective is to help marketing biocides (ensure working systems) or whether it's main purpose is to protect the environment. The definition of a biocide in the BPR is "any substance or mixture, in the form in which it is supplied to the user, consisting of, containing or generating one or more active substances, **with the intention**[9] of destroying, deterring, rendering harmless, preventing the action of, or otherwise exerting a controlling effect on, any harmful organism by any means other than mere physical or mechanical action". It is very difficult to prove the real intentions of a supplier thus there is a focus on the marketing of the product. This leads to bias especially in the emission scenarios, as only emissions of a compound are considered that are marketed as biocides while those fractions of the same compound that are not marketed as biocide (i.e., with the intention to destroy…) but e.g. a detergent or underlie rather the cosmetics regulation than the BPR are not considered. – Of course the target organisms are affected by the final concentrations and not by the intentions with which the compounds are marketed.

However, most environmental NGOs advocate that all biocidal compounds should be assessed as such.

Waste/reuse strategies

Considering sustainability, building materials should be recycled after use. – While this is in principle happening, biocides in construction materials make the recycling more difficult, as proper recycling would need to be able to exclude introduction of biocides from old uses into new structures where they might not be needed or even detrimental.

[8] Echa, Guidance on the Biocidal Products Regulation, Volume IV: Environment, Part A: Information Requirements, 2018

[9] Emphasis by author of this brief

5 References

Bester, K., Vollertsen, J., Bollmann, U.E., (2014) Water driven leaching of biocides from paints and renders, Pesticide Research No. 156, https://www2.mst.dk/Udgiv/publications/2014/02/978-87-93178-11-3.pdf

Bester, K., Mongelli, A., Vollertsen J., (2022) Emissioner af kvaternære ammoniumforbindelser (QUAT-Fate), unpublished results

Bollmann, U.E., Minelgaite, G., Schlüsener, M., Ternes, T., Vollertsen, J., Bester, K., 2016. Leaching of Terbutryn and Its Photodegradation Products from Artificial Walls under Natural Weather Conditions. Environmental Science & Technology 50, 4289-4295.

Bollmann, U.E., Minelgaite, G., Schlüsener, M., Ternes, T.A., Bester, K., 2017a. Photodegradation of octylisothiazolinone and semi-field emissions from facade coatings. Scientific Reports 7, 41501.

Bollmann, Ulla E.; Fernández-Calviño, David; Brandt, Kristian K.; Storgaard, Morten Swayne; Sanderson, Hans; Bester, Kai., 2017b. Biocide Runoff from Building Facades: Degradation Kinetics in Soil. Environmental Science & Technology, 51, 3694-3702

Bollmann, Ulla E.; Bester, Kai; Vollertsen, Jes; Urbanczyk, Michal; Rudelle, Elise A. (2018) Transport and transformation of biocides in construction materials: Factors controlling release and emissions, Pesticide Research No.177, https://www2.mst.dk/Udgiv/publications/2018/11/978-87-7038-007-2.pdf

EU 2012, Regulation No 528/2012 of the European Parliament and of the Council of 22 May 2012 concerning the making available on the market and use of biocidal products, Official Journal of the European Union, *L 167,. 1–123*

Vollertsen, J., Bester, K., Rudelle, E.A., Bollmann, U., Minelgaite, G., Stephansen, D.A., Haaning Nielsen, A., Lauge Pedersen, M., (2017): Biocider i urbane småsøer, MST, BEKF nr. 170, https://www2.mst.dk/Udgiv/publikationer/2017/02/978-87-93529-70-0.pdf