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Desorption of biocides from renders modified with acrylate and silicone

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HIGHLIGHTS

- Partitioning of biocides between polymeric renders and water is described.
- The partitioning constants are correlating to the K_{ow} in some cases.
- For triazines the fraction of polymer in the render influences the partitioning.
- The render fraction also influences carbamates and isothiazolinones.
- For the phenylureas the partitioning is not influenced by the polymer content.

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ABSTRACT

Biocides are used in the building industry to prevent algal, bacterial and fungal growth on polymericrenders and thus to protect buildings. However, these biocides are leached into the environment. To better understand this leaching, the sorption/desorption of biocides in polymeric renders was assessed. In this study the desorption constants of cybutryn, carbendazim, iodocarb, isoproturon, diuron, dichloro-N-octylisothiazolinone and tebuconazole towards acrylate and silicone based renders were assessed at different pH values. At pH 9.5 (porewater) the constants for an acrylate based render varied between 8 (isoproturon) and 9634 (iodocarb) and 3750 (dichloro-N-octylisothiazolinone), respectively. The values changed drastically with pH value. The results for the silicone based renders were in a similar range and usually the compounds with high sorption constants for one polymer also had high values for the other polymer.

Comparison of the octanol water partitioning constants (K_{ow}) with the render/water partitioning constants (K_d) revealed similarities, but no strong correlation.

Adding higher amounts of polymer to the render material changed the equilibria for dichloro-*N*-octylisothiazolinone, tebuconazole, cybutryn, carbendazim but not for isoproturon and diuron.

1. Introduction

Biocides are used to protect facade coatings like organic modified renders (plasters) and paints from deterioration by organisms (algae, fungi and bacteria). These renders have become very popular for buildings with enhanced thermal insulation (Reichel et al., 2004). To achieve the biocidal protection, the compounds in question must be present in the surface film on the respective material to reach the organisms that try to settle there (Burkhardt et al., 2009). The properties needed for this lead to the use of compounds that are to some extent soluble in water. Currently several groups of compounds are used to achieve the wanted effect (Paulus, 2005): triazines such as terbutryn and cybutryn; phenylureas such as diuron and isoproturon; azole fungicides, such as tebuconazole and propiconazole; carbamates such as carbendazim and iodocarb, and isothiazolinones such as methylisothiazolinone, chloro-methylisothiazolinone, *N*-octylisothiazolinone (OIT), dichloro-*N*-octylisothiazolinone (DCOIT). Due to their properties these biocides may also be washed off the protected surfaces by rainwater during wet weather (Schoknecht et al., 2009; Burkhardt et al., 2012a; Wangler et al., 2012). This effect is called leaching. The leached biocides may reach separated sewer systems and are then discharged into surface waters (Wittmer et al., 2010; Coutu et al., 2012; Bollmann et al., in prep.). In these surface waters they may affect aquatic organisms (Mohr et al., 2008; Burkhardt et al., 2009). To minimise adverse effects it would be necessary to understand the desorption equilibria between the organic modified render materials and the water.

While leaching has been studied utilising bigger systems with forced artificial rain as well as controlled rain exposure (Burkhardt et al., 2011, 2012a; Wangler et al., 2012), smaller systems have also

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been used to study equilibria on paint systems (Schoknecht et al., 2009). Three steps together will in reality control the leaching: (1) partition between render and water; (2) transport of the biocides from the deeper layers to the surface (3) wash off the available biocides from the surface. In this study we focussed on equilibrium partitioning.

Organically modified renders contain calcium carbonate, sand, an organic binding phase such as acrylates and silicones, as well as other additives. This work was conducted to study which effects the organic binding phase (acrylates and silicones) of the renders have on the desorption of biocides. Often, sorption and desorption processes or environmental risk assessments are based on the octanol/water (K_{ow}) partitioning coefficients of the respective compounds. In this study we wanted to use desorption constants (K_d) and its form that is normalised to the organic fractions, $K_{OM,}$ as they are well known from pesticides in soil (Karickhoff, 1981; Spark and Swift, 2002; Weber et al., 2004).

For these reasons we conducted experiments with commercial renders with modified acrylate and silicone content. The two-phase model considers desorption of the target compounds between the water phase (C_w) and the facade render (C_s).

2. Materials and methods

2.1. Materials

Compounds included in this study: cybutryn (irgarol 1051), tebuconazole, isoproturon, diuron, carbendazim, iodocarb, dichloro-*N*-octylisothiazolinone, and carbendazim-D4, isoproturon-D6, irgarol-D9, tebuconazole-D6 as internal standards (suppliers see supplementary materials Table S1). The molecular formulas, physical and chemical properties of the compounds are summarised in Table 1. For the chromatography, as well as the experiments, water from the millipore apparatus in house and methanol gradient grade from Merck, Darmstadt, Germany was used. For the experiment renders containing about 10% polymeric binder, calcium carbonates and sand were used (for more details see Section 2.2).

2.2. Facade render characterisation

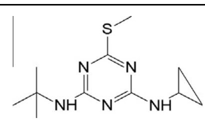
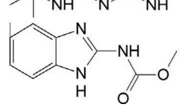
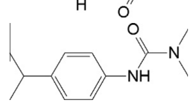
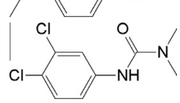
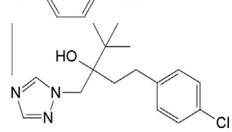
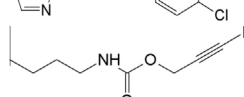
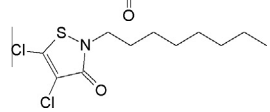
In the study two commercially available facade renders with acrylate (KHK, Quick-Mix, Osnabrück, Germany) and silicone resin binder (HECK SHP KC1, BASF Wall Systems, Marktredwitz, Germany) were applied. The content of organic binder was determined by measuring the losses during combustion at 550 °C. This temperature releases carbon from organic matter but no carbon from calcium carbonate. The initial organic content was 10% in the dry acrylate render, while it was 15% in the silicone render. The used renders contained none of the studied biocides, however the acrylate render contained amounts of octylisothiazolinone (OIT) typically used in commercial products while the silicone render contained MI & BIT, and Zn-Pyrithion. The dried acrylate render had a surface area of 1.12 $m^2\ g^{-1}$ (determined as BET experiment following Brunauer–Emmett–Teller (Brunauer et al., 1938), a density of 1.79 g mL^{-1} and a calcium carbonate content of 66%, while the dried silicone render had a BET surface of 0.63 $m^2\ g^{-1}$, a density of 1.53 g mL^{-1} and a calcium carbonate content of 25%.

To increase the acrylate content a water based dispersion of thermoplastic acrylate polymer on the basis of methylmethacrylate and *n*-butylacrylate (Plextol D498, Synthomer Deutschland, Marl, Germany) was added.

2.3. Desorption experiments

The renders were spiked with different concentrations of biocides, and the well mixed systems were air dried in the laboratory in 5 mm films for two days instead of normal industrial application, thus resulting in realistic hardened renders. The thus dried and spiked materials were homogenised in a mortar on the

Table 1
Biocides covered within this study: Name, Acronym, Activity, octanol–water partition coefficient (log K_{ow}),[a] water solubility (WS).[a]

Substance (Acronym)	Formulae	Activity	Physico-chemical properties
Cybutryn, Irgarol 1051		Algaecide	Log K_{OW}: 4.07 WS: 20 mg L^{-1}
Carbendazim		Fungicide	Log K_{OW}: 1.55 WS: 3112 mg L^{-1}
Isoproturon		Algaecide	Log K_{OW}: 2.84 WS: 92 mg L^{-1}
Diuron		Algaecide	Log K_{OW}: 2.67 WS: 102 mg L^{-1}
Tebuconazole		Fungicide	Log K_{OW}: 3.89 WS: 97 mg L^{-1}
Iodocarb		Fungicide	Log K_{OW}: 2.45 WS: 436 mg L^{-1}
Dichloro-*N*-octylisothiazolinone		Bactericide/fungicide	Log K_{OW}: 3.59 WS: 27 mg L^{-1}

[a] Calculated with EPI SuiteTM v4.10 of the US EPA (http://www.epa.gov/oppt/exposure/pubs/episuitedl.htm).