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# Determination of diffusion coefficients of biocides on their passage through organic resin-based renders

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## HIGHLIGHTS

- The diffusion of biocides through organic resin-based renders is described.
- The rate of the leaching is generally determined by the rate of transport of biocide in the water-filled pores.
- The organic modifier in the render influences the diffusion driven transport of biocides.

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## ABSTRACT

In this study the diffusion coefficients of isoproturon, diuron and cybutryn in acrylate and silicone resin-based renders were determined. The diffusion coefficients were determined using measuring concentrations of biocides in the liquid phase after being in contact with renders for specific time intervals. The mathematical solution of the transient diffusion equation for an infinite plate contacted on one side with a limited volume of water was used to calculate the diffusion coefficient.

The diffusion coefficients through the acrylate render were $8.10 \cdot 10^{-9}$ $m^2$ $s^{-1}$ for isoproturon, $1.96 \cdot 10^{-9}$ $m^2$ $s^{-1}$ for diuron and $1.53 \cdot 10^{-9}$ $m^2$ $s^{-1}$ for cybutryn. The results for the silicone render were lower by one order of magnitude. The compounds with a high diffusion coefficient for one polymer had likewise high values for the other polymer.



## 1. Introduction

Currently, the attention of researchers and the Regulation of the European Parliament and of the Council (Regulation (EU). No 528, 2012) has been focused on the release of biocides from façade coatings. Biocides are used to protect façade coatings like organic modified renders and paints from deterioration by algae, fungi and bacteria (Reichel et al., 2004; Paulus, 2005). Natural weather conditions cause their release from applications such as coatings. Some compounds used as biocides are toxic to aquatic organisms and long-term adverse effects in the aquatic environment cannot be excluded already for low concentrations (Mohr et al., 2008). Burkhardt et al. (2007) showed that release from building materials is a major source of biocide pollution concerning urban waters. Storm water is often directly discharged into surface water excluding wastewater treatment plant.

The purpose of the biocide product regulation is to improve the free movement of biocidal products within the European Union while ensuring a high level of protection of both human and animal health and the environment (Regulation (EU). No 528, 2012). The laboratory leaching test procedure includes the evaluation of risk assessment for the authorization of active substances and biocidal products, on one side and optimized leaching processes may ensure long-term efficacy of materials coupled with minimized emissions on the other side (Schoknecht et al., 2013). Coated external surfaces are only exposed to water during dew formation and driving rain events and dryness in between rain periods. The critical input parameters required for estimating emissions are leaching rates. Release of biocidal compounds from different materials was demonstrated in laboratory and/or field studies (Konstantinou and Albanis, 2004; Schoknecht et al., 2009; Wittmer et al., 2011; Burkhardt et al., 2012; Wangler et al., 2012; Schoknecht et al.,

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2013; Styszko et al., 2014, 2015). Indirect conclusions on the release of these substances from materials can be made from their occurrence in water samples. Research of surface water and waste water indicates emissions of active substances into water (Bester and Lamani, 2010; Wittmer et al., 2010; Bester et al., 2011; Botta et al., 2012; Coutu et al., 2012; Bollmann et al., 2014a, 2014b).

A crucial step for the release of biocides is their transport to the façade coating surface (Erich and Baukh, 2016). According to Erich and Baukh (2016), the release process combined three processes in one fully coupled finite element model: water uptake, dissolution of biocides and transport of biocide by diffusion and advection. Diffusion controlled release was demonstrated in immersion studies by Schoknecht et al. (2009, 2013) and Wangler et al. (2012). In our last study transport processes of biocides through acrylate and silicone renders were considered under (Styszko et al., 2015) three different kinds of cycles. Transport depends on the availability of water, and diffusion through the water-filled pores is probably the dominant mechanism under applied experimental conditions. Evaporative driven transport of biocides through render materials is less relevant in comparison to the transport of biocides through the water-filled pores (Styszko et al., 2015).

The aim of the present study was the calculation of the diffusion coefficients for transport of biocides through the render based on experiments presented in already published work (Styszko et al., 2015). The experiments were performed with commercial acrylic and silicone resin-based renders.

## 2. Materials and methods

### 2.1. Materials

See Table 1 for data on the active components (isoproturon, diuron and cybutryn) that were investigated in the laboratory experiments. Isoproturon (99.9%) and diuron (98%) were purchased from Sigma Aldrich. Cybutryn (traded as Irgarol 1051, 99%) was purchased from Dr. Ehrenstorfer GmbH. Water from the in-house Millipore apparatus was used in the high performance liquid chromatography (HPLC) and in the leaching experiments. Methanol (Merck, Darmstadt, Germany) was used in gradient grade quality as an HPLC eluent.

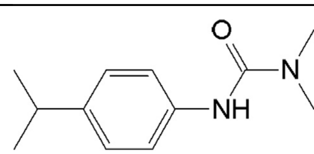
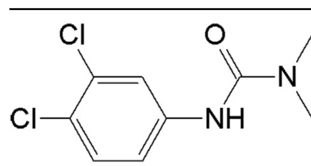
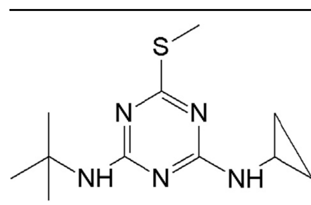
### 2.2. Characterization of renders

Typically, the main components of polymer enhanced renders are carbonates (30–60%), polymeric binder (10–15% either acrylate or silicone) and sand in different grain sizes (Styszko et al., 2015). The total content of biocides in render ranges from 5 to 10 g kg$^{-1}$ and a mixture of several biocides is used (Burkhardt et al., 2011).

Two commercially available façade renders with acrylate (KHK, Quick-Mix. Osnabrück, Germany) and silicone resin binder (HECK SHP KC1, BASF Wall Systems. Marktredwitz, Germany) were applied in the current study. The full characteristics of renders used in this work were presented in the previous paper (Styszko et al., 2014). The initial organic content was 10% in the dry acrylate render, while it was 15% in the silicone render. The contribution of calcium carbonate in dried acrylate render was 66% and 25% in silicone render. In the dried state, the specific surface areas of acrylate and silicone renders were 1.12 m$^2$ g$^{-1}$ and 0.63 m$^2$ g$^{-1}$, respectively. The density of dried acrylate render was 1.79 g mL$^{-1}$ and silicone render was 1.53 g mL$^{-1}$.

The previous works showed that the partitioning of the biocides in the render-water system for most compounds is dependent on the acrylate-water partitioning and the acrylate fraction in the render (Styszko et al., 2014; Bollmann et al., 2015). As described in paragraph 1, the release of biocides from the render is assumed to be a multistep process. The acrylate-water partitioning is only linked to the transfer of biocides from the render material into the water phase, either inside the pores or first on the render surface. During the leaching experiments described in our previous paper (Styszko et al., 2015) the renders sorbed water. The total mass of water sorbed by the render during 144 h of the experiment described in paragraph 2.3 was about 0.49 g and 0.4 g for silicone and acrylate renders, respectively.

**Table 1**
Name, acronym, molecular formulas, octanol-water partition coefficient (Log $K_{OW}$)[a], acrylate-water distribution coefficients (Log $K_{AcW}$)[b], acrylate/silicone resin-based render-water distribution coefficient ($K_{d(acrylate)}$/$K_{d(silicone)}$)[c], water solubility (WS)[a] of tested biocides.

| Compounds (acronym) | Formulae | Physical and chemical properties |
|---|---|---|
| Isoproturon (IP) |  | Log $K_{OW}$: 2.84<br>Log $K_{AcW}$: 1.66<br>$K_{d(acrylate)}$: 8.1<br>$K_{d(silicone)}$: 9.8<br>WS: 92 mg L$^{-1}$ |
| Diuron (DR) |  | Log $K_{OW}$: 2.67<br>Log $K_{AcW}$: 2.19<br>$K_{d(acrylate)}$: 17.9<br>$K_{d(silicone)}$: 21.4<br>WS: 102 mg L$^{-1}$ |
| Cybutryn. Irgarol 1051 (IRG) |  | Log $K_{OW}$: 4.07<br>Log $K_{AcW}$: 2.87<br>$K_{d(acrylate)}$: 26.0<br>$K_{d(silicone)}$: 121.4<br>WS: 20 mg L$^{-1}$ |

[a] Calculated with EPI SuiteTM v4.10 of the US EPA (http://www.epa.gov/oppt/exposure/pubs/episuitedl.htm).
[b] Bollmann et al. (2015).
[c] Styszko et al., (2014).