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Determination of biocides as well as some biocide metabolites from facade run-off waters by solid phase extraction and high performance liquid chromatographic separation and tandem mass spectrometry detection

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ABSTRACT

Biocides are used to protect buildings, boats, and other materials from microbial infestations. A huge variety of compounds are being used: isothiazolinones, e.g., to prevent bacterial growth in paints, triazines and phenylureas against algal growth on water exposed materials while carbamates are used against fungal investations. However these biocides can be leached from the respective materials. As these are very effective compounds it is important to know the concentrations of these biocides in the leachates as well as their leaching behaviour to assess their risk to the environment. In this study, a method for the determination of biocides from facade material run-off water by means of high performance liquid chromatography coupled to tandem mass spectrometry (HPLC–MS/MS) was developed. Due to the amphiphilic character and the expected varying pH-values in the samples, the extractions as well as the HPLC-method development proved to be demanding. The water samples (leachates) were buffered with a phosphate buffer to pH 7. As some of the biocides are very hydrophilic, different SPE cartridges were tested to identify the SPE material with the highest recovery rates for all compounds. For gaining a good separation, analyte trapping was performed on the HPLC column. Quantification was performed using a mass spectrometer in multi-reaction monitoring with two transitions per compound. The final recovery rates were conducted using a cartridge with a divenylbenzyl polymer sorbent. A combination of methanol and acetonitrile as eluents was used to reach recovery rates in the range of 70–100%. The limit of quantification for the compounds of interest ranged from 0.01 to 0.1 μg/L.

1. Introduction

With the increasing demands on thermal insulation, increasingly more vulnerable materials containing high concentrations of organic polymers are used in construction. These materials are, however, susceptible to infestations of bacterial, algal, and fungal biofilm growth. These films can, e.g., change a white surface into brown, green or black. Thus such surfaces are protected by biocides. Biocides are, like pesticides, used to control harmful organisms. However, in opposite to pesticides they are used for non-agricultural purposes [1]. A variety of compounds is being used: isothiazolinones, e.g., to prevent bacterial growth in paints to increase shelf life and to stabilise the paint films (in-can and film preservatives). Triazines and phenylureas are used against algal growth on water exposed surfaces (film preservatives). Carbamates are utilised against fungi (film preservatives). All of these compounds are used in plasters, renders and paints [2,3] (Table 1). To reach the planned effect, the biocides have to migrate from the building materials into the target cells through the surface water film on the materials [4]. During this process the biocidal compounds can be leached of or washed away by rainwater [5–7]. Such rainwater originated run-off waters are currently managed by infiltrating directly into the soil or by direct discharge into surface waters. Thus buildings become potentially a source for pollution of surface and ground waters and long term contamination is possible [8].

However, biocides are not only effective on target organisms, but they are also toxic to other aquatic organisms in surface waters [9–11]. Some of the studied compounds such as diuron are also prioritised in the water framework directive and thus a monitoring of concentrations as well as potential sources is necessary [12].

As the respective materials (paints, plasters and renders) are supposed to keep this property for a long time, biocides are only expected in relatively high concentrations in run-off water at the beginning and at lower concentrations later in the lifetime of the building [μg/L]. The expected concentrations are thus quite

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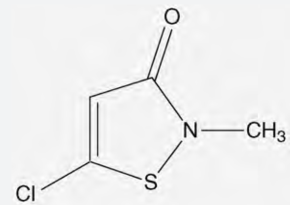
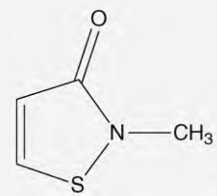
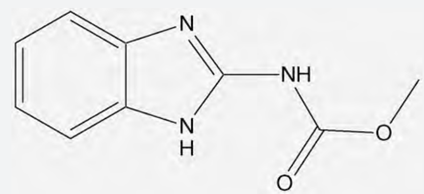
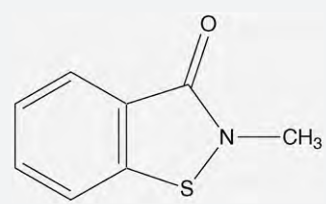
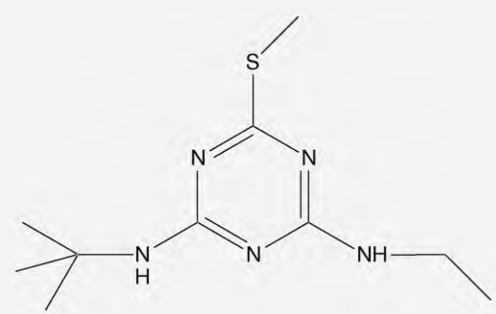
Table 1
Compounds studied.

Common name (acronym)	Systematic name	Structural formulae	CAS no.	log Kow	Usage
Chloro-methyl-isothiazolinone (CMI)	5-Chloro-2-methyl-isothiazol-3(2H)-one		26172-55-4	<3	Preservative formulations for rinse-off application, such as shampoos and liquid hand soaps [4]
Methyl-isothiazolinone (MI)	2-Methyl-isothiazol-3(2H)-one		2682-20-4	<3	Similar functions as CMI [4]
Carbendazim (CD)	Methyl-benzimidazol-2-yl carbamate		10605-21-7	1.51 (pH 7)	Film preservative, also used to protect citrus fruit [5]
Benzo-isothiazolinone (BIT)	Benzo[*d*]isothiazol-3(2H)-one		2634-33-5	1.77	Water based coatings [4]
Terbutryn (TB)	*N*-(1,1-Dimethylethyl)-*N′*-ethyl-6-(methylthio)-1,3,5-triazine-2,4-diamine		886-50-0	3.44	Aquatic herbicide for control of submerged and free-floating weeds and algae [6]