Release of biocides from urban areas into aquatic systems

Rejets de biocides utilisés en zones urbaines dans l'environnement aquatique

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RESUME

Les biocides sont des produits employés couramment en milieux urbains pour la protection des matériaux. Les facteurs influençant le lessivage de ces substances et leur devenir dans les réseaux d'assainissement sont encore actuellement mal connus. Plusieurs biocides ont été suivis à différentes échelles de travail dans le cadre du projet URBIC, allant de l'étude de toiture et de façade, de la station d'épuration ou du milieu récepteur. Les produits les plus souvent détectés ont été la carbendazim, le diuron et le mecoprop. Des tests de lessivage de membranes bitumeuses, utilisées pour les toitures plates, ont été réalisés. Les taux de mecoprop (produit d'inhibition de la croissance racinaire) varient d'un facteur 100 entre plusieurs produits testés. La connaissance de ces processus de lixiviation et des quantités de biocides utilisés est indispensable pour une protection efficace des milieux récepteurs par le biais de mesures techniques ou de solution de contrôle à la source.

ABSTRACT

Biocidal products are widely used in urban areas for material protection. Carbendazim and diuron are representatives for biocides in paints and plaster of facades. Factors influencing release of biocides and their fate in urban sewer systems are not well understood at present time. We therefore investigated several biocides at different scales: facades and roofs, effluent and sludge from wastewater treatment plants and receiving waters (project URBIC). Carbendazim, diuron and mecoprop were often detected in the different compartments. Bitumen sheets for roof waterproofing treated with the root protection agent mecoprop were investigated more specifically. Initial laboratory tests resulted in leaching rates differing by a factor of 100 between different products. The knowledge on leaching processes and occurrence of biocides from material protection products in urban water systems is a prerequisite for efficient implementation of technical measures or at-source controls.

KEYWORDS

Biocides; leaching ; risk assessment ; source control ; urban runoff.

1 INTRODUCTION

Biocides are substances widely used for material protection products (MPPs). They have a specific mode of action against algae and fungi to reduce microbial deterioration. Plant protection products (PPP) used in urban and rural areas may have the same active ingredients. The PPPs contain active ingredients appropriate for both agricultural and non-agricultural purposes (Figure 1). MPPs including such biocides have widespread applications in urban areas, e.g. for treatment of wood, concrete, paints, and roofs (Lassen et al., 2001). Their use as fungicides and algicides in facades (paints and plaster) is the current state of art for material protection of buildings. Similar applications of MPPs are known or expected for plastic membranes on flat roofs. In bitumen sheets for roof waterproofing, herbicidal products containing Mecoprop (MCPP) are often used for preventing root penetration. The leaching process of MPPs is expected to be the main source of biocides in urban areas. However, there is a lack of knowledge in this field.

Some compounds applied as biocides were detected in urban sewer systems (Burton and Pitt 2001, Clark et al., 2005). MCPP, diuron, and terbutryn were frequently found in effluents of urban wastewater treatment plants (WWTP) (Gerecke et al., 2002) (Figure 1). All these substances are active ingredients in MPPs. Nevertheless, most information on the leaching of biocides from facades and plastic roofs is available from a few laboratory studies (Cadmus, 1982; Lindner, 1997; Schoknecht et al., 2003). To our knowledge, investigations under field conditions and studies on the fate of these substances in urban drainage systems have not been carried out yet. Only MCPP was detected on field scale in roof runoff at concentrations of up µg/L (Bucheli et al., 1998) and its occurrence in river water was shown to originate from flat roofs (Gerecke et al., 2002).

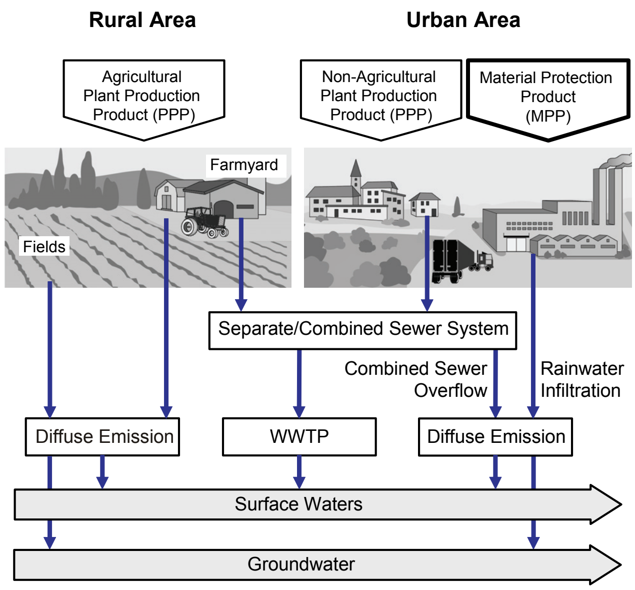

Figure 1: Pathways of pesticides (PPP) and material protection products (MPP) in rural and urban environment. MPPs are containing biocides.

However, the studies on leaching of MCPP seem to be not representative for the current composition of different bitumen sheets for roof waterproofing. Moreover, leaching rates vary according to the type of the roof (green roofs, gravel roofs). The current construction of buildings (e.g. thermal insulation of buildings, limited or missing roof overhang) provides advantageous conditions for growth of algae and fungi on facades (Burkhardt et al., 2005). Therefore, the use of biocidal products increased in recent years and may represent an important source of contamination for the environment.

In fact, infiltration of runoff from roofs and paved surfaces as well as the separate sewer systems are promoted in urban water management (Figure 1: rainwater infiltration). This leads to concern since biocides might enter and contaminate aquifers or surface waters. Therefore, the infiltration of roof runoff from bitumen sheets for roof waterproofing containing root protection agents is not allowed in Switzerland. However, to develop efficient measures for water protection close to the source (source control) or at the outlet of WWTPs, knowledge of the leaching behaviour of biocides included in MPPs and their fate in the urban sewer systems is required (Figure 1).

The aim of our study "Biocides in Urban Water Systems" (URBIC) is the determination and evaluation of sources, pathways and fates of biocides in urbanized areas in order to minimize their environmental impact. URBIC focus on facades and flat roofs as possible sources of biocides and the occurrence of important active ingredients in urban sewer systems.

While parts of this study have already been completed and published, other investigations are still running. Therefore, we present part of our results obtained within studies on WWTPs and surface water as well as laboratory results from the leaching experiments on bitumen sheets for roof waterproofing.

2 MATERIAL AND METHODS

The present study includes experiments at different scales: laboratory, small-scale model systems (facades or roofs) and watershed level (waste water treatment plant and receiving waters).

The laboratory study with bitumen sheets for roof waterproofing based on material samples (16 x 10 cm) which were shaken in deionised water and artificial ageing in a weather simulation chamber. Each of the three elutions lasted for 168 h at room temperature and each of the two ageing steps for 300 h with 15 temperature cycles between -10 to +50°C during 20 h. The procedure was conducted twice. MCPP-analysis was performed with solid phase extraction (SPE) and HPLC-UV.

For field systems, leaching behaviour is investigated at two buildings with known composition of the biocides in their coatings and roof materials. The fate of the compounds after leaching is followed up by sampling runoff in the separated stormwater system. The biocides are determined by LC-MS/MS.

Substances determined in WWTPs, surface waters and at the sources are mainly carbendazim, Irgarol 1015, diuron and isothiazolinones. For MCPP, laboratory studies will include bituminous roof sealing membranes with different properties (MPPs, concentration, thickness, surfacing). The leaching behaviour will be investigated at two buildings with known composition of the biocides in coatings and roof materials. The fate of the compounds after leaching is followed up by sampling runoff in the stormwater drains of a separate sewer system.

Sludge samples were collected from the sludge storage tanks at several locations in Switzerland. The samples were taken at different depths in the sludge, with 8 to 15 samples per container, and were homogenized to get a composite. The samples were stored in glass bottles at +4°C. Waste water was sampled by 24 h flow proportional composites of influent and secondary effluent with automated samplers during one week in each of April 2001 and 2002, respectively. Sampling was performed in dry weather conditions. Discharge of stormwater was sampled during three storm events with an automatic sampling device.

Analyses of biocides in sludge and water were performed on two GC/ECD. Conditions for analyses have been described by Plagellat et al. (2004). Limits of detection (LOD) and limits of quantification (LOQ) were between 1 and 5 ng/L in water and between 40 and 60 µg/kg in sludge. LOD and LOQ were determined and adjusted by the recovery rates. The relative standard deviations (RSD) were below 13% for all compounds and all matrices. Absolute recoveries were determined by the standard addition method described by Plagellat et al. (2004).

3 RESULTS AND DISCUSSION

One specific source of a biocide has partly been evaluated. MCPP used in bitumen sheets for roof waterproofing as a root protection agent was investigated. In our experiments, 16 different roof sealing membranes leach MCPP in significant concentrations (Figure 2). It is noteworthy that the lowest and highest concentrations differed by a factor of 100. The observed leaching rates may enhance use of optimized products. In fact, this point plays an important role for planning at the source control measures. Such measures at the source are most efficient and sustainable for the protection of aquatic systems.

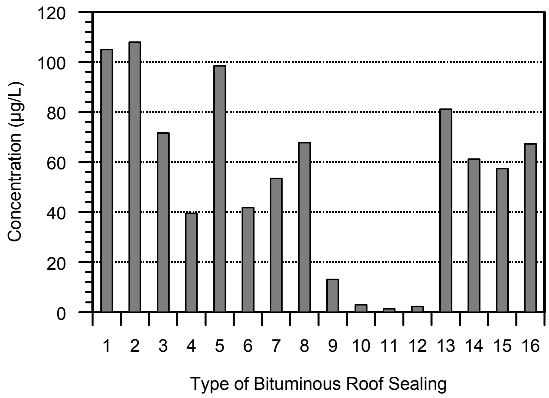

Figure 2: Leaching of Mecoprop from different types of bituminous roof sealing membranes. Under same experimental conditions the concentrations ranged from 1.0 to nearly 110 µg/L.

Biocides were found in sewage sludge of WWTPs receiving almost exclusively domestic wastewater from a rural catchment area with a separate sewer system (type A, Figure 2; Plagellat, 2004). A moderate release from private households is expected to occur. Higher specific loads of biocidal products were observed in WWTPs where stormwater and domestic/industrial wastewater was treated due to a combined sewer system (type B and C, Figure 3). This indicates that these compounds were washed off from building parts treated with paints or coatings containing MPPs and entered the sewer with surface runoff. The release from non-agricultural sources was strengthened by the fact that almost half of sewage sludge samples taken in wintertime, when plant protection products are not applied exhibited, higher concentrations of diuron and carbendazim than corresponding summer samples (Plagellat, 2004).

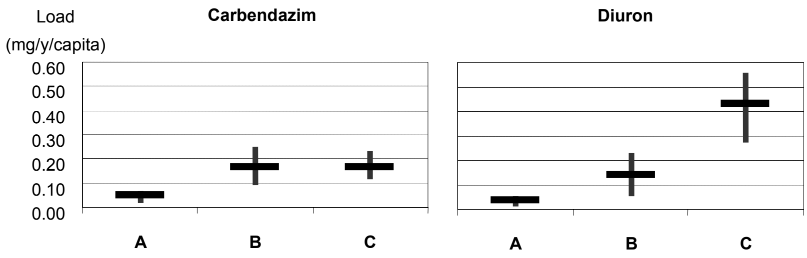

Figure 3: Loads (mg per year and per inhabitant) of carbendazim and diuron in sewage sludge obtained from wastewater treatment plants (WWTPs) with different characteristics of the catchment. Type A: Almost exclusively private households connected to WWTP with separate sewer system; type B: Like A, but additionally connected to sewer system; Type C: private households and industry connected to WWTP with a combined sewer system.

Carbendazim, diuron and MCPP were detected in the effluent of WWTPs at concentrations up to the range of µg per liter (Table 1). The occurrence is not surprising due to low elimination rates for carbendazim (12 to 69%; Kupper et al., 2006) in WWTPs. A release of these compounds to surface waters may also occur during heavy rainfalls by the discharge of combined sewer overflow or storm water from separate sewers (Table 1). In general, the first flush exhibits significant higher concentrations. Nevertheless, it seems plausible that after rainfall the tailing of the concentration curve might be extended over a few days. Preliminary results from monitoring of facades runoff and the occurrence of biocides in a separate sewer underline this fact. The concentrations of Irgarol 1051 were in the range of effluent concentrations of diuron displayed inTable 1.

	Samples	**Diuron** (ng/L)	**Carbendazim** (ng/L)	**Mecoprop** (ng/L)
8 WWTPs Zurich: **Effluent**	~800	120 (14-970)	n.a.	260 (43-3200)
WWTP Emmental: **Effluent**	7		464 (48-982)	n.a.
WWTP Chevilly: **Effluent**	7	n.n.	9 (4-11)	n.a.
WWTP Uster: **Combined sewer overflow**	3*	60 (43-81)	n.a.	n.a.

Table 1: Concentrations (ng/L) of biocides in effluents of WWTPs and combined sewer overflow in Switzerland. Three storm events were sampled at WWTP Uster (*); n.a. = not. analyzed.

Accordingly, several active ingredients used in MPPs have been detected in surface waters in Switzerland (Table 2). In contrast to agricultural pesticides, the occurrence of biocidal products from urban areas in surface water is often continuous over the year and the emission does not follow a seasonal pattern. The evolution of concentrations is shown in Figure 4 for diuron and isoproturon. However, a similar pattern might occur for other MPPs. Lindner (1997) has studied residual diuron concentrations in surfaces treated with paints. The determined diuron losses were larger during seasons with a high temperature due to enhanced leaching rates under temperate conditions. This is in line with the pattern observed in Figure 4.

Diuron	**Carbendazim**	**Diazinon**
Mecoprop	Propiconazole*	**Diethyltoluamide (DEET)**
Terbuthryn	Tebuconazole*	Permethrin
Terbuthylazin	Difenconazole*	Benzotriazole*

Table 2: Active ingredients of biocidal products detected in surface waters of Switzerland. Bold letters: Frequently detected. *Measurements carried out within the International Commission for the Protection of Lake Geneva (CIPEL), personal communication, P. Edder, Service de Protection de la Consommation (Geneva).

In receiving waters, aquatic organisms are therefore continuously exposed to biocides and PPPs in concentrations which might exceed ecotoxicologically based water quality criteria (Chèvre et al., 2006). Furthermore, considering mixtures of hazardous compounds for risk assessment, the risk induced by emissions of agricultural PPPs coincides with the continuous risk of biocides from urban areas resulting in a significant pressure to the aquatic ecosystem.

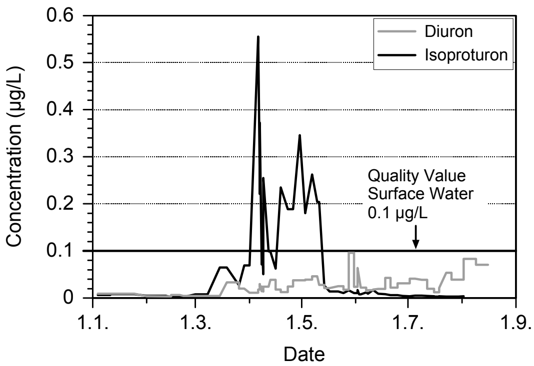

Figure 4: Concentration of diuron (µg/L) measured in a medium size river (Aa Mönchaltorf) compared to the Water Quality Criteria (WQC) proposed in Switzerland (Chèvre et al., 2006).

4 CONCLUSION AND OUTLOOK

With regard to sustainable water protection it is important to account for both rural and urban sources. WWTP sludge is considered as an adequate reflection of biocidal releases from urban areas. Concentration peaks in receiving waters indicate that in some cases ecotoxicological thresholds were already exceeded. To minimize their environmental impact the main sources have to be identified and evaluated. We demonstrated that the choice of a different product could be a good solution, as illustrated for MCCP. This has not been done so far for other sources.

Overall, current knowledge on biocides originating from urban areas and MPPs, respectively, is still incomplete. To establish measures for source control in a most efficient and sustainable way, specific sources have to be investigated. We expect that the results of the URBIC study will contribute to a better understanding on the urban sources and control measures. This may lead to a substantial reduction of contaminant.

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