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Occurrence and overlooked sources of the biocide carbendazim in wastewater and surface water☆

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ABSTRACT

Carbendazim is a fungicide commonly used as active substance in plant protection products and biocidal products, for instance to protect facades of buildings against fungi. However, the subsequent occurrence of this fungicide and potential endocrine disruptor in the aqueous environment is a major concern. In this study, high resolution mass spectrometry shows that carbendazim can be detected with an increasing abundance from the source to the mouth of the River Rhine. Unexpectedly, the abundance of carbendazim correlates poorly with that of other fungicides used as active ingredients in plant protection products (r^2 of 0.32 for cyproconazole and r^2 of 0.57 for propiconazole) but it correlates linearly with that of pharmaceuticals (r^2 of 0.86 for carbamazepine and r^2 of 0.89 for lamotrigine). These results suggest that the occurrence of carbendazim in surface water comes mainly from the discharge of treated domestic wastewater. This hypothesis is further confirmed by the detection of carbendazim in wastewater effluents (n = 22). In fact, bench-scale leaching tests of textiles and papers revealed that these materials commonly found in households could be a source of carbendazim in domestic wastewater. Moreover, additional river samples collected nearby two paper industries indicate that the discharge of their treated process effluents is also a source of carbendazim in the environment. While characterizing paper and textile as overlooked sources of carbendazim, this study also shows the biocide as a possible ubiquitous wastewater contaminant that would require further systematic and worldwide monitoring due to its toxicological properties.

1. Introduction

Biocides comprise a large number of chemicals specifically designed for their toxicological properties, which allow them to eliminate or limit the population of certain organisms. However, their extensive application worldwide is raising environmental and public health concern since compounds like the fungicide carbendazim can be transported and detected in soil and water.

Carbendazim is a benzimidazole fungicide that used to be commonly employed in agriculture to protect plants, vegetables, cereals and fruits against fungal diseases (Pan et al., 2012; Singh et al., 2016). In some countries, carbendazim could also be used as worm control agent to protect amenity turf such as tennis courts or golf courses (Singh et al., 2016). Furthermore, carbendazim is also frequently applied as biocide for the product types (PT) 7 (film preservative), PT 9 (as preservative for fiber, leather, rubber and polymerized materials) and PT 10 (preservative for construction materials like those used for the facades of buildings) as defined in the EU regulation number 528/2012 (Burkhardt et al., 2011; Coutu et al., 2012; Jungnickel et al., 2008; Schoknecht et al., 2009). Moreover, other applications not reported in the literature might also exist.

In the European Union (EU), carbendazim falls under different regulations depending on the purpose of its application (Fig. 1). On the first hand, as an active substance in plant protection products, carbendazim was initially approved since January 2007 and regulated by the directive 91/414/EEC. This approval was renewed in June 2011, when the new and current regulation (EC 1107/2009) came into effect, but it expired in November 2014 and the maximum period of grace ended in May 2016. Therefore, nowadays carbendazim should no longer occur in plant protection products used in the EU. On the other hand, as an active substance in biocidal

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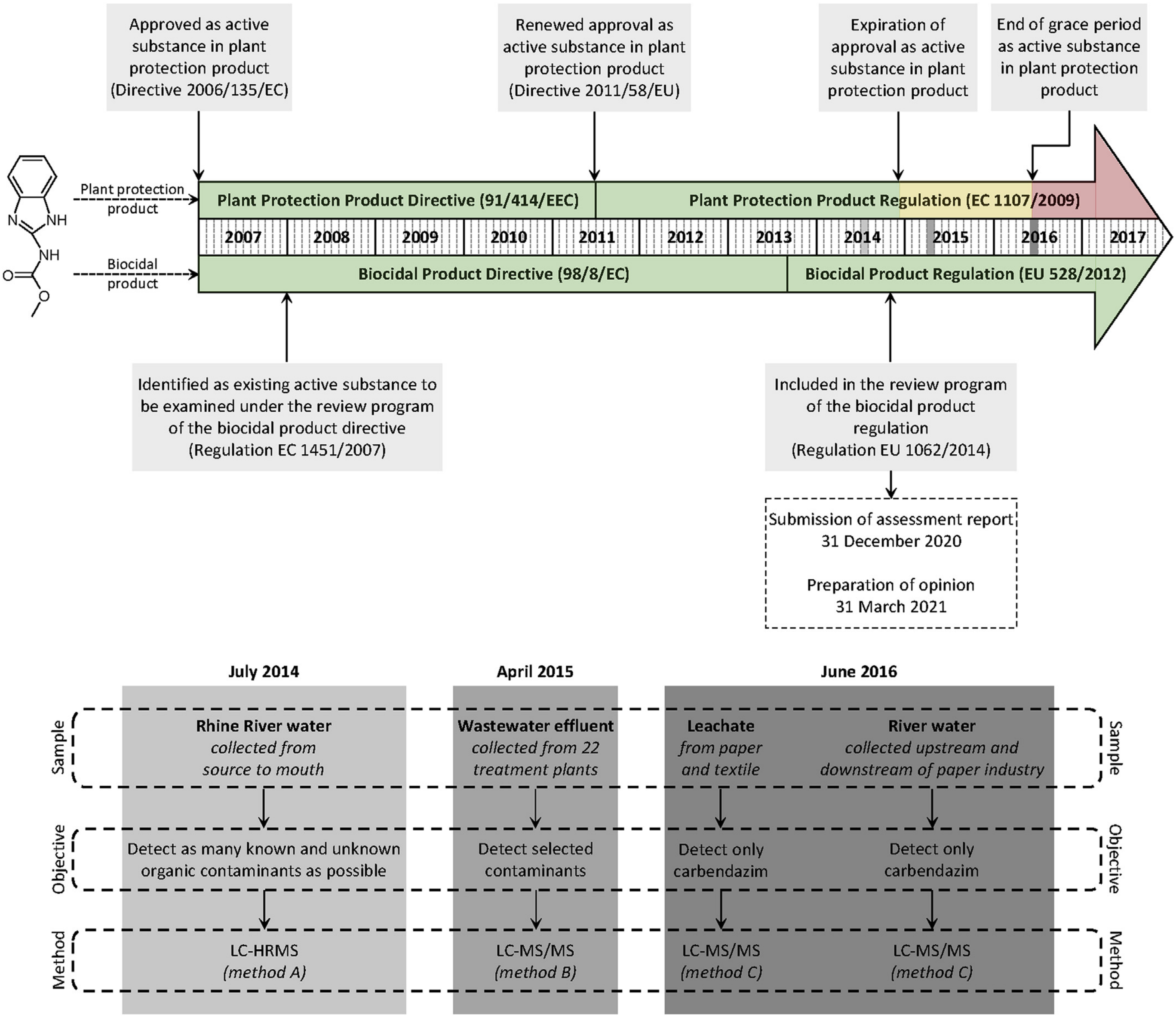

Fig. 1. Overview of regulation, sample collection and analytical methods.

products, carbendazim was acknowledged in December 2007 and added to the list of substances to be examined under the review program of the biocidal product directive 98/8/EC. In September 2013, this directive was repealed by regulation EU 528/2012 and carbendazim was only included in the review program of active substances in November 2014. With assessment reports to be submitted by December 2020, carbendazim is currently being reviewed for its application for PT 7, 9 and 10.

Carbendazim mostly affects the growth of fungi, but it is also an endocrine disruptor for other organisms (McKinlay et al., 2008). Rather than binding to steroid receptors, carbendazim acts on human ovarian cells by interfering with microtubule formation and it increases estrogen production through an intensification of aromatase activity (Morinaga et al., 2004; Yamada et al., 2005). Premating exposure to carbendazim could also lead to birth defects in the offspring via mechanisms linked to androgens and androgen receptors (Lu et al., 2004; McKinlay et al., 2008). Moreover, recent studies also linked carbendazim exposure to oxidative stress (Singh et al., 2016), DNA damage in *Daphnia magna* (Silva et al., 2015), and alteration of locomotor activity in Zebrafish larvae at levels down to 160 ng/L (Andrade et al., 2016).

The usual applications of carbendazim make it likely to be released during rainfall events while subsequent runoff carries it to receiving waters where its biological properties are a potential threat to environmental and human health. For instance, the occurrence of carbendazim in wastewater and surface water has been reported in Brazil (Montagner et al., 2014), Chile (Palma et al., 2004), China (Chen et al., 2014; Liu et al., 2015), Colombia (Hernández et al., 2012), Denmark (Bollmann et al., 2014), Germany (Launay et al., 2016; Wick et al., 2010), Greece (Kalogridi et al., 2014), Portugal (Gonzalez-Rey et al., 2015), Romania (Chitescu et al., 2015), Serbia (Antic et al., 2015; Duјaković et al., 2010), Spain (Campo et al., 2013; Ccanccapa et al., 2016; Masiá et al., 2015) and Switzerland (Singer et al., 2010). While most studies reported concentrations in surface water ranging from 10 ng/L to 50 ng/L, concentrations from 600 ng/L to 6000 ng/L were also reported in specific areas of Spain where carbendazim was largely applied in agriculture (Masiá et al., 2015; Readman et al., 1997). Despite these