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Leaching of azoxystrobin and its degradation product R234886 from Danish agricultural field sites

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ABSTRACT

The objective was to estimate leaching of the fungicide azoxystrobin (methyl (αE)-2-[[6-(2-cyanophenoxy)-4-pyrimidinyl]oxy]-α-(methoxymethylene)benzene-acetate) and one of its primary degradation products R234886 ([(E)-2-(2-[6-cyanophenoxy)-pyrimidin-4-yloxyl]-phenyl-3-methoxyacrylic acid], major fraction) at four agricultural research fields (one sandy and three loamy) in Denmark. Water was sampled from tile drains, suction cups and groundwater wells for a minimum period of two years after application of azoxystrobin. Neither azoxystrobin nor R234886 were detected at the sandy site, but did leach through loamy soils. While azoxystrobin was generally only detected during the first couple of months following application, R234886 leached for a longer period of time and at higher concentrations (up to 2.1 μg L^{-1}). Azoxystrobin is classified as very toxic to aquatic organisms and R234886 as very harmful. Our study shows that azoxystrobin and R234886 can leach through loamy soils for a long period of time following application of the pesticide and thereby pose a potential threat to vulnerable aquatic environments and drinking water resources. We thus recommend the inclusion of azoxystrobin and R234886 in pesticide monitoring programmes and further investigation of their long-term ecotoxicological effects.

1. Introduction

The threat to the aquatic environment posed by agricultural and related use of pesticides is a much discussed issue. In Denmark, where the drinking water supply is exclusively based on groundwater, the Danish Groundwater Monitoring Programme (Jørgensen and Stockmarr, 2009; Brüsch, 2010) has demonstrated that pesticides or their degradation products are present in about 5% of the abstraction wells used for the drinking water supply in concentrations exceeding the EU limit value (0.1 μg L^{-1}) for these substances in both drinking water (European Commission, 1998) and groundwater (European Commission, 2006). Monitoring of five Danish streams revealed the presence of pesticides or their degradation products in almost all samples (Bøgestrand, 2007). Both banned and approved substances have been detected. Detection of the latter indicates that although thorough environmental risk assessments are conducted by the Danish Ministry of the Environment, the approval procedures used may be inadequate to ensure that pesticides and their degradation products do not leach to the aquatic environment. In a recent US study of fungicides in stream water the most frequently detected compound was azoxystrobin (Battaglin et al., 2011).

Azoxystrobin has been used as a fungicide in Denmark since 1998, mainly in barley and wheat. Total annual consumption was 31 tonnes in 2008 and 14 tonnes in 2009 (Ministry of the Environment, 2010), having declined from almost 94 tonnes in 1999. Azoxystrobin and its degradation products are not included in the Danish National Monitoring and Assessment Programme for the Aquatic and Terrestrial Environment. In the USA, where azoxystrobin has been marketed since at least 1998, consumption exceeded 230 tonnes in 2006. There the fungicide is mainly used in rice and potato production, although it is also used to treat vegetables and fruit. For example, 47% of all strawberry fields were treated with azoxystrobin in 2002 and 40% of all cucumber fields in 2004 (National Agricultural Statistical Services, 2010).

Azoxystrobin is defined as moderately to highly persistent in soil (DT_{50} 121–262 d, field studies) with medium to low mobility (K_d 2–20 L kg^{-1}) (EFSA, 2010). The high persistence was confirmed by van Beinum et al. (2006), who estimated DT_{50} to be 152 d (laboratory study). Studies undertaken by EFSA (2010) reveal that up to 29% of applied azoxystrobin degrades to R234886 ([(E)-2-(2-[6-cyanophenoxy)-pyrimidin-4-yloxyl]-phenyl-3-methoxyacrylic acid], Fig. 1) in the soil and that R234886 is moderately to highly persistent (DT_{50} 18–44 d) with very high to high mobility (K_d 0.5–14 L kg^{-1}). Moreover the studies revealed two minor (<9% of

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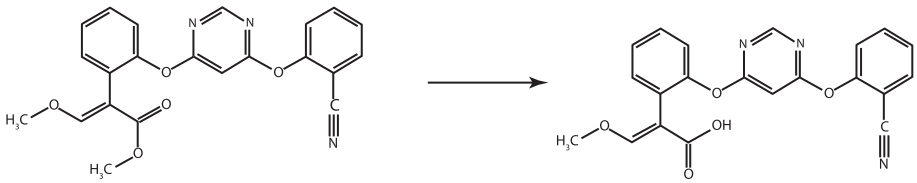

Fig. 1. Pathway for degradation of azoxystrobin to R234886 (adapted from EFSA, 2010).

applied azoxystrobin) photolytic degradation products, R401553 and R402173 that have low to very low persistence (DT_{50} < 10 d) and very high to medium mobility (K_d 0.3–18 L kg^{-1}).

Azoxystrobin is classified as very toxic to aquatic organisms, with less than 1 mg L^{-1} being sufficient to kill 50% of a fish population (EC_{50} determined by 96-h flow-through exposure) or affect 50% of invertebrates (EC_{50} determined by 48-h stationary exposure) and algae (EC_{50} determined by 72-h stationary exposure) within a short time frame (EFSA, 2010). In pesticide monitoring studies in Germany, Liess and von der Ohe (2005) classified azoxystrobin as one of the more toxic substances and reported that it had lethal to sublethal effects on the invertebrate communities investigated. Further evidence of the toxicity of azoxystrobin to macroinvertebrates is provided by modelling in combination with monitoring data (Schriever et al., 2007). All three degradation products of azoxystrobin are considered harmful to aquatic organisms (acute toxicity 10–100 mg L^{-1}; EFSA, 2010).

The scientific literature contains very few studies of the fate and transport of azoxystrobin in the aquatic environment. These studies only address azoxystrobin, moreover, and not its primary degradation products. Larsbo et al. (2008) followed leaching pathways of azoxystrobin in a series of lysimeters representing golf greens – a surface often treated with this fungicide in the Nordic countries. The studies showed that azoxystrobin persisted in the system for seven months after application in October, being detected in concentrations of up to 8.6 μg L^{-1}. A number of pesticide screening studies have been carried out in Lower Saxony, Germany (an area similar to Denmark in terms of climate, geology, land use and pesticide management practice) using 20 different watercourse locations (Berenzen et al., 2005; Liess and von der Ohe, 2005; Schriever et al., 2007). Following runoff events, azoxystrobin was detected in stream water at concentrations as high as 11.1 μg L^{-1} (Liess and von der Ohe, 2005) and 29.7 μg L^{-1} (Berenzen et al., 2005). Contamination pathways were not determined in any of these investigations, however, and neither macropore transport nor preferential flow were addressed.

To our knowledge, no controlled studies have been conducted to quantify long-term leaching of azoxystrobin and its three primary degradation products through the vadose zone into the aquatic environment under field conditions. Given their ecotoxicological and toxicological effects there is an obvious need to evaluate leaching of these substances. The present study thus examined the long-term leaching of azoxystrobin and its most persistent degradation product R234886 at four different field sites in order to assess the leaching risk associated with agricultural use of azoxystrobin.

2. Materials and methods

Leaching of azoxystrobin and its degradation product R234886 was studied at four Danish experimental field sites previously established to facilitate risk assessment of pesticide leaching under field conditions. Three of these field sites have loamy soil (Silstrup, Estrup and Faardrup), and the fourth has sandy soil (Jyndevad). See the Supplementary material Fig. S1 for monitoring design and Table S1 for soil characteristics. The sites are described in detail in Kjær et al. (2005) (Jyndevad, Estrup and Faardrup) and Kjær et al. (2007) (Silstrup and Estrup).

2.1. Site description

The loamy sites Silstrup, Estrup and Faardrup are situated on flat or slightly sloping glacial tills with a shallow groundwater table. During the monitoring period the groundwater table was located 0.5–3.5 m below ground surface (b.g.s.) at the Silstrup site (Fig. 2B), 0.5–4.5 m b.g.s. at the Estrup site (Fig. 3B), and 1.0–3.0 m b.g.s. at the Faardrup site. Tile drains were installed 1 m b.g.s. at all three sites in the 1940s or 1960s.

The sandy Jyndevad site is a practically flat, coarse, meltwater deposit with local occurrences of thin clay and silt beds. The groundwater table was located 1.5–2.5 m b.g.s. during the monitoring period.

The three loamy sites are characterised by preferential transport through macropores, while other forms of preferential transport may take place at the sandy site (Rosenbom et al., 2009). The sites vary in size from 1.3 to 2.4 ha.

2.2. Agricultural management

All four experimental field sites are cultivated in accordance with conventional agricultural practice in the area. To prevent fungal attacks in early summer, azoxystrobin was applied once at Jyndevad (May 2005) and Faardrup (June 2004) and three times at Silstrup (June 2004, 2005 and 2009) and Estrup (June 2004, 2006 and 2008) at the maximum permitted dose of 250 g a.i. ha^{-1} (1 L ha^{-1} Amistar). See Supplementary material Table S2 for more detail regarding dates and crops.

2.3. Monitoring

The water balance and pesticide transport and leaching have been monitored continuously at all four sites since at least May 2000. Precipitation is measured at each site, while additional climatic data are obtained from automatic climate stations located 0.5–3.0 km from the sites. Monitoring data are supported by hydrological modelling (MACRO 5.1; Larsbo et al., 2005), providing an overall water balance and a description of water dynamics in the unsaturated zone (Kjær et al., 2011). The qualitative monitoring programme encompasses numerous pesticides and their degradation products. Azoxystrobin and R234886 were included in the monitoring programme at Silstrup from May 2004 to July 2010, at Estrup from May 2004 to June 2009, at Faardrup from May 2004 to July 2006, and at Jyndevad from April 2005 to April 2007. To avoid artefactual leaching of pesticides to groundwater wells, all sampling equipment was installed from or within the buffer strips surrounding the treated area, and soil sampling was restricted to the upper 20 cm (the plough layer). Additional information about sampling methods and monitoring design is available in Lindhardt et al. (2001) and Kjær et al. (2005, 2007) and in the Supplementary material Fig. S1.