Science of the Total Environment 524–525 (2015) 394–399

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Occurrence of fungal metabolites — fumonisins at the ng/L level in aqueous environmental samples

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HIGHLIGHTS

- Fumonisins B_1 was detected in all types of water samples.
- It was observed seasonal variability of fumonisins B_1 concentration in water samples.
- Fumonisins B_2 and B_3 in water samples were not detected.
- Toxigenic fungi were not found in water samples.

ARTICLE INFO

Article history:
Received 2 November 2014
Received in revised form 6 February 2015
Accepted 4 March 2015
Available online xxxx

Editor: Daniel Wunderlin

Keywords:
Mycotoxins
Fumonisins
HPLC
Drainage ditches
Aqueous matrices

ABSTRACT

The B-series fumonisins (FBs) are some of the most prevalent mycotoxins produced as a secondary metabolite by *Fusarium* species growing on cereals. For decades they have been studied extensively in food and feed products, but there is no information about their occurrence in the aquatic environment or about how these mycotoxins are transported to the surface water and the groundwater. The aim of this study was to clarify the causes of fumonisin occurrence in aquatic ecosystems by examining the relation between mycotoxin contamination of crops and their levels in the aquatic environment. Water samples were collected from drainage ditches and wells or watercourses located in agricultural areas in the Wielkopolska region, Poland. Our research conducted on an annual basis showed the seasonal variability of fumonisin B_1 concentration in the analyzed water samples, with the highest concentration in the post-harvest season (September to October) at 48.2 ng L^{-1}, and the lowest in winter and spring at 21.9 ng L^{-1}. Fumonisins B_2 and B_3 in water samples were not detected. Cereal samples were collected in the harvest season from each agricultural area close to tested water bodies. Mycotoxins were present in all cereal samples at concentrations from 43.3 to 1055.9 ng g^{-1}. Our results confirm that fumonisins are transported to aquatic systems by rainwater through soil. On the basis of available literature, this is the first report concerning the presence of fumonisin B_1 in different aquatic environments. To date their ecotoxicological effects are largely unknown and require further investigation.

1. Introduction

Contamination in aquatic ecosystems is mainly associated with substances formed as a result of human activity and currently the greatest amounts of contaminants are transferred to waters with sewage. However, there are also other compounds, to date not considered to be a health risk or a threat to human life and thus not covered by any legal regulations. For several years now, monitoring studies have been conducted worldwide aiming at determination of the scale of water contaminations with natural toxic compounds found in the aquatic environment in nanogram amounts. Recently, the group of these compounds has been extended to include products of fungal biosynthesis, i.e. mycotoxins (Schwarz et al., 2010).

Mycotoxins — secondary metabolites of microscopic fungi — naturally occur in various cereals, fruits, vegetables and organic material in the soil, but can also be formed under moist conditions during storage (Barkai-Golan and Paster, 2008; Hoerger et al., 2009; Irzykowska et al., 2012; Waśkiewicz and Stępień, 2012; Wawrzyniak and Waśkiewicz, 2014). Research conducted so far has focused mainly on the occurrence of mycotoxins in food and feed as the most important sources of these compounds because of their potential threat to human and animal health (Goliński et al., 2009, 2010). Important classes of mycotoxins are formed by *Fusarium*, *Aspergillus* and *Penicillium* spp. and comprise of aflatoxins, ochratoxins, trichothecenes (mainly deoxynivalenol), fumonisins and zearalenone (Barkai-Golan and Paster, 2008; Goliński et al., 2009, 2010; Wawrzyniak and Waśkiewicz, 2014; Yoshinari et al.,

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http://dx.doi.org/10.1016/j.scitotenv.2015.03.015
0048-9697/

2014). Although this topic has been very well investigated and documented, very few studies have been published on their occurrence in different environmental matrices, and their ecotoxicological effects are largely unknown (Bucheli et al., 2005; Gromadzka et al., 2009, 2012; Waśkiewicz et al., 2012).

The B-series fumonisins produced by *Fusarium verticillioides* and *Fusarium proliferatum*, cause different toxicological effects in both humans and animals (Soriano and Dragacci, 2004; Voss et al., 2009). Consumption of feeds contaminated with fumonisins causes a number of mycotoxicoses, including leukoencephalomalacia in horses, pulmonary edema in swine, altered hepatic and immune function in cattle, as well as liver cancer and neural tube defects in experimental rodents (Logrieco et al., 2003; Desjardins et al., 2007). Particularly fumonisin B_1 is toxic to the liver and kidneys in many species, causing apoptosis followed by mitosis in the affected tissues, and it is also toxic to the cardiovascular system in pigs and horses (Voss et al., 2009). Epidemiological studies also suggest that these toxins could be associated with human esophageal cancer in some regions of the world, where maize contaminated with FBs is used as the staple food (Torres et al., 2007). Taking into consideration available toxicological evidence, the International Agency for Research on Cancer classified FB_1 is probably carcinogenic to humans (class 2B carcinogen) (IARC, 2002). The European Commission Scientific Committee on Food (European Commission, 2007) has evaluated fumonisins and established a provisional maximum tolerable daily intake of 2 μg kg^{-1} of body weight per day for the total amount of FB_1, FB_2, and FB_3, either alone or in combination. The European Union recently regulated fumonisins (as the sum of FB_1 and FB_2) in maize-based products and unprocessed maize so that if no specific concentration had been fixed before 1 October 2007, maximum concentrations from 200 to 2000 μg kg^{-1} would apply thereafter (European Commission, 2005). Most reports concerning the presence of FBs in cereals focus primarily on maize samples (Abbas et al., 2006; Arino et al., 2007; Schjøth et al., 2009). Nevertheless, in recent years there are increasingly frequent studies on occurrence of fumonisins in different edible plants (e.g. onion, garlic, asparagus, pea seed) (Irzykowska et al., 2012; Waśkiewicz and Stępień, 2012; Waśkiewicz et al., 2013b) and in other cereals, mainly in wheat (Cendoya et al., 2014a,b; Jaksic et al., 2012; Stankovic et al., 2012). Until now, little information has been provided on wheat serving as the host for fumonisin producers. On the contrary, *Fusarium graminearum*, *Fusarium culmorum*, *Fusarium avenaceum* and *Fusarium poae* have been considered as major pathogens of this crop, but none of these species is capable of synthesizing fumonisins (Boenisch and Schäfer, 2011; Goliński et al., 2009, 2010; Wagacha and Muthomi, 2011). Many recent studies have concentrated on the variability of *F. proliferatum* and *F. verticillioides* populations occurring in the natural environment, especially in the geographical and ecological contexts (Jurado et al., 2010; Rocha et al., 2011; Waśkiewicz and Stępień, 2012; Waśkiewicz et al., 2013b).

Although the occurrence of FB_s has been studied extensively in cereals and cereal products, there is a lack of information concerning the presence of fumonisins in the aquatic environment. The first analytical method for the analysis of FB_1 in soils was published by Madden and Stahr in 1993, and several other publications have reported the quantification of FB_1 in soil and silage (Benedetti et al., 2006; Garon et al., 2006; Richard et al., 2009).

The aim of this study was to clarify the causes of fumonisin occurrence in aquatic ecosystems by examining the relation between mycotoxin contamination of crops and their levels in the aquatic environment.

2. Materials and methods

2.1. Collection of water samples

Water samples were collected in the Wielkopolska region, Poland. Seven water sampling points were established in five different parts of the region (Fig. 1). Water samples were collected in an annual cycle, at monthly intervals, from water reservoirs such as ditches, drainage wells or lakes and rivers located in agricultural areas. An exception in this respect was provided by sample collection in July, when due to the harvest being in progress the frequency was increased to twice a month, at 2-week intervals. Sample collection was performed at the same previously established locations, by immersing a 1-liter scoop to

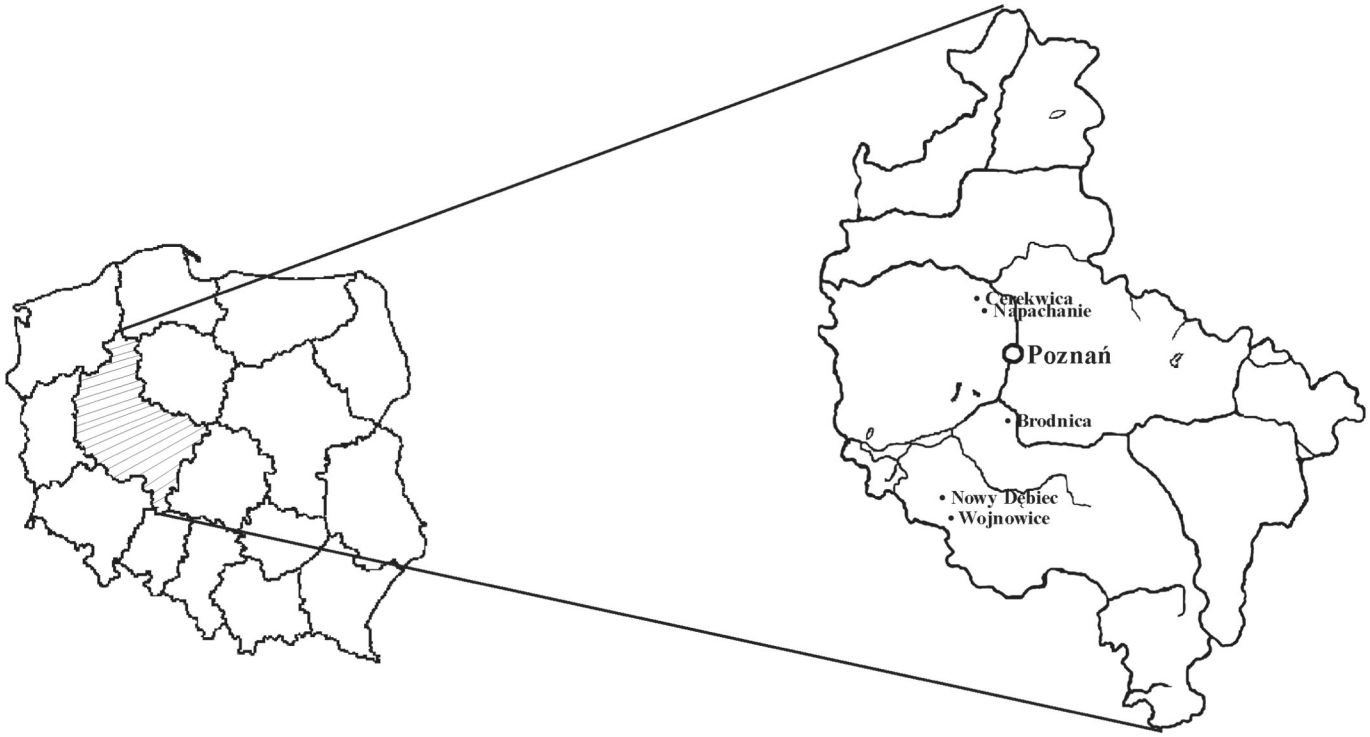

Fig. 1. Distribution of water sample collection points in the Wielkopolska region.