Science of the Total Environment 470–471 (2014) 669–676

Contents lists available at ScienceDirect

Science of the Total Environment

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

Mycotoxins: Diffuse and point source contributions of natural contaminants of emerging concern to streams

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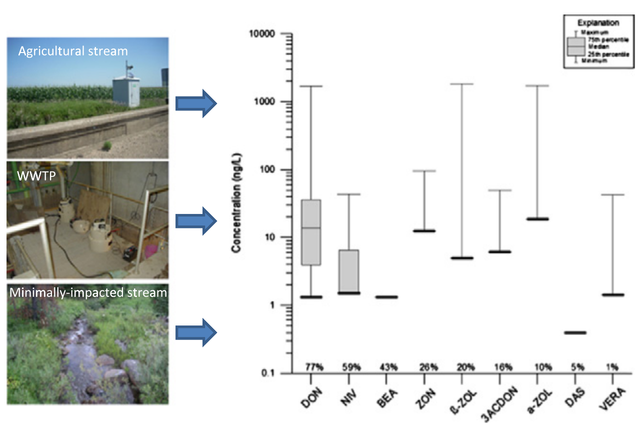
HIGHLIGHTS

- A total of 116 water samples were collected at 32 streams and 3 wastewater treatment plants during 2010.
- The detections of mycotoxins were nearly ubiquitous (94% of samples) even though basin size spanned 4 orders of magnitude.
- The most frequently detected mycotoxins included deoxynivalenol (77%), nivalenol (59%), and beauvericin (43%).
- Levels exceeding 100 ng/L were measured during spring snowmelt conditions in agricultural settings and in WWTP effluent.
- Both diffuse and point sources are important environmental pathways for mycotoxin transport to streams.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 August 2013
Received in revised form 20 September 2013
Accepted 22 September 2013
Available online 29 October 2013

Editor: Damia Barcelo

Keywords:
Mycotoxins
Streams
United States

ABSTRACT

To determine the prevalence of mycotoxins in streams, 116 water samples from 32 streams and three wastewater treatment plant effluents were collected in 2010 providing the broadest investigation on the spatial and temporal occurrence of mycotoxins in streams conducted in the United States to date. Out of the 33 target mycotoxins measured, nine were detected at least once during this study. The detections of mycotoxins were nearly ubiquitous during this study even though the basin size spanned four orders of magnitude. At least one mycotoxin was detected in 94% of the 116 samples collected. Deoxynivalenol was the most frequently detected mycotoxin (77%), followed by nivalenol (59%), beauvericin (43%), zearalenone (26%), β-zearalenol (20%), 3-acetyl-deoxynivalenol (16%), α-zearalenol (10%), diacetoxyscirpenol (5%), and verrucarin A (1%). In addition, one or more of the three known estrogenic compounds (i.e. zearalenone, α-zearalenol, and β-zearalenol) were detected in 43% of the samples, with maximum concentrations substantially higher than observed in previous research. While concentrations were generally low (i.e. <50 ng/L) during this study, concentrations exceeding 1000 ng/L were measured during spring snowmelt conditions in agricultural settings and in wastewater treatment plant effluent. Results of this study suggest that both diffuse (e.g. release from infected plants and manure applications from exposed livestock) and point (e.g. wastewater treatment plants and food processing plants) sources are important environmental pathways for mycotoxin transport to streams. The ecotoxicological

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0048-9697/$ – see front matter. Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.scitotenv.2013.09.062

impacts from the long-term, low-level exposures to mycotoxins alone or in combination with complex chemical mixtures are unknown.

1. Introduction

Mycotoxins are naturally occurring toxic secondary metabolites of fungal species (e.g. *Aspergillus* spp., *Fusarium* spp., and *Penicillium* ssp.) that can grow on a wide variety of crops including wheat (*Triticum* ssp.) and corn (*Zea mays*) (Goswami and Kistler, 2004; Murphy et al., 2006). Previous research has documented mycotoxins as potentially important, but underinvestigated, environmental contaminants (Lagana` et al., 2004; Bucheli et al., 2008; Gromadzka et al., 2009; Kolpin et al., 2010; Schenzel et al., 2012b).

Mycotoxin infestations cause head blight in cereal grains and stem and ear rot in corn that lead to substantial crop damage worldwide. In addition, the presence of mycotoxins lowers the quality of food and feedstuffs by deteriorating the nutritional content and potentially affecting animal health (Bennett, 1987; Hussein and Brasel, 2001). Fungal infestations in crops have increased in recent years because of factors such as changes in tillage practices, decreased crop rotations (Champeil et al., 2004), and climate change (Madgwick et al., 2011). While the number of potential toxic metabolites of fungi has been estimated to be in the thousands, only several hundred have been identified to date (Jestoi, 2008).

Mycotoxins can exhibit a broad range of effects including carcinogenicity, neurotoxicity, and developmental toxicity. In particular, zearalenone (ZON) and its metabolites α-zearalanol (α-ZOL) and β-zearalanol (β-ZOL) have estrogenic activity similar to that of natural estrogens (Le Guevel and Pakdel, 2001; Metzler, 2011). Its pronounced hormonal activity has prompted some scientists to characterize ZON as a mycoestrogen (Bennett and Klich, 2003). In fact, α-ZOL is a potent estrogen commonly used in the United States for growth promotion in cattle. It is estimated that over 97% of beef cattle produced in the United States receive hormone supplements to enhance growth (Balter, 1999). The presence of α-ZOL and β-ZOL in both treated and control cattle (Bartelt-Hunt et al., 2012) indicates that runoff from livestock facilities or fields receiving livestock manure applications could be of environmental concern. Recent studies have documented the potential deleterious effects to environmental and human health from mycotoxin exposure (Frizzell et al., 2011; Johns et al., 2011; Metzler et al., 2010; Pietsch et al., 2011; Schwartz et al., 2010). Experiments exposing ZON to zebrafish (*Danio rerio*) confirm the estrogenic potential of ZON to influence sexual differentiation and reproduction (Schwartz et al., 2011). In addition, the developmental effects on zebrafish suggest the potential for ZON to interact with other ontogenic pathways (Bakos et al., 2013).

While extensive research has been conducted on the production of mycotoxins and their occurrence in agricultural products such as food and feed (Pittet, 1998; Streit et al., 2013), little has been done to determine their environmental fate and distribution (Bucheli et al., 2008; Hartmann et al., 2008; Kolpin et al., 2010; Schenzel et al., 2012a; Qu et al., 2012). Potential environmental pathways include the release from infected plants (Hartmann et al., 2008; Bucheli et al., 2008; Schenzel et al., 2012a), manure from exposed livestock (Seeling et al., 2005; Hartmann et al., 2008), and human waste via wastewater treatment plants (Schenzel et al., 2012b). Previous research has documented the presence of mycotoxins in tile drains (Lagana` et al., 2004; Hartmann et al., 2008; Schenzel et al., 2012a), streams (Bucheli et al., 2008; Kolpin et al., 2010; Maragos, 2012; Schenzel et al., 2010, 2012b) and municipal effluent (Wettstein and Bucheli, 2010; Schenzel et al., 2012b) providing evidence of both diffuse and point sources of mycotoxins to the environment.

The purpose of this report is to describe the occurrence of a broad spectrum of 33 mycotoxins (ten trichothecenes, five aflatoxins, four alternaria toxins, three resorcyclic acid lactones, two ochratoxins, two ergot alkaloids, two fumonisins, two penicillium toxins, and three miscellaneous mycotoxins) measured in 116 samples collected during 2010 from a network of 32 streams and three wastewater treatment plant (WWTP) effluents. The sampling network was selected to assess mycotoxin occurrence in streams impacted by agricultural runoff and WWTP effluent. In addition, two streams in minimally impacted reference settings were also selected to increase the understanding of sources of mycotoxins to streams. This study provides the broadest investigation on the spatial and temporal occurrence of mycotoxins in streams conducted in the United States to date.

2. Materials and methods

2.1. Sampling sites

To determine the prevalence of mycotoxins in streams in the United States, 116 samples from 32 streams and three WWTP effluents were collected (Fig. 1, Table SI-1). To understand the temporal distribution of mycotoxins in agricultural-impacted rivers and streams, a network of 17 sampling sites across Iowa was selected to provide a range of basin sizes and geographic distribution across the state (Fig. 1, Table SI-1). These sites include 15 interior stream basins and two sites on the large border rivers of Iowa (Missouri and Mississippi Rivers) that also include extensive basin areas outside of Iowa. This stream network drains about 90% of Iowa. There were roughly 5.69 million ha of corn, 3.48 million ha of soybean, 0.46 million ha of forage crops (e.g., alfalfa, grass), 19.3 million swine, 3.98 million cattle, and 69.2 million poultry produced in Iowa in 2007 (US Department of Agriculture National Agricultural Statistics Service, 2009). Thus, Iowa was an ideal location to assess the occurrence of mycotoxins in streams having extensive agricultural activities such as crop and livestock production. The 17 agricultural sites in Iowa were sampled on a relatively high-frequency basis (e.g. 5 times) from March to November, 2010 to capture concentration patterns through the growing season (Fig. SI-1, Table SI-2). Additional opportunistic samples, however, were also collected at select study sites in Iowa when conditions warranted. Sites were generally sampled within a 2-week window during each collection period. For comparison to the Iowa results, a second agricultural basin was sampled in Indiana (Fig. 1, Table SI-1). This basin was primarily in corn and soybean agriculture with roughly 50 livestock facilities (particularly swine and cattle) present in the basin (Bernot et al., 2013). The seven agricultural sites in Indiana (Bernot et al., 2013) were sampled in July (six sites) and in October (six sites) during the 2010 crop growing season (Table SI-2). To document the importance of WWTPs as sources of mycotoxins to streams, three sets of sampling sites in New York (Fig. 1, Table SI-1) were selected consisting of one stream site upstream of the WWTP outfall, one effluent site, and one stream site downstream of the WWTP outfall. Each site was sampled once during this study. Finally, two streams from remote sites in Montana and Wisconsin (Fig. 1, Table SI-1) in areas having minimal direct impact from urban and agricultural activities were sampled once during this study.

All study sampling sites were selected because they: (1) were located at a US Geological Survey (USGS) stream gage in order that continuous streamflow could be provided, and/or (2) were being sampled as part of other ongoing USGS water-quality investigations. All stream samples were collected by USGS personnel using standard depth and