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Characterization of Missouri surface waters near point sources of pollution reveals potential novel atmospheric route of exposure for bisphenol A and wastewater hormonal activity pattern ☆

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HIGHLIGHTS

- Assessed contaminants in surface water near chemical release sites.
- Anti-hormonal receptor activities were predictive of wastewater inputs.
- Bisphenol A concentrations were greater in surface water near airborne releases.
- Airborne release of bisphenol A may represent underestimated human exposure source.

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ABSTRACT

Surface water contamination by chemical pollutants increasingly threatens water quality around the world. Among the many contaminants found in surface water, there is growing concern regarding endocrine disrupting chemicals, based on their ability to interfere with some aspect of hormone action in exposed organisms, including humans. This study assessed water quality at several sites across Missouri (near wastewater treatment plants and airborne release sites of bisphenol A) based on hormone receptor activation potencies and chemical concentrations present in the surface water. We hypothesized that bisphenol A and ethinylestradiol would be greater in water near permitted airborne release sites and wastewater treatment plant inputs, respectively, and that these two compounds would be responsible for the majority of activities in receptor-based assays conducted with water collected near these sites. Concentrations of bisphenol A and ethinylestradiol were compared to observed receptor activities using authentic standards to assess contribution to total activities, and quantitation of a comprehensive set of wastewater compounds was performed to better characterize each site. Bisphenol A concentrations were found to be elevated in surface water near permitted airborne release sites, raising questions that airborne releases of BPA may influence nearby surface water contamination and may represent a previously underestimated source to the environment and potential for human exposure. Estrogen and androgen receptor activities of surface water samples were predictive of wastewater input, although the lower sensitivity of the ethinylestradiol ELISA relative to the very high sensitivity of the bioassay approaches did not allow a direct comparison. Wastewater-influenced sites also had elevated anti-estrogenic and anti-androgenic equivalence, while sites without wastewater discharges exhibited no antagonist activities.

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1. Introduction

The contamination of surface water sources is nearly ubiquitous, with surface water investigations in the United States and European Union revealing organic wastewater pollutants in 80% and 97% of samples, respectively (Kolpin et al., 2002; Loos et al., 2009). Frequent among these contaminants are endocrine disrupting chemicals (EDCs), which are able to interfere with some aspect of hormone action (Zoeller et al., 2012). As of 2013, approximately 1000 synthetic and naturally occurring chemicals with EDC activity had been identified (The Endocrine Disruption Exchange, n.d.), with exposure linked to a number of adverse health effects (Guillette et al., 1994; Ottinger et al., 2008; Vandenberg et al., 2012). EDCs are capable of acting at much lower concentrations than chemicals without EDC activity that are tested at very high doses in traditional toxicological risk assessments. In addition, EDCs can exhibit non-monotonic dose response curves (resulting in quantitatively and qualitatively different outcomes at low versus high concentrations), and may exert greater effects during critical windows of development, when exposure can derail normal development and lead to adult disease (Vandenberg et al., 2012; Welshons et al., 2003; Myers et al., 2009; vom Saal et al., 2007).

EDCs that interact with the estrogen and androgen receptors are common in surface water around the globe (Kolpin et al., 2002; Loos et al., 2009; Van der Linden et al., 2008). Major sources for these compounds include wastewater effluents (Furuichi et al., 2004; Murk et al., 2002; Belfroid et al., 1999; Pawlowski et al., 2004; Kuch and Ballschmiter, 2001; Williams et al., 2003; Cargouet et al., 2004), industrial discharges (Calafat et al., 2008; Vandenberg et al., 2010; Kassotis et al., 2014), agricultural operations (Hayes et al., 2011; Hayes, 2002; Hayes et al., 2010; Loos et al., 2010), and natural sources (Kolodziej et al., 2004; Kolpin et al., 2014; Sychrová et al., 2012). Two hormonally active contaminants that are routinely found in surface water are ethinylestradiol (EE2), an estrogen receptor agonist (Folmar et al., 2002; Thorpe et al., 2003) used in many oral contraceptives, and bisphenol A (BPA; 4,4′-isopropylidenediphenol, Chemical Abstract Number 80-05-7), a selective estrogen receptor modulator with agonist/antagonist activity as well as antagonist activities for the androgen receptor and other receptor activities (Vandenberg et al., 2012; vom Saal et al., 2007; Reif et al., 2010; Richter et al., 2007; Zoeller et al., 2005), that is used in the production of plastic and numerous other consumer products (Calafat et al., 2008; Latini, 2005; Pak et al., 2007). Both chemicals contribute to estrogenicity in surface water (Johnson and Williams, 2004; Johnson et al., 2000), in part due to the failure of routine wastewater treatment plant (WWTP) processes to adequately remove these and similar compounds from wastewater (Kuch and Ballschmiter, 2001; Westerhoff et al., 2005; Campbell et al., 2006; Braga et al., 2005). Some researchers have found BPA and EE2 to be significant contributions to estrogenicity in surface water, accounting for up to 50% of activity (Cargouet et al., 2004; Sun et al., 2008). However, many others have not found these two chemicals to contribute significant activities and instead report estrone, estradiol, nonylphenol, and/or octylphenol as major contributors (Furuichi et al., 2004; Hashimoto et al., 2005; Cespedes et al., 2005), while others have been unsuccessful in accounting for the majority of observed activity (Murk et al., 2002; Wang et al., 2011). Additionally, another significant source of BPA release into the aquatic environment includes groundwater leachates from common landfills. Indeed, nearly all landfill leachates tested in a recent national survey across the United States contained BPA (95%), with concentrations as great as mg/L (Masoner et al., 2014). BPA contributes up to 84% of the estrogenicity of these leachates, suggesting that the relative contributions in water are likely source dependent (Kawagoshi et al., 2003). Surface water concentrations are reported for these two estrogenic EDCs at between 0.1–1.5 ng/L for EE2 and 3–30 ng/L for BPA (Murk et al., 2002; Belfroid et al., 1999; Kuch and Ballschmiter, 2001; Cargouet et al., 2004; Bhandari et al., in press). Moreover, EE2 and BPA have been reported in surface water at concentrations known to cause adverse effects in wildlife (Petrovic et al., 2004; Papoulias et al., 1999; Colborn, 1995, 2003).

Reporter gene assays have been utilized to assess total receptor activities of complex mixtures of chemicals in the environment (Pawlowski et al., 2004; Zhao et al., 2011; Soto et al., 2003). Reporter gene assays do not provide quantification of any particular chemical or analyte; however, they provide a highly sensitive detection system for multiple chemicals with a specific receptor-mediated mechanism of action and can be used to target hormonally active chemicals for subsequent analytical identification. This is particularly important as the types and concentrations of contaminants in water vary widely (Kolpin et al., 2002; Loos et al., 2009, 2010; Barnes et al., 2008; Lapworth et al., 2012). As estrogenic or androgenic disrupting chemicals can act additively (Silva et al., 2002; Rajapakse et al., 2002; Christiansen et al., 2008; Kortenkamp and Faust, 2010; Ermler et al., 2011), there is a particular cause for concern over mixtures of hormonally active contaminants with a similar mode of action in water. Chemical mixtures in water can also include receptor antagonists coming from wastewater (Ihara et al., 2014; Liscio et al., 2014; Bellet et al., 2012), agricultural operations (Orton et al., 2011), and other sources (Chen et al., 2014). Receptor-based assay systems provide an integrated assessment of hormonal and anti-hormonal activities within a particular receptor group. Receptor-based cell assays do not offer the level of complexity known to regulate endocrine function of vertebrates in vivo; however, they do offer an initial estimate of receptor-mediated transcriptional response of an intact cell.

The goals of this study were to assess the water quality at potentially threatened sites across Missouri and to ascertain whether the type of point source contamination to surface water could be determined based on receptor activities and chemical concentrations present in the water sampled from each location. Six sites were selected for investigation, including two nearby permitted atmospheric release sites of BPA, and four downstream of current or historical WWTP effluent discharge sites (Fig. 1, Table 1). At each site, grab water samples were collected to ascertain chemicals present at a given point in time, and passive samplers were deployed to measure chemicals present in the water at the specific location over approximately 35 days. We hypothesized that 1) concentrations of BPA and EE2 would be greater near permitted airborne release sites and WWTP effluent inputs, respectively, and 2) that BPA and EE2 would be responsible for the majority of estrogenic and BPA for the majority of anti-androgenic receptor activities observed in water samples collected near the respective site types. Concentrations of BPA and EE2 were compared to observed receptor activities of individual chemical standards to assess the contribution to total receptor-based activities. Further, quantitation of a comprehensive set of wastewater compounds was performed to help characterize each site. Altogether, receptor activities and individual chemical concentrations were analyzed to determine point source pollution potential and contamination signatures.

2. Materials and methods

2.1. Selection of sampling sites

Water sampling sites were selected based on their proximity to: 1) Superfund National Priorities List (NPL) locations with reported atmospheric discharges of BPA; or 2) downstream from current or historical municipal wastewater treatment plant discharges. NPL sites are defined under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) as sites warranting further investigation. Missouri NPL discharges of BPA were identified from the U.S. Environmental Protection Agency (US EPA) Toxic Release Inventory (http://www2.epa.gov/toxics-release-inventory-tri-program) with watersheds within the immediate area (<16 km) of the NPL site. Two NPL sites with BPA discharges were selected and water-sampling locations identified for collection of water grab samples and passive water