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Fate of trace organics in a wastewater effluent dependent stream

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HIGHLIGHTS

- The fate of TOrCs and estrogenicity in the Lower Santa Cruz River is presented.
- Estrogenicity and some TOrCs are attenuated with distance of travel in the river.
- Estrogenic compounds are degraded by indirect photolysis.
- Hydrophobic TOrCs tend to accumulate in riverbed sediments.
- Riverbed sediment quality is periodically affected through storm-related scouring.

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ABSTRACT

Trace organic compounds (TOrCs) in municipal wastewater effluents that are discharged to streams are of potential concern to ecosystem and human health. This study examined the fate of a suite of TOrCs and estrogenic activity in water and sediments in an effluent-dependent stream in Tucson, Arizona. Sampling campaigns were performed during 2011 to 2013 along the Lower Santa Cruz River, where TOrCs and estrogenic activity were measured in aqueous (surface) and solid (riverbed sediment) phases. Some TOrCs, including contributors to estrogenic activity, were rapidly attenuated with distance of travel in the river. Those TOrCs that are not sufficiently attenuated and percolate to ground water have in common low biodegradation probabilities and low octanol–water distribution ratios. Independent experiments showed that attenuation of estrogenic compounds may be due in part to indirect photolysis caused by formation of organic radicals from sunlight absorption. Hydrophobic TOrCs may accumulate in riverbed sediments during dry weather periods, but riverbed sediment quality is periodically affected through storm-related scouring during periods of heavy rainfall and runoff. Taken together, evidence suggests that natural processes can attenuate at least some TOrCs, reducing potential impacts to ecosystem and human health.

1. Introduction

For more than thirty years, it has been known that pharmaceuticals, personal care products and other trace organic contaminants (TOrCs) survive conventional wastewater treatment and persist in the environment to varying degrees (Richardson and Bowron, 1985; Ahel et al., 1994a; Kolpin et al., 2002). More than any other group of trace organics in municipal wastewater, endocrine disrupting compounds (EDCs) have attracted the attention of health professionals and the public (Heberer, 2002; Teske and Arnold, 2008; Sumpter and Jobling, 2013). These compounds interfere with normal endocrine function by blocking signaling/response (antagonists) or stimulating inappropriate activity (agonists). Chemicals present in municipal wastewater that promote estrogenic response include natural steroidal estrogens such as estrone (E_1), 17β-estradiol (E_2) and estriol (E_3), and anthropogenic mimics such as 17α-ethinylestradiol (EE_2) and alkylphenols (APs) (Routledge and Sumpter, 1996; Teske and Arnold, 2008). All these compounds share similar chemical structure: presence of phenolic rings, similar molecular weight, and significant hydrophobicity (log $D_{OW} > 3$).

Early evidence of endocrine disrupting activity in treated wastewater arose from elevated incidence of intersex characteristics (compromised gonadal growth, spermatogenesis, sperm motility, and fertilization success) among male fish in rivers of the United Kingdom (Purdom et al., 1994; Jobling et al., 1998). E_2 and EE_2 elicit physiological changes in continuously exposed organisms at levels that are routinely measured in conventionally treated municipal wastewater effluent

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(Sanchez et al., 2011). Factors that influence the removal of EDCs and other TOrCs during wastewater treatment have been widely studied. Simulations of conventional treatment have not, however, been entirely successful in predicting chemical-specific removal efficiencies during municipal wastewater treatment (Rojas et al., 2010).

Gross et al. (2004) studied the fates of TOrCs in an effluent dominated stream and wetland in southern California, measuring attenuations of ibuprofen, gemfibrozil and chlorinated tris-propylphosphates as well as the conversion of alkylphenol polyethoxylates to APs. Fono et al. (2006) measured the attenuations of ethylenediaminetetraacetate (EDTA), gemfibrozil, ibuprofen, metoprolol, naproxen, and total adsorbable organic iodide in the Trinity River, an effluent dominated stream in Texas. Although the iodated compounds were conserved, others decreased in concentration by 60–90% during two weeks of travel over 500 km. In a more recent Arizona survey, Chiu and Westerhoff (2010) found that surface water concentrations of sucralose, sulfamethoxazole, acetaminophen, cotinine, dilantin, caffeine, DEET and oxybenzone exhibited seasonal trends. Oxybenzone and sucralose concentrations were generally higher in summer months due to increased recreational use of surface water resources.

Candidate mechanisms for the attenuation of trace organics during in-stream transport include biodegradation, photolysis and adsorption on riverbed sediments (Barber et al., 2013; Hanamoto et al., 2013; Writer et al., 2013). Conditional rate constants representing relative compound biodegradability have been based on either direct measurement (Salveson et al., 2010) or moiety-specific contributions to biological transformation rates (ASTreat 1.0, a windows based computer model designed by Procter and Gamble Company, McAvoy, 1999). The contribution of sorption on organic solids should be directly related to compound hydrophobicity, as reflected by octanol/water partitioning (K_{OW} or D_{OW}) (Ying et al., 2002; Snyder et al., 2003). It is expected that, other factors being equal, compound hydrophobicity would lead to accumulation in river sediments due to both sedimentation and the retention of contaminants during infiltration. Direct photolysis and indirect photolysis also contribute to in-stream compound disappearance (Watts and Linden, 2008; Wols and Hofman-Caris, 2012). Direct photolysis occurs when a compound undergoes transformation as a result of light absorption. This is envisioned as a two-step process in which the absorption of light energy promotes the compound to an excited state, after which either chemical transformation occurs or the excited compound devolves to its original ground state. Indirect photolysis is initiated through light absorption by other chemicals, leading to production of reactive intermediates such as hydroxyl or organic radicals that react chemically with the target compound (Wols and Hofman-Caris, 2012). Jasper and Sedlak (2013) hypothesized that radicals formed by direct photolysis of dissolved organic matter could be responsible for indirect photolysis of TOrCs. Schwarzenbach et al. (2003) analyzed how radicals (hydroxyl, carbonate, organics, etc.) produced by direct photolysis of certain compounds may attack TOrCs and degrade them.

The Santa Cruz River (SCR) is an effluent dependent stream in Tucson, Arizona (Fig. 1). Except during widespread precipitation events, the only source of river water is the treated wastewater from two wastewater treatment facilities. The SCR is located in an inner valley created by dissected pediments and alluvial deposits. Consequently, the riverbed is made up of fine sand and gravel eroded from surrounding mountains. Prior to 2014, the Pima County Regional Wastewater Reclamation Department's (PCRWRD) two major wastewater treatment plants discharging to the SCR were the Roger Road Wastewater Treatment Plant (RRWTP; trickling filter, treatment capacity of 1.80 m^3/s) and the Ina Road Water Reclamation Facility (IRWRF; activated sludge, treatment capacity 1.64 m^3/s). The plants are the main wastewater treatment facilities for the City of Tucson, with about half

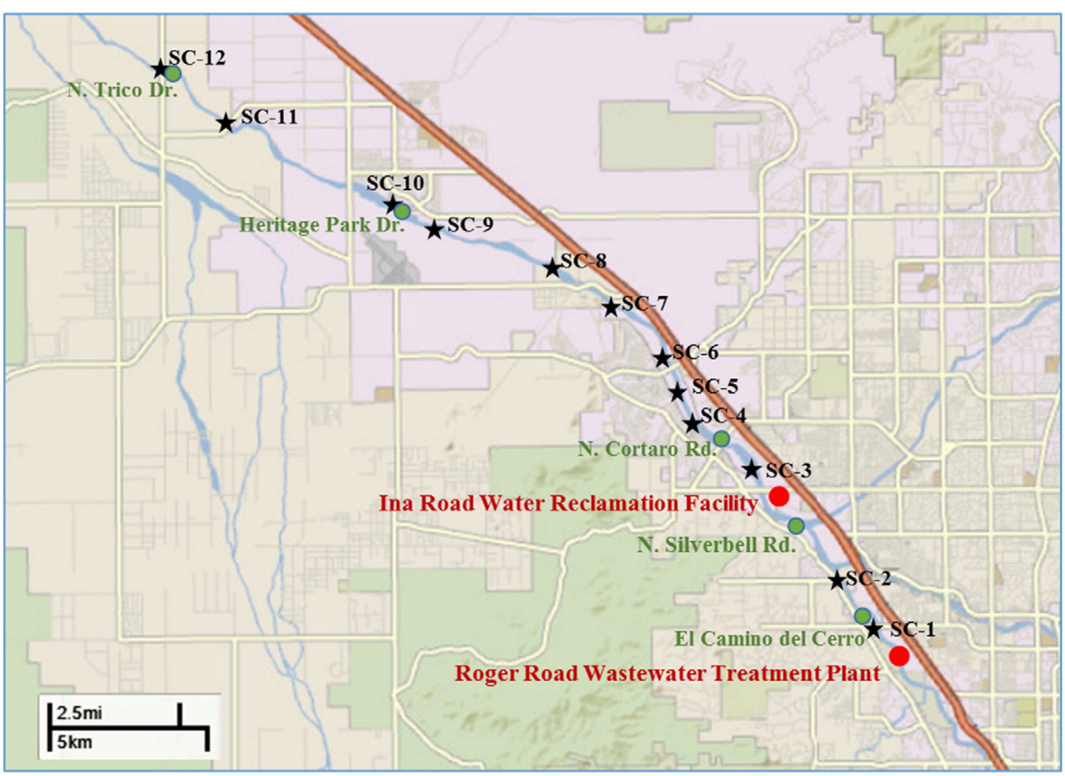

Fig. 1. Wastewater treatment facilities and sampling sites along the Santa Cruz River (blue line) in Tucson, AZ. Red dots: major water reclamation facilities; black stars: sampling sites in the 2011 campaign (river water and groundwater wells); green dots: river water sampling sites in the 2012–13 campaigns. Relative distances for all sampling points are reported in Tables 4 and 5. In February 2014, the Roger Road Wastewater Treatment Plant (RRWTP) was replaced by the Agua Nueva Water Reclamation Facility (WRF); and the Ina Road Water Reclamation Facility (IRWRF) was similarly upgraded and renamed Tres Rios WRF. Except during periods of widespread rain, the SCR only flows along the northwest direction from the RRWTP, and the tributaries seen in the figure are completely dry.