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# Sorption of isoflavones to river sediment and model sorbents and outcomes for larval fish exposed to contaminated sediment

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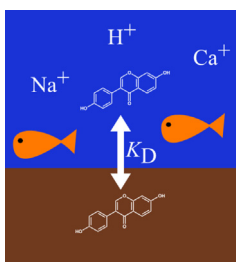
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### HIGHLIGHTS

- Isoflavones sorb to the mineral and organic components of sediments.
- Sorption to minerals is dependent on pH and ionic strength.
- Sorbed isoflavones do not adversely affect fish larvae.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Isoflavones are compounds whose presence in the aquatic environment is increasingly recognized and may be of concern due to their potential to act as endocrine disruptors. Sorption to particles may be a relevant removal mechanism for isoflavones. This work investigated the influence of pH, ionic strength, and sediment composition on sorption of genistein and daidzein, two key isoflavones, using sorption isotherms and edges. The effect of sorbed isoflavones on the survival, growth, and predator avoidance performance of larval fathead minnows (*Pimephales promelas*) was assessed. Sorption to goethite and kaolinite was pH-dependent, with a maximum near pH 7 for both compounds. Sorption to montmorillonite was ionic-strength dependent but largely pH-independent. Overall, sorption to sediments is likely to sequester less than 5% of isoflavones in a discharge. No statistically significant effects were observed for larvae exposed to sorbed isoflavones, suggesting that sorption to sediments reduces exposure to isoflavones.

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## 1. Introduction

Isoflavones are one type of phytoestrogen, a class of compounds derived from plants that have been shown to cause reproductive and immunosuppressive effects [1–3]. Isoflavones including genistein, daidzein, biochanin A and formononetin (Table 1) have been detected in municipal wastewater and industrial effluents, drainage waters from pastures and fields, and surface waters at concentrations ranging from 2 ng L<sup>-1</sup> to 151,000 ng L<sup>-1</sup> [4–13]. The photochemical fates of genistein, daidzein, biochanin A, and formononetin have been studied [14,15]. The photolytic half-lives of these isoflavones vary across 2–3 orders of magnitude, depending on environmental conditions including sunlight intensity, pH, quantity and characteristics of dissolved organic matter, and concentration of reactive oxygen species. While the potential exists for photochemical degradation of isoflavones in the aquatic environment, rates of direct and indirect photolysis do not explain the wide variety of observed concentrations in surface waters and effluents [16]. Long photolytic half-lives (up to 120 h for genistein in deionized water at pH 8.5 and latitude 40° N) [15], suggest that other removal or attenuation mechanisms are worth investigating.

Because isoflavones have relatively low aqueous solubility (e.g., 0.81 mg L<sup>-1</sup> for genistein, 2.54 mg L<sup>-1</sup> for daidzein), sorption to suspended particles or sediments is a possible mechanism for removal of these compounds from the water column [17,18]. Previous work has addressed the organic carbon–water ( $K_{oc}$ ) or octanol–water ( $K_{ow}$ ) partitioning coefficients for some isoflavones. The log  $K_{oc}$  of daidzein was found to be 3.29, using a Pahokee Peat column [19]. The log  $K_{ow}$  values for genistein and daidzein were measured as 3.04 and 2.51, respectively, determined by octanol–water partitioning [20]. Experimental values are approximately within a factor of two of the values predicted values from EPI Suite [21]. The partitioning coefficient values suggest that these compounds may sorb to organic-rich phases.

Clay and iron oxide minerals are major components of soils in the intermediate and advanced stages of weathering, and related sediments [22]. The phenolic, estrogenic compounds estrone, 17 $\alpha$ -ethinylestradiol (EE2), and bisphenol A all show pH-dependent sorption to montmorillonite, but not kaolinite or goethite [23]. Estradiol, a human estrogen, shows pH-dependent sorption to goethite, but not to kaolinite or montmorillonite [24]. Oxytetracycline, a phenolic antibiotic, shows pH-dependent sorption to goethite, montmorillonite, and kaolinite [25,26]. Thus, the presence of phenolic functional groups on the isoflavones suggests that pH may influence sorption behavior. The pK<sub>a</sub> values of isoflavones range from 7 to 13 [14,15], indicating that deprotonation will occur at environmentally relevant pH values and must be considered when evaluating sorption to mineral surfaces.

A number of studies on the effects of free, aqueous isoflavones on adult fish have been conducted. Genistein has been shown to affect the gonadal development of male and female Japanese

medaka (*Oryzias latipes*) at concentrations from 1 to 1000  $\mu$ g L<sup>-1</sup> [1]. In another study, it was shown to affect the behavior of male fighting fish (*Betta splendens*). Fish exposed to genistein at concentrations from 1 to 1000  $\mu$ g L<sup>-1</sup> built smaller nests and behaved less aggressively towards a mirror stimulus than unexposed fish [3]. Fighting fish exposed to 1  $\mu$ g L<sup>-1</sup> and 1000  $\mu$ g L<sup>-1</sup> produce more dopamine in their forebrain than unexposed fish [29]. Larvae exposed to aqueous isoflavones had lower survival and adult fish exposed to degraded isoflavones reproduced at lower rates than control fish [30,31]. Sorption to sediments, however, may not represent a true removal mechanism for isoflavones. Because developing fish in the larval stage spend more time in or near sediments, isoflavones sorbed to settled particles may pose as great or greater a risk than free, aqueous isoflavones. Indeed, larval fish exposed to steroid estrogens have been shown to exhibit altered predator avoidance behavior [32] which may be linked to upstream neuroendocrine disruption in the central nervous system. Although the exact mechanism of the disruption of predator avoidance performance is not known, the previously demonstrated sensitivity of this assay to estrogen exposure and the inherent ecological relevance of this predator avoidance as an endpoint justify the use of this assay in the present study. In this study the sorption of isoflavones to mineral surfaces and river sediment is assessed, with the role of pH being critically evaluated. Additionally, the potential risk posed by sediment-phase isoflavones to larval fish is investigated.

## 2. Materials and methods

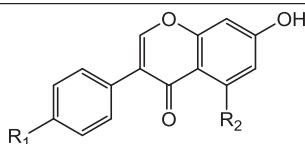
### 2.1. Chemicals

Genistein (96%) and daidzein (95%) were purchased from TCI America. Formononetin (99%) was purchased from Acros Organics. Biochanin A (99.3%) and 3-morpholinopropane-1-sulfonic acid (MOPS, 99.5%) were purchased from Sigma. Sodium chloride (99%), sodium bicarbonate (99.7%), methanol (99.9%) and hydrochloric acid (37%) were purchased from Sigma-Aldrich. Calcium chloride (99%), ammonium acetate (97%), potassium hydroxide (88%), potassium chloride (99.4%), and sodium hydroxide (98.6%) were purchased from Mallinckrodt. Ethanol (91%) was purchased from Fisher. Acetonitrile (100%) was purchased from J.T. Baker.

Goethite was synthesized according to Anschutz and Penn [33]. The goethite has a point of zero net proton charge (pznpc) of 8.47 (pK<sub>a1</sub> = 6.7 and pK<sub>a2</sub> = 10.3) and a surface area of 118.5  $\pm$  2.6 m<sup>2</sup> g<sup>-1</sup> as measured by BET and 248  $\pm$  90 m<sup>2</sup> g<sup>-1</sup> geometrically [34]. Montmorillonite (SWy-2) was obtained from the Source Clay Minerals Society and prepared homoionically using either sodium chloride or calcium chloride, according to Wang and Arnold [36]. Kaolinite was used as purchased from Riedel de Haen. Sediment was collected from the Mississippi River at the East River Flats in Minneapolis, MN on September 26, 2012. The sediment was dried at

**Table 1**  
Structure and pK<sub>a</sub> values of isoflavones and estimates of log  $K_{oc}$  and log  $K_{ow}$ <sup>a</sup>.

Compound	R <sub>1</sub>	R <sub>2</sub>	pK <sub>a</sub>	log $K_{ow}$ <sup>b,c</sup>	log $K_{oc}$ <sup>d</sup>
Genistein	OH	OH	6.7, 9.6, 13.0 <sup>a</sup>	2.84 (3.04)	3.248, 3.485
Daidzein	OH	H	7.4, 9.9 <sup>a</sup>	2.55 (2.51)	2.921, 3.367 (3.29) <sup>e</sup>
Formononetin	OCH <sub>3</sub>	H	7.0 <sup>f</sup>	3.11	3.120, 3.065
Biochanin A	OCH <sub>3</sub>	OH	7.0, 12.3	3.41	3.452, 3.183



<sup>a</sup> From Ref. [15].

<sup>b</sup> Estimated via EPI Suite [21].

<sup>c</sup> Experimental values from Ref. [19] in parentheses.

<sup>d</sup> Estimated via EPI Suite [21]. The first value is from the log  $K_{ow}$  method [27] and the second from the MCI method [28].

<sup>e</sup> Experimental values from Ref. [20] in parentheses.

<sup>f</sup> Estimated to be the same as pK<sub>a1</sub> for biochanin A.

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