



## **Emerging steroid estrogens in rural subsurface environment: distribution, environmental risk and sorption behavior**

Xiaoming Song (1), Yujuan Wen (1), Yuanyuan Wang (1), Yuesuo Yang (1,2)

(1) Key Laboratory of Regional Environment and Eco-restoration, Shenyang University, Ministry of Education, Shenyang 110044, China, (2) College of Environment and Recourses, Jilin University, Changchun 130012, China

Steroid estrogens (SEs) known as emerging contaminants being characterized with low concentration, high toxicity, and polymorphism in environment, posed high risk and uncertainty to eco-environment and human health. Livestock and poultry manure account for about 90% of the natural SEs in environment, which will enter the soil-groundwater subsurface environment through processes of fertilization, irrigation and other pathways, subsequently migrate and transform in groundwater system posing risk to rural distributed potable supplies.

The recent work on the fate/transport, penetration and risk assessment of the SE contamination in subsurface environment was reviewed, including investigation of the distribution of estrone (E1) and  $17\beta$ -estradiol ( $17\beta$ -E2) in a suburban farm around Shenyang City as case studies, penetrating processes of the SEs from surface to vadose zone and groundwater, risk quantification of these emerging organic compounds. Both field and lab based approaches and quantitative modelling were utilized in the studies for various contamination sources, pathways and targets in considering in-situ remediation of the problems. Investigations showed that the horizontal distribution of E1 and  $17\beta$ -E2 were similar in groundwater, the concentration in the west of the site center was relatively low, and the surroundings were relatively high at a site, indicating no significant transverse dispersion at these cases. The concentration of E1 changed less, but  $17\beta$ -E2 was significantly increased in silt and silty sand layers in the vadose zone profiles, demonstrating impact of geology on penetration of SEs into groundwater. Both E1 and  $17\beta$ -E2 concentrations changed abruptly at the interface of geology layers. The ecological risk quotients values of both soil and groundwater indicated a very high ecological risk associated with SEs, but the non-carcinogenic harm quotients did not exceed the acceptable level of non-carcinogenic human health risk. Incorporating the temporal and spatial evolution of physical-chemical-biological environmental parameters at the sites, sorption and biodegradation were suggested the controlling roles in the fate and transport of SEs in the soil-groundwater system. Therefor the sorption behavior of E1 and  $17\beta$ -E2 to the agricultural soil and its sequentially extracted humic substances was further examined. The elemental composition, Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy combined with the sorption-desorption data showed that the sorption of E1 and  $17\beta$ -E2 was controlled by the non-specific interactive hydrophobic partition, and significant correlations between alkyl carbon contents (both surface and bulk) of sorbents with their sorption coefficients ( $n$  and  $\log K_{oc}$ ) suggested that alkyl carbon contents could dominate SEs sorption rather aromatic carbon content. Specific sorption, such as the hydrogen bond and  $\pi$ - $\pi$  bond interaction, was the main reason for nonlinear sorption, whereas the micropore filling and its specific sorption in condensed organic matter might be the major cause of slow sorption and desorption hysteresis. The sorption capacity of two compounds correlated negatively with the surface polar of sorbents, suggesting the O-containing polar functionalities distributed on sorbent surface may reduce the accessibility of high affinity sorption sites.