

# Sorption of antibiotics and natural estrogens onto reservoir sediment

Department of Civil Engineering, Gifu University  
Graduate School of Engineering, Gifu University  
River Basin Research Center, Gifu University  
Department of Civil Engineering, Gifu University

Member of JSCE  
Member of JSCE

○ Roza Amelia  
Reni Desmiarti  
Fusheng Li  
Chihiro Yoshimura

## 1. Introduction

Veterinary antibiotics and natural estrogens, as emerging environmental micro-contaminants, are greatly concerned because of their potential adverse effects on ecosystems and human health. Veterinary antibiotics such as oxytetracycline (OTC) and tetracycline (TC) are primarily used in swine farming for prevention of infections. OTC and TC are released to the environment with animal waste through direct deposition and direct land application. OTC was detected up to the 100 µg/L in stream waters in a small catchment area with many livestock farms (Matsui et al., 2008).

Natural estrogens, such as 17β-estradiol (E2) and estrone (E1), are introduced into natural water sources via animal wastes, biosolids applied to agricultural fields and effluent from sewage treatment plants (STPs). E2 and E1 were found to vary in the range of 10-100 ng/L in effluents of STPs and surface water (Tanaka et al., 2003). However, the information on the fate and behavior of OTC and natural estrogens in relatively close freshwater environmental systems is scarce, where both sorption and degradation may play significant roles. Thus, this study focused on the sorption of natural estrogens (E1 and E2) and antibiotics (OTC and TC) on sediment of natural reservoir.

## 2. Materials and Methods

### 2.1 Sediment and water samples

The sediment and water were collected from the Miharu Dam of Fukushima, Japan on July 2004, at two sampling sites: St. A (located in the downstream) and St. B (located in the midstream). St. B was 100 m upstream of St. A. Sediments were collected using a gravity core sampler with an internal diameter of 4 cm and a length of 50 cm. All collected cores were transported

to the laboratory using a core container supplied consistently with nitrogen to prevent sediments from being oxidized by air.

In the laboratory, the sediment portion (with a thickness of about 30-35 cm for most cores) was sliced vertically from its top into 2 cm thickness layers. Totally, fifteen sediment layers were obtained. For the purpose of this study freeze-dried sediment samples were used. The dried sediments were stored at 5°C, and sterilized in a 105°C-controlled oven for one hour just before experiment. Water samples were transported to the laboratory in cool and were stored immediately in the dark at 5°C till use.

### 2.2 Experiments

Sorption experiments for OTC, TC, E2 and E1 were done in a temperature-controlled room at 20°C by batch equilibrium sorption method. After sterilization in an oven (110°C, 3h), the 2 mL of filtered water (0.2 µm PTFE membrane filter) was added into each 5 mL glass vial following the addition of 0.2 g of dried sediment which was weighed for each compounds. The initial concentrations for each compound were set at 5, 10, 30, 50 and 100 µg/L. Sorption was equilibrated by shaking with a mechanical shaker for 24 h. After equilibration, each vial was centrifuged at 3500 rpm for 10 min; the supernatant was filtered through a 0.45 µm membrane filter. The obtain filtrate was subjected to analysis for OTC, TC, E2 and E1 by an Agilent 1100 series LC/MSD system (HP1100MSD).

## 3. Results and Discussion

### (1) Vertical distribution of surface area

The size distribution of sediment particles was measured using a Hybrid Particle Counter. Using the

**Table 1.** Sediment characteristics and sorption parameters for natural estrogens and antibiotics

Location	Total OC (%, w/w)	Particle Size (µm)			Compound	MW	Freundlich Constant			K <sub>oc</sub> <sup>*</sup> µg/kgC in sediment
		0.5-1	1-2	<2			K <sup>*</sup> (µg/kg-sediment)(L/µg) <sup>1/n</sup>	1/n <sup>*</sup>	R <sup>2</sup>	
St.A	2.19	73.37%	20.09%	6.54%	E1	270.37	6.88±0.53	1.52±0.04	0.95-0.98	314.19±24.24
					E2	272.39	5.71±0.64	1.51±0.04	0.92-0.98	260.80±29.39
					OTC	460.4	1.13±0.12	1.57±0.04	0.93-0.97	51.67±5.69
					TC	444.4	0.50±0.19	1.77±0.15	0.92-0.98	22.72±8.92
St.B	2.16	82.68%	12.10%	5.22%	E1	270.37	5.52±0.68	1.58±0.05	0.92-0.98	255.72±31.43
					E2	272.39	4.26±0.41	1.64±0.04	0.92-0.98	196.99±19.14
					OTC	460.4	0.48±0.12	1.79±0.08	0.87-0.97	22.38±5.47
					TC	444.4	0.21±0.04	1.02±0.07	0.91-0.98	9.56±1.75

\*The measured values for all these parameters are given in the form of mean value± standard deviation from experiments using sediment layers of 0-2, 2-4, 4-8, 8-10, 14-16, and 25-28 cm.

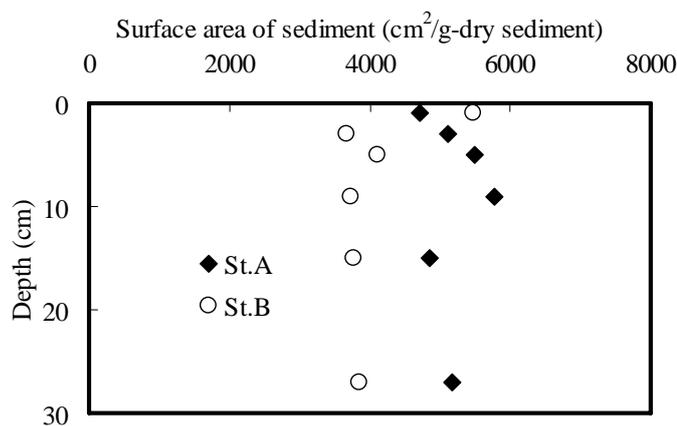


Fig 1. Vertical distribution profiles of sediment surface area

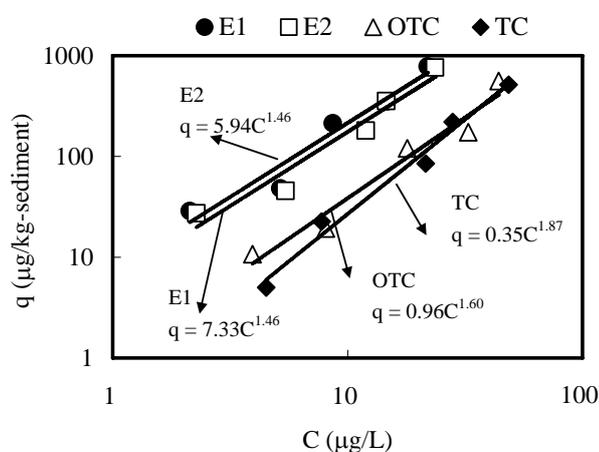


Fig 2. Sorption isotherm of estrogens and antibiotics for the sediment layer (0-2 cm) in St.A.

particle size distribution data, the surface area of each sediment layer could be calculated. The vertical distribution of particle area in sediment from St. A and St. B are given in Fig.1. Particle area in St. A had higher values than in St. B for most layers, hinting the sorption capacity in sediment of St. A might be higher than in St. B.

## (2) Sorption behavior of OTC, TC, E2 and E1

The sorption isotherms of the four compounds onto the surface layer sediment (0-2 cm) are given in Fig.2. The relation between the liquid and the solid phase concentrations was linear when plotted in logarithmic scales and was thus described using the following Freundlich equation.

$$q = K C^{1/n} \quad (1)$$

Where  $q$  is the concentration of a chemical adsorbed by the soil ( $\mu\text{g}/\text{kg}$ );  $C$  is the liquid phase concentration ( $\mu\text{g}/\text{L}$ );  $K$  is the Freundlich constant ( $(\mu\text{g}/\text{kg-sediment})(\text{L}/\mu\text{g})^{1/n}$ ); and  $1/n$  is Freundlich exponent. Many studies have shown that the sorption capacity of compounds depends on the carbon content of soils. Therefore,  $K$  values were further calibrated by the

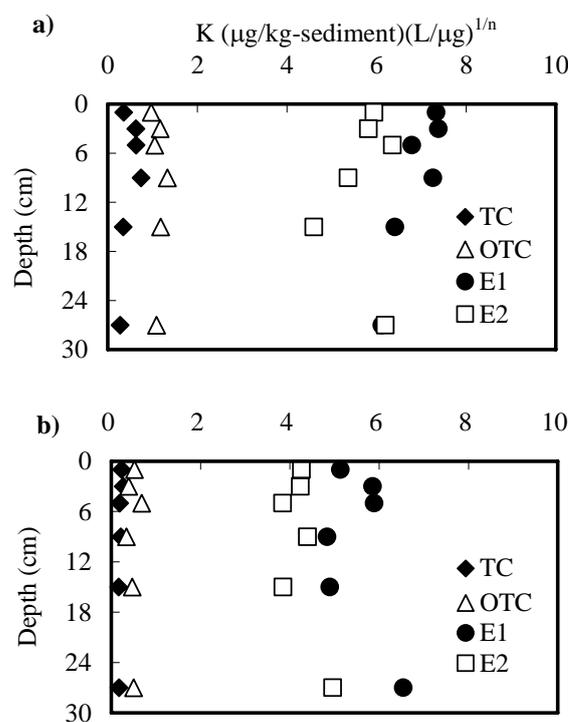


Fig 3. Vertical distribution profiles of sorption parameter  $K$  for sediment at (a) St. A (b) St. B

organic carbon content of sediments, and the calibrated  $K$  values ( $K_{oc}$ ) is also displayed in Table 1. The sorption capacity depended on the physicochemical properties of the compounds and the sediment (Table 1). Less polar compounds tend to have higher adsorption on sediments. The determine parameters for  $K$  and  $1/n$  are displayed in Table 1.

From this table, E1 had the highest  $K$  and  $K_{oc}$  values, while TC had the lowest  $K$  and  $K_{oc}$  values in both sites (St. A and St. B). In each layer of sediment, E1 had the highest sorption capacity, and TC had the lowest sorption capacity (Fig.3).

## 4. Conclusion

The sorption capacity of OTC, TC, E2 and E1 was measured. The Freundlich constant ( $K$ ) followed the order of  $E1 > E2 > OTC > TC$ . A general trend of enhanced sorption capacity with sediment surface area was not confirmed. For further laboratory studies, the effect of pH and comparison in other soils of different origin will be performed.

## References

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