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Marine Pollution Bulletin - Revised version of a Shorter Research Note

Water-sediment partitioning of flumequine and florfenicol, two antibiotics used in salmon aquaculture in Chile

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Abstract

The water-sediment partitioning of flumequine and florfenicol, two antibiotics used in salmon aquaculture is a critical driver of their fate and environmental impact. Batch experiments, were carried out using pure water or seawater, with or without sediment, and at summer and winter temperatures of Chilean fjords. Log K_d (partition between water and sediment) of florfenicol in seawater varied from 0.62 ± 0.69 to 0.67 ± 0.13 , and Log K_{OC} (partition between water and organic fraction of sediment) from 2.15 ± 0.29 to 2.19 ± 0.13 . Difference between K_{OC} and the octanol-water partition constant (K_{OW}) showed that for florfenicol, adsorption onto the surface of particles was more significant than the absorption driven by hydrophobicity whilst hydrophobic absorption was a major driver of flumequine sorption. Flumequine

Log K_d (0.92 ± 0.25 to 1.36 ± 0.10) and Log K_{OC} (from 2.44 ± 0.25 to 2.89 ± 0.10) demonstrated its greater affinity than florfenicol to particles and potential accumulation into marine sediments.

Keywords:

Emerging pollutant, sorption, florfenicol, flumequine, K_d and K_{OC} .

Introduction

Chile is the second most important salmon producer in the world (Food and Agriculture Organization, 2018). As such, it is a major consumer of antibiotics per biomass of salmon produced (antibiotic consumption index of 0.05%, or weight antibiotics/harvested salmon, Miranda *et al.*, 2018). Our understanding of the impact of these emerging pollutants used by aquaculture in coastal waters is limited to a few studies addressing their presence (Buschmann *et al.*, 2012; Jara *et al.*, 2021) and the development of bacterial resistance genes (Miranda and Zemelman, 2002; Miranda and Rojas 2007; Cabello *et al.*, 2016). Florfenicol and flumequine are amongst the antibiotics mostly used in salmon farming in Chile. They are administered to salmon through incorporation into food pellets and approximately 5% of unconsumed pellets can be deposited into sediments (Cabello *et al.* 2013; Miranda *et al.* 2018).

The impact of antibiotics depends on the way they reach the environment, and their on subsequent partition between the dissolved phase (truly dissolved, complexed, absorbed to dissolved organic carbon) and particles (suspended, sinking and sedimentary). Surface processes (adsorption) such as ion exchange, cation and hydrogen binding all govern reverse exchanges between water and particles for those antibiotics with ionic charges, whilst diffusive exchanges such as absorption to the organic phase drive the sorption of neutral antibiotics (Cao *et al.* 2015). The dissolved-particle partition constant (K_d) and the octanol-water partition constant (K_{OW}) provide information on the tendency of chemicals to be affected by the aforementioned processes, but these constants are not presently available for all antibiotics. For instance, K_d values for flumequine and florfenicol are only available for terrestrial soils and not for marine sediments. For florfenicol, log K_{OW} values reported in the literature vary between -0.17 and 1.63.

This lack of fundamental information difficult predicting the fate of these antibiotics in marine ecosystems housing salmon aquaculture .

In soils, the dependence of the sorbed fraction of antibiotics to their water concentration is described either by linear relationships (K_d , $C_s = K_f C_w$) or by Freundlich isotherms (K_f , $C_s = K_f C_w^{1/n}$). In the concentration range up to 10 mg/ L, the Freundlich isotherm fitted the sorption of norfloxacin to marine sediments, whilst sorption was also well described by the linear relationship with R^2 values of between 0.94 and 0.98 (Cao *et al.*, 2015). Our aim is to describe realistic marine antibiotic behavior, in the mg/L range. In this range, the sorption of florfenicol and flumequine is linear, and described by K_d (Cao *et al.*, 2015).

In the present study, batch experiments mimicking sorption-desorption between water and sediments were carried out at the ppm level, over a range of conditions (temperature and salinity) typical of Chilean fjords. In Puyuhuapi, the lowest monthly average temperature was 8°C in August 2013 and summer temperatures were up to 18°C in January 2013 and up to 15°C in December 2013 (e.g. Schneider *et al.*, 2014, Pinilla et al., 2020). Experimental temperatures were at 8 and 15°C. Salinity in Puyuhuapi varies seasonally as a result of admixture of river water and fjord water (Schneider *et al.*, 2014). Lowest and highest salinity values between 2013 and 2015 were 4 and 28 PSU (Pinilla et al., 2020). For the experiment, a first salinity condition was selected to minimize antibiotic complexation (pure water, salinity of 0 PSU), and coastal seawater of salinity 31 was used to reconstruct seawater conditions. Pure water does not represent *in situ* conditions, but rather a control condition to help deciphering complexation from sorption processes. The objectives were to provide experimental data on partition constants of florfenicol and flumequine between water and sediment particles (K_d), and between water and the organic matter associated with particles (K_{OC}).

Material and Methods

1.1 Seawater and sediment sampling

Seawater was collected from the surface, and marine sediment was collected at ca 90m depth on the 8th October, 2018 at the Oceanographic Time Series Station 18 (36° 29.94' S, 73 °07.8' W) of the COPAS Center (ANID Chile).

1.2 Water and sediment sterilization

Sterile and dark conditions were set to avoid biodegradation and photodegradation. All glassware was cleaned by calcination to 450°C for 4 h and exposed to UV radiation for 30 minutes before use. Natural seawater was filtered through a PVDF membrane filter of 0.22 µm pore size and autoclaved. Natural marine sediments were autoclaved and exposed to UV radiation for 30 minutes before use. Ultrapure water was obtained from a Milli-Q device (18Ω).

1.3 Sediment-water batch experiments

Experiments were carried out in the Laboratory of Marine Organic Geochemistry at the University of Concepción, under constant orbital agitation (200 rpm) on a Thermo Scientific Chamber MaxQ 6000 set at 8°C or 15°C. . Experiments started on the 23rd of October, 2018. Forty mL of seawater (salinity =31 PSU) or of ultrapure water (milliQ water, salinity =0 PSU) were added to glass tubes of 80 mL. In half of the tubes, 3 g of wet marine sediments were added in half of the vials to prepare the water + sediment treatments. Each treatment was set in triplicate. Control treatments consisted of vials containing pure water or seawater, with or without sediment, but without antibiotic addition. A mixture of flumequine (Sigma-Aldrich CAS 42835-25-6) and florfenicol (Sigma-Aldrich CAS 73231-34-2) was prepared as a primary stock solution of 40 mg L⁻¹ of each antibiotic.. The target experimental concentration was around 1 mg L⁻¹. Previous tests showed that part of the antibiotics was lost by sorption on vial walls. Therefore, for the first experiment, carried out at 8°C, florfenicol and flumequine were added to non control batch at an initial concentration of 1.4 mg L⁻¹. For the second series of batch experiments, carried out at 15°C, the initial concentration was selected at a slightly lower value of 1.2 mg L⁻¹ of florfenicol and flumequine in order to adjust the equilibrium concentration closer to 1 mg L⁻¹. This value ensured good analytical detection and representativity of *in situ* concentrations. Initial concentration differences between both experiment series have no effect on the partition coefficients, because they are relative values of concentrations. Flasks were gently mixed, maintained for 30 min in dark conditions, and 1 mL of water was sampled for the initial time. Further sampling times were defined according to other batch experiment studies (Guaita *et al.*, 2011; Cao *et al.*, 2015) and our own preliminary tests at 1, 2, 3, 4, 24, and 48h.

1.4 Analysis of antibiotics

Each water sample was diluted 10 times into an acetonitrile: water mixture (50:50, v/v), and a subsample of 1 mL was directly injected in the UHPLC-MS.

Antibiotics were detected using a Shimadzu (Kyoto, Japan) Nexera X2 LC-30 AD UHPLC system coupled to a single quadrupole mass spectrometer LCMS-2020 with an electrospray ionization (ESI) interface. The mobile phase A was Milli-Q + Formic acid 0.1%, and B was Acetonitrile + Formic Acid 0.1%. The analysis started using 10% B for 1 min, increasing to 70% in 3 min, this percentage was maintained for 10 min, and finally decreased to 10% B in 5 min. on the analytical column was a Kinetex EVO C18 core-shell column (Phenomenex, Torrance, CA, USA) (150 mm x 2.1 mm, 2.6 μm) connected to a Kinetex C18 guard column. The columns were maintained at 40° C. Ionization ESI in positive and negative mode was used simultaneously to measure florfenicol (negative) and flumequine (positive). Mass spectrometry analysis was implemented in selected ion monitoring acquisition mode, at m/z 262 $[\text{M}+\text{H}]^+$ to target the molecular ion of flumequine and at 356 $[\text{M}-\text{H}]^-$ to monitor the molecular ion of florfenicol. Reproducibility was 3 to 5 % (coefficient of variation), routinely determined from three to five replicate analyses (Jara *et al.*, 2021). Detection and quantification limits were calculated using signal-to-noise ratios (S/N) of 3 and 10, respectively. Detection limits for florfenicol was 2 ng L^{-1} and 12 ng L^{-1} for flumequine. Limits of quantification for florfenicol was 6 ng L^{-1} and 36 ng L^{-1} for flumequine.

1.5 Statistical analyses

Tests of both homogeneity of variances (Levene test) and normality of variables (Shapiro–Wilk test) were not fulfilled. We therefore tested for significant differences between categorical factors (matrix, antibiotic type, and temperature) using the nonparametric Kruskal–Wallis test (95% significance), and for differences between experimental treatments (Seawater, pure water, seawater + sediment, and pure water + sediment) using the paired sample Wilcoxon test (95% significance).

1.6 Calculation of K_d and K_{OC}

When the difference between treatment with and without sediment was proven to be significant using the Wilcoxon test, concentrations of sorbed antibiotics were calculated as the difference between the concentration of a dissolved antibiotic in a given condition without

sediment and the same condition with sediment. The difference was calculated for each replicate at each of the equilibrated times (4, 24, and 48 h). For instance, for the condition seawater (SW), 8°C (W for winter), at 4H and the first replicate (R1), the sorbed concentration of flumequine (FLU) was calculated as:

$$[\text{FLU}_{\text{in sed SW W}}]_{4\text{H}, \text{R1}} = ([\text{FLU}_{\text{SW W}}]_{4\text{H}, \text{R1}} - [\text{FLU}_{\text{SW W+SED}}]_{4\text{H}, \text{R1}}) / \text{SedW}$$

where,

$[\text{FLU}_{\text{SW W}}]_{4\text{H}, \text{R1}}$ is the dissolved antibiotic concentration in the first replicate of the treatment without sediment sampled at 4H, expressed in $\mu\text{g L}^{-1}$;

$[\text{FLU}_{\text{SW W+SED}}]_{4\text{H}, \text{R1}}$ is the dissolved antibiotic concentration in the first replicate of the same treatment with sediment, sampled at 4H, expressed in $\mu\text{g L}^{-1}$;

SedW is the dry weight of sediment used in the treatment, expressed in kg L^{-1} ;

$[\text{FLU}_{\text{in sed SW W}}]_{4\text{H}, \text{R1}}$ is the calculated content of flumequine sorbed to the sediment, expressed in $\mu\text{g kg}^{-1}$, for the condition SW W, at 4H, for the first replicate.

The dissolved-particle partition constant K_d was calculated as the ratio of sorbed antibiotic concentration to the dissolved antibiotic concentration, for a given condition and a given replicate:

$$K_{d, \text{FLU } 4\text{H}, \text{R1}} = [\text{FLU}_{\text{in sed SW W}}]_{4\text{H}, \text{R1}} / [\text{FLU}_{\text{SW W}}]_{4\text{H}, \text{R1}}$$

where, $K_{d, \text{FLU } 4\text{H}, \text{R1}}$ is expressed in L (of seawater)/ kg (of dry sediment)

The organic carbon partition constant K_{OC} represents the ratio of sorbed antibiotic concentration in the organic phase, divided by the dissolved antibiotic concentration, for a given treatment and a given replicate:

$$K_{OC, \text{FLU } 4\text{H}, \text{R1}} = ([\text{FLU}_{\text{in sed SW W}}]_{4\text{H}, \text{R1}} / [\text{FLU}_{\text{SW W}}]_{4\text{H}, \text{R1}}) / \text{OC} = K_{d, \text{FLU } 4\text{H}, \text{R1}} / \text{OC}$$

where, OC is the concentration of organic carbon in the dry sediment, expressed in kg/kg and $K_{OC, \text{FLU } 4\text{H}, \text{R1}}$ is expressed in L (of seawater)/ kg (of organic carbon). At station 18, $\text{OC} = 0.03 \text{ kg kg}^{-1} = 3\%$.

Results

Florfenicol and flumequine were not detected in the control treatments. All experiments with antibiotic amendment were characterized by a steep decrease of dissolved antibiotic concentration during the initial 3 hours of the experiment (Figure 1), followed by little variation between 4 and 48 hours. However, the concentration of florfenicol increased at the final sampling

time under all conditions. We assumed that partition equilibrium was reached at 4h, and therefore replicates at 4h, 24h, and 48h were used to calculate partition coefficients. The Kruskal Wallis statistical tests performed on these equilibrium concentrations showed that temperature, salinity, and antibiotic type contributed to the observed variances, producing significant differences between the concentration in each condition, for each factor (Kruskal Wallis; $p < 0.05$).

Florfenicol concentrations were statistically similar in pure water + sed and in pure water alone (Figure 1) thus partition constants were not calculated for pure water conditions. In contrast, florfenicol showed significant sorption to the sediments in seawater. In addition, whether sediment was present or not, florfenicol concentration was significantly lower in seawater than in pure water (20 to 40% lower at 8°C and 4 to 15% lower at 15°C Figure 2, Table 1).

For all experimental conditions, flumequine concentrations were significantly lower in presence of sediment (Table 1). Flumequine showed greater decreases in concentration than florfenicol, suggesting a higher sorption tendency. After stable conditions were reached, $49 \pm 10\%$ of flumequine was sorbed to sediments in pure water, and $19 \pm 6\%$ in saline water, whilst the percentage of adsorbed florfenicol in saline water was less than $10 \pm 2\%$ (Figure 1).

The influence of temperature on sorption was complex, with non-significant effects on dissolved florfenicol and flumequine in pure water without sediment. In contrast, flumequine concentrations decreased significantly at 15°C compared to 8°C in seawater conditions (Table 1). For florfenicol, the initial drop in concentration appeared to be more pronounced at 8°C and similar both with and without sediment. These observations are suggestive of enhanced adsorption onto vial walls at 8°C compared to 15°C. The proportion of flumequine sorbed to sediments was lower in summer temperature conditions, and in seawater compared to pure water (Table 1).

The sorption coefficient K_d describes the reversible tendency of compounds to adsorb onto particles. In seawater, $\text{Log } K_d$ for florfenicol varied between 0.62 ± 0.69 and 0.67 ± 0.13 (Table 2), while previous K_d from freshwater environments are reported as 2.9 in seawater (Na *et al.*, 2013). K_{OC} is the organic carbon-normalized sorption coefficient and indicates the tendency of the compounds to sorb on the organic fraction of the particles. The range of $\text{Log } K_{OC}$ measured for florfenicol in this study was 2.15 ± 0.29 to 2.19 ± 0.13 .

Log K_d calculated for flumequine varied between 0.92 ± 0.25 and 1.36 ± 0.10 with lower values observed in seawater (Table 2), while K_d values of flumequine were only available for the humic fraction of soils in the literature, and correspond to log K_d 3.4 to 4.0 (Tolls, 2001). Log K_{OC} values of flumequine calculated for pure water and seawater ranged between 2.44 ± 0.25 and 2.89 ± 0.10 , while log K_{OC} values representing flumequine sorption to humic acids in soils were higher, from 3.4 to 4.4 (Tolls 2001).

Discussion

The half-life of florfenicol and flumequine is one week and ~ 150 days, respectively (Hektoen *et al.*, 1995; Halling- Sorenson *et al.*, 1998), suggesting that the initial decreases in concentration observed in the present experiments were not related to degradation. The initial concentration decreases cannot be attributed to complexation because they occur in all conditions, even in pure water devoid of ions, and likely reflect adsorption of part of the antibiotics to the walls of experimental vessels. Equilibrium times in our experiments (ca 4 h) are in good agreement with previous observations (>2 h, Guaita *et al.*, 2011; within 6 h, Cao *et al.*, 2015). The partition constants K_d and K_{OC} point to a sorption capacity of flumequine that is twice that of florfenicol, thus implying greater storage potential of flumequine in sediments in the vicinity of salmon farms. Sorption could be related to cation availability and complexation, pH, dissolved organic matter (MacKay and Seremet, 2008; Guaita *et al.*, 2011; Jia *et al.*, 2013; Na *et al.*, 2013). Various studies addressing the sorption of veterinary antibiotics to soils have shown that surface processes (ad-sorption) play a more important role than organic carbon absorption driven by hydrophobicity (Tolls 2001). However, some data from the marine environment contrast with this conclusion. In the Bohai and Yellow Seas for example, the formation of cation bridges between oxolinic acid and calcium and magnesium explained the adsorption of oxolinic acid to intertidal sediments, but failed to explain the adsorption of other quinolones (Lang *et al.*, 2018) which were neither explained by sediment types, pH, nor organic carbon content (Lang *et al.*, 2018). When sorption of a compound is driven by hydrophobic diffusive exchange (*id es* absorption), environmental Log K_{OC} approaches the theoretical partition constant Log K_{ow} . Florfenicol Log K_{OC} calculated from the present study was 2 to 3 units higher than other published values for Log K_{OC} (0.37 in Endris, 2004; 2013). Either hydrophobic absorption contributes to only a low percentage of the florfenicol association with particles, while the major

florfenicol-particle interaction is due to surface-driven processes, or published values of Log K_{ow} of florfenicol are underestimated.

Log K_{OC} of flumequine estimated in our batch experiments are also higher than published values, although by only more or less one unit on the Log scale. Our data contribute to a better definition of partition constants of antibiotics in the marine environment, but further research is required to better clarify these estimates and to understand the processes underlying their variability.

Comparing the partition in pure water with that in seawater provides evidence for the formation of complexes with marine ions for florfenicol (significant Wilcoxon tests), whilst this was not observed for flumequine (non-significant Wilcoxon tests). The pK_a for florfenicol's is 6.3, and its basic ionized form dominates both in pure water (pH=7.2) and in seawater (pH=8.2, pH=8.7 in sediment slurries). The decrease in concentration of this basic, negatively charged form of florfenicol in seawater is likely due to the formation of complexes with marine cations. Variable difference between pure and seawater concentration suggests that $16 \pm 8\%$ and $10 \pm 8\%$ of the florfenicol was complexed in winter and summer, respectively. Sulfamethazine also forms complexes which increase its affinity to particles (Wegst-Uhrich *et al.*, 2014). Similarly, in the present batch experiments, florfenicol in seawater appears to bind to particles and form complexes. The pK_a of flumequine is 9.3, and its acid neutral form dominates under all experimental conditions. The non-significant difference between flumequine concentrations in pure- and sea-water conditions argues against the complexation of flumequine. However, the complexation of flumequine with Cu (II) has been reported during experiments in soils (Guaita *et al.*, 2011). Marine sediments may leach cations that are not present in seawater such as Cu^{2+} , and the potential complexation of flumequine cannot be ruled out in the presence of sediment. Further research is also needed to explain why flumequine sorption to sediment is lower in seawater ($19 \pm 6\%$) than in pure water ($49 \pm 10\%$) (Figure 2).

The role of temperature on antibiotic behavior was explored for the first time to our knowledge. Dissolved concentrations of florfenicol were significantly different at 8°C and 15°C in all treatments (Table 1). Flumequine dissolved concentrations showed no significant differences at both temperatures in pure water treatments, but were significantly different in marine conditions, either with or without sediments (Table 1). Moreover, the proportion of sorbed flumequine increased from $19 \pm 6\%$ under summer temperatures to $30 \pm 6\%$ under temperature conditions typical of Chilean fjords in winter. The underlying processes driving these novel findings are

presently unknown, but there are clear seasonal implications for the retention of flumequine in the vicinity of aquaculture activities.

Conclusions

Analytical difficulties limit our understanding of the environmental impact of emerging pollutants, and specifically those antibiotics used by salmon farming in Chilean fjords (Jara *et al.*, 2021). Although further *in situ* studies are clearly needed, batch experiments offer an alternative to empirically describing the sorption behavior of antibiotics in the coastal environments. The present study has shown that flumequine has a higher sorption tendency than florfenicol, and the fate of flumequine will therefore be more associated with processes such as particle transport and deposition onto the seafloor. In contrast, florfenicol shows a lower tendency to bind to particles, and the fate of this antibiotic will be to a greater extent related to hydrodynamic processes such as dispersion and water mass transport by currents. The discrepancy between K_{OC} and K_{OW} indicates that reversible absorption to organic carbon is not the dominant process driving sorption of florfenicol to sediment particles in seawater. However, other surface-driven processes (ion exchange, cation and hydrogen binding, and complex formation) are likely to drive partition processes (Tolls 2001). The present study therefore provides experimental partition constants for flumequine showing that diffusive absorption to organic carbon is an important driver of the association of this compound with sediments.

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Table 1. Wilcoxon test results comparing concentrations of florfenicol (FLO) and flumequine (FLU) in batch experiments. Experimental conditions are PW: in pure water; SW: in seawater; PW+SED: in pure water + sediments and SW+SED: in seawater + sediments. The number on the first cell row represents the Z value from Wilcoxon test, and the number on the second row is the critical value (p level). Where $p < 0.05$, the concentrations are significantly different and are highlighted in bold, and marked by *.

Table 2. Dissolved-particle partition constant (K_d) and organic carbon partition constant (K_{OC}) of florfenicol and flumequine, determined empirically using batch experiments. Units of constants are $L\ Kg^{-1}$.

Figure captions

Figure 1. Florfenicol and flumequine dissolved concentrations (average \pm SD) in batch experiments with (orange square) and without (blue diamond) added marine sediments: A) and E) pure water at 8°C; B) and F) pure water at 15°C; C) and G) Seawater at 8°C and D) and H) Seawater at 15°C.

Figure 2. Box plot showing the means, standard errors, and standard deviations for dissolved concentration of flumequine and florfenicol in each treatment. A) 8°C (winter conditions) and B) 15°C (summer). FLU: Flumequine, FLO: Florfenicol, PW: pure water (pure water), SW: Seawater, and SED: with wet sediment added to the tube.

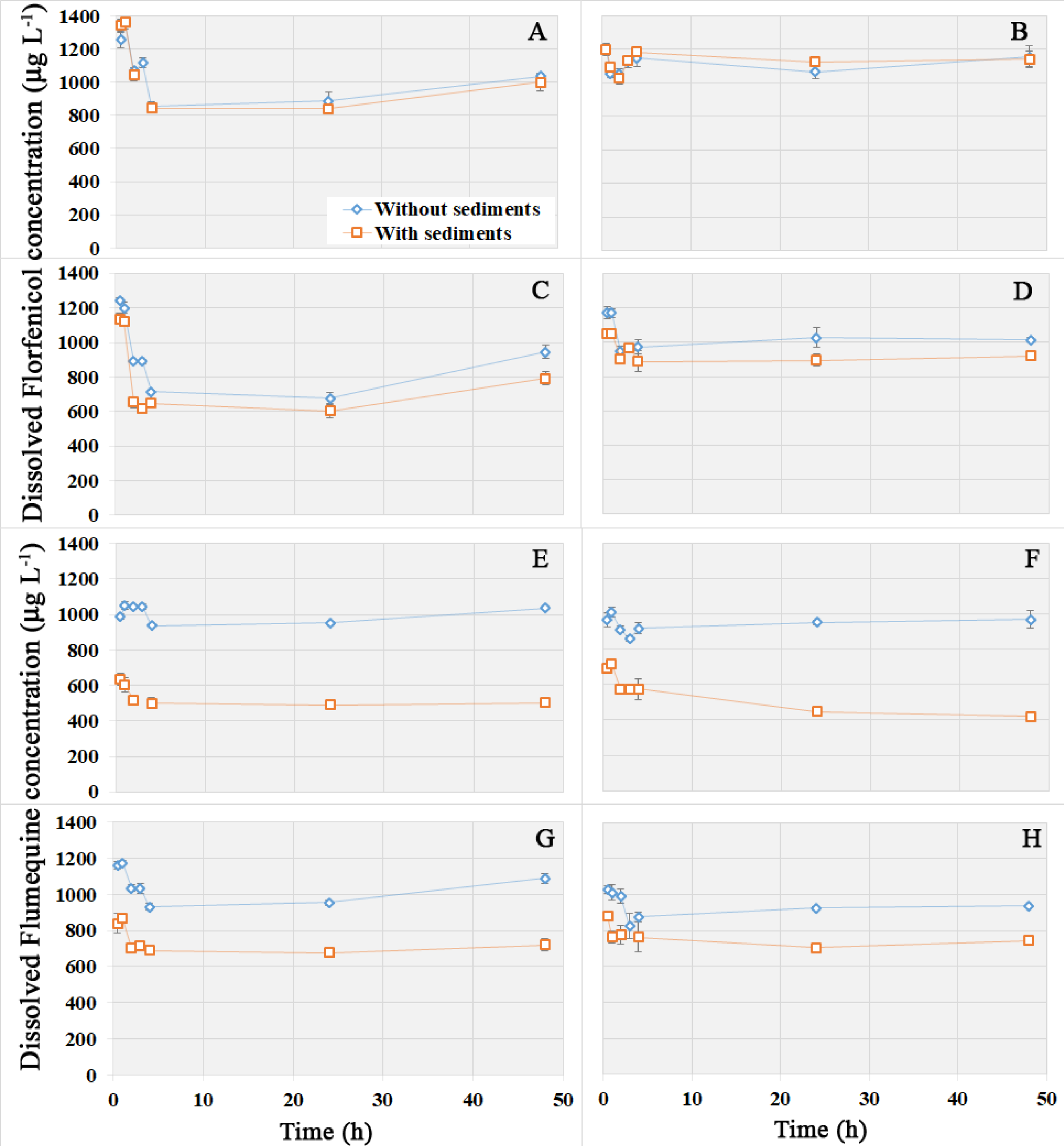


Table 2.

	Temperature	Florfenicol		Flumequine	
		8° C	15° C	8° C	15° C
Log K _a	Pure Water	-	-	1.30 ± 0.03	1.36 ± 0.10
	Seawater	0.62 ± 0.29	0.67 ± 0.13	1.07 ± 0.06	0.92 ± 0.25
Log K _{oc}	Pure Water	-	-	2.82 ± 0.03	2.89 ± 0.10
	Seawater	2.15 ± 0.29	2.19 ± 0.13	2.60 ± 0.06	2.44 ± 0.025