

Partitioning kinetics of polar organic contaminants to Oasis HLB® as a function of pH and ionic strength for optimisation of passive sampling and solid phase extraction approaches

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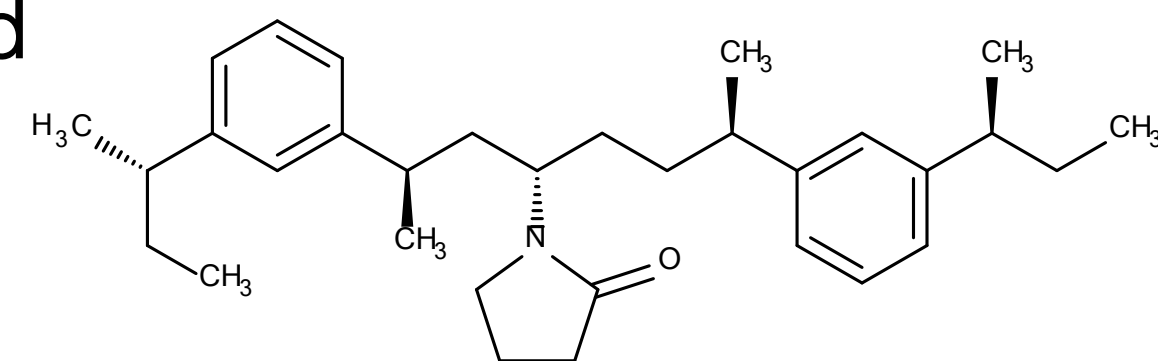
Introduction

▪ **Aim: To characterise the partitioning of polar organic contaminants to the adsorbent material Oasis HLB® as a function of pH and ionic strength**

▪ The application of polymers plays a critical role in the analysis of organic contaminants

▪ The relative affinity of the chemical to the polymer in the sorbent-liquid system is key parameter for both SPE and passive sampling

▪ Oasis HLB® is one of the most commonly used sorbents for solid phase extraction (SPE) and polar organic chemical integrative sampler (POCIS)



▪ Target compounds include 21 compounds classed as priority substances in the EU water framework directive

37 biocides

6 pharmaceuticals

4 industrial chemicals

▪ Therefore, the equilibrium sorption behaviour of a range of organic contaminants to Oasis HLB® in aqueous systems at environmentally relevant concentrations was investigated

Experimental design

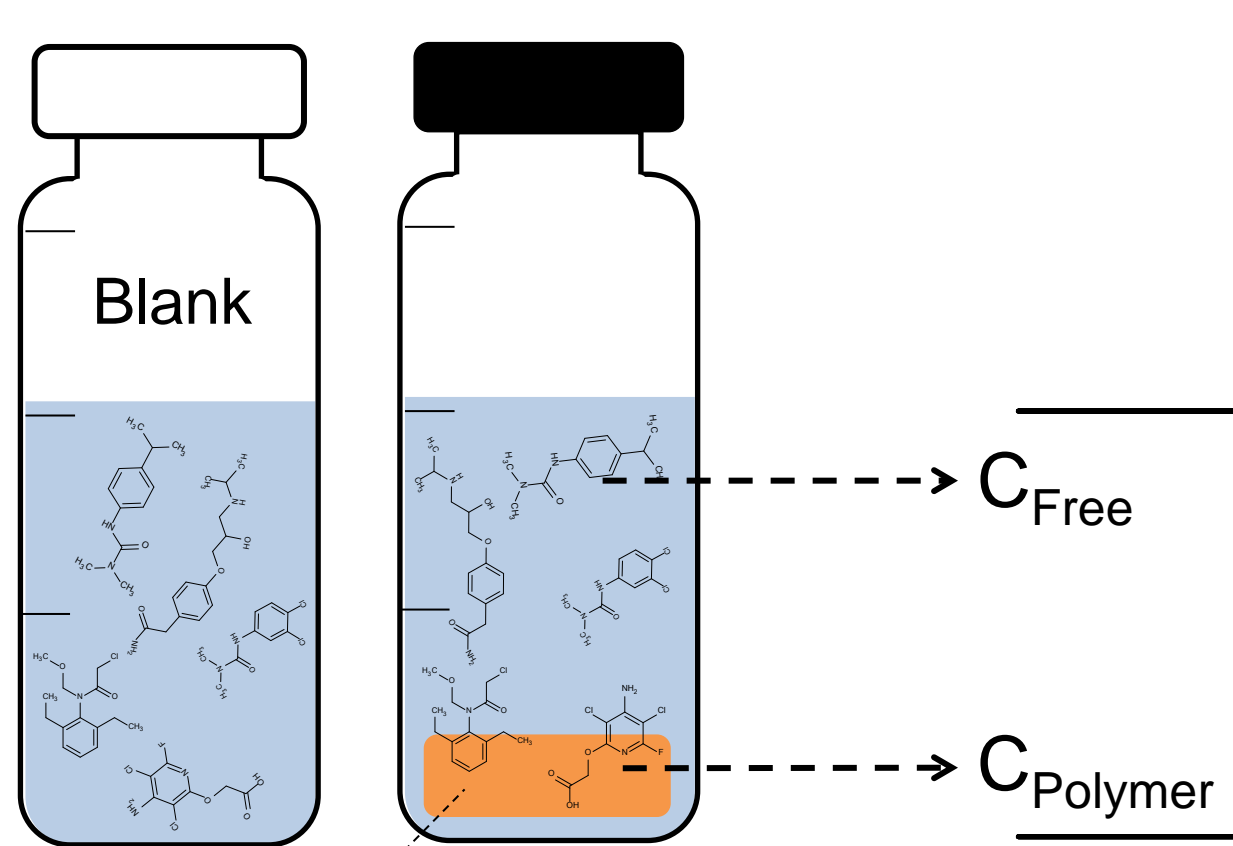
▪ Partitioning to Oasis HLB® was measured in batch experiments in HPLC vials

▪ Forty seven polar organic compounds were spiked at a nominal concentration of 100 µg/L (solvent 1 % v/v)

✓ **pH setup:** acetic acid and ammonium acetate were used to make buffers with pHs from 5 to 8. NaCl was added to ensure that these all had the same ionic strength

✓ **Ionic strength setup:** NaCl was used for all experiments at concentrations (salinity) of 0 (Milli-Q water), 5, 15, 25, 35 ‰

✓ After equilibrium was reached, the total and dissolved concentrations were measured directly in the aqueous phase (See Figure 1)



Oasis HLB® settled to the bottom of the vial

Figure 1. A simple schematic of the batch experiment

$$K_D = \frac{C_{\text{Polymer}}}{C_{\text{Free}}} = \frac{C_{\text{Total}} - C_{\text{Free}}}{C_{\text{Free}}}$$

- K_D : Partitioning ratio to Oasis HLB®
- C_{Free} : Target compound measured directly by external quantification
- C_{Total} : Quantification relative to labelled standard

▪ Analysis was carried out by HPLC coupled to a triple quadrupole mass spectrometer equipped with an electrospray ionisation source (ESI)



Conclusions

▪ Partitioning ratios of polar organic contaminants to Oasis HLB® were determined as a function of pH and ionic strength providing their relative affinities to this polymer.

▪ These are being interpreted as a function of the compound and system properties to try and drive predictive relationships

▪ This information is useful to optimise SPE and passive sampling approaches

Results

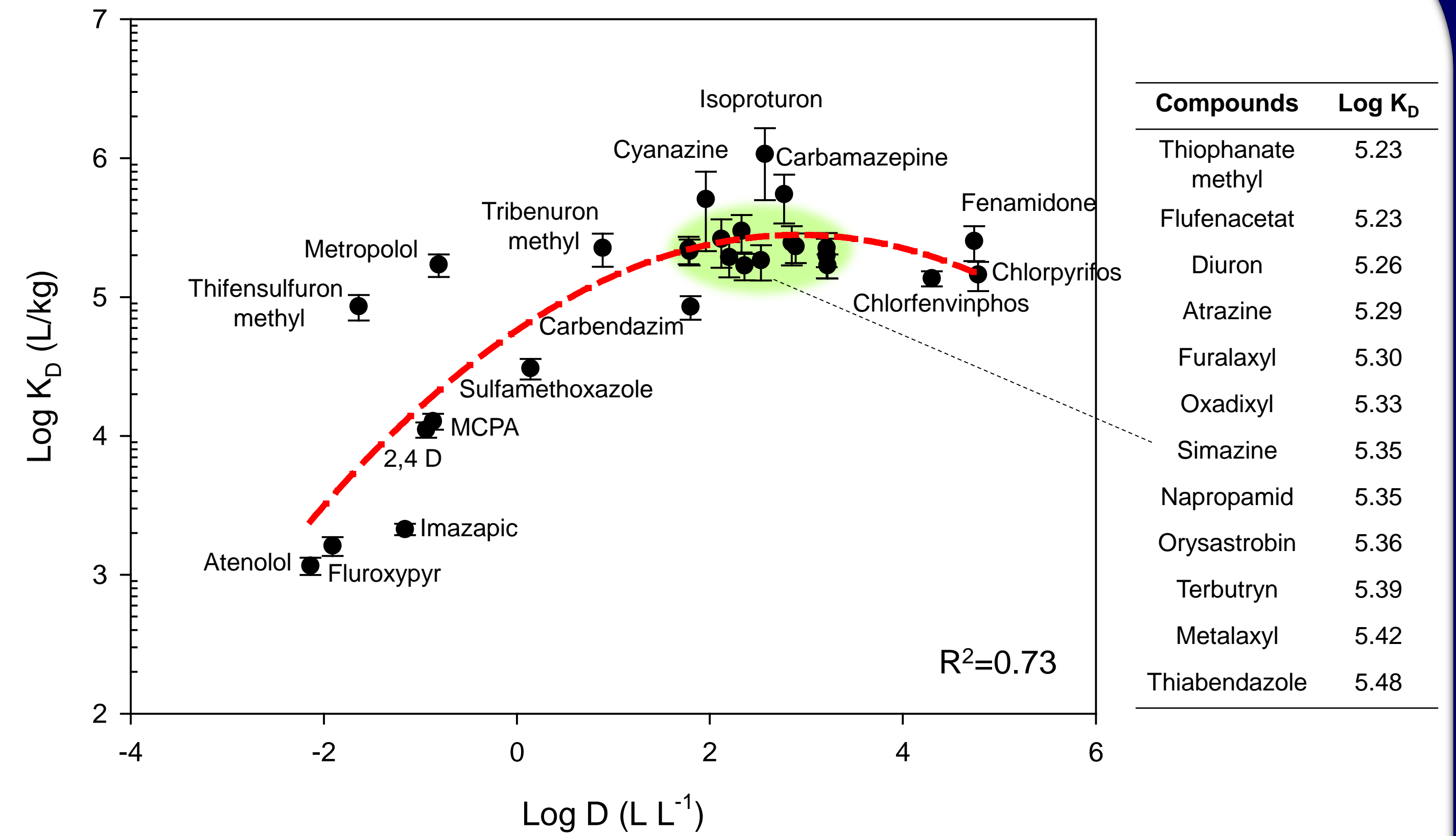


Figure 2. Partitioning ratios ($\text{Log } K_D, \text{L kg}^{-1}$) of the target compounds at pH 7 and 20°C plotted against the octanol-water distribution coefficients ($\text{log } D, \text{L L}^{-1}$) values taken from Marvin sketch 6.2.2 (<http://www.chemaxon.com>)

- $\text{Log } K_D$ values in pH 7 buffer at 20°C ranged over 3 orders of magnitude, from 3.04 L kg^{-1} (atenolol) to 6.03 L kg^{-1} (isoproturon)
- Many compounds with higher log D values exhibited similar log K_D values of between 5 and 6
- A quadratic trend was observed between log K_D and log D, a proxy of pH dependent lipophilicity of chemical

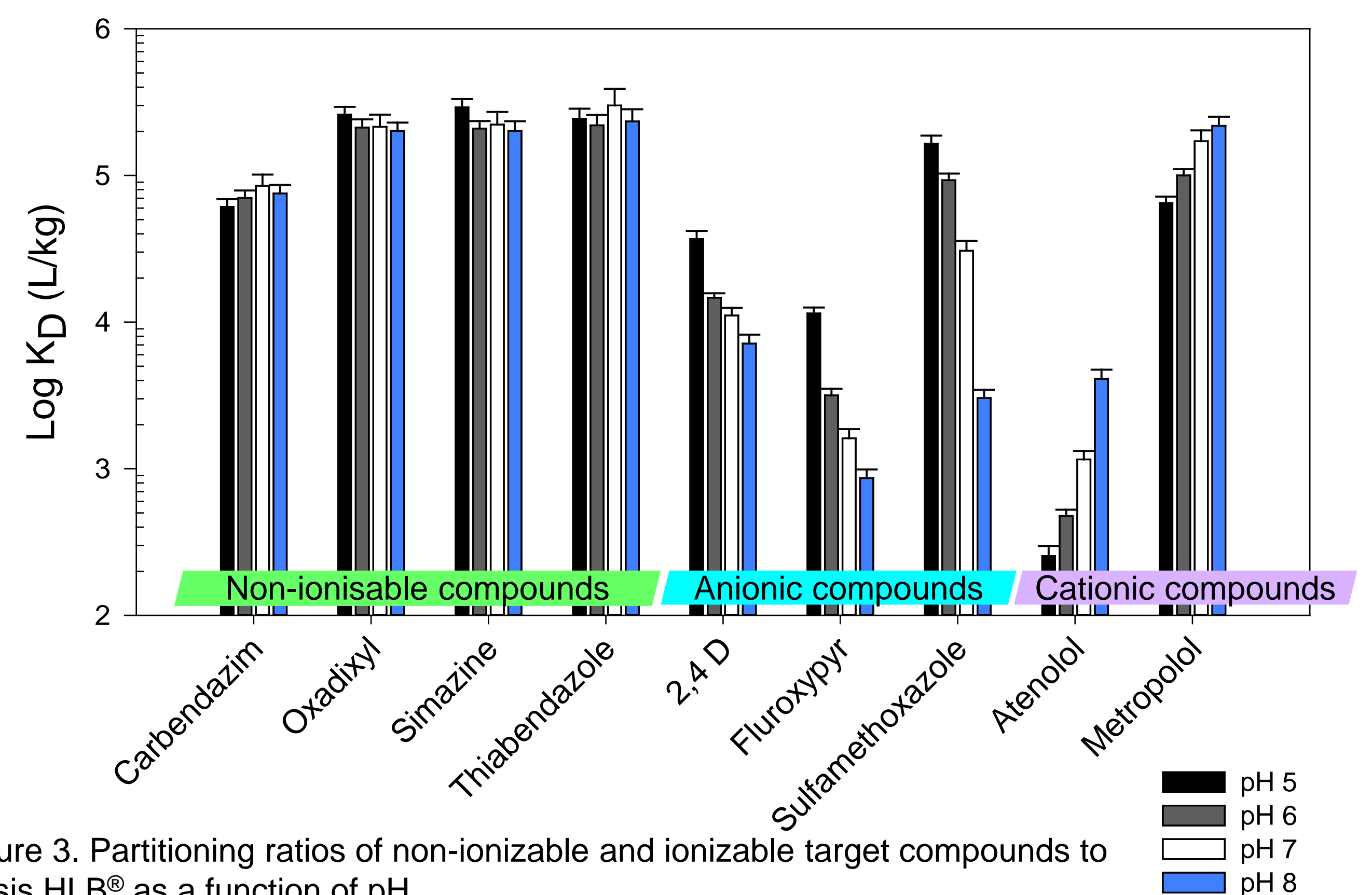


Figure 3. Partitioning ratios of non-ionizable and ionizable target compounds to Oasis HLB® as a function of pH

- Non-ionizable compounds did not display any trends with pH
- Anionic compounds showed a decrease in partitioning ratios with increasing pH with the exception of thiophanate methyl and tribenuron methyl
- The cationic compounds, atenolol and metoprolol, showed an increase in their partitioning ratios with increasing pH

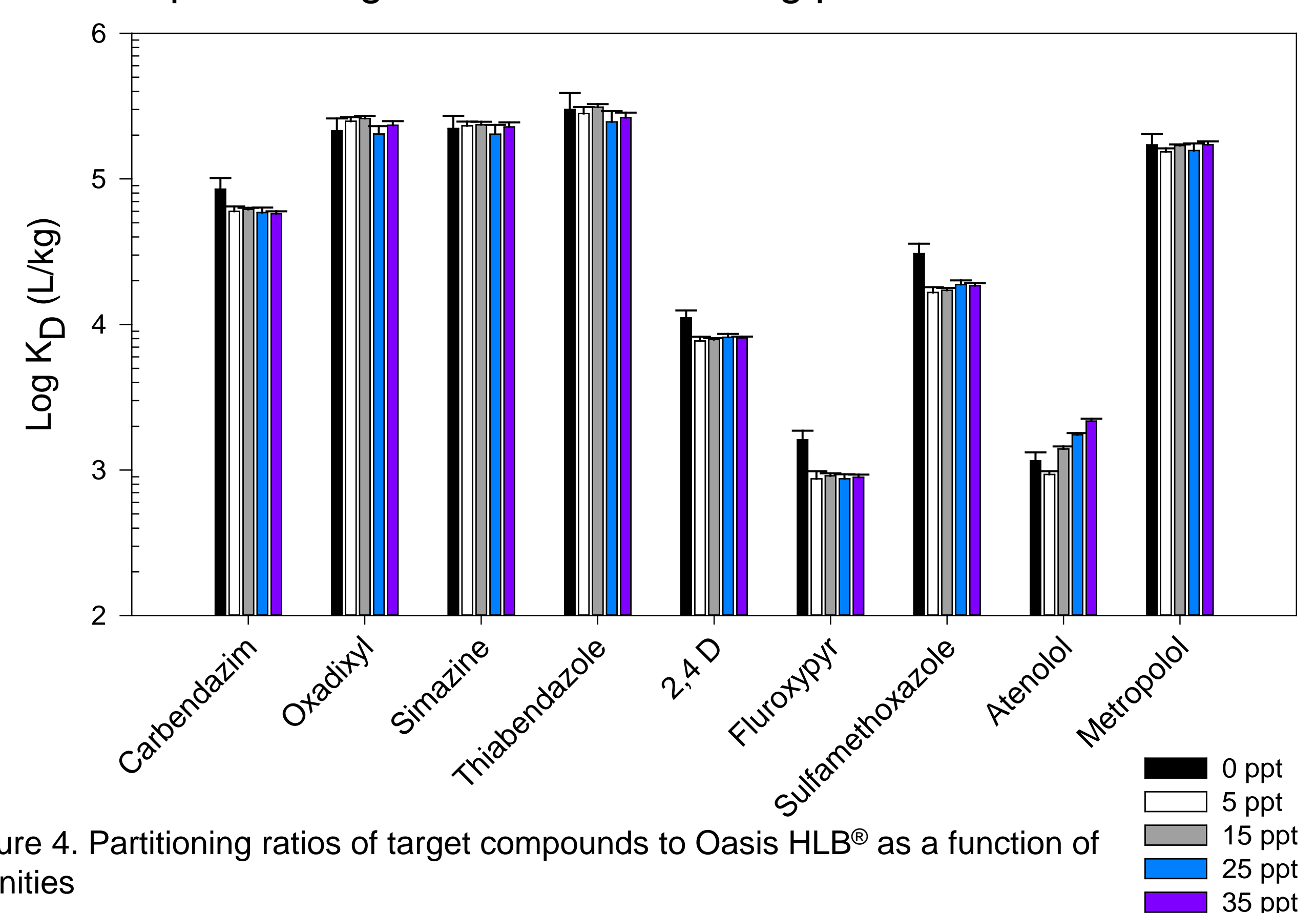


Figure 4. Partitioning ratios of target compounds to Oasis HLB® as a function of salinities

- Partitioning ratios presented in Figure 4 showed similar values with increasing salinity
- A small decrease in the partitioning ratios was observed for some compounds. This can be explained by the “salting-out” effect