

Environmental Chemistry

Influence of Salinity on the Partitioning Behavior of Six Commonly Used Pesticides in Fish Eggs

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Abstract: Salinity has been reported to impact the octanol–water partition coefficient of organic contaminants entering aquatic ecosystems. However, limited data are available on the impacts of salinity on their partitioning from the aqueous phase to adjacent organic compartments. The pesticides bifenthrin, chlorpyrifos, dicloran, myclobutanil, penconazole, and triadimefon were used to investigate the effects of salinity on their partitioning to capelin (*Mallotus villosus*) eggs in 5 practical salinity units (PSU) versus 25 PSU artificial seawater (ASW). The partitioning coefficient was significantly higher in 25 versus 5 PSU ASW for bifenthrin, chlorpyrifos, dicloran, penconazole, and triadimefon by 31%, 28%, 35%, 28%, and 20%, respectively, while for myclobutanil there was no significant difference. Moreover, pesticide partitioning to store-bought capelin eggs was consistent with the partitioning observed for the standard assay species, inland silversides (*Menidia beryllina*) eggs, after partitioning between the eggs and exposure solution had reached a state of equilibrium. The present study illustrates the importance of considering the influence of salinity on the environmental partitioning and fate of hydrophobic organic contaminants in aquatic ecosystems. *Environ Toxicol Chem* 2024;43:299–306. © 2023 SETAC.

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INTRODUCTION

Pollutants in estuarine areas experience variations in salinity depending on the size of the rivers flowing into estuaries and the salinity of adjacent marine waters. Such variations in water chemistry can affect the physicochemical properties and, consequently, the fate and toxicity of aquatic pollutants (Goff et al., 2017; Jing et al., 2014; Saranjampour et al., 2017). Pesticides frequently enter aquatic ecosystems through agricultural surface runoff, where they can travel downstream and ultimately be deposited in estuarine systems (Kuivila & Hladik, 2008). Due to the larger number of crops and high human population along coastlines, more pesticides have been used within close proximity to estuaries in recent years, leading to increased pesticide pollution in these ecosystems (Hutton et al., 2021; Kuivila & Hladik, 2008). However, the influence of salinity on the fate of pesticides in estuarine systems is poorly understood. It is important to consider the effects of salinity on the fate of pesticides as, depending on the compound, many

pesticides are categorized as being highly toxic to a range of non-targeted organisms, including those found in estuarine systems (e.g., estuarine shrimp, oysters, crabs, birds, and fish; Bringer et al., 2021; DeLorenzo et al., 2009; Hutton et al., 2021; Osterberg et al., 2012; Parsons et al., 2010).

While current regulation does require pesticides to undergo fate and toxicity testing prior to being registered for use, these tests are primarily conducted using fresh water with much less emphasis placed on estuarine or coastal ecosystems that also commonly receive run-off (US Environmental Protection Agency [USEPA], 2016). Although the effects of salinity on the fate and toxicity of pesticides are not well-understood, salinity has been shown to significantly impact the toxicity and behavior of pesticides in certain cases. For example, the fungicide triadimefon was found to be significantly more toxic to inland silversides (*Menidia beryllina*) in 15 practical salinity units (PSU) seawater versus 5 PSU seawater (Hutton et al., 2021). Similarly, the herbicide atrazine demonstrated to be significantly more toxic to sheepshead minnow (*Cyprinodon variegatus*) in higher salinity (15 PSU) versus lower salinity (5 PSU) seawater (Hall et al., 1994). While the effects of salinity on the toxicity of aquatic pollutants are variable and likely caused by a combination of physiological and chemical factors, prior research suggests one contributing

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factor could be higher bioaccumulation rates driven by salinity (Derby et al., 2022; Jeon et al., 2010). For instance, the bioaccumulation of the pyrethroid permethrin in the crustacean *Hyalella azteca* was reported to be over two times greater in 6 versus 0.2 PSU seawater (Derby et al., 2022). Likewise, the bioaccumulation of multiple perfluorinated compounds in Pacific oyster (*Crassostrea gigas*) tissues were found to be over two times greater in 34 versus 10 PSU seawater (Jeon et al., 2010).

One potential explanation for why some pesticides bioaccumulate more in seawater versus freshwater is that an increase in salinity is reported to reduce the aqueous solubility of organic contaminants in certain cases (Turner & Rawling, 2001). Such decreases in aqueous solubility have been shown to increase chemical partitioning from the aqueous phase to the organic phase and impact chemical partitioning coefficients (e.g., K_{ow} , K_d , and K_{oc} ; Brunk et al., 1996; Saranjampour et al., 2017). The octanol-water partition coefficient ($\log K_{ow}$) is a chemical partitioning coefficient that serves as a relative indicator of the tendency of a chemical in the aqueous phase to adsorb to soil and/or the tissues of organisms (USEPA, 2012). By increasing a chemical's $\log K_{ow}$, a chemical becomes less hydrophilic and more lipophilic (Hutton et al., 2021; Saranjampour et al., 2017; USEPA, 2012). Consequently, organic contaminants such as pesticides could have a higher affinity for the lipids of an organism in seawater versus freshwater environments (Hutton et al., 2021; Saranjampour et al., 2017). This in turn could enhance the partitioning of pesticides from the aqueous phase to the organic phase, including the tissues of aquatic organisms. As a result, the enhanced partitioning of pesticides to the tissues of aquatic organisms could potentially intensify their toxicity in saltwater environments. However, whether the tendency of pesticides to partition more onto the organic phase in saltwater is significant enough to enhance their sorption onto the tissues of organisms is not well understood. Thus, evaluating the influence of salinity on the partitioning behavior of pesticides in aquatic environments warrants further research.

The goal of the present study was to better understand the influence of salinity on the partitioning behavior of four fungicides (dicloran, penconazole, myclobutanil, and triadimefon) and two insecticides (bifenthrin and chlorpyrifos) between the aqueous and organic phase. Specifically, we characterized the partitioning of each pesticide from 5 and 25 PSU artificial seawater (ASW) to capelin (*Mallotus villosus*) eggs. Pesticide partitioning in capelin eggs (available in large quantities commercially) versus silverside eggs (available in lesser quantities) was also compared to determine if capelin eggs were a suitable proxy for silverside eggs when used as a lipid source to evaluate salinity effects on pesticide partitioning. Our study can help guide whether regulatory environmental fate assessments of organic contaminants should place a larger emphasis on the effects of salinity. It also has the potential to help characterize the effects of future saltwater intrusion related to global climate change on the behavior of pesticides in estuarine environments.

MATERIALS AND METHODS

Standards, solvents, and tissues

Bifenthrin, chlorpyrifos, dicloran, myclobutanil, penconazole, and triadimefon were purchased from Chem Service with purities above 99%. Capelin eggs were purchased from the Gourmet Food Store (SKU: 1502401) and inland silverside eggs were obtained from broodstock maintained in the Brander laboratory at the Hatfield Marine Science Center (Newport, OR, USA) per protocols described previously (Brander et al., 2016; DeCourten et al., 2020). Tissues were stored frozen prior to the start of the partitioning experiments. All solvents used (acetonitrile, dichloromethane, ethyl acetate, and hexane) were obtained from VWR and were reagent grade or better. Instant Ocean® was used as ASW and mixed in sterilized deionized water according to directions on the package. Experiments were conducted in sterilized 250 ml amber glass jars with polytetrafluoroethylene (PTFE)-lined caps purchased from Thermo Fisher Scientific. Tissues were extracted in sterilized 50 ml polypropylene centrifuge tubes purchased from VWR.

25 versus 5 PSU partitioning experiments with capelin eggs

The partitioning behavior of each pesticide was analyzed across a salinity gradient of 5 and 25 PSU (a gradient applicable to many estuarine organisms) to evaluate the influence of salinity on their sorption onto capelin eggs. This was conducted through six individual experiments, one for each pesticide. The first step of each experiment was to measure 0.5 g of capelin eggs in 48 250-ml amber glass jars with 24 labeled "5 PSU" and the remaining 24 "25 PSU". Second, 7400 ml of autoclaved deionized water was measured and spiked with the desired concentration of one of the pesticides and thoroughly stirred in a 10-L glass carboy. The desired dosing concentration of the pesticide in each experiment was based on the lethal concentration required to kill 10% (LC10) of an inland silverside population in 5 PSU seawater previously determined by Hutton et al. (2021; Table 1). Next, the spiked 7400 ml pesticide

TABLE 1: The the lethal concentration required to kill 10% (LC10), measured dosing concentration (C_{water}), $\log K_{ow}$, and water solubility (in deionized water) of each pesticide used for the partitioning experiments

Compound	LC10 (ppb)	C_{water} (ppb)	$\log K_{ow}$	Water solubility (ppm)
5 versus 25 PSU capelin partitioning experiments				
Bifenthrin	0.0227	0.021 ± 0.001	6.4	0.1
Chlorpyrifos	0.137	0.146 ± 0.007	4.7	1.4
Dicloran	0.288	0.270 ± 0.011	2.8	6.3
Myclobutanil	4.3	4.37 ± 0.16	2.9	132
Penconazole	0.235	0.249 ± 0.006	3.7	73
Triadimefon	118	111.5 ± 0.9	3.8	64
Silverside versus capelin partitioning experiments				
Myclobutanil	4.3	4.51 ± 0.21	2.9	132

Values after ± indicate standard error ($n = 4$; Hutton et al., 2021).

solution was divided into two separate 3600-ml pesticide solutions for the 5 and 25 PSU egg exposures; the remaining 200 ml was used to extract and measure the concentration of pesticide in the solutions. Eighteen grams of Instant Ocean® artificial sea salt was dissolved in one of the 3600-ml pesticide solutions to obtain a salinity of 5 PSU; 90 g of artificial sea salt was dissolved in the other 3600-ml pesticide solution to obtain a salinity of 25 PSU. The 5 PSU pesticide solution was then used to pour 150 ml of the solution into each of the 24 glass jars labeled “5 PSU” containing 0.5 g of capelin eggs. Likewise, the 25 PSU pesticide solution was used to pour 150 ml of the solution into each of the 24 glass jars labeled “25 PSU” containing 0.5 g of capelin eggs. Immediately after exposing the eggs to the 5 and 25 PSU pesticide solutions, all samples were stored in a dark incubator set at 20 °C. The 0.5-g egg samples were removed from each jar containing the 5 or 25 PSU pesticide solutions after 4, 24, 48, and 72 h of exposure for most experiments; however, eggs were exposed up to 144 h in cases where pesticide partitioning between the dosing solution and eggs had not reached a state of equilibrium by 72 h. During exposure, the 5 and 25 PSU pesticide solutions in each of the 150 ml samples were statically renewed every 24 h. Pesticide was extracted from the egg tissues immediately on removing the tissues from the 5 and 25 PSU pesticide solutions at each time point and analyzed by gas chromatography-tandem mass spectrometry (GC-MS/MS). Each experiment was conducted in quadruplicate or triplicate depending on the compound ($n \geq 3$). Welch's *t*-test ($\alpha = 0.05$) determined any significant statistical differences in the final concentration of pesticide recovered from the eggs in the 25 and 5 PSU ASW solutions.

Inland silverside versus capelin egg partitioning experiments

While inland silversides are typically used by regulatory agencies as the standard toxicity assay species for investigating salinity effects, their spawning is a time-consuming process that often produces a limited mass of eggs, therefore to ensure the store-bought capelin eggs were a suitable proxy for inland

silverside eggs for use in the partitioning experiments, a separate exposure experiment was conducted to compare pesticide sorption onto capelin versus inland silverside eggs. This was primarily to confirm the additives in the store-bought capelin eggs (i.e., monosodium glutamate, Yellow No. 6, sugar, and salt) did not significantly distort the trends observed in the 25 versus 5 PSU partitioning experiments (Gourmet Food Store, 2023). The design of this experiment was therefore similar to the previously described design for the 25 versus 5 PSU partitioning experiments with capelin eggs. Myclobutanil was selected for these exposures due to the enhanced sensitivity of the GC-MS/MS method and because the partitioning of myclobutanil between the dosing solution and capelin eggs (in the previously described experiments) reached equilibrium before 144 h (Figure 1). The first step was to measure 0.25 g of inland silverside eggs in nine 250-ml amber glass jars labeled “silversides” and 0.25 g capelin eggs in nine 250-ml amber glass jars labeled “capelin.” The egg mass for these exposures was less than the mass for the previously described exposures (0.5 g) due to the length of time required for the silverside population to produce eggs at the Hatfield Marine Science Center. Second, 2900 ml of autoclaved deionized water was measured and spiked to the LC10 of myclobutanil, 4.3 parts per billion (ppb; measured concentration was 4.51 ± 0.21 ppb) and thoroughly stirred in a 10-L glass carboy (Table 1). Two hundred milliliters of the spiked myclobutanil solution was saved for use in water extractions to measure the concentration of myclobutanil in the solution. Then, 67.5 g of Instant Ocean® artificial sea salt was dissolved in the remaining 2700 ml to obtain a salinity of 25 PSU. This 25 PSU pesticide solution was then used to pour 150 ml of the solution into each of the nine glass jars containing 0.25 g of silverside eggs and each of the nine glass jars containing 0.25 g capelin eggs. Immediately after exposing the capelin and silverside eggs to the 25-PSU myclobutanil solution, all samples were stored in a dark incubator set at 20 °C. The 0.25-g capelin and silverside egg samples were removed from each jar containing the 25-PSU myclobutanil solutions after 24, 48, and 72 h of exposure. During exposure, the 25-PSU myclobutanil solution in each of the 150-ml samples was statically renewed every 24 h. Pesticide

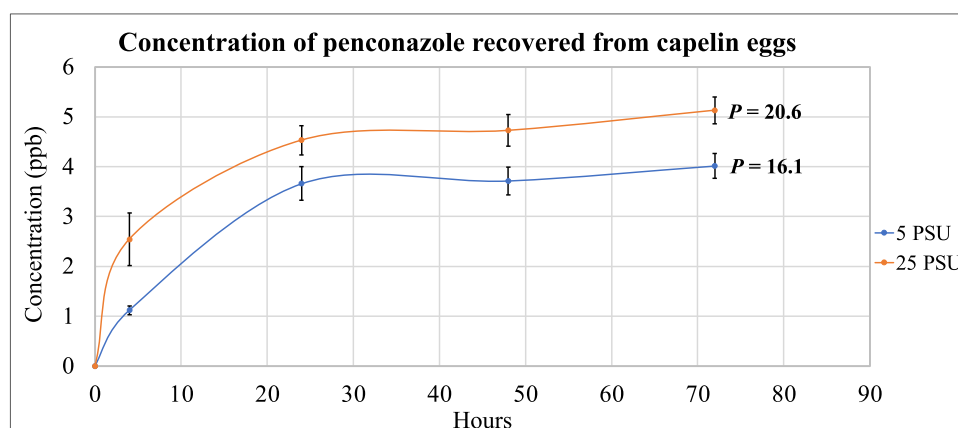


FIGURE 1: The partitioning coefficient (*P*) and concentration of myclobutanil recovered from capelin eggs in 5 and 25 PSU after 4, 24, 48, 72, and 96 h of exposure. Error bars indicate standard error ($n = 3$).

was extracted from the egg tissues immediately on removing the tissues from the 25 PSU myclobutanil solution at each time point and analyzed by GC-MS/MS. These exposures were conducted in triplicate ($n = 3$).

Analytical confirmation of pesticide solutions

Each pesticide solution was analyzed to ensure they were accurately spiked to the LC10 of each compound. Pesticide residues were extracted from 50-ml aliquots of each pesticide solution (prior to adding sea salt) using C18 solid phase extraction (SPE) cartridges (100 mg of sorbent, 3 ml of reservoir volume) from Thermo Fisher. Cartridges were preconditioned with 3 ml of methanol and 3 ml of deionized water prior to adding the sample and placed on a vacuum manifold to capture the analytes. Residual pesticide was eluted from each cartridge with 2 ml of dichloromethane for all compounds. The extracts were transferred into 2-ml borosilicate glass vials obtained from Agilent and immediately analyzed by GC-MS/MS. This was conducted in quadruplicate for each dosing solution; SPE recoveries were 91% or greater for each compound ($n = 4$). Measured concentrations deviated from expected concentrations by less than 10% for each compound in all partitioning experiments (Table 1).

Tissue extractions for capelin and inland silverside eggs

Pesticide was extracted from the egg tissues using a modified quick, easy, cheap, effective, rugged, and safe (QuEChERS) method immediately on removing the eggs from their respective pesticide solutions in ASW (5 or 25 PSU; Varela-Martinez et al., 2020). For each 150-ml sample, the pesticide solution containing the eggs was poured through a fine steel mesh strainer to capture the eggs and dispose of the solution. The eggs were immediately washed with deionized water to ensure no residual pesticide solution remained on the egg surfaces and were transferred into a sterilized 50-ml polypropylene centrifuge tube (capped). Next, 4.5 ml of an extraction solvent mixture composed of 80% ethyl acetate and 20% hexane was poured into each centrifuge tube containing the eggs. The eggs and solvent mixture were rigorously vortexed at high speed for 1 min with a Vortex Genie 2 (VWR) then sonicated in warm water ($\approx 35^\circ\text{C}$) for 15 min with a Branson 2210 sonication bath. Each extract was then transferred to individual 40-ml borosilicate glass vials with PTFE-lined caps. These steps were repeated two more times for each sample, each time with 4.5 ml of fresh extraction solvent and stored in the 40-ml borosilicate glass vials after vortexing and sonication. Each sample extract contained in the 40-ml glass vials was then stored in the freezer prior to sample preparation and analysis.

To prepare the extracts for analysis, each extract was removed from the freezer and immediately transferred to a graduated 15-ml borosilicate glass evaporation tube. Extracts were blown down under a gentle stream of nitrogen gas to a final volume ranging between 200 and 400 μL depending on

the compound. The extracts were transferred into 2-ml borosilicate glass vials (with PTFE septum caps) containing 400- μL salinized-glass inserts and analyzed by GC-MS/MS. Extraction recoveries of pesticide residues were determined prior to the start of the exposures by directly spiking unexposed eggs to 5 ppb of each pesticide. Recoveries of pesticide residues from spiked capelin eggs averaged $87 \pm 5\%$ for bifenthrin, $89 \pm 4\%$ for chlorpyrifos, $70 \pm 3\%$ for dicloran, $92 \pm 5\%$ for myclobutanil, $89 \pm 2\%$ for penconazole, and $80 \pm 3\%$ for triadimefon ($n = 5$). Recoveries of pesticide residues from spiked silverside eggs varied by less than 5% of these values ($n = 3$).

GC-MS/MS analysis

A Bruker Scion TQ 456-GC-MS/MS (Billerica) was used to measure pesticides in the tissue extracts. Residues were separated on an RXI-5MS column (length 30 m, internal diameter 0.25 mm, and film thickness 0.25 μm) programmed at 90°C for 3 min and then ramped up $5^\circ\text{C}/\text{min}$ to 300°C , where the temperature was held for 10 min. The carrier gas was ultra-purity helium, and the collision gas was ultra-purity argon. External standards were used to quantify the concentration of pesticide in each sample which were run daily. The limit of detection for bifenthrin was 0.1 ppb and for all other compounds was 0.5 ppb or lower. Additional information regarding the retention time for each pesticide as well as the parent ion and quantification ion for each MRM method is given in Supporting Information, Table S1.

RESULTS AND DISCUSSION

Capelin egg exposures in 25 versus 5 PSU pesticide solutions

The concentration of pesticide recovered from the eggs exposed to the 25 PSU solutions was consistently higher than the concentration of pesticide recovered from the eggs exposed to the 5 PSU solutions for all six pesticides (Figures 1–6). A partitioning coefficient was calculated for the final time point of each exposure after pesticide partitioning between the exposure solution and the eggs had reached a state of equilibrium (characterized by negligible change in concentration with exposure time). The partitioning coefficient (P) is defined in the form:

$$P = C_{\text{egg}}/C_{\text{water}}$$

where C_{egg} refers to the final concentration of pesticide recovered from the eggs and C_{water} refers to the measured dosing concentration of pesticide in the exposure solution. (Tables 1 and 2).

With the exception of myclobutanil, the partitioning coefficient for each pesticide in 25 PSU ASW was significantly higher ($p < 0.05$) than in 5 PSU ASW. This suggests salinity can enhance the partitioning of organic contaminants between the aqueous and organic phase, in this case capelin egg tissues. The enhanced partitioning of the selected pesticides to capelin eggs may be explained, in part, by the tendency of salinity to increase the $\log K_{\text{ow}}$ of certain organic contaminants. For example, the

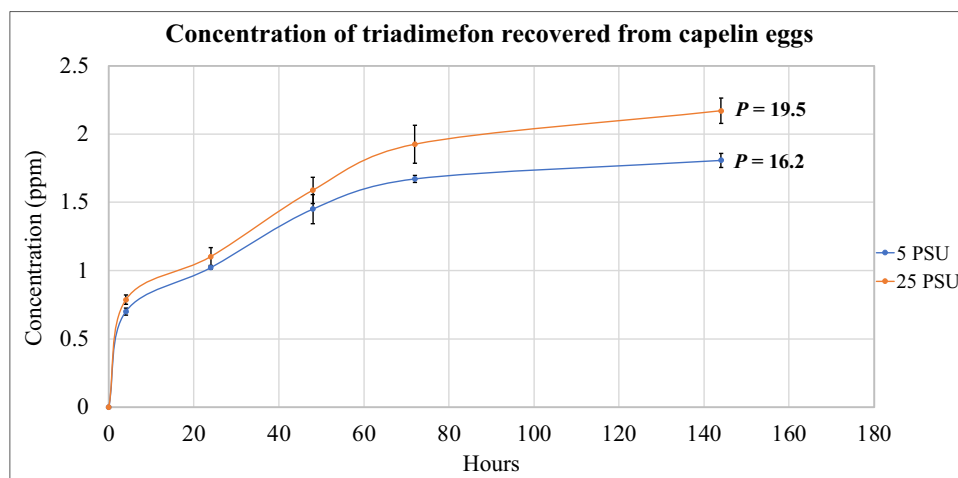


FIGURE 2: The partitioning coefficient (P) and concentration of bifenthrin recovered from capelin eggs in 5 and 25 PSU after 4, 24, 48, and 72 h of exposure. Error bars indicate standard error ($n = 3$).

pesticides atrazine, bifenthrin, fipronil, and cypermethrin and the crude oil constituent dibenzothiophene have all been reported to have increased $\log K_{ow}$ values in ASW compared with distilled-deionized water (Saranjampour et al., 2017). Such increases in $\log K_{ow}$ have been reported to increase the partitioning propensity of aqueous organic contaminants to adjacent organic compartments (e.g., sediment organic matter and tissues of aquatic organisms) in certain cases (Saranjampour et al., 2017; Turner & Rawling, 2001). For instance, salinity has also been shown to increase the soil adsorption coefficient (K_d) and dissolved organic matter partition coefficient (K_{dom}) of organic contaminants including 2,2',5,5'-tetrachlorobiphenyl and phenanthrene (Brunk et al., 1996; Turner & Rawling, 2001). These studies suggest the enhanced partitioning of organic contaminants with escalating salinity could be, in part, a result of the "salting-out" effect experienced by such contaminants due to their decreased solubilities in saltwater. It follows a decrease in water solubility for an aqueous hydrophobic organic contaminant could cause an increase in the amount of contaminant that

partitions onto adjacent organic compartments if it is significantly closer to its solubility limit. This is because the fraction of organic contaminant that can no longer dissolve in the aqueous solution must move elsewhere, preferentially to compartments of similar polarity (i.e., organic compartments; Abelman et al., 2005). It is important to note the water solubilities and $\log K_{ow}$ values reported for the pesticides investigated in the present study reflect their solubility limits in deionized water because their water solubilities in seawater are poorly characterized (Table 1). Nonetheless, salinity has been shown to significantly reduce the solubility of organic contaminants; hence, it is reasonable to suspect the selected pesticides have significantly lower solubilities in the ASW solutions used in the present study (Saranjampour et al., 2017).

While it was anticipated that pesticides with the highest $\log K_{ow}$ values would exhibit the highest partitioning coefficients (in both 5 and 25 PSU ASW), this trend was only observed for some of the pesticides. For example, bifenthrin had the highest $\log K_{ow}$ (6.4) and the highest partitioning coefficient in 5 (20.9 ± 0.7) and

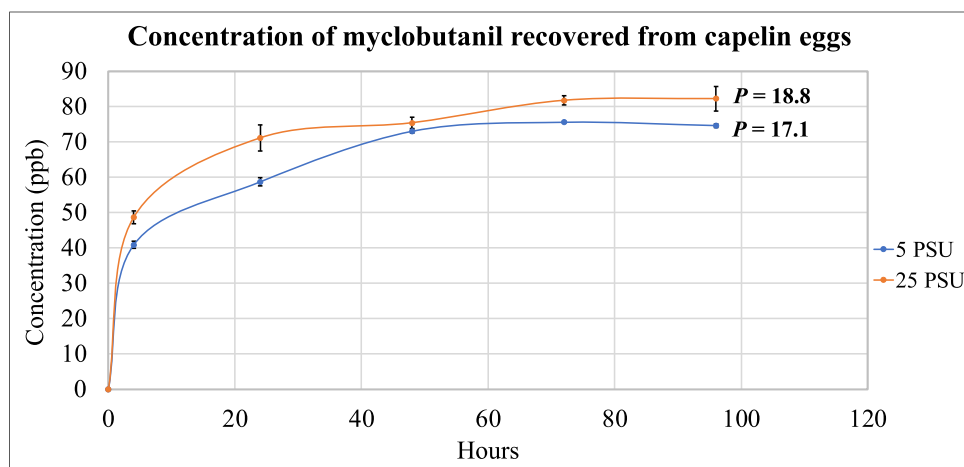


FIGURE 3: The partitioning coefficient (P) and concentration of chlorpyrifos recovered from capelin eggs in 5 and 25 PSU after 4, 24, 48, and 72 h of exposure. Error bars indicate standard error ($n = 3$).

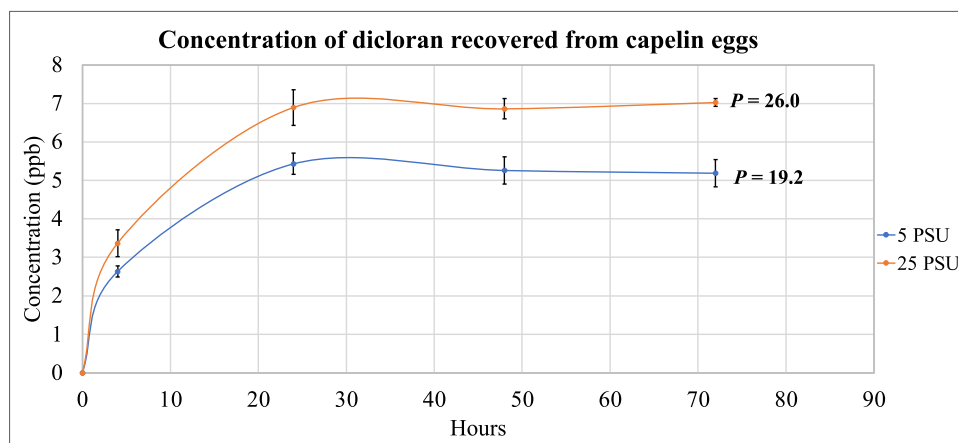


FIGURE 4: The partitioning coefficient (P) and concentration of dicloran recovered from capelin eggs in 5 and 25 PSU after 4, 24, 48, and 72 h of exposure. Error bars indicate standard error ($n = 4$).

25 (27.4 ± 1.3) PSU ASW compared with all other pesticides (Tables 1 and 2). However, dicloran, which had the lowest $\log K_{ow}$ of all the pesticides (2.8), had a higher partitioning coefficient in both the 5 and 25 PSU ASW solutions compared with chlorpyrifos, myclobutanil, penconazole, and triadimefon. For example, chlorpyrifos had a $\log K_{ow}$ value of 4.7, but its partitioning coefficient in 5 (16.6 ± 1.1) and 25 (21.3 ± 0.5) PSU ASW was lower than that of dicloran in 5 (19.2 ± 1.3) and 25 (26.0 ± 0.3) PSU ASW. These results suggest the partitioning behavior of the selected pesticides was not solely dependent on their $\log K_{ow}$. Other factors such as variability in dosing concentrations, water solubilities, and pesticide extraction recoveries could have played a role in causing these deviations from the otherwise expected trend of increased partitioning potential with increased $\log K_{ow}$ (Hutton et al., 2021; Saranjampour et al., 2017). Nonetheless, there was a clear trend of increased pesticide partitioning to capelin eggs with increased salinity for all pesticides.

Capelin versus inland silverside egg exposures in 25 PSU myclobutanil solution

While some variability existed in the initial uptake of myclobutanil between capelin and silverside eggs in the 25 PSU solution, both yielded similar final concentrations of myclobutanil after reaching a state of equilibrium with the exposure solution (Supporting Information, Figure S1). Specifically, the final concentration of myclobutanil ($\pm$ the standard error) in capelin eggs and silverside eggs (C_{egg}) after 72 h of exposure was 80.2 ± 0.7 and 77.32 ± 3.2 ppb ($n = 3$), respectively. With a measured dosing concentration (C_{water}) of 4.51 ± 0.21 ppb, this corresponds to a partitioning coefficient of 17.8 ± 0.2 and 17.1 ± 0.7 for capelin and silverside egg tissues, respectively. No significant difference ($p > 0.05$) was found between these partitioning coefficients. This suggests the additives in store-bought capelin eggs and potential differences in the shape, size, and lipid content of capelin eggs versus silverside eggs

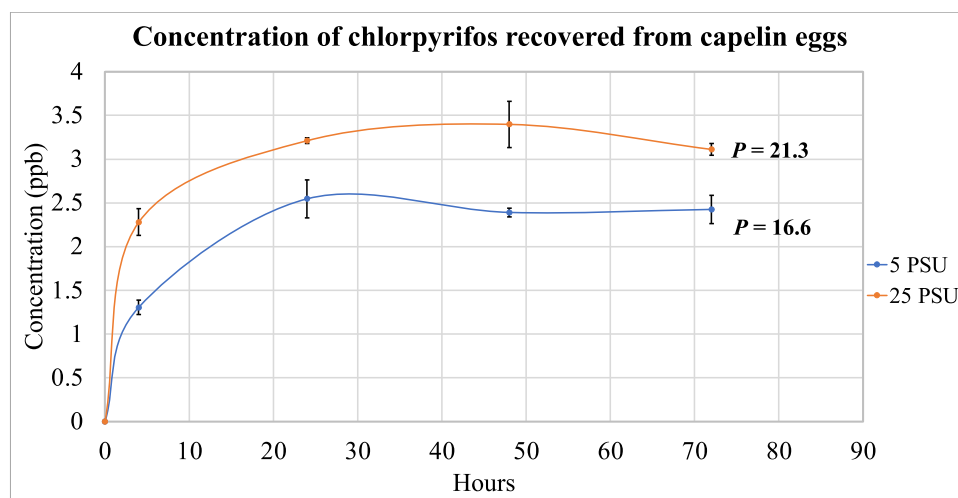


FIGURE 5: The partitioning coefficient (P) and concentration of penconazole recovered from capelin eggs in 5 and 25 PSU after 4, 24, 48, and 72 h of exposure. Error bars indicate standard error ($n = 4$).

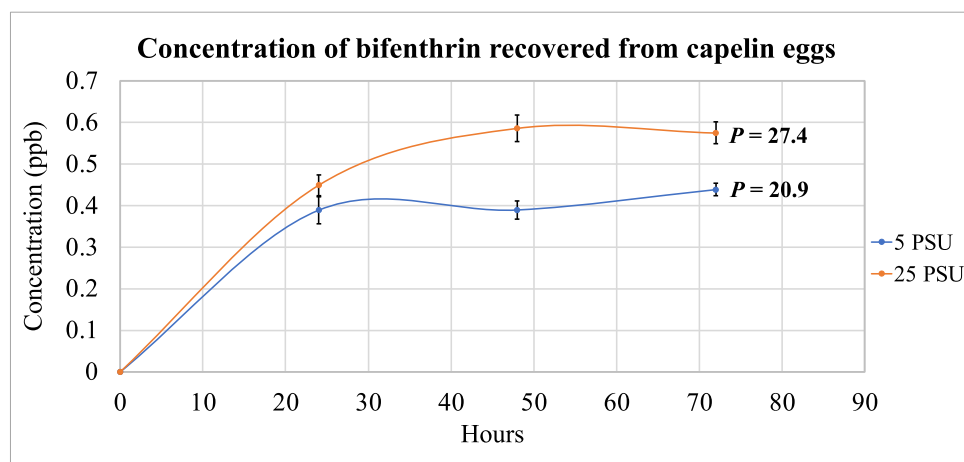


FIGURE 6: The partitioning coefficient (P) and concentration of triadimefon recovered from capelin eggs in 5 and 25 PSU after 4, 24, 48, 72, and 144 h of exposure. Error bars indicate standard error ($n = 4$).

do not significantly impact equilibrium concentrations of pesticides in the egg tissues (C_{egg}). However, considerable differences in the concentration of myclobutanil extracted from capelin versus silverside eggs prior to reaching a state of equilibrium with the exposure solution were observed. The largest concentration difference between the two tissue types was after 24 h of exposure to the 25 PSU myclobutanil solution with 45.1 ± 1.9 and 64.7 ± 4.2 ppb detected in capelin and silverside egg tissues, respectively (values after $\pm$ indicate standard error). It is possible this initial variation in the pesticide uptake rate was due to the smaller size observed for the silverside eggs compared with the capelin eggs. A smaller egg size requires more eggs to obtain the same mass per sample, which ultimately results in more egg surfaces being available for pesticide sorption (increased surface area). This is one potential explanation for why more myclobutanil was recovered from the silverside eggs after 24 h of exposure. This variability, however, was not observed after 48 or 72 h of exposure to the 25 PSU myclobutanil solution.

Hence, for the purpose of evaluating the impacts of salinity on the sorption of pesticides onto silverside eggs, capelin eggs appear to be a suitable substitute for comparing partitioning coefficients (at equilibrium) across a salinity gradient. Caution should be exercised, however, if capelin eggs are used to gauge pesticide uptake in silverside eggs; these results indicate the concentration of myclobutanil in the two tissue types varied considerably prior to reaching a state of equilibrium with the exposure solution.

CONCLUSION

Salinity did appear to significantly enhance the partitioning of bifenthrin, chlorpyrifos, dicloran, penconazole, and triadimefon to capelin eggs with partitioning coefficients ranging from 20% to 35% higher in 25 versus 5 PSU ASW. In addition, for the purpose of investigating pesticide partitioning behavior, capelin eggs are a suitable substitute for inland silverside eggs after partitioning between the eggs and exposure solution have reached a state of equilibrium. The enhanced partitioning of the selected pesticides to capelin eggs observed in the 25 PSU ASW solution suggest salinity can impact the partitioning potential of organic chemicals and should be considered in their regulatory fate and transport assessments. However, this does not necessarily imply their potential to accumulate in living organisms increases with salinity. Differences in the metabolic activity and water consumption of aquatic organisms often vary with salinity and can impact the uptake of a chemical in an organism (Kültz, 2015; Lavado et al., 2014). Future research should evaluate the potential effects of this enhanced partitioning on the accumulation of organic contaminants in estuarine/marine organisms to determine whether these organisms may be differentially impacted by such contaminants depending on the salinity of exposure. In particular, salinity-corrected K_{ow} values may be useful in future toxicological risk assessments of estuarine/marine organisms because the bioaccumulation potential of organic contaminants may be increased in higher salinity systems due to reduced solubility.

TABLE 2: The final pesticide concentration recovered from egg tissues at equilibrium (C_{egg}) and the partitioning coefficient (P) for each pesticide in the 5 versus 25 PSU partitioning experiments with capelin eggs

Compound	Salinity (PSU)	C_{egg} (ppb)	P
Bifenthrin	5	0.438 ± 0.015	20.9 ± 0.7
	25	0.575 ± 0.026	27.4 ± 1.3
Chlorpyrifos	5	2.42 ± 0.16	16.6 ± 1.1
	25	3.11 ± 0.07	21.3 ± 0.5
Dicloran	5	5.19 ± 0.35	19.2 ± 1.3
	25	7.03 ± 0.10	26.0 ± 0.3
Myclobutanil	5	74.7 ± 0.5	17.1 ± 0.1
	25	82.2 ± 3.5	18.8 ± 0.8
Penconazole	5	4.02 ± 0.25	16.1 ± 1.0
	25	5.13 ± 0.27	20.6 ± 1.1
Triadimefon	5	$1,809 \pm 51$	16.2 ± 0.5
	25	$2,171 \pm 92$	19.5 ± 0.8

Values after $\pm$ indicate standard error ($n = 4$).

The present study emphasizes the importance of considering salinity effects on the environmental partitioning of organic contaminants in aquatic systems and highlights the need to account for these effects in regulatory assessments evaluating chemical transport in estuarine ecosystems.

Supporting Information—The Supporting Information is available on the Wiley Online Library at <https://doi.org/10.1002/etc.5780>.

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