Environmental Science & Technology

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Preferential Partitioning of Per- and Polyfluoroalkyl Substances in Freshwater Ice

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Cite This: *Environ. Sci. Technol.* 2024, 58, 15214−15223

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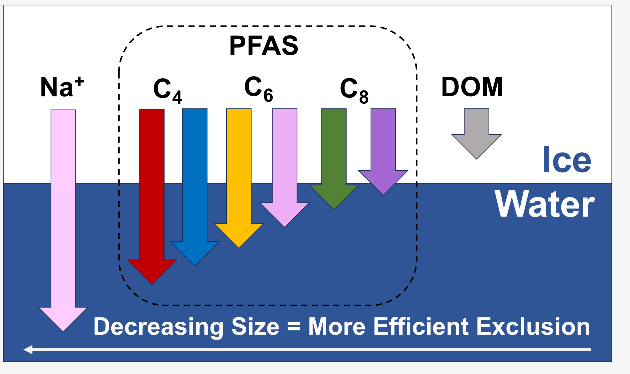

ABSTRACT: Millions of lakes worldwide freeze, yet the fate of per- and polyfluoroalkyl substances (PFAS) in ice in freshwater systems is poorly understood. We quantified concentrations of 36 PFAS, dissolved organic carbon (DOC), and inorganic ions in ice and water in seven freshwater lakes to investigate the preferential exclusion of ions during freezing. PFAS concentrations in ice are typically lower than in the water column, demonstrating that these chemicals are excluded from ice as it freezes. However, there is preferential partitioning of both PFAS and DOC relative to cations with average sodium-normalized enrichment factors (EF) ranging from 2.74 for perfluorobutanoate (PFBA; a C_4 perfluorocarboxylic acid) to 4.01 for perfluorooctanesulfonate (PFOS; a C_8 perfluorosulfonic acid), with a similar EF value of 4.14 for DOC. Laboratory experiments and seasonal measurements of PFAS in the water column indicate that PFAS concentrations in ice are a function of aqueous PFAS concentrations, with lower EF values observed in waters with higher PFAS concentrations. Understanding PFAS behavior in freshwater ice is important for predicting contaminant fate during winter and spring periods, with implications for exposure to PFAS during the winter and release of PFAS when ice melts in freshwater systems.

KEYWORDS: *PFAS, ice, partitioning, freshwater, lakes, environmental fate*

■ INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS), which are a class of >9000 synthetic chemicals, are widely distributed in the environment due to their persistence and long history of commercial[1−5] and industrial[6−9] use. Potential sources for contamination include direct emissions,[10−12] precipitation,[13−15] and dry deposition.[16−18] These chemicals are of concern due to their toxicity at low concentrations[19−22] and ability to bioaccumulate.[23,24]

Over 50 million of the ∼117 million lakes in the world freeze each year,[25,26] yet ice−water partitioning of PFAS in freshwater systems is poorly understood. Freshwater lakes are often drinking water sources and serve the community for recreational use, including ice fishing during winter. Ice cover alters the physical structure and chemical composition of lakes by decreasing light penetration and preventing wind-driven mixing.[27] Importantly, the exclusion of solutes from ice can alter lake biogeochemistry. For example, rejection of salts in ice can impact seasonal salinity trends,[28] while rejection of mercury from ice can serve as a pollution source in lakes where a large fraction of the water freezes.[29] Studies in the Arctic have similarly identified melting sea ice as a potential source of PFAS to under-ice seawater.[30−32] However, PFAS behavior in frozen freshwater lakes has not been investigated. An understanding of PFAS accumulation in freshwater ice is important for assessing potential exposure to PFAS during winter months and for predicting PFAS release during the spring, as well as for broadly understanding PFAS fate in lakes that freeze.

The behavior of inorganic ions, metals, and dissolved organic matter (DOM) during freezing may provide insight into PFAS behavior in ice. Dissolved solutes are typically excluded from ice rather than being incorporated into the crystal lattice.[33,34] For example, inorganic ions (e.g., sodium and chloride)[27,28,35] and metals[29,36] are excluded from freshwater ice under both field and laboratory conditions, with similar trends observed in seawater.[34,37−41] The relative exclusion of efficiency of inorganic ions has been attributed to differential diffusivity of each ion.[42] Interestingly, DOM is enriched in ice relative to inorganic ions in freshwater[27,43] and in seawater.[37,38,41,44,45] DOM is a complex mixture of biologically derived molecules that share properties with PFAS, such as an amphiphilic nature and negatively charged

Received: May 9, 2024
Revised: August 7, 2024
Accepted: August 8, 2024
Published: August 13, 2024

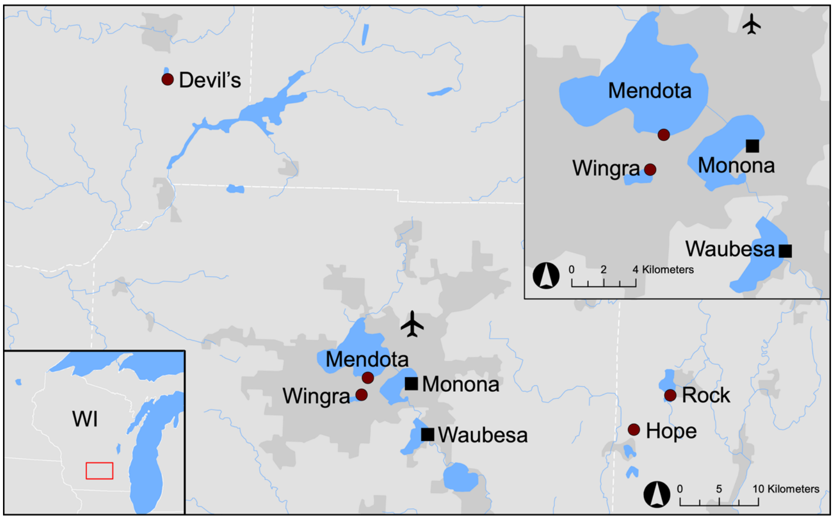

Figure 1. Map of sites where samples were collected from Wisconsin lakes created using ArcGIS (10.6.1). Data provided by the National Atlas of the United States, USGS. The hydrologically connected lakes in Dane County (i.e., Mendota, Wingra, Monona, and Waubesa) are shown in the inset. Sites with low PFAS concentrations are indicated with red circles. AFFF-impacted sites are indicated with black squares. The Dane County Regional Airport and adjacent Truax Field Air National Guard Base are indicated with a black airplane symbol. Coordinates for each sampling location can be found in Table S2 in the Supporting Information.

moieties (e.g., carboxylate functional groups), with ions that have similar molecular weights as many PFAS (i.e., 200−650 Da).[46−49] Furthermore, preferential partitioning of DOM to natural foams and the surface microlayer follows similar trends as PFAS as a function of chain length.[50] Thus, we hypothesized that PFAS would behave similarly as DOM and be retained in ice relative to inorganic ions.

Previous measurements of PFAS in ice are limited to sea ice formed in the laboratory[33,51] and the Arctic Ocean,[30,31] as well as ice collected from ice caps[5,52−55] and glaciers[56] in the Arctic. Summed PFAS concentrations in sea ice range 0.2−2.2 ng/L, which are higher than underlying seawater in some locations.[30,31] Arctic sea ice is dominated by perfluorocarboxylic acids (PFCAs) with smaller amounts of perfluorosulfonic acids (PFSAs), suggesting that atmospheric deposition is the major source of PFAS.[30,31] Interestingly, sea ice contains longer chain PFCAs that are absent from seawater[30] and short chain PFAS are more readily released from sea ice when it melts.[31] Similar preferential enrichment of longer chain PFCAs in sea ice has also been observed under laboratory conditions.[33,51] Thus, PFAS chain length likely influences its ability to be excluded from ice.

There are several key differences between marine and freshwater systems that may influence PFAS behavior in ice. First, freshwater lakes can have higher concentrations of PFAS due to their proximity to PFAS sources [e.g., release of aqueous film-forming foam (AFFF)[7,57]]. Second, there are physical differences between ice formed from freshwater compared to seawater.[58] In ice formed from seawater, dissolved solutes may concentrate in the liquid brine phase, become incorporated into the ice as inclusions, or trapped in grain boundaries.[27,38,59] While gravity drainage (i.e., brine convection) causes solutes to be rejected into underlying seawater,[34,60,61] freshwater ice does not have a large fraction of porous brine channels due to its lower ionic strength. Chemical sorption to ice surfaces, which has been proposed as a mechanism for PFAS partitioning in sea ice,[33] may therefore play a more important role than gravity drainage in freshwater systems. Finally, pack ice in the Arctic Ocean represents the accumulation of ice, and therefore PFAS, over years,[30] in contrast with freshwater lakes which are highly dynamic and only represent a single season.

Understanding PFAS behavior in freshwater ice is important for predicting contaminant fate during winter and spring periods. This study therefore quantifies PFAS, DOM, and inorganic ions in ice and water of freshwater lakes to investigate how PFAS partitions within ice relative to inorganic ions and DOM. Study lakes include two sites with elevated PFAS concentrations and five lakes with lower PFAS inputs to investigate the role of PFAS concentration in partitioning to ice. Additionally, laboratory experiments are used to further investigate the chain length and concentration dependence of PFAS partitioning to ice.

■ MATERIALS AND METHODS

Standards and Reagents. Chemicals used for sample preparation and analysis are described in Supporting Information Section S1. Ultrapure water (18.2 MΩ·cm) was supplied by a Milli-Q water system.

Field Sample Collection. Ice and water samples were collected from seven lakes in Wisconsin, USA in February 2023, with additional water samples collected in summer 2022 and spring 2023 (Figure 1; Tables S2 and S3). Sectioned ice samples were collected by drilling a hole with an auger to a known depth, stopping to collect ice shards from the drilling in a 1 L polypropylene bottle, and repeating until the auger broke through the ice to the water underneath; see Section S3 for quality control measures. Underlying water samples were collected by submerging a closed 500 mL polypropylene bottle >12 cm below the surface, opening the bottle to collect the water, and then closing the bottle while underwater.

PFAS Quantification. Water and melted ice samples were analyzed for 36 PFAS (Table S1). Analytes include compounds relevant to regulations[62] and newer species.[63] Environmental water and ice samples were extracted following a modified version of U.S. Environmental Protection Agency method 1633 (Section S1.2.2).[64] Briefly, samples were amended with mass-labeled surrogates, extracted by solid-phase extraction

https://doi.org/10.1021/acs.est.4c04636
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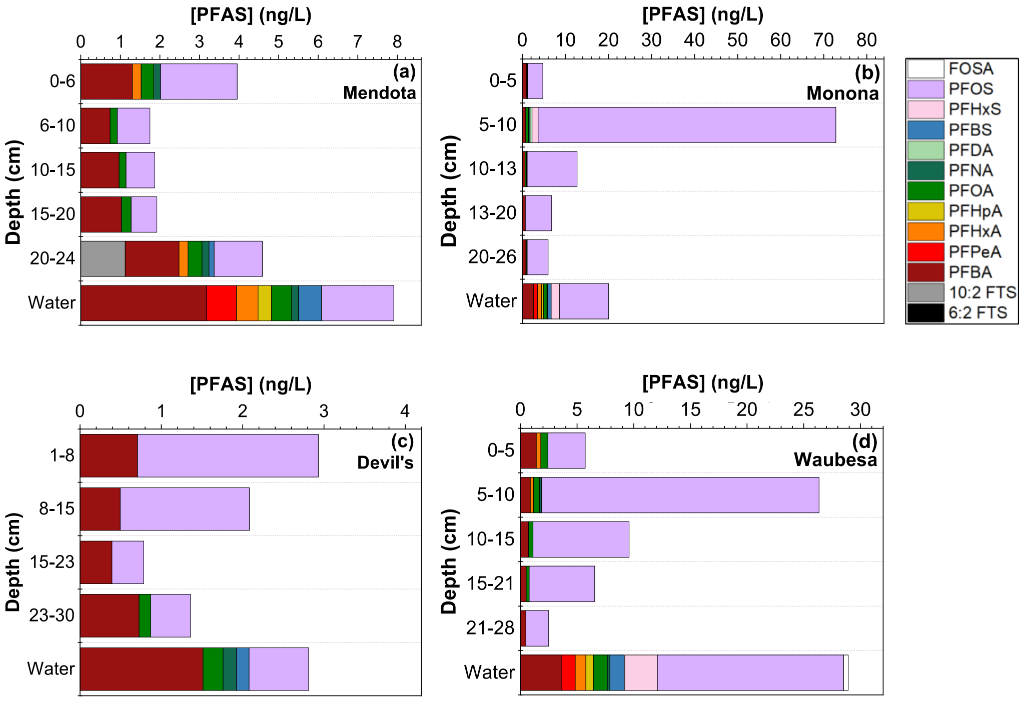

Figure 2. Concentration of PFAS throughout the ice column and in underlying water in (a) Lake Mendota, (b) Lake Monona, (c) Devil's Lake, and (d) Lake Waubesa. The surface of the ice (i.e., ice/air interface) is denoted as 0 cm. Samples for each lake were collected on the same day from the same location. PFAS data for the other three study lakes are presented in Figure S6.

(SPE) onto weak anion exchange cartridges (Waters Oasis WAX), and eluted with 60 mM ammonium hydroxide in methanol. The eluent was passed through carbon cleanup cartridges (ENVI-Carb). Extracts were concentrated to 1 mL under nitrogen, amended with mass-labeled internal standards, and analyzed by liquid chromatography−tandem mass spectrometry (LC−MS/MS; Section S1.3). Quality control for PFAS quantification is discussed in Section S3.

Background Water Chemistry Analysis. Water and melted ice samples were analyzed for cation and anion concentrations. Sample pH, dissolved organic carbon (DOC) concentrations, and UV−visible spectra were also measured for field samples. Instrumental methods are provided in Section S1.4.

Laboratory Ice Experiments. Two sets of laboratory experiments were conducted using filtered (0.45 μm, nylon) Lake Mendota water. First, PFAS and cation partitioning as a function of time was studied in lake water amended with ~10 μg/L each of C_4, C_6, and C_8 PFCAs and PFSAs. This concentration was selected to enable PFAS analysis by LC−MS/MS without the need for SPE due to sample volume limitations. The stock solution (40 mL) was distributed into uncapped falcon tubes and transferred to the freezer. Triplicate sacrificial tubes were removed at 60, 75, 85, 95, and 105 min. At each time point, water was pipetted into a clean falcon tube and ice was allowed to melt separately. Samples were diluted with methanol (80:20 MeOH/sample) prior to LC−MS/MS analysis for PFAS. A second set of experiments was conducted with larger volumes (1 L) of ambient Lake Mendota water, as well as lake water amended with nominal concentrations of 1, 10, 50, and 4000 ng/L each of PFBA, PFHxA, PFOA, PFBS, and PFOS. Triplicate reactors were removed after 8 h (i.e., when ~40% of the water was frozen); water and ice were transferred to separate polypropylene bottles. Solutions with amended PFAS concentrations ≤50 ng/L were extracted by SPE prior to PFAS analysis, whereas the remaining solutions were analyzed directly as described above.

RESULTS AND DISCUSSION

Sampling Locations. The seven lakes range widely in size, trophic status, and potential PFAS inputs (Table S3).[65] Four of the lakes are in Dane County, Wisconsin and are hydrologically connected (inset of Figure 1). Lakes Mendota and Wingra [hydraulic residence time (θ) = 4.4 and 1.3 years, respectively] both feed into Lake Monona (θ = 1.1 years). Lake Monona drains into Lake Waubesa (θ = 0.2 years). While the lakes share many characteristics (e.g., all are eutrophic drainage lakes), they have different potential PFAS loadings. Lake Monona receives PFAS from Starkweather Creek, which is impacted by historical AFFF use for firefighting and training at the Dane County Regional Airport and Truax Field Air National Guard Base.[66−70] Lake Waubesa is also highly impacted because it is directly downstream of Lake Monona and is expected to display similar trends in water chemistry; both lakes have fish advisories for PFOS.[71] In contrast, Lakes Mendota and Wingra are not currently associated with known PFAS sources.

The three remaining lakes have low expected PFAS concentrations and are included to investigate PFAS partitioning to ice in unimpacted systems. Hope Lake and Devil's Lake are seepage lakes with no inlets or outlets (Table S3). Therefore, the only sources of water are precipitation, stormwater runoff, and groundwater, which are expected to be low in PFAS.[13] Rock Lake is a mesotrophic drainage lake with a long hydraulic residence time (θ = 6 years); this rural lake is not currently linked to known PFAS sources.

PFAS Concentrations in Water and Ice. PFAS concentrations range widely in the seven lakes (Figure 2 and

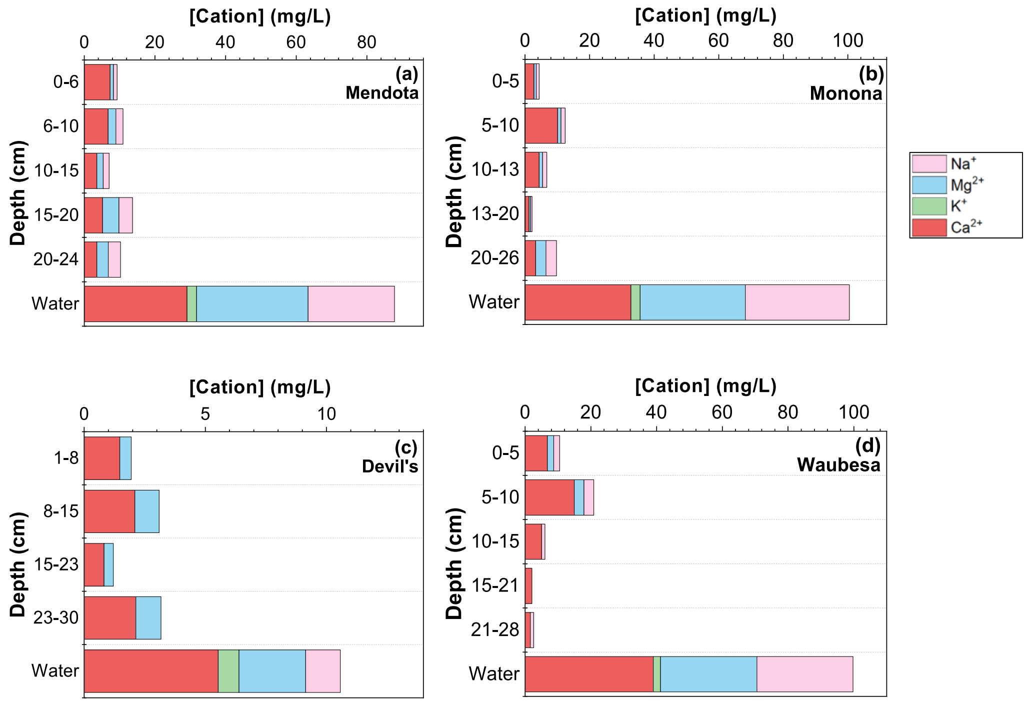

Figure 3. Cation concentrations throughout the ice column and in underlying water in (a) Lake Mendota, (b) Lake Monona, (c) Devil's Lake, and (d) Lake Waubesa. The surface of the ice (i.e., ice/air interface) is denoted as 0 cm. Samples for each lake were collected on the same day from the same location. Cation data for the other three study lakes are presented in Figure S1.

S6; Table S14). PFAS concentrations are low in five of the lakes (i.e., Mendota, Wingra, Devil's, Hope, and Rock), with average aqueous concentrations of 5.6 ± 2.2 ng/L (sum of 36 PFAS). These concentrations agree with available data on Lake Wingra, Devil's Lake, and Lake Mendota.[66,67] Higher winter aqueous concentrations of 20.0 and 28.9 ng/L are observed in Lakes Monona and Waubesa, respectively, as expected based on AFFF impacts to both lakes.[66−70] Only 13 of the 36 PFAS are detected in these samples, with frequent detections of PFOS (97% of samples) and PFBA (89%; Table S15).

In lakes with lower PFAS, PFAS concentrations within the ice are always lower than in the water column. For example, PFAS concentrations are 2.8 ± 1.4 ng/L in ice and 7.9 ng/L in water in Lake Mendota (sum of 36 PFAS; Figure 2a) and 1.8 ± 0.9 ng/L in ice and 2.8 ng/L in water Devil's Lake (Figure 2c). Similar trends are observed for the other three lakes with low PFAS concentrations (Figure S6). There are fewer individual PFAS in ice above the limit of detection compared to the water column. While eight PFAS are detected in water in the five lakes, ice is dominated by PFBA and PFOS. There is no trend in isomers of PFOS; (51 ± 15) % of PFOS in ice is linear, whereas (48 ± 5) % of PFOS in water is linear (Table S16).

Cation concentrations are similarly low in ice compared to water in the five lakes. The cation concentration (sum of sodium, calcium, magnesium, and potassium) for Lake Mendota ranges 8−16 mg/L in ice and is 85 mg/L in water (Figure 3a), while the cation concentration in Devil's Lake ranges from 1 to 3 mg/L in ice and is 11 mg/L in water (Figure 3c). Similar trends observed in the other nonimpacted lakes (Figure S1) and for anions (Figure S2).

These results indicate that both PFAS and inorganic ions are excluded during ice formation in freshwater lakes. The rejection of inorganic ions from ice is consistent with observations made under field conditions in lakes[28] and marine systems,[39−41] as well as under laboratory conditions with freshwater[27,35] and seawater.[34,37,38] While PFAS concentrations in freshwater ice have not been previously reported, there are inconsistent trends with PFAS measurements in ice compared to water in marine environments. For example, PFAS concentrations can be either higher[30,31] or lower[31] in Arctic sea ice cores compared to underlying seawater.

While there is variability in PFAS concentrations in each lake, concentrations at the surface of the ice are consistently higher than deeper in the ice column for these five lakes. This C-shape in PFAS concentrations in ice cores from more pristine lakes is similar to trends observed in laboratory sea ice freezing experiments[33] and for long-chain PFAS in Arctic sea ice.[31] There are three possible mechanisms that could influence PFAS accumulation at the ice surface. First, snow on top of a frozen lake can melt and refreeze to form ice, serving as an atmospheric PFAS source as observed in Arctic sea ice,[30] ice caps,[5,52−55] and glaciers.[56] However, the type of PFAS detected in these lakes suggests that atmospheric deposition is not the major source because ice is dominated by PFOS (i.e., a long chain PFSA), whereas precipitation in the region and globally is dominated by PFCAs.[13−15] Second, ice sublimation could result in elevated PFAS concentrations when water leaves as vapor and ionic species remain behind.[72] Finally, the direction of ice formation can potentially influence PFAS concentrations. Because PFAS can partition to the air−water interface,[50,73−79] it is possible that PFAS may be trapped at the ice surface as it freezes from the top down. While more work is needed to distinguish between the latter two mechanisms in freshwater systems, it is likely that one or both influenced the elevated PFAS concentrations in the ice surface.

PFAS concentrations in ice in Lakes Monona and Waubesa (i.e., the highly impacted lakes) range widely. Four of the ice samples in Lake Monona have lower PFAS concentrations

https://doi.org/10.1021/acs.est.4c04636
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(4.8−12.7 ng/L) compared to the water (20.0 ng/L; Figure 2b). However, a concentration of 75 ng/L is observed at 5−10 cm, which is 3.6 times higher than in water. A similar spike in ice PFAS concentration is observed at the same depth in Lake Waubesa (i.e., 26.3 ng/L compared to 2.5−9.6 ng/L in other ice samples; Figure 2d). Lake Waubesa is hydrologically connected to Lake Monona and serves as a quality assurance measure of the trends observed in the upstream lake. In contrast, cation concentration trends largely agree with the other studied lakes and are 4.8−45.7 times lower in ice compared to the water column (Figure 3b,d). Interestingly, PFAS concentrations at the ice surface (0−5 cm) are lower than the concentrations at ∼5−20 cm depth in Lakes Mendota and Waubesa. It is possible that deposition of snow, followed by melting and refreezing into ice, could dilute PFAS at the ice surface given the lower concentrations of PFAS in wet deposition in the region.[13]

We hypothesize that elevated concentrations observed at 5−10 cm ice depth in Lakes Monona and Waubesa may be attributable to seasonal differences in aqueous PFAS concentrations. PFAS concentrations are 2.6 and 2.8 times higher, respectively, in samples collected during summer 2022 compared to winter 2023 (Figure 4a). Thus, higher aqueous

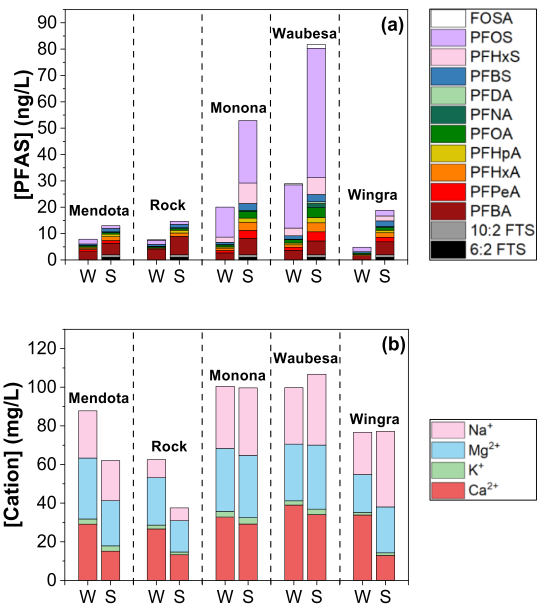

Figure 4. (a) PFAS and (b) cation concentrations in the water column of five different lakes in the winter and summer.

concentrations in the lakes at ice onset could lead to elevated PFAS concentrations in ice. In contrast, cation concentrations are either slightly higher or equal in the winter compared to the summer samples (Figure 4b), in agreement with trends in cation concentrations in ice samples in all lakes. However, higher PFAS concentrations are also observed in the three other lakes in summer compared to winter (i.e., Mendota, Rock, Wingra; Figure 4a), yet there is not a clear increase in PFAS in shallow ice in these systems (Figures 2a and S6). The large variability in aqueous PFAS concentrations in the two available time points suggests that there are seasonal differences in PFAS loadings to these lakes; the summer concentration measurements may not reflect PFAS concentrations at the time of ice onset. Samples collected immediately at the time of ice onset are needed to validate the concentration dependence of PFAS partitioning in the field and further investigation of the causes of seasonal differences in aqueous PFAS concentrations are warranted.

PFAS and DOC Enrichment Factors. To evaluate the impact of PFAS structure on partitioning to ice, we calculate enrichment factors (EF) between the deepest ice sample and the water column (i.e., paired samples that are assumed to be at equilibrium). EF for partitioning of PFAS,[33] nutrients,[39,44] metals,[39] and DOM[37,44] to ice in marine systems are typically normalized to salinity or ion concentrations to enable comparison with small, well-characterized ions. Therefore, PFAS concentrations are normalized to sodium concentrations in each matrix:

$$\text{Enrichment Factor} = \frac{[\text{PFAS}]_{\text{ice}}/[\text{Na}^+]_{\text{ice}}}{[\text{PFAS}]_{\text{water}}/[\text{Na}^+]_{\text{water}}} \quad (1)$$

EF values are calculated for PFAS with the highest frequencies of detection (i.e., PFBA, PFOA, and PFOS), as well as DOC (Figure 5a). Mean EF values are 2.74 (range = 0.98−3.90) for PFBA, 3.14 (2.15−4.86) for PFOA, 4.01 (3.07−4.64) for PFOS, and 4.14 (2.77−6.10) for DOC (Table S9). These mean values are consistently >1, which means both PFAS and DOC are preferentially retained in ice relative to sodium. Similar EF values are obtained when PFAS concentrations are normalized to chloride (Figure S4).

PFAS structure influences the preferential enrichment of PFAS in ice, with the highest enrichment observed for PFOS (i.e., a C_8 PFSA) and the smallest enrichment for PFBA (i.e., a C_4 PFCA). Long chain PFAS have been detected in Arctic sea ice, but not in snow or underlying seawater, suggesting preferential partitioning based on chain length in marine environments.[30] Similarly, enrichment of longer chain PFCAs relative to salinity has been observed in sea ice under laboratory conditions[33,51] and attributed to the preferential ability of long chain PFAS to sorb to ice surfaces,[33] as observed in sediments.[57,80] While the preferential retention of long chain PFAS in ice formed from seawater[30,31,33,51] agrees with our observations in freshwater lakes (Table S9), there are important distinctions between these systems. First, the salinity-normalized EF values in sea ice are lower than our field measurements (i.e., median values of 1.8 for both PFOS and PFOA in laboratory sea ice measurements[33] compared to 3.14 and 4.01 for PFOS and PFOA, respectively, in this study; Table S9). Second, preferential enrichment of PFOS compared to PFOA was not observed in sea ice,[33] which is surprising because PFSAs partition more strongly than PFCAs to the surface microlayer,[50,75] sea spray aerosols,[81] and sediments.[57,80] These differences may be attributable to differences in ionic strength (e.g., extent of brine channels) and/or physical differences in ice crystalline orientation in freshwater versus seawater.[35,38,58] Collectively, our data indicate that long chain PFCAs, as well as PFSAs compared to PFCAs, are preferentially retained in ice in freshwater lakes relative to cations.

DOC (i.e., a measure of DOM concentration) is preferentially retained by ice with similar averaged sodium-normalized EF values as PFOS (i.e., 4.14 and 4.01, respectively). This result is consistent with DOC enrichment in ice relative to inorganic ions in freshwater[27,43] and in seawater.[37,38,41,44,45] Cation- or salinity-normalized enrichment values range from ∼1 to 8 in freshwater[27,43] and ∼1 to 4 in seawater,[37,44] in agreement with our measurements.

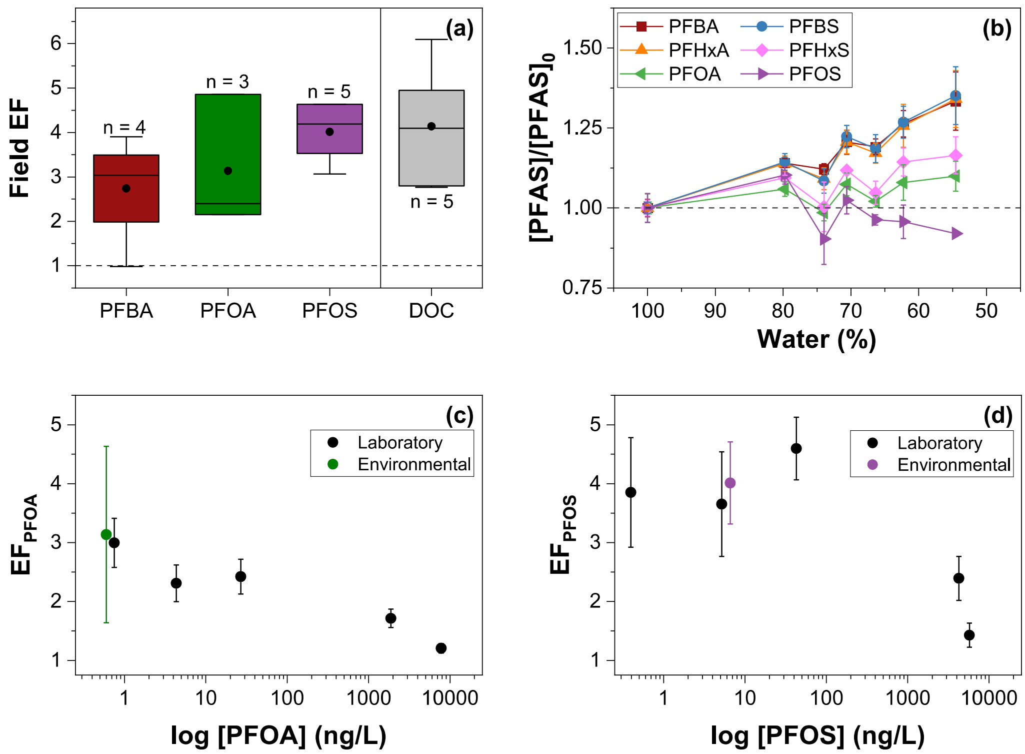

Figure 5. (a) Calculated field EF for PFBA, PFOA, PFOS, and DOC between the deepest point in the ice and the water (i.e., paired samples). Lines of the boxes represent the first and third quartiles. The line within each box represents the median and solid points correspond to the average. Whiskers represent minimum and maximum values. (b) PFAS concentrations in water during laboratory experiments as a function of water depletion (i.e., time of freezing); concentrations are normalized to initial aqueous PFAS concentration. (c) PFOA and (d) PFOS EF values as a function of initial PFAS concentration under laboratory conditions and field conditions. Note that the *x*-axis is on a log scale. Error bars in panels (b−d) correspond to the standard deviation of triplicate samples (laboratory samples) or the standard deviation of all values from different lakes (environmental samples).

Consistently, DOM in ice is lower specific UV absorbance ($SUVA_{254}$) and E_2:E_3 than DOM in water (Table S6). While these trends suggest that DOM in ice is less aromatic[82] and lower in apparent molecular weight,[83] more work is needed to evaluate these proxies in frozen DOM. Interestingly, the negative relationship between $SUVA_{254}$ and E_2:E_3 commonly observed in aquatic systems[84] is not observed in this data set (Table S6). The trends in $SUVA_{254}$ are consistent with past observations that humic-like, terrestrially derived (i.e., highly aromatic) DOM is less efficiently incorporated into ice in freshwater[27,43] and seawater[37,44] as assessed using fluorescence and specific absorbance. However, the E_2:E_3 trends are contrary to observations that DOM retained in sea ice is lower in molecular weight than DOM in bulk seawater as determined using size exclusion chromatography.[37,45]

Ice Partitioning Under Controlled Conditions. Laboratory experiments with Lake Mendota water (Table S7) amended with selected PFCAs and PFSAs are used to quantify PFAS and cation partitioning to ice as a function of time and PFAS concentration. PFAS concentrations are constant in ice as it forms (Figure S7a) and are 1.6 times lower than initial aqueous concentrations on average. In contrast, PFAS concentrations in water increase as ice forms (Figure 5b), demonstrating that PFAS are concentrated in water as they are excluded from ice in these small volumes. Collectively, the moles of PFAS increase in ice and decrease in water as ice forms (Tables S19 and S20; Figure S9).

PFAS structure determines its extent of exclusion during freezing. PFBA, PFBS, and PFHxA are excluded readily, as demonstrated by their increasing aqueous concentration as ice freezes (Figures 5b and S8), while PFHxS shows modest exclusion from ice. In contrast, PFOA shows no exclusion and PFOS shows preferential uptake by ice with decreasing water percentage. The preferential exclusion of smaller PFAS from ice agrees with observations in lakes (Figure 5a).

Cations are also excluded from ice under controlled conditions. As observed for PFAS, cation concentrations are constant within ice as it freezes (Figure S7b) and increase in water as more ice is formed (Figure S7c). Similar increases in aqueous ion concentrations have been observed in laboratory freezing experiments.[27,35] Although the differences in slopes are not significant, sodium and potassium are more readily excluded than divalent cations.

Freezing experiments conducted with PFAS concentrations ranging 4 orders of magnitude demonstrate that PFAS EF values calculated using paired samples are modestly impacted by PFAS concentration (Figures 5c,d, and S10). For example, average EF values for ∼1 ng/L PFAS are 1.81 ± 0.27 for PFBA, 2.99 ± 0.42 for PFOA, and 3.85 ± 0.93 for PFOS (Table S22). These values are within the ranges of the EF values calculated under field conditions for these compounds. Average EF values decrease by 20% on average as the nominal PFAS concentration increases to 10 ng/L (Table S22). At the highest PFAS concentration of ∼10,000 ng/L, EF values decrease by 54% on average relative to the lowest PFAS concentration studied (i.e., 1.14 ± 0.01 for PFBA, 1.20 ± 0.08 for PFOA, and 1.43 ± 0.21 for PFOS; Table S21). Average EF values of the other studied PFAS are 1.09 ± 0.05 for PFHxA,

https://doi.org/10.1021/acs.est.4c04636
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1.09 ± 0.05 for PFBS, and 1.23 ± 0.06 for PFHxS under the same condition.

Both laboratory and field data indicate that longer chain PFAS are preferentially retained in ice relative to shorter chain PFAS and that PFSAs (e.g., PFOS) are preferentially retained compared to PFCAs (e.g., PFOA). Furthermore, PFAS enrichment in ice decreases with increasing initial PFAS concentration over large ranges in PFAS concentration, with small changes in EF values observed over the concentration range observed in lakes (Figure 5 and S10). The agreement between laboratory and field data demonstrate that laboratory experiments provide a practical method to evaluate and confirm trends in PFAS behavior (e.g., the impact of PFAS structure on exclusion from ice). Furthermore, these data support our hypothesis that PFAS concentrations in ice are driven by PFAS concentrations in water when it freezes and indicate that ice is more efficient at rejecting PFAS when these compounds are present at higher concentrations.

■ ENVIRONMENTAL IMPLICATIONS

As many lakes experience freezing in the winter, it is important to understand how PFAS partition within ice to describe their environmental fate. While PFAS concentrations in ice are typically lower than in the underlying water column, PFAS are preferentially retained in ice relative to cations and thus do not follow conservative behavior expected for small ions. Similar trends are observed for DOM. Elevated PFAS concentrations observed at the ice surface relative to deeper ice in some cases may be attributable to sublimation or air−water interfacial partitioning. Our combined laboratory and environmental results suggest that PFAS concentrations found within ice reflect concentrations in water at the time of freezing, with preferential retention of longer chain PFAS.

The results of this study have implications for human and ecosystem exposure to PFAS, as well as for PFAS fate in freshwater systems. We observed higher PFAS concentrations in ice in Lakes Monona and Waubesa (Figure 2b,d), which are highly impacted lakes. However, we expect that dermal contact with contaminated ice during ice fishing is likely a minor exposure pathway, particularly compared to ingestion of fish in these lakes.[71]

The ability of ice freezing and melting to impact PFAS concentrations in lakes will vary based on lake morphology. In cases where a large fraction of the lake freezes, preferential exclusion of PFAS from ice could result in elevated aqueous concentrations as observed in our laboratory experiments (Figure 5b) and as observed for mercury.[6] However, this process is expected to be minor in the large lakes included in this study because ice is a small fraction of the volume (e.g., ice cores of <30 cm compared to average depths of <5−13 m; Table S3). We observed the opposite trend of lower aqueous PFAS concentrations in winter compared to summer (Figure 4a), which may be attributable to decreased runoff during the winter or potentially limitation of atmospheric deposition to lakes due to the physical barrier formed by ice at the lake surface. More research is needed to identify the factors that determine seasonal variability of PFAS concentrations in these lakes.

While melting ice has been identified as a potential source of PFAS to Arctic seawater,[30−32] our data suggests that melting ice is more likely to lead to modest dilution of PFAS concentrations in freshwater lakes. As with the potential for elevating aqueous concentrations during freezing, the extent of dilution of PFAS in water in the spring when ice melts will vary based on the volume of ice, with larger impacts expected in lakes with larger ice volumes. As a result, it is important to monitor fish and consider health advisories on a seasonal basis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.4c04636.

File 1 (.docx) includes additional experimental details; cation, anion, DOC, and PFAS concentrations for all lakes and laboratory experiments; and pH, E_2/E_3, and $SUVA_{254}$ values for all lakes. (PDF)

File 2 (.xlsx) includes PFAS concentrations in environmental samples (XLSX)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Josie Jauquet, Emily Schmitt, and Samuel Bieber for assistance with sample preparation, James Lazarcik for maintaining instrumentation, Jonathan Remucal for map preparation, Patrick Gorski and the Wisconsin Department of Natural Resources for assistance with sampling on Hope Lake and Devil's Lake, and Martin Shafer for helpful discussions. Funding for this study was provided by Wisconsin Sea Grant (R/HCE-47) and a National Science Foundation Graduate Research Fellowship (K.G.).

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