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Influence of Temperature, Sunlight and Wind on the Mobilization of Propylene Glycol From Airport De-Icers by Rainfall

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ABSTRACT

Commercial anti-icers and de-icers (CADs) are essential for safe winter operation; yet, their mobilization remains poorly understood, limiting the ability of airport operators to optimize treatment processes, thus presenting a significant risk to freshwater ecosystems. This study investigated the impact of meteorological conditions and durations on CAD mobilization during rainfall. Two common commercial formulations were subjected to a range of controlled meteorological conditions, including temperature (+18°C, +5°C and −5°C), wind and sunlight, over 1 or 2 weeks, followed by simulated rainfall, where glycol in runoff was analysed by HPLC every minute. Exposure to sunlight and wind substantially decreased propylene glycol mobilization (6.9%–45.3% decrease). However, higher temperatures increased runoff concentrations of the anti-icing fluid (31.6%–36.9% increase). There were significant differences in mobilization rates between commercial products ($p < 0.045$). Weathering duration had a minimal effect on mobilization. These results offer critical insights for airport operators in contaminant mobilization and treatment.

1 | Introduction

The application of commercial anti- and de-icing chemicals (CADs) is a critical requirement for ensuring safe winter operations at airports to prevent and remove ice on aircraft and ground surfaces (ACRP 2020; International Standards Organisation (ISO) 2020; Secretary of State for Transport 2018). In a given de-icing season, more than one million litres of CADs are used on aircraft and another million litres are used on ground surfaces at a typical international airport (Castro et al. 2005; Freeman et al. 2015; United States Environmental Protection Agency 2012). Freeze-point depressants (FPDs)—commonly propylene glycol, ethylene glycol or acetate/formate salts—are the active ingredients in CADs (Fay and Shi 2012; Schweigert and Poissonnier 2016) that lower the freezing point of water to prevent the build-up of snow and ice (Barbelli et al. 2012; Stefl and George 2014). Depending on viscosity and holdover time, CADs are further categorized for de-icing (for removal of frozen material) or anti-icing (for prevention of ice build-up) for both aircraft and ground surfaces. Aircraft CADs are classified into different types depending on their intended use (ACRP 2009; Freeman et al. 2015): Type I are exclusively utilized for de-icing aircraft (International Standards Organisation (ISO) 2007a); Type II

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Summary

- A laboratory experiment to quantify the impacts of weathering on de-icer mobilization.
- Sunlight and wind significantly decreased anti-icer mobilization.
- Higher temperatures resulted in more anti-icer mobilization.
- Differences were observed between de-icers and anti-icers.
- This initial study provides valuable insights for airport operators and stormwater management.

offer extended anti-icing properties but remain primarily used for de-icing; Type III are a compromise between them but are less commonly used; and Type IV are primarily anti-icers (International Standards Organisation (ISO) 2007b).

After application, approximately 75%–80% of CAD fluids drip or are deflected onto surrounding surfaces (Castro et al. 2005; Switzenbaum et al. 2001), with the remaining fluid dispersed, for example, by wind or jet blasts (Wayson et al. 2000) or containing additives designed to shear excess CADs during take-off (2010; ACRP 2009; United States Environmental Protection Agency 2012). Subsequent rain events mobilize residues into airport drainage systems, due to the high water solubility of FPDs (Figure 1) (ACRP 2009; Corsi et al. 2001). Given the prevalence of impervious surfaces (e.g., asphalt and concrete), runoff volumes can be high, especially as drainage systems are designed to transport water away from critical areas (ACRP 2009, 2012). Consequently, large volumes of surface runoff may overwhelm surface water treatment systems, such as moving bed biofilm reactors (Hassani et al. 2014) and aerated wetlands (Freeman 2016). The biological mechanisms that break down FPDs in these treatment systems operate most effectively under steady contaminant loading and flows (Tchobanoglous et al. 2021); therefore, storage reservoirs are often used to buffer influxes, but predicting contaminant loads remains challenging (ACRP 2012; Shi et al. 2017).

In the case of ineffective treatment, organic pollution from CADs can lead to severe ecological consequences in receiving waters, most notably the proliferation of undesirable river biofilms (URBs, also called 'sewage fungus') (ACRP 2014; Exton et al. 2023; Nott et al. 2020), which thrive on high biochemical oxygen demand (BOD) inputs (Exton et al. 2024a; Quinn and Mcfarlane 1985). URBs rapidly alter community structure (Gray 1985), deplete dissolved oxygen (Curtis et al. 1971; Hickey 1988a) and stress macroinvertebrates and fish (Gray and Hunter 1985; Hickey 1988b; Quinn and Mcfarlane 1989). URBs are diverse polymicrobial, heterotrophic biofilms used as bioindicators of organic pollution that proliferate rapidly in saprobic rivers, dominating the ecosystem (Exton et al. 2024a). Although URBs have been shown to proliferate in rivers contaminated with inadequately treated CAD runoff (Exton et al. 2023; Nott et al. 2020) and key taxa can utilize common FPDs for growth (Exton et al. 2024b), the specific mechanisms by which they utilize the carbon source have not been directly studied. Further environmental damage can arise from the proprietary additives in CAD formulations—often non-ionic surfactants, flame retardants, corrosion inhibitors (Corsi et al. 2006; Samuels et al. 2006) or thickeners (Adeola et al. 2009; Seeland et al. 2011)—which pose toxic risks to aquatic biota (ACRP 2009; Pillard 1995; Pillard and DuFresne 1999), despite being a minor constituent in formulations (Ramakrishna and Viraraghavan 2005; United States Environmental Protection Agency 2012).

However, substantial knowledge gaps remain regarding how environmental conditions between application and precipitation events influence subsequent CAD mobilization (Freeman et al. 2015). Therefore, we present an initial investigation into the mobilization of CADs during rainfall following exposure to different meteorological treatments. During the time between CAD application and rainfall, airport operators observed that deposited CADs often form thick, sticky residues (pers.

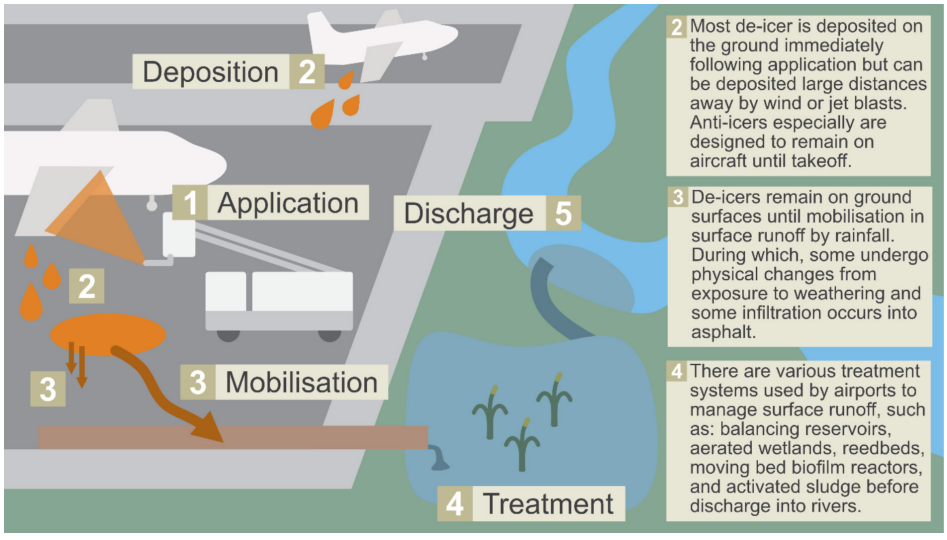

FIGURE 1 | Schematic overview of the main transport pathway of airport de-icers: (1) application of de-icers; (2) deposition on ground surfaces; (3) mobilized in surface runoff; (4) de-icer containing surface runoff is treated; (5) treated effluents are discharged into receiving waters.

communication, M. Murphy). Sunlight may promote evaporation of volatile or water fractions (Ingram et al. 2017; Kawamura and Mackay 1987) and photochemical reactions; wind may hasten drying through convection (Sutton and Simpson 1934); and colder temperatures may increase viscosity, altering the physical and chemical properties of CADs. Propylene and ethylene glycol, common FPDs in CADs, are expected to be non-volatile from water and dry surfaces (Lyman 1990). Such changes could influence how quickly or completely the glycol fraction is released during the next storm, yet systematic data on this behaviour remain limited, posing additional challenges for the effective treatment of airport surface runoff.

This study aims to determine how key meteorological conditions affect the mobilization of CADs from a surface by rainfall in a laboratory setting. We hypothesized that (i) sun and wind weathering treatments would lead to greater evaporation of the water fraction, resulting in drier and less soluble residues; (ii) lower temperatures would reduce mobilization due to increased viscosity of CAD residues; (iii) prolonged exposure to meteorological treatments would further exacerbate influences on CAD mobilization rates, such as increased dehydration (sun and wind) or viscosity (low temperature); and (iv) the more viscous Type IV aircraft anti-icers would have lower mobilization rates than Type I aircraft de-icers (Type I).

2 | Methods

This study was conducted under highly controlled conditions to reduce the influence of external complications (such as substrate effects) and directly examine the impact of environmental treatments (temperature, sunlight and wind) over two durations (1 and 2 weeks) on the mobilization of airport anti-/de-icers by rainfall. The substrate (i.e., tile) on which the CADs were dispensed was carefully selected to ensure that only rainfall and surface runoff processes would impact mobilization. An artificial rainfall tower was used to generate controlled, repeatable rainfall events of known intensity and duration. The rainfall test container was designed to collect all rainwater and any CAD mobilized by raindrop impact and runoff. Runoff was sampled every minute during the 5-min mobilization tests for quantification of CADs using high-performance liquid chromatography (HPLC).

2.1 | Sample Preparation

For each sample, 5 mL CAD was spread evenly across a tile using a precision pipette, leaving an approximately 1 cm border along each edge as a buffer to minimize the likelihood of spillage.

The CADs used in this study were Kilfrost DF Plus (Kilfrost LTD 2019a) and Kilfrost ABC S Plus (Kilfrost LTD 2019b) (herein referred to as 'DF' and 'S+') as they are common aircraft de- and anti-icers, respectively. Both are propylene glycol based but with different proportions of the FPD (96.99%v/v for DF and 44.28%v/v for S+) and additives. DF is a Type I de-icing fluid with an orange dye, whereas S+ is primarily a Type IV anti-icer but can also be used for de-icing purposes and is coloured green—dyes are added by the manufacturer for easy identification.

TABLE 1 | A summary of the meteorological conditions in each treatment.

Treatment	Cold	Cool	Warm	Sun	Wind
Temperature	−5°C	+5°C	+18°C	+18°C	+18°C
Sunlight	✗	✗	✗	✓	✓
Airflow	✗	✗	✗	✗	✓

A glazed, matt ceramic tile [Matrix Antique White Matt Tile (14.8×14.8 cm), Topps Tiles] was selected as the substrate following initial testing during method development (Section 2.3.). These tiles were broadly non-porous with minimal surface texture, allowing us to isolate weather conditions as the experimental variables. The tiles were then placed into clear plastic containers [18×25×9 cm, Beaufort (104601)], which were either left open or closed for exposure to different environmental conditions.

2.2 | Artificial Meteorological Conditions

Three aspects of weather were evaluated: temperature, sunlight and airflow (Table 1). First, the effect of temperature was determined by positioning tiles inside sealed, clear plastic containers and placing them within a temperature-controlled freezer, fridge or glasshouse. The threshold for automatic de-icing at airports is typically 5°C (pers. communication, M. Murphy). Therefore, temperatures of +5°C ('cool') and −5°C ('cold') were chosen to represent the threshold temperature and a colder winter temperature in the UK. For the 'warm' temperature treatment, a glasshouse was used (+18°C). Samples (i.e., CADs applied to tiles) were sealed inside plastic containers to reduce the impact of variable humidities in the different settings. Additionally, an opaque cover (i.e., cardboard box) was placed over the sealed containers in the glasshouse for the 'warm' treatment to block the influence of sunlight (Supplementary A-1c). Thus, all temperature treatments occurred in the absence of sunlight exposure.

Second, the effects of sunlight ('sun') and airflow ('wind') were tested in the 'warm' conditions of the glasshouse (+18°C). For the 'sun' treatment, the same sealed, plastic containers were used, without an opaque cover. For the 'wind' treatment, containers were instead left open, without a lid or opaque cover, and a desk fan was positioned to provide additional airflow (Supplementary A-1a,b). The 'warm' treatment served as the control for the 'sun' and 'wind' treatments, that is, no sunlight exposure or wind.

Weathering was tested over 2 durations: 1 and 2 weeks. Identical samples and meteorological conditions were used for both exposure durations to evaluate the effect of exposure time between CAD application and rainfall event. In addition, freshly applied samples ('untreated') were also tested as an overall control for no weathering and were exposed to rainfall immediately after CAD application.

2.3 | Rainfall Simulation and Runoff Sampling

The gravity-fed rainfall tower (CHAP Soil Science Unit, Cranfield University, UK) is approximately 9 m tall with

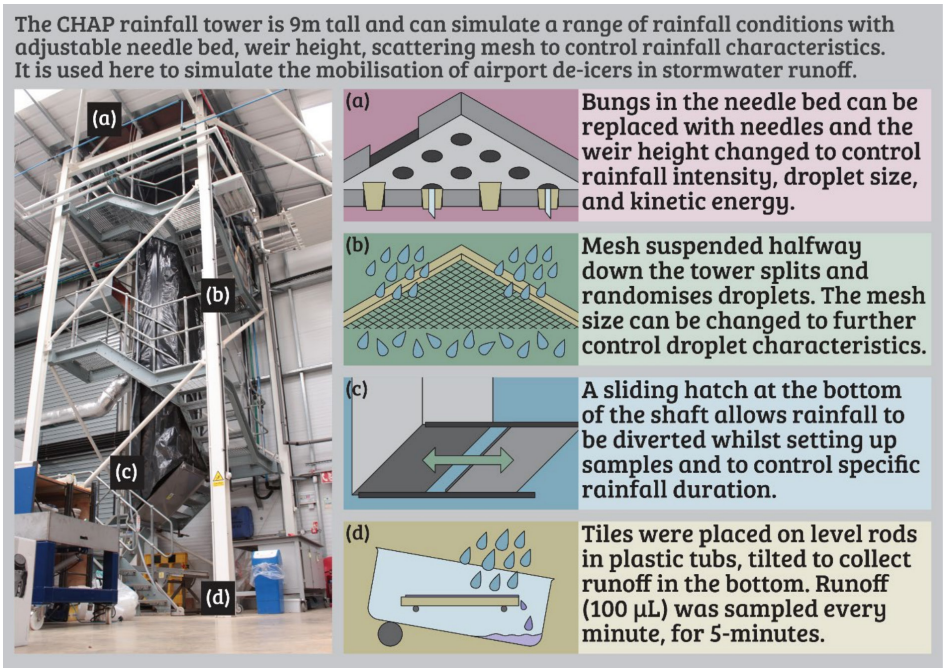

FIGURE 2 | The labelled key features of the CHAP rainfall tower and diagrams of each key feature, including (a) the needle bed and weir, (b) the mesh layer, (c) cover hatch and (d) runoff trays.

a head tank that fills a needle bed with de-ionized water (Figure 2). Rainfall characteristics (such as droplet size, kinetic energy and intensity) can be controlled through the weir height, number of needles used and size of needles. Droplets then fall from hypodermic needles and hit a suspended mesh, which splits and randomizes them before hitting the ground as artificial rainfall. The height of the rainfall tower is to allow droplets to reach terminal velocity under gravity when they impact the sample.

After exposure of CADs to different treatments, tiles were placed in a runoff tray [a modified 18×25×9 cm plastic container, Beaufort (104601); Supplementary A-1a,b and Figure 2d] under the rainfall tower and exposed to the artificial rainfall (12.26 ± 0.90 mm/h, 5 min). The runoff tray was designed to allow for straightforward collection of runoff by tilting the container to direct flow to a single sampling point, with internal posts to maintain the tiles horizontal position. The runoff tray, therefore, had a larger surface area than the sample tiles, so the ratio of surface areas was used to determine the dilution factor which was accounted for in future calculations (i.e., to determine the amount of CAD lost from tiles) (Supplementary A-2c). Over the 5-min period, 38.68 mL of rainfall was collected in total within the runoff tray, with 22.38 mL (58%) directly impacting the sample tile. Every minute, runoff was briefly mixed by pipette and a sample taken (100 µL) before diluting to 1 mL (i.e., 1:10 dilution) with ultrapure de-ionized water; diluted runoff samples were refrigerated (4°C) overnight and analysed the following day.

The rainfall tower was calibrated to ensure evenly distributed rainfall of the desired intensity (Allton et al. 2007). Firstly, a 28-mm weir was chosen for the needle bed, and the configuration of needles was optimized for even rainfall across the target area. The distribution was evaluated using pre-weighed catchment cups arranged in a grid under the rainfall tower. After running the tower for several minutes to equilibrate rainfall, the sliding hatch was opened to collect rainfall in catchment cups for 15 min before closing the hatch, drying the outside of collection cups and re-weighing to accurately determine the mass of water, from which intensity (mm/h) was calculated (Equation (1)). Before every use, a 5-min 'performance check' was undertaken to ensure similar rainfall intensity between each set of experiments.

$$intensity\ (mm/hr) = \frac{rain\ collected\ (cm^3)}{surface\ area\ (cm^2) \times time\ (hr)} \times 10 \quad (1)$$

2.4 | Replication and Analyses

To mitigate the potential for variability between samples, three replicates for each condition were prepared and tested (direct replication); a fourth tile was also prepared in case of any problems during the treatments, such as the tile not quite being level leading to unintended spillage of the CAD from the tile. Sample tiles were chosen at random for rainfall treatment and analysis.

2.4.1 | Laboratory Analysis

Diluted runoff samples were analysed by HPLC (Agilent Technologies 1200 series, USA) (10.0 µL injection volume, 0.400 mL/min flow rate, 21–24 bar, 60°C) using a ROA Rezex Phenomenex (150×7.8 mm) column with a refractive index detector and H_2SO_4 (0.5 mM) mobile phase. Propylene glycol (extra pure, analytical specification, Fisher Chemical) was diluted in ultra-pure de-ionized water to make standards of 3.0%v/v,

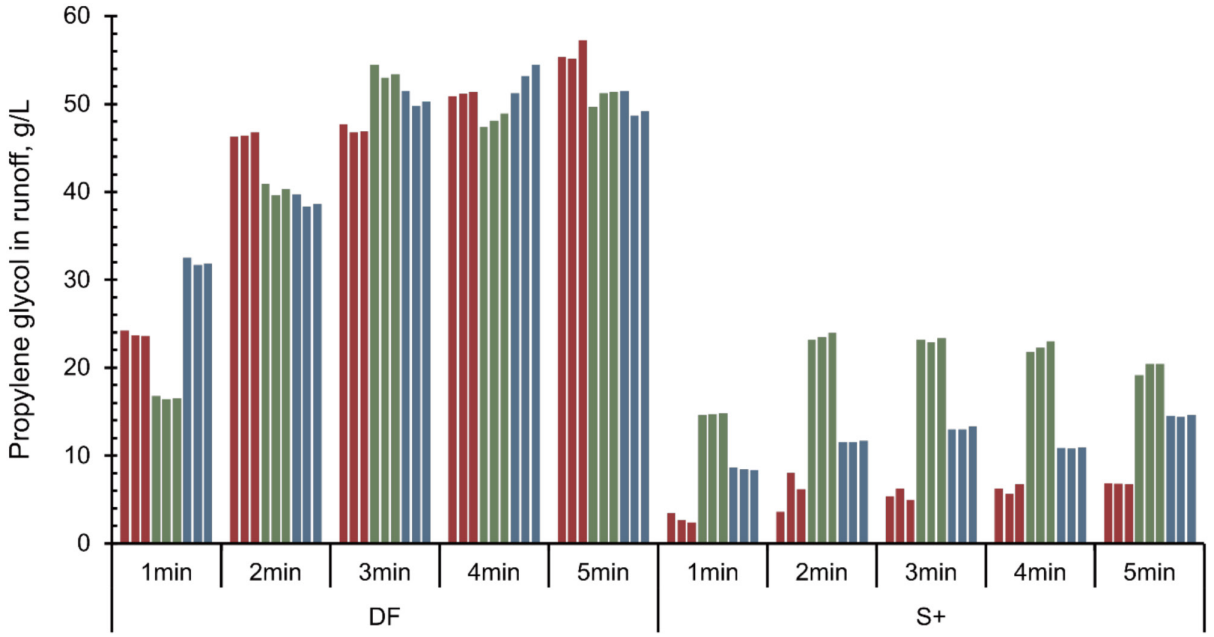

FIGURE 3 | Comparing replicates of propylene glycol concentration in runoff to test homogenization of runoff for cold-2wk samples of the airport de-icer **Kilfrost DF Plus (DF)** and **anti-icer Kilfrost** ABC-S Plus (S+). Colour denotes each tile (direct replicates), and clustered columns of each colour are runoff replicates for that tile (sample replicates).

2.5%v/v, 2.0%v/v, 1.5%v/v, 1.0%v/v and 0.5%v/v (52.0–312.0 g/L propylene glycol) to create the calibration curve. Further information, including calibration curves and quality control information, is provided in Supplementary B-1.

2.4.2 | Data Analysis and Statistics

Peaks for each sample were integrated, and propylene glycol concentration was calculated from the calibration curve in the ChemStation companion software (Agilent Technologies Inc., USA). Data were transformed (e.g., to account for runoff-tray and runoff sample dilutions) and plotted in Microsoft Excel (Equation (2)). The density of propylene glycol is 1.04 g/mL (National Institute of Standards and Technology 2008) and has been used in volume-mass calculations throughout. Mobilization per minute was calculated using the change in mass of propylene glycol in runoff between sequential measurements (i.e., ΔProG/min). The 'percentage mobilization' of propylene glycol relative to starting concentration was calculated using the percentage of propylene glycol in each CAD. Statistical analyses were performed in SPSS Statistics (IBM, New York). Data did not fulfil the assumptions of ANOVA (data were not normally distributed, Shapiro–Wilk test, $p = 0.0002$), so the Kruskal–Wallis test of difference was used to compare treatment conditions after 5 min of rainfall, with pairwise comparison post hoc test.

$$vol.\,ProG\,(mL) = undiluted\ conc.\,(mL/L) \times vol.\,rain\,(L/min) \times time(min) \quad (2)$$

2.5 | Method Development

These experiments were designed as a preliminary investigation to assess the changes in the erodibility of de-icers following exposure to weather conditions. Several factors in the experimental needed to be tested to ensure consistency between sample runs, including substrate type, CAD application volume and runoff homogenization.

Firstly, the choice of substrate for the tests was important, in terms of surface texture and porosity. Although a more realistic substrate would be similar to materials found at an airport (concrete and bitumen), their semi-porous and textured nature would likely impact runoff and repeatability—especially at the small volumes tested. Therefore, initial testing was conducted to find a suitable material. Unglazed domestic house tiles were proposed [Quarry Autumn Blend Tile (15.0 × 15.0 cm), Topps Tiles (709218)], as an approximation for airfield ground surfaces whilst maintaining regular uniformity between samples (Supplementary A-3a). However, during initial testing, a large proportion of CAD appeared to infiltrate into the porous tiles, which would have substantially affected runoff and variability in mobilization measurements. Consequently, glazed, matt tiles were tested to provide a non-porous surface but maintain some texture to the surface—these were found to be more suitable following some initial tests (Supplementary A-3b). Aluminium and glass plates were also tested; however, CADs quickly clumped together, and the surface was highly slippery, thus increasing the likelihood of spilling material from them during transport and invalidating those samples (Supplementary A-3c). Therefore, glazed, matt tiles were selected as the substrate [Matrix Antique White Matt Tile (14.8 × 14.8 cm), Topps Tiles (696128)].

Secondly, it was important to match the volume of CAD applied to the tile size to maximize the volume applied whilst not introducing other sources of error (e.g., from spills). Different amounts of CAD were therefore trialled: 2, 5 and 10 mL. We found that using only 2 mL often resulted in the CAD mostly being removed from the tile by various kinds of weathering, whereas 10 mL often spilt off the tile during weathering or when

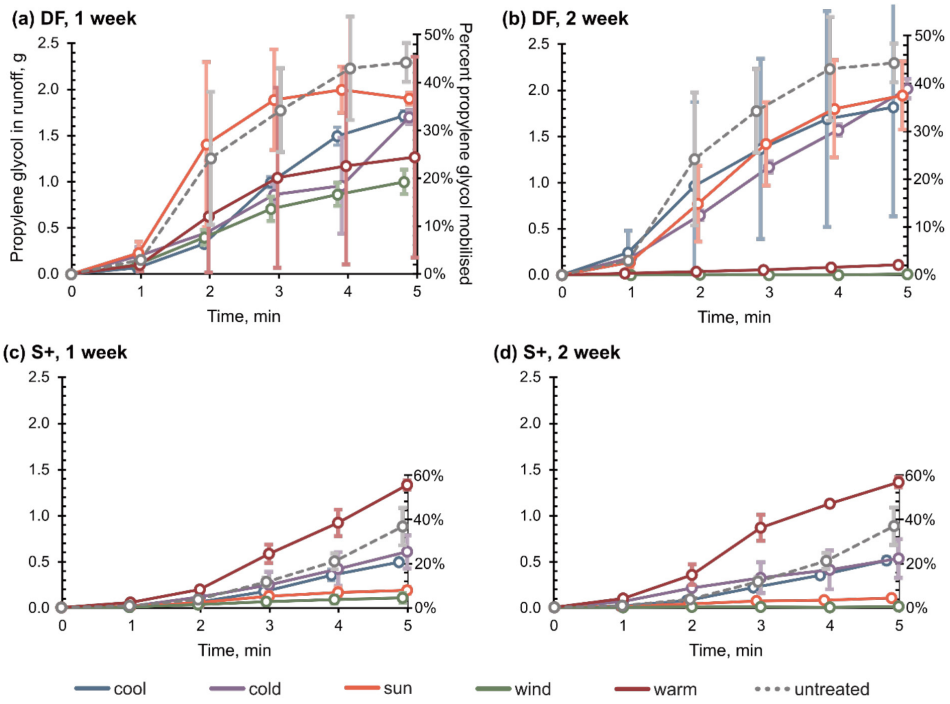

FIGURE 4 | Mean cumulative amount of propylene glycol in runoff from the aircraft de-icer **Kilfrost DF Plus (DF)** and **anti-icer Kilfrost** ABC-S Plus (S+) following exposure to meteorological conditions for 1–2 weeks. (a) DF, 1 week; (b) DF, 2 weeks; (c) S+, 1 weeks; (d) S+, 2 weeks. Error bars denote 1 standard deviation from the mean. Second y-axis shows the percentage propylene glycol mobilized from tiles relative to starting concentration in the commercial formulation.

transporting to the rainfall tower. The loss of material for both 2 and 10 mL applications would lead to inaccuracies in results, so 5 mL aliquots were deemed optimal. Runoff rates of 5 mL CAD were then visually assessed to determine sampling duration and frequency, which found substantial removal of CAD within the first couple of minutes, and often all CAD was visibly gone within 5 min. Therefore, it was decided that runoff should be sampled every minute for 5 min.

Third, before sampling for HPLC analysis, runoff was mixed by pipette. To verify this was effective homogenization, triplicate samples were collected at each time point for the cold-2wk treatments (sample replicates) (Figure 3), alongside the three tiles for each treatment condition (direct replicates). Analysis of runoff concentrations revealed minimal variability among sample replicates (standard deviation was 0.15–1.33 g/L for DF and 0.05–1.80 g/L for S+) that was smaller than variability between tiles [direct replicates; standard deviations were < 3.1% of the mean of sample replicates for all but one tile with S + CAD (red columns for S + in Figure 3)]. Therefore, the pre-sampling mixing procedure was deemed effective, allowing for a single, well-mixed sample to be considered representative of runoff from each sample tile at each time point in subsequent treatments.

3 | Results

Simulated meteorological treatments had a significant impact on the mobilization of CADs in runoff, with the greatest effects observed in those experiencing 'drying effects' (i.e., sun and wind). After treatments, some differences between treatments were initially discernible in visual observations of tiles (e.g., Supplementary A-4). Both DF and S+ became visibly more viscous in 'cold' and 'cool' treatments, likely a result of the lower temperature, and were most pronounced in 'cold' conditions (−5°C) where there was also some visible CAD loss (Supplementary A-4c). There was minimal change in appearance for 'warm' samples with some changes for DF after 2 weeks. However, in 'sun' and 'wind' treatments, there were profound changes to both CADs (Supplementary A-4b). There was a substantial drying out of the CADs and samples had the appearance of a thin, dry film rather than a viscous liquid; these effects were most prominent in 'wind', which had both sun and wind influences. For many 'wind' samples, especially in S+, little CAD remained visible on tiles after 2 weeks, which may suggest a loss of propylene glycol through evaporation. However, propylene glycol is described as non-volatile in water and has a Henry's law constant of 1.3×10^{-8} atm·m^3/mol, implying that it would not readily evaporate under these treatments. There were also substantial visual differences between the two CADs tested.

3.1 | Influence of Specific Meteorological Conditions on CAD Mobilization

The treatment type, the duration of weathering, the choice of CAD and rainfall duration all had impacts on the mobilization of propylene glycol in runoff (Figure 4). After 5-min of rainfall, there was often no longer CAD visible on tiles; however, HPLC results indicate that, after 5-min of rainfall, < 60% of propylene glycol was mobilized in runoff.

Firstly, for DF, there was substantial mobilization of propylene glycol in all treatments. However, there was negligible propylene

glycol mobilization in both 'warm' and 'wind' 2-week treatments (Figure 4b). Visual observations of tiles suggest this could be a consequence of drying effects and loss of CAD to evaporation but remain unclear why this was not influential on 'sun' samples, which were sealed (like 'warm') but uncovered (like 'wind'). There were also limited differences between different winter temperatures (−5°C and +5°C), indicating that a colder temperature does not play a substantial role in influencing the mobilization of CADs ($p \geq 0.545$; Table 2a). The large standard deviation in warm-1wk reflects high variability between replicates, with some replicates having negligible mobilization and some having substantial amounts of mobilization. Furthermore, after 1-week treatment duration, there were no significant differences in runoff amount after 5 min of rainfall between any treatment in DF samples ($p \geq 0.388$; Table 2a). After a 2-week treatment duration, there were significant differences between wind-2wk, warm-2wk and all other weathering treatments after 5-min rainfall ($p \leq 0.020$; Table 2a). Untreated-0wk samples generally had more propylene glycol in runoff, as would be expected, demonstrating that weathering treatments affected CAD mobilization. However, only comparisons with wind-2wk and warm-2wk yielded any significant difference ($p < 0.001$ and 0.007, respectively).

Secondly, for S+ samples, treatments had an impact on runoff. Exposure to 'cool' and 'cold' treatments results in approximately 21.7%v/v–26.5%v/v of propylene glycol mobilization after 5 min compared to untreated-0wk (38.5%v/v) and 'warm' (58.4%v/v–59.2%v/v) treatments (Figure 4). In contrast, 'sun' and 'wind' treatments had substantially lower mobilization amounts (0.5%v/v–8.3%v/v), resulting in a significant difference between sun-2wk and wind-2wk when compared to warm-2wk samples ($p \leq 0.040$; Table 3).

Comparing the two CADs, there was substantially less propylene glycol in S+ samples' runoff (Figure 4c,d) compared to DF. This was not unexpected, as S+ has a much lower FPD concentration (~442.8 g/L propylene glycol in S+, compared to 969.9 g/L in DF) and, as an anti-icer, is much more viscous. Therefore, comparing the percentage of propylene glycol mobilized from the tile relative to its starting concentration, there is a lower disparity between DF and S+, but some significant differences

TABLE 2 | Pairwise comparisons from Kruskal–Wallis test of difference (p values stated) in the amount of propylene glycol in runoff after 5-min rainfall (mL) comparing different weathers. For (a) Kilfrost DF Plus for 1 and 2 weeks and (b) Kilfrost ABC-S Plus for 1 and 2 weeks, where * indicates a significant difference ($p = 0.05$).

(a) Kilfrost DF Plus

	1wk					2wk				
	Cool	**Cold**	**Warm**	**Sun**	**Wind**	**Cool**	**Cold**	**Warm**	**Sun**	**Wind**
Cool		1.000	0.388	0.735	0.388		0.545	0.020	0.714	0.004*
Cold			0.388	0.735	0.388			0.003*	0.812	<0.001*
Warm				0.267	1.000				0.007*	0.589
Sun					0.267					0.001*
Wind										

(b) Kilfrost ABC-S Plus

	1wk					2wk				
	Cool	**Cold**	**Warm**	**Sun**	**Wind**	**Cool**	**Cold**	**Warm**	**Sun**	**Wind**
Cool		0.880	0.290	0.619	0.400		0.897	0.261	0.342	0.160
Cold			0.364	0.517	0.321			0.321	0.280	0.125
Warm				0.120	0.057				0.038*	0.012*
Sun					0.730					0.650
Wind										

TABLE 3 | Pairwise comparisons from Kruskal–Wallis test of difference (p values stated) on the percentage of propylene glycol mobilized in runoff, relative to starting concentration in the CADs comparing Kilfrost DF Plus to Kilfrost ABC-S Plus, after 5-min rainfall, where * indicates a significant difference ($p = 0.05$).

(a) 1 week					(b) 2 weeks				
Cool	**Cold**	**Warm**	**Sun**	**Wind**	**Cool**	**Cold**	**Warm**	**Sun**	**Wind**
0.437	0.666	0.045*	0.101	0.388	0.231	0.244	0.001*	0.040*	0.966

remain (Figure 4), for example, warm-1wk, warm-2wk and sun-2wk treatments (Table 3). Expressing mobilization as a percentage of propylene glycol concentration provides a direct basis for comparison between CADs; however, the two products are used for different purposes (anti-icing vs. de-icing) and, therefore, in different quantities. As such, the more relevant metric for environmental management and airport operators is the amount of FPD in runoff (e.g., g/L) and biological oxygen demand (BOD_5).

3.2 | Effect of Weathering Duration on CAD Mobilization

Generally, the duration of each treatment had little influence on the amount of propylene glycol mobilized, except for 'wind' treatment of DF (Figure 4a,b). Although there were visible differences in the samples for some treatments (e.g., 'sun', 'wind' and 'warm' became thin, dry films), the only condition where the duration of weathering had a significant influence on the amount mobilized after 5-min rainfall is the aforementioned 'wind' treatment of DF ($p = 0.033$; Table 4).

3.3 | The Impact of Rainfall Duration on CAD Mobilization

Longer durations of rainfall broadly resulted in increased mobilization of propylene glycol from tiles (Figure 4). Whereas there was generally a consistent increase in the amount mobilized per minute for S+ ($\bar{x} = 0.107 \pm 0.132$ g/min, mean ± standard deviation), there was greater variation for DF ($\bar{x} = 0.266 \pm 0.298$ g/min; Figure 5). High variability was observed in the runoff values for some treatments (e.g., cold-1wk minute-5, warm-1wk minute-2 and cool-2wk minute-2), but these observations were not consistent for most conditions and their direct replicates. This variability may reflect poor homogenization in a small number of samples as there is no discernible trend in meteorological treatment, CAD, date sampled or minutes rainfall.

TABLE 4 | Pairwise comparisons from Kruskal–Wallis test of difference (p-values stated) in the amount of propylene glycol (mL) in runoff comparing 1-week to 2-week weathering durations at 5-min rainfall. For (a) Kilfrost DF Plus, (b) Kilfrost ABC-S Plus, where * indicates a significant difference ($p = 0.05$).

(a) Kilfrost DF Plus					(b) Kilfrost ABC-S Plus				
Cool	**Cold**	**Warm**	**Sun**	**Wind**	**Cool**	**Cold**	**Warm**	**Sun**	**Wind**
0.897	0.635	0.110	0.900	0.033*	1.000	0.983	0.948	0.650	0.574

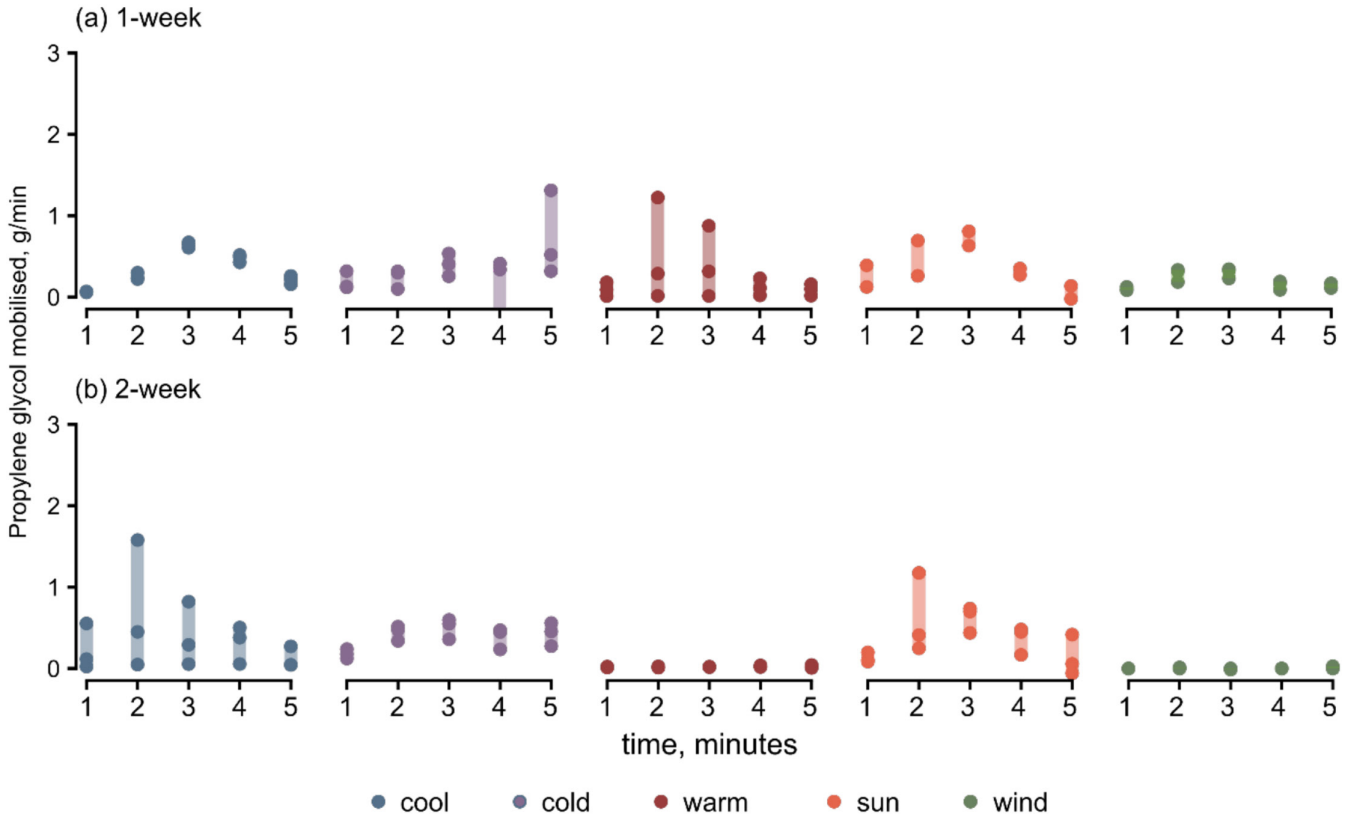

FIGURE 5 | Mobilization rate per minute of propylene glycol from Kilfrost DF Plus ('DF') airport de-icer in rainfall following exposure to different meteorological conditions for (a) 1-week and (b) 2-week duration of weathering for all replicates.

4 | Discussion

The most influential factors affecting propylene glycol mobilization were (1) the specific CAD tested and (2) the treatments associated with 'drying effects' (i.e., 'sun' and 'wind'). The duration of weathering was much less influential. Whereas temperature-related treatments (i.e., 'cold', 'cool' and 'wind') were otherwise identical, 'sun' and 'wind' were combinations of meteorological factors. 'Sun' combined the 'warm' treatment with the presence of sunlight and 'wind' added airflow to 'sun' treatments. Therefore, further evaluation is required to extrapolate individual influences (Table 1).

This study found that exposure of CADs to wind significantly affects their mobilization from a surface during rainfall—with sunlight sometimes having a substantial influence—(Figure 4 and Table 2), partially supporting Hypothesis 1: 'Sun and wind weathering treatments will cause higher evaporation of the water fraction, drying out the sample and making it less soluble'. For DF samples, the 1-week 'sun' treatment resulted in a similar amount of propylene glycol in runoff compared to other treatments, with a higher-than-expected amount mobilized in the earlier stages of rainfall (i.e., after 2–4 min of rainfall). In contrast, 'sun' treatments of S+ resulted in approximately a quarter of the amount of propylene glycol mobilized in runoff compared to 'cool' and 'cold' treatments and a seventh to a fourteenth of 'warm' treatments, suggesting that each CAD could be affected differently by sunlight. These observations may be a consequence of the higher viscosity of the S+ anti-icer. There was consistently slightly less propylene glycol mobilized with the presence of airflow ('wind' treatments) compared to other treatments (Figure 4). In the wind-2wk treatment, negligible propylene glycol was detected in runoff for both DF and S+, resulting in a significant difference between it and sun-2wk samples for DF de-icer ($p = 0.001$; Table 2).

These findings, along with observations of thin, dry films forming on 'sun' and 'wind' tiles, indicate that the combined influence of sunlight and air convection substantially reduced CAD mobilization in runoff, which has important implications for airport operators' treatment strategies. Understanding the timing of higher organic loads in effluents is crucial for the effective treatment of surface runoff at airports, especially during periods of intensive de-icing activities. Consequently, these findings have direct implications for airport treatment strategies, as they demonstrate that exposure to meteorological conditions affects the quantity of CADs released in runoff. For instance, not all CADs may be mobilized during the initial rainfall event, so even in the absence of de-icing activity between rainfall events, treatment systems should anticipate the presence of CADs in runoff. Future research should expand on this and examine repeat rainfall-drying effects.

It was also hypothesized that lower temperatures would result in lower mobilization of propylene glycol due to increasing viscosity (Hypothesis 2). Our experiments found significant differences between temperatures, but these varied by CAD. For DF, slightly less propylene glycol was mobilized after 1 week of 'warm' treatment than 'cool' or 'cold' conditions (Figure 4a,b); however, after 2-week exposure, there are significant differences compared to other treatments, with only trace amounts of propylene glycol mobilized in warm-2wk ($p \leq 0.020$; Table 2). Conversely, S+ samples, consistently exhibited the highest mobilization of propylene glycol in 'warm' treatments. The amount of propylene glycol mobilized was even higher than untreated-0wk samples, which were subjected to rainfall immediately after CAD application (Figure 4c,d). It is therefore difficult to draw definitive conclusions regarding the impact of temperature, given the contrasting behaviours of the two CADs in 'warm' treatments. Nevertheless, higher proportions of propylene glycol were detected in runoff compared to other meteorological effects tested, suggesting temperature plays a less significant role than sunlight or airflow in CAD mobilization.

The results did not show a significant reduction in propylene glycol mobilization with increased weathering exposure, contrary to Hypothesis 3 (Figure 4 and Table 4). The only significant difference observed was for the 'wind' treatment of the DF de-icer, which exhibited unusually high mobilization of propylene glycol compared to all other wind-exposed treatments. A potential explanation for the lack of influence is that the surface changes induced by weathering may have reached a plateau relatively quickly. For instance, drying effects from sunlight or airflow could cause the de-icers to form films or become substantially more viscous more rapidly than predicted. Therefore, the duration of exposure may not play as critical a role as the nature of the initial weathering process itself. However, the duration of exposure may be more influential in larger-scale experiments or field studies owing to the greater CAD quantity and deposition depth, which would form an interesting avenue for future work.

Calculation of percentage propylene glycol mobilization was particularly important for testing Hypothesis 4: 'Type IV aircraft anti-icers will be less readily mobilized by rainfall than Type I aircraft de-icers (Type I) because they are more viscous'. There were fewer differences between CAD type than hypothesized (Figure 4 and Table 3) with significant differences only in 'warm' treatments where there was considerably higher mobilization, as a percentage of propylene glycol deposited, in S+ samples than DF ($p \leq 0.045$).

In all samples tested, < 60% of propylene glycol was mobilized in runoff after 5-min rainfall. Visual inspection of tiles indicated that some CAD often remained on tiles after rainfall; however, other factors may affect the amount of mobilized propylene glycol on glazed ceramic tiles, such as evaporation of the water fraction and either volatility or photodegradation of the FPD. The evaporation of water from the CAD in sunlight and airflow would increase the FPD concentration and viscosity of the CAD (Saleh et al. 1999); thus, more rainfall would be required to mobilize CADs—a possible explanation for the lower mobilization rates in 'sun' and 'wind' treatments, especially for the already more viscous S+ anti-icer. Propylene glycol is reportedly non-volatile in water and dry substrates (Lyman 1990) with a Henry's law constant of 1.3×10^{-8} atm·m^3/mol (Daubert and Danner 1989), indicating that it would not readily evaporate when exposed to weathering treatments. Therefore, evaporation is unlikely to be a significant transport vector. In addition, propylene glycol is not thought to undergo photodegradation in water or soil matrices (West et al. 2014) but has been reported as undergoing photolysis in the presence of a TiO_2 catalyst (Kim and Hoffmann 2008). Furthermore, in all HPLC chromatograms of runoff samples,

there were no additional peaks observable, an initial indication that there was no, or very limited, chemical degradation of propylene glycol. However, further work, such as untargeted mass spectrometry (e.g., QTOF), could better determine whether chemical degradation occurs and provide a much improved understanding of the additives used in the commercial products and how these might affect the physical transport, chemical fate and environmental impacts of CAD use.

The controlled experimental approach employed in this study—using uniform sample tiles to isolate influences of individual meteorological conditions—provides a valuable foundation and preliminary investigation, despite not fully replicating the complexity of real airport surfaces, weather conditions and scale of CAD use [~500 L of CAD used on an Airbus A380 aircraft and ~30 000 L CAD used on a runway (ARM Ltd. 2023)]. Future research should develop on these findings, employing more realistic substrates (e.g., rough and semi-permeable asphalt, tarmac or concrete) on a larger scale (i.e., larger CAD volumes) and undertaking all treatments with a full-factorial cross in more environmentally representative conditions whilst also measuring additional physicochemical parameters such as viscosity, photodegradation and conducting comprehensive mass-balance analyses. Further studies may also wish to explore other transport pathways, such as CADs that are not immediately deposited on stands (approximately 30%) (ARM Ltd. 2023), to further aid winter operation strategies by airport operators. Moreover, the mobilization data presented here could enhance existing models, such as HardSPEC (UK Health and Safety Executive n.d.; Hollis et al. 2003), to better simulate the sorption, degradation and delayed runoff of CADs under variable weather conditions. Such modified models could then have substantial benefits—for example, informing enhanced monitoring protocols and operational procedures—thereby supporting airport operators in maintaining aircraft safety whilst minimizing environmental pollution risks.

Nevertheless, this initial study provides valuable insights for airport operators. Depending on the type and volume of CAD applied, as well as the weather conditions between application and rainfall, the timing and concentration of FPDs in surface water runoff may vary considerably. This variability underscores the importance of anti-icer/de-icer reporting by de-icing contractors to those managing treatment systems. Integrating such reporting into predictive models alongside meteorological forecasts (informed by findings presented here) could improve the prediction of contaminant loading and enhance the preparedness of treatment systems. Moreover, incorporating online water quality monitoring within drainage networks could refine these models using machine learning, offering a dynamic approach to optimizing treatment efficiency and minimizing environmental risks whilst ensuring continued operational safety in winter conditions.

5 | Conclusions

This study generated new evidence on how meteorological conditions affect the mobilization of CADs deposited on airport surfaces. Our laboratory experiments show that the largest contributor to propylene glycol mobilization was the specific CAD used. The more viscous Kilfrost ABC-S Plus (S+) anti-icer resulted in substantially less mobilization from the sample tile compared to the Kilfrost DF Plus (DF) de-icer, even adjusted for its propylene glycol content.

Comparing different meteorological conditions revealed that warmer temperatures (+18°C) can increase the mobilization of CADs compared to colder, winter temperatures (+5 and −5°C). Exposure to sunlight and airflow had a more pronounced effect on mobilization, and CADs visibly formed thin, dry films as opposed to the viscous liquid of freshly applied CADs. The duration of exposure to weathering had minimal impact on CAD mobilization, suggesting that weather-induced changes occur more rapidly after CAD application than initially anticipated.

Addressing the central objective of this study, these findings demonstrate that weathering of CADs between application and rainfall leads to a notable, and in some cases significant, reduction in the mobilization of FPDs in surface runoff. These findings offer critical insights for airport operators, enhancing their understanding of CAD transport across airfields and informing the management of treatment systems to further mitigate the environmental impact of airport de-icing.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

Supporting data for this study can be accessed through the Cranfield University repository (CORD) at 10.57996/cran.ceres-2596.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section. **Appendix S1:** Photos of experimental setup. **Appendix S2:** HPLC calibration curves and quality control.

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Influence of temperature, sunlight and wind on the mobilization of propylene glycol from airport deicers by rainfall

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