General Response:

We thank the Referees for their time to provide comments and feedback on this manuscript. We have edited the manuscript to address and incorporate their suggestions. In many cases, we realize that the clarity of our writing could be improved to address comments where the Reviewers had to make assumptions about technical details of our technique, and its validation. The Introduction has been thoroughly streamlined, as have sections of the Results and Discussion. We think that the manuscript contents are now clear, reflect the necessary corrections, and that the work is improved to a state we think meets the expectations for publication in Atmospheric Measurement Techniques. We hope the Editor and Reviewers agree. Our responses to specific comments from the Reviewers below are highlighted in yellow, while additions and alterations to our manuscript or in cases where we are redirecting concerns to existing discussion are highlighted, bolded, and underlined in green for additional clarity.

Editor

This manuscript has been reviewed by two referees. They believe that the instrument you developed is of great interest and that the work is well conducted. Nevertheless, they both feel that the current manuscript contained a lot of redundant materials and should be substantially shortened. I agree with them very much; in addition, the structure of this manuscript should be further improved, as also pointed out by the two referees.

As a result, in addition to the revised manuscript and point-to-point reply, could you please also provide a summary of major changes you make in the revision (in order to make it easier for the referees and also the handling editor)? Thank you very much.

You - as the contact author - are requested to individually respond to all referee comments (RCs) by posting final author comments (ACs) on behalf of all co-authors no later than 28 March 2024 (final response phase).

We thank the Editor for their contribution to the discussion on changes required for this manuscript. We have collected the major points that required addressing from all parties to provide a succinct summary of the modifications to the revised manuscript. Listed below are the five major changes made to the manuscript:

1. The Introduction (Section 1.0) has been revised for clarity and substantially shortened to be better focused on the topic(s) of this manuscript. The following are the major modifications:
   a. In the original manuscript, the Introduction was 2,261 words total and the revised Introduction section is now 1,783 words total, a reduction by over 1/5th.
   b. Any discussion/mention of those chemical species (e.g., POPs, nitrates/sulfates, and ON) not specifically studied in this work has been moved and integrated succinctly into the new Conclusions and Future Directions (Section 4.0).
   c. Small – yet impactful – modifications were made to the preexisting information within the last paragraph of the Introduction to better addresses comments made by
either Reviewer regarding the mixing of system validation and the scientific data analysis. The Authors believe that the location of these new modifications clarify and emphasize that sample preservation is based on established methodologies and that comparison to previously reported values in the literature is the primary metric for validation of the chemical measurements within this work.

2. A new subsection has been included within the Materials and Methods – more specifically, to the NL-BELT field site descriptions (Section 2.3).

Sample Preservation (Section 2.3.1) has been added to the manuscript to address Reviewer comments regarding topics such as sample preservation and method validation.

This is a re-working and expansion on the last paragraph in Section 2.3 of the original manuscript. This subsection details our use of mercuric chloride (HgCl$_2$) as a sample preservation technique and cites its established efficacy in previous studies. With the well-established and long-studied nature of this preservation method, and its use for over a decade within the aquatic and soil biogeochemical work at NL-BELT, the Authors felt that additional tests were not needed to verify the temporal preservation efficacy of collected samples.

We highlight in this new section the role of selective use of HgCl$_2$ within our replicate samplers as a method of internal sample validation (i.e. comparing samples in sterilized vs. unsterilized containers). We also highlight the versatility of our modular design as being open for use with many other established sample preservation methods, which ultimately allows it to become analyte specific without burdening researchers with laborious method re-development.

3. Within the Results and Discussion section comparing collected samples volumes (3.3), the paragraph detailing our intercomparison of ECCC and DAYMET measurements has been moved to the Supporting Information.

This comparison can now be found in Section S2, “Deposition Comparison: This Work, DAYMET, and ECCC.”

4. A rather minor, yet substantive, comment made regarding the paragraph in Section 3.3 discussing the presented triplicate sampler RSD values has been modified.

The variability observed in the samples is now briefly revised and better addressed, with the preexisting sentences were reordered for better flow.

5. The paragraph examining cation exchange capacity has been completely removed from the Results and Discussion section analyzing precipitation pH within the collected NL-BELT samples (3.4.1). The Authors agree that it serves only our own scientific objectives at NL-BELT was unnecessary and tangential to the manuscript contents.
Review 1

Overview:

This manuscript describes the development of an autonomous precipitation collector (excluding snow) that can be deployed off-grid in remote areas and is suitable for measuring pH, conductivity, and DOC (Dissolved Organic Carbon) in wet deposition with a monthly resolution. The collector was deployed and tested over a period of 2 years (2015-2016 on the NL-BELT network) for open fall and throughfall depositions.

General comments:

The subject is scientifically interesting and is well within the scope of the journal. But I think the presenting quality and arguments for validation of this system should be substantially improved before it can be accepted for publication in AMT:

The text is very dense, overly detailed, and often confusing, even off-topic, making it challenging to understand and preventing a clear presentation of the study’s results. Moreover, certain parts of the text resemble a promotional brochure (e.g., in the "general design advantages" section) or a technical manual (e.g., 3.2.1) that does not appear suitable for a scientific article. I have the impression that this is a study report that has simply been slightly reformatted for submission to AMT (without even sorting through the relevant or irrelevant information for the purpose of this paper). A scientific article about a new method/system should demonstrate that the developed tool meets the expectations and requirements set to address scientific questions, rather than being a comparison with commercial tools or a series of technical information. For example, in 3.2.1, it doesn’t matter that commercial samplers consume 100 times more; what is relevant here is the autonomy of your device.

We appreciate the thorough and thoughtful comments of the Reviewer. Where applicable, we have modified the text to be less dense, more concise, and less confusing for the readership. Given that there are no affordable commercial solutions for this type of sampling equipment, the manuscript needs to necessarily argue the rationale for the component selection and design. These sections aim to convey the unique features and advantages of our design, which is essential for assessment and effective uptake by the scientific community, particularly with respect to modular components. This is a central thrust of making instrumentation Open Access and research tools globally accessible.

We respectfully disagree with the position of the Reviewer on this point, as there are many manuscripts in this journal, and others related to instrument development, that are similarly detailed where novel platforms have been developed. As such, comparison with commercially available tools is relevant to underscore the application of our device in a broader context. When it comes to autonomy of using these samplers off-grid, power requirements are surely a fair comparison for stating why current commercial solutions are not viable.

The "Results" section mixes the points about the system validation and the scientific data analysis. The results/discussion section could be divided into two parts for clarity:
- A section titled "Validation": I believe there would be a significant benefit in simplifying the argument and presenting, point by point, the performance parameters. The article aims to demonstrate that the developed collectors are suitable for autonomously measuring conductive rain deposition in remote areas, so the key points of this demonstration could be highlighted:

1. Autonomous off-grid operations: low power consumption + opening conditions for the collection of wet deposition (time taken to open or close...)
2. Representativeness of the conductive rain collector for deposition measurement: Define what constitutes conductive rain compared to "common" rain.
3. Validation of measured chemical parameters: Verify the preservation of chemical species even after a month, including pH, conductivity, and DOC.

We thank the Reviewer for their comments. We must note a major oversight on the part of the Reviewer and in our emphasis of method validation before proceeding further with our responses. Validation throughout this manuscript was conducted by controlling and observing in two ways:

i) Microbes will transform bioavailable molecules and so we microbially sterilized two out of three sample replicates with HgCl₂, which is standard practice for biogeochemical handling of environmental water samples for chemical characterization. This technique has been in use for over a decade within our aquatic and soil biogeochemical work at NL-BELT (Ziegler et al., 2017; Bowering et al., 2020; Bowering et al., 2022; Bowering et al., 2023). We then compare those sterilized results against a replicate that was not administered HgCl₂ to ascertain whether microbial issues exist for measurement metrics (e.g., conductivity, pH, DOC). Generally, we did not find a difference between measurements that were microbially sterilized versus those that were not for the presented measures, but this is not a given for other molecules. Given the longstanding history of this approach, we do not feel that extensive restructuring of the manuscript into the Reviewer’s three sections is warranted.

We also strongly emphasize that this approach may not work for other molecules of interest to the atmospheric deposition community (e.g., those that are volatile). Sample preservation approaches should be conducted by users of this new platform based on their scientific objectives and review of the literature. We are not in a position to detail all preservation techniques. Please see our detailed response to comment 3 below and the newly added Section 2.3.1 entitled “Sample Preservation.”

ii) We perform comparisons to the literature for validation of our measurements against longstanding measurement techniques used by academics and regulatory agencies globally. We do not see a scientific contribution that validates precipitation pH measurements as a worthwhile activity, given that the control experiments we have conducted to ensure our samples are preserved have been made in line with methodologies that have been in place since the 1960s.
We have addressed the numbered points offered by the Reviewer in detail as follows:

1. The time it takes for the system to open, based on several years of qualitative observation, has been added to the section entitled “Heated Precipitation Sensor” (2.1.2):

   An output of 12 VDC is sent to the digital control board by the relay when rain is sensed, or 0 VDC in its absence, for signal processing and motor control (Figure S7). **When rain is sensed, the lid of each sampler in the array is simultaneously opened (<5 seconds) and is dependent on the rotational rate of the lid motor.** To increase the sensitivity of this sensor and to extend the sampling duration when conductive atmospheric constituents are completely washed out of the atmosphere, a sloped tin chute (e.g., Home Depot SKU# 1001110514) was added to extend the surface of the rain sensor.

2. For improved clarity, we will redefine what constitutes conductive rain compared to "common" rain in Section 3.1 (General Design Advantages):

   The chute does this by accumulating water-soluble materials between rain events that require time to be completely washed off and through the release of ions from the material itself, which ages under environmental conditions. As the conductivity of the precipitation falls below the sensor threshold—**conductive precipitation being that which initially contains high solute levels that progress through trace level concentrations,** the added ions from the chute prolong the collection of rain past this time point. In rainfall events where extended atmospheric wash-out occurs, **where precipitation becomes ultrapure water,** the sampler lids will eventually close—preventing dilution of the sample while maintaining the collection of analytes of interest.

3. Section 2.3 (Continuous Monthly Collection of Remote Samples at NL-BELT) was revised to include a new ‘Sample Preservation’ subsection (Section 2.3.1). This subsection addresses our use of a well-established sample preservation technique and clarifies why additional tests were not done to verify the preservation of collected chemical species over time. We believe that this new subsection, in addition to the small modifications made to clarify the motivations and objective of our approach in the final paragraph of the Introduction addresses the comments made by both Reviewers regarding their initial confusion on the mixing of system validation and the scientific data analysis. Please see below for the modifications made to the Introduction as well as the new additions to Section 2.3.1 specifically pertaining to sample preservation and validation:

1.0. Introduction (final paragraph)
The materials used can be easily changed in order to optimize collection and preservation of a wide array of target analytes, such as DOC, when using high density polyethylene and mercuric chloride (HgCl$_2$). We demonstrate that these platforms are capable of continuous operation off-grid for monthly wet deposition collection of precipitation across the Newfoundland and Labrador Boreal Ecosystem Latitudinal Transect (NL-BELT) during snow-free periods in 2015 and 2016.

The captured fraction compared to total volume deposited is used to gain insight into how these samplers can limit analyte dilution effects and improve method detection limits, such as rejecting 50% of the total volume delivered as ultrapure precipitation leading to a factor of two improvement. Chemical parameters of pH, conductivity, and DOC fluxes collected according to established preservation protocols were then compared to prior measurements to validate this proof-of-concept system. Measurement methods for pH and conductivity of rainwater are very well-established in the literature and serve as a baseline reference to ensure that the samples collected by the new devices presented in this work are consistent with what is expected in samples from a remote coastal environment, given the selective sampling strategy. We then move away from these well-established parameters to quantify DOC fluxes using established biogeochemical preservation techniques for fresh water and groundwater to demonstrate the potential of these samplers in application to automated collection of analytes of emerging importance and interest in the remote locations of our latitudinal transect.

### 2.3.1 Sample Preservation

Four of the six sample containers (two each of OF and TF) were biologically sterilized using 1 mL of a saturated aqueous solution of mercuric chloride (HgCl$_2$) to preserve against biological growth and loss of bioavailable nutrients over the collection periods. Unsterilized sample containers (without HgCl$_2$) were used for measurements of recalcitrant species and to assess any matrix effects exerted on target analyte quantitation. The use of HgCl$_2$ as a sample preservation technique has been long-studied and well-established (Kirkwood, 1992; Kattner, 1999); thus, additional tests to verify the preservation of collected chemical species over time were not performed. The analysis of deposition collected in unsterilized and
sterilized containers, however, serves as a method for internal sample validation - as does our evaluation of measurement outcomes in comparison to those reported within the literature.

Filtered samples were transferred to new clean HDPE containers and stored for up to two months at 4°C in a cold room until analysis. The target analytes in this work are non-volatile and the described sample collection methods consider this analyte property, as well as their interactions with container materials. The versatility of the system design allows for the use of different collection materials, keeper solvents for volatile organics, etc., so that the experimental design can be analyte specific, depending on end user needs. Sample preservation approaches should thus be identified by users of this new platform based on their scientific objectives and review of the literature (Galloway and Likens, 1978; Peden et al., 1986; Dossett and Bowersox, 1999; Wetherbee et al., 2010). In addition to the internal validation approach described here, we aim to demonstrate that the precipitation samplers in this work are suitable for measuring conductive deposition on- and off-grid. Below we highlight autonomous off-grid operations, determine the fraction of conductive rainfall collected from the total volume of precipitation, and validate our measurements through comparison to the literature.

A section titled "Application": to demonstrate the usefulness of the collector in identifying canopy effects, through a comparison of the obtained data with the literature and between OF and TF for pH, conductivity, and DOC.

We thank the Reviewer for their suggestion. We believe that our existing Sections 3.3 and 3.4 demonstrate the ‘Applications’ of our collector in identifying canopy effects as well as comparing our measurements to those reported within the relevant literature. The extent of this analysis serves as an example of how the samplers may be used, which will be exploited in our future work to explicitly consider canopy effects on deposited species. For brevity, as both Reviewers and the Editor have requested reduced content, we have opted not to separate and expand the discussion of canopy effects with respect to the observed OF and TF deposition.

Instead, we have tried to emphasize this in our Conclusions and Future Directions (Section 4.0): Comparability and complementariness of our results to well-established and current measurements of interest like DOC, demonstrate their efficacy and potential application to the study of processes such as canopy-precipitation interactions through the collection of open fall and throughfall replicates.
The samples collected in this work from this new instrumentation, specifically, are expected to be used further in several upcoming complementary and novel environmental monitoring studies. Not only will this future work extend our biogeochemical analysis, but it will also assist in our studying of the transport of other anthropogenic pollutants of emerging interest which are beyond the scope of describing this new platform.

In addition to presenting quality, the developed arguments do not justify the scientific quality of the proposed measurements. The validation of the system's operation and measurement is somewhat fragmented and, as such, not very convincing. Specifically, three points are missing in the developed arguments:

1. This is a rain collection system where the opening/closing is controlled by a resistive sensor which is activated from the conductivity of the rain. However, the operational range of the sensor is not specified (it triggers at 1 mohm.cm, it is the only information). Thus, there is no definition of what is being truly measured.

We thank the Reviewer for highlighting this point, but it is also somewhat confusing. A threshold for generating a response would exist in all sensors, so the one we have provided represents the lower limit of the range. This is common practice for many instrumental techniques, where the detection limit is reported. We will note that all standard deposition samplers in government monitoring networks use the same sensing approach for precipitation (often without a design to increase their sensitivity; e.g., NADP, CAPMoN, etc.; (Canadian Air and Precipitation Monitoring Network, 1985b)). Without a specific reference to other programs’ definitions, and some sort of example expectation from the Reviewer, is it hard to ascertain what might be most useful to address their concern. As such, we have retained our original lower limit conductivity definition and added the equivalent concentration in sodium chloride. We think this clarifies the work and hope the Reviewer agrees.

We have added the following to Section 2.1.2, “Heated Precipitation Sensor”:

The detection of rain modulates the opening and closing of the collection units by an interdigitated resistive sensor (M152; Kemo Electronic GmbH, Geestland, Germany; Figures S6 to S8). This approach is consistent with established precipitation detection techniques used by government monitoring programs (e.g., CAPMoN; Canadian Air and Precipitation Monitoring Network, 1985a, 1985b). The rain sensor detects conductive deposition by the completion of a conductive circuit when electrolytes bridge the connection between the interdigitated gold electrodes. The sensor is supplied with 12 VDC from the power system to trigger a relay when precipitation conductance above 1 MΩ·cm conductivity is detected.
(determined experimentally, see Section S1). This is equivalent to approximately 8 µM sodium chloride. The sensor detection limit reflects an upper limit of precipitation ion loading because the design of the rain chute leads to an increase in surface area of more than a factor of 25 on which solutes can accumulate to enhance the ionic content of the deposited water. An output of 12 VDC is sent to the digital control board by the relay when rain is sensed, or 0 VDC in its absence, for signal processing and motor control (Figure S7).

2. The time it takes for the system to open is also not mentioned. We know that the first seconds of rain contain strong concentrations, so if the opening occurs 30 seconds after the start of the rain, a significant amount of information will be lost.

The Reviewer mentioned this point in a prior comment, which has already been addressed with a technical addition to the paper. We thank the Reviewer for this comment, and we understand the need to communicate that the samplers open readily when rain is sensed, for the facts they mention here. The opening of the lid is fast (<5 seconds) and is dependent on the rotation rate of the motor selected. We typically use 2 to 6 rpm motors, depending on their availability from our suppliers. We hope the inclusion of this information in our revision is satisfactory.

3. The system is dedicated to measuring monthly fluxes of chemical species, but no information is provided on the preservation of the tested parameters (pH, conductivity, and DOC) between each sample retrieval.

We agree with the Reviewer, and we have now included a new subsection (Section 2.3.1) to address our use of a well-established sample preservation technique for microbially labile DOC, and hence, why additional tests were not done to verify the preservation of collected chemical species over time. We have also now clearly acknowledged that other analytes may require other considerations, depending on their chemical and physical properties (e.g., volatility).

We have also noted in our responses above that our comparison to long-standing reports of a parameter such as precipitation pH, using calibrated meters and standard collection/storage/analysis techniques from the literature (Dossett and Bowersox, 1999; Wetherbee et al., 2010) means that further evaluation of the preservation is not warranted, as the outcomes (i.e., the samples will be stable) are predictable. Given that both Reviewers have also indicated that the manuscript is too long, we do not feel that adding more results to this work are warranted. They have taken the time and attention to identify redundant components of the original work and we feel that it is important to emphasize where we find suggested additions to also be redundant. Especially results that fail to make substantive contributions to this field. We hope that our efforts to improve clarity in our justified approach, guidance for the community, and doing so concisely for the overall improvement of the manuscript are agreeable and meaningful changes to address the concerns of the Reviewer.

Specific comments:
Introduction

The introduction is very general and is organized into different paragraphs discussing the importance of monitoring atmospheric deposition of various chemical species (nitrates/sulfates (L83-91), POP (L119-129), ON (L157-165)) that are not subsequently addressed in the study, as only pH, conductivity, and DOC are studied here. If these species need to be detailed, it should be done in the conclusion to demonstrate that the developed system could also be used to study them. Please refocus the introduction on aspects related to your study.

We thank the Reviewer for this comment and Reviewer 2 raised similar concerns. The Introduction has been revised and the mention/discussion of studying the deposition of various chemical species (POPs, ON, etc.) not specifically studied in this work has been moved and integrated into the newly titled Section 4.0, “Conclusions and Future Directions” (see below). In the original manuscript, the Introduction was 2,261 words total, and the revised Introduction section is now 1,783 words total.

4.0 Conclusions and Future Directions (last paragraph):

For the broader deposition-motivated community, the instrument design also allows for easy cost-effective modification of the number of replicate samplers, the material composition of all surfaces the aqueous samples interact with, as well as preservation strategies - depending on the analyte of interest. For example, the lack of organic nitrogen measurements within universally established sampling and measurement procedures serves as a general example of the substantial knowledge gaps that may result when translating limited data sets to the wider global picture. This includes incomplete speciation and quantification across precipitation, aerosol, and gas phases. Monitoring systems that support U.S. deposition assessments (e.g., the NADP) only characterize the inorganic fraction of wet deposition. Additionally, modern emerging issues that require the continuation of existing deposition measurements or expansion of observation programs revolve around identifying and quantifying compound classes of concern, such as persistent organic pollutants. As reported in the literature, the deposition of these types of pollutants (e.g., polychlorinated biphenyls, polycyclic aromatic hydrocarbons, etc.) can be monitored using suitable collectors made of amber-coloured glass or stainless steel (Fingler et al., 1994; Amodio et al., 2014) - modifications which can be applied to the sample design detailed here. The samples collected in this work from this new instrumentation, specifically, are expected to be used further in several upcoming complementary and novel environmental monitoring studies. Not only will
this future work extend our biogeochemical analysis, but it will also assist in our studying of the transport of other anthropogenic pollutants of emerging interest which are beyond the scope of describing this new platform.

L.148-151: The justification for developing this new collector is based on comparisons with commercial devices, mentioning the cost and difficulty of making measurements in remote areas. It would be interesting to mention that precipitation collectors have already been developed to address specific questions about atmospheric fluxes. Here are a few examples:


We thank the Reviewer for directing our attention to these overlooked studies. We have added these in locations where we think they best fit in the manuscript.

1. We mention two of the five references listed above (Laquer, 1990; Germer, 2007), amongst others, within a modified Introduction paragraph to better address the preexisting precipitation collectors that have been more broadly developed for a variety of scientific objectives:

Over the past 60 years, the precipitation chemistry community has made advancements in deposition collectors to better understand atmospheric processes (Siksna, 1959). While bulk deposition collection (i.e., a collection bucket or jug fitted with a funnel open at all times; Hall, 1985) is both a simple and economically feasible sampling method utilized by monitoring networks, it is subject to bias through collection of inputs other than atmospheric...
deposition (e.g., bird droppings, insects, plant debris). As a result, bulk collectors can overestimate total deposition and underestimate wet deposition in a variety of locations (Lindberg et al., 1986; Richter and Lindberg, 1988; Stedman et al., 1990). Sequential precipitation collection methods include manually segmenting samplers (requiring only a shelter, clean surface, and an operator), linked collection vessels (sample containers that are filled in sequence via gravitational flow), amongst others and have been developed to analyze rainwater composition and measure parameters such as pH and conductivity (Gatz et al., 1971; Reddy et al., 1985; Vermette and Drake, 1987; Laquer, 1990). Sequential sampler designs have also been adapted to collect precipitation in remote field sites (Germer et al., 2007; Sanei et al., 2010). Although it is a more costly and time intensive method when compared to bulk deposition collection, the major appeal of measuring isolated wet deposition is the ability to isolate this individual atmospheric process.

While several precipitation collectors have been similarly developed to address specific scientific objectives—e.g., the quantitation of dust in wet and dry deposition (Laurent et al., 2015; Brahney et al., 2020), determination of ions and DOC in a tropical rainforest (Germer et al., 2007) and urban environments (Audoux et al., 2023), here we present a more general design for modular adaptability. When compared to other precipitation collection apparatuses, the automated precipitation sampler developed in this work has several advantages. Most notable is the ability to collect integrated samples at remote locations by exploiting its off-grid capabilities. ... In rainfall events where extended atmospheric wash-out occurs, where precipitation becomes ultrapure water, the sampler lids will eventually close – preventing dilution of the sample while maintaining the collection of analytes of interest. A recent study has found that rainfall events could exhibit variability and the lower atmosphere can be supplied with aerosols due to specific sources, atmospheric dynamics, and meteorological conditions (Audoux et al., 2023). If this occurs, the automated lid will reopen to sample the polluted air masses. In application to trace pollutants, this also reduces methodological sample preparation
time as it decreases the extent to which additional handling steps, like solid-phase extraction, are required prior to analytical determinations.

2.1.2 Heated Precipitation Sensor

Could you add information about time and delay between resistivity sensor activation and opening of the tip?

We thank the Reviewer for this suggestion, and we understand the need to include this information within the manuscript. As the Reviewer has mentioned this point in prior comments, it has been already addressed with a technical addition to the paper (see Section 2.1.2, “Heated Precipitation Sensor”).

Results and Discussion

3.0 Results and Discussion

The paragraph begins with a summary of the strategies used for validation. Wouldn't it be better to place these points at the beginning of each section to avoid redundancy?

We thank the Reviewer for their comment. Due to the detailed nature of Section 3.0, we thought including this summary would effectively preface each of the following subsections. Additionally, with these important details summarized at the beginning of the Results and Discussion section, this benefits those readers who would choose only to skim through the paper to points of particular interest to them. As such, we have opted to retain this section.

3.1 General Design Advantage

L518-543: This entire section mentions the advantages of the system without any results validating these claims. For example, regarding sample preservation, have you conducted tests on the preservation of reactive, volatile, or biologically transformed species (L538)? Similarly, you argue the possibility of detecting ultra-traces through the resistivity sensor systems (collection even at low conductivity and avoidance of dilution) and the types of materials used. I have no doubt that low-conductivity rains are collected, but what about the quality of the samples in the container? Could you provide information on field blanks, for example?

I believe that if you have a 'Validation' section, this part should be supported by your data.

We thank the Reviewer for their comment. This section was addressed in response to previously made Reviewer comments via a technical addition to the paper (see Section 2.3.1., Sample Preservation).

With respect to field blanks, we have an existing statement on how these were prepared in Section 2.4 ‘Cleaning and Preparation of Sample Containers’ and have added a minor clarification that
these were used to perform blank subtractions on measurements of all relevant metrics (e.g., conductivity and DOC here):

Field and method blanks were collected through the addition of DIW to cleaned containers, and/or sample handling devices, in order to quantify appropriate method detection limits and to identify any sources of systematic or random contamination. **Blank subtraction was applied to measurements, where appropriate.**

An example of an appropriate mention of how field blanks were used for considering conductivity (Section 3.4.2, first paragraph):

The conductivity of saturated HgCl\(_2\) in water (at 0.1% vol/vol) was 13.6 ± 0.4 µS/cm, which is also comparable to **but statistically higher than** our field blanks (\(p = 0.0015;\) unpaired t-test) and less than what was observed for our samples (\(p < 2 \times 10^{-6}\) for each site considered separately and also across all sites; unpaired t-test).

### 3.3. Comparison of Sample Collection Volumes

L647: It is announced that the automatic collectors and total deposition collectors are colocated, but if I understand correctly, the values discussed in this paragraph only concern the volumes obtained with the total deposition collectors in OF?

The Reviewer understands correctly that this paragraph deals with the fraction of total deposition collected in the automated samplers. This paragraph demonstrates the extent to which atmospheric washout can potentially dilute bulk samples, making the determination of trace analytes challenging and often then subject to complex and error-prone sample concentration methods. We refer the Reviewer to the existing introductory text in the Methods (Section 2.3) describing the colocation of the samplers:

One array of six automated collection units (3 OF, 3 TF) were deployed within one forested experimental field site located in each of the four watershed regions of the NL-BELT (24 samplers in total) between 2015 and 2016. Additionally, between one to three total deposition samplers were located at each of the four field sites (Table 1, Figure S10).

In Section 3.3 itself we have clarified the comparators in the second paragraph, alongside expectations:
The wet deposition volumes collected for the snow free period using the automated precipitation samplers did not follow the trends in total deposition (Figure 4), as might be expected (e.g., due to pollutant loading, rainfall quantity/rate, and scavenging processes). For the 2015 collection period from June through October, the summed volumes of OF precipitation, from south to north across the NL-BELT, were 25.4, 10.9, 20.4, and 2.2 L, while in 2016 they were 17.3, 30.4, 13.5, and 5.1 L. While the total and OF fractions would typically be much closer to unity in more polluted regions, it would be expected in these remote NL-BELT field sites for the differences to be driven by complex, non-linear processes that cannot be easily disentangled. Here we present three reasons as to why the measured wet OF deposition volumes do not follow the total deposition trend across the transect.

We thank the Reviewer for their comment. We agree with the suggestion that this comparison (L673-701 in the original manuscript) be removed and we have relocated it to the Supporting Information. This significantly simplifies and focuses this section and we thank the Reviewer for encouraging us to do so with this comment.

The text in Section 3.3 of the manuscript now simply refers to this material, presenting only the most important results of the comparison.

The automated samplers were collocated with total deposition samplers and deployed across the experimental forests of four NL-BELT regions during the 2015 and 2016 growing seasons to observe deposition trends. In addition, we briefly compare these observations to the long-term climate normals reported by ECCC and estimated deposition at 1 km x 1 km resolution from the DAYMET reanalysis model (Table 1, Section S2). Three automated samplers were deployed in the open to collect incident precipitation (OF) and another three under the experimental forest site canopy (TF). ... The total deposition samplers were installed in HR in late 2014 and the automated samplers were then set up at PB. Despite this, there is good agreement between the trends in predicted deposition values by DAYMET with the measured values, although the absolute amounts
from these are systematically lower in all of our observations (Section S2). Regardless, by following the recommended siting criteria from the NADP and CAPMoN as best as possible, the very strong agreement of our temporal trends at both annual and monthly timescales with both comparators demonstrates the suitability of the total deposition samplers and, therefore, the automated samples for use in quantifying deposited chemical species of atmospheric interest into the experimental sites.

In my opinion, the comparison between total deposition and collector values (and their differences) is the best argument to show that the automatic collectors effectively capture all rainfall. The question is what is the representativity of the “conductive” rains collected here compared to the conventional rainfall collection?

We thank the Reviewer for this comment. We assume that the conventional rainfall referred to by the Reviewer is bucket-based bulk deposition, collected on an event basis, rather than integrated sampling. If this is the case, our conductive rain is the fraction containing solutes above the sensor detection threshold stated in the main manuscript (addressed previously, see above).

The representativeness is exactly that defined by the sensor threshold, excluding ultrapure water from precipitation during washout events, which serves to dilute analytes in a sample. In more polluted regions, for example, we would expect the total and open fall fractions to be much closer to unity (see response and manuscript additions made to the comment immediately before this one). At the remote locations of the NL-BELT experimental forests - knowing that the region is subject to intense rainfall - it is not surprising that the collected fractions are smaller than found in the total deposition samplers. The fact that we do not see any comparisons where open fall volume exceeds that of the total also satisfies the basic premise of our comparison.

L733-753: The RSD obtained on the triplicates of the rain collectors of 10 samples out of 33, or 1/3 of the samples, have an RSD greater than 40%. This indicates a very high variability in the collected volumes. It would be interesting to discuss the reasons for this variability, which is crucial to estimate the performance/artifacts of your device (it's unfortunate that the data are in supplementary material). No analysis is done on these high RSD values. Is it for the same period of the year, e.g., when the winds are strongest? Is it at a specific site? Did the replicates use the same sensor, or is each system independent of the other? Could the observed variability in the replicates be due to different closing or opening times? Has simultaneity been tested?

We thank the Reviewer for their comment, and we agree that the high RSD values should be addressed better. To do so, we will answer your questions posed individually as follows:

i. Is it for the same period of the year, e.g., when the winds are strongest?

Winds are highly variable throughout the year. Storms can be accompanied by winds up to 140 km/hr in any month. Siting of samplers was conducted according to standard requirements of government sampling statements, so subject to the same potential artifacts. Government agencies
tend to only collect a single sample, so potential uncertainty in volume and analyte deposited quantities likely goes unreported (see addition to Section 3.3. below).

ii. Is it at a specific site?

No; it occurs at many of the sites and varies over the sampling periods.

iii. Did the replicates use the same sensor, or is each system independent of the other? Could the observed variability in the replicates be due to different closing or opening times? Has simultaneity been tested?

As described in Sections 2.1.2 and 2.3, each array of 6 samplers (3 OF, 3 TF) are controlled by the same sensor and the sampler lids all open within 5 seconds of detected conductive rainfall. Thus, after several years of qualitative observations, the observed variability is not a result of different sampler lid opening and closing times (i.e., a lack of simultaneity).

The following modifications have been made to Section 3.3 in the manuscript to communicate the information we have provided above for questions (i) and (ii). In addition to the new text underlined and bolded, some sentences from the original manuscript were reordered in this modified paragraph for better flow:

The automated OF wet deposition volumes collected each year have peak values that range from 1 to 4 L with an overall variability of ± 33% for any triplicate of samples across the entire dataset. Across our 33 sample collection periods, our replicate relative standard deviations (RSDs) follow a log-normal distribution where volume reproducibility is typically within ± 12.5% and almost always within ± 31.5% (Figure S11). A few outliers with higher variability skew the overall view of volume precision. Out of 33 OF samples collected, 10 have RSDs greater than 40.5% with 2 of those 10 having RSDs greater than 100%. Those values greater than 40.5% had no systematic relationship with site or time of year. Wind speeds were considered as a possible source of variability. The prevailing winds over Atlantic Canada are known to be southwesterly in the summer – intensifying during the autumn months – and westerly to northwesterly in the winter (Bowyer, 1995; Jacob, 1999; Randall, 2015). Strong wind speeds (i.e., >100 km/hr) could occur on an event basis during any time of the year and, thus, could contribute to the variability seen at each field site. Wind is known to generate bias in gauge-based precipitation measurements where unshielded precipitation gauges can catch less than half of the amount of a shielded gauge (Colli et al., 2016). A windscreen design for obtaining rainfall rates – and thus, volumes – to be more reproducible could be considered in future deployments of our developed
samplers, similar to recently reported innovations for smaller rainfall rate devices (Kochendorfer et al., 2023). This would, however, increase costs and logistical considerations in deploying the developed devices which currently operate synonymously to deposition systems employed by government monitoring programs. **Our siting approach is consistent with these, which often deploy a single sampler without wind protection.** Thus, by employing replicates, we are able to better ascertain the environmental variability. In addition, collection of replicate samples allows our observations to span a wider physical area, reducing the impact of confounding variables such as wind speed in comparison to a more typical sample size of one for many field collections. Imperfect siting and lack of shielding is necessary where remote field sampling prevents the setup of such infrastructure. As a result, the deployment of triplicate samplers provides researchers with a better opportunity to implement quality control as they can reduce bias in the event of dynamic OF. While the effect of wind is reduced, additional factors can drive variability when the samplers are placed under a forest canopy for TF collection.

The comparison between total volumes and precipitation volumes shows a clear difference. The explanations given for these differences are not quantified, while they could provide information on the quality of the collection and, therefore, on the definition of conductive rains (and provide information on the dilution parameter). For example, is there a link between the total collected volume and the difference between total/conductive deposition? Is it related to the site? This type of analysis could be done with scatterplots between total volume and rain, with different colors for each site to highlight if biases are site-related, then with colors by season.

Similar to our response to a comment above, the difference between open fall and total volume is not simple (e.g., pollutant loading, rainfall quantity/rate, scavenging processes). It is generally true that in more polluted regions, we would expect the total and open fall fractions to be much closer to unity. However, at the remote locations of the NL-BELT experimental forests, we expect the differences (as shown in Figure 4) to be driven by complex, non-linear processes that cannot be easily disentangled.

To better communicate this point, we have made the following modifications in Section 3.3:

The wet deposition volumes collected for the snow free period using the automated precipitation samplers did not follow the trends in total deposition (Figure 4), as might be expected (e.g., due to pollutant loading, rainfall quantity/rate, and scavenging processes). For the 2015 collection period from June through October, the summed volumes of OF precipitation, from south to north across the NL-BELT, were 25.4, 10.9, 20.4, and 2.2 L, while in 2016 they were 17.3, 30.4, 13.5, and 5.1 L. **While the total and OF fractions would typically be much closer to unity in more**
polluted regions, it would be expected in these remote NL-BELT field sites for the differences to be driven by complex, non-linear processes that cannot be easily disentangled. Here we present three reasons as to why the measured wet deposition volumes do not follow the total deposition trend across the transect.

Could you discuss these differences considering technical aspects? For example, the closing/opening of the collector lids is conditioned by the conductivity of the rainwater, assuming that concentrations in the rains decrease as the rain progresses. However, it has already been demonstrated that this is not necessarily the case (e.g. Audoux et al., 2023 see before). There can be refeeding of the lower layers with aerosols or mixtures of air masses that induce increases in conductivity during rain. The question is, what will be the behavior of the collector in this case? Is there a risk that the lid closes and reopens, or not? Are these phenomena that you observe from the datalogging?

We thank the Reviewer for this question. We acknowledge that the lower layers of the atmosphere can be supplied with aerosols, or that the arrival of contaminated air masses can increase the conductivity during a washout event. In that case, the lid of our samplers would re-open and sample the conductive precipitation, as the sensor is always active and the discriminating factor between sample collection (or not). We have witnessed this phenomenon firsthand in the field during deployment. To better address this topic, we have modified Section 3.1 to include the following underlined text:

In rainfall events where extended atmospheric wash-out occurs, where precipitation becomes ultrapure water, the sampler lids will eventually close – preventing dilution of the sample while maintaining the collection of analytes of interest. A recent study has found that rainfall events could exhibit variability and the lower atmosphere can be supplied with aerosols due to specific sources, atmospheric dynamics, and meteorological conditions (Audoux et al., 2023). If this occurs, the automated lid will reopen to sample the polluted air masses. In application to trace pollutants, this also reduces methodological sample preparation time as it decreases the extent to which additional handling steps, like solid-phase extraction, are required prior to analytical determinations.

It is known that the conductivity of a solution depends on temperature, and here the temperatures can vary greatly between seasons. The sensor is one of the key elements in the autonomy of your system. Have you tested how temperature affects the sensor's response? Could this have an influence on the differences observed between sites or with total depositions?

We thank the Reviewer for highlighting this point. The sensor surface is heated during detected precipitation events, which would mitigate the majority of ambient temperature effects. The operational temperature range provided by the manufacturer, based on a personal communication
with their support team, is -10 °C to +55 °C. Based on many years of qualitative observations, we have not noticed seasonal temperatures influencing the response of the sensor and know that similar considerations are not made by commercial systems on the market, or by government agency samplers. Lastly, the automated deposition samplers were decommissioned during the winter at the NL-BELT so we felt that this information was not relevant to include in the main text. It is noteworthy to mention that we have deployed these automated samplers year-round, since this initial study, in temperatures below –10 °C in Toronto and they continue to detect snow and ice deposition without issue. To do so, we have heated our chute to melt any deposited snow or ice, which again prevents any temperature-dependent conductivity detection issues. This will be featured in future studies reporting on winter deposition of pollutants of interest.

In addition, we have included the operating temperature range provided by the manufacturer of (-10°C to +55°C) in Table S2 within the Supporting Information.

L718: The authors rely on acquired data that are not collected simultaneously with their samples and justify the discrepancies due to the heterogeneity of precipitation. However, this heterogeneity is known. Why choose to use ECCC measurement sites that are not collocated with NL-BELT sites to do this validation work for the collectors since it is certain that there will be a discrepancy between the two?

We thank the Reviewer for highlighting this. We agree with their assessment and, as described above, have moved this comparison to the Supporting Information.

L733-776: This part pertains to the application of the collectors and no longer their validation; I think it should appear in a different section.

We thank the Reviewer for their comment. As there is now a separate “Sample Preservation” subsection (2.3.1), we believe that this particular analysis can remain where it is within the main text.

3.4. Characterizing Chemical Parameters from NL-BELT

I think the validation part of the chemical measurement should be in a separate section and thoroughly discuss:

Could you present sample preservation tests for pH, conductivity, and DOC? How can you ensure that concentrations are maintained over time despite all precautions taken? For example, have you taken a sample after rain and observed it after a month outdoors, considering temperature and sunlight variations (the choice of black color may lead to high temperatures inside the units during summer)? Could this have an impact on chemical parameters, such as the desorption of organic species from the surface of particles in the rain? The system is designed to limit evaporation, but is this really the case? Have you tested volumes pre- and post-sampling?

The Reviewer mentioned this point in a prior comment, which has already been addressed with a technical addition to the paper (Section 2.3.1, Sample Preservation). This subsection addresses our
use of a well-established sample preservation technique and hence, why additional tests were not
done to verify the preservation of collected chemical species over time. We believe that this new
subsection addresses all further comments made by either Reviewer regarding system validation,
as do the references we have provided, should they have further interest in this topic.

L995: This paragraph should be positioned earlier (in the validation section) to show the agreement
between the values measured here with this new system and the values expected from the literature.

We respectfully disagree with the Reviewer in this case. After the thorough restructuring of the
manuscript, we believe this paragraph is most effective in its current position.

A significant portion of these (Section 3.4) results is applicable and pertains to the study of canopy
effects on deposition fluxes and should be placed in a separate section and discussed accordingly.

We thank the Reviewer for this suggestion. For brevity, as previously mentioned, we have opted
not to separate the discussion of canopy effects with respect to the observed OF and TF deposition.
The measurements are meant to demonstrate the extended application of these samplers, not to
study canopy-precipitation interactions in detail. This is the subject of a future manuscript and
beyond the scope of this work, as we have noted in the revised Conclusions and Future Directions
(Section 4.0) in a prior response above.

Reviewer 2

Overview:

The paper outlines the design of an automatic precipitation sampler for off-grid use. It is suitable
for measuring pH, conductivity, and dissolved organic carbon. The new sampler was tested in the
Newfoundland and Labrador Boreal Ecosystem Latitudinal Transect over a two-year period for
open-fall and throughfall precipitation. A notable disadvantage to this sampler is the inability to
collect snowfall, limiting year-round monitoring of precipitation.

We understand the Reviewer’s concern regarding the inability to sample snowfall. We share the
same opinion. In fact, since the first iteration, we have modified the funnels and rain sensor chute
by installing heating cables to detect, melt, and therefore sample snowfall. This requires a constant
power demand in excess of 4 A and, therefore, access to grid power. Since this alteration of the
system is still in the testing/development phase, and is not applicable to off-grid sampling, we have
decided to exclude the modifications from the current manuscript. This is a substantial engineering
challenge and would also undermine our desire to communicate on how to obtain a widely
accessible automated deposition sampling method (i.e., cheap).

General comments

This work is of great interest to atmospheric scientists and is within the scope of the journal.
Overall, this work is appropriate for acceptance in AMT following the revisions outlined below.
The revisions mostly focus on reformatting, reducing lengthy descriptions, and improving clarity (particularly in the introduction and results/discussion sections).

We thank the Reviewer for the positive feedback and appreciate the time they have taken to provide these comments. Please see below where we address these points in our responses and manuscript alterations. Where appropriate, to retain concision, we refer the Reviewer to prior responses above where overlapping concerns with the other Reviewer occur.

Specific comments

Introduction:

Overall, the introduction is very lengthy. Finding ways to pare down this material would allow for clarity of the important topics related to this work.

We agree with the Reviewer. It is challenging to speak to a broad audience while also retaining a focused Introduction. We appreciate the thoughtfulness of the Reviewer in their suggestions that follow and have done our best to reduce the content of the Introduction. The other Reviewer made a similar suggestion and we have managed to reduce the word count of the Introduction from 2,261 words to 1,783 words in the revision. We hope that this is satisfactory.

Line 74-91: It seems like this paragraph is trying to introduce pH, conductivity, and DOC, however it is hard to separate the information of these three topics from each other. The discussion of pH, conductivity, and DOC are mixed together, making it hard for the reader to parse out the relevant information for each topic. This paragraph needs to be revised and simplified.

We agree with the Reviewer. Given the established measurements of pH and conductivity, we feel that removing the majority of this paragraph to better focus on the deposition collectors themselves would address this comment accordingly as well as the other comments pertaining to the dense and general nature of the Introduction.

Line 119-132: This paragraph discusses persistent organic pollutants (POPs), which the authors do not monitor during the testing period presented in this work. This paragraph could be removed from the introduction and incorporated later as a future use for the sampler.

Line 152-165: This paragraph discusses monitoring reactive nitrogen in atmospheric deposition, however this was not a focus of the precipitation characteristics (pH, conductivity, and DOC) that was highlighted in the results. If this does in fact connect with those three characteristics, those connections need to be made clearer, or this paragraph can be removed.

Response to comments pertaining to L119-132 and L152-165:

We thank the Reviewer for these comments and Reviewer 1 raised similar concerns. The Introduction has been refocused and the mention/discussion of studying the deposition of various chemical species (POPs, ON, etc.) not specifically studied in this work has been either removed
completely or integrated into a succinct addition in the revised Conclusions and Future Directions (Section 4.0).

Methods

2.1.2 Heated Precipitation Sensor

Line 305-306: Is the conductivity that triggers the sensor typically for that of precipitation (both in your geographic region and others)? I wonder about the variability of precipitation globally and if this would cause differences in sampling. In addition, what is the time delay for the lid opening once triggered?

We thank the Reviewer for this comment and Reviewer 1 raised similar concerns. While we acknowledge that conductivity in precipitation could vary depending on sampling locations, the threshold that we report represents the lower limit of the range and this excludes our modification to its design to increase the sensitivity of the sensor by adding the chute. We do not expect precipitation conductance to fall below our threshold unless there is a washout event in the atmosphere that effectively consists of ultrapure water. We note that established sensors on deposition samplers used by government monitoring programs that rely on conductivity would be similarly impacted. As such, we have retained our original lower limit conductivity definition and added the equivalent concentration in sodium chloride. We think this clarifies the operation of the samplers, their detection limits, and hope the Reviewer agrees.

We have added the following to Section 2.1.2 Heated Precipitation Sensor:

The detection of rain modulates the opening and closing of the collection units by an interdigitated resistive sensor (M152; Kemo Electronic GmbH, Geestland, Germany; Figures S6 to S8). This approach is consistent with established precipitation detection techniques used by government monitoring programs (e.g., CAPMoN; Canadian Air and Precipitation Monitoring Network, 1985a, 1985b). The rain sensor detects conductive deposition by the completion of a conductive circuit when electrolytes bridge the connection between the interdigitated gold electrodes. The sensor is supplied with 12 VDC from the power system to trigger a relay when precipitation conductance above 1 MΩ·cm conductivity is detected (determined experimentally, see Section S1). This is equivalent to approximately 8 µM sodium chloride. The sensor detection limit reflects an upper limit of precipitation ion loading because the design of the rain chute leads to an increase in surface area of more than a factor of 25 on which solutes can accumulate to enhance the ionic content of the deposited water. An output of 12 VDC is sent to the digital control board by the relay when rain is sensed, or 0 VDC in its absence, for signal processing and motor control (Figure S7).
Additionally, Reviewer 1 raised the point regarding the opening and closing times of the lid. We thank the Reviewer for this comment, and we understand the need to communicate that the samplers open rapidly when rain is sensed, for the facts they mention here. The opening of the lid is fast (<5 seconds) and is dependent on the rotation rate of the motor selected. We typically use 2 to 6 rpm motors, depending on their availability from our suppliers. We hope the inclusion of this information in our revision is satisfactory.

An output of 12 VDC is sent to the digital control board by the relay when rain is sensed, or 0 VDC in its absence, for signal processing and motor control (Figure S7). **When rain is sensed, the lid of each sampler in the array is simultaneously opened (<5 seconds) and is dependent on the rotational rate of the lid motor.** To increase the sensitivity of this sensor and to extend the sampling duration when conductive atmospheric constituents are completely washed out of the atmosphere

Results and Discussion

3.1. General design advantage

Overall, I think the results and discussion could be reformatted. It was confusing to read and keep track of the sampler’s validation results and how you were actually applying the sampler to gain new information (like TF and OF comparisons). I appreciate the “General Design Advantages” section to highlight the ability to use this sampler in remote locations and to collect replicates.

We thank the Reviewer for recognizing our rationale for including the “General Design Advantage” section in the manuscript. This is contrary to the comments made by Reviewer 1, as they felt that this section resembles a promotional brochure or technical document. Given the conflicting opinions of the Reviewers, we have elected to retain our preference of having this section in the manuscript.

Below, we have attempted to address the Reviewer’s detailed comments on improving the Results and Discussion section of the manuscript. We hope they find these to be acceptable.

3.3. Comparison of Sample Collection Volumes

Line 681: If there is a lot of data missing from the ECCC monitoring site, why would you choose this dataset for your comparisons?

We thank the Reviewer for their comment. The Authors initially believed that although a lot of data was missing from the monitoring site in question, it was still better to include any available data for collocated sampling sites. Upon reflection, we now agree that this is not a suitable comparison to include within the main text but is instructive information to include in the
Supporting Information. In also addressing comments made by Reviewer 1, suggesting that our comparison of total deposition with ECCC and DAYMET data is tangential to the central topics of this paper, Section 3.3 was greatly simplified by moving the ECCC/DAYMET comparison to the Supporting Information (Section S2). We agree with both Reviewers that while this was instructive for our biogeochemistry and hydrology work at the NL-BELT, that it is not instructive for the wider scientific community.

Line 689-690: The R² values are presented in a confusing manner, especially the ones found in parentheses. Please make it more clear which value corresponds to which site.

We thank the Reviewer for their comment. As mentioned above, to address comments made by both Reviewers, Section 3.3 was greatly simplified by moving the ECCC/DAYMET comparison to the Supporting Information. Regarding the R² values, the way in which they are presented in the Supporting Information has been revised for simplicity as follows:

**S2. Deposition Comparison: This Work, DAYMET, and ECCC**

The DAYMET observations are representative of a larger spatial scale, where our discrete samplers could be subject to heterogeneity in deposition (e.g., orographic precipitation, driven by topography like steep slopes) or impacted by meteorological conditions not captured by the model (e.g., undercatch driven by local winds). The temporally resolved volume comparisons at sampling interval timescales better-demonstrates comparability, despite the systematic differences. The month-to-month relationships between DAYMET and our observations, as well as between ECCC and our observations, all show strong correlations with linear regressions having R² values, from north to south, of 0.72, 0.99, 0.99, and 0.86, and N/A, 0.94, N/A, and 0.93, respectively (Table S3). The discrepancy between DAYMET, ECCC, and our observations for total deposition were highest in the most northerly site, where the experimental site was located on a steep slope, with only 43% of the predicted volume collected. At all of the sample collection sites on the island of Newfoundland, a consistent difference was observed with 65 ± 4% of the estimated volume collected, except at GC where our measurements and those from ECCC are identical and starkly contrasting to DAYMET.

Caption of Table S3:

**Table S3.** Collected precipitation volumes from NL-BELT in bulk deposition samplers for rainwater were deployed for one to two months, while snow was collected as an integrated sample throughout the winter because sites were not accessible. The Environment and Climate Change Canada (ECCC) precipitation data was obtained for identical sampling intervals. The DAYMET model for North America (1 km x 1 km resolution) for precipitation was obtained for the identical sampling intervals, which utilizes interpolated
and extrapolated data from daily weather observations to predict inputs at the NL-BELT locations. Linear regression results for slope (m) and correlation coefficient \( R^2 \) between observations and DAYMET (italics), and observations and ECCC (where possible; underlined), were calculated. For sampling periods where a measurement was compromised or not collected for a given interval in this work, these are reported as with ‘-’ and an estimated volume from the regression relationship with ECCC is reported in parentheses when used to replace compromised samples.

Overall, Section 3.3 Comparison of Sample Collection Volumes is very long and feels repetitive. This section should be made more concise.

We thank the Reviewer for their comment and appreciate their suggestions. We have moved the ECCC/DAYMET comparison to the Supporting Information, resulting in a more succinct Section 3.3 (1,893 words now reduced to 1,675).

3.4. Characterizing Chemical Parameters from NL-BELT

Line 815-819: Mentioning and comparing the pH of the TF samples to the pH of the soil in that area seems like extraneous information. Why are you making this comparison? If it’s truly needed, provide some justification or explanation as to why this is important.

We thank the Reviewer for their comment, and we agree that this is extraneous information to include here, as was the comparison in the prior section. Again, while there is value in this for our ongoing work at the NL-BELT, we agree that it was a misplaced idea on our part to include it in the main text of manuscript.

We have removed this material entirely from Section 3.4.1 and incorporated it into Table 1 as “footnote a” for contextual purposes:

*Soil pH for the organic and mineral soil horizons determined by addition of 400 μL of aqueous 0.5 M CaCl\(_2\) to a 50:50 w/w slurry of dried soil in deionised water. Note: the four remote NL-BELT sites are dominated by balsam fir trees underlain by humo-ferric podzol soil with pH ranging between 3.0 and 4.5.*

Section 3.4.2 – Most other sections have a comparison of OF and TF samples, but this one does not. Was that intentional? A brief statement comparing these two would be great.

We thank the Reviewer for their comment and this brief statement has been included within Section 3.4.2:

In all the collected OF and TF precipitation samples, across all four NL-BELT sites, the average measured conductivity values ranged from 21 to 166 μS/cm following no apparent seasonal or temporal trend (Figure 6). Additionally, the conductivity in both OF and TF also appear to vary across the field sites - only within the 2016 TF samples does the conductivity
**appear to increase with decreasing latitude.** Yet, with the typical conductivity of surface and drinking waters being between 1 to 1000 µS/cm (Lin et al., 2017), and typically below 200 µS/cm in stream water measurements within the watersheds of each of the NL-BELT sites, our observations are comparable and fall within the expected range. Our field blanks – encompassing a variety of materials and apparatuses, and our cleaning procedures, routinely produced conductivities of 9 ± 5 µS/cm.

Line 893-894: p-values to support your statements that the conductivity of HgCl₂ in water is comparable to field blanks and less than your samples would strengthen this argument. The Reviewer is making a request that may not be as informative as they wish it to be, but we have decided to incorporate the results of a statistical comparison in line with their request. Our measurements of HgCl₂ in water at the saturation limit is an upper boundary. This is the measured value of 13.6 ± 0.4 µS/cm is expected to be much higher than its impact on any sample where the small volume of such solutions (1 to 5 mL) is diluted by the total volume of collected precipitation. Thus, the comparison and resulting statistics are expected to be skewed towards similarity as they do not account for this physical reality.

In addition, our field blanks show less conductive contamination compared to this upper limit of saturated HgCl₂ statistically, and the samples are significantly higher (p = 7.65 x 10⁻⁸; unpaired t-test). Therefore, the results hold up in line with expectations of high-quality analytical performance, despite the above stated caveat. We have added brief statistical outcomes from unpaired t tests to the main manuscript:

**Our field blanks – encompassing a variety of materials and apparatuses, and our cleaning procedures, routinely produced conductivities of 9 ± 5 µS/cm.** The conductivity of saturated HgCl₂ in water (at 0.1% vol/vol) was 13.6 ± 0.4 µS/cm, which is also comparable to but statistically higher than our field blanks (p = 0.0015; unpaired t test) and less than what was observed for our samples (p < 2 x 10⁻⁶ for each site considered separately and also across all sites; unpaired t-test).

Line 958-963: You mention wildfire plumes being a potential cause of increased DOC levels in precipitation. Was there a wildfire event near your sites during your sampling period to warrant mentioning this possibility? Or would the possibility of increased DOC still be observed some amount of time after a wildfire event? In order to justify including this argument, I would like to see if you could make a potential correlation to an actual event that may explain this.

We thank the Reviewer for highlighting the very important link between wildfire plumes and increased DOC deposition. The province of Newfoundland and Labrador does experience wildfires, forest fire season is in effect from May to September each year. Based on 20 years of
wildfire data, there are on average 118 wildfires burning 22,993 hectares in Newfoundland and Labrador each year (Government of Newfoundland and Labrador, 2023). We strongly believe this argument is warranted since (i) there has been an increase in wildfire activity across North America and (ii) several studies have now linked increased organic and inorganic carbon deposition to wildfire events. (Wagner et al., 2021; Coward et al., 2022; Barton et al., 2024). Given the variability in atmospheric transport from these fire locations (typically in Labrador, but also reaching Quebec and further west), it is challenging to provide deep insight regarding the magnitude of impact in monthly integrated samples without detailed back trajectory analysis driven by known precipitation intercepting these airmasses. So, although we did not make a quantitative determination of wildfire plumes during the campaign, it would be unusual not to include wildfires as a possible reason for increased DOC deposition.

The discussion on DOC seems less than a validation of instrument performance, but rather a capability of the sampler. Unless you have DOC data from your sampling locations to compare to, this seems like new information for remote sampling sites.

We thank the Reviewer for this comment. We may have miscommunicated our approach and would now like to clarify it. In Section 3.4, we aimed to highlight the sampler’s capability to accurately quantify precipitation pH, conductivity, and DOC fluxes, with a special interest in demonstrating the capacity to discern and investigate canopy effects. To validate our new DOC measurements, we compared our observed fluxes to other studies in forested regions. We strongly feel that this section is a validation of the instrument performance and re-emphasize that future applications for these samplers are stated in the Conclusions and Future Directions (Section 4.0), as further scientific inquiry is beyond the scope of this work.

To add clarity to the manuscript, we have added the following text in Section 3.4.3 (paragraph following Figure 7):

Additionally, we cannot rule out that the chemical speciation differs between OF, TF, and SF even if the DOC values are similar, but such insights require more selective instrumentation for chemical analysis (e.g., high resolution mass spectrometry).

**The ability to accurately determine DOC in OF and TF precipitation demonstrates the capability of the automated deposition samplers. To validate our measurements, we compared our observed fluxes to other studies in different forest types.** Mean annual DOC fluxes were generally similar to those reported in some other boreal forests (Table 3).

Line 1014: what evidence do you have that supports the same that the automated system better maintains the integrity of DOC in samples?

We thank the Reviewer for highlighting this and we welcome the opportunity to clarify our approach. Our rationale in stating that the automated system maintains the integrity of DOC in the collected samples is because we have followed the standard approach used by biogeochemists to study DOC in soil and freshwater samples, by microbiially fixing them through the addition of
HgCl$_2$. In addition, we have outlined apparatus cleaning procedures to minimize contamination. Finally, the sampler design also prevents the intrusion of forest litter and other materials that could potentially influence the levels of DOC in forested regions if these were to be submerged in the collected aqueous precipitation sample, leading to bias due to leaching of organic compounds from these solid organic materials. This is particularly important if the objective is to selectively quantify DOC in wet deposition.

To better address this comment, we have made a small addition to the final paragraph of Section 3.4.3 which now reads:

The automated system better maintains the integrity of DOC in the samples. This was achieved by following standard procedures for biogeochemical sample preservation (i.e., adding HgCl$_2$) (Argentino et al, 2023), employing a rigorous cleaning procedure, and preventative design against the intrusion of forest litter which could result in a positive bias for DOC in the collected precipitation.

Additionally, we’ve added a new subsection “Sample Perseveration” (2.3.1) to address comments regarding topics such as sample preservation and our approach to method validation.

Technical Corrections Starting with section 3.4.3 – it is mentioned that flux (with the units: mg C m$^{-2}$ d$^{-1}$) is used. However, at several points in this discussion flux is given as mg C m$^{-2}$ a$^{-1}$. I’m providing a list locations I’ve found this mistake, but please check throughout the manuscript for places I may have missed:

Lines 50, 921, 925, 944, 955, 966, 997, 998, 100

We thank the Reviewer for this comment; however, we think there was some miscommunication with our approach and we would like the opportunity to clarify. The deposition fluxes were calculated daily; however, this was summed for each sampling period and reported as an equivalent annual flux with units of (mg m$^{-2}$ a$^{-1}$). We have checked the values and units throughout the manuscript and Supporting Information to confirm that they are correct in all locations.

To clarify, the text at the end of the first paragraph of Section 3.4.3 now reads:

The concentrations were converted to elemental fluxes using the volume of precipitation collected, the area of the funnel and the number of sampling days of each sampling period (Figure 7). The total flux for each sample period was summed and reported as an equivalent annual flux with the following units: mg m$^{-2}$ a$^{-1}$. Annual fluxes ranged from 600 to 4200 mg C m$^{-2}$ a$^{-1}$ across the study sites for the snow free period (Table S4).
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Cost Effective Off-Grid Automatic Precipitation Samplers for Pollutant and Biogeochemical Atmospheric Deposition

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Abstract

An important transport process for particles and gases from the atmosphere to aquatic and terrestrial environments is through dry and wet deposition. An open-source, modular, off-grid, and affordable instrument that can automatically collect wet deposition samples allows for more extensive deployment of deposition samplers in fieldwork and would enable more comprehensive monitoring of remote locations. Precipitation events selectively sampled using a conductivity sensor powered by a battery-based supply are central to off-grid capabilities. The prevalence of conductive precipitation - that which initially contains high solute levels and progresses through trace level concentrations to ultrapure water in full atmospheric washout, depends on the sampling location but is ubiquitous. This property is exploited here to trigger an electric motor via limit switches to open and close a lid resting over a funnel opening. The motors are operated via a custom-built and modular digital logic control board, which have low energy demands. All components, their design and rationale, and assembly are provided for community use. The modularity of the control board allows operation of up to six independent wet deposition units,
such that replicate measurements (e.g., canopy throughfall) or different collection materials for
various targeted pollutants can be implemented as necessary.

We demonstrate that these platforms are capable of continuous operation off-grid for integrated
monthly and bimonthly collections performed across the Newfoundland and Labrador Boreal
Ecosystem Latitudinal Transect (47° to 53° N) during the growing seasons of 2015 and 2016.
System performance was assessed through measured power consumption from 115 volts of
alternating current (VAC; grid power) or 12 volts of direct current from battery supplies during
operation under both standby (40 or 230 mA, respectively) and in-use (78 or 300 mA, respectively)
conditions. In the field, one set of triplicate samplers was deployed in the open to collect incident
precipitation (open fall) while another set was deployed under the experimental forest canopy
(throughfall). The proof-of-concept systems were validated with basic measurements of rainwater
chemistry including: i) pH ranging from 4.14 to 5.71 in incident open fall rainwater; ii)
conductivity ranging from 21 to 166 μS/cm; and iii) dissolved organic carbon concentrations in
open fall and canopy throughfall of 16 ± 10 mg/L and 22 ± 12 mg/L, respectively; with incident
fluxes spanning 600 to 4200 mg C m⁻² a⁻¹ across the transect. Ultimately, this demonstrates that
the customized precipitation sampling design of this new platform enables more universal
accessibility of deposition samples to the atmospheric observation community—e.g., those
who have made community calls for targeting biogeochemical budgets and/or contaminants of
emerging concern in sensitive and remote regions.

1.0 Introduction

Atmospheric deposition is the central loss process for particles and gases to terrestrial and
aquatic surfaces (Pacyna, 2008). Particles and gases can be deposited by both dry and wet
deposition processes. Dry deposition is facilitated by the direct interaction of gases and particles
with boundary layer surfaces such as water, vegetation, and/or soil, while wet deposition involves
in-cloud scavenging and below-cloud interception of gases and aerosols by, e.g., rain droplets and
snow crystals (Fowler, 1980; Lovett and Kinsman, 1990). Dry and wet deposition are global
processes coupled to regional synoptic scale conditions, but their relative importance depends on
local sources and global transport of atmospheric analytes of interest. Dry deposition consists of a
variety of mechanisms for particles and gases, with fine mode particles and their chemical
constituents (compared to ultrafine and coarse mode particles) being more likely to undergo
atmospheric long-range transport prior to being deposited (Farmer et al., 2021). Wet deposition occurs when such long-lived atmospheric particles and gases are included and/or scavenged into cloud water and transported to the surface of the Earth in precipitation (e.g., snow and rain). With the size and number of droplets in the atmosphere largely controlling the rate, wet deposition depends on a variety of meteorological factors affecting precipitation, such as the size distribution and concentration of ice and droplet nucleating particles, as well as the solubility, concentration, and reactivity of gases (Lovett, 1994). Ultimately, deposition plays an important role in pollutant distribution and biogeochemical cycling of long-studied major nutrients (e.g., nitrogen and sulfur in acid rain) and those with increasing recognition of importance such as dissolved organic carbon (DOC) (Meteorological Service of Canada, 2005; Vet et al., 2014; Safieddine and Heald, 2017; United States Environmental Protection Agency, 2020).

Recognizing the significance of atmospheric trace chemical deposition has led to the establishment of monitoring networks. For example, long-term wet deposition monitoring networks, like the Canadian Air and Precipitation Monitoring Network (CAPMoN) and the National Atmospheric Deposition Program (NADP), aim to provide critical data on the spatial and temporal patterns of wet and dry deposition. As a result, this has allowed for the estimation of regional and continental deposition rates of species regulated by national or international policies (Lovett, 1994). Data from these networks have been critical to understanding the efficacy of policy to reduce environmental issues like acid rain (Likens and Butler, 2020). In particular, the Oslo and Geneva protocols have achieved an 80% decrease in both North American and European SO$_2$ emissions since 1980 (Grennfelt et al., 2020). Despite these successes, reduction in acid deposition has had unexpectedly slow recovery in ecosystems leaving them sensitized – necessitating continued deposition monitoring (Stoddard et al., 1999; Kuylenstierna et al., 2001).

Over the past 60 years, the precipitation chemistry community has made advancements in deposition collectors to better understand atmospheric processes (Siksna, 1959). While bulk deposition collection (i.e., a collection bucket or jug fitted with a funnel open at all times; Hall, 1985) is both a simple and economically feasible sampling method utilized by monitoring networks, it is subject to bias through collection of inputs other than atmospheric deposition (e.g., bird droppings, insects, plant debris). As a result, bulk collectors can overestimate total deposition and underestimate wet deposition in a variety of locations (Lindberg et al., 1986; Richter and Lindberg, 1988; Stedman et al., 1990). Sequential precipitation collection methods
include manually segmenting samplers (requiring only a shelter, clean surface, and an operator), linked collection vessels (sample containers that are filled in sequence via gravitational flow), amongst others and have been developed to analyze rainwater composition and measure parameters such as pH and conductivity (Gatz et al., 1971; Reddy et al., 1985; Vermette and Drake, 1987; Laquer, 1990). Sequential sampler designs have also been adapted to collect precipitation in remote field sites (Germer et al., 2007; Sanei et al., 2010). Although it is a more costly and time intensive method when compared to bulk deposition collection, the major appeal of measuring isolated wet deposition is the ability to isolate this individual atmospheric process. Further innovation can reduce bias and improve the preservation of samples, such as the use of sensors to automate isolation of collected precipitation or the addition of polymeric mesh barriers to reduce debris input in windy environments (Lovett, 1994) - yet commercial solutions often come at a substantial expense.

When targeting biogeochemically relevant species in deposition collectors, additional standard practices have been developed to improve the representativeness of sample composition. First, an appropriate monitoring site must be selected. Three categories of siting criteria, established by organizations such as CAPMoN and the NADP, are of particular importance: (i) site representativeness and physical characteristics, (ii) distance from potential pollution sources, and (iii) operational requirements (Canadian Air and Precipitation Monitoring Network, 1985a; National Atmospheric Deposition Program, 2009). This means that each site must be a location that receives precipitation representative of the hydrologic area; is ideally not within 500 m of local pollution sources, such as wood-burning stoves, garbage dumps, and vehicle parking lots; and is accessible for daily collections, maintenance, and can be serviced by reliable 115 volts of alternating current (VAC) electrical power (Canadian Air and Precipitation Monitoring Network, 1985a; National Atmospheric Deposition Program, 2009). Despite these guidelines, there are many reasonable scenarios in which these siting conditions cannot be met. As an example, remote sample collections are often required for global assessments on persistent contaminants or nutrients of biogeochemical importance. Remote locations, however, can result in sampling sites with no power provision, infrequent sample collection, and/or the infrastructure-bearing location itself being a source of the targeted pollutants. As a result, innovation in collection strategies such as time-integrated off-grid sampling, with modularity in the deployment of replicates, as well as
materials for quantitative collection of environmental targets, is still needed to expand and/or modify networks to meet current and future monitoring and policy needs.

In biogeochemical cycles, for example, improvement of constraints in atmospheric carbon linkages to terrestrial and aquatic processes is necessary. This would play a critical role in correctly assessing climate feedbacks and reducing uncertainty in Earth system models. The measurement of atmospheric DOC transport to surfaces has been limited and impedes landscape scale carbon balance from being obtained (Casas-Ruiz et al., 2023). The pool of compounds from which DOC is derived in the atmosphere has also been limited and is only recently seeing an increase in research intensity. Reactive organic carbon (ROC) is defined as the sum of nonmethane organic gases and primary and secondary organic aerosols (Safieddine and Heald, 2017). The major removal mechanism of water-soluble organic compounds produced through oxidation from the atmosphere is by dry deposition of particle-bound pollutants and scavenging by rainfall (Jurado et al., 2004, 2005). When ROC is scavenged into rainfall, it becomes DOC and enters terrestrial and aquatic systems. Deposition measurements of ROC compounds are needed since they play a crucial role in the formation of secondary species such as ozone, particulate matter, and carbon dioxide (CO$_2$) (Safieddine and Heald, 2017; Heald and Kroll, 2020).

There are several evolving drivers around studying atmospheric ROC; for example, light-absorbing organic carbon that can affect global radiative balance and undergo photochemical transformations in the condensed phase (Saleh, 2020; Wang et al., 2021; Washenfelder et al., 2022; George, 2023). Reactive organic carbon can also influence cloud formation and contribute to precipitation acidity (Avery et al., 2006; Ramanathan and Carmichael, 2008). Measurements of speciated ROC are difficult due to the chemical complexity of emitted compounds and oxidation products (Heald and Kroll, 2020). To circumvent this, monitoring and quantifying DOC can be used as a proxy to estimate the total ROC in precipitation. However, quantitative measurements of DOC in precipitation samples are sparse due to its relatively low concentration of 0.1 to 10 mg C L$^{-1}$ (Iavorivska et al., 2016; Safieddine and Heald, 2017). Recently, calls for carbon closure on atmospheric processing of ROC make this measurement of increasing importance (Kroll et al., 2011; Heald et al., 2020; Barber and Kroll, 2021). Similarly, to obtain net landscape or watershed carbon exchange, studies require effective methods for capturing and preserving atmospheric DOC deposition to constrain biogeochemical linkages at global interfaces as outlined above.
In this work, we present the design of a custom-built automated array of precipitation samplers that can be operated both on- and off-grid for wet deposition collection. The purpose of these samplers is to enable cost-effective collection of integrated water-soluble conductive atmospheric constituents deposited in remote environments without grid power or routine access. A sensor interfaces with a custom-built motor control board capable of operating up to six independent wet deposition units such that canopy throughfall (TF) and incident precipitation (open fall, OF) measurements are possible to collect in replicate. The materials used can be easily changed in order to optimize collection and preservation of a wide array of target analytes, such as DOC, when using high density polyethylene and mercuric chloride (HgCl$_2$). We demonstrate that these platforms are capable of continuous operation off-grid for monthly wet deposition collection of precipitation across the Newfoundland and Labrador Boreal Ecosystem Latitudinal Transect (NL-BELT) during snow-free periods in 2015 and 2016. Extremes in system performance were evaluated by testing the power consumption of a sampling array from spring through fall when paired with a solar top-up system, and during snow-free winter conditions using only a battery. The two years of field samples were collected using an array of six collection units, with triplicate collection of both incident precipitation and throughfall from rain passing through a forest canopy. Samples were analyzed in terms of deposition volumes relative to total bulk volumes, reproducibility of replicate samples, and to determine the fraction of conductive rainfall within the total volume of precipitation at these remote sites. The captured fraction compared to total volume deposited is used to gain insight into how these samplers can limit analyte dilution effects and improve method detection limits, such as rejecting 50% of the total volume delivered as ultrapure precipitation leading to a factor of two improvement. Chemical parameters of pH, conductivity, and DOC fluxes collected according to established preservation protocols were then compared to prior measurements to validate this proof-of-concept system. Measurement methods for pH and conductivity of rainwater are very well-established in the literature and serve as a baseline reference to ensure that the samples collected by the new devices presented in this work are consistent with what is expected in samples from a remote coastal environment, given the selective sampling strategy. We then move away from these well-established parameters to quantify DOC fluxes using established biogeochemical preservation techniques for fresh water and groundwater to demonstrate the potential of these samplers in
application to automated collection of analytes of emerging importance and interest in the remote locations of our latitudinal transect.

2.0 Materials and Methods

2.1 Precipitation Sampling Array Components

Each automated precipitation sampling setup can be operated as an array, here being used in groups of up to six collection units (Figure 1). A collection unit is a simple opaque doored box. The box protects the sample containers against exposure to direct sunlight and provides a mounting location for the funnel and lid, while also facilitating easy exchange of sample containers. The collection units can be fitted with stabilizing legs that allow them to be bolted to concrete or pinned by retaining rods when on soil. In both cases, this prevents tipping and loss of sample during high winds or wildlife-sampler interactions (e.g., Figures 2 and S1). The collection of precipitation is facilitated by a funnel mounted through the top of the sampling unit. The funnel tip extends into the opening of the sample collection container placed inside. The connection can be sealed to better preserve volatile analytes with tubing that passes through a sealed grommet (P/N 9280K34, McMaster-Carr) to enter the sample collection container and minimize evaporative losses. Precipitation events are sampled selectively by modulating the position of a lid over the funnel with an electric motor. The collection unit motors are operated by a digital control board, which interfaces with a precipitation sensor and requires 12 volts of direct current (VDC) power supplied to this system. Switches detecting the lid position ensure complete opening or closure of the funnel mouth for each collection unit.
Figure 1. Schematic of custom-built automated precipitation sampling array components for off-grid wet deposition collection. The pink arrows denote the direction of electrical signal and power exchanged between components. The curved black arrow indicates the rotation of a motorized lid to obtain open (O) or closed (C) sampler configurations.

2.1.1 Collection Units

The collection unit materials to date have been made of both 3/8” plywood and black polyacrylate sheeting. The materials have demonstrated high durability on the order of four years under field conditions (Figures S1 and S2). Opaque materials were explicitly selected to minimize photochemical reactions and growth of photosynthetic microorganisms within the sample. The dimensions of the collection unit are detailed in Figure 2. Each can accommodate sample containers up to 20 L in volume for collection in locations with large monthly wet deposition volumes, such as in Newfoundland and Labrador (Table 1).
Figure 2. Detailed collection unit schematic with all dimensions provided in inches. Further specifications for the lid dimensions can be found in Figure S3. The shaded 3D rendering depicts both open and closed states for the lid, positioning of legs to secure it to surfaces, placement of corner brackets, and the door handle and hinges.

The box panels can be joined using hardware inserts (P/N 1556A54 and 1088A31, McMaster-Carr, Aurora, OH), 3D printed corners (Figure S4), or along the box edges with screws if using wood. The door is attached with two hinges (P/N 1549A57, McMaster-Carr) and held closed with a magnetic contact (P/N 1674A61; McMaster-Carr) or hooked latch. The electric motor controlling the lid is enclosed in a standard polyvinylchloride electrical junction box, which is attached to a short paddle mounted on one side of the collection unit. Here we used an electric worm-gear motor (12 VDC, 2 revolutions per minute; TS-32GZ370-1650; Tsiny Motor Industrial Co., Dong Guan, China) mounted inside the enclosure with matching hex bolts (P/N 91251A146, McMaster-Carr) that passed through the weather-tight cover while the drive shaft protrudes through a 3/8” hole drilled in the cover. The drive shaft has a flat edge to affix the lid rod using a short set screw (Figure S5) that is cemented semi-permanently in place with thread locking compound (P/N 91458A112; Loctite Threadlocker Blue 242; McMaster-Carr). The lid rod is 3/8” aluminum machined on one end to allow connection to the motor drive shaft (Figure S5) with four threaded holes along its length to affix the lid (Figure S3). The lid rod passes through a second mounting paddle on the box that keeps the lid level and capable of isolating the funnel from the
atmosphere in the absence of precipitation. The lids used here were made of 1/8” Lexan polycarbonate sheet.

Selective precipitation sampling is performed using a logic-based assessment of sensor and switch states (defined in Figure S6) by the control board quadNOR gate chip (Fairchild Semiconductor P/N DM74LS02) which activates the H-bridge motor driver chipset (Figure S7). A 12 VDC signal drives the clockwise or counterclockwise rotation of the motor, installed in a suitable port of the junction box, via a cable from the control board, which passes through a weather-tight compression fitting (e.g., Home Depot SKU# 1000116446). The motor rotation signal is interrupted when the lid makes contact with one of two weather-tight limit switches (P/N SW1257-ND; Omron, Digi-Key Electronics, Thief River Falls, MN) mounted on opposite ends of a horizontal armature connected to the vertical motor mounting paddle (Figure 2). The switches controlling the lid location ensure that the funnel is completely open or covered as necessary for precipitation collection. The funnels used in this work are 20 cm in diameter and made from high-density polyethylene (HDPE; Dynalon, P/N 71070-020, VWR International, Mississauga, ON). A 7" x 5" piece of filtration mesh (P/N 9265T49, McMaster-Carr) that was tied together as a fitted cone insert with Nylon thread (e.g., fishing line) to prevent large debris entering the sampler containers when used, for example, in the collection of TF precipitation under a forest canopy when accompanying litterfall is also expected. The exit of the funnel directs the collected precipitation into the narrow-mouth opening the container inside the collection unit, such as 20 L HDPE jugs or 10 L HDPE jerricans (Bel-Art Products; P/N 11215-314, VWR International).

2.1.2 Heated Precipitation Sensor

The detection of rain modulates the opening and closing of the collection units by an interdigitated resistive sensor (M152; Kemo Electronic GmbH, Geestland, Germany; Figures S6 to S8). This approach is consistent with established precipitation detection techniques used by government monitoring programs (e.g., CAPMoN: Canadian Air and Precipitation Monitoring Network, 1985a, 1985b). The rain sensor detects conductive deposition by the completion of a conductive circuit when electrolytes bridge the connection between the interdigitated gold electrodes. The sensor is supplied with 12 VDC from the power system to trigger a relay when precipitation conductance above 1 MΩ·cm conductivity is detected (determined experimentally, see Section S1). This is equivalent to approximately 8 µM sodium...
chloride. The sensor detection limit reflects an upper limit of precipitation ion loading because the design of the rain chute leads to an increase in surface area of more than a factor of 25 on which solutes can accumulate to enhance the ionic content of the deposited water.

An output of 12 VDC is sent to the digital control board by the relay when rain is sensed, or 0 VDC in its absence, for signal processing and motor control (Figure S7). When rain is sensed, the lid of each sampler in the array is simultaneously opened (<5 seconds) and is dependent on the rotational rate of the lid motor. To increase the sensitivity of this sensor and to extend the sampling duration when conductive atmospheric constituents are completely washed out of the atmosphere, a sloped tin chute (e.g., Home Depot SKU# 1001110514) was added to extend the surface of the rain sensor. The sensor was placed at the end of the chute and sealed in place with caulking to allow water droplets to move easily from the chute onto the sensor.

The angle of the chute can be adjusted to control the momentum of collected droplets so that they collect on the sensor surface and only flow off it when the rate of precipitation exceeds the sensor evaporation capability. When soil is available, two bent rods can be used to hold the chute at the optimized angle of 10° (Figure S2). They are inserted into the soil and the chute is affixed to the tops of the rods with zip ties passed through small holes drilled in the sides of the chute, which are subsequently sealed with caulking. When soil is unavailable, for example in urban environments, we have created a mounting frame to hold the chute at the optimized angle of 10° (Figure S8). When precipitation is detected the sensor surface draws current up to 1.0 ampere (A) into a heater to actively evaporate water from its surface so that it accurately detects the active period of rain events. The heated sensor has undergone preliminary field tests and is also capable of detecting ice and snow, provided they contain electrolytes.

2.1.3 Power Supply Systems

Power for this system can be supplied from a battery at 12 VDC or using a 115 VAC to 12 VDC transformer power supply (P/N 285-1818-ND; TDK-Lambda Americas, Digi-Key Electronics). Depending on the duration of sampling and the time of year, the battery capacity can be changed to suit power needs (Section 3.2.2). To provide sufficient power density in this study, over one to two month-long collection periods, the battery capacity was carefully matched; with top-up options implemented when prolonged or high-frequency precipitation was expected. Absorbent glass mat (AGM) marine deep cycle batteries can withstand discharge events down to
less than 60 % capacity and are robust under nearly all environmentally relevant temperatures (≤ -20°C to 40°C). Additionally, these batteries interface easily with solar charging options as they are able to accept high current input. Monthly collections in Newfoundland were powered with 76 amp-hour (Ah) AGM batteries (Motomaster Nautilus; Ultra XD Group 24 High-Performance AGM Deep Cycle Battery, 12 VDC) topped up by a 40 W solar panel interfaced with a charge controller to prevent overcharging (Coleman; Model # 51840, max current of 8 A at 14 VDC).

For collections made every second month in Labrador, a 120 Ah battery with the same solar top-up strategy was used to ensure continuous operation. For either remote field deployment, batteries and charge controllers were housed in a Pelican™ case (Model 1440, Ocean Case Co. Ltd., Enfield, NS) fitted with weathertight bulkhead cord grips (P/N 7529K655, McMaster-Carr) through which charging and power cables were passed (Belden, Coleman; S/N 7004608, 70875227, Allied Electronics, Inc., Ottawa, ON). Humidity in all weatherproof cases was minimized by exchanging reusable desiccant packs (Ocean Case Co. Ltd.) when depleted batteries were exchanged for fully charged replacements. Solar panels were repositioned monthly to optimize orientation for solar power provision. Using either power source, the control board converts and distributes the 12 VDC to the other components in the precipitation sampling array.

2.1.4 Custom Control Board

A custom control board to operate a six-collection unit array was designed based on prior digital logic circuits for standalone collectors (VandenBoer, 2009). The 12 VDC battery or transformer output is supplied directly to the rain sensor and relay, as well as to the motor drivers for lid opening (Figure S9). Each collection unit is controlled independently to ensure lids are fully opened or closed, thereby requiring six replicate motor driver control circuits that respond to their independent switch signals. The remainder of the signaling and digital logic operates on 5 VDC which is produced by on-board voltage regulators (Micro Commercial Co; P/N MC7805CT-BP, Digi-Key Electronics). The lid switches are provided with 0 and 5 VDC to indicate collection unit open or closed status (Omron Electronics; P/N D2FW-G271M(D), Digi-Key Electronics). The signals from the sensor and switches connect to the board through four-conductor cable (Belden; S/N 70003678, Allied Electronics Inc.) passed through weathertight bulkhead cord grips and secured to screw terminals (Figure S9). The sensor and switch signal inputs interface with a quad NOR GATE chipset (Texas Instruments; P/N 296-33594-5-ND, Digi-Key Electronics) to trigger
the motor driver (STMicroelectronics; P/N 497-1395-5-ND, Digi-Key Electronics) such that it rotates or remains stationary. The additional resistors, capacitors, and diodes are necessary to maintain stable signaling throughout the printed circuit board (Figure S9, Table S1).

The custom control board was housed in a Pelican™ case (1400 NF; Pelican Zone, Mississauga, ON) fitted with cut-to-use foam inserts and a reusable desiccant pack that was also exchanged alongside those for the battery cases. All collection units, sensors, and power supply cables were passed through eight weathertight bulkhead cord grips and fixed to screw terminals on the board. The opposing ends of the cables were fitted with weathertight Bulgin Buccaneer 400 or 4000 Series circular cable connectors (Table S2; Allied Electronics, Inc.) to allow easy field installation with mated connectors on the cables originating from each of the previously mentioned array components. Connected cables could then be buried in shallow soil trenches to reduce the attention of gnawing animals, as well as potential entanglement hazards with other wildlife. Precipitation events were logged from the control boards using a HOBO 4-channel analog data logger (UX120-006M; Onset®, Bourne, MA) that records the sensor, switch, and motor voltages. The fourth channel is reserved to monitor battery or power supply voltages over time (Section 3.2).

2.2 Power Demand and Management Tests

Power demand was calculated based on the cumulative component requirements prior to the selection of batteries. This was to ensure adequate capacity to collect samples over one to two month-long field deployments and are sufficient for an assumed worst-case scenario of one week of constant rain without solar power charge restoration. Solar panel power production capacity was determined based on the calculated energy required to recharge the battery. As a result, we selected the 40 W panel which could complete charging at 14 VDC with a week of direct sunlight at 8 hours per day. The power demand for a six-sampler array was measured in standby and during operation with a digital power meter (Nashone PM90, Dalang Town, China) in real-time when supplying 12 VDC with a transformer. Contrasting power demand tests were performed under different environmental conditions and power management configurations. The first was performed using the 76 Ah AGM battery with a solar top-up in an urban environment from July through August 2018, while the other was performed using a 103 Ah AGM battery alone from January through February 2019.
2.3 Continuous Monthly Collection of Remote Samples at NL-BELT

One array of six automated collection units (3 OF, 3 TF) were deployed within one forested experimental field site located in each of the four watershed regions of the NL-BELT (24 samplers in total) between 2015 and 2016. Additionally, between one to three total deposition samplers were located at each of the four field sites (Table 1, Figure S10). The watersheds span 5.5° latitude from the southernmost site Grand Codroy (GC), through the colocated Pynn’s Brook (PB) and Humber River Camp 10 (HR) sites, to Salmon River (SR) as the highest latitude site on the island of Newfoundland. The northernmost forested watershed, Eagle River (ER), is located in southern Labrador and extensive details characterizing each of the four sites can be found in Ziegler et al. (2017). All sampling locations are far from anthropogenic pollutant point sources, except for the ubiquitous presence of marine sea spray from the nearby marine coastlines. The total deposition samplers were identical to the automatic collection units except that they were not fitted with a motor arm and lid, so they did not require a source of power. Three of the six automated samplers were deployed in the open at a distance from the forest stand, equal to or greater than the height of the trees, in line with CAPMoN and NADP guidelines. The other three automated samplers were placed under the canopy to collect TF precipitation within the forest sites. These samplers actively collected wet deposition into integrated monthly (Newfoundland) or two-month (Labrador) samples during snow-free periods (approximately June through November). The arrays were collected and stored during the winter months while total deposition samplers remained in field locations year-round. It is also important to note that during the growing season, sample collections were made at the same time – that is, OF and TF deposition were collected on a single day at each sampling site and within a few days of each other across the transect. Collected sample volumes were compared between the automated samplers and total deposition collectors for each collection interval as a check on proper function (i.e., less than or equal volumes in automated samples). During each site visit, the slope of the sensor was confirmed to be correct, sample containers were collected and replaced with clean units, the battery and desiccant packs replaced with fully recharged devices, and the entire array confirmed operational.

Table 1. NL-BELT sampling site details provide locations and identifiers, alongside those from long-term weather stations operated by Environment and Climate Change Canada (ECCC). Soil pH was determined from samples collected at the same time as precipitation. Mean annual temperature was derived from ECCC climate normals. Annual total deposition precipitation
volumes were either measured for the 2015-16 period (ECCC, This Work) or calculated by the Oak Ridge National Lab DAYMET archive.

<table>
<thead>
<tr>
<th>Sampling Site</th>
<th>Sampling Site Location</th>
<th>Station (Climate ID)</th>
<th>Station Location</th>
<th>Soil pH(^a)</th>
<th>MAT (°C)(^b)</th>
<th>Average Annual Precipitation (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grand Codroy (GC)</td>
<td>47°50'43.1&quot;N 59°16'16.0&quot;W</td>
<td>Stephenville A (8403801)</td>
<td>48°32'29.00&quot; N 58°33'00&quot; W</td>
<td>3 to 4</td>
<td>5.0(^c)</td>
<td>53.2</td>
</tr>
<tr>
<td>Pynn’s Brook (PB)</td>
<td>49° 05' 13.20&quot;N 57° 32' 27.60&quot; W</td>
<td>South Brook Pasadena (8403693)</td>
<td>49°01'00&quot; N 57°37'00&quot; W</td>
<td>3 to 4</td>
<td>4.6(^d)</td>
<td>21.4</td>
</tr>
<tr>
<td>Salmon River (SR)</td>
<td>51°15'21.6&quot;N 56°08'16.8&quot;W</td>
<td>Plum Point (40KE88)</td>
<td>51°04'00&quot; N 56°53'00&quot; W</td>
<td>3 to 4</td>
<td>2.4(^e)</td>
<td>47.1</td>
</tr>
<tr>
<td>Eagle River (ER)</td>
<td>53°33'00.0&quot;N 56°59'13.2&quot;W</td>
<td>Cartwright A (8501100)</td>
<td>53°42'30&quot; N 57°02'06&quot; W</td>
<td>3 to 4</td>
<td>0(^f)</td>
<td>56.3</td>
</tr>
</tbody>
</table>

\(^a\) Soil pH for the organic and mineral soil horizons determined by addition of 400 μL of aqueous 0.5 M CaCl\(_2\) to a 50:50 w/w slurry of dried soil in deionised water. *Note: the four remote NL-BELT sites are dominated by balsam fir trees underlain by humic ferric podzol soil with pH ranging between 3.0 and 4.5.*


\(^c\) At least 20 years of measurements.

\(^d\) The World Meteorological Organization’s “3 and 5 rule” (i.e., no more than 3 consecutive and no more than 5 total missing for either temperature or precipitation).

\(^e\) Annual precipitation averages determined using ECCC daily precipitation reports.

\(^f\) Large quantity of missing data for this location from January 2015 to December 2016 prevents any reliable estimate.

\(^g\) Estimated deposition rates converted to volume using DAYMET (Thornton et al., 1997, 2021, 2022).

\(^h\) Volumes merged for 2015 and 2016 at PB and HR.

### 2.3.1 Sample Preservation

Four of the six sample containers (two each of OF and TF) were biologically sterilized using 1 mL of a saturated aqueous solution of mercuric chloride (HgCl\(_2\)) to preserve against biological growth and loss of bioavailable nutrients over the collection periods. Unsterilized sample containers (without HgCl\(_2\)) were used for measurements of recalcitrant species and to assess any matrix effects exerted on target analyte quantitation. The use of HgCl\(_2\) as a sample preservation technique has been long-studied and well-established (Kirkwood, 1992; Kattner, 1999); thus, additional tests to verify the preservation of collected chemical species over time were not performed. The analysis of deposition collected in unsterilized and sterilized containers, however, serves as a method for internal sample validation - as does
our evaluation of measurement outcomes in comparison to those reported within the literature. Collected sample volumes were measured with a 1000 ± 10 mL graduated cylinder and aliquots were collected for chemical analysis via transfer to precleaned 500- or 1000-mL HDPE containers (Nalgene; VWR International). Samples were stored at 4°C before returning to the laboratory where they were filtered with a 1000 mL Nalgene vacuum filtration system (P/N ZA-06730-53; ThermoFisher Scientific, Waltham, MA), fitted with 0.45 µm polyethersulfone filters (PES, P/N HPWP 04700, EMD Millipore), to remove suspended solids. Filtered samples were transferred to new clean HDPE containers and stored for up to two months at 4°C in a cold room until analysis. 

The target analytes in this work are non-volatile and the described sample collection methods consider this analyte property, as well as their interactions with container materials. The versatility of the system design allows for the use of different collection materials, keeper solvents for volatile organics, etc., so that the experimental design can be analyte specific, depending on end user needs. Sample preservation approaches should thus be identified by users of this new platform based on their scientific objectives and review of the literature (Galloway and Likens, 1978; Peden et al., 1986; Dossett and Bowersox, 1999; Wetherbee et al., 2010). In addition to the internal validation approach described here, we aim to demonstrate that the precipitation samplers in this work are suitable for measuring conductive deposition on- and off-grid. Below we highlight autonomous off-grid operations, determine the fraction of conductive rainfall collected from the total volume of precipitation, and validate our measurements through comparison to the literature.

2.4 Cleaning and Preparation of Sample Containers

All sample collection and storage containers, as well as all sample handling apparatuses, were made of HDPE or polypropylene for the quantitative analysis of target analytes. Prior to use in handling samples, these were all acid-washed in 10 % v/v HCl (P/N BDH7417-1; VWR International) followed by six sequential rinses with distilled water and ten rinses with 18.2 MΩ·cm deionised water (DIW; EMD Millipore Corporation, Billerica, MA, USA). Containers were dried by inversion on a clean benchtop protector overnight, or with protection from dust using lint-free lab wipes over container openings when necessary. Field and method blanks were collected through the addition of DIW to cleaned containers, and/or sample handling devices, in
order to quantify appropriate method detection limits and to identify any sources of systematic or random contamination. Blank subtraction was applied to measurements, where appropriate.

2.5 Measurements of pH and Conductivity

The pH and conductivity of each sample was determined using a ThermoScientific™ Orion Versa Star meter (ORIVSTAR52) interfaced with a pH electrode (Model: 8157BNUMD, Ultra pH/ATC Triode, ROSS) and 4-electrode conductivity cell (Model: 013005MD, DuraProbe, ROSS). Prior to use, the probes were calibrated daily with standard solutions specific for these probes (ThermoScientific™ Orion™ conductivity standard 1413, and pH 4, 7, and 10 buffers) and then stored between analyses according to manufacturer directions. Aliquots of 15 mL of precipitation from archived samples were subsampled into 40 mL polypropylene Falcon tubes. This was followed by immersion of a cleaned electrode for the conductivity measurement, followed by the pH probe measurement to prevent conductivity bias due to potassium chloride migration across the glass frit of the pH probe. Readings were recorded once signals had stabilized.

2.6 Measurements of Dissolved Organic Carbon (DOC)

Measurements of DOC were performed by catalytic combustion of samples in a platinum bead-packed quartz furnace at 720°C to quantitatively produce CO₂, followed by non-dispersive infrared absorption spectrophotometry using a Shimadzu Total Organic Carbon (model: TOC-V) analyzer and an autosampler (model: ASI-V). Cleaning of materials prior to DOC determination follows the same procedure as for the sample containers. Precipitation aliquots of at least 12 mL were transferred to clean and combusted (500°C, 5 hours) 40 mL borosilicate glass vials, then capped and stored at 4°C until analysis. Prior to analysis, vial caps were replaced with cleaned polytetrafluoroethylene-lined septa. Inorganic dissolved carbon (e.g., H₂CO₃) was purged from samples by acidification to pH 2 with HPLC grade H₃PO₄ (20 % v/v) and bubbling with an inert carrier gas. Samples were analyzed in triplicate and quantified using calibrations spanning 0.1 to 10 or 10 to 100 ppm (mg C L⁻¹) with potassium hydrogen phthalate (KHP), depending on the relative sample concentration range. Accuracy and precision were assessed using 1 and 10 ppm KHP check standards analyzed every 10 injections, respectively. Calibrations were performed at the beginning of every analysis day.
3.0 Results and Discussion

In addition to the general design advantages in the section that follows, we present the results of various physical and chemical parameters to validate this new open source custom-built modular system. The power consumption and snow-free performance testing are used to demonstrate the off-grid capabilities of these samplers, as are the two-year datasets. The lower power requirements are compared to existing commercial samplers and paired with solar top-up to prolong the use and reduce the need to replace batteries on timescales shorter than planned sampling duration (i.e., < 1 month). We then evaluate the automated wet deposition volumes, in which the samplers prevent dilution during atmospheric washout events, compared to total volumes collected from co-located samplers to depict the fractionation by volume as a function of time. We also investigate the advantages of replicates collected across the four watersheds, using deployments of triplicate samplers under field conditions. The ratio of collected TF to OF replicates highlights the ability of these samplers to capture the dynamic nature of precipitation interacting with forest canopies. Simple pH and conductivity measurements are then used as benchmarks to situate the NL-BELT data within the established literature to emphasize the robust operation of the samplers and impact of the selective sampling. Fluxes of DOC are also interrogated across all four sampling sites as we demonstrate the potential of these samplers to make measurements of more complex analyte pools that are of current interest to the atmospheric measurement community.

3.1 General Design Advantages

While several precipitation collectors have been similarly developed to address specific scientific objectives—e.g., the quantitation of dust in wet and dry deposition (Laurent et al., 2015; Brahney et al., 2020), determination of ions and DOC in a tropical rainforest (Germer et al., 2007) and urban environments (Audoux et al., 2023)—here we present a more general design for modular adaptability. When compared to other precipitation collection apparatuses, the automated precipitation sampler developed in this work has several advantages. Most notable is the ability to collect integrated samples at remote locations by exploiting its off-grid capabilities. Our approach also maximizes the sensitivity of the rain sensor as long as electrolytes remain in the water reaching it. The chute ensures that even if the precipitation contains ultra-trace analyte quantities, they are still collected and quantified for an extended period when
high-purity water may be deposited during an atmospheric wash-out event. The chute does this by accumulating water-soluble materials between rain events that require time to be completely washed off and through the release of ions from the material itself, which ages under environmental conditions. As the conductivity of the precipitation falls below the sensor threshold – conductive precipitation being that which initially contains high solute levels that progress through trace level concentrations – the added ions from the chute prolong the collection of rain past this time point. In rainfall events where extended atmospheric wash-out occurs, where precipitation becomes ultrapure water, the sampler lids will eventually close – preventing dilution of the sample while maintaining the collection of analytes of interest. A recent study has found that rainfall events could exhibit variability and the lower atmosphere can be supplied with aerosols due to specific sources, atmospheric dynamics, and meteorological conditions (Audoux et al., 2023). If this occurs, the automated lid will reopen to sample the polluted air masses. In application to trace pollutants, this also reduces methodological sample preparation time as it decreases the extent to which additional handling steps, like solid-phase extraction, are required prior to analytical determinations.

The six replicate measurements used in each array provide a means of assessing sampling reproducibility (e.g., canopy TF has expected heterogeneity) and for multiple analyte classes to be targeted. Various analytes, with different chemical properties and/or contamination considerations, can be targeted by changing the materials used for the components that encounter the sample (i.e., lids, funnels, and sample holding containers). Replicate collection can also allow for selective sample preservation when quantifying deposited chemical species that may be reactive, volatile, or biologically transformed. The modularity of the overall system design also allows the collection units to be dismantled entirely and easily reassembled on-site, minimizing logistical issues and costs for transport to remote regions. Lastly, these collection units are cost-effective. We were able to produce four arrays, each consisting of six collection units, at a fraction of the cost of a single equivalent commercial off-grid automated precipitation sampling unit.

With the majority of commercial precipitation samplers requiring a source of electricity, on-grid sample collection necessitates high infrastructure costs and/or samplers being positioned closer than desired to point sources of anthropogenic pollution. As a result, especially in remote locations, site selection becomes heavily restricted and expensive when factoring in all the standard criteria, particularly with respect to the need for an easily accessible power source. Thus,
the off-grid capabilities of our samplers lend dexterity to these systems and makes deposition
sampling that follows standard siting guidelines, like those of CAPMoN or NADP but without
power, more accessible to the global atmospheric research community (Vet et al., 2014). To further
highlight and validate their capabilities, a series of fundamental performance parameters were
collected and are discussed in detail in the sections that follow.

3.2 Power Consumption and Performance Testing

3.2.1 Power Consumption of Instrumental Setup

The simplicity of the automated precipitation samplers allows for low power consumption
during operation, which is particularly important for off-grid operation. The motors operating and
rain sensor heating during active precipitation are the most energy-intensive elements of the system
(Table 2). The integrated contribution of the motor over a month-long sampling period is however
negligible compared to other components, since it is operational for short periods of 5 to 10
seconds with a current usage of only 38 mA. The continuous need to provide 5 VDC to the digital
logic via step-down from 12 VDC is actually the largest power consuming component of the setup
in the absence of rain. When the samplers are in the closed position, under rain-free conditions,
the power consumption of the entire array is 4.66 Watts (W) and 2.86 W for transformed 115 VAC
and battery 12 VDC supplies, respectively. The provision of 12 VDC to the board with a
transformer for the 115 VAC application results in greater total power requirements. These values
increase to 10.00 W and 5.04 W with the detection of a conductive liquid on the precipitation
sensor as it heats the sensor surface to capture the active period of the event. Based on the measured
power consumption, a fully charged 103 Ah AGM battery would provide at most 447 hours (or 18
days) in standby mode under rain free conditions and 294 hours (or 12 days) if the heated surface
of the sensor is in continuous use (Table 2). The lower range limit is unlikely since the sensor only
operates for the duration of a rain event, after which the battery is available for solar top-up again.
In the fieldwork conducted here, battery life was extended through the addition of 40 W solar
panels to the systems. The entire array was confirmed to be operational at the end of monthly (SR,
PB, and GC) and two month (ER) integrated sampling periods on an ongoing basis, prior to
exchange with a new fully charged battery, for two years.
Table 2. Measured voltage, current, and power consumption of the rain sensor and circuitry in both the idle and maximally operational state when connected to a 12 VDC battery or transformed 115 VAC. Total power demand was measured for wet and dry sensor scenarios.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Rain Sensor</th>
<th>AC Outlet</th>
<th>DC Battery</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage (V)</td>
<td>12 DC</td>
<td>12 DC</td>
<td>114 AC</td>
<td>DC</td>
</tr>
<tr>
<td>Current (A)</td>
<td>0.008</td>
<td>0.120</td>
<td>0.040</td>
<td>AC</td>
</tr>
<tr>
<td>Power (W)</td>
<td>0.10</td>
<td>1.44</td>
<td>4.56</td>
<td>DC</td>
</tr>
</tbody>
</table>

In comparison to two commercial samplers used by national monitoring networks, the power requirements of our new samplers are substantially lower. The first commercial sampler we reviewed draws a maximum of 2 A, with a ceramic heater housed within the sampler case that draws 0.8 A constantly, resulting in an upper limit power demand of 230 W (at 115 VAC) and a lower limit of 92 W. The commercial sampler can be upgraded to utilize a thermostated space heater for winter operation, drawing an additional 4.2 A (480 W), resulting in a maximum power demand of about 800 W when using a 115 VAC power supply. A second commercial precipitation sampler reviewed is used by national monitoring networks and draws approximately 5 A, resulting in a power requirement of 575 W at 115 VAC. The commercial and standard precipitation samplers for deposition monitoring programs have much higher power requirements compared to those presented in this work. The commercial samplers utilize 80 to 100 times more power. With our lower power requirements, the new automated samplers prove to be advantageous in both on- and off-grid sampling yet are disadvantaged in being unable to collect snow in the winter.

3.2.2 Precipitation Sampler Performance Tests and Data Logging

In addition to low power consumption during precipitation sampling, a supplied battery can obtain constant power renewal when outfitted with a solar top-up that is kept exposed to sunlight by proper orientation. At NL-BELT, adjustments were made for this during each site visit during sample collection. During the solar top-up tests below, voltages of the sensor and batteries were consistently monitored. Over a test period of 22 days, no appreciable decline in battery performance of a 76 Ah unit was observed despite the detection of more than 10 rain events during that period (Figure 3a).
Figure 3. Performance of off-grid precipitation samplers during sample collections from (a) 13 July to 7 August 2018, using a 76 Ah battery and solar panel top-up and (b) 22 January to 13 February 2019 with a 103 Ah battery and no solar panel. Battery voltage (shaded orange) is elevated above 12 VDC when charging, or decreases over time when no solar panel is used and precipitation is sensed/colllected. The 12 VDC rain sensor relay signal (purple) and the open sampling lid switch voltage (blue) indicate active periods of detected precipitation. The black dashed line indicates the 60% efficiency cut off, 7.2 V, at which the battery should be recharged.

In comparison, winter sampling with these devices is not recommended without substantial investment in a sufficient power density provided high-performance cold weather batteries. The lack of sunlight during winter at higher latitudes also negates the use of effective small scale solar top-up. Our tests show that when the samplers were deployed without a solar backup under snow-free winter conditions (temperatures ranging from -17.8 to 7°C), with a 103 Ah battery, the off-grid system only lasted for 17 days. At this point, the larger capacity battery was fully depleted by frequent snow and rainfall – probably due to the heated precipitation sensor requiring additional energy to phase change snow and ice to water and then to evaporate that water. This depletion occurred despite housing the battery in an insulated enclosure during the test. In addition, on days 6 and 16, the precipitation sensor relay was activated but the lid did not rotate to the open position (Figure 3b, blue trace). This could have been because the precipitation event was not intense
enough for the lid to open fully and trigger the 5 V lid open switch or because of snow and ice buildup around the lids resulting in them being unable to physically open. Overall, these samplers may be possible to deploy during the winter if line power can be supplied. Such a deployment would further necessitate that the sampling funnel be heated to render a liquid sample for collection in the jugs in addition to the sensor chute to prevent snow and ice accumulation. A heated funnel would also prevent snow or ice accumulation on top of the automated lids. Together, such power-hungry requirements for winter operation exceed simple off-grid use with a battery package that is easily transported into and out of remote field sites.

3.3 Comparison of Sample Collection Volumes

The automated samplers were colocated with total deposition samplers and deployed across the experimental forests of four NL-BELT regions during the 2015 and 2016 growing seasons to observe deposition trends. In addition, we compare these observations to the long-term climate normals reported by ECCC and estimated deposition at 1 km x 1 km resolution from the DAYMET reanalysis model (Table 1, Section S2). Three automated samplers were deployed in the open to collect incident precipitation (OF) and another three under the experimental forest site canopy (TF). The mean OF volumes of triplicate measurements from south to north were 1.42, 1.38, 1.31, and 0.79 L, whereas the corresponding TF volumes were generally similar in magnitude at 0.96, 0.98, 1.02, and 1.13 L, for the 2015-16 sampling period (Figure 4). It is evident that the volume of precipitation decreased as latitude increased for OF samples, whereas the opposite relationship was observed in TF samplers, although the absolute volumes are more comparable in magnitude. The total deposition volumes collected were as expected, decreasing from south to north in agreement with the expectations from the long-term normals and comparable to the estimates from the DAYMET model (Table 1), where the largest integrated volume of precipitation was collected at the lowest latitude (GC) and a lower amount at the highest latitude (ER), with the intermediate sites (HR and PB) having the lowest inputs overall during this observation period. Total annual deposition volumes collected by our deployed samplers from south to north in 2015 were 39.5, 39.4, 31.9, and 17.5 L, while in 2016 they were 51.7, 37.8, 32.8, and 34.2 L. Total deposition volume collected from HR was used for comparison to automated sample volumes collected at PB in 2015, as they both share the same watershed. This approach had to be taken, as the HR site was initially planned for full experimental use before becoming inaccessible in early 2015. The relative
error between the two sites for samples collected in 2016 was ± 15% (24.6 L in PB and 32.2 L in HR), comparable to the reproducibility we observe for replicates collected within a given site (see below). The total deposition samplers were installed in HR in late 2014 and the automated samplers were then set up at PB. Despite this, there is good agreement between the trends in predicted deposition values by DAYMET with the measured values, although the absolute amounts from these are systematically lower in all of our observations \[\text{Section S2}\]. Regardless, by following the recommended siting criteria from the NADP and CAPMoN as best as possible, the very strong agreement of our temporal trends at both annual and monthly timescales with both comparators demonstrates the suitability of the total deposition samplers and, therefore, the automated samplers for use in quantifying deposited chemical species of atmospheric interest into the experimental sites.

The wet deposition volumes collected for the snow free period using the automated precipitation samplers did not follow the trends in total deposition (Figure 4), as might be expected (e.g., due to pollutant loading, rainfall quantity/rate, and scavenging processes). For the 2015 collection period from June through October, the summed volumes of OF precipitation, from south to north across the NL-BELT, were 25.4, 10.9, 20.4, and 2.2 L, while in 2016 they were 17.3, 30.4, 13.5, and 5.1 L. While the total and OF fractions would typically be much closer to unity in more polluted regions, it would be expected in these remote NL-BELT field sites for the differences to be driven by complex, non-linear processes that cannot be easily disentangled. Here we present three reasons as to why the measured wet OF deposition volumes do not follow the total deposition trend across the transect. First, these samplers are designed specifically to collect only conductive precipitation (i.e., containing conductive atmospheric compounds) not total/bulk precipitation. As a result, the OF wet deposition volume collected across the sites is mostly below 50% of total volumes collected, while TF volumes are similar in magnitude or lower than that of OF (Figure 4). The wet deposition fraction collected was variable within and between regions, sometimes less than 10%, despite large volumes collected in total and presumably due to intense atmospheric washout that this region is well-known for. Second, the NL-BELT total deposition trend estimated using the ECCC long-term climate normals represents a 30-year period (Bowering et al., 2022) while the automated volume measurements here represent two years of targeted conductive precipitation collection. The combined summed volumes of targeted conductive wet deposition across the 2015 and 2016 field seasons were 42.7, 41.3, 33.9, and 7.3
L, somewhat better reflect the expected precipitation trends within the transect (Table 1). Lastly, our monthly automated wet deposition sample collection periods occurred from June through November and so it is temporally incomplete with respect to the substantial amount of precipitation volume deposited as snow delivered during the winter (Table S3). The discrepancies between the long-term trends and our shorter-term observations therefore make sense as they are sensitive to interannual changes in synoptic scale transport and rainwater solute loadings, as exemplified by the volumes collected in SR in 2015 (Figure 4b) and PB in 2016 (Figure 4c). Overall, for the automated sampler observations on a per-year basis, there is no consistent trend between site latitude and the volume collected in either OF or TF. This is unsurprising as they are dependent on the conditions that drive the rate of atmospheric wash-out and presence of conductive solutes.

The automated OF wet deposition volumes collected each year have peak values that range from 1 to 4 L with an overall variability of ± 33% for any triplicate of samples across the entire dataset. Across our 33 sample collection periods, our replicate relative standard deviations (RSDs) follow a log-normal distribution where volume reproducibility is typically within ± 12.5% and almost always within ± 31.5% (Figure S11). A few outliers with higher variability skew the overall view of volume precision. Out of 33 OF samples collected, 10 have RSDs greater than 40.5% with 2 of those having RSDs greater than 100%. Those values greater than 40.5% had no systematic relationship with site or time of time. Wind speeds were considered as a possible source of variability. The prevailing winds over Atlantic Canada are known to be southwesterly in the summer – intensifying during the autumn months – and westerly to northwesterly in the winter (Bowyer, 1995; Jacob, 1999; Randall, 2015). Strong wind speeds (i.e., >100 km/hr) could occur on an event basis during any time of the year and, thus, could contribute to the variability seen at each field site. Wind is known to generate bias in gauge-based precipitation measurements where unshielded precipitation gauges can catch less than half of the amount of a shielded gauge (Colli et al., 2016). A windscreen design for obtaining rainfall rates – and thus, volumes – to be more reproducible could be considered in future deployments of our developed samplers, similar to recently reported innovations for smaller rainfall rate devices (Kochendorfer et al., 2023). This would, however, increase costs and logistical considerations in deploying the developed devices which currently operate synonymously to deposition systems employed by government monitoring programs. Our siting approach is consistent with these, which often deploy a single sampler without wind protection, Thus, by employing replicates,
In addition, collection of replicate samples allows our observations to span a wider physical area, reducing the impact of confounding variables such as wind speed in comparison to a more typical sample size of one for many field collections. Imperfect siting and lack of shielding is necessary where remote field sampling prevents the setup of such infrastructure. As a result, the deployment of triplicate samplers provides researchers with a better opportunity to implement quality control as they can reduce bias in the event of dynamic OF. While the effect of wind is reduced, additional factors can drive variability when the samplers are placed under a forest canopy for TF collection.

To demonstrate canopy dynamics impacting interception volumes within the sampling sites, the ratio of throughfall to open fall (TF/OF) volume was compared amongst our total pool of 31 samples. This group of samples encompassed the monthly average TF/OF values for each set of triplicate samplers, at all four sites, from 2015 to 2016. These measurements were then split into two separate populations – samples that have a TF/OF less than one (n=24) and those that have a TF/OF greater than one (n=7). The samplers were positioned identically between years and no single sampler was reproducibly found in the second population. In the first population, the fraction collected was 56 ± 21% (ranging from 19 to 88%), likely due to the known processes of canopy and stem interception (Eaton et al., 1973; Howard et al., 2022). For example, in two young balsam fir-white birch mixed forest stands, the amount of precipitation intercepted by the forest canopy, in similar snow-free conditions, was estimated to be 11 ± 5% (Hadiwijaya et al., 2021). In mature boreal forests, 9% to 55% of rainfall can be intercepted by the canopy (Pomeroy et al., 1999). Relevant to deposition of atmospheric constituents, Pomeroy et al. (1999) also reported that up to 70% of intercepted rainfall may evaporate directly from the canopy, which can leave behind non-volatile rainfall solutes. Wet deposition that undergoes stemflow (SF) proceeds down the branches, stems, and/or trunks of a plant, transferring precipitation and nutrients from the canopy to the soil at the trunk or stem base (Ciruzzi and Loheide, 2021). These known mechanisms of canopy interception ultimately reduce the amount of precipitation reaching the ground as TF, and thus, this explains the smaller volumes found in our samplers compared to the OF measured simultaneously. In contrast, the fractions that ranged from 108% to 424%, averaging 186%, demonstrates a different aspect of the highly dynamic nature of canopies where they can sometimes intercept rainfall like an impermeable surface to act as a funnel, guiding large volumes of precipitation on to the ground, or in this case into the TF samplers (Metzger et al., 2019).
Figure 4. Average volume collected from replicate automated samplers deployed from June 2015 to October 2016, from north (N) to south (S), at the NL-BELT field sites: (a) ER, (b) SR, (c) PB, and (d) GC. The red trace represents open fall, teal for throughfall, and light green for total deposition (the sum of conductive and non-conductive precipitation). The total precipitation volumes depicted for PB, from July 2015 to November 2015, were collected at the nearby HR site in the same watershed since no total deposition measurements were in place at PB during this period. The missing volume for GC in 2015 was estimated from the determined ECCC station linear relationship and is presented as a broken line. The fraction of precipitation collected as open fall or throughfall, compared to the total deposition (right axis), are represented by diamonds of the corresponding color. Error bars represent the standard deviation of three measurements from replicate samples. The axis break spans the winter months when the off-grid automated samplers were stored.

3.4 Characterizing Chemical Parameters from NL-BELT

In addition to assessing physical parameters, chemical parameters were also evaluated in this work. Conductivity and pH are measurements commonly made on precipitation samples collected from the field and so incorporating them into our analysis is useful for instrumental validation. Additionally, with increasing recognition of their importance as a proxy for ROC estimation, and in biogeochemical carbon budget closure, DOC flux measurements were used to compare against a limited number of prior reports, each using different sampling or data interpretation strategies. These chemical measurements were also made in an underrepresented
part of the world in terms of atmospheric deposition sampling and are useful additions to the overarching study of precipitation chemistry.

3.4.1 Precipitation pH

The deposition of atmospherically persistent pollutants and biogeochemically relevant species to the Earth’s surface, or even NO$_3^-$ and SO$_4^{2-}$ historically, can affect the environmental health of soil, air, and water. With the pH range of natural rainwater in equilibrium with atmospheric CO$_2$ expected to be between 5.0 to 5.6, acid rain is defined by values lower than this (Han et al., 2019). Traditionally, the extent of acidity depended on the intercepted atmospheric concentrations of HNO$_3$ and H$_2$SO$_4$. In any case, monitoring acidity and deposition is especially relevant in remote regions, where major uncertainties and gaps in deposition measurements and global ion concentrations exist (Escarré et al., 1999; Vet et al., 2014). A change in pH can modify the chemical state of many pollutants, altering their transport, bioavailability, and solubility (Guinotte and Fabry, 2008). For example, this can increase exposure and toxicity of metals and nutrients in marine habitats which can go undetected for longer periods in remote areas.

Most TF samples were observed to have slightly higher pH than those from OF which had pH values ranging from 4.14 to 5.71 (Figure 5, Table 1). The TF precipitation pH, on average, ranged from 4.74 to 5.99 with rare exceptions falling outside of that range (e.g., July and September 2015 PB pH of 3.69 and 4.26, respectively, and the July 2015 GC with pH of 4.12). Excluding these exceptions, there are no major variations observed spatially between the four sites, or temporally between seasons or years (Figure 5). The pH values reported at each of the NL-BELT field sites are comparable to recent OF measurements made at CAPMoN sites in Nova Scotia and Newfoundland and Labrador, where the reported pH of precipitation ranged from 4.44 to 5.19 (Houle et al., 2022). The more basic TF overall is expected, as it has been found that up to 90% of H$_3$O$^+$ in precipitation can be absorbed by leaves while passing through the canopy (Cappellato et al., 1993). Foliar leaching, the release of ions from leaves, has been commonly reported for base cations such as Mg$^{2+}$, K$^+$, and Ca$^{2+}$ while being minimally observed for other ions such as Cl$^-$ and SO$_4^{2-}$ (Carlson et al., 2003). Mechanisms for foliar leaching include passive cation exchange of H$_3$O$^+$ with, for example, cells in the interior of the leaf (Burkhardt and Drechsel, 1997). Additionally, alkaline dust – deposited on the leaves of the canopy, can decrease the acidity of TF precipitation. Such dust can accumulate on leaf surfaces as a result of anthropogenic (i.e., industrial
processes) or natural (i.e., wind erosion) sources (Csavina et al., 2012), so that precipitation passing through the canopy can interact with it (e.g., CaCO$_3$); thus, neutralizing acidic species and increasing the TF pH observed in our automated samplers.

**Figure 5.** Average pH values from replicate samples collected at each NL-BELT field site, from north (N) to south (S), at (a) ER, (b) SR, (c) PB, and (d) GC, from June 2015 to August 2016. Open fall collections are represented using the solid blue trace whereas the orange trace is the pH of the precipitation collected as throughfall under the balsam fir canopy.

The pH of the collected precipitation appears to be similar in both TF and OF as a function of time – despite the potential for foliar leaching and dust dissolution in the canopy. The same chemical components may be setting the pH, as these measurements do not vary much seasonally, geographically, or temporally. As pH is a long-studied measurement, its purpose in this work was to validate the sample quality from our described collection approach, rather than drive any scientific objective. Nevertheless, while the NL-BELT measurements demonstrate a recovery compared to rainwater pH in 1980s eastern North America – prior to NO$_x$ and SO$_2$ regulation (pH from 4.1 to 5.0; Barrie and Hales, 1984), the present-day pH remains lower than expected for natural rainwater (~5.6; Boyd, 2020). Keeping in mind the successful environmental policies limiting SO$_2$ and NO$_x$, leading to considerable decreases in atmospheric concentrations of H$_2$SO$_4$
and HNO₃, a modern view on the trajectory of continental U.S. cloud water composition and pH has recently been reported (Lawrence et al., 2023). Across the U.S. and eastern Canada, measurements of anion molar charge equivalents have been lower than cations – a potential explanation being an increase in the presence of weak organic acids which commonly have pKa values near 4 (Feng et al., 2021), an outcome we have also observed in aerosol sample chemical composition from Atlantic Canada (Di Lorenzo et al., 2018). With the frequency of acid rain having a pH < 5 decreasing over the past 20 years, these recently reported measurements depict deposition composition shifting away from a ‘linear’ chemical regime dominated by H₃O⁺ and SO₄²⁻ towards a ‘non-linear’ regime designated by low acidity, moderate to high conductivity, potentially weak acid-base buffer systems, and increasing base cation and TOC concentrations (Lawrence et al., 2023). It would seem the evolving chemical contributors to global rainwater pH remain an open line of investigation.

3.4.2 Precipitation Conductivity

In all the collected OF and TF precipitation samples, across all four NL-BELT sites, the average measured conductivity values ranged from 21 to 166 µS/cm following no apparent seasonal or temporal trend (Figure 6). Additionally, the conductivity in both OF and TF also appear to vary across the field sites - only within the 2016 TF samples does the conductivity appear to increase with decreasing latitude. Yet, with the typical conductivity of surface and drinking waters being between 1 to 1000 µS/cm (Lin et al., 2017), and typically below 200 µS/cm in stream water measurements within the watersheds of each of the NL-BELT sites, our observations are comparable and fall within the expected range. Our field blanks – encompassing a variety of materials and apparatuses, and our cleaning procedures, routinely produced conductivities of 9 ± 5 µS/cm. The conductivity of saturated HgCl₂ in water (at 0.1% vol/vol) was 13.6 ± 0.4 µS/cm, which is also comparable to but statistically higher than our field blanks (p = 0.0015; unpaired t test) and less than what was observed for our samples (p < 2 x 10⁻⁶ for each site considered separately and also across all sites; unpaired t-test). Even with this background correction applied, the conductivity values presented here are expected to be similar to or higher than what would typically be found in rainwater (4 to 150 µS/cm; Beverland et al., 1997) as the rain sensor deliberately selects for precipitation containing ionic chemical components with conductivity greater than 1.0 µS/cm, while excluding pure water during atmospheric washout,
which would dilute the dissolved solutes in the wet deposition sample and lower the resulting conductivity values. The overall comparability between our range and those previously reported, where the lower limit is slightly higher in our dataset, demonstrates that the principle of operation of our instrument is robust. It decisively collects precipitation with the property of conductance indicating dissolved ionic solutes of interest to atmospheric chemical processes.

Figure 6. Average conductivity measured from replicate automated samplers at the NL-BELT field sites, from north (N) to south (S), at (a) ER, (b) SR, (c) PB, and (d) GC, from June 2015 to October 2016. The green trace represents open fall samplers whereas the purple trace represents throughfall samples. The error bar represents the standard deviation between replicate measurements. The dashed black line represents the upper threshold of conductivity (13.6 µS/cm) that arises due when an addition of saturated aqueous HgCl₂ is made to microbially sterilize samples. Note that all samples have conductivities equivalent to or higher than 13.6 µS/cm.

3.4.3. Wet Deposition of Dissolved Organic Carbon (DOC) at NL-BELT

The concentration of DOC in OF and TF precipitation, across all four sites, ranged from 3 to 46 mg L⁻¹ and 5 to 65 mg L⁻¹ with averages of 16 ± 10 mg L⁻¹ and 22 ± 12 mg L⁻¹, respectively (Table 3). Concentrations are influenced by the volume collected and are not useful when discerning deposition trends and/or mechanisms. The concentrations were converted to elemental fluxes using the volume of precipitation collected, the area of the funnel and the number of
The total flux for each sample period was summed and reported as an equivalent annual flux with the following units: mg m\textsuperscript{-2} a\textsuperscript{-1}. Annual fluxes ranged from 600 to 4200 mg C m\textsuperscript{-2} a\textsuperscript{-1} across the study sites for the snow free period (Table S4).

The TF DOC fluxes were enhanced compared to the corresponding OF samples as precipitation was intercepted by the forest canopy, with fluxes higher in TF samples by 600, 400, and 400 mg C m\textsuperscript{-2} a\textsuperscript{-1} at GC, SR, and ER, respectively (Table S5). The accumulation of water-soluble organics on forest canopies that increases DOC detected in TF could originate in part from organic carbon-containing compounds aged through oxidation reactions in the atmosphere, which increases their water solubility and propensity for surface interactions. In periods without substantial rain, these oxidized organics deposit effectively to the high surface area of forest canopies, contributing to the elevated DOC measured in TF. Additionally, non-volatile organics left behind from evaporated precipitation intercepted by the canopy could also contribute. Conversely, other mechanisms within the forest could result in enhanced DOC in TF. Recently, Cha et al. (2023) utilized a mass balance approach to determine whether DOC deposition is driven by canopy leaching (i.e., soluble tree resin, leaf exudates, internal tissues and microbes) or dissolution of dry deposited gases and PM\textsubscript{2.5} on plant foliage into rainwater. It was found that canopy leaching is the major contributor to TF DOC, accounting for ~83% of throughfall DOC. Whereas, PM\textsubscript{2.5} and rainwater only accounted for ~3 and 14%, respectively, while dry deposited gases were not considered. This suggests that internal cycling of DOC within the forest could be an important source of DOC to the throughfall soil interface (Cha et al., 2023). It is possible that a similar mechanism may be responsible for the elevated levels of DOC in TF at the NL-BELT sites, but we cannot explicitly distinguish between internal cycling versus external deposition in the current study.

A notable exception was observed at PB, where the DOC fluxes in the open fall sample were enhanced up to 1800 mg C m\textsuperscript{-2} a\textsuperscript{-1} when compared to the TF in 2016. This may be attributed to a difference in forest type within this NL-BELT region being black spruce (\textit{Picea mariana}) instead of balsm fir (Bowering et al., 2023). Some studies have suggested that forest type could be a major factor affecting DOC variability (Arisci et al., 2012; Sleutel et al., 2009). Specific differences in canopy height, leaf area index, canopy structure and the shape of leaves and needles could drive DOC differences between forest types (Smith, 1981; Erisman and Draaijers, 2003;
Sleutel et al., 2009). The elevated levels in OF samples relative to TF within PB are consistent with idea of uptake and/or leaching of canopy DOC in the internal cycling of DOC, while the enhanced TF at the rest of the sites is more difficult to observational constrain the participating processes.

Episodic events, such as polluted air masses from wildfires could also result in elevated deposition of DOC. It is estimated that ~116 – 385 Tg C a⁻¹ is produced globally due to the incomplete combustion of biomass during landscape fires (Santín et al., 2016; Coward et al., 2022). Several studies have associated enhanced DOC levels with wildfires (Gao et al., 2003; Moore, 2003; Wonaschütz et al., 2011; Myers-Pigg et al., 2015). More recently, Coward et al. (2022) measured DOC in Pacific surface waters along the California coastline and observed 100 to 400 % increases in DOC concentration, when compared to pre-wildfire conditions. It is possible that a similar biomass burning plume that underwent atmospheric washout, could be responsible for the enhancement in the observed DOC at NL-BELT, overlaid on a background more typical of seasonal oxidation of biogenic DOC. This also coincides with the seasonal variability observed in OF samples from the same summer where elevated levels of DOC were measured. For instance, the DOC deposition at PB for August 2016 was 4800 mg C m⁻², whereas the total deposition for the same year was 7800 mg C m⁻² a⁻¹. This single period accounts for 62% of the total DOC deposition at this site. This underscores the pivotal role that episodic transport may play in influencing the dynamics of DOC deposition, particularly with a warming future where wildfires are more prevalent.

The deposition trend observed in the current study also highlights the complexity of the varied drivers of atmospheric ROC, in which some months have more DOC in TF versus OF and occasionally the opposite is observed. Generally, we observed similar fluxes in both samples – suggesting that the amount of deposited carbon is comparable. Although the volume of precipitation captured in TF samplers are generally lower when compared to the corresponding OF samplers, the deposition flux of DOC is greater in TF samplers. With DOC enhanced in TF samples, the values reported here could be an underestimation of the amount of carbon reaching the forest floor during precipitation events due to competing processes within the canopy. One such process is stemflow (SF), where a fraction of precipitation intercepted by the forest canopy is funneled over the bark of the tree surface to the base of the tree stem (Oka et al., 2021). Although, SF was not measured in the current study, several studies have demonstrated that DOC
concentrations are enhanced in SF when compared to the corresponding TF and bulk precipitation samples (Stubbins et al., 2017; Van Stan and Stubbins, 2018; Ryan et al., 2021). Additionally, we cannot rule out that the chemical speciation differs between OF, TF, and SF even if the DOC values are similar, but such insights require more selective instrumentation for chemical analysis (e.g., high resolution mass spectrometry).

Figure 7. Average DOC fluxes (mg m$^{-2}$ d$^{-1}$) in replicate samples collected at the NL-BELT field sites, from north (N) to south (S), at (a) ER, (b) SR, (c) PB, and (d) GC, from June 2015 to August 2016. The yellow trace represents samplers that were placed in the open without any obstruction whereas the blue trace represents samplers that were placed under the canopy. Error bars represent the standard deviation of three measurements from three independent samples.

The ability to accurately determine DOC in OF and TF precipitation demonstrates the capability of the automated deposition samplers. To validate our measurements, we compared our observed fluxes to other studies in different forest types. Mean annual DOC fluxes were generally similar to those reported in some other boreal forests (Table 3). These include Finland, with work in stands that consisted mainly of Scots pine (Pinus sylvestris L.) (mean OF 2.32; TF, 4.35 g C m$^{-2}$ a$^{-1}$; Pumpanen et al., 2014), as well as in Mont St. Hilarie, Québec (mean OF 0.49; TF 2.05 g C m$^{-2}$ a$^{-1}$; Dalva and Moore, 1991), which also consisted of a variety of tree species.
species such as yellow birch (*Betula alleghaniensis*), red maple (*Acer rubrum*), and sugar maple (*Acer saccharum*). Conversely, the annual fluxes were orders of magnitude lower than measurements made at the University of Georgia (23 to 48 g C m\(^{-2}\) a\(^{-1}\)) which has a subtropic climate consisting mainly of southern live oak (*Quercus virginiana* Mill.) and eastern red cedar (*Juniperus virginiana* L.) occasionally hosting dense epiphytes (Van Stan et al., 2017). This highlights the potential variability to expect when measuring DOC in different forest systems, as the annual DOC fluxes vary depending on factors such as climate, tree species composition, and environmental conditions.

These results underscore the pivotal role the off-grid custom-built automated deposition samplers can play in advancing scientific research, particularly in precipitation monitoring and analysis. The automated system enabled long term continuous sample collection in remote locations, which was previously challenging to attain due to the need for frequent human intervention and resources required to regularly access these experimental forest stands. These samplers also allowed us to compare DOC through replicate measurements in TF and OF samples which sheds light on the potentially different DOC deposition chemistries within the NL-BELT region. The automated system better maintains the integrity of DOC in the samples. This was achieved by following standard procedures for biogeochemical sample preservation (i.e., adding HgCl\(_2\)) (Argentino et al., 2023), employing a rigorous cleaning procedure, and preventative design against the intrusion of forest litter which could result in a positive bias for DOC in the collected precipitation. The use of replicates also results in more robust scientific conclusions and broader applicability of the results, and they can be obtained for a fraction of the cost of a commercial equivalent, highlighting the contribution these automated systems are capable of when applied to current precipitation monitoring. As a result, these samplers show promise in the quantification of biogeochemical and anthropogenic chemical species of interest, which will be visited in future manuscripts drawing from the samples presented in this dataset, and others since obtained, but are beyond the scope of this manuscript in demonstrating the performance of this new instrumentation.

**Table 3.** Concentrations (mg C L\(^{-1}\)) and annual fluxes (g C m\(^{-2}\) a\(^{-1}\)) of DOC in precipitation (P), open fall (OF), throughfall (TF), and stemflow (SF) collected at forested sites. Where volumes are not available for other studies, fluxes are not possible to calculate. The values reported in the current study are the estimated DOC flux for the wet deposition sampling period (~June through
October) for each year and therefore represents the lower limit of DOC deposition, as the dataset excludes snow.

<table>
<thead>
<tr>
<th>Site</th>
<th>Type</th>
<th>Mean Concentration (mg C L⁻¹)</th>
<th>Annual Flux (g C m⁻² a⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grand Codroy, NL, Canada</td>
<td>OF</td>
<td>12.83</td>
<td>1.56</td>
<td>This study</td>
</tr>
<tr>
<td>(2015 to 2016)</td>
<td>TF</td>
<td>23.40</td>
<td>2.20</td>
<td></td>
</tr>
<tr>
<td>Pynn’s Brook, NL, Canada</td>
<td>OF</td>
<td>19.98</td>
<td>4.21</td>
<td></td>
</tr>
<tr>
<td>(2015 to 2016)</td>
<td>TF</td>
<td>21.24</td>
<td>2.44</td>
<td></td>
</tr>
<tr>
<td>Salmon River, NL, Canada</td>
<td>OF</td>
<td>16.14</td>
<td>1.33</td>
<td></td>
</tr>
<tr>
<td>(2015 to 2016)</td>
<td>TF</td>
<td>21.00</td>
<td>2.65</td>
<td></td>
</tr>
<tr>
<td>Eagle River, NL, Canada</td>
<td>OF</td>
<td>11.59</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>(2015 to 2016)</td>
<td>TF</td>
<td>28.26</td>
<td>0.86</td>
<td></td>
</tr>
<tr>
<td>Mont St. Hilaire, QC, Canada</td>
<td>P</td>
<td>2.00</td>
<td>0.49</td>
<td>Dalva and Moore, 1991</td>
</tr>
<tr>
<td>(1987)</td>
<td>TF</td>
<td>12.13</td>
<td>2.05</td>
<td></td>
</tr>
<tr>
<td>SF</td>
<td></td>
<td>40.10</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Northern China</td>
<td>P</td>
<td>2.4 to 3.9</td>
<td>1.4 to 2.7</td>
<td>Pan et al., 2010</td>
</tr>
<tr>
<td>(2007 to 2008)</td>
<td>TF</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Coulissenhieb, Northeast Bavaria</td>
<td>P</td>
<td>2.70</td>
<td>-</td>
<td>Michalzik and Matzner, 1999</td>
</tr>
<tr>
<td>(1995 to 1997)</td>
<td>TF</td>
<td>15.20</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Hobcaw Barony, South Carolina</td>
<td>P</td>
<td>1.20</td>
<td>-</td>
<td>Chen et al., 2019</td>
</tr>
<tr>
<td>USA (2014 to 2015)</td>
<td>Pine TF</td>
<td>26.00</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oak TF</td>
<td>38.8</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>University of Georgia, USA</td>
<td>TF Epiphyte Oak</td>
<td>17</td>
<td>23**</td>
<td>Van Stan et al., 2017</td>
</tr>
<tr>
<td>2015 to 2016</td>
<td>TF Bare Cedar</td>
<td>20</td>
<td>32**</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TF Epiphyte Cedar</td>
<td>54</td>
<td>48**</td>
<td></td>
</tr>
<tr>
<td>SMEARII Site, Southern Finland</td>
<td>P</td>
<td>3.24</td>
<td>2.32</td>
<td>Pumpanen et al., 2014</td>
</tr>
<tr>
<td>(1998 to 2012)</td>
<td>TF</td>
<td>10.10</td>
<td>4.35</td>
<td></td>
</tr>
</tbody>
</table>

** Estimated DOC yield for 2016 (g C m⁻² a⁻¹) where sampled storms values (g C event⁻¹) were scaled to an annual deposition value using meteorological data and a linear rainfall-DOC yield relationship.

4.0 Conclusions and Future Directions

This paper presents a cost-effective automated deposition sampler for continuous collection of precipitation. An open-source procedure and schematics for building these samplers is provided alongside the rationale for selecting the materials in the current study to target analytes of scientific interest in wet deposition samples. These low-power systems are demonstrated in being capable of continuous off-grid use for sample collection over two years at the NL-BELT experimental sites, with replacement of battery power packs monthly or bimonthly, with on-grid
performance also provided for comparison. The resulting systems enhance the accessibility of automated wet deposition samplers to scientists globally and this work highlights their robust performance in collecting and preserving rainwater conductivity and pH, alongside providing measurements of DOC from this understudied region that builds a broader picture of the atmosphere-surface exchange of this biogeochemical pool across the NL-BELT. Comparability and complementariness of our results to well-established and current measurements of interest like DOC, demonstrate their efficacy and potential application to the study of processes such as canopy-precipitation interactions through the collection of open fall and throughfall replicates. The capacity to autonomously collect wet deposition, in addition to traditional bulk deposition samples can shed light on competing wet and dry deposition processes. Should on-grid capacity suit scientific objectives, these samplers are anticipated to be possible for use year-round when paired with more power-intensive strategies to facilitate solid to liquid phase transfer for detected and collected precipitation in the winter.

For the broader deposition-motivated community, the instrument design also allows for easy cost-effective modification of the number of replicate samplers, the material composition of all surfaces the aqueous samples interact with, as well as preservation strategies - depending on the analyte of interest. For example, the lack of organic nitrogen measurements within universally established sampling and measurement procedures serves as a general example of the substantial knowledge gaps that may result when translating limited data sets to the wider global picture. This includes incomplete speciation and quantification across precipitation, aerosol, and gas phases. Monitoring systems that support U.S. deposition assessments (e.g., the NADP) only characterize the inorganic fraction of wet deposition. Additionally, modern emerging issues that require the continuation of existing deposition measurements or expansion of observation programs revolve around identifying and quantifying compound classes of concern, such as persistent organic pollutants. As reported in the literature, the deposition of these types of pollutants (e.g., polychlorinated biphenyls, polycyclic aromatic hydrocarbons, etc.) can be monitored using suitable collectors made of amber-coloured glass or stainless steel (Fingler et al., 1994; Amodio et al., 2014) - modifications which can be applied to the sample design detailed here. The samples collected in this work from this new instrumentation, specifically, are expected to be used further in several upcoming complementary and novel environmental monitoring studies. Not only will
this future work extend our biogeochemical analysis, but it will also assist in our studying of
the transport of other anthropogenic pollutants of emerging interest which are beyond the
scope of describing this new platform.

Data availability. The data are available from the corresponding author (TV) on request.

Author contributions. AC, DP, and ML performed the data analysis. AC and DP wrote the
manuscript with contributions from all authors. Sampler design and construction were led by TV,
with assistance from BP and RH for initial prototypes, DP and ML for the revised iteration, and
AC for the final modular control boards. Sample collection and associated characterization
measurements were performed by BP and TV. Conceptualization and conduct of the sampling
experiments were made by TV, CY, KE, and SZ. All authors were involved in examining and
reviewing the results. All authors were involved in editing the paper.

Competing interests. The contact author has declared that none of the authors has any competing
interests.

5.0 Acknowledgements

Funding for this work was provided by the Newfoundland and Labrador Department of
Agrifoods and Forestry, Centre for Forestry Science and Innovation (Project 221269), and the
Harris Centre at Memorial University. T. C. VandenBoer was supported for this work in-part
through a Government of Canada Banting Postdoctoral Fellowship. Fieldwork sample collection
by B. K. Place was supported by funding from Polar Knowledge Canada through the Northern
Scientific Training Program. Additional financial support for full redesign of the samplers was
provided through Environment and Climate Change Canada Grants & Contributions
(GCXE20S009). A. A. Colussi acknowledges support for this work through a Natural Sciences
and Engineering Research Council of Canada (NSERC) Graduate Scholarship – Master’s program
(CGSM) and Ontario Graduate Scholarship (OGS). M. Lao acknowledges support for this work
through a NSERC Undergraduate Student Research Award (USRA). We thank C. M. Laprise and
C. Conlan for aid in the collection and organization of samples for analysis, supported in part by
the Memorial University Career Experience Program (MUCEP) and V. Sitahai through a York
University Dean’s Undergraduate Research Award (DURA). T. C. VandenBoer, C. J. Young and
S. E. Ziegler were supported through the NSERC Discovery (RGPIN-2020-06166; RGPIN-2018-
05990; RGPIN-2018-05383) and Strategic Partnerships (479224) Programs. The authors would also like to thank B. Hearn, D. Harris, A. Skinner, C. Young, J. J. MacInnis, J. Warren, and L. Souza for their invaluable assistance in sampling site access and set up, off-season storage of collection units, sample collection and analysis, and meteorological reanalysis. We thank H. Hung and C. Shunthirasingham for productive discussions on modular design and considerations for collection of persistent pollutants.

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Supporting Information for

Cost Effective Off-Grid Automatic Precipitation Samplers for Pollutant and Biogeochemical Atmospheric Deposition

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ǂ Now at: Climate Change Impacts and Adaptation Division, Lands and Minerals Sector, Natural Resources Canada, Ottawa, ON

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Figure S1. Automated precipitation array stationed at the Air Quality Research Station, York University, Toronto, consisting of: (A) weather-proofed control board, (B) 40 W solar panel, (C) rain sensor, and enhanced sensitivity chute, and (D) an automated collection unit fixed to concrete with lag sleeves and bolts during a rain event.

Figure S2. Automated precipitation samplers deployed at NL-BELT. The (A) weatherproof control board was powered by (B) an off-grid AGM battery. The (C) sensor chute modulated the
opening of the samplers for precipitation collection with (D) a 40 W solar panel to recharge the power package between (E) precipitation events when the lids open to collect wet deposition.

**Figure S3.** Dimensions (in inches) for automated collection unit lid, with mounting holes on the bottom edge to secure it to the aluminum lid rod.
Figure S4. Dimensions (in millimeters) of 3D printed corner options: (A) double corner to affix panels adjoining the door and (B) multi corner used to secure three panels throughout the remainder of the collection unit.

(a) End-On View  
\[ \text{3/8'' Al-rod} \rightarrow \begin{array}{c} \frac{3}{4}'' \text{ I.D. milled hole} \\ \frac{1}{2}'' \text{ deep} \end{array} \]

(b) Cross-Section View  
\[ \begin{array}{c} \frac{3}{4}'' \text{ I.D. milled hole} \\ \frac{1}{2}'' \text{ deep} \end{array} \]

Figure S5. Aluminum rod milling schematics showing (A) end-on view for motor drive shaft and (B) cross section for situating the setscrew to hold the rod to the drive shaft of the motor.

(a) Lid Open Switch 5 V  
\[ (1 = \text{Open}; 0 = \text{Closed}) \]

(b) Lid Closed Switch 5 V  
\[ (0 = \text{Open}; 1 = \text{Closed}) \]

(b) Power In  
\[ 12 \text{ V (8/160mA)} \]

(c) Relay Signal Out  
\[ +12 \text{ V / 0 V} \]

(b) Rain Sensor  
\[ 0 = \text{Dry}; 1 = \text{Wet} \]

(c) Driver Signals, 12 V (0.01 - 0.04 A)  
\[ D_1, D_2 \]

(c) Lid Motor  
\[ 1/0 = \text{Open}; 0/1 = \text{Close} \]

Figure S6. Voltage and logic states of the (a) lid switches, (b) precipitation sensor, and (c) lid motor used to drive digital decision making on custom control boards.
Figure S7. (a) Input layout for digital logic control of precipitation sampler using three NOR gates to operate a H-bridge motor driver and (b) corresponding truth table to input and output logic states for switches and rain sensor (yellow), first NOR gate (green), second NOR gate (blue), and third NOR gate (red) to control 12 VDC from the motor driver to the motor terminals (D1 and D2).

S1. Measuring Conductivity Threshold of Kemo Electronic Rain Sensor.

A simple procedure determined the conductivity threshold of the 12 VDC Kemo Electronic rain sensor. A 1000 µS/cm stock standard was prepared by dissolving 0.225 g of sodium chloride in 500 mL deionized water, ensuring thorough mixing for homogeneity. A series of conductivity standards were then prepared by diluting the stock standard with deionized water (DIW) to different levels near the suspected threshold of the sensor (0.75, 0.8, 0.9, 1.0, 2.0, 3.0, 4.0, and 5.0 µS/cm). Prior to this testing, the rain sensor was flushed with copious amount of DIW to remove any conductive substance from the surface of the sensor - this was also repeated in between trials. The result from testing with these solutions determined that the conductivity threshold for the relay is 1.0 µS/cm, as the rain sensor was observed to be only partially activated at 0.9 µS/cm and the result was not consistent.
Figure S8. Design and dimensions (in mm) of the mounting chute for the rain sensor. The chute slope is fixed at an optimized angle of $10^\circ$, that maintains water on the surface of the sensor throughout a rain event but allows excess water to flow over the sensor when necessary. We also tested $15^\circ$ and $20^\circ$ through manual observation but found that rainwater would flow over the sensor too rapidly – limiting or even preventing detection of wet deposition events.
Figure S9. Technical schematics for all printed circuit board components required to control (a) one precipitation collector with all components and connections to chips indicated and (b) a complete six-unit array composed of replicate layouts.
Table S1. List of required components, part numbers, and quantities required to assemble a single printed circuit board.

<table>
<thead>
<tr>
<th>Component</th>
<th>Part Identification</th>
<th>Description</th>
<th>Quantity</th>
<th>Unit Price (CAD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Integrated Circuit 1 (IC1)</td>
<td>74AC02N = SN7402n</td>
<td>Four channels, two input NOR gate</td>
<td>1</td>
<td>3.52</td>
</tr>
<tr>
<td>Integrated Circuit 7 (IC7)</td>
<td>L298N</td>
<td>Dual Full Bridge Driver</td>
<td>1</td>
<td>7.41</td>
</tr>
<tr>
<td>Integrated Circuit 2 (IC2), Integrated Circuit 3 (IC3)</td>
<td>7805TV = MC7805CT-BP</td>
<td>5V regulator, TO220</td>
<td>2</td>
<td>0.67</td>
</tr>
<tr>
<td>Diode 1, Diode 2, Diode 3, Diode 4</td>
<td>1N4004</td>
<td>Diode</td>
<td>4</td>
<td>0.14</td>
</tr>
<tr>
<td>Resistor 1, Resistor 2, Resistor 3</td>
<td>10k</td>
<td>resistor, %1, 1/4W</td>
<td>3</td>
<td>0.21</td>
</tr>
<tr>
<td>Capacitor 1, Capacitor 12</td>
<td>100nF cap</td>
<td>Capacitor, 0.1Uf / 50V</td>
<td>2</td>
<td>0.35</td>
</tr>
<tr>
<td>Capacitor 3, Capacitor 5</td>
<td>1Uf Cap</td>
<td>Capacitor, 1Uf, 50V</td>
<td>2</td>
<td>0.84</td>
</tr>
<tr>
<td>Capacitor 2, Capacitor 4</td>
<td>10Uf</td>
<td>Capacitor, %10, 10Uf, 50V</td>
<td>2</td>
<td>1.84</td>
</tr>
</tbody>
</table>
Table S2. List of specific components, manufacturers, and specifications required to construct precipitation collection arrays.

<table>
<thead>
<tr>
<th>Components</th>
<th>Description</th>
<th>Selection Rationale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boxes</td>
<td><strong>Material:</strong> 3/8” Acrylic or Plywood <strong>Dimensions:</strong> (33.78 W x 33.78 L x 42.94 H) cm See Figure 2 for more details</td>
<td>Acrylic and plywood were chosen for their low cost and durability against a variety of environmental conditions. Both materials are opaque to minimize light intrusion.</td>
</tr>
<tr>
<td>Collection</td>
<td><strong>Material:</strong> High Density Polyethylene <strong>Brand:</strong> Bel-Art Products <strong>Dimensions:</strong> (19 H x 26 W x 36 H) cm; <strong>Volume:</strong> 10 L</td>
<td>Large volume collection of precipitation and resistance of material to environmental degradation. Quantitatively transfers analytes such as inorganic ions and DOC.</td>
</tr>
<tr>
<td>Container</td>
<td><strong>Brand:</strong> Dynalon <strong>Dimensions:</strong> 9.4” W x 8.68” H; 20 cm diameter</td>
<td>Guides conductive precipitation into the collection container. Material is matched to maintain quantitative analyte transfer.</td>
</tr>
<tr>
<td>Funnel</td>
<td><strong>Material:</strong> High Density Polyethylene <strong>Brand:</strong> Dynalon <strong>Dimensions:</strong> 9.4” W x 8.68” H; 20 cm diameter</td>
<td></td>
</tr>
<tr>
<td>Sampler Lids</td>
<td><strong>Materials:</strong> Lexan <strong>Brand:</strong> Kraloy, Carlon® Lamson &amp; Sessions <strong>Dimensions:</strong> See Figure S3 for more details <strong>Voltage:</strong> 12 V</td>
<td>Prevents foreign material entering the collection container when closed. Lexan was chosen due to its high flexibility and impact resistance. Acrylic was determined to be too fragile and not suitable for environmental conditions with elevated winds.</td>
</tr>
<tr>
<td>Geared Box DC</td>
<td><strong>Brand:</strong> Tsiny Motor Industrial Co. Ltd. TS-32GZ370-1650 <strong>Operating voltage range:</strong> 6-24 VDC <strong>Nominal voltage:</strong> 12 VDC <strong>Speed:</strong> 2-8 RPM</td>
<td>The worm gear motor is connected to the aluminum rod and sampler lids to open and close them when conductive precipitation is detected by the rain sensor.</td>
</tr>
</tbody>
</table>
Table S2 (cont’d). List of specific components, manufacturers, and specifications required to construct precipitation collection arrays.

<table>
<thead>
<tr>
<th>Components</th>
<th>Description</th>
<th>Selection Rationale</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Collection Units (cont’d)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Lid Rod</strong></td>
<td><strong>Material</strong>: Aluminum</td>
<td>The aluminum rod is attached to the motor and facilitates the opening and closing of the Lexan lids. The rod is attached to the motor by a 8/32 threaded 1/4” set screw.</td>
</tr>
<tr>
<td></td>
<td><strong>Outer diameter</strong>: 3/8”</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Inner diameter</strong>: 1/4”</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Depth</strong>: 1/2” deep</td>
<td></td>
</tr>
<tr>
<td><strong>Lid Limit Switches</strong></td>
<td><strong>Brand</strong>: Omron Electronics</td>
<td>Snap action switches are used to detect the open and closed position of the motorized sampler lids. Weatherproofing keeps them watertight.</td>
</tr>
<tr>
<td></td>
<td><strong>Part Number</strong>: D2FW-G271M(D)</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Max Current</strong>: 1 A</td>
<td></td>
</tr>
<tr>
<td><strong>Funnel Mesh</strong></td>
<td><strong>Material</strong>: HDPE</td>
<td>When the automated sampler is in the open position, these cone-shaped filters prevent debris from entering the collection jug.</td>
</tr>
<tr>
<td></td>
<td><strong>Brand</strong>: McMaster-Carr</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Part Number</strong>: 9265T49</td>
<td></td>
</tr>
<tr>
<td><strong>Lag shields, lag bolts and washers</strong></td>
<td><strong>Lag shields dimensions</strong>: 3/8” x 1-3/4”</td>
<td>These are utilized to secure precipitation collectors to concrete. This prevents unit tipping during storms or from animal interactions.</td>
</tr>
<tr>
<td></td>
<td>(Requires masonry drill bit: 5/8”)</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Lag bolt and washer dimensions</strong>: 1/2”</td>
<td>Tent pegs or rebar may be alternatively used to secure the samplers into soils.</td>
</tr>
<tr>
<td><strong>Power System</strong></td>
<td><strong>Brand</strong>: Coleman 40W Folding Panel</td>
<td>The solar panel recharges the off-grid battery. This can be repositioned to optimize sunlight exposure and maximize recharging capabilities.</td>
</tr>
<tr>
<td></td>
<td><strong>Output Voltage</strong>: 17.1 V, 2.3 amps</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Dimensions</strong>: (79 L x 35.1 W x 1.8 H) cm</td>
<td></td>
</tr>
</tbody>
</table>
**Table S2 (cont’d).** List of specific components, manufacturers, and specifications required to construct precipitation collection arrays.

<table>
<thead>
<tr>
<th>Components</th>
<th>Description</th>
<th>Selection Rationale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar Charge Controller</td>
<td><strong>Brand:</strong> Coleman</td>
<td>The ability of the solar panel to deliver charge to the battery or stop when it is fully charged is regulated. The controller prevents the battery from overcharging.</td>
</tr>
<tr>
<td></td>
<td><strong>Load Charge:</strong> 8.5 A</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Cut-out:</strong> 14.2 V</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Cut-in:</strong> 13 V</td>
<td></td>
</tr>
<tr>
<td>103 Ah off-grid battery</td>
<td><strong>Brand:</strong> Motomaster Nautilus Ultra XD Group 31 High Performance AGM Deep Cycle Battery (103 Ah)</td>
<td>The 99.99% lead AGM (absorbed glass mat) was used for long lasting power and reliability for field testing without a solar panel.</td>
</tr>
<tr>
<td></td>
<td><strong>Voltage:</strong> 12 V</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Dimensions:</strong> (33 L x 18 W x 25 H) cm</td>
<td></td>
</tr>
<tr>
<td>76 Ah Off-grid battery</td>
<td><strong>Brand:</strong> Motomaster Nautilus Ultra XD Group 24 High Performance AGM Deep Cycle Battery (76 Ah)</td>
<td>The 99.99% lead AGM with 76 Ah battery was used for field testing while being charged with a solar panel for long periods.</td>
</tr>
<tr>
<td></td>
<td><strong>Voltage:</strong> 12 V</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Dimensions:</strong> (27.6 L x 17.1 W x 22.2 H) cm</td>
<td></td>
</tr>
<tr>
<td>Transformer</td>
<td><strong>Brand:</strong> TDK Lambda Americas</td>
<td>The transformer replaces an off-grid battery and converts 115 VAC to 12 VDC. This can be used when sampling in locations with grid power available.</td>
</tr>
<tr>
<td></td>
<td><strong>Voltage:</strong> 115 VAC to 12 VDC</td>
<td></td>
</tr>
</tbody>
</table>
Table S2 (cont’d). List of specific components, manufacturers, and specifications required to construct precipitation collection arrays.

<table>
<thead>
<tr>
<th>Components</th>
<th>Description</th>
<th>Selection Rationale</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rain Detection</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| Heated Precipitation Sensor | **Brand:** Kemo Electronic M152  
**Voltage:** 12 V  
**Dimensions:** (6.5 x 4.5 x 3.6) cm | A waterproof conductive sensor that becomes activated and switches on a relay when in contact with conductive rain or snow. The sensor relay triggers the control board so that the sampler lids rotate open. The operating temperature range provided by the manufacturer is -10 to +55°C. |
| Sensor Chute                | **Dimensions:** (see Figure S8)                                              | Increases surface area of precipitation sensor to activate the relay. Delays lid closing by providing more conductive ions to the sensor surface when atmospheric wash out may occur. |
| **Digital Control Board**  |                                                                             |                                                                                                         |
| Control Boards              | See Figure S9 for more details.                                             | Controls communication between the motors, power supply, and rain sensor (12 VDC), as well as the two limit switches (5 VDC). |
| Control Board Protective Case | **Brand:** Pelican ™ 1450 Case  
**Material of body:** polypropylene  
**Exterior Dimensions:** (41.8 L x 33 W x 17.3 D) cm  
**Interior Dimensions:** (37.2 L x 26 W x 15.5 D) cm  
**Weight with foam (polyurethane):** 2.9 kg | The 1450 case contains custom foam for cable accommodations with automatic pressure equalization valve to balance interior pressure. It is watertight, crushproof, and dustproof with double throw latches and a rubber handle. |
| Reusable Hydrosorbent Silica Gel Beads | **Brand:** Pelican Case Desiccant  
**Canister Dimensions:** (1.3 L x 5.1 W x 10.2 H) cm  
**Mass:** 40 g | The silica gel beads absorb moisture to prevent water damage to the control board; when clear, must reactivate in an oven for 3 hours at 300°F. |

Table S2 (cont’d). List of specific components, manufacturers, and specifications required to construct precipitation collection arrays.

<table>
<thead>
<tr>
<th>Components</th>
<th>Description</th>
<th>Selection Rationale</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Digital Control Board</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control Boards</td>
<td>See Figure S9 for more details.</td>
<td>Controls communication between the motors, power supply, and rain sensor (12 VDC), as well as the two limit switches (5 VDC).</td>
</tr>
</tbody>
</table>
| Control Board Protective Case | **Brand:** Pelican ™ 1450 Case  
**Material of body:** polypropylene  
**Exterior Dimensions:** (41.8 L x 33 W x 17.3 D) cm  
**Interior Dimensions:** (37.2 L x 26 W x 15.5 D) cm  
**Weight with foam (polyurethane):** 2.9 kg | The 1450 case contains custom foam for cable accommodations with automatic pressure equalization valve to balance interior pressure. It is watertight, crushproof, and dustproof with double throw latches and a rubber handle. |
| Reusable Hydrosorbent Silica Gel Beads | **Brand:** Pelican Case Desiccant  
**Canister Dimensions:** (1.3 L x 5.1 W x 10.2 H) cm  
**Mass:** 40 g | The silica gel beads absorb moisture to prevent water damage to the control board; when clear, must reactivate in an oven for 3 hours at 300°F. |
### Miscellaneous

| Data logger | **Brand**: ONSET® HOBO 4-channel analog data logger  
| **Part #**: UX120-006M  
| **Program**: HOBOware | To collect and offload data from the control board using one of four channels. This work: CH1 – battery voltage, CH2 – motor driver voltage, CH3 – rain sensor voltage, CH4 – limit switch voltage. |
| Cable Connectors | **Brand**: Bulgin (400 or 4000 Series Buccaneer) IP68 Sealed  
| **Electrical Circular Cable Connectors**: PXP4010/03P/3540 and PSP4011/03S/3540  
| **SA3349, SA3350, SA3348, SA3347**  
| **Material**: Polyamide UL94-V0 body, gold contacts  
| **Cable acceptance**: 3 mm – 7 mm  
| **Contact insertion**: crimp or solder | Waterproof and dustproof cable connectors provide electrical connections from the control board to the battery, solar panel, and sampler motors and switches. Different numbers of contacts represent different cable requirements within the system (2- or 3-contact = battery and solar panel cables, 6- or 8-contact = rain samplers). |
| Extension Cables | Any commercial outdoor-rated extension cord | To increase distance from VAC power source to sampling location. |
Figure S10. Map of the NL-BELT highlighting the four watershed regions where sampling occurred: Grand Codroy (GC), Pynn’s Brook (PB), Salmon River (SR), and Eagle River (ER).
S2. Deposition Comparison: This Work, DAYMET, and ECCC

Sufficiently continuous measurements from ECCC stations near each site are challenging to obtain for the 2015-16 period. When available with greater than 80% coverage, the ECCC datasets both agree and disagree with our observations in GC and SR, respectively, suggesting that there is substantial deposition volume heterogeneity at the scale of ~10 km in this region. In SR, the disagreement with our measurements is identical to the DAYMET model which uses ECCC observations as input data, while at GC the ECCC measurements are identical to ours (Table S3). Further, the discrepancy in the PB or ER average annual precipitation volume between ECCC and those of this work and DAYMET are not possible to interrogate due to the large quantity of data missing from the ECCC monitoring station (35.22% in ER and 39.65% in HR/PB; Table S3). The DAYMET observations are representative of a larger spatial scale, where our discrete samplers could be subject to heterogeneity in deposition (e.g., orographic precipitation, driven by topography like steep slopes) or impacted by meteorological conditions not captured by the model (e.g., undercatch driven by local winds). The temporally resolved volume comparisons at sampling interval timescales better-demonstrates comparability, despite the systematic differences. The month-to-month relationships between DAYMET and our observations, as well as between ECCC and our observations, all show strong correlations with linear regressions having $R^2$ values, from north to south, of 0.72, 0.99, 0.99, and 0.86, and N/A, 0.94, N/A, and 0.93, respectively (Table S3). The discrepancy between DAYMET, ECCC, and our observations for total deposition were highest in the most northerly site, where the experimental site was located on a steep slope, with only 43% of the predicted volume collected. At all of the sample collection sites on the island of Newfoundland, a consistent difference was observed with 65 ± 4% of the estimated volume collected, except at GC where our measurements and those from ECCC are identical and starkly contrasting to DAYMET. Overall, parsing these comparisons is difficult and demonstrates that there may be up to 55% additional uncertainty in deposited species, should given measurements of a species be scaled for a watershed like ER by concentration in total deposition samples. We propose, that by isolating only the deposited analytes and using analyte fluxes instead of concentrations in precipitation samples, that uncertainty issues in representing volumes, improves overall deposition budget certainties.
Table S3. Collected precipitation volumes from NL-BELT in bulk deposition samplers for rainwater were deployed for one to two months, while snow was collected as an integrated sample throughout the winter because sites were not accessible. The Environment and Climate Change Canada (ECCC) precipitation data was obtained for identical sampling intervals. The DAYMET model for North America (1 km x 1 km resolution) for precipitation was obtained for the identical sampling intervals, which utilizes interpolated and extrapolated data from daily weather observations to predict inputs at the NL-BELT locations. Linear regression results for slope (m) and correlation coefficient ($R^2$) between observations and DAYMET (italics), and observations and ECCC (where possible; underlined), were calculated. For sampling periods where a measurement was compromised or not collected for a given interval in this work, these are reported as with ‘-’ and an estimated volume from the regression relationship with ECCC is reported in parentheses when used to replace compromised samples.

<table>
<thead>
<tr>
<th>Date (mmm-yy)</th>
<th>Grand Codroy</th>
<th>Pynn’s Brook/Humber River</th>
<th>Salmon River</th>
<th>Eagle River</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This Work (L)</td>
<td>DAYMET (L)</td>
<td>ECC (L)</td>
<td>This Work (L)</td>
</tr>
<tr>
<td>Jun-15</td>
<td>22.68</td>
<td>40.98</td>
<td>23.80*b</td>
<td>23.44</td>
</tr>
<tr>
<td>Jul-15</td>
<td>2.92</td>
<td>3.38</td>
<td>2.06</td>
<td>2.24</td>
</tr>
<tr>
<td>Aug-15</td>
<td>6.86</td>
<td>8.08</td>
<td>7.20</td>
<td>5.06</td>
</tr>
<tr>
<td>Sep-15</td>
<td>(5.17)*</td>
<td>2.93</td>
<td>5.17</td>
<td>3.05</td>
</tr>
<tr>
<td>Oct-15</td>
<td>1.71</td>
<td>4.31</td>
<td>4.44</td>
<td>-</td>
</tr>
<tr>
<td>Nov-15</td>
<td>3.57</td>
<td>5.92</td>
<td>4.92</td>
<td>5.66</td>
</tr>
<tr>
<td>May-16</td>
<td>26.00</td>
<td>28.15</td>
<td>25.38</td>
<td>15.62</td>
</tr>
<tr>
<td>Jun-16</td>
<td>1.83</td>
<td>4.21</td>
<td>3.79</td>
<td>4.25</td>
</tr>
<tr>
<td>Jul-16</td>
<td>5.81</td>
<td>3.96</td>
<td>6.10</td>
<td>3.13</td>
</tr>
<tr>
<td>Aug-16</td>
<td>5.19</td>
<td>4.10</td>
<td>3.98</td>
<td>4.67</td>
</tr>
<tr>
<td>Sep-16</td>
<td>7.79</td>
<td>5.17</td>
<td>4.06</td>
<td>4.97</td>
</tr>
<tr>
<td>Oct-16</td>
<td>5.10</td>
<td>6.69</td>
<td>5.30</td>
<td>5.15</td>
</tr>
</tbody>
</table>

m, $R^2$ 0.62, 0.859; 1.02, 0.934 0.60, 0.990; - 0.68, 0.987; 0.67, 0.941 0.43, 0.719; -

*aSample compromised by wildlife-sampler interaction.

*bThese values result from periods where <80% of the observation days report collected data. Partial volumes from the available data are presented.

*cThese values result from periods where <50% of the observation days report collected data. Partial volumes from the available data are presented.
Figure S11. Thirty-three sets of triplicate open fall samples were collected across the NL-BELT between 2015 and 2016. (a) The replicate relative standard deviations (RSDs) appear to follow a log-normal distribution where reproducibility is typically within ± 12.5% and almost always within ± 31.5%. (b) A variable ‘x’ is said to have a lognormal distribution if $y = \ln(x)$ is normally distributed. The RSDs were treated as variable ‘x’ and then log-transformed, resulting in a mean ($\mu$) and standard deviation ($\sigma$) of 2.81 and 1.41, respectively. The probability density function for the log-normal, plotted against these log-transformed values, is defined by the two parameters $\mu$ and $\sigma$, where $x > 0$. As a result, one of the 33 RSD values was excluded from this plot as it became a negative value after being log-transformed.
Table S4. Sum of DOC fluxes (mg C m\(^{-2}\) a\(^{-1}\)) in wet deposition samples for 2015 and 2016 at GC, PB, SR, and ER. The average DOC flux error (mg C m\(^{-2}\) a\(^{-1}\)) propagated by summing the errors across the sampling sites to obtain the annual values.

<table>
<thead>
<tr>
<th>Site</th>
<th>Year</th>
<th>OF Deposition Flux (mg C m(^{-2}) a(^{-1}))</th>
<th>TF Deposition Flux (mg C m(^{-2}) a(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC</td>
<td>2015</td>
<td>1800 (± 800)</td>
<td>3700 (± 2400)</td>
</tr>
<tr>
<td></td>
<td>2016</td>
<td>1400 (± 800)</td>
<td>700 (± 700)</td>
</tr>
<tr>
<td>PB</td>
<td>2015</td>
<td>600 (± 300)</td>
<td>1800 (± 600)</td>
</tr>
<tr>
<td></td>
<td>2016</td>
<td>7800 (± 7700)</td>
<td>3000 (± 3600)</td>
</tr>
<tr>
<td></td>
<td>2016</td>
<td>4000 (± 1700)</td>
<td>1700 (± 1500)</td>
</tr>
<tr>
<td>ER</td>
<td>2015</td>
<td>100 (± 100)</td>
<td>1600 (± 2200)</td>
</tr>
<tr>
<td></td>
<td>2016</td>
<td>1000 (± 800)</td>
<td>100 (± 30)</td>
</tr>
</tbody>
</table>

Table S5. Average DOC flux (mg C m\(^{-2}\) a\(^{-1}\)) for 2015 to 2016 at GC, PB, SR, and ER. The difference between calculated fluxes in TF and OF samples are also included.

<table>
<thead>
<tr>
<th>Site</th>
<th>OF Flux (mg C m(^{-2}) a(^{-1}))</th>
<th>TF Flux (mg C m(^{-2}) a(^{-1}))</th>
<th>TF - OF</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC</td>
<td>1600</td>
<td>2200</td>
<td>600</td>
</tr>
<tr>
<td>PB</td>
<td>4200</td>
<td>2400</td>
<td>-1800</td>
</tr>
<tr>
<td>SR</td>
<td>3000</td>
<td>2600</td>
<td>400</td>
</tr>
<tr>
<td>ER</td>
<td>500</td>
<td>900</td>
<td>400</td>
</tr>
</tbody>
</table>