

COMPARISON OF WETNESS SENSING METHODS DURING ATMOSPHERIC EXPOSURE

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SUMMARY: This paper reports on the results of a set of experiments that examine TOW determinations using three indirect sensing methods during short-term outdoor and laboratory atmospheric exposure. The objective of the study was to better elucidate the accuracy and comparability of TOW determination methods. Replicate sets of indirect resistance and galvanic multi-electrode sensors along with inert gold surfaces were exposed to an outdoor coastal marine environment followed by laboratory humidity chamber exposure. Output was compared between sensor types and to optical micrographs of the sensor and inert surfaces during exposure. Cumulative TOW estimates varied widely between the different methods. Results indicate that output of the resistance-type sensors was dependent on aerosol loading and surface wettability. Additionally, sensor output and optical microscopy indicated that the outdoor exposed sensors remained wet down to at least 13% RH, far below the ISO 9223 TOW threshold.

Keywords: wetness, time, atmospheric, sensor, humidity

1. INTRODUCTION

This paper reports on the initial results of a set of experiments that examine time of wetness (TOW) determinations using three indirect sensing methods during short term outdoor and laboratory atmospheric exposure. Time of wetness is generally defined as the amount of time a metal surface remains wet during atmospheric exposure. Practical definitions associated with TOW determination vary widely.

Practical definitions represented in literature and practice can be categorized by the way in which TOW is treated—either as an environmental parameter or a surface parameter. As an environmental parameter, TOW is defined in terms of climatic variables, such as relative humidity (RH) and temperature. A widely used definition of this type is given by ISO 9223, which defines TOW as the cumulative time during which the relative humidity of the ambient environment is greater than 80% at temperatures above 0°C [1]. This definition is based on the concept of a critical relative humidity above which the corrosion rate becomes significant. The basis for 80%RH as a threshold is unclear and has previously been demonstrated to be an inaccurate estimate of actual surface wetness [2-4].

A range of complimentary techniques are available to provide information on TOW. For instance, measurements of moisture can be made on a sensor in proximity to a surface of interest as a means of an indirect estimate of TOW. Resistance and galvanic-type sensor are commonly used for this purpose. These sensors consist of thin metal electrodes separated by an insulating material. Electrolyte present on the surface causes measureable change in the sensor electrical properties by bridging the electrodes. Time of wetness is defined as the time which a certain voltage, current, or impedance threshold is exceeded during the exposure period. A variety of sensor designs and associated definitions are seen in practice. Thresholds are often defined as the baseline response of the clean sensors at low humidity levels.

It is unclear exactly how the presence of microscopic amounts of electrolyte (aerosol deposits) on the surface of any of these sensors relates to their output. Detection is in part controlled by the wettability of the sensors (electrolyte

bridging) and amount of electrolyte. Given multi-site and inter-institutional field data, including TOW parameters, are commonly utilized for atmospheric corrosion modeling, an understanding of the comparability of various TOW determination methods is imperative.

This paper reports on the initial results of a set of experiments that examine TOW determinations using three indirect sensing methods during short term outdoor and laboratory atmospheric exposure. The objective of the study was to better elucidate the accuracy and comparability of TOW determination methods. Replicate sets of indirect resistance and galvanic sensors and inert surfaces were exposed to an outdoor coastal marine environment followed by laboratory humidity chamber exposure. Output was compared between sensor types and to optical micrographs of the inert and sensor surfaces during exposure.

2. EXPERIMENTAL

Three indirect TOW sensing methods and associated definitions were utilized for these experiments. The first method was comprised of Wetcorr sensors (NILU) connected to a resistance circuit which in turn output a frequency read and logged using a DT80 datalogger (Thermo Fisher Scientific). The wetcorr sensor, herein referred to as a grid sensor, consists of an interdigitated pair of gold alloy electrodes on a sintered alumina backing. The sensing area measures around 20 x 20 mm with 130 μm spacing between the electrodes. All sensor readings were normalized against an open circuit reading on the measurement circuit to remove noise and temperature effects. The sensor was defined as being wet above a reading of 0.5Hz relative to open circuit, to exclude background noise[5].

The second method utilized Campbell Scientific 237L leaf wetness sensors connected to a CR1000 data logger manufactured by the same company. The leaf sensors consist of interdigitated gold alloy electrodes deposited on a fiber-reinforced plastic circuit board. The overall sensing area measures around 50 x 50 mm with approximately 1 mm electrode spacing. A manufacturer-supplied program was employed to send an excitation voltage to the sensor and measure the resistance across the electrodes in a half-bridge configuration. Maximum resistance was measured on clean and dry sensors as $>7.3 \text{ M}\Omega$. Below this value the sensor was considered wet. It is important to note that it is common practice to paint these sensors with a latex paint to increase sensitivity, but this was not done so as to give more comparable results to the grid method[6].

The third method utilized coiled ribbon galvanic sensors manufactured by CSIRO [7]. The sensors consist of Al and Cu ribbon formed in a spiral pattern and set in epoxy with a 400 μm polymer insulating spacer between them. The sensing area is around 450 mm. Sensor output was monitored using zero-resistance ammeters connected to a DT80. Prior to the initiation of experiments, output of the clean, unexposed sensors to be used was measured over a period of four days at $45 \pm 2\% \text{RH}$ and $20 \pm 1^\circ\text{C}$ with an average output of $0.01 \mu\text{A}$ and standard deviation of $0.013 \mu\text{A}$. This value was going to be used as the dry baseline- currents above which would define the sensor as wet. Unfortunately, issues with current baseline fluctuations during the experiment prevented use of this definition as discussed later.

Triplicates of each of the sensors were cleaned and mounted on plates for exposure. Cleaning involved mild non-ionic detergent in water followed by deionized water ($18.2 \text{ M}\Omega \cdot \text{cm}$) and absolute ethanol rinses. In an attempt to achieve similar thermal characteristics amongst the different types, the grid and galvanic sensors were adhered with silicone to non-functioning leaf sensors prior to mounting. All sensors were then attached with Nylon standoffs onto randomly assigned locations of two aluminium plates. Additionally, a Vaisala HMP60 probe was connected to a DT80 logger and deployed with the sensors to monitor ambient RH and temperature.

The sensor arrays were exposed to both outdoor and controlled laboratory environments. Outdoor exposure was carried out at the CSIRO Highett atmospheric site located in suburban Melbourne, Australia. The location is characterized by light industrial activity and is 3km west of Port Phillip Bay. Average measured soluble salt deposition for the site is $8 \text{ mg} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$ [7]. The arrays were mounted on either an open or sheltered rack, both of which faced North at 45° . Prior to initiating experiments the sensors were exposed, unsheltered, for 11 days as a means of aging them. They were then rinsed after exposure with deionized (DI) water using a wash bottle.

Laboratory exposure was carried out in a Weis WK480/10 circulating air environmental chamber. The sensor plates were laid flat in the chamber and subjected to cyclic humidity ramps using nearly the full achievable range of the chamber ($12\text{--}95\% \text{RH}$) at $23 \pm 1^\circ\text{C}$. A 500x digital optical microscope was placed in the chamber and trained on one of the grid sensors. Images were taken at two minute intervals during each exposure. The resulting images were compiled into a time-lapse video that was viewed for visible surface changes related to wetting or drying (e.g., droplet formation, crystallization, etc.). Wetting and drying points were determined as the time at which visible change could first be distinguished (wetting) or no longer observed (drying).

Experiments were comprised of three consecutive exposure sequences. The first sequence consisted of an 8 day open outdoor exposure followed by two chamber exposures in the lab. The first chamber exposure was carried out immediately after the sensors were removed from the field. A subsequent chamber exposure was carried out after the sensors were rinsed with DI water. The second sequence consisted of a 4 day sheltered outdoor exposure followed by chamber exposure immediately after take-down. The third was an 18 day open outdoor exposure followed by a chamber exposure immediately after take down. Between outdoor exposures the sensors were rinsed with DI water using a wash bottle in an attempt to remove aerosol contamination. Data was sampled and logged at one minute intervals for all sensors. Climatological data was collected from an Australian Bureau of Meteorology weather station 5km from the exposure site to aid in interpretation of the results.

Additionally, two gold-coated quartz crystal microbalance (qcm) sensors (Qsense) were deployed alongside the sensors during the sheltered outdoor exposure. The qcm sensors were first cleaned with an aqueous ammonia and hydrogen peroxide solution followed by rinsing and soaking in DI water to ensure particulate residue was removed, which was afterwards confirmed using optical microscopy. The qcm sensors were mounted in Teflon holders such that the gold coated sensing side, with a circular area of 154 mm², was exposed. The mounted qcms were placed alongside the TOW sensors on the aluminium plates and taken down 15 hours after the start of the sheltered exposure and at the end of the exposure. The qcms were examined after exposure using optical microscopy to determine particle and watermark size distributions. Magnification used during examination limited resolution during image analysis to 10 µm.

3. RESULTS AND DISCUSSION

Sensor output logged during exposures is shown in Figures 1 and 2. Table 1 gives TOW estimates during the outdoor exposure based on the definitions set above. Comparability to TOW determinations and sensor performance along with the RH range in which the deposited aerosols remained wet are discussed below.

3.1 TOW Comparability

During the experiments, output from the galvanic sensors consistently exceeded the initial current measured on the dry and cleaned sensors prior to them. Additionally the baseline current was found to fluctuate between 0.2 to 0.6 µA with peak height variable and sometimes in this range during the exposures. This made it unclear as to when the sensors were wet or dry, which in turn prevented the determination of TOW. Baseline fluctuations were often, but not always, in the form of abrupt jumps during drying events, especially noticeable in the humidity chamber runs, **Figure 3**. Interestingly, response was nearly identical between galvanic sensors with regard to peak position and magnitude during each exposure period. The origin of the baseline current is unclear. It may have been due to moisture retention by the sensor construction materials or by corrosion product accumulated on the surface, which was visibly bridging the electrodes during inspection after the first exposure. The latter case would represent an actual surface measurement, meaning 100% TOW for all exposures. Further investigation is required.

Data from the leaf and grid sensors allowed for definitional calculation of TOW during the outdoor exposures, with results indicating wide variation in the estimates, Table 1. Values between replicate grid sensors are within a few percent at most for both of the open exposures, while those between the leaf sensors vary up to nine percent. The range of TOW values is considerably greater between and among sensors during the sheltered exposure as opposed to the open exposures. The variability in TOW could be due to a number of reasons including sensitivity of the measurement electronics or the associated TOW definitions, insufficient bridging of electrodes by electrolyte, or variations in surface RH between sensor types.

3.2 Sensor Performance

Sensor output data along with optical microscopic examination of the exposed qcms and grid sensors indicate that variation in TOW is likely due to electrolyte bridging effects. Bridging is a function of aerosol size, loading density and wettability. Given the sheltered exposure produced the highest TOW variability, the results from this period are examined here in more detail with regard to these factors.

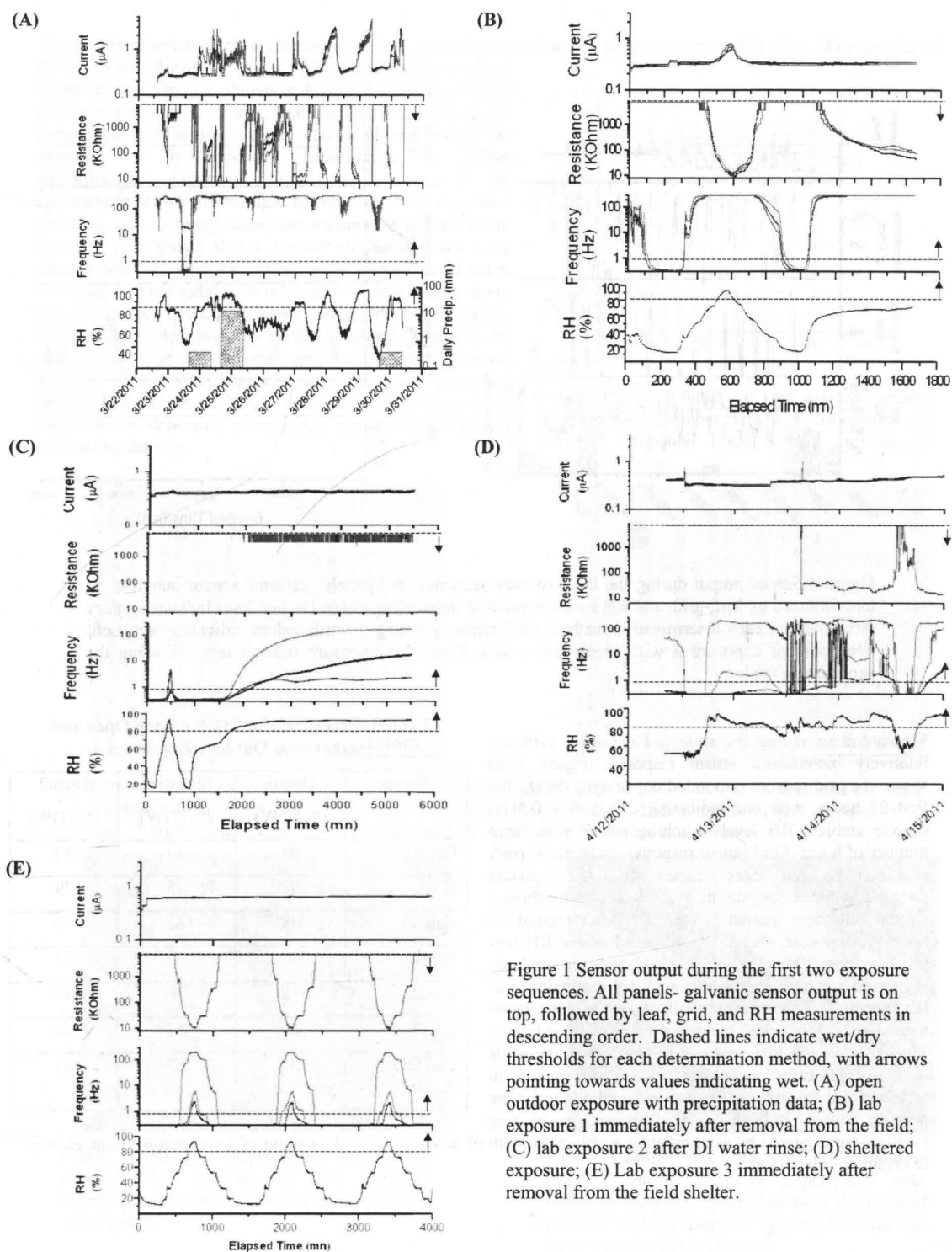


Figure 1 Sensor output during the first two exposure sequences. All panels- galvanic sensor output is on top, followed by leaf, grid, and RH measurements in descending order. Dashed lines indicate wet/dry thresholds for each determination method, with arrows pointing towards values indicating wet. (A) open outdoor exposure with precipitation data; (B) lab exposure 1 immediately after removal from the field; (C) lab exposure 2 after DI water rinse; (D) sheltered exposure; (E) Lab exposure 3 immediately after removal from the field shelter.

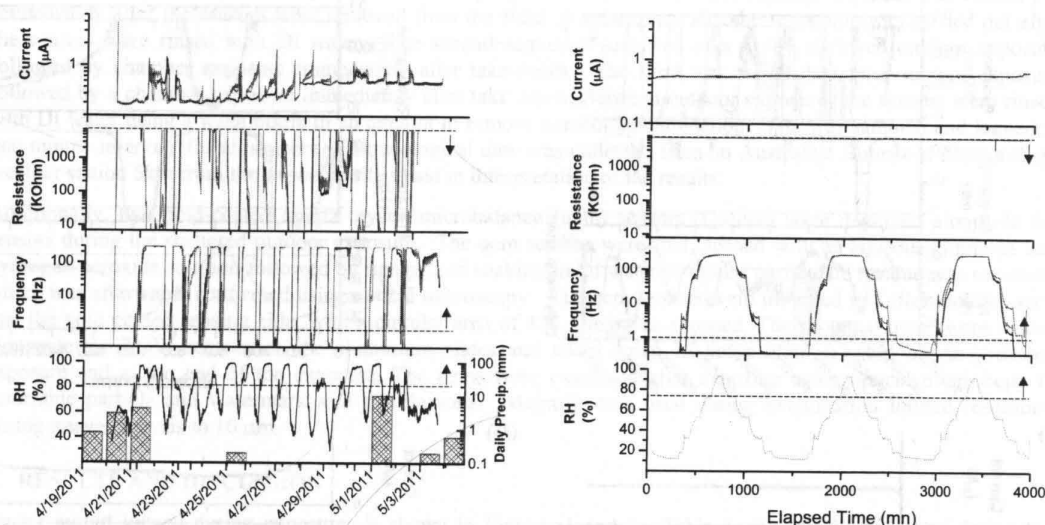


Figure 2 Sensor output during the last exposure sequence. All panels- galvanic sensor output is on top, followed by leaf, grid, and RH measurements in descending order. Dashed lines indicate wet/dry thresholds for each determination method, with arrows pointing towards values indicating wet. Left, open outdoor exposure 2 with precipitation data. Right, lab exposure immediately following the exposure on the left.

Measurements during the sheltered exposure evidence relatively inconsistent sensor response. Figure 1(D) shows the grid sensors responded out of sync during the first 24 hours, with one indicating dry (below 0.5Hz) despite ambient RH levels reaching above 90% for a number of hours. Grid sensor response, in terms of peak locations, becomes more concurrent as the exposure progresses. Measurements from the leaf sensors show a similar but more dramatic disparity. After around 30 hours of exposure, and during a period where RH was no less than 70%, one of the leaf sensors suddenly registered wet and indicated as such for the majority of the exposure. This occurred while the other leaf sensors indicated dry along with the grid sensors at some points. The fact that the leaf sensor read wet while the grids read dry indicates something besides differences in measurement sensitivity between the methods to be the primary cause. It appears that these sudden wetting events were triggered by accumulating a critical amount of wet aerosol or deposition of a wet aerosol large enough to bridge the electrodes.

Table 1. Percentage of TOW during Open and Unsheltered Outdoor Exposures

Sensor	Open1 (%TOW)	Sheltered (%TOW)	Open2 (%TOW)
Grid1	98	39	80
Grid2	97	65	79
Grid3	100	83	79
Leaf1	75	1	53
Leaf2	78	5	49
Leaf3	69	57	48
RH(ISO 9223)	36	65	45

The results of microscopic examination of the exposed qcm and sensor surfaces support this idea. Micrographs of the qcms pulled after 15 hours and upon completion of the sheltered exposure are shown in Figure 4 with an overlaid grid sensor electrode pattern. Although deposit sizes appear comparable, the loading density clearly increases over the exposure as is expected. Examination at higher magnifications, Figure 5, reveals dark specks in the micrographs which are thought to represent both deposited particles, and, in many cases, the watermarks around them. Figure 5 also shows that a number of the deposits were actually wet during the examination which was carried out at 45-50%RH. Additionally, it is clear from this image along with those taken of the grid sensor during chamber exposures that visible droplets are only partially wetting, Figure 6. In other words they are not spreading out as thin, electrode bridging films. Assuming the non-visible wet deposited aerosols behaved similarly, this means that sensor response is dependent on deposited aerosol size, shape (contact angle) and loading density.

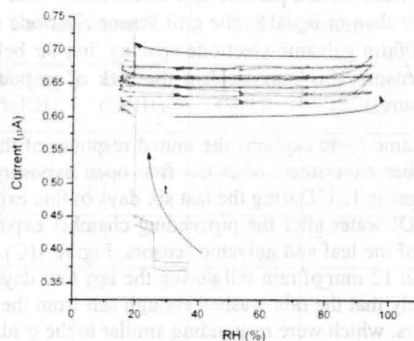


Figure 3 current output of two galvanic sensors during RH chamber cycling following the sheltered exposure. Black arrows indicate the direction of time.

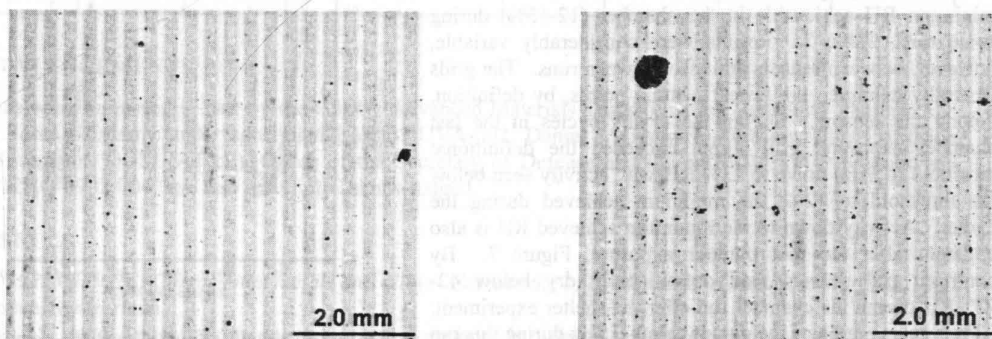


Figure 4 optical micrographs of deposits (black specks) on the qcms deployed during the sheltered exposure overlaid with an image of the electrode grid spacing at the same scale. Left, deposits on qcm exposed for first 15 hours. Right, deposits on qcm exposed the duration of the shelter experiment.

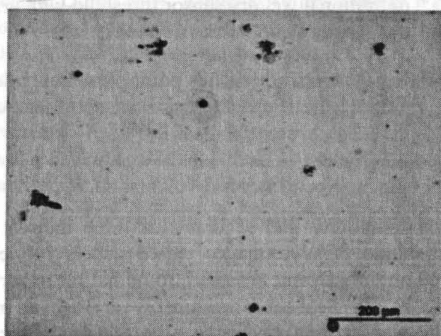


Figure 5 detail of deposits on qcm sensor exposed the duration of the sheltered experiment, showing examples of watermarks and droplets.

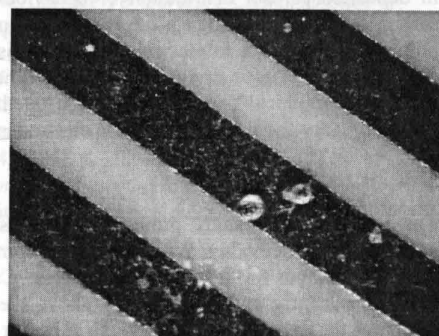


Figure 6 optical micrograph of grid sensor at 94%RH during chamber experiment after sheltered exposure. Electrolyte is in the form of partially wetting droplets. Spacing between the electrodes (white) is 130 µm.

Image analysis of a low magnification micrograph of the qcm exposed for the entire sheltered period was carried out to estimate wetted particle size distribution. Out of the nearly 1400 spots analyzed in a 61mm² area, only 13 were greater than or equal to the grid sensor electrode spacing of 130µm. One spot, measuring 650µm, was greater than the 400µm galvanic electrode spacing, but far below the 1mm leaf sensor spacing. Given similar distributions on the sensors, this may explain the lack of response from the galvanic and two leaf sensors during the sheltered exposure.

The same logic explains the muted response of the sensors after wash-off periods during the other exposures. The chamber experiment after the first open exposure is the only one in which all sensors appreciably responded to changes in RH. During the last six days of that exposure only 0.3 mm of rain fell on the sensors. Rinsing the sensors with DI water after the proceeding chamber experiment resulted in muted to nil sensor response, especially in the case of the leaf and galvanic sensors, Figure 1(C). Although the second outdoor exposure was longer than the first, around 12 mm of rain fell during the last four days of exposure and, of that, 0.4mm fell on the last day, Figure 2. It is likely that the rain washed enough salt from the surface to again cause a lack of response on the galvanic and leaf sensors, which were responding similar to the grids up to a day before take-down.

3.3 Deposited Aerosol Wetting Behaviour

Results from the RH chamber experiments indicate that the sensors were likely wet, or at least conductive, down to the minimum RH achievable in the chamber (12-15%) during some runs, Table 2. Results were considerably variable, however, between sensors and also between runs. The grids generally exhibited the lowest wetting points, by definition, among the sensors. During the drying cycles in the last chamber exposure, grid output exceeded the definitional threshold (0.5Hz) down to 13% RH with activity seen below the threshold to 12%, the minimum achieved during the cycles. Activity down to the minimum achieved RH is also apparent after the first outdoor exposure, Figure 7. By contrast, grid sensors read definitionally dry below 42-72%RH during the chamber run after the shelter experiment. Closer examination of the output below 0.5Hz during this run reveals lack of sensor response below 33%RH. Time-lapse video on one sensor, however, showed noticeable wetting and drying events down to 21%RH. Assuming no difference in deposited aerosol distribution or behaviour between the sensors, these results indicate the varying drying and wetting points are likely due to electrolyte bridging issues. As the deposits contract upon drying they will, at some point, stop bridging the electrodes. This point presumably depends on the geographical deposit distribution on the sensors, the ability of the droplet to wet and spread across the insulating gap, and the spacing of the electrodes.

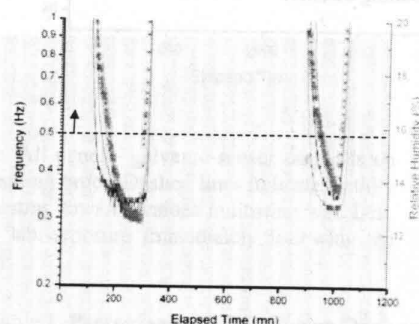


Figure 7 detail of grid sensor output at minimum RH levels reached during lab exposure 1. Relative humidity is plotted as hatched points. Dashed line represents definitional wet/dry sensor threshold with arrow pointing towards values defined as wet.

4. CONCLUSIONS

The results of this study provide further insight into the comparability and accuracy of three indirect TOW determination methods. With respect to comparability, cumulative TOW estimates varied widely between the different methods for the outdoor exposures. Currents measured on the galvanic sensors throughout the experiments were consistently and considerably above the initial baseline of the clean and presumably dry sensor prior to initiating the experiments. Although a higher current baseline was present during the experiments, it fluctuated, preventing confident determination of TOW. The reason for this is unclear, but the non-zero current readings may be indicating that the sensors were consistently wet, possibly due to moisture retention of surface corrosion products or within the sensors themselves. Output on the other sensors appears to be linked to aerosol loading and the wettability of their surfaces. Grid sensor output indicates surfaces may have been wet down to at least 13%RH after outdoor exposure, far below the ISO 9223 TOW threshold. Further work is necessary to examine comparability during long-term outdoor exposure, correlate sensor output with actual surface conditions, and, in general, develop an informed understanding of TOW parameter used in atmospheric monitoring and modeling.

Table 2. Wetting and Drying points as per TOW Definitions and Microscopy during Lab Exposure

Sensor	Lab Exposure 1		Lab Exposure 2 (clean)		Lab Exposure 3		Lab Exposure 4	
	Wetting (%RH)	Drying (%RH)	Wetting (%RH)	Drying (%RH)	Wetting (%RH)	Drying (%RH)	Wetting (%RH)	Drying (%RH)
Grid1	18	19	90	70	81	74	13	33
Grid2	21	20	78	75	68	61	13	33
Grid3	17	17	78	75	53	42	13	24
Time-lapse micrographs of Grid 2 surface	78	35	-	-	34	21	20	23
Leaf1	54	52	-	-	-	-	-	-
Leaf2	49	44	-	-	-	-	-	-
Leaf3	57	52	-	-	44	42	-	-

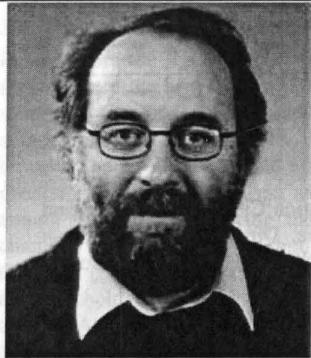

5. ACKNOWLEDGEMENTS

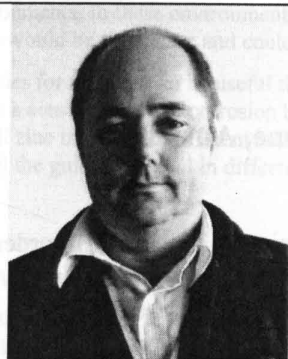
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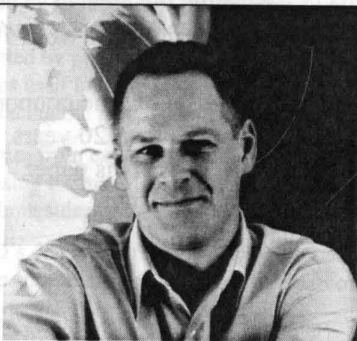
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7. AUTHOR DETAILS

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