Desiccated microclimates for heritage metals: creation and management

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Abstract

Since the early 1970s, archaeologists, conservators and curators have turned to published guidance for methods of safeguarding archaeological metals in the short and long term. Much of this has appeared in editions of the ubiquitous handbook *First Aid for Finds*, the most recent of which dates to 1998. A central message across all guidance has been to dry metals post-excavation and prevent their corrosion during storage by desiccating the environment around them. This has been proven crucial for iron, with reports of catastrophic loss of collections arising from inappropriate storage environments.

There has long been agreement that an effective, low cost option for desiccation is the packing of artefacts in boxes with a desiccant. Though advice on the detail of how to achieve this has evolved over time, what has not changed is the lack of quantified evidence for the methods proposed.

Informed by a survey of current practice in the sector, this study investigated quantitatively the many variables involved in creating desiccated microclimates for storage of heritage metals. This paper presents the results of an evaluation of the airtightness of a range of commercially available boxes, the optimum mass of desiccant, the effect of external environments, and preliminary data on the efficiency and risk of drying damp objects with silica gel. A second paper will report the effect of stacking boxes on their airtightness and present data on the accuracy and long-term reliability of humidity indicator cards.

The guidance arising from laboratory testing of the hardware and methods for desiccated storage is designed to be achievable and adaptable. Combining these findings with corrosion rate data for iron artefacts allows the escalation of risk to objects from decisions in the storage process to be calculated. Together, these papers offer an evidence-based and practice-focused update to *First Aid for Finds*.

Keywords

Metals; Wrought Iron; Cast Iron; Copper Alloy; Storage; Desiccation; Guidelines; Corrosion; Preventive

Introduction

Post-excavation corrosion of archaeological metals: relative humidity and risk

Most archaeological metals occur as small finds, encrusted in thick but porous corrosion layers (Bertholon 2001; Neff *et al.* 2004; Bellot-Gurlet 2008). In temperate climates, excavation from damp burial environments necessitates rapid drying of iron to prevent its corrosion in the oxygen rich atmosphere (Turgoose 1982). Immediate post-excavation procedures centre on the safe packaging of objects to ensure they remain unchanged for post-excavation study and publication (Watkinson, Neal 1987; Sease 1994; Perrin *et al*. 2014; CIfA 2014). Key to this is minimising the risk of corrosion processes which lead to loss of metal, growth of disfiguring corrosion products and, ultimately, the break-up of objects.

Controlling the corrosion of archaeological and historical metals is a longstanding problem within the heritage sector and much research has focused on methods of achieving this. Water, oxygen and soluble salts are necessary for electrolytic corrosion to occur (Evans 1981; Scully 1990; Revie, Uhlig 2008) and eliminating any of these from the objects and their environment will prevent corrosion. Removing water is more reliable than treatments to remove soluble salts and more practical than anoxic methods (Watkinson, Lewis 2005; Watkinson 2010; Rimmer *et al.* 2013a; Watkinson, Rimmer 2014; Watkinson et al. 2019). This explains why an enduring approach for controlling metallic corrosion is to eliminate water from the ambient environment by desiccation. Whether by manipulation of relative humidity (RH) or oxygen, creating “safe” storage for these artefacts involves a complex set of decisions (Figure 1).

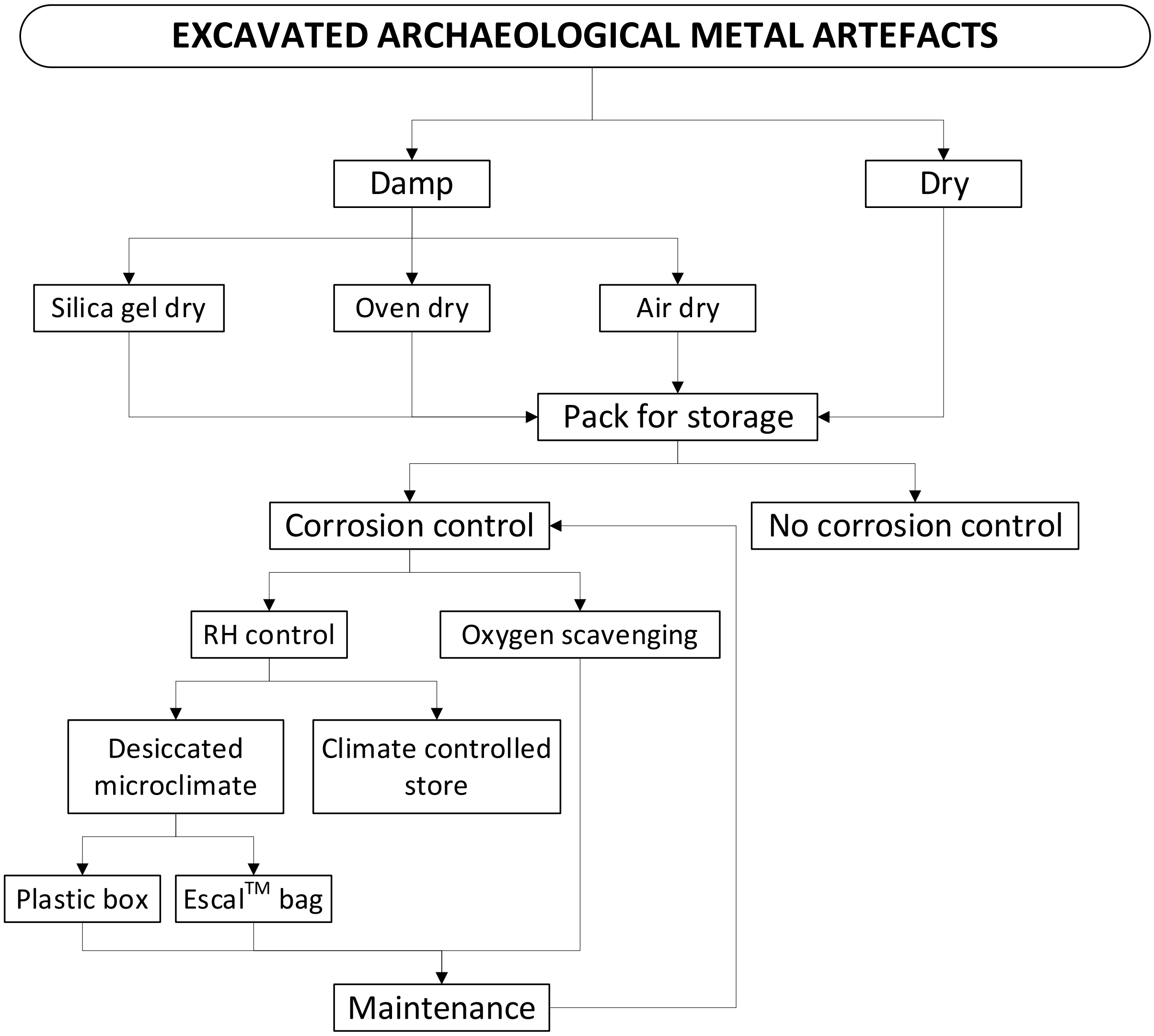

Figure 1: Options for storage of archaeological metals post-excavation

If corrosion control is to be achieved via desiccation, the crucial question becomes: how much water must be removed from the environment to ensure safety of the artefacts? As post-excavation corrosion is a particular concern for iron and copper alloy artefacts, attention has focused on determining experimentally the RH at which corrosion occurs for these metals. Complete prevention of archaeological iron corrosion can be achieved by creating and maintaining an RH below 12%, the corrosion threshold for iron (Watkinson and Lewis 2005). Above this RH value, the risk of corrosion begins, rising slowly to 50% RH beyond which it increases rapidly to a rate that may be 90x faster at 80% RH than at 30% RH (Figure 2) (Watkinson et al. 2019). For copper alloys, an RH below 28% is required to prevent corrosion (Thickett 2016).

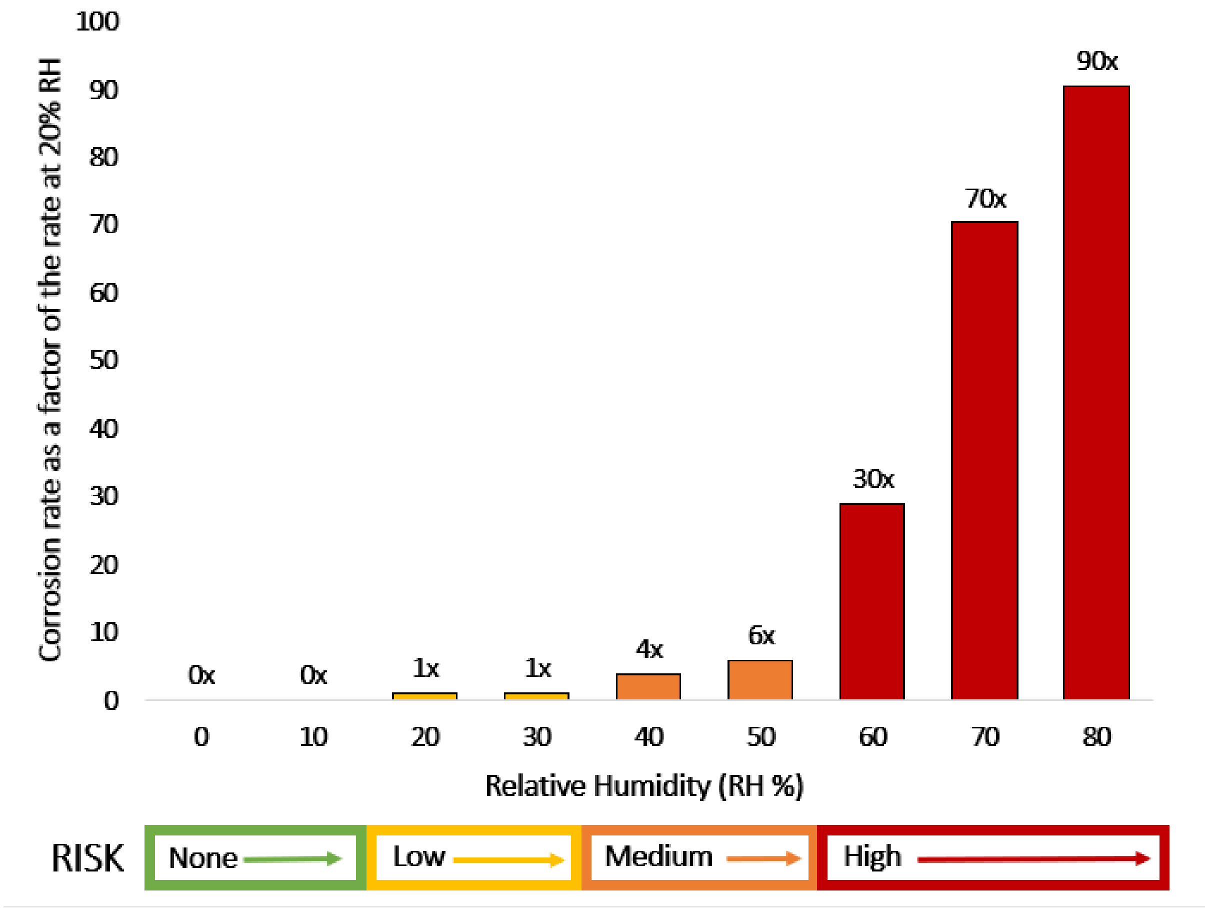

Figure 2. Schematic of expected corrosion risk for archaeological iron as a function of relative humidity (based on data from Watkinson et al. 2019; Watkinson and Lewis 2004).

Although desiccation is proven to prevent corrosion, procedures for producing low RH environments around heritage artefacts remain largely empirical and are based on theory rather than quantitative study in practice. With archaeological artefacts relying on appropriate storage and display conditions for their survival, evidence-based management protocols are essential to ensure that corrosion threshold RH values are not exceeded.

Current practices in storage of archaeological metals

Desiccated storage has long been recommended for safeguarding archaeological metal artefacts (Leigh 1972; Watkinson and Neal 1987; Logan 2007; Rimmer et al. 2013b). The most common approach to achieving this is understood anecdotally to be enclosing artefacts in airtight plastic storage boxes with dry silica gel as a desiccant. A recent survey of practitioners in the sector investigated this and identified that low RH storage is widespread but varies greatly in the procedures employed for creating, maintaining and managing desiccated microclimates (Whitehead 2018). The survey gathered approximately 90 replies from 23 countries across 6 continents from a range of professionals (including conservators, collections assistants and managers, curators, archaeologists, finds officers and archivists) and volunteers in archaeology units, historic houses, museums, private practice, government institutions and universities. This is a broad capture of responses from those working with or managing archaeological metalwork collections internationally. Examining the results gives an insight into current practices in storage of archaeological metals:

1. 71% separate metals from other finds for storage.
2. 53% dry metal artefacts post-excavation, of whom 64% air dry and 36% dry with silica gel.
3. 74% have stores with climate control, of which 43% are controlled by HVAC, 49% by dehumidifier and 8% by conservation heating.
4. RH of the stores varies widely (Figure 3):

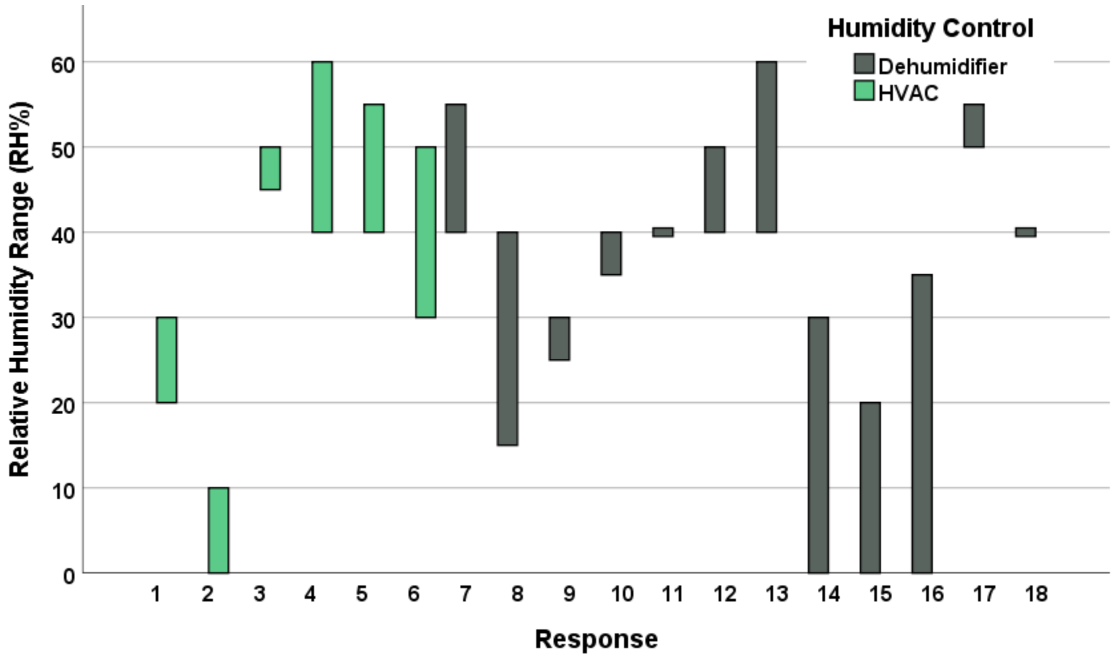

Figure 3: RH ranges of stores controlled by HVAC and dehumidifiers.

5. 63% use low RH storage for metals, of whom 83% use this for iron and copper alloy and 17% for iron only.
6. The range of target RH values for those using low RH storage is also variable and places some artefacts (particularly iron) at risk of corrosion (Figure 4).

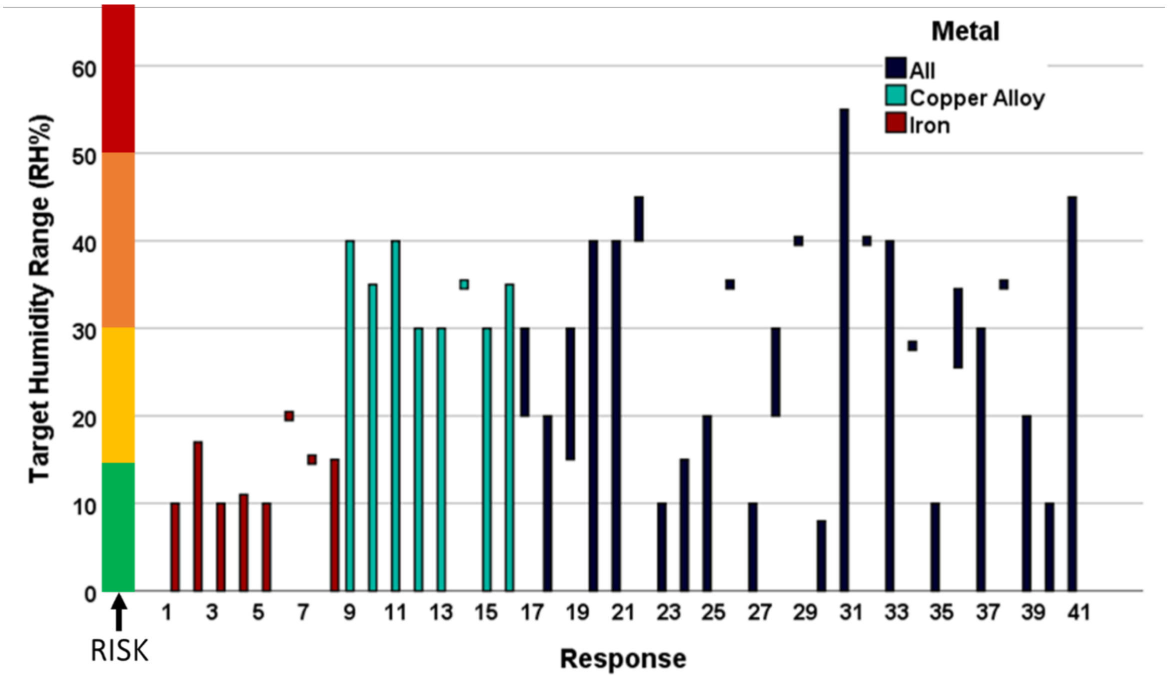

Figure 4: Target RH ranges for respondents using low RH storage for iron, copper alloy and all metals with risk levels (None, Low, Medium, High) for iron artefacts indicated as per Figure 2.

7. Of the 63% employing low RH storage, 17% rely on their climate-controlled storerooms, 36% store objects in plastic boxes with desiccant and 22% combine these measures. Other responses (14%) included storing in vacuum plastic bags with desiccant or in cardboard boxes with objects in polyethylene bags with silica gel.
8. Of those using plastic boxes with desiccant, 35% report using Stewart boxes, 17% Tupperware, 11% Crystal boxes and 4% each Lock & Lock, Rubbermaid, Ikea, Rotho and supermarket.
9. A wide range of storage box volumes are used, often multiple by the same respondent (Figure 5):

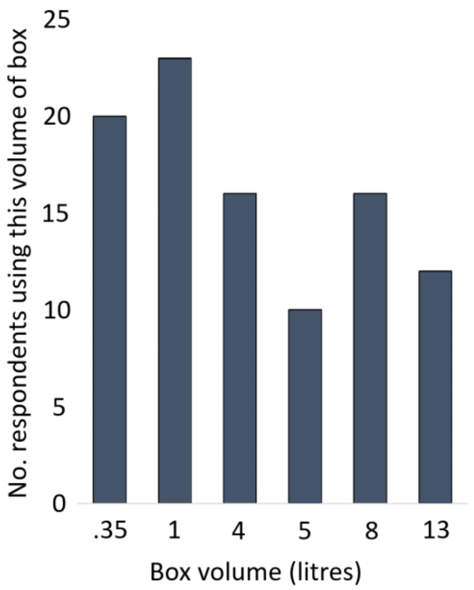

Figure 5: Number of respondents using these volumes of box for metal finds in store.

10. Of those using silica gel as a desiccant within boxes, 40% either do not control the amount within the box (33%) or do not know how much is used. Of the 60% who do control the amount, First Aid for Finds proportions (Watkinson and Neal 1998) are cited most frequently, others have algorithms based on box leakage, some use a percentage of box volume (5%, 20%, 33%) and as little as 100g/13l box is cited.
11. 14% of those using silica gel put this free into a box, 41% contain it within polyethylene bags and 46% use pre-sealed sachets.
12. Silica gel requires regeneration to maintain desiccation; 33% aim to regenerate every 6 months, 17% annually, 4% every 2 years, 20% on an ad hoc basis and 9% when indicated by colour of the silica gel or indicator card.

What is clear from the survey data is that practices differ widely between institutions and individuals, yet each of these variables in storage of metals will affect corrosion rate and long-term survival of the artefacts. When asked about use of guidelines to direct their practice in storing archaeological metals, 38% of respondents did not follow any published guidance or did not know and those that did cited First Aid for Finds (Watkinson, Neal 1998) predominantly, plus English Heritage (Rimmer et al. 2013b) or a range of in-house institutional guidelines. None of these are based on a complete dataset evidencing effectiveness of the methods for safe storage of artefacts.

With millions of archaeological metal artefacts held worldwide and long-term in museums and other repositories, developing successful management strategies for their safe storage is essential to preserve their heritage value. These strategies should be effective, predictable, feasible and based on quantified data. This research investigates the most commonly reported method of post-excavation storage which is the creation of desiccated microclimates within plastic boxes. The variables in setting up these microclimates are considered and investigated in turn over the course of two papers, beginning here with choice of storage box and influence of external RH, mass of silica gel and use of silica gel for drying objects.

Variables in creating a desiccated microclimate

The procedure for creating a desiccated microclimate is empirically straightforward and conceptually simple; dry desiccant is placed in a box that can be sealed against the external environment and it adsorbs moisture entering the box, buffering its interior to maintain a low humidity.

RH exchange occurs by movement of water vapour via three dominant pathways: through cracks, holes and small openings, through solid walls, or through gaps and larger openings (Thomson 1977; Michalski 1994; Tencer 1994). Low water vapour permeability of plastics used in commercial storage boxes (Begley et al. 2008: 1409; Maier, Calafut 1998: 4; Barrie 1968: 284; Shashoua 2008: 247) means that the main route for water vapour exchange between the interior of a plastic storage box and its external environment is expected to be through the opening at the box seal (Thickett, Odlyha 2010), driven primarily by differences in water vapour concentrations between the two environments (Burrows et al. 2009; Tencer 1994).

Variables in a successful microclimate are likely to be the:

- storage box;
- type, amount and distribution of desiccant;
- amount of water contained in the artefacts within the box;
- external RH around the box;
- frequency with which the desiccant is replaced or regenerated;
- frequency with which the box is opened.

These variables are largely procedural, but the box type and desiccant are hardware choices to be made when purchasing materials for creating microclimates.

Storage boxes

Microclimate boxes should be air-tight and produce low water vapour exchange rates to retain a stable RH for as long as possible, minimising the frequency of silica gel regeneration and maximising protection of objects (Calver et al. 2005). They should have an efficient seal, be translucent or transparent allowing contents to be visible, stack without compromising seal effectiveness, retain their properties over time and be low cost. While the need to identify the most airtight box has long been accepted, the various types and brands of box recommended have relied upon anecdotal reporting rather than quantitative data (Watkinson, Neal 1987, 1998; Rimmer et al. 2013b), with the exception of limited testing of Stewart Plastics boxes (Thickett, Odlyha 2010). The lack of testing is due in part to the wide range of variables that will determine if a box is suitable (Table 1) which necessitate investigations of large numbers of box types.

<table>
<tr><th>Variable</th><th colspan="2">Comment</th></tr>
<tr><td>Box material</td><td colspan="2">Manufacturers use different polymer systems and gradings to achieve performance specifications such as flexibility, transparency, ageing, permeability, toughness, brittleness, shrinkage, dimension retention and response to temperature. Factors that will influence properties include molecular weight, chain branching, density and plasticiser (internal or additive). Degradation of box materials over time may change their properties during the use life of a box.</td></tr>
<tr><td>Box lid material</td><td colspan="2">Manufacturers may vary plastics between lid and box body or use the same plastic to manage factors such as rigidity and transparency, aiming for either more rigid lids to support stacking or greater transparency to facilitate viewing of the box contents.</td></tr>
<tr><td rowspan="3">Seal mechanism</td><td colspan="2">Boxes may employ a range of different seal mechanisms which will influence the airtightness of the box.</td></tr>
<tr><td>Snap lid - interference seal</td><td>An interference seal involves a close fit between the lid and the box lip and exerts a degree of tension across the lid. It is closed by applying pressure to push the lid onto the raised seal. Its effectiveness will depend on many factors including malleability of the plastic and the tolerance of the seal at the manufacturing stage. The density and rigidity of the plastic used may be critical to performance, as will the physical design of the lid and box, since a more rounded corner on the lid might be expected to produce a better fitting seal than a design using a right angle.

Advantage: Simple design and cheap manufacture but requires close tolerances for a tight fit and effective seal.

Disadvantages: Repeated opening and closing may lead to wear and reduced seal tightness. Any loss of plasticiser over time would be expected to influence seal quality due to dimensional changes.</td></tr>
<tr><td>Locking clip and may involve malleable polymer liner</td><td>This design uses a close-fitting seal but its effectiveness relies on clips, located on the box body or its lid, to create pressure to force a close fit between the top and bottom of the seal. The female part of the seal may be lined with a malleable polymer (elastomer) to form a gasket that will deform onto the lip.

Advantages: Secure fixing of the lid with no room for error either in its initial closure or in later movement influencing its quality. Less physical wear due to use.</td></tr>
</table>

		Disadvantages: More expensive to produce. There are multiple methods of clip manufacture and their positioning will influence the evenness of pressure on the seal and, potentially, distortion of the box. Pressure must be even along the seal for a uniform performance. There may be more opportunity for breakage, depending on the clip design. It may form part of the lid or box body as one extrusion or have been attached as a separate fitting. Geometry may interfere with stacking. Malleable polymer gaskets are likely to be more highly plasticised which will lead to faster ageing relative to original properties and shorter operational lifespan.
Box geometry and length of seal	Boxes are sold on volume and designed for specific functions that are not related to heritage. A tall, deep box will have a smaller seal area than a shallow box of the same volume. For boxes employing the same sealing method, a shorter seal length to box volume would be expected to produce a better performance. For management purposes, boxes often need to be stacked and are usually heavy when full of silica gel and metal artefacts. Box geometry, ability of lids to nest and rigidity of the plastic will influence the effectiveness of seals when boxes are stacked. Size of box is likely to be an influential variable in selection of boxes for a store based on size of objects and available space.	

Table 1. Plastic box design variables.

Desiccant

An ideal desiccant to produce an effective microclimate must be able to adsorb moisture at low RH, adsorbing any water in the microclimate during the set-up and offsetting higher RH entering the box through its seal, while at the same time leaving sufficient space within the box to maximise the free volume for objects. It should desiccate the environment to below corrosion thresholds, perform predictably to planned regeneration intervals and maintain a low RH for as long as possible to minimise regeneration needs.

Silica gel beads are the most common desiccant used in microclimates according to this survey. Silica gel is an amorphous silicon dioxide that can adsorb/desorb moisture until in equilibrium with the surrounding air (Weintraub 2002; Yang 2003). It has an excellent capacity to adsorb water, up to 35-40% of its own weight, due to a large network of polarised hydroxyl groups on the silanol sites (S-OH) sites (Zhuralev 1987; Chuang, Maciel 1997; Christy 2010). Atmospheric moisture adsorbs primarily on the surface of the gel, first directly to the OH^- sites, forming a monolayer of water, then by water binding to water molecules on the surface, forming several layers of adsorbate (Zhuralev 2000; Christy 2010). Surface adsorption can also occur through capillary condensation, but the level of capillary condensation depends on the size of the pores of silica gel (Li *et al.* 2007; Alcañiz-Monge et al. 2010). Some silica gels include an agent that will change colour upon saturation of the gel, such as the largely banned cobalt chloride (blue-pink) and currently used methyl violet (orange-green). Aside from its desiccation efficiency, the use of silica gel is favoured in microclimates as it can be regenerated indefinitely by removal of adsorbed water at elevated temperatures, making the surface ready for rehydration (Yeh et al. 1992; Ng et al. 2001). Silica gel is often discussed in generic terms but its properties and use will determine its final performance (Table 2).

Variable	Comment
Surface area	Will affect the number of hydroxyl groups available on the surface for moisture to adsorb. The number of hydroxyl group on the surface is proportionate to the surface area (Zhuralev 1987). Different gels have different surface area.
Pore size	Pore size of the silica gel will determine the efficacy of adsorbing moisture and maintaining equilibrium in different RH environments. Meso- (2-50nm) and macroporous (>50nm) silica gel adsorb/desorb water through capillary condensation more readily than microporous (≤2nm) gels (Li et al. 2007; Alcañiz-Monge et al. 2010). Regular density (RD) gel is used most frequently for desiccated storage of archaeological metals as its large surface area (measured in Brunauer–Emmett–Teller, BET) and small pore size produces an excellent capacity to adsorb water in the lower RH regions (Li et al. 2007; Alcañiz-Monge et al. 2010). At lower RH, water molecules are primarily adsorbed in monolayers, meaning that higher surface area offers more sites for hydroxyl groups for water to adsorb (Li et al. 2007). Desorption will only occur slowly as any adsorbed water in the micropores will bond firmly to water, yielding a high desorption activation energy.
RH and moisture content during set-up	On the principle that silica gel has a saturation point (35-40% of its dry weight), the moisture content within the box must not exceed the capacity of the silica gel to adsorb the moisture within the box, equilibrating or becoming saturated before desiccation is achieved.
Quantity of silica gel	The quantity of silica gel within a fixed volume will influence both the extent to which it can desiccate it and the rate at which this occurs. As the number of hydroxyl groups across the surface is finite, they may become saturated to the point that they cannot uptake any more moisture, which is why using an appropriate quantity of silica gel is critical for successful desiccation of the microclimate.

Packing of silica gel	There are multiple ways of including silica gel in a plastic box to create a microclimate. As shown in the survey, pouring it in loose in the box bottom is less common, more often it is contained in pierced plastic bags or is within a porous textile bag in which it can be regenerated. Access of the air to the surface of the gel is important so both the size of the hole/porosity of the bag and the area occupied by the gel will influence its adsorption/desorption rate. Hole punching protocols for plastic bags can vary from piercing with a sharp object to using a hole punch of the type used for paper. The size of hole will determine how fast moisture can leave the object and enter the atmosphere in the box, where the silica gel will adsorb it. The success of the silica gel is dependent on access to the hydroxyl groups on the silica gel surface, meaning that the greater the surface area of the gel, the more responsive it should be.
Drying procedure	When drying, all adsorbed water will need to leave the structure to achieve full desiccation. Gel drying protocols should ensure this occurs.
Airtightness of box	As silica gel will equilibrate with the ambient environment, the longevity of the desiccation will be determined by the airtightness of boxes and external RH.

Table 2. Variables affecting the performance of silica gel as a desiccant

Existing guidance to underpin decision-making for setting up and use of microclimates

Boxes

Unlike display cases, whose performances have been rigorously studied and standardised (BS EN 15999-1:204; Brimblecombe, Ramer 1987; Cassar, Martin 1994; Camuffo et al. 2000; Thickett et al. 2006; Thickett et al. 2007; Watts et al. 2007; Schieweck, Salthammer 2011; Romano et al. 2015), few studies have investigated quantitatively the efficiency of plastic boxes for creating and retaining specific microclimates. The heritage sector is reliant on out-of-date, conflicting and unevidenced guidelines to inform decision-making when selecting materials and methods for object storage. Following publication of *First Aid for Finds* in 1987, which first advised the use of Stewart Sealfresh boxes to maintain microclimates post-excavation, the sector has largely been using these boxes for this purpose (Watkinson, Neal 1987). Despite their popularity, anecdotal reports over the last 20 years have identified issues with these snap-seal boxes. This includes difficulty ensuring proper closure, embrittlement and cracking of lids, and lids failing to seal effectively when boxes are stacked. These factors must compromise the efficiency of microclimate retention.

Studies (Larkin et al. 1998, Thickett, Odlyha 2010; Thickett 2012) have confirmed these reports and identified the new polypropylene (PP) design of Stewart Sealfresh is less suited to microclimate control than the pre-2005 low density polyethylene (LDPE) version (Larkin et al. 1998; Thickett, Odlyha 2010; Bugge-Jensen 2011). In comparative tests involving selected polythene boxes, Stewart Sealfresh was not identified as the most appropriate box choice, relative to the criteria governing microclimate storage (Bugge Jensen 2011; Thickett 2012; Thunberg 2014). As a result, current heritage microclimate guidelines now offer general advice to use commercial polythene or polypropylene boxes for microclimates but do not specify a brand (Senge 2011; Rimmer et al. 2013b; Butterworth, Greaves 2018; Cook 2019). More recently, boxes featuring elastomers and locks that clip into place have been recommended as a more airtight alternative to snap-lid boxes (Senge 2011; Rimmer et al. 2013b).

Despite the existence of guidelines and their widespread adoption, the evidence-base for using polythene boxes for storage purposes remains limited (Thickett 2012: Senge 2014: Thunberg 2014). The number of published studies is small, no standard procedure for investigating box performance has been established and variables affecting performance of polythene boxes have not been discussed exhaustively. The focus on establishing a *best in test*, rather than investigating the factors affecting box performance, limits end-user understanding of these microclimates and methods to optimise them. Consequently, heritage professionals are choosing between boxes whose microclimate retention performance has never been studied rigorously, creating uncertainty about their efficacy. Without a robust evidence base for prediction of storage box performance, establishment of reliable microclimate maintenance regimes for storage cannot be achieved.

Desiccant

Throughout conservation literature, few articles explain how silica gel works for microclimate purposes and the interaction of silica gel with the ambient environment. Existing studies are outdated and often relate to retaining display environments at mid-range humidities (La Fontaine 1984; Yu et al. 2001; Weintraub 2002). The heritage sector must turn to publications outside conservation for a detailed understanding of silica gel as a material, especially when employed as a desiccant at very low humidities.

Existing guidelines provide a range of often conflicting recommendations on silica gel use which are rarely evidence-based. While the relationship between quantity of silica gel and the volume and airtightness of boxes is acknowledged to affect performance and calculations are offered, the goal of desiccation, suitable materials to use and management routines specific to heritage metals have never been reported in detail.

With no clear understanding of how silica gel can be used to achieve specific goals, it is not surprising that the practice of including silica gel in microclimates throughout the sector is highly inconsistent (Whitehead 2018).

While silica gel is a relatively cheap method of achieving desiccation, ineffective use can have serious cost-implications regarding the staff-time required to monitor and regenerate the gel. Predictability of the performance of both box and desiccant is critical for producing efficient maintenance regimes. At a time when funding for the heritage sector has been cut and museums are increasingly reliant on staff without professional qualifications for day-to-day maintenance (Museums Association 2015), unpredictability of microclimates could have a significant impact on collections and resources spent on storage maintenance. Understanding the longevity of desiccation measures, and the inherent risk when maintenance timescales slip, embeds resilience into planning and permits an evidence-based appraisal of priorities for resource allocation.

Aim and objectives of the study

A range of experiments were designed to examine quantitatively the effect of variables in creation of microclimates on the efficiency, longevity and predictability of their desiccation, specifically:

- To quantify the ability of selected widely available commercial polythene boxes to maintain microclimates without a buffer and with silica gel desiccant, considering the variables of gel quantity and external RH.
- To determine how drying damp archaeological small finds in a desiccated microclimate impacts on the microclimate itself.

This was achieved by:

- Measuring the RH exchange rate of a selected range of commercial storage boxes and relating this to box design.
- Recording the RH within boxes containing varying amounts of desiccated silica gel over 9 months at 20^{o}C and 50% external RH.
- Recording the RH within boxes containing varying amounts of desiccated silica gel and damp archaeological artefacts.

Method

Investigated boxes

The six box types chosen for this study were Addis Clip & Close, Araven, Lock & Lock, Sistema Klip IT, Stewart Gastronorm and Stewart Sealfresh (Table 3, Figure 6). The boxes are affordable, readily available from commercial stores or online and come in a range of sizes. All boxes can be nested when empty, offer easy access through their re-sealable lid and, except for Araven, permit a clear view of contents through their transparent bodies (Larkin *et al.* 1998). Addis Clip & Close, Lock & Lock and Sistema Klip IT seal using clips and elastomers, representing a range that might be selected if following the current best-practice guidelines (Rimmer et al. 2013b). Stewart Sealfresh are effectively the control in this study, having been in use for decades in the United Kingdom. Along with the newer Stewart Gastronorm and Araven boxes, they represent the snap-seal closing system recommended previously. Five different volumes of boxes were investigated; 1l, 2l, either 5l or 6.5l and 13/14l depending on manufacturer availability. These volumes are commonly used in museum stores and archaeological archives (Whitehead 2018). Five boxes of each volume within a brand were investigated, 90 boxes in total. All boxes were tested directly after purchase and were therefore in a 'new' condition.

These boxes reflect the variation in design of closure and seal that are commercially available and would be acceptable when following current storage guidelines. The designs utilise different numbers and locations of locks, with different elastomers fitted in varying ways between body and lid (Table 3).

Box (Acronym used in results section)	Body/ lid material	Elastomer	Size (l)	Volume (cm^3)	Seal length (cm)	No. of locks	Lock hinge attachment	Lock length (cm-total)	Total area of seal covered by lock (%)
Addis Clip & Close (ACC)	PP/PP	Silicone rubber rectangular, hollow, tight fit in lid	**1.1**	1150	70	4	Lid	48.4	69
			2	2050	72			48.4	67
			5.2	5485	102			72	71
Araven (AR)	PP/PE	None	**1**	965	48	N/A			
			2	1725	59				
			6	5950	92				
			14	14100	123				
Lock & Lock (LL)	PP/PP	Silicone rubber rectangular, hollow, tight fit in lid	**1**	1140	64	4	Lid	46	72
			1.9	2050	64			46	72
			5.5	5900	101			75	74
Sistema Klip IT (SKI)	PP/PP	Round, solid, loose in lid	**1**	930	57	2	Body	17	29
			2	2100	77			23	32
			5	5250	94	4	Body	46	51
Stewart Gastronorm (SG)	PP/PP	None	**0.9**	900	57	N/A			
			1.6	1650	68				
			5.7	5900	100				
			14	13700	123				
Stewart Sealfresh (SS)	PP/PP	None	**1**	1050	66	N/A			
			2.25	2380	80				
			6.5	6700	104				
			13	14450	120.5				

Table 3. Characteristics of boxes. PP: polypropylene; PE: polyethylene.

Figure 6: 1 litre examples of Addis Clip & Close, Araven, Lock & Lock, Sistema Klip IT, Stewart Gastronorm and Stewart Sealfresh. For dimensions, see Table 3.

Evaluating airtightness

Rationale for test parameters

Airtightness was evaluated by setting a low internal RH within each box and then measuring the rate of equilibration with a higher external RH. This is an appropriate measure, as RH is the main agent of decay controlled using microclimates (Thickett et al. 2005; Camuffo 1998). To evaluate box airtightness accurately, any interaction between atmospheric moisture in the boxes and other materials was avoided by studying the boxes empty (Giani 2005; Weintraub 2002; Camuffo 1998).

An internal RH value of 20% was chosen to model the low RH environments recommended for storage of metal objects within boxes. 20% RH also represents the lowest value that can be reliably maintained by the climatic chamber. The experiment was repeated for equilibration with two different external RH values. An RH of 50% represents an 'ideal' mid-range collection environment often sought in museums and evidenced in the survey responses. Repeating the investigation at 80% RH modelled an uncontrolled storage environment, as 80% is the median ambient RH in the United Kingdom (Met Office 2014). The difference in water vapour partial pressure between the internal and external environments allowed RH to be the sole driving force for the exchange to take place (Table 4). The internal and ambient temperature was kept at 20^{o}C.

RH %	20	50	80
Water vapour pressure (mbar)	4.7	11.7	18.7

Table 4. Water vapour pressure of the investigated environments at 20^{o}C assuming normal atmospheric pressure (1012.5mbar).

Calibration of equipment

The investigation relied on dataloggers and climatic chambers which were calibrated prior to the experiment. The Binder KBF720 (±1.5% RH ±0.1^{o}C) climate chambers underwent a three-point calibration process by a manufacturer-approved engineer. The MadgeTech RHTemp101A (±3% RH ±0.5^{o}C manufacturer information) data loggers were then two-point calibrated at 20% RH and 80% RH within a climatic chamber using the process dictated by the proprietary MadgeTech 4 software. The agreement between data loggers and both climatic chambers post-calibration was examined through the range 20-80% RH. The calibration protocol reduced the error of the dataloggers to ±1% RH and ±0.2^{o}C.

Method

A MadgeTech RHTemp101A data logger programmed to record RH and temperature at 10-minute intervals over the test period was placed inside each box. For each data logger, an alarm triggering a blinking light had been set to the RH value of the external environment (50/80% RH) to indicate full equilibration and determine the end of the test.

A Binder KBF720 climate chamber was used to establish 20% RH inside the boxes. The boxes were placed in the climate chamber with their lids propped open by a Plastazote® block (50x20x10mm) enclosed in a polythene bag, placed in the right-hand corner of one of the short sides of each box (Figure 7). This arrangement allowed the air in the climate chamber to enter the box, which was later closed by using the Plastazote® block as a pulling tool to close the lid, with the polyethylene bag reducing friction during this action. Boxes were spaced at a minimum of 30mm allowing the lids/locks to be clipped without disturbing the boxes on either side.

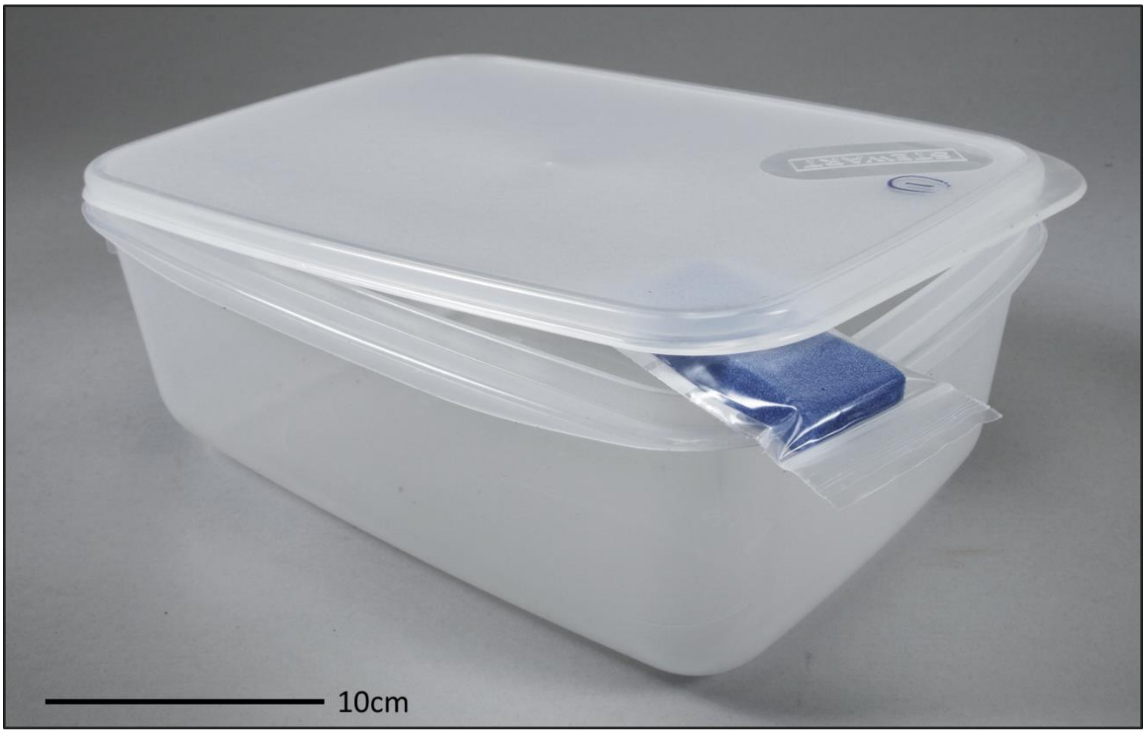

Figure 7: 1 litre Stewart Sealfresh illustrating the method of propping the lid open with a Plastazote® block to acclimatise the interior.

All boxes in the climate chamber were undisturbed for a minimum of four hours to establish a 20% RH environment inside them prior to closing, which took place one minute before a known data logging point. The climate chamber was opened, the Plastazote® blocks were quickly pulled and the lids secured, producing an audible click-sound. For 1l and 2l boxes, three boxes were closed at each opening of the chamber, while 5-6.5l and 13-14l boxes were closed two at a time. This minimised the effect of forced convection from opening the climate chamber. 50-minute intervals separated each opening of the chamber to permit the environment to stabilise and maintain 20% RH.

Closed boxes were transferred to a second Binder KBF720 climate chamber which maintained the desired ambient RH value (50% RH or 80% RH) at 20^{o}C throughout the test period. The boxes remained inside the climate chamber until the logger alarm within a box was triggered. The entire test procedure was repeated twice for all manufacturers, box sizes and ambient RH values (Table 5).

Group	Box size (litre)	Ambient RH (%)	No. box designs	No. boxes tested of each design
GR1	1	50	6	5
GR2		80	6	5
GR3	2	50	6	5
GR4		80	6	5
GR5	5	50	6	5
GR6		80	6	5
GR7	13	50	3	5
GR8		80	3	5

Table 5. Sample sets for determining box leakage.

Influence of silica gel quantity on internal RH

Rationale for test parameters

Having examined the humidity exchange rate of empty boxes, the influence of different masses of silica gel on the internal environment of boxes over time was investigated. This was examined using one brand and size of storage box, Lock & Lock 1litre. A mixture of 50% non-indicating and 50% self-indicating regular density silica gel (<0.2% methyl violet – orange to green, GeeJay Chemicals) was used (Table 6) in four different quantities. These were calculated to encompass the range of quantities identified in the sector survey (Whitehead 2018) and the frequently used 88g per litre recommended in *First Aid for Finds* (Watkinson and Neal 1998). A doubling series was employed for the tests (44g; 88g; 176g; and 352g).

Method

The silica gel was desiccated using a 60l Snol 60/300LFN (2kW, 10^{o}C-300^{o}C, ±0.3^{o}C) oven with a horizontal air flow fan and temperature controller VC7 ProWIC at 105^{o}C. Full desiccation was ensured by establishing a constant weight indicating that the gel did not desorb any more moisture. The required mass of silica gel for each box was divided between two pierced polyethylene resealable bags placed one at either end of the box. Bag size was chosen according to the amount of silica gel to be used so that each bag was approximately half full and a constant silica gel/bag ratio could therefore be achieved (Table 6). All bags were pierced on both sides with a 1mm diameter nail at 30mm x 20mm intervals to allow airflow between the gel and the atmosphere within the box.

Ten 1l Lock & Lock boxes were tested for each mass of silica gel with a total of 40 boxes used. A MadgeTech RHTemp101A (±1% RH ±0.2^{o}C – calibration details above) data logger programmed to record RH and temperature at 10-minute intervals over the test period was placed inside each box. Closed boxes were transferred to a Binder KBF720 (±1.5% RH ±0.1^{o}C) climate chamber which maintained 50% RH and 20^{o}C. The experiments were run for 280 days to represent long-term storage and encompass a range of maintenance intervals indicated by survey results.

Regular density silica gel		**Lock & Lock 1l (1140cm^3)**				
BET surface area (m^2/g)	600	*Box number*	1-10	11-20	21-30	31-40
Average bead size (mm)	2-5	*Silica gel (g)*	44	88	176	352
Average pore diameter (nm)	2-3	*g/1000cm^3* *(to nearest g)*	39	77	154	309
Pore volume (ml/g)	0.35-0.45	*Size of bags (mm)*	96 x 77	130 x 90	155 x 103	250 x 125
Density (kg/m^3)	700-750	*Number of holes*	18	30	30	56

Table 6. Properties of regular density silica gel, details of bagging method and quantities of gel used in experimental work to determine impact of silica gel quantity on RH control within the box.

Storing or drying damp objects with desiccated silica gel

Rationale for test parameters

Drying damp archaeological artefacts in an enclosed box with desiccant is a common practice but the efficiency of the silica gel in drying the objects and the environment within the box during drying is not known. Depending on factors intrinsic to iron objects and the nature of the burial environment, the extent and porosity of overlying corrosion products will vary. Along with the water table of the site relative to the burial context of the objects, these factors will dictate the amount of water within freshly excavated archaeological artefacts. Roman iron nails from two sites were available for this test. Those from one site (GG) had voluminous corrosion products and soil overlying a metal core. Those from the second site (SWA) had thin, closely adhering corrosion products and very little soil. Their capacity to hold water was very different and represented opposite ends of the spectrum of possible post-excavation scenarios. They were tested here as separate and mixed site groups.

To align with the investigation of silica gel masses above, the same mixture of 50% non-indicating and 50% self-indicating regular density silica gel (<0.2% methyl violet – orange to green, GeeJay Chemicals) was used in the 1litre Lock & Lock boxes. Two masses of silica gel were examined, the 88g/litre recommended by *First Aid for Finds* (Watkinson, Neal 1998) and double that figure with 176g/litre. The four boxes tested contained:

- Box 1 – data logger, ten damp nails (5 GG, 5 SWA), 88g silica gel;
- Box 2 – datalogger, ten damp nails (5 GG, 5 SWA), 176g silica gel;
- Box 3 – datalogger, ten damp nails (SWA only), 176g silica gel;
- Box 4 – datalogger, ten damp nails (GG only), 176g silica gel.

To verify the rate of water loss from the artefacts during drying, boxes 3 and 4 were opened at intervals and the objects weighed to record loss of water mass. This allows correlation with previously published experimental results (Thickett, Odlyha 2010). Boxes 1 and 2 were not opened during the test to examine the environment within the boxes without changes of air caused by opening. This was a pilot investigation for a larger scale project involving a large number of archaeological nails to be published in a forthcoming paper.

Method

Forty nails were selected for this test and radiographed to ensure that they retained an iron core overlain by corrosion products. The mass of each nail within a designated 103 x 155mm resealable polyethylene bag pierced at 30mm x 20mm intervals with a 1mm nail was determined using a Mettler Toledo AX504 balance (0.1 mg readability). The nails were removed from the bags, laid in a deep tray and impregnated by immersion in deionised water under vacuum. They were subsequently laid out on a drying rack to drain, dabbed with a paper towel to remove any excess water, each returned to its original polyethylene bag and the mass of each nail determined again using the same balance. Close observation verified that no loss of corrosion products or soil occurred which would have affected object masses.

Five damp iron nails in individual bags from each of the two sites were selected for both boxes 1 and 2. These were chosen to be of approximately even balance of larger and smaller nails from both sites. For Box 1, 88g silica gel was divided equally between two 130 x 90mm resealable polyethylene bags pierced at 30mm x 20mm intervals with a 1mm nail and placed at either end of a 1 litre Lock & Lock box. The ten nails were placed between the silica gel bags with a MadgeTech RHTemp101A (±1% RH ±0.2°C) data logger programmed to record the RH and temperature at 10 minute intervals (Figure 8). This process was repeated for Box 2 with 176g silica gel divided between two 155 x 103mm resealable polyethylene bags pierced in the same manner and the iron objects and datalogger set up as for Box 1. Boxes 3 and 4 both contained ten nails from a single site (Box 3, SWA; Box 4, GG) but were otherwise identical to Box 2 in set up procedure.

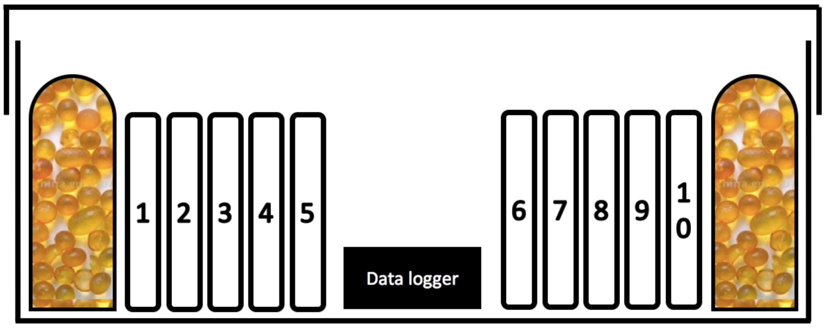

Figure 8. Schematic representation of the positioning of silica gel in pierced bags (left and right), damp objects in pierced bags (1-10) and data logger in 1l Lock & Lock test boxes.

The boxes were placed in a Binder KBF720 (±1.5% RH ±0.1°C) climate chamber set to 50% RH and 20°C to represent an environment that is often sought for museum and store interiors. Boxes 1 and 2 were undisturbed for the duration of the test period for those boxes (54 days). Boxes 3 and 4 were opened ten times over a period of 30 days and the mass of each nail recorded to measure loss of water from the nail. The boxes were opened at days 2, 5, 7, 9, 12, 14, 16, 19, 21 and 30 when water loss was complete then remained closed until the end of the test period of 70 days.

Results

Box leakage

The average RH within the five boxes of each of the six makes over the test period for 1l, 2l, 5-6.5l and 13-14l sizes has been plotted for 50% and 80% external RH environments (figures 9-12). The internal RH for each box increases over time until equilibration with the external RH, therefore all boxes exhibit leakage.

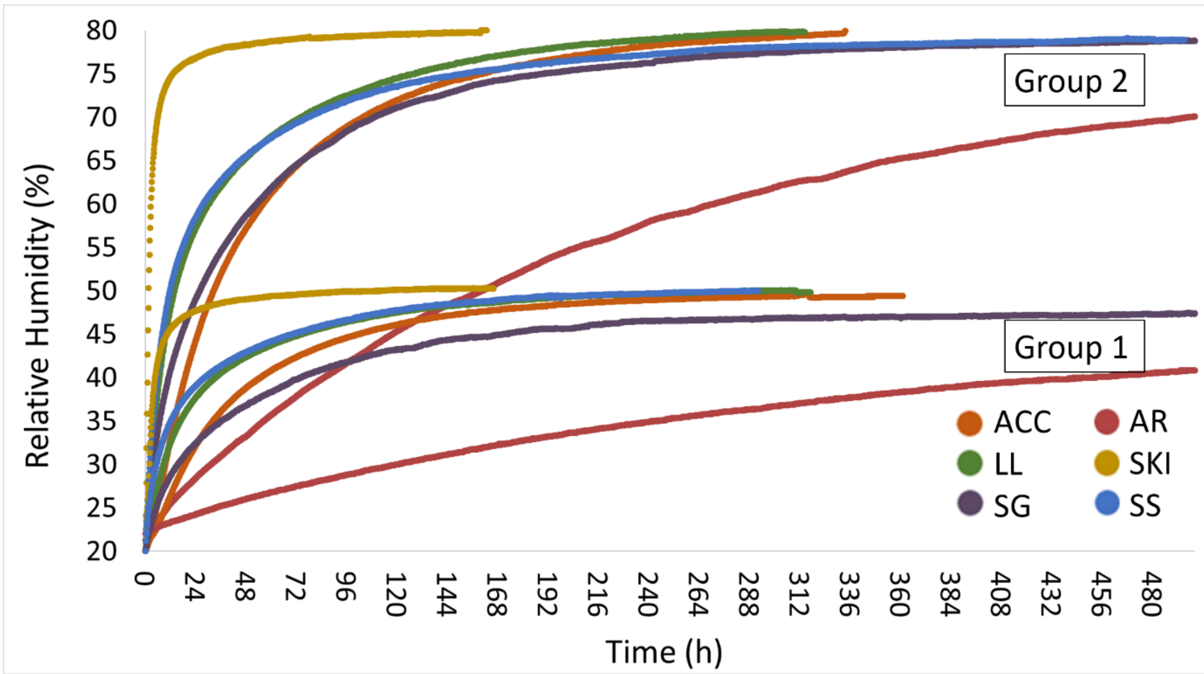

Figure 9: Average change in the internal RH of 5 x 1 litre boxes each for ACC, LL, SKI, SS, SG and AR. Box interiors initially conditioned to 20% RH; Group 1 boxes placed in 50% RH, Group 2 boxes at 80% RH both at 20^{o}C.

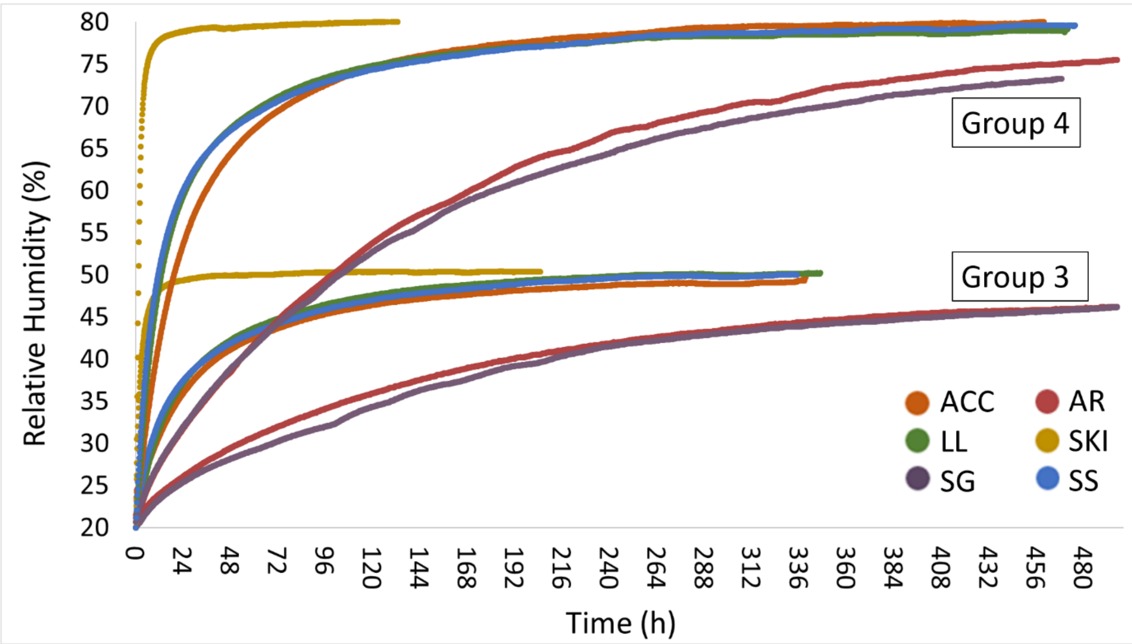

Figure 10: Average change in the internal RH of 5 x 2 litre boxes each for ACC, AR, LL, SKI, SG and SS. Box interiors initially conditioned to 20% RH; Group 3 boxes placed in 50% RH, Group 4 boxes at 80% RH both at 20^{o}C.

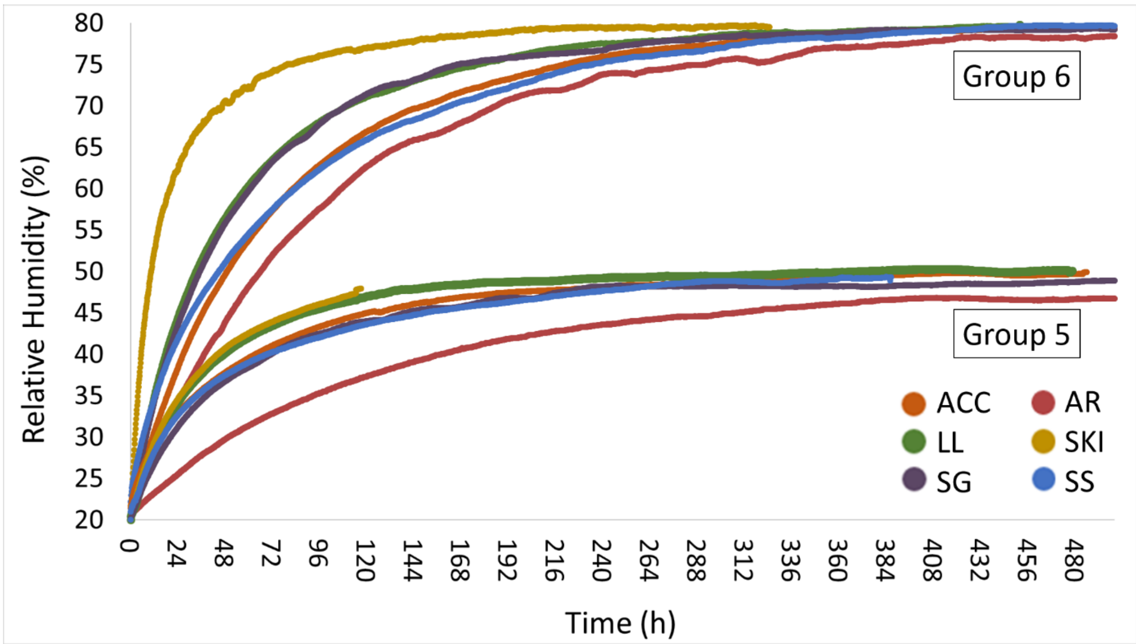

Figure 11: Average change in the internal RH of 5 x 5 litre boxes each for ACC, AR, LL, SKI, SG and SS. Box interiors initially conditioned to 20% RH; Group 5 boxes placed in 50% RH, Group 6 boxes at 80% RH both at 20°C.

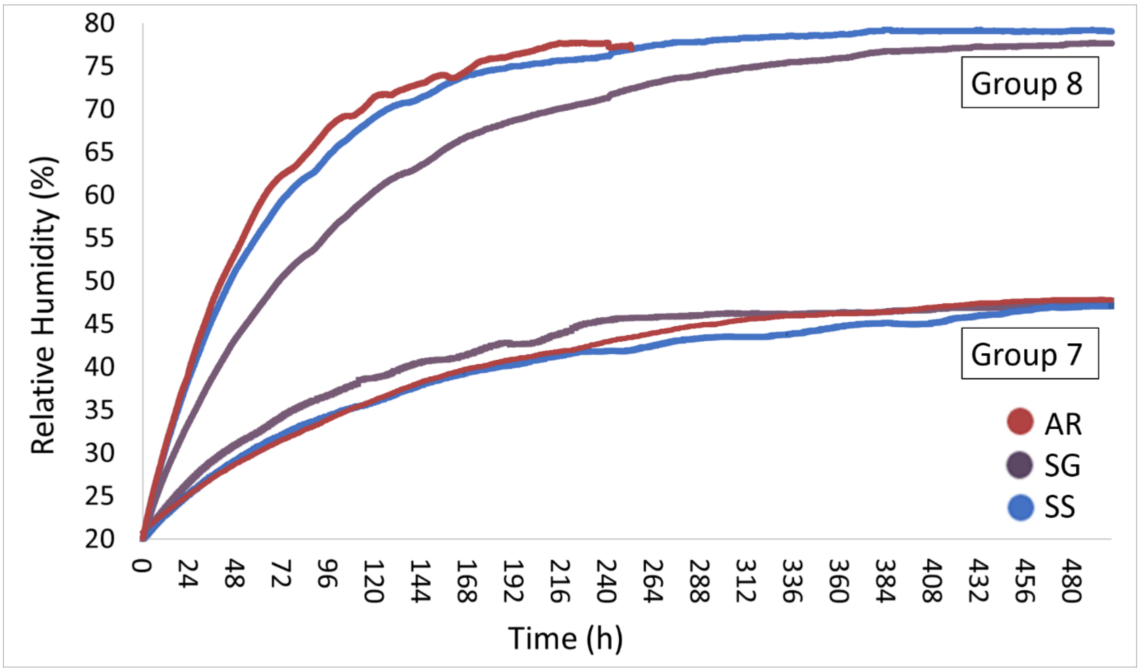

Figure 12: Average change in the internal RH of 5 x 13-14 litre boxes each for AR, SG and SS. Box interiors initially conditioned to 20% RH; Group 7 boxes placed in 50% RH, Group 8 boxes at 80% RH both at 20°C.

Silica gel mass

Figure 13 records RH as a function of time for individual 1l Lock & Lock boxes containing 44g, 88g, 176g and 352g of silica gel. Battery failures within RH loggers during the experiment made it impossible to return data for all the boxes tested.

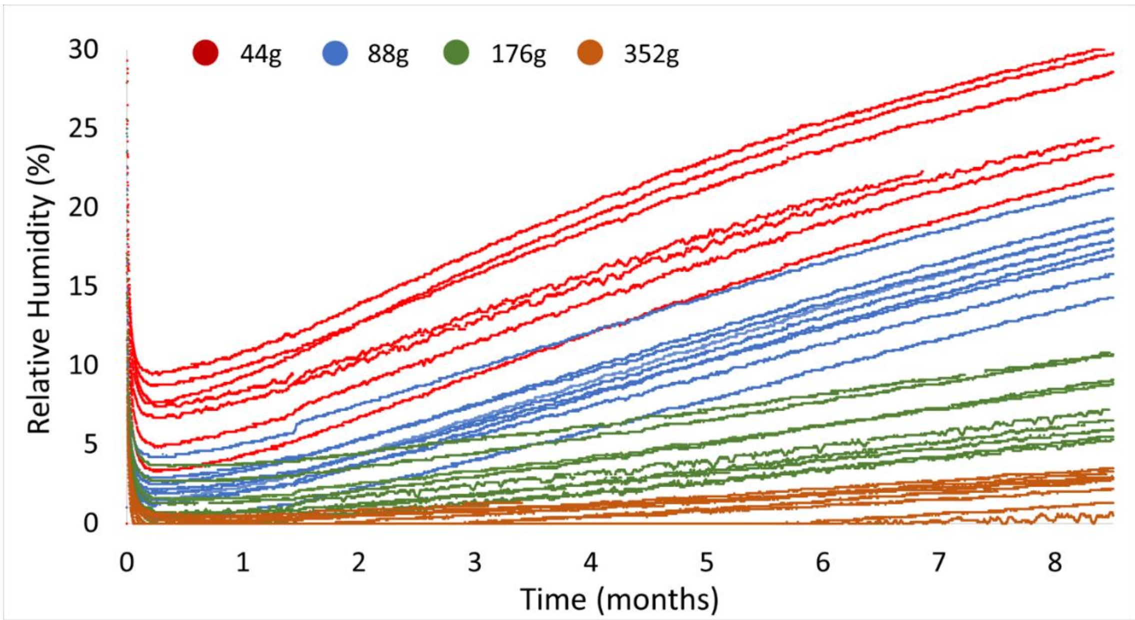

Figure 13: Internal RH within 10 individual 1l Lock & Lock boxes each for: 44g; 88g; 176g; 352g in a 50% RH external environment.

Damp objects

The internal RH within 1l Lock & Lock boxes 1 and 2 containing 88g and 176g of silica gel and ten damp archaeological iron nails per box is recorded in Figure 14.

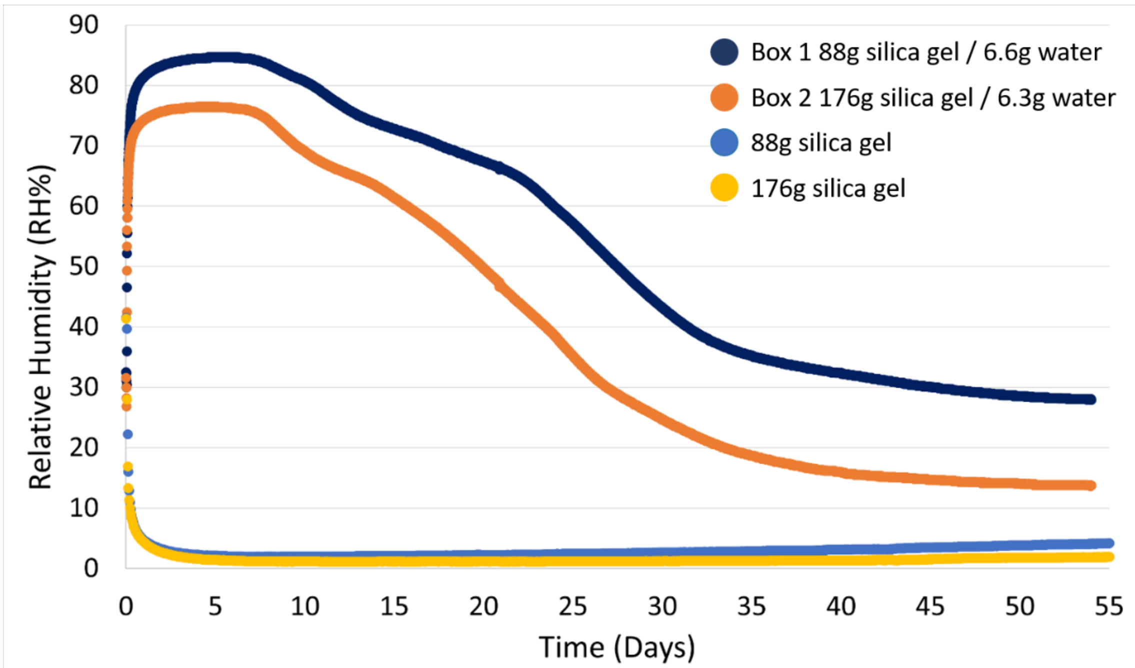

Figure 14: The internal RH for boxes containing 10 archaeological nails with 88g and 176g silica gel. Box 1 contained 6.6g water within objects and 88g silica gel. Box 2 contained 6.3g water within objects and 176g silica gel. For comparison, the average data for boxes containing 176g silica gel (as given in Figure 13) is plotted.

The internal RH within 1l Lock & Lock boxes 3 and 4 containing 176g of silica gel and ten damp archaeological iron nails per box is recorded in in Figure 15 including the average cumulative loss of water from the nails in each box.

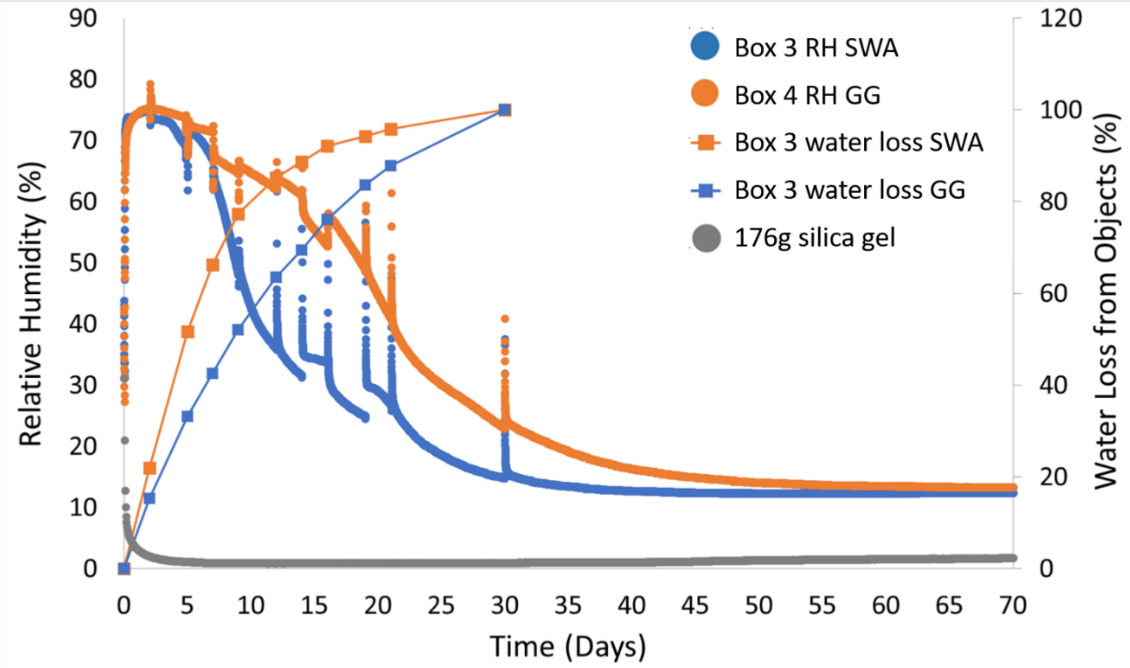

Figure 15: The internal RH for boxes containing 10 archaeological nails with 176g silica gel and the average cumulative water loss from objects as a percentage of their total water content. Box 3 contained 4.2g water within objects and Box 4 contained 6.1g water within objects. For comparison, the average data for boxes containing 176g silica gel (as given in Figure 13) is plotted.

Discussion

Evaluating airtightness

Figures 9-12 demonstrate clearly that none of the box types investigated here is fully airtight and an internal humidity of 20% RH increases until equilibration with the ambient 50% or 80% RH in all cases. The rate of equilibration, or RH exchange, varies between boxes and is seen to be influenced by:

- External environment (RH%)
- Box size
- Brand design

The data for each box has a logarithmic gradient which reduces over time. This confirms that the RH exchange function of all boxes is reliant on diffusion (whether through the box body material or the seal), with rates being driven by the magnitude of difference between internal and external water vapour pressures; the lower the gradient between internal and external RH, the slower the exchange rate. The logarithmic gradients indicate that the exchange rate reduces, or decays, exponentially over time. Consequently, as a simple measure of box airtightness, the hygrometric halftime ($t_{1/2}$) of the equilibration process can be employed. This is the time taken for the RH inside each box to reach the half-way point between the starting (20%) and ambient (50% or 80%) RH values. The average $t_{1/2}$ for all box brands and volumes at 50% and 80% RH is given in Table 7.

	Average $t_{1/2}$							
Ambient humidity (% RH)	**1l**		**2l**		**5 - 6.5l**		**13-14l**	
	50	***80***	***50***	***80***	***50***	***80***	***50***	***80***
ACC	32	33	21	19	33	49		
AR	242	159	107	100	93	66	108	42
LL	17	14	18	13	27	33		
SKI	3	2	2	1	27	12		
SG	36	27	111	108	39	32	66	76
SS	13	12	19	12	31	45	110	45

Table 7. Average $t_{1/2}$ (to nearest hour) for all box brands and volumes at ambient 50% and 80% RH. The $t_{1/2}$ is therefore the average time taken for the internal RH value to reach 35% with external 50% RH and to reach 50% with external 80% RH. Datalogger error ±1% RH.

To draw comparisons between the box performance in 50% and 80% RH external environments, it is necessary to consider leakage over the same RH range for both sets of data. Taking as an end point the time at which the internal RH of all boxes reaches 50%, $t_{1/2}$ values are calculated as the time taken for internal RH to reach 35%. Plotting these values of $t_{1/2}$ as boxplots allows examination of the influence of external RH and the consistency of the performance of a specific brand and size (figures 16-22).

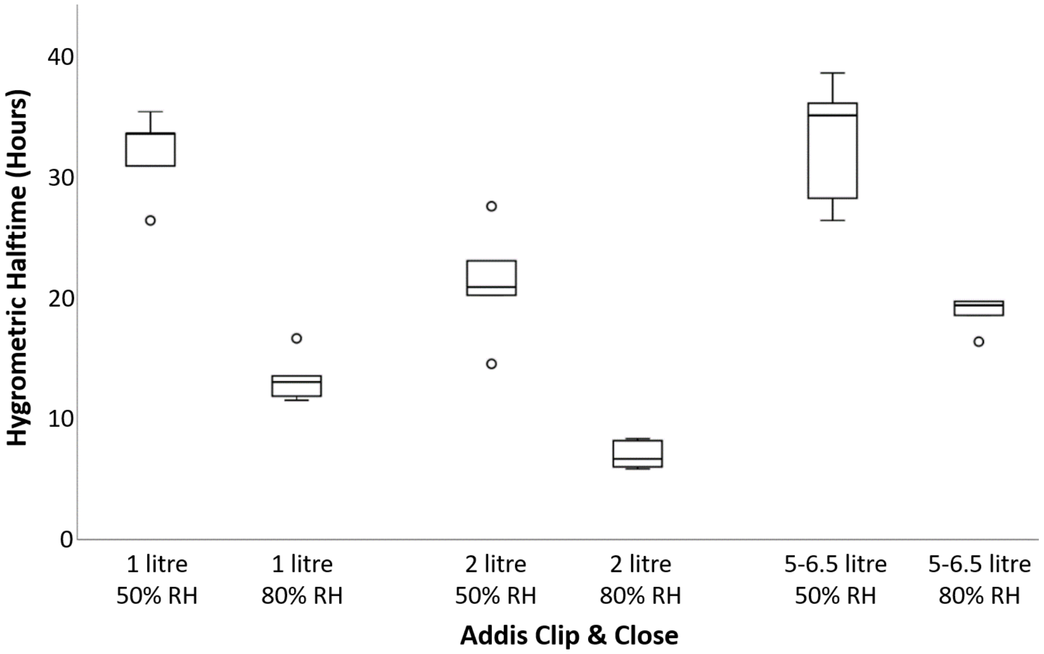

Figure 16: Boxplot of values of $t_{1/2}$ to 50% RH internally for all Addis Clip & Close (ACC) (1, 2 and 5-6.5l) boxes in 50% RH and 80% RH external environments measured as the time taken (to the nearest hour) for the internal environment to reach 35% RH. In all boxplots presented here, the box represents the interquartile range, the horizontal line within the box denotes the median and the upper and lower whiskers show the maximum and minimum values. A circle represents an outlying value (lying between 1.5 and 3 times the interquartile range from the upper or lower quartile) and an asterisk represents an extreme value (more than three times the interquartile range from the upper or lower quartile). All values are considered in discussion.

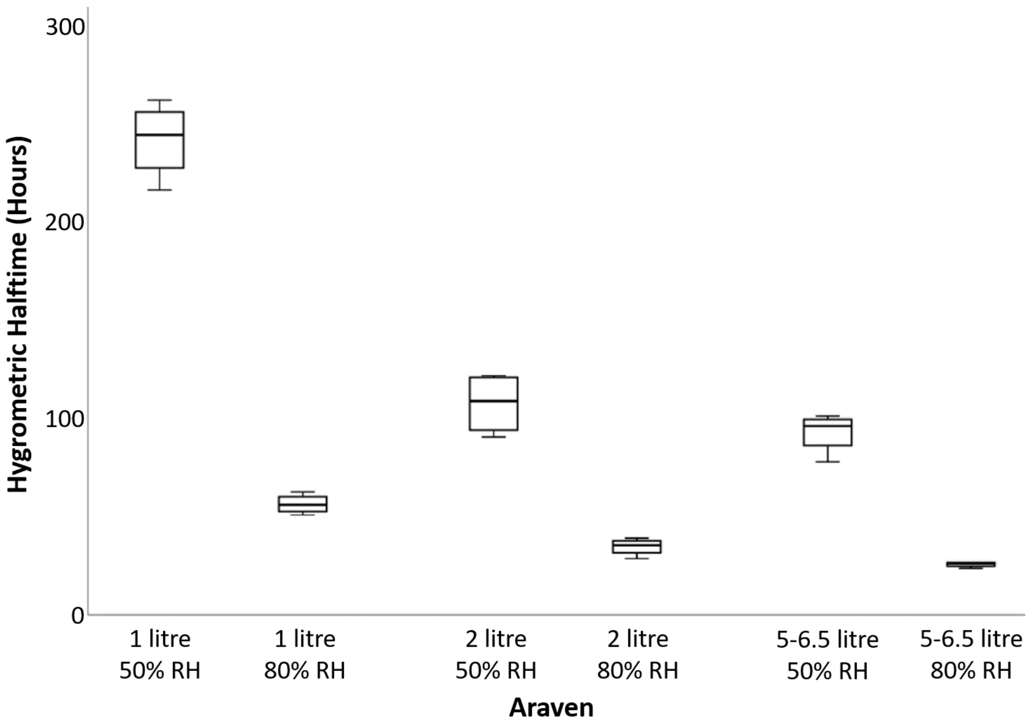

Figure 17: Boxplot of values of $t_{1/2}$ to 50% RH internally for all Araven (AR) (1, 2 and 5-6.5l) boxes in 50% RH and 80% RH external environments measured as the time taken (to the nearest hour) for the internal environment to reach 35% RH.

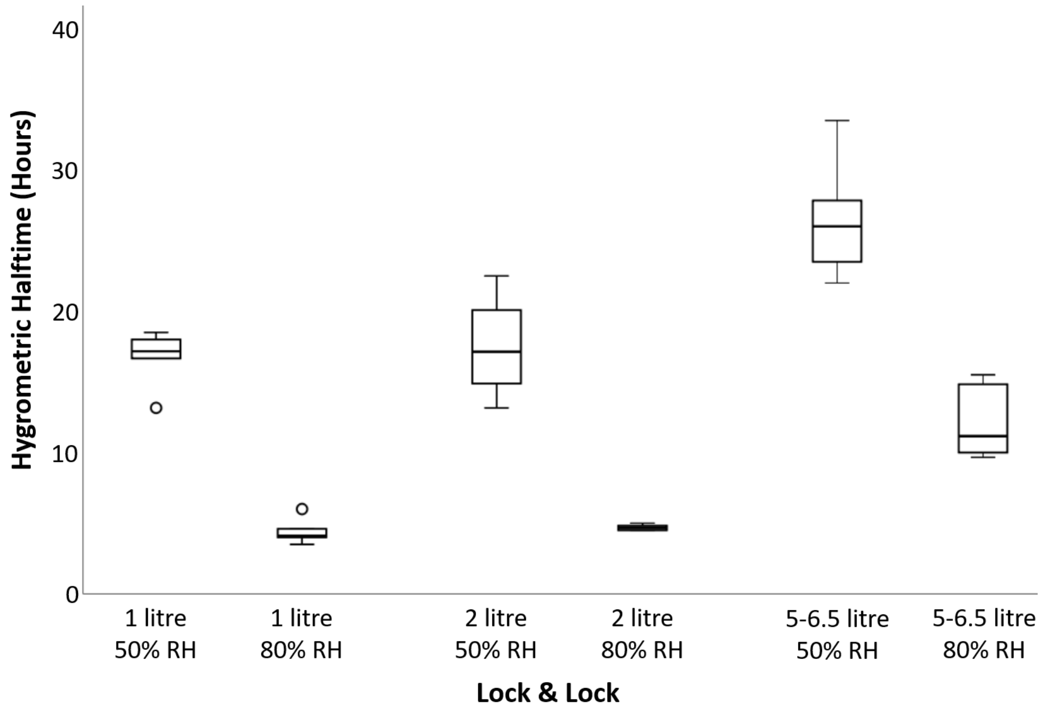

Figure 18: Boxplot of values of $t_{1/2}$ to 50% RH internally for all Lock & Lock (LL) (1, 2 and 5-6.5l) boxes in 50% RH and 80% RH external environments measured as the time taken (to the nearest hour) for the internal environment to reach 35% RH.

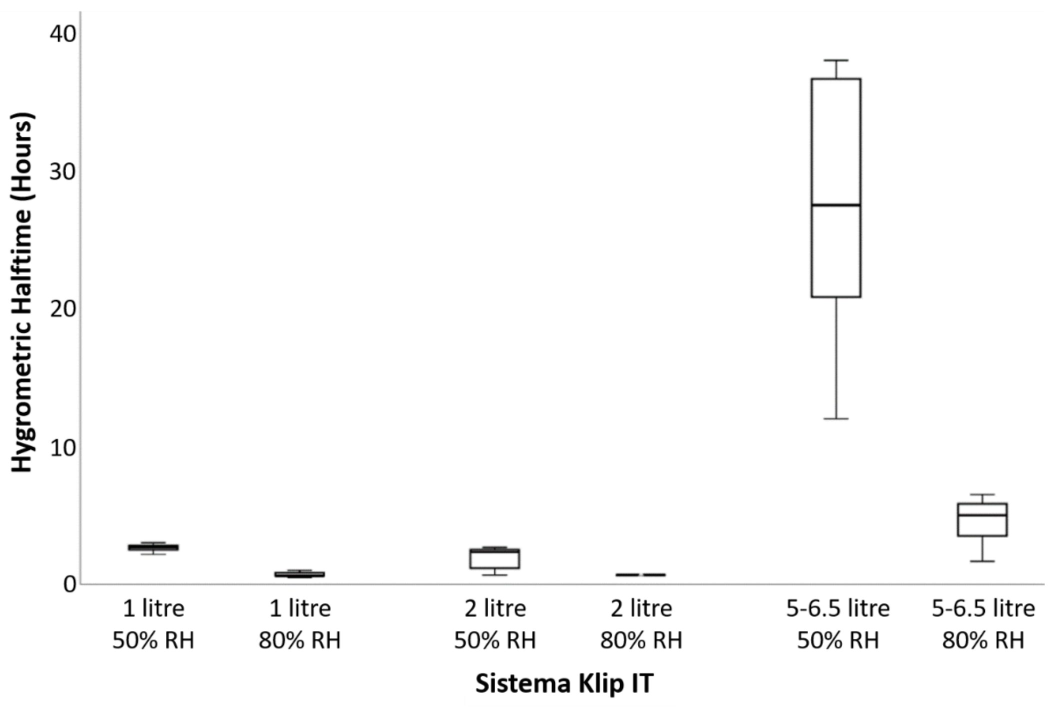

Figure 19: Boxplot of values of $t_{1/2}$ to 50% RH internally for all Sistema Klip IT (SKI) (1, 2 and 5-6.5l) boxes in 50% RH and 80% RH external environments measured as the time taken (to the nearest hour) for the internal environment to reach 35% RH.

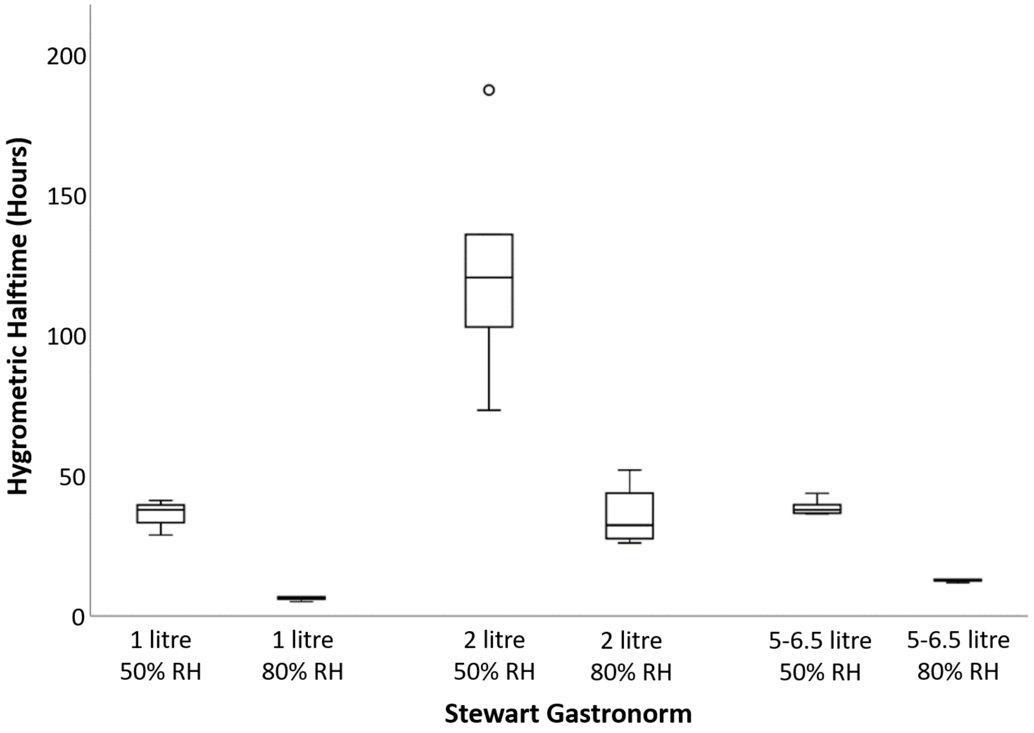

Figure 20: Boxplot of values of $t_{1/2}$ to 50% RH internally for all Stewart Gastronorm (SG) (1, 2 and 5-6.5l) boxes in 50% RH and 80% RH external environments measured as the time taken (to the nearest hour) for the internal environment to reach 35% RH.

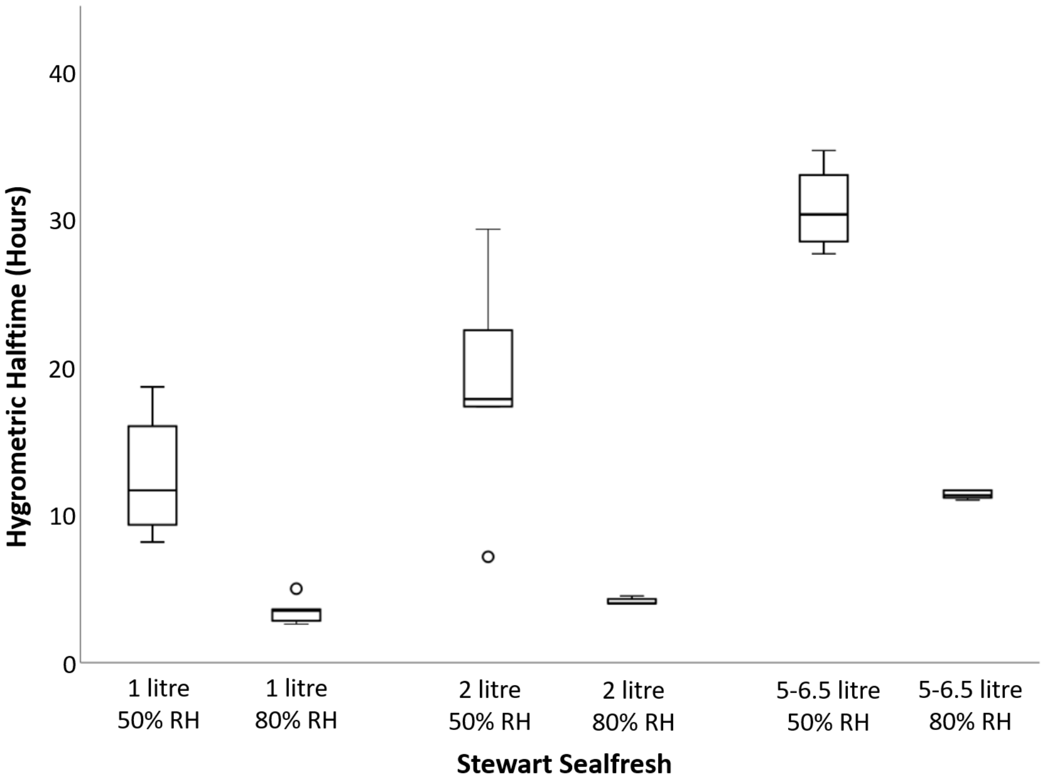

Figure 21: Boxplot of values of $t_{1/2}$ to 50% RH internally for all Stewart Sealfresh (SS) (1, 2 and 5-6.5l) boxes in 50% RH and 80% RH external environments measured as the time taken (to the nearest hour) for the internal environment to reach 35% RH.

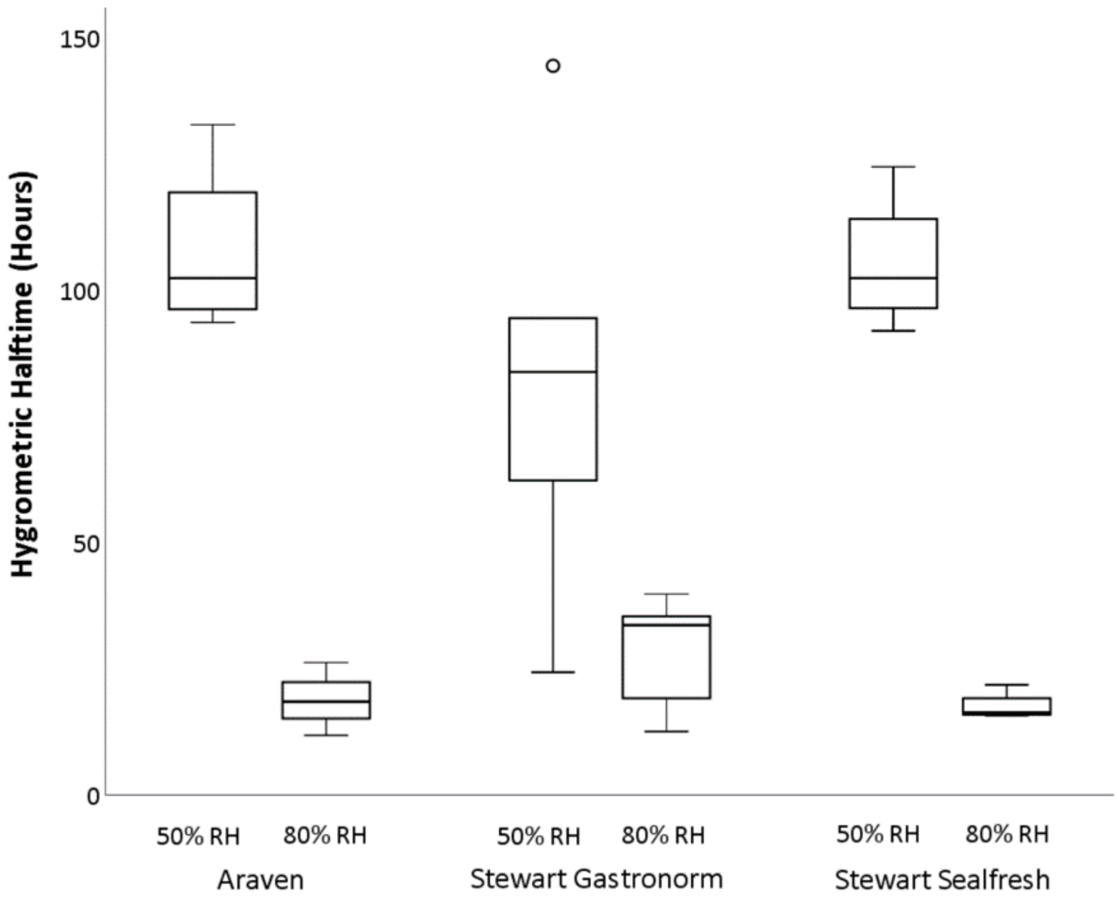

Figure 22: Boxplot of values of $t_{1/2}$ to 50% RH internally for all Araven (AR), Stewart Gastronorm (SG) and Stewart Sealfresh (SS) 13-14 litre boxes in 50% RH and 80% RH external environments measured as the time taken (to the nearest hour) for the internal environment to reach 35% RH.

External environment

While the equilibration time is longer overall for the boxes in an ambient environment of 80% RH than 50% RH, the internal increase from 20-50% RH occurs more rapidly at 80% RH (figures 9-12). This results in a significant decrease in $t_{1/2}$ calculated at the point the internal RH for all boxes reaches 35% which can be seen in boxplots for each box brand and volume (figures 16-22) with average values of $t_{1/2}$ at 35% given for groups of boxes in Table 8.

	Average $t_{1/2}$ at 50% RH to nearest hour							
	1l		**2l**		**5 - 6.5l**		**13-14l**	
Ambient humidity (% RH)	***50***	***80***	***50***	***80***	***50***	***80***	***50***	***80***
ACC	32	13	21	7	33	19	-	-
AR	242	56	107	35	93	26	107	18
LL	17	4	18	5	27	12	-	-
SKI	3	1	2	1	27	5	-	-
SG	36	7	111	36	39	13	66	30
SS	13	4	19	4	31	13	110	18

Table 8: Average $t_{1/2}$ (to nearest hour) for all box brands and volumes at ambient 50% and 80% RH over the range 20-50% RH taken as the point at which internal RH reaches 35%.

Consequently, important corrosion thresholds will be crossed at a much faster rate in an uncontrolled storage environment than one in which the external environment is controlled to a lower RH. This effect is seen to differing extents across all boxes (Table 9).

% Decrease in $t_{1/2}$ at 80% RH				
Brand	**1l**	**2l**	**5-6.5l**	**13-14l**
ACC	59	67	42	-
AR	77	68	72	83
LL	76	72	56	-
SKI	67	50	81	-
SG	81	68	67	55
SS	70	79	58	84
Average	**73**	**70**	**63**	**74**

Table 9. Decrease in $t_{1/2}$ *when external environment increases from 50% RH to 80% RH.*

Consistency of performance

Examining figures 16-22, it is clear that the consistency of performance (as $t_{1/2}$) varies with box type, ambient environment, and volume of box, meaning that none of the investigated brands provide a predictable RH exchange rate. Figures 23-28 indicate some brands have comparable airtightness as boxplots are overlapping and the faster exchange rate at 80% RH means that the variation in box performance within a group diminishes between 20-50% RH. Summing up the total $t_{1/2}$ by type in 1l, 2l and 5-6.5l, Lock & Lock demonstrated the smallest variation in performance while Araven proved to be the least predictable box type in 50% RH and Stewart Gastronorm proved to be least predictable in 80% RH (Figure 29).

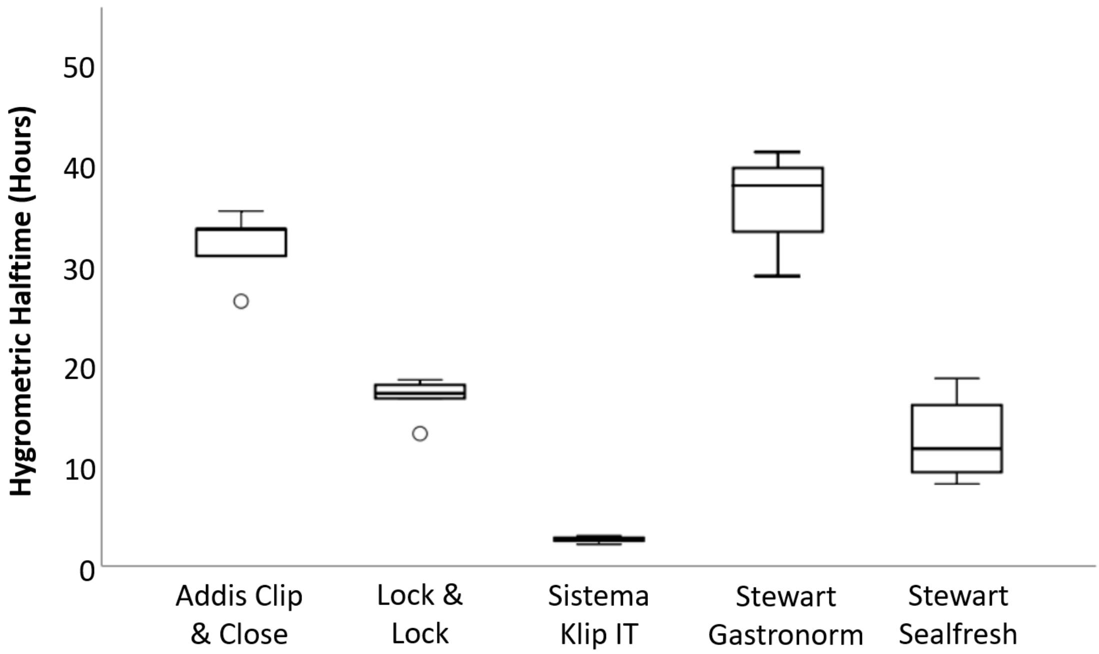

Figure 23: Boxplot of hygrometric halftime values for 1l Addis Clip & Close, Lock & Lock, Sistema Klip IT, Stewart Gastronorm and Stewart Sealfresh boxes in a 50% RH external environment for comparison of performance. Araven 1l boxes are excluded due to their significantly greater halftime.

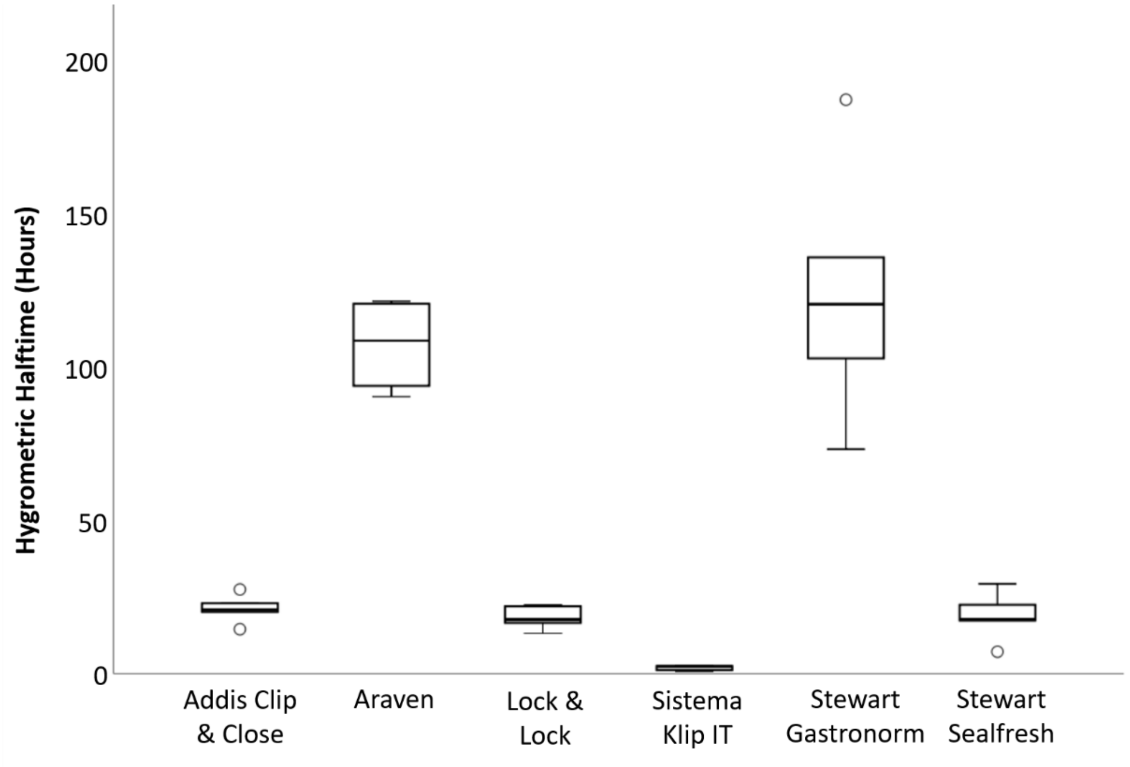

Figure 24: Boxplot of hygrometric halftime values for 2l Addis Clip & Close, Lock & Lock, Sistema Klip IT, Stewart Gastronorm and Stewart Sealfresh boxes in a 50% RH external environment for comparison of performance.

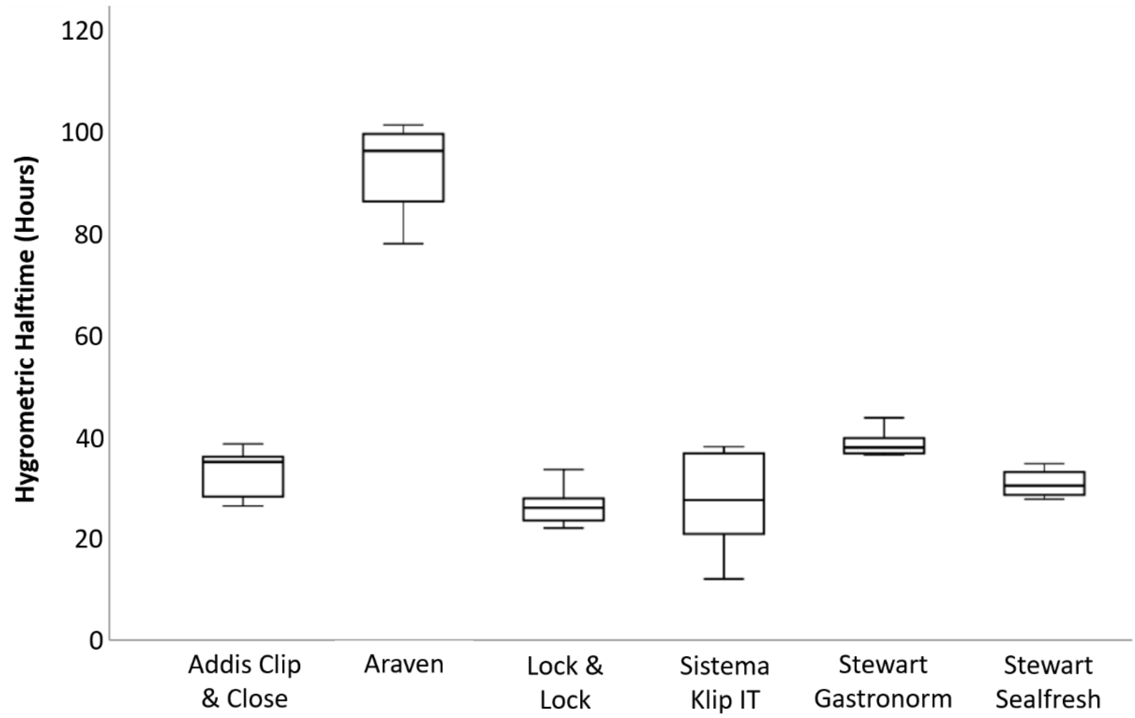

Figure 25: Boxplot of hygrometric halftime values for 5-6.5l Addis Clip & Close, Lock & Lock, Sistema Klip IT, Stewart Gastronorm and Stewart Sealfresh boxes in a 50% RH external environment for comparison of performance.

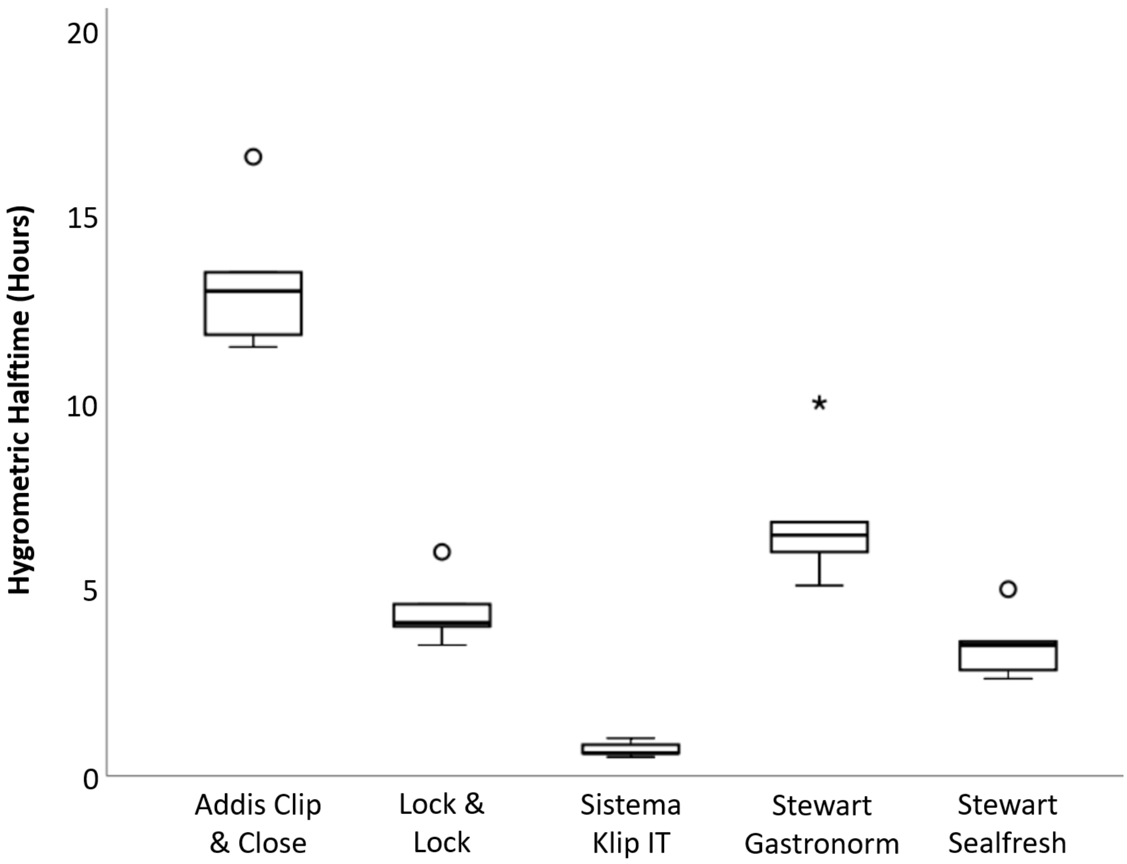

Figure 26: Boxplot of hygrometric halftime values for 1l Addis Clip & Close, Lock & Lock, Sistema Klip IT, Stewart Gastronorm and Stewart Sealfresh boxes in an 80% RH external environment for comparison of performance. Araven 1l boxes are excluded due to their significantly greater halftime.

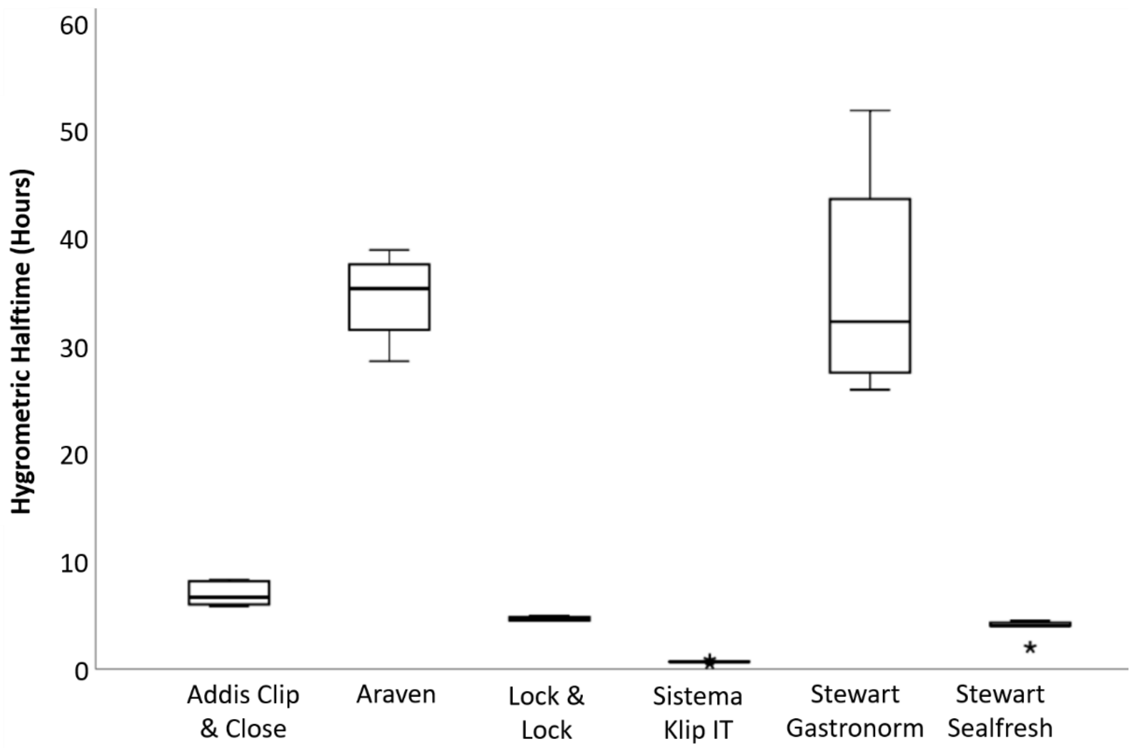

Figure 27: Boxplot of hygrometric halftime values for 2l Addis Clip & Close, Lock & Lock, Sistema Klip IT, Stewart Gastronorm and Stewart Sealfresh boxes in an 80% RH external environment for comparison of performance.

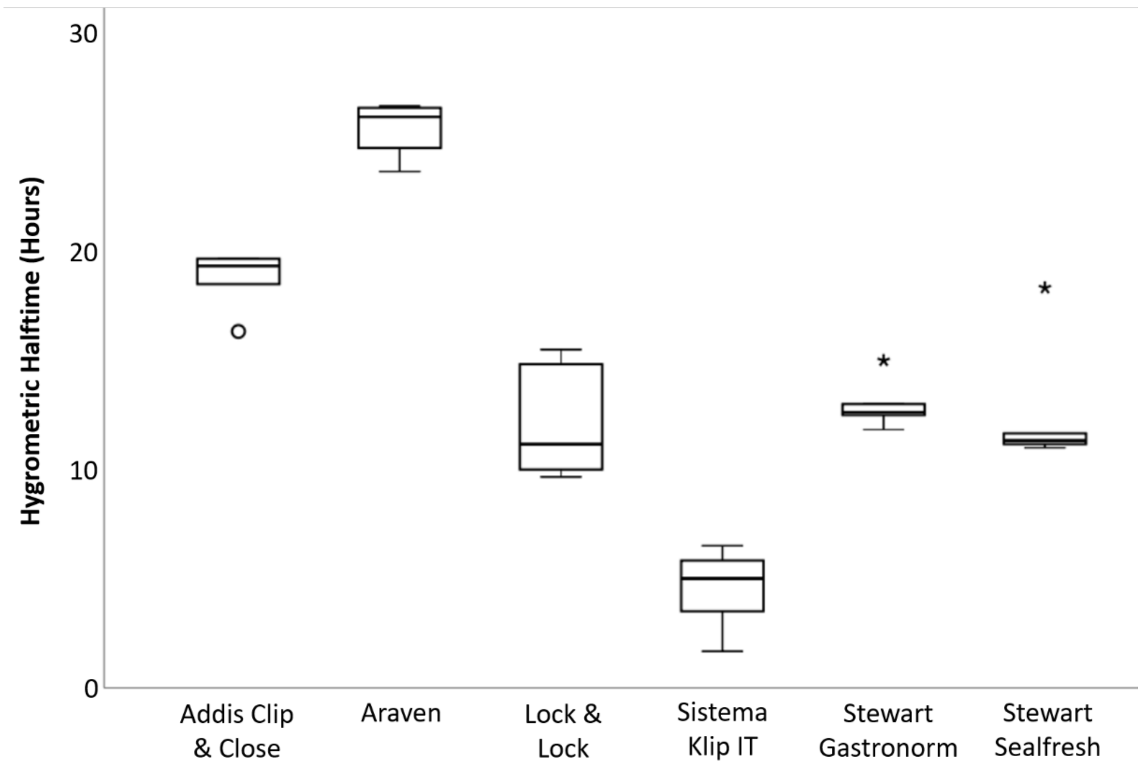

Figure 28: Boxplot of hygrometric halftime values for 5-6.5l Addis Clip & Close, Lock & Lock, Sistema Klip IT, Stewart Gastronorm and Stewart Sealfresh boxes in an 80% RH external environment for comparison of performance.

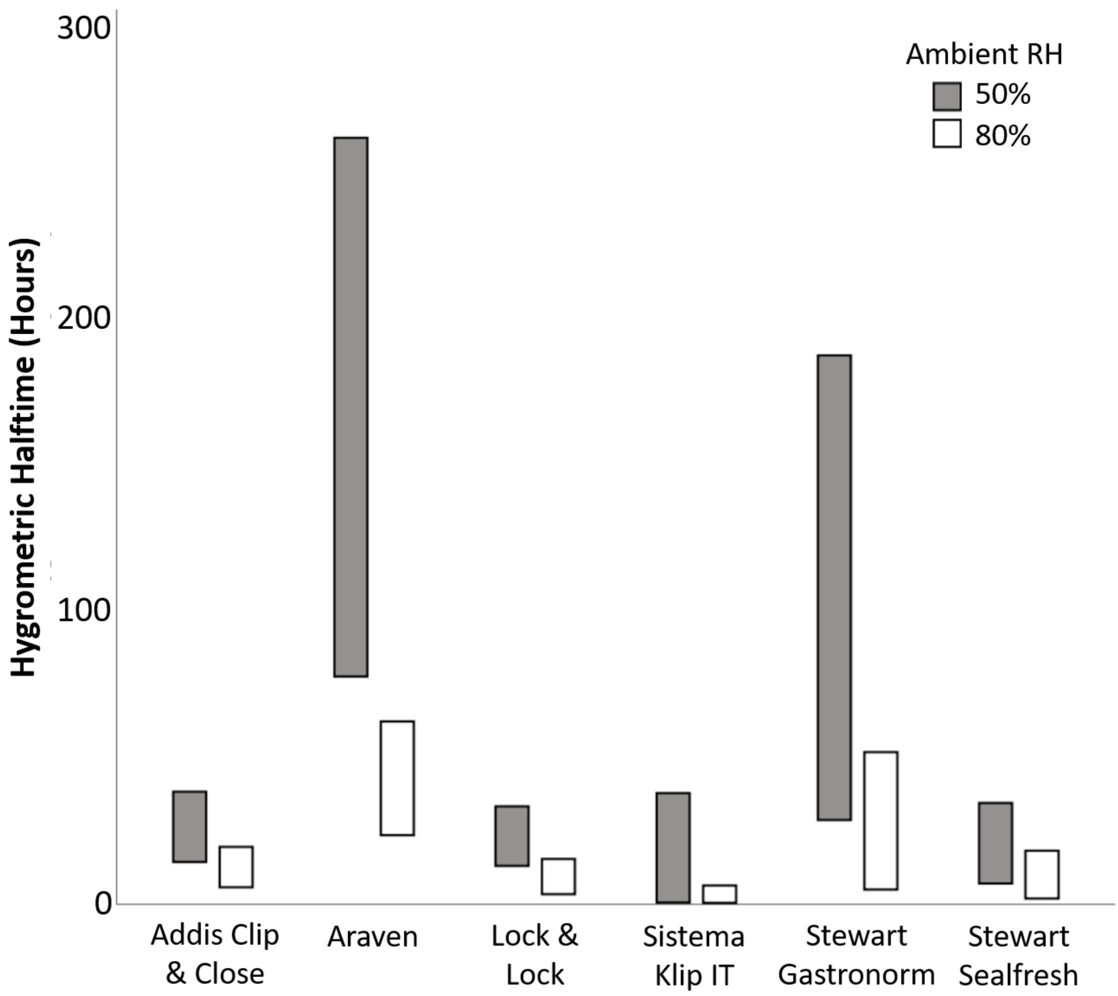

Figure 29. Range of $t_{1/2}$ of all 1, 2 and 5-6.5 litre box volumes within a type to demonstrate the overall variation (in hours) of performance between all sizes of the investigated brands in both 50% RH and 80% RH. 13l boxes are excluded from this comparison as the size is not available across all the box types.

Variation in performance of boxes can have significant implications for management of microclimates, as larger variation results in unpredictability of microclimate performance unless all boxes in use are tested for their individual airtightness. This will be particularly problematic where a range of box sizes are used in a store. Understanding that boxes have a range of performances calls for increased monitoring of microclimates.

Size of box

Table 7 and figures 9-12 and 16-22, demonstrate that larger boxes produce a slower RH exchange rate due to the increased volume of air to be exchanged. The increased surface areas of larger boxes did not have a negative impact on the exchange rate, confirming that permeation is not the main route for RH exchange. The relationship between volume and exchange rate in 1-2l boxes is less clear as the volumetric difference is not large enough to display a trend. Slight differences in volume of brands within each group may affect the relative ranking of boxes to each other, but generally the difference between brands becomes smaller with larger size boxes (figures 23-28). The fact that different volumes of box type produce different RH exchange rates can be used when planning maintenance regimes, where smaller boxes will require more frequent monitoring and regeneration of desiccant. This finding suggests that for microclimate management purposes, boxes of larger volume are a better choice and have the added benefit of fewer boxes to manage.

Despite this generic rule, inconsistencies within and between brands across the range of box volumes indicate that design variables must influence final performance of boxes.

Design variables influencing performance

Brand performance

The relationship between box types varies according to ambient environment and box size as a result of performance inconsistencies within a brand and slight differences in volumetric relationships (Table 1, figures 16-22). It is possible to produce a ranking of average airtightness of box types for each volume and external RH but this ignores the issues of consistency across boxes of each type and the slim margins by which one box type out performs another in many cases, considering the data logger error of ±1% RH. General trends across the data show that Araven, Stewart Gastronorm and Addis Clip & Close exhibit the greatest airtightness across the box sizes and in both external environments.

Box material

For box construction the properties of plastics used for forming the box need to be considered, along with any differing materials associated with the lid closure. All boxes were made of polypropylene (PP), apart from Araven which had a PP box body and a polyethylene (PE) lid. Both PP and PE are highly impermeable to moisture due to their high degree of crystallinity (Begley *et al.* 2008: 1409; Maier, Calafut 1998: 4; Barrie 1968: 284; Shashoua 2008: 247). All brands made entirely of PP are expected to have a similar buffering capacity through the box body and lid, despite small compositional differences. The PE lid may offer a small advantage due to its higher density.

Different composition of fillers, reinforcement material and additives can alter PP and PE properties and its affinity for moisture permeation (Barrer 1968: 200; Becker et al 1996: 177). They may increase water uptake and change permeability trends if not fully incorporated in the material structure, exposing polar groups accessible for water molecules to diffuse through the material (Tripathi 2013: 60; Barrer 1968: 200). Chemical reactions of the filler or impurities can have a negative impact on the polymer, as can the nature of the filler. Large surface areas of fillers and additives, plus high pH, polarity and content of reactive iron oxides, also increase the likelihood of polymer degradation and greater water uptake (Tripathi 2002: 60; Maier, Calafut 1998: 49). Additives may also be exhausted or migrate from the plastic over time, creating pathways for permeation to occur (Shashoua 2008: 57, 159). Some investigation of the impact of aging on exchange rate has been carried out (Thickett, Odlyha 2010) but an expanded study using the method reported in this paper to measure changes in box performance as a function of aging is needed and will be undertaken.

Seal mechanism

Araven, Stewart Gastronorm and Stewart Sealfresh boxes performed better than, or as well as, boxes with locking mechanisms. This casts doubt on the recommendation in existing guidelines to use boxes with locking mechanisms (Senge 2011; Rimmer et al. 2013b). The comparable performance of snap seal boxes may be a combined result of similar box design variables as locking boxes, including a raised seal in their seal mechanism. The raised seal will improve the RH exchange rate by closing any gaps where the body and the lid meet. The worst performing box, Sistema Klip IT, does not have this feature and partly explains the rapid RH exchange.

On the other hand, Araven, Stewart Gastronorm and Stewart Sealfresh models all demonstrate a larger range of performance between same sized boxes than brands with locking mechanism (Figure 29), indicating that gaskets and locking lid may produce a more predictable performance than boxes without these features.

Clip & Close and Lock & Lock have hollow, rectangular silicone elastomers that fit snugly into a recess in the lid and are easily deformed by pressure exerted by the lock. Their large seal/lock ratio provides an even pressure around the seal (Table 1, Figure 6). This facilitates a close seal and minimises airflow. The Sistema Klip IT elastomer is round and does not fit tightly in the rectangular recess in the lid. It is also solid and requires more pressure from the locks to deform, but these are only two in number on the 1 and 2 litre versions and lock loosely onto the top of the lid. The combination of these features has a detrimental effect on the airtightness of Sistema Klip IT boxes. It is noticeable that Sistema Klip IT performance improves slightly in the 5 litre version which has four clips (figures 9-11).

Volume/seal ratio

The ratio between volume and seal length must be considered consistent between the investigated brands and is therefore not thought to be a determining factor of brand performance in this study (1l: 5-6.3% of total volume, 2l: 3.1-4% of total volume, 5-6.5l: 1.5-1.8% of total volume, 13-14l: 0.8-0.9% of total volume).

With the seal expected to be the main route for diffusion between external and internal box environments, the decreasing volume to seal ratio in larger boxes is expected to play a role in their improved ability to retain a microenvironment.

Close examination of box design is essential when developing management routines or purchasing new boxes to ensure that the box design provides an airtight seal. Identifying whether there are gaps between the lid and the box, how a gasket fits within the lid, determining lock length to seal ratio and estimating the amount of pressure exerted by the locks, should be routine practice. Choosing a box shape may be influenced by the nature of the material to be stored within it but volume to seal length ratio is an important consideration, with a smaller seal length preferable for minimising RH exchange.

Management practices

While box properties will be intrinsic to the manufacturer's choice of materials and their box design, the performance of the box also relates to management procedures in their application for desiccated storage. Using data on box performance to develop management guidance is the goal of ongoing work in Cardiff. Stacking boxes is expected to have an impact on seal performance. Two high stacking of Stewart boxes, with the upper box containing 10kg of soil, was reported to have no influence on air exchange of the old-style design of Stewart boxes loosened the lid on the new design (Thickett, Odlyha 2010). Stacking is normal storage procedure for most institutions and seal performance of boxes can reasonably be expected to differ according to design, illustrating the need for significant further research in this area to produce quantitative data for management guidance. This research took place in a controlled climate at static 20°C, changes in temperature (fluctuations or extreme values) may affect RH exchange rates of boxes and further work will investigate this.

Silica gel quantity

Varying the amount of silica gel (Figure 13) impacts the following characteristics of the microclimate:

- The lowest RH that can be achieved;
- RH exchange rate within the box;
- The consistency of performance between boxes of the same brand.

The lowest RH that can be achieved within a microclimate is related to the adsorption capacity of the silica gel which increases with its quantity as the number of adsorption sites, where water molecules can form a monolayer, increases. In the experimental design here, the rate of desiccation is initially very rapid and falls below 10% RH within the first day of setting up the microclimate within all boxes (Figure 13). Adsorption stops at the point where the gel reaches equilibrium with the vapour pressure of the surrounding air. This occurs at a rate that slows as the multi-layer adsorption of water molecules occurs (Christy 2010; Li et al. 2007:874).

The time taken to reach the lowest desiccation point and the lowest RH achieved by the silica gel vary with quantity of silica gel, with more silica gel producing a lower RH (Table 10, Figure 30). The doubling system employed in the experiment, from 44g to a maximum of 352g of gel, highlights that lower desiccation levels are obtained by using more gel. The decrease in RH when increasing gel from 44g to 88g might be identified as moving from inadequate to adequate amounts of gel, whereas the reduction in minimum RH when increasing gel from 176g to 352g is minor. While this may not be considered good cost benefit in terms of the lowest RH achieved, it is offering enormous cost benefit elsewhere by maintaining low RH over a long time period.

Box	**Silica gel (g)**	**Days to reach min RH**	**Min RH**	**End RH (267 days)**
1-10	44	7	7	28
11-20	88	7	2	19
21-30	176	8	1	8
31-40	352	8	0	3

Table 10. Variation in time taken to reach minimum RH, the minimum RH value and end RH based on the average of all boxes investigated

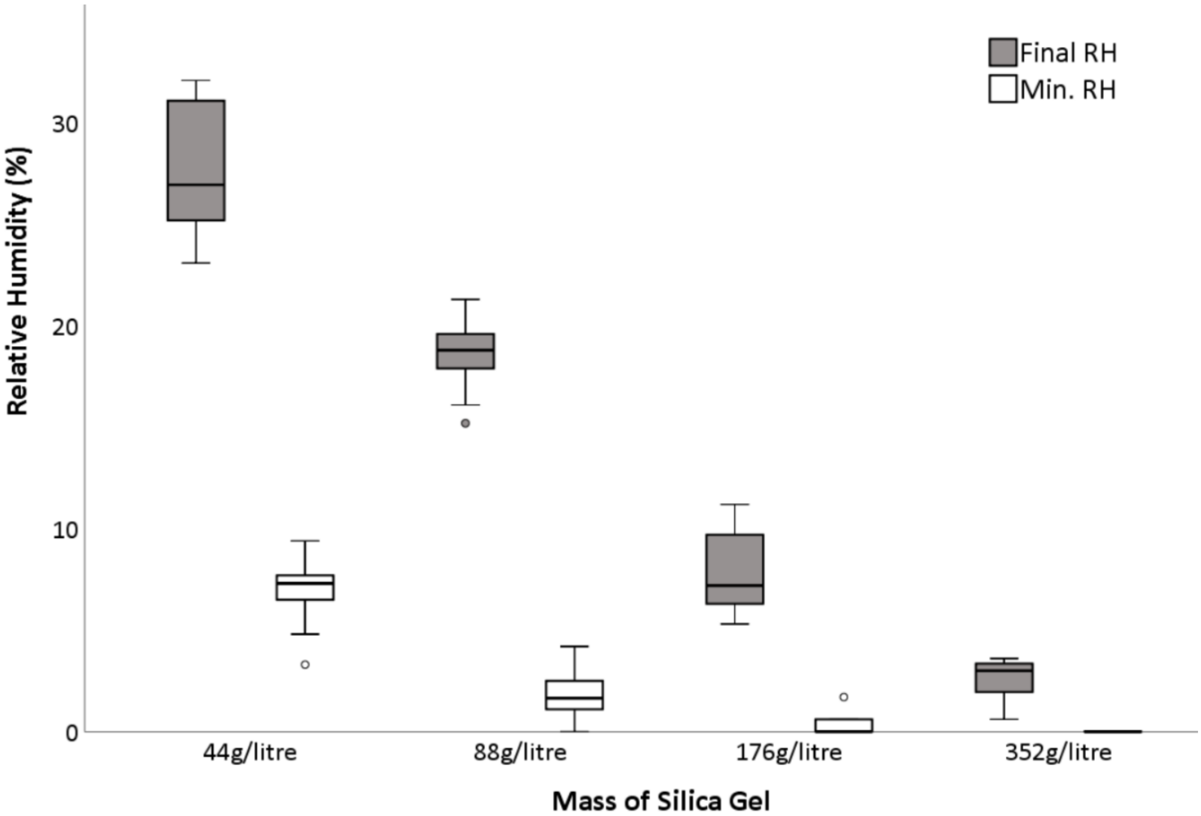

Figure 30. Boxplots outlining the lowest RH achieved and the RH at the end of the test (267 days), illustrating the consistency of performance between 10 boxes containing 44g, 88g, 176g and 352g of silica gel (40 boxes in total).

The range of RH data that is produced across different boxes is likely to be the combined product of differences between individual box humidity exchange rates, small discrepancies in the mass of silica gel and the error value for each data logger. All boxes were within the same climatic chamber so this should not lead to differences across the values measured. However, there is no overlap between the silica gel mass groups in terms of final RH at the end of the test with the possible exception of two boxes out of the 40 (44g and 88g) which may overlap if the 1.5% RH error is applied.

After reaching the minimum RH achievable within the box, air ingress gradually raises the box RH according to the amount of silica gel, with larger quantities of gel buffering against rising RH more effectively than smaller quantities (Table 10, Figure 13). The increase in RH in monthly intervals from the desiccation point demonstrates a good linear fit for all quantities of silica gel (R^2= >0.99) and a forecast was therefore fitted to identify when RH passes the crucial 15% RH corrosion threshold for archaeological iron and continues through the corrosion risk escalation (Figure 31).

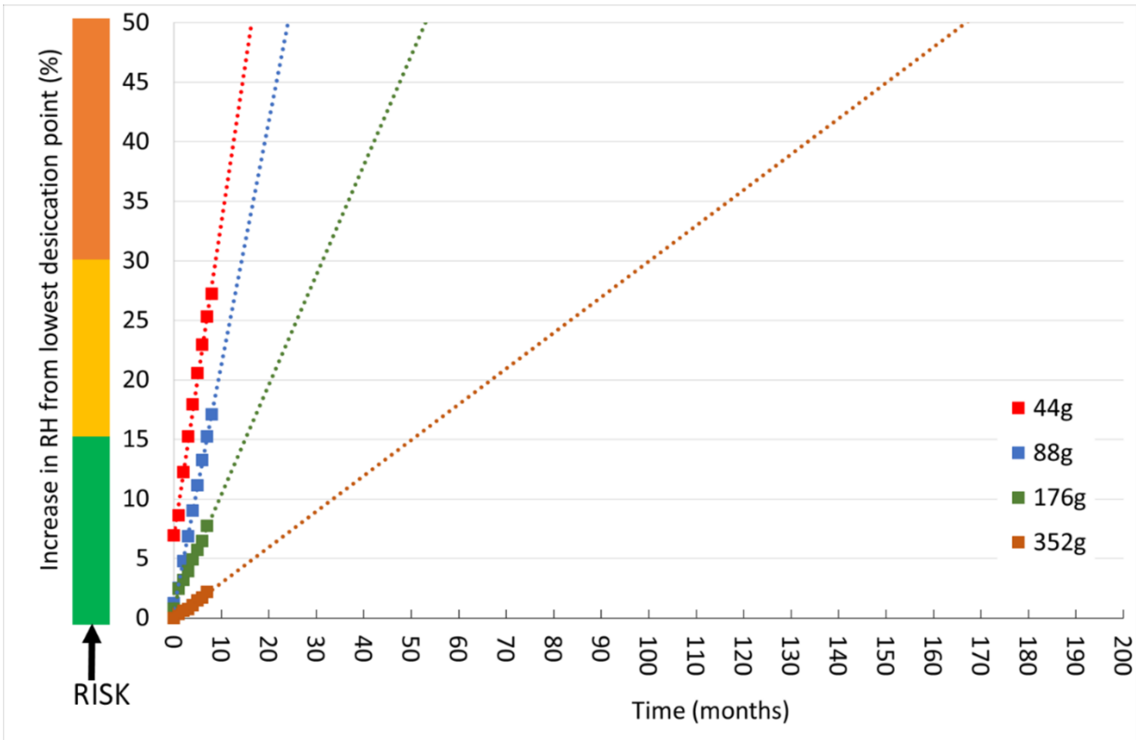

Figure 31: RH increase (squares) and forecast (dotted line) of average RH increase within boxes containing 44g, 88g, 176g, and 352g silica gel from their lowest desiccation point in a 50% RH environment. The first value represent average lowest RH achieved as indicated in Table 10.

Although the rate of RH increase will deviate from the linear as the gradient between internal box and ambient RH decreases (figures 9-12), planning for RH control using a linear forecast allows a worst-case scenario to be accounted for. A linear forecast is likely to be accurate for an ambient store environment in which RH is not controlled to 50% RH or below and the gradient between internal and external RH remains large as the RH threshold for high risk to iron artefacts is approached (Figure 2). Using the linear forecast also accommodates differences in humidity exchange rates between boxes and may allow for any increase in humidity exchange rate due to degradation of the box material over time.

The consistency of box performance is influenced by the quantity of silica gel used. In Figure 13 the wide range for the lowest RH achieved by 10 boxes using 44g of silica gel and the even wider range of their RH end value at 267 days, demonstrates boxes are performing inconsistently. Yet, for the 352g of silica gel within the same box design these ranges are exceptionally small, demonstrating that increasing the quantity of silica gel compensates for differences in airtightness between boxes, offering more consistent and predictable performance (Figure 30).

This investigation used silica gel contained in pierced polyethylene bags as do 41% of the survey respondents. The rate at which silica gel desiccates the environment inside a box may vary with the pre-sealed sachets used by 46% of survey respondents or enclosing it loose within the box. This is under investigation, as is the effect of different size and number of holes in the polyethylene bags.

Storing damp objects

The results (figures 14,15) identified five determinable steps that occur when enclosing wet objects within a microclimate containing silica gel as a buffer:

- RH increases rapidly;
- High RH is maintained;
- Gradual desiccation occurs;
- Desiccation point is achieved;
- RH increases.

Figures 14 and 15 shows that immediately after enclosing damp objects within a box, there is a rapid increase in RH driven by the moisture released by the objects which causes RH to reach between 75-85% RH in these boxes depending on the total amount of water in objects, the amount of silica gel and the opening of the box (Table 11). There is a delay in the adsorption of moisture, and the box environment appears to initially equilibrate to the high humidity environment caused by a rapid moisture release in the damp objects, maintaining a high RH in the box (Figure 14).

Sample type	***None***		***Damp iron objects***			
Amount of water (g)	***0***	***0***	***6.6***	***6.3***	***4.2***	***6.1***
Amount of silica gel (g)	***88***	***176***	***88***	***176***	***176***	***176***
Box opened	No	No	No	No	10x	10x
Initial high RH (%)	-	-	85	77	75	76
Lowest RH (%)	2	1	28	14	12	13
Days to reach 15% RH	0.15	0.10	-	43	30	44
Days to reach lowest RH	7	8	54	54	47	55

Table 11: Highest and lowest RH and time taken to achieve lowest RH in boxes containing damp archaeological objects with 88g and 176g silica gel and the average lowest humidity achieved within boxes containing silica gel and no damp artefacts.

RH starts to decrease after 7-8 days in boxes 1 and 2 and at the first opening (6 days) with boxes 3 and 4. During this time at high humidity, corrosion can be expected to have been instigated and damage may have occurred on archaeological metals (Watkinson *et al.* 2019; Watkinson, Lewis 2005). Regular opening of boxes 3 and 4 is likely to have caused the shorter plateau at highest RH and the faster fall in RH, although the lower total mass of water in the boxes is also seen to be a major contributor to these effects when the differences between boxes 3 and 4 are considered. Following the high humidity plateau, the time taken for the RH to drop to 15% is between 30 and 44 days depending on the amount of water in the artefacts and the mass of silica gel in the box. In the case of 88g silica gel and 6.6g water, the RH never approaches 15%. During the time at high humidity, corrosion can be expected to have been instigated and damage may have occurred on archaeological metals (Watkinson *et al.* 2019; Watkinson, Lewis 2005).

In addition to the high humidity period, the inclusion of damp artefacts also reduces the lowest RH that is achieved. In the case of 88g silica gel, where damp artefacts are included the RH levels off at around 28% RH as compared with 2% RH with no water in artefacts. With 176g silica gel, the inclusion of 4g or 6g of water in the box limits the lowest RH to 12-14% as compared to 1% with no damp objects. Ten artefacts were included in each box but many more could be accommodated in a 1 litre box. The small size of the artefacts also limited the amount of water in the boxes in this test, particularly with SWA iron nails in which had very thin, closely adhering corrosion products capable of holding little water. This should be seen as a best case scenario for drying groups of archaeological artefacts with silica gel in a box. It is notable that the self-indicating silica gel remained orange throughout, its colour was not reflective of the internal RH of the box.

Archaeological metal artefacts should be dried before being contained in a storage box with silica gel. This can be achieved by air drying in a relatively low RH ambient environment or drying in an oven at temperatures ≤90°C. Ensure that air can circulate around the artefacts to increase the rate of drying. Further work is investigating the rates of drying by these methods and the risk of any damage to artefacts.

Application to object storage scenarios

The results of this study show that a large range of variables will influence the efficacy of a microclimate. While more research is in progress to expand the evidence-base on the performance of microclimates, it is possible to provide some general guidance based on these initial results.

Setting up microclimates

- <u>Always</u> dry objects before placing them in a microclimate.

- Oven dry below 90°C or air dry until the artefacts reach a constant mass.
- If possible, use box types with known leakage rates or test before use.
- Boxes with locking lids may produce a more consistent performance.
- Generally, the larger the box, the slower the RH exchange and the better the microclimate performance.
- Visual examination of design can be an aid to estimate airtightness. Look for:
    - Gaps between box and lid or any other feature that may compromise the seal;
    - Large lock to seal ratio;
    - Locks that are stiff to close and exist on all 4 sides of the box;
    - Gaskets that are easily deformable.
- Distribute silica gel in thin layers.
- Distribute silica gel across a series of bags.
- Choose a quantity of silica gel that suits your management routines. For an average performing box in a controlled store (50% RH), this study indicates that:
    - 44g/l will on average reach 15% RH threshold after 3 months;
    - 88g/l will on average reach 15% RH threshold after 7 months;
    - 176g/l will on average reach 15% RH threshold after 12 months;
    - 352g/l will on average reach 15% RH after 48 months.
- Choose silica gel according to the desiccation goal of the microclimate. For an average performing box in a controlled store (50% RH), this study indicates that:
    - 44g/l will on average achieve 7% RH;
    - 88g/l will on average achieve 2% RH;
    - 176g/l will on average achieve 1% RH;
    - 352g/l will on average achieve 0% RH.
- In an uncontrolled store (80% RH), to compensate for the increased RH exchange rate of boxes, include 70-80% more silica gel than advised to use at 50% RH in smaller (1-2l) and larger (13-14l) boxes and 60-70% more silica gel in medium boxes (5-6.5l). If unsure, reduce risk by doubling the amount of gel.
- Increase predictability of box performance by increasing the amount of silica gel.
-

In stores containing microclimates

- If possible, monitor the ambient RH in the store.

- Design a maintenance regime with a schedule for reconditioning of silica gel based on box volume, ambient store RH, humidity exchange rate of boxes (if known) and degree of risk to objects deemed acceptable.
- Record how much silica gel is currently kept within boxes and when it was last regenerated.
- Monitor the RH within boxes closely, for example with humidity indicator strips but be aware that their performance may change with ageing (Thickett, Odlyha 2010).
- Do not rely on colour change of indicating silica gel to decide when it should be regenerated or as an indicator of internal box RH.

Conclusion

Surveying the sector revealed that a wide range of individuals have responsibility for ensuring the safekeeping of archaeological metals in store and that their methods for doing so vary just as widely. Practitioners and volunteers alike are turning to guidance that is largely out of date, is not usually based on quantified evidence and does not assist them in making cost-benefit decisions about hardware and maintenance regimes for their particular storage environments.

This study was designed with the aim of producing the quantified data that would reveal the most crucial variables in establishing and managing microclimates and how those variables can be manipulated to achieve maximum longevity of desiccation. In doing so, it has begun to address the anecdotal practices within conservation that hitherto have dictated procedure for establishing desiccated microclimates within plastic boxes. Further, it has demonstrated clearly that quantitative data collected in real time experimental studies is necessary for developing informed management practices and estimating risk. This sets important baselines for further study into the practical use of microclimates to achieve desiccated storage.

The large variation in performance of boxes in a relatively small sample set prompts larger sample sets to be investigated, including a broader range of sizes and brands. The compromising effect of ambient environment is also being recorded more extensively and studies are underway that reflect practical use of microclimates in collection storages, such as measuring the effects of stacking and ageing of boxes. The limitations in predicting microclimate behaviour also highlights the importance of routine monitoring and the efficacy of equipment designed to do this, such as humidity indicator cards, is being investigated thoroughly.

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