

## Microbial damage of tsunami-affected objects in the Great East Japan Earthquake 2011 and problems with fungicidal fumigation

Rika Kigawa\* and Yoshinori Sato

### Abstract

Vast areas of land were affected by the major tsunami that followed the Great East Japan Earthquake in March 2011. Many cultural objects and documents were severely damaged by the tsunami, and many paper-based objects and paintings were left for weeks or in some cases for months before they were salvaged. However, probably because of salts in the seawater together with the low environmental temperatures in March in the Tohoku area, such seawater-soaked paper objects seem to have less fungal damage than that found on objects damaged by freshwater (rain or river water). However, there were cases in which severe fungal infestation was seen on paper-based objects and paintings that had been left wet for months. Examples of such damage are introduced here as an overview. As an early response to prevent microbial damage, drying of the objects or freezing of paper-based documents is strongly recommended. Cleaning the soiled objects can be the next step.

Since some objects were contaminated by wastes or were very moldy, treatment by fumigation with a fumigant such as ethylene oxide (EO) or propylene oxide (PO) was considered. However it was thought that such fumigants might react with chloride or water in seawater, resulting in the generation of highly toxic chlorohydrins or glycols which can attract water. We therefore investigated the risk of the generation of such chemical residues in seawater-soaked paper objects and books, including those actually affected by the tsunami. We found that residual chlorohydrins and glycols were at low levels in most of the dried paper samples, but higher levels of chlorohydrins and glycols were detected in the samples that had been fumigated in a wet condition. It is therefore

recommended that damaged objects be fumigated in a well-dried condition if such sterilization is necessary.

### Preface

In March 2011, many victims lost their lives to the Great East Japan Earthquake and the accompanying tsunami. We offer our sincere condolences for all those who have been affected by these disasters. Japan is still dealing with the aftermath of the earthquake and tsunami, and in this report we describe the impact these disasters have had on cultural properties, especially biological damage, in our roles as staff who are responsible for rescuing cultural objects.

The knowledge we have gained through our post-disaster activities is detailed below according to the categories of the affected objects. We hope this knowledge will be helpful for the salvage of cultural properties should other disasters occur.

### Microbial impact on tsunami-soaked objects

The impact of the March 2011 tsunami on cultural objects includes the effects of being soaked in water for long periods, as also occurs due to river overflows, flooding, rain water leakage, etc. Microbial damage by mold and bacteria is a significant concern, and in addition, the water that a tsunami brings is seawater. The salts in the seawater must be considered, and in the case of a tsunami, the salty seawater brings along various soils and other wastes, meaning that the water may well be contaminated with dirt and in some cases sewage. Under these circumstances, we need to consider what types of early response are appropriate

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\* Corresponding author

Center for Conservation and Restoration Techniques, National Research Institute for Cultural Properties, Tokyo,  
13-43 Ueno Park, Taito-ku, Tokyo, 110-8713 Japan,  
E-mail: rkigawa@tobunken.go.jp, Tel: +81-3-3823-4875, Fax: +81-3-3822-3247

to minimize the biodeterioration of the cultural properties.

Some benefits of seawater should be noted. The salts in seawater suppress the growth of hydrophilic microorganisms (Higashijima et al., 2012), and some actual examples of this suppression are discussed later in this report. There are also detrimental effects of seawater, of course; for example, the salts may remain in the seawater-soaked objects, documents, etc.

When there are salts in soaked objects and the objects are dirty with soil and/or other contaminants, a natural response would be to wash the objects with freshwater. However, if the object tends to not dry quickly (e.g., documents), washing off the salts may cause mold to grow more easily. Great care needs to be taken regarding the proper timing and method of the washing, i.e., for the removal of salts.

### The microbial damage to objects soaked by the tsunami

Some specific examples of the microbial damage to cultural properties by the 2011 tsunami are described here. Examples from a temple named

Ryuzo-in in Kashima City of Ibaraki Prefecture are shown in Figure 1. At the temple, the tsunami water level rose to approx. 1 meter (Fig. 1a). The water traces inside the house wall are seen (Fig. 1b), even after cleaning. After the water receded the salts remained in large quantities on the grounds of the temple yard (Fig. 1c). We suspect that salts also remained in the documents and objects after they were dried.

#### *Books and documents: examples and initial responses*

We went to Ryuzo-in Temple on May 2, 2011, about 7 weeks after the tsunami occurred (March 11). The documents shown in Figure 1d were air-dried on a table there but they were still wet or damp when we arrived. A visual inspection revealed no mold growth. In cases involving freshwater flooding, there would be more significant mold growth.

At the Nara National Research Institute for Cultural Properties (NRICP), Yohsei Kohdzuma's team has done extensive work on freeze-drying documents that were damaged by the tsunami (Fig. 2). We visited the Institute in March 2012 to examine those documents. We saw that on the documents



Fig.1 Examples of the March 2011 tsunami damage at Ryuzo-in Temple in Kashima City of Ibaraki Prefecture, Japan.a: The tsunami rose to approx.1 m.b: The water traces inside the house wall.c: The salts remained on the ground of the yard.d: Air-dried documents on a table, still wet or damp (photographed on May 2, 2011). Courtesy: Ryuzo-in Temple, The Board of Education, Kashima City.

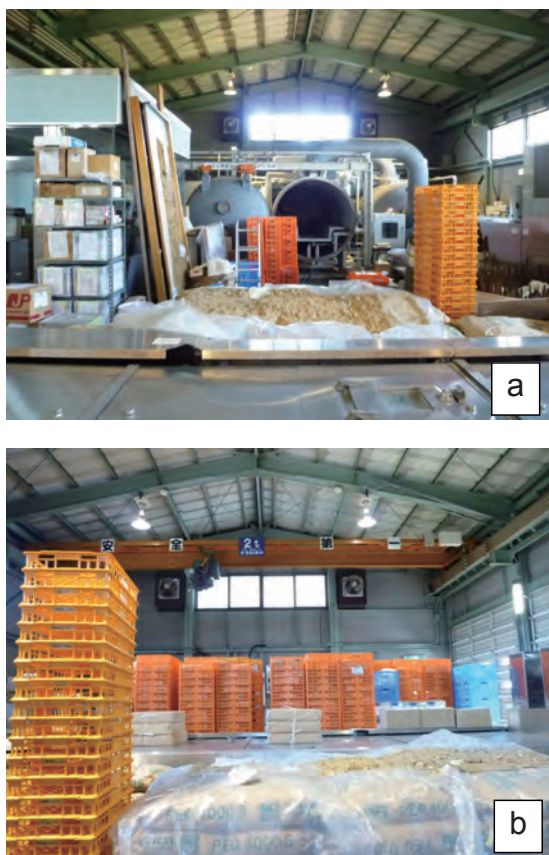


Fig.2 Nara National Research Institute for Cultural Properties.a: Freeze-drying machine.b: Freeze-dried documents (photographed on March 14, 2012).Courtesy: Nara National Research Institute for Cultural Properties.

salvaged in May 2011 in Kesen-numa, Miyagi Prefecture, after the freeze-drying there was not much trace of mold (Fig. 3). The condition of the documents which were rescued at an early stage was quite good. It seems that if documents are dried very quickly after being soaked in seawater, the prognosis can be positive.



Fig.3 The documents which were salvaged in May 2011 in Kesen-numa, Miyagi Prefecture, after-freeze-dried (photographed on March 14, 2012).Courtesy: Nara National Research Institute for Cultural Properties.

However, our examination of the documents that were salvaged at a later stage (i.e., the end of June 2011, when it was hot and humid) and kept in a damp cupboard revealed that the documents suffered very severe mold damage (Fig. 4). Similar damage was seen on documents salvaged in Oarai-machi, Ibaraki Prefecture (Fig. 5); we observed mold that was so dark that the documents looked as if they had been burned.

At another location (Kamaishi City, Iwate Prefecture), administrative documents were affected by the tsunami. With the cooperation of Mutsumi Aoki of the National Institute of Japanese Literature, we investigated the microbes on damaged documents. These documents were salvaged from April to May 2011, a rather early stage, and the volunteers of Mutsumi Aoki's group had put them upright and air-dried them (Fig. 6). Because of the early response, the documents were in fairly good condition.

At the same time, mold growth was seen on some documents that were in comparatively bad condition before the tsunami and had then been soaked for a prolonged time in the tsunami seawater. Black and red spots (Fig. 7a) were seen on most of these documents. There was a very particular, peculiar type of microbial damage on the affected documents (for details, Sato et al., submitted). When we opened the documents, red spots that look like a smear of ink were visible (Fig. 7b). Some of the documents from another location (Rikuzen-takata City, Iwate Prefecture) had been frozen. Microbial damage that was identical to the above-described red spots was seen on documents that were waiting for cleaning treatment (an example is shown in Fig. 8). Even though the locations are different, the paper documents





Fig.4 Documents salvaged on June 23, 2011, in Ishinomaki, Miyagi Prefecture, in the hot and humid season. They had been kept in a damp cupboard (photographed on March 14, 2012). Courtesy: Nara National Research Institute for Cultural Properties.



Fig.5 Document salvaged in Oarai-machi, Ibaraki Prefecture (photographed on September 5, 2011). Courtesy: The Board of Education, Oarai-machi, Ibaraki Prefecture.



Fig.6 Administrative documents salvaged from April to May 2011, air-dried, Kamaishi City, Iwate Prefecture (photographed on August 7, 2012). Courtesy: Kamaishi City, Iwate Prefecture and Mutsumi Aoki of the National Institute of Japanese Literature.

that had been soaked in tsunami seawater for a long time exhibited a very similar, peculiar type of microbial damage.

Figure 9 is pictures taken in August 2012 at the city hall of Rikuzen-takata. The city hall building was to be demolished, and the last salvaging activities of the administrative documents in the building were being conducted in August 2012. Those documents had remained wet in the city hall building for approx. 17 months, and when we examined them, even though there were severe growths of microbes we could see a pattern of microbial damage similar to the pattern described above (Fig. 9). More specifics about the microorganisms will be given in the report by Sato et al. (submitted).

As noted above, in the case of documents soaked

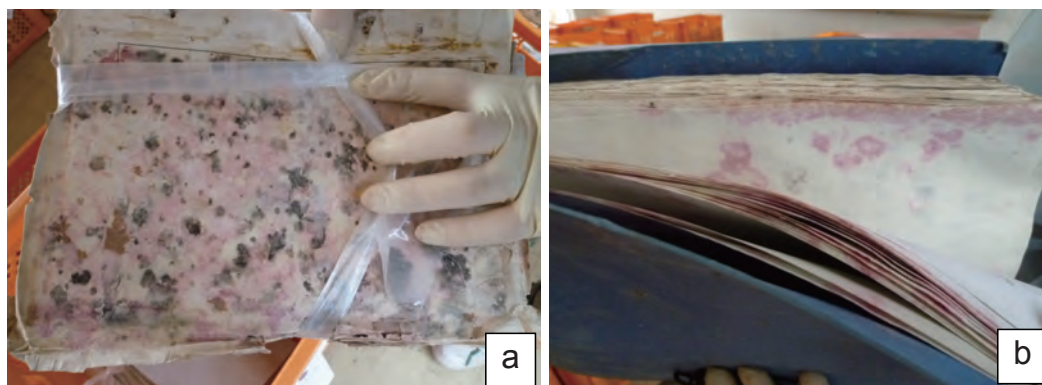


Fig.7 Microbial damage to some documents which had been soaked for a prolonged time.a: Black and red spots on documents.b: Red spots that look like a smear of ink (photographed on August 7, 2012).Courtesy: Kamaishi City, Iwate Prefecture and Mutsumi Aoki of the National Institute of Japanese Literature.

in seawater, it is clear that the mold growth is suppressed at an early stage compared to documents soaked in freshwater. However, if the wet stage is prolonged, there can be extensive microbial damage. Seawater from a tsunami occasionally has traces of sewage or other contaminants, and these can provide nutrients to the microbes.

On May 10, 2011, two months after the disaster, our institute had a meeting to share information (National Research Institute for Cultural Properties, Tokyo, 2011a) and we discussed how early rescue activities should be conducted in order to minimize microbial damage. We proposed a flow chart for initial responses (Fig. 10) (Kigawa and Sato 2011) with reference to the existing literature (e.g., Aoki 2011, Imazu 1998, Mori et al. 1998).

Regarding tsunami-soaked documents, almost-

dry documents and books should be air-dried as quickly as possible. Damp documents and books should be placed upright and opened slightly if necessary to enhance the drying. Because the 2011 tsunami and earthquake damage covered a vast region, in the most of the affected areas there was no infrastructure such as water supply or electricity that would enable us to conduct preservation activities; the priority was to try to access the damaged materials and air-dry them with the described strategies (Aoki 2012).

When the documents are wet and especially when mold growth is significant and the smell is bad, the documents should be prioritized for freezing, and they should be freeze-dried. For documents soaked in seawater but without much mold, especially in early stage, squelch-drying (Hadgraft and Welch 1999, Onodera et al. 2012) can be also applied as an option. However, if the number of the affected materials is large, the materials can be frozen and freeze-dried. Yohsei Kohdzuma's group at the Nara NRICP has successfully conducted this process with large numbers of documents.

When the infrastructure has not yet returned to normal conditions, and if freezers are not available, it would be better to try to air-dry soaked documents as quickly as possible by available measures, even if they have started to become moldy.

It is tempting to wash dirty documents with freshwater, but we contend that the timing of such washing should be carefully considered. If drying or freezing documents can be accomplished immediately after the washing, these provide the best options. However, if the conditions do not allow such



Fig.8 An example of documents from Rikuzen-takata City in Iwate Prefecture (photographed on June 8, 2012).Courtesy: Masaru Kumagai and Fumito Honda, Rikuzen-takata City Museum, Iwate Prefecture.





Fig.9 The city hall building of Rikuzen-takata City, Iwate Prefecture, and the salvaged administrative documents after about 17 months (photographed on August 8, 2012). Courtesy: Rikuzen-takata City, Iwate Prefecture.

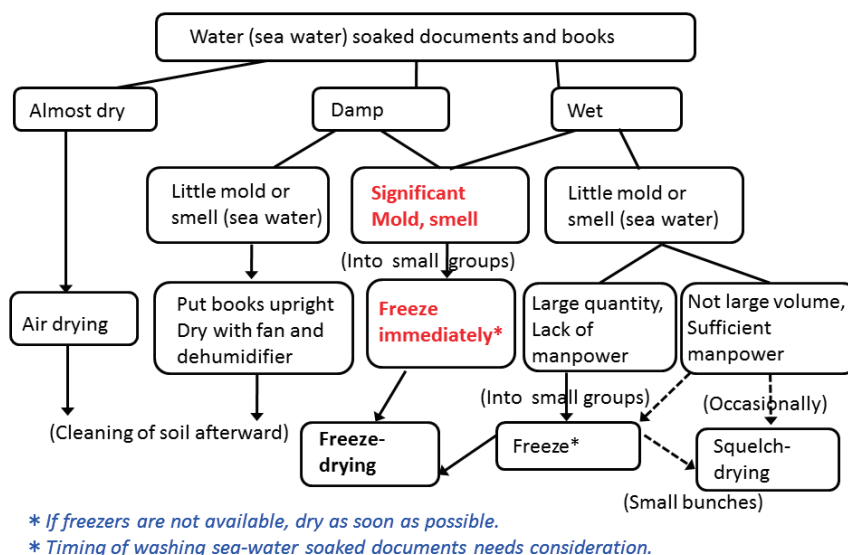


Fig.10 Proposed flow chart for initial responses for salvaging documents soaked in water or sea water (partly modified from Kigawa and Sato 2011).

treatments, simply drying or freezing the documents immediately without washing them can be a better option. Some of the tsunami-soaked documents were washed in freshwater, and they became moldy much faster than unwashed ones in the drying process (M. Aoki, pers. comm.), probably because they lost sea

salts which could have suppressed the growth of hydrophilic microorganisms. As electricity and water supply were not available in the salvaging site in Kamaishi, they did not wash the affected documents, considering the risk of mold outbreak (Aoki 2013).

These treatments concern paper documents and



Fig.11 Examples of tsunami-affected Japanese paintings, Ryuzo-in Temple, Ibaraki Prefecture. a: A locker in which hanging scrolls had been stored. b: A thin hanging scroll, almost dry. c: A hanging scroll made of thicker cloth, still significantly wet and damaged by mold (photographed on May 2, 2011). Courtesy: Ryuzo-in Temple, The Board of Education, Kashima City, Ibaraki Prefecture.

similar materials. Electronic media, natural history collections and other types of objects must be considered differently.

#### ***Japanese paintings: examples and initial responses***

Examples of Japanese painting from Ryuzo-in Temple in Ibaraki Prefecture is shown in Figures 11–13. Valuable hanging scrolls had been stored in a locker (Fig. 11a). The locker was inundated with tsunami water, and the scrolls were soaked in the seawater. We went to the temple on May 2, 2011,

about 7 weeks after the disaster struck. Most of the scrolls were still a bit damp. When we unrolled the scrolls, the thin ones were almost dry and there was no significant mold damage (Fig. 11b). This status is unthinkable under a freshwater-soaked situation, so it was very surprising for us to see how minor the mold growth was.

On the other hand, some hanging scrolls made of thicker cloth were still significantly wet, and some had prominent mold growth (Fig. 11c). The results of the investigation of the mold species are described



Fig.12 Drying of scrolls, on May 2, 2011. Courtesy: Ryuzo-in Temple, The Board of Education, Kashima City, Ibaraki Prefecture.





Fig.13 Mild drying process of fragile, still-wet scrolls (photographed on May 2, 2011). Courtesy: Ryuzo-in Temple, The Board of Education, Kashima City, Ibaraki Prefecture.

elsewhere (Wada et al. 2013). The only treatment method that was available at the moment was to dry the scrolls. For the scrolls that could be unrolled, we asked skilled restorators to unroll them. The scrolls that could be hung on the wall were put up on a sunny day (Fig. 12).

We put the scrolls which were still very wet and could not be hung on a wall down flat on water-absorbent paper (Fig. 13, top). A thin layer of polyester

paper was inserted before another clean water-absorption paper was placed on the scrolls (Fig. 13, top and middle), and we put newspaper as a weight on top (Fig. 13, bottom) and dried the scrolls slowly in this manner (for 1–2 weeks). This was the early response for the scrolls; a more thorough restoration of these scrolls will be conducted eventually.

Figure 14 shows the microbial damage inside of a Japanese folding screen from another location that had been soaked by tsunami water. It suffered very significant microbial damage, including the black- and red-colored microbial damage. Details about the microbes will be described in another paper (Sato et al. 2014).

### *Oil paintings: examples*

The oil paintings in Figure 15 are from Rikuzentakata City in Iwate Prefecture. The Japanese Council of Art Museums decided to rescue the oil paintings, and they were salvaged in July 2011. There were some art pieces which remained wet for four months (from March to July 2011). The activity was reported in other literature (Hamada 2012, Ito 2012).

There was no significant mold damage on the surface of the oil paintings (Fig. 15), but the back of the canvases showed extensive damage from mold after the paintings had been wet for months (Fig. 16). However, if we compare the situation to those of oil paintings which had been soaked in a past flood with freshwater, the mold damage still seemed to be less (T. Kijima, pers. comm.). It is also of interest that regarding the morphological stability of the canvases, the dimensional change of the canvases of oil paintings that had been soaked in seawater was much less than that of oil paintings that had been soaked in freshwater in other occasions (T. Kijima, pers. comm.). To investigate the morphological stability of canvases, we placed oil painting canvases in freshwater and in seawater. We found that the dimensional stability was better in the canvases which had been soaked in seawater (data not shown).

### **Caution when handling tsunami-soaked moldy objects**

When cleaning tsunami-affected moldy objects, documents and artwork, several factors must be borne in mind. The impact of the mold on human health is





Fig.14 Microbial damage inside of a Japanese folding screen salvaged from Ishinomaki, Miyagi Prefecture (photographed on August 19, 2011). Courtesy: Kentaro Ohbayashi.

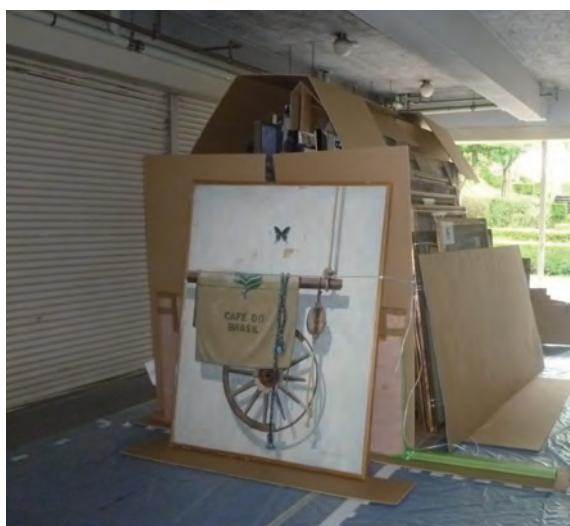


Fig.15 Oil paintings salvaged in July 2011, from Rikuzen-takata, Iwate Prefecture (photographed on July 15, 2011). They were collected for fungicidal fumigation in a treatment bubble. Courtesy: The Japanese Council of Art Museums, and Rikuzen-takata City Museum, Iwate Prefecture.

the highest priority; the necessary steps must be taken to protect staff from incurring infections or allergies. In addition to microbes, harmful micro-dusts such as asbestos in construction materials may be present on the objects. The staff working to rescue the objects must be vigilant about not ingesting contaminants.

In light of this danger, we have promoted the use of certified dust-proof masks by all staff who are involved in the cleaning, rather than casual-type masks. Information about the masks has been

distributed and is available on our website (<http://www.tobunken.go.jp/japanese/rescue/20120319.pdf>) (National Research Institute for Cultural Properties, Tokyo (2012)). Figure 17 is a photo that we took, courtesy of Yohsei Kohdzuma of Nara National Research Institute for Cultural Properties; the Non Profit Organization (NPO), books preservation and restoration staff working to clean the freeze-dried documents are wearing the protective masks and gear for their safety.

Figure 18 shows the cleaning going on in Rikuzen-takata City Museum. The affected books were cleaned using liquid agents so that the dispersal of microorganisms could be prevented.

Many steps have been taken for the safety of the cleaning staff. After the March 2011 earthquake and tsunami, we have not heard of an incident where someone got ill after cleaning the tsunami-affected objects and documents; however, after an earlier earthquake in Japan, there was a case in which volunteers were involved in cleaning a mushroom factory without wearing proper masks; they had inhaled toxic fungi and about twenty people got ill and some of them were hospitalized because of fever, malaise and cough, and one person got serious *Aspergillus* pneumonia (Shimaoka et al. 2006, Kawasaki et al. 2012). Working with damaged cultural properties requires thorough protection against such fungal dusts, toxins and other dangerous substances.



Fig.16 Backside of the canvases (photographed on July 15, 2011).Courtesy: The Japanese Council of Art Museums, and Rikuzen-takata City Museum, Iwate Prefecture.



Fig.17 Staff working to clean the freeze-dried documents, Nara National Research Institute for Cultural Properties (photographed on April 13, 2012). Courtesy: Nara National Research Institute for Cultural Properties.



Fig.18 Cleaning of moldy documents, Rikuzen-takata City Museum (reopened at Oide Elementary School) (photographed on June 8, 2012).Courtesy: Masaru Kumagai and Fumito Honda, Rikuzen-takata City Museum, Iwate Prefecture.

## Problems of biocidal fumigation of tsunami-soaked objects

In addition to concerns about infections in cases with significant mold or bacterial growth, the impact from sewage, contaminated soil and other materials must also be considered. In some situations, biocidal (fungicidal) fumigation has been used to treat damaged objects. Ethylene oxide and propylene oxide have been used as fumigants for cultural properties,

but for seawater-soaked objects and documents, the fumigants may react with ingredients of the seawater, and some toxic substances may be generated as a result.

More specifically, water may react with ethylene oxide or propylene oxide and generate glycol, i.e., ethylene glycol (EG) or propylene glycol (PG) respectively, which are moisture-retaining. Another problem is that chloride is present in seawater, and the chloride can react with ethylene oxide as well as propylene oxide to create toxic substances called





Fig.19 Experiments of fungicidal fumigation of seawater-soaked, wet or dried paper or documents.

ethylene chlorohydrin (ECH) and propylene chlorohydrin (PCH). ECH is known to be carcinogenic, and both ECH and PCH may remain as residues in the treated documents and objects.

Fumigation of oil paintings was being planned after the 2011 disaster. Some of the paintings were still damp or wet at the time. Before a large-scale fumigation was conducted, we decided to check the levels of glycol and chlorohydrin generation resulted from fumigation of seawater soaked objects. Such toxic products are thought to be generated in larger amounts when the materials were wet.

We conducted an experiment in July 2011 in which we fumigated various materials in the wet state (with seawater) and in the dried state. We used paper materials such as cardboard soaked in seawater from

Rikuzen-takata City, and sample documents were soaked in 3.5 % (weight/volume) seawater. The results of the fumigation were compared between the samples which were dried and those which were still wet. Table 1 shows the list of samples used, and the experimental treatment conditions are described in Table 2.

Table 3 shows the results of the analysis of residual toxic substances after fumigation with ethylene oxide. The toxic substances were not detected in the control samples, which were not fumigated. When we fumigated the samples that were dry, EG and ECH were generated, although at low levels. These toxic substances were generated in larger quantities in the wet documents (Table 3).

The results of the propylene oxide fumigation

Table 1 The samples used for the July 2011 fungicidal fumigation tests

Sample	Description	Weight
Cardboard paper	Cardboard paper, soaked by the tsunami, from Rikuzen-takata, Iwate Prefecture, sampled in the wet state. ( July15, 2011) Wet or dried pieces.	Wet: approx. 65 g Dried: approx. 50 g
Documents	The same lot of documents, artificially soaked in 3.5% (w/v) sea salt solution. Wet or dried pieces.	Wet: approx. 300 g Dried: approx. 125 g

Table 2 The experimental treatment conditions used to compare the wet and dry samples

Treatment	Sample	Treatment conditions	Total amount of fumigants used
1. Non-treated	Dried cardboard and documents	Non-treated (Control)	—
2. EO fumigation	Dried cardboard and documents	Kept approx. 1.0 % volume EO, for 48 hours	540 g/m <sup>3</sup>
3. EO fumigation	Wet cardboard and documents	The same amount of EO with 2.	540 g/m <sup>3</sup>
4. EO fumigation	Wet documents	Kept approx. 1.0 % volume EO, for 48 hours (total amount of EO is a bit more than 2 and 3 as wet samples absorbed more EO gas)	555 g/m <sup>3</sup>
5. PO fumigation	Dried cardboard and documents	Kept approx. 1.6 to 2.0 % volume PO, for 48 hours	103 g/m <sup>3</sup>
6. PO fumigation	Wet cardboard and documents	The same amount of PO with 5.	103 g/m <sup>3</sup>
7. PO fumigation	Wet documents	Kept approx. 1.6 to 2.0 % volume PO, for 48 hours (total amount of PO is larger than 5 and 6 as wet samples absorbed more PO gas)	153 g/m <sup>3</sup>

EO: Commercial ethylene oxide gas for fumigation (EO:15 wt%, HCF-134a 85% wt%, Nippon Ekitan Corp., Tokyo, Japan). PO: Propylene oxide, Kanto Chemical Co., Inc., Tokyo, Japan.

are shown in Table 4. We compared the results obtained with the dried samples and the wet samples, and we found that PG was generated in larger quantities in the wet documents. There was also slightly more PCH generation in the wet samples.

## Dry objects well if biocidal fumigation is being considered

To evaluate the results obtained here, we referred to the U.S. Food and Drug Administration (FDA) standards on the residual substances for ethylene

Table 3 Residual ethylene oxide (EO), ethylene glycol (EG) and ethylene chlorohydrin (ECH) after the EO fumigation of seawater-soaked paper and documents (ppm)

Treatment	Samples	EO	EG	ECH (method A)	ECH (method B)
1. Non-treated	Dried CB paper 1	N.D.	N.D.	N.D.	N.D.
	2	N.D.	N.D.	N.D.	
	Dried document 1	N.D.	N.D.	N.D.	N.D.
	2	N.D.	N.D.	N.D.	
2. EO 1.0% volume	Dried CB paper 1	N.D.	43	9	N.D.
	2	N.D.	52	N.D.	
	Dried document 1	N.D.	43	16	N.D.
	2	N.D.	42	19	
3. The same amount of EO as 2	Wet CB paper 1	N.D.	205	6	N.D.
	2	N.D.	127	N.D.	
	Wet document 1	N.D.	192	52	39 ppm
	2	N.D.	127	35	
4. EO 1.0% volume	Wet document 1	N.D.	335	32	25 ppm
	2	N.D.	377	27	

N.D.: Not detected.

EO, EG and ECH (method A): Pieces (approx. 2 g each) were put into 10 mL of ethanol solution, and soluble chemicals were extracted at 70°C for 3 h on a shaker. After being maintained at 70°C for 30 min, the gaseous phase was analyzed for EO, and the solution's EG and ECH levels were determined by gas chromatography (GC-2014, Shimadzu, Kyoto, Japan). Detection limits: EO 1 ppm, EG 3 ppm, ECH 1 ppm. Detailed description of the procedures is in Kigawa et al. 2012.

ECH (method B): The remaining bulk samples were finely shred and extracted in acetonitrile and analyzed by gas chromatograph/mass spectrometry-selected ion monitoring (GC/MS-SIM). Detection limit: ECH 5 ppm. Detailed description of the procedures is in Kigawa et al. 2012.



Table 4 Residual propylene oxide (PO), propylene glycol (PG) and propylene chlorohydrin (PCH) after the PO fumigation of seawater-soaked paper and documents (ppm)

Treatment	Samples	PO	PG	PCH (method A)	PCH (method B)
1. Non-treated	Dried CB paper 1	N.D.	N.D.	N.D.	N.D.
	2	N.D.	N.D.	N.D.	
	Dried document 1	N.D.	N.D.	N.D.	N.D.
	2	N.D.	N.D.	N.D.	
5. PO1.6-2.0% volume	Dried CB paper 1	N.D.	43	N.D.	N.D.
	2	N.D.	44	N.D.	
	Dried document 1	N.D.	64	10	6
	2	N.D.	69	7	
6. The same amount of PO as 5	Wet CB paper 1	N.D.	39	N.D.	N.D.
	2	N.D.	28	N.D.	
	Wet document 1	N.D.	295	17	12
	2	N.D.	268	10	
7. PO1.6-2.0% volume	Wet document 1	N.D.	498	12	9
	2	N.D.	589	12	

N.D.: Not detected.

PO, PG and PCH (method A): Pieces (approx. 2 g each) were put into 10 mL of ethanol solution, and soluble chemicals were extracted at 70°C for 3 h on a shaker. The solution was analyzed for PO, PG and PCH by gas chromatography. Detection limits: PO 1 ppm, PG 9 ppm, PCH 3 ppm. Detailed description of the procedures is in Kigawa et al. 2012.

PCH (method B): The remaining bulk samples were finely shred and extracted in acetonitrile and analyzed by GCMS-SIM. Detection limit: PCH 5 ppm. Detailed description of the procedures is in Kigawa et al. 2012.

Table 5 Proposed maximum residue limits (ppm) for EO, EG and ECH

Medical device	EO	EG	ECH
Implant Small (<10 grams)	250	5,000	250
Implant Medium (10–100 grams)	100	2,000	100
Implant Large (>100 grams)	25	500	25
Intrauterine device	5	10	10
Intraocular lenses	25	500	25
Devices contacting mucosa	250	5,000	250
Devices contacting blood (ex vivo)	25	250	25
Devices contacting skin	250	5,000	250
Surgical scrub sponges	25	500	250

Cited from: U.S. Department of Health, Education, and Welfare, and the U.S. Food and Drug Administration, 1978.

oxide fumigation (Table 5) (U.S. Department of Health, Education, and Welfare; Food and Drug Administration, 1978). To the best of our knowledge, standards for the residues of propylene oxide fumigation do not yet exist, so we considered the results in reference to the standards for ethylene oxide fumigation. Proposed maximum residue limits for medical devices and materials are shown in Table 5. For example, the maximum residue limit for intraocular lenses is 25 ppm for ECH and 500 ppm for EG. For devices which would be in contact with blood, the maximum limit is 25 ppm for ECH and 250 ppm for EG. The residue limits for medical devices contacting skin are much higher: 250 ppm for ECH and 5,000 ppm for EG.

When we compare the standards with the results we obtained for materials that were fumigated after drying, our data would meet the residue limits for intraocular lenses and also medical devices that come into contact with blood. However, in the present wet samples, the generation of both ECH and EG increased and occasionally went beyond the maximum residue limits for intraocular lenses and for devices contacting blood, but their levels were still lower than the residue limits for medical devices which would contact skin.

In summary, if fumigation is necessary, the objects or documents should be dried before conducting the fumigation. If the objects are dried well, the FDA maximum residue limits for medical devices which would contact blood can be met. In the

case of wet documents, there is a larger generation of toxic substances.

Our results are also posted on the National Research Institute for Cultural Properties, Tokyo (2011b) website, at <http://www.tobunken.go.jp/japanese/rescue/110829.pdf>.

## Conclusion

When documents and objects are soaked in tsunami seawater, the salts in the seawater usually suppress the growth of many types of hydrophilic microorganisms. However, when the wet state is prolonged or when contamination by soil or sewage is prominent, microbial damage can occur. In order to prevent microbial damage, the objects/documents should be dried or frozen as soon as possible, especially in the case of paper materials such as documents and books.

If there is a plan to wash the objects, the washing should be done only when the objects can be dried or frozen immediately after the washing, because when the salt content is washed away, mold may grow more easily.

Proper protection must be used by the staff who handle moldy or possibly moldy materials, including the use of certified dust-protective masks. If biocidal fumigation by ethylene oxide or propylene oxide is considered, the documents or objects must be well dried first in order to prevent the generation of harmful residues by the fumigation.

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## References

- Aoki, M.: Rescuing system and restoration techniques of large amount of water-damaged archives. In: *Report of salvaging water-damaged archives*, eds. Amakusa Archives, Amakusa City, Kumamoto Prefecture. Revised manuscript (in Japanese) (2011)
- Aoki, M.: Rescue and recovery of tsunami-damaged documents in the Great East Japan Earthquake. Report from the National Research Institute of Japanese Literature. In: *Activity Reports 2011*, Committee for Salvaging Cultural Properties Affected by the 2011 Earthquake off the Pacific Coast of Tohoku and Related Disasters, c/o National Research Institute for Cultural Properties. pp. 121-130 (in Japanese) (2012)
- Aoki, M.: Salvaging activity of tsunami-damaged documents in the Great East Japan Earthquake, *Annual bulletin of National Institute of Japanese Literature, volumes of archival study*, 9 (in Japanese) (2013)
- Hadgraft, N. and S. Welch: Vacuum-packing and its implication for library, archive and related materials. *Paper Conservation News*, 89, pp. 12-14 (1999)
- Hamada, T.: Rescuing activity of disaster affected art works of Rikuzen-takata City museum by Japanese Council of Art Museums. (in Japanese). In: *Activity reports 2011*: Committee for Salvaging Cultural Properties Affected by the 2011 Earthquake Off the Pacific Coast of Tohoku and Related Disasters, c/o National Research Institute for Cultural Properties. pp. 156-160 (2012)
- Higashijima, K., C. Hori, K. Igarashi, T. Enomae and A. Isogai: First aid for flood-damaged paper using saltwater: The inhibiting effect of saltwater on mold growth, *Studies in Conservation*, 57 (3), pp. 164-171 (2012)
- Imazu, S.: Freeze-drying of disaster-affected documents. *Shufuku*, Oka bokko-do, (in Japanese) pp. 36-39 (1998)
- Ito, Y.: Rescuing activity by Japanese Council of Art Museums – First-aid treatments and restoration of



- disaster-affected art works (in Japanese). In: *Activity reports 2011: Committee for Salvaging Cultural Properties Affected by the 2011 Earthquake Off the Pacific Coast of Tohoku and Related Disasters*, c/o National Research Institute for Cultural Properties. pp. 161-164 (2102)
- Kawasaki, S., Y. Shimaoka, T. Ishida, and O. Kobayashi: Analysis of an epidemic outbreak case of organic dust toxic syndrome among volunteers worked at an *enoki* mushroom factory damaged by the earthquake disaster, *Annals of the Japanese Respiratory Society*, 1 (4), pp.287-293. (in Japanese) (2012)
- Kigawa, R. and Y. Sato: Proposed flow chart of first aid rescue of water or seawater-soaked paper objects. In: *The digest of the meeting for salvaging disaster-affected cultural objects to share information about various options for first-aid treatments, minimizing biodeterioration and preparing for appropriate later restoration*. May 10, 2011, National Research Institute for Cultural Properties, Tokyo. (in Japanese) (2011) <http://www.tobunken.go.jp/~hozon/rescue/summary110613-2.pdf>. Accessed June 21, 2013.
- Kigawa, R., C. Sano, Y. Sato, M. Inuzuka, N. Hayahawa, T. Kotajima, E. Yamanashi, A. Tanaka, M. Morii, K. Okada and T. Ishizaki: Problems in disaster response of seawater-soaked objects: Evaluation of a risk on generation of chlorohydrin and glycol by ethylene oxide or propylene oxide fumigation in tsunami-soaked paper objects and books, *Science for Conservation*, 51, pp. 121-133 (in Japanese) (2012)
- Mori, K., E. Sato and I. Oka: Restoration report of Hanmoto daihan-nyakyo, Amidadera temple (Examples of water-damaged ancient Japanese documents), *Shufuku*, Oka bokko-do, pp. 30-35 (in Japanese) (1998)
- National Research Institute for Cultural Properties, Tokyo: *Handouts of the meeting for salvaging disaster-affected cultural objects to share information about various options for first-aid treatments, minimizing biodeterioration and preparing for appropriate later restoration*. May 10, 2011. National Research Institute for Cultural Properties, Tokyo (in Japanese) (2011a) <http://www.tobunken.go.jp/~hozon/rescue/rescue20110510.html>. Accessed July 2, 2013.
- National Research Institute for Cultural Properties, Tokyo: *Results of investigation on the risk of generation of carcinogenic chemicals by fungicidal fumigation of wet documents and objects soaked by sea water*, August 26, 2011. Committee for Salvaging Cultural Properties Affected by the 2011 Earthquake off the Pacific Coast of Tohoku and Related Disasters, c/o National Research Institute for Cultural Properties, Tokyo (in Japanese) (2011b) <http://www.tobunken.go.jp/japanese/rescue/110829.pdf>. Accessed July 2, 2013.
- National Research Institute for Cultural Properties, Tokyo: *Precautions for handling disaster-affected moldy objects to protect human health, and for prevention of further mold damage*. March 19, 2012. Committee for Salvaging Cultural Properties Affected by the 2011 Earthquake off the Pacific Coast of Tohoku and Related Disasters, c/o National Research Institute for Cultural Properties, Tokyo (in Japanese) (2012) <http://www.tobunken.go.jp/japanese/rescue/20120319.pdf>. Accessed July 2, 2013.
- Onodera, Y., Y. Sato, H. Tanimura, C. Sano, T. Kotajima, M. Hayashi and R. Kigawa: Examination of the squelch-drying technique to restore wet paper documents affected by tsunami, *Science for Conservation*, 51, pp. 135-155 (in Japanese) (2012)
- Sato, Y., M. Aoki and R. Kigawa: Microbial deterioration of tsunami-affected, paper-based objects: A case study. (submitted)
- Shimaoka, Y., T. Ishida, S. Kawasaki and O. Kobayashi : An autopsy case of aspergillus pneumonia after inhalation of a great deal of dust in a mushroom factory, *The Journal of the Japanese Respiratory Society*, 44 (9), pp.659-664. (in Japanese) (2006)
- U. S. Department of Health, Education, and Welfare, Food and Drug Administration (FDA), USA: Federal Register: Ethylene oxide, ethylene chlorohydrin, and ethylene glycol. Proposed Maximum Residue Limits and Maximum Levels of Exposure. (1978)
- Wada, T., Y. Sato, T. Itokawa and R. Kigawa: Identification of filamentous fungi growing on tsunami-affected hanging scrolls owned by Ryuzoh-in, Kashima City, Ibaraki Prefecture, *Science for Conservation*, 52, pp.149-158 (in Japanese) (2013)