

Atmospheric corrosion of historical organ pipes: influence of acetic and formic acid vapour and water leaching on lead

A. Niklasson ^a, L-G. Johansson ^b, J-E. Svensson ^c

^{a, c} Department of Environmental Inorganic Chemistry, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

^b Department of Chemistry, Göteborg University, SE-412 96 Göteborg, Sweden,

Abstract

A field campaign and laboratory exposures have been performed. Comparably high concentrations of acetic and formic acid vapour are present in the wind system of heavily corroded baroque organs in Europe. The corrosivity of these gases is investigated in lab exposures of polished samples. Corrosion rate was measured gravimetrically and the corrosion products were analysed qualitatively and quantitatively. The atmospheric corrosion of lead is strongly accelerated by traces of acetic acid (ethanoic acid). The results imply that acetic acid vapour is a very important corrosive agent for lead pipes in historical organs. Formic acid (methanoic acid) is slightly less corrosive than acetic acid. Water leaching has no apparent effect on the corrosion rate of lead in the presence of acetic acid vapour.

Keywords: Atmospheric corrosion, lead, acetic acid, formic acid, water leaching, organ pipe

1. Introduction

The atmospheric corrosion of ancient lead organ pipes in European churches has recently attracted attention. The organ heritage found in all countries of Europe includes more than 10,000 historically valuable organs and they are all important parts of the cultural heritage. A unique organ, originally built 1467, rebuilt 1636-37 to its present state by the famous organ builder Friedrich Stellwagen, gives a relevant illustration of the problem, see Figure 1. After more than 500 years, the irreplaceable lead-tin pipes from 1467 are suffering from very aggressive corrosion. When a pipe is corroding it gradually develops cracks and holes, and finally collapses and there is no other way to solve the problem than replacing the historic pipes with modern ones – and a part of the sounding cultural heritage is forever lost. The corrosion of lead-tin alloy organ pipes appears to be accelerating all over Europe.

We are partners in the EC project “Collapse” - Corrosion of Lead and Lead-Tin Alloys of Organ Pipes in Europe. The aim of the project is to identify which factors cause the atmospheric corrosion of organ pipes by combining field work with laboratory investigations. In addition, laboratory experiments within COLLAPSE also aim at identifying and testing a set of surface treatments for the protection of lead-rich pipes from corrosion (Chiavari et al., 2004).

Corresponding author: TEL: +46(0)317722859; FAX: +46(0)317722853; email: annikan@chem.chalmers.se



Figure 1. Heavily corroded organ pipe from the Stellwagen organ in Lübeck. (Photo: Ibo Ortgies, GOArt)

Compared to an ordinary indoor atmosphere, the church environment to which these organs are exposed is characterized by relatively low temperature and high relative humidity. Another characteristic is the presence of wood structures. Wood is known to emit a variety of organic vapours, including acetic acid (Arni et al., 1965).

Studies of the degradation of lead were initiated in 1923 (Vernon, 1927). High concentrations of organic acid vapours are known to be corrosive to lead (Graedel, 1994, Tétreault et al., 1998, 2003, Black et al., 1999, 2000). We have previously shown in laboratory studies that low concentrations of acetic acid vapours (0.1–1 ppm) accelerate the atmospheric corrosion of lead, the mass gain being a linear function of time and concentration (Niklasson et al., 2004:1).

In the present work we present results from field investigations regarding mapping of the environment inside of the organ wind system. In addition metal coupons were exposed inside the organs. Laboratory studies were performed in order to investigate the influence of low concentrations of acetic or formic acid vapour on the atmospheric corrosion of lead. In addition, we investigated if the corrosion rate can be reduced by water leaching (cleaning) of exposed samples. The combined input from field investigations and laboratory experiments is essential in order to identify the corrosive factors. This in turn gives us the possibility to prohibit the corrosion by changing the corrosive environment and by applying surface protection treatments.

2. Experimental

2.1 Field studies

Field campaigns have been performed in four geographical areas and countries in Europe. Heavily corroded and slightly corroded organs were selected and the environmental conditions inside of the organ wind system were compared. Temperature and relative humidity were logged during one year. The concentration of different air pollutants were measured at four different positions in each church: In the pallet box, outside the wind chest, in the bellows room and in the church room. Samples of carboxylic acids and aldehydes were collected by pumping known volumes of air on alkaline traps. These measurements were performed in collaboration with the SP (Swedish National Testing and Research Institute). Polished samples that mimic the material used in the historical organ pipes have been exposed in several organs up to one year. The samples were brought in for corrosion product analysis and corrosion rate determination. Water-soluble anions were determined by ion chromatography.

2.2 Laboratory studies

2.2.1 Influence of organic acid vapours

Lead of electrolytic grade (99.95% purity) was used in all experiments. The concentration of acetic acid was 170 ppb and the concentration of formic acid was 195 ppb. The concentration of pollutant gases is given in ppb (parts per billion, v/v). The samples had a geometrical area of 20 cm² (30×30×2 mm). A hole was drilled in each sample for suspension. The samples were polished mechanically on 220 mesh SiC paper in water and then on 1000 mesh in ethanol. Then they were ultrasonically cleaned in ethanol two times, each cleaning lasting two minutes, dried and stored in a desiccator over silica gel. Within 24 hours the samples were weighed and put into the exposure chambers. In each experiment eight samples were exposed. The exposure time was four weeks. The laboratory exposures are performed to provide detailed information regarding the interplay of different environmental factors in the corrosion process such as pollutant concentration, humidity, and temperature.

The experimental set-up is presented in Figure 2. The apparatus is entirely made of glass and teflon. There are eight parallel chambers through which the gas is sequentially distributed, the whole gas flow passing through each chamber in turn for 15 seconds. The gas flow was 1000 ml/min in all experiments, corresponding to a gas velocity of 7 mm/s. Each sample was suspended on a nylon string in the middle of the chamber. Only one sample was exposed in each chamber. The chambers have an inner diameter of 55 mm and a volume of 0.4 l. The corrosion chambers are immersed in a water tank held at 22.00 °C. The temperature in the room was kept at 25 °C to avoid condensation in the parts of the system outside the water tank. Relative humidity (RH) was regulated by mixing dry air and air saturated with water vapour. RH was 95% in all exposures and was controlled with an accuracy of ± 0.3 %. Pure carbon dioxide was added from a gas bottle and a CO₂-analyser (BINOS 1000) was used to monitor the concentration (350 ppm v/v) in the exposure gas. To monitor the corrosion process, the samples were weighed during exposure. The wet mass gain was recorded rather than the dry mass gain in order to minimise the disturbance of the corrosion process. The dry mass gain signifies the weight gain of samples stored over a desiccant at ambient pressure and room temperature for one week after exposure.

The amount of water-soluble anions in the corrosion product layer was determined by ion chromatography, IC. The chromatograph used was an IONPAC AD9-SC Analytic Column. To determine the amounts of carbonate in the corrosion products, some of the samples were transferred to an acid desorption cell consisting of a three-necked flask made of Pyrex glass containing 1M HClO₄ (aq). Immersing the samples in the acid quantitatively converted carbonate to carbon dioxide. A stream of nitrogen was used to expel the carbon dioxide from the solution and carry it to the CO₂ analyzer (Binos 100). The sensitivity of this analysis corresponded to 10×10^{-9} mol CO₂/sample. By introducing weighed amounts of BaCO₃(s) into the system, the precision of the analysis was found to be ± 2 %. Crystalline corrosion products were analysed by X-ray diffraction (XRD). A Siemens D5000 power diffractometer (CuK_α radiation) was used. The diffractometer was equipped with a grazing incidence beam attachment combined with a Göbel mirror. With this technique it is possible to analyse very thin oxide films.

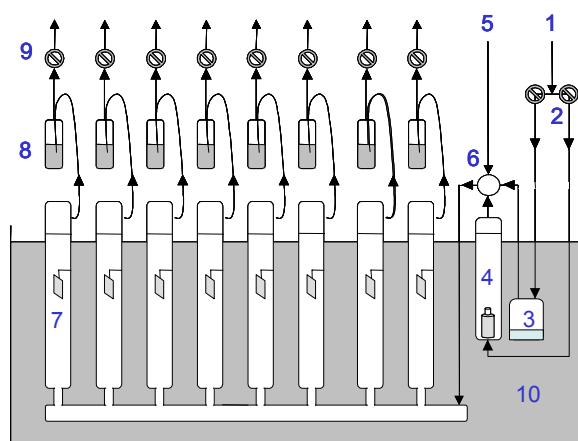


Figure. 2 Experimental set-up for corrosion exposures. (1) dried purified air; (2) flow control; (3) humidifier; (4) vessels for permeation tubes; (5) CO₂ inlet; (6) mixer; (7) eight exposure chambers; (8) wash bottles, (9) eight-channel solenoid valve; (10) water tank at constant temperature.

2.2.2 Effect of water leaching

The development of methods to clean the corroded pipe metal surface is a necessary part of the conservation procedure. Cleaning the corroded pipe is done primarily to decrease the rate of corrosion by removing corrosion compounds (salts) from the surface. The insoluble corrosion products (e.g. lead white) are not to be removed. Cleaning should not affect the metal itself. This is very important for the surfaces in the pipe mouth area. The sound is generated in the mouth area (lower and upper lip and the languid) and the tone quality is extremely sensitive to changes in the mouth area geometries, edges and surface structure. In order to investigate if water leaching is beneficial or not several different exposures were performed, see Table 1. In all the experiments samples of pure lead was exposed to gaseous acetic acid, HAc, (170 ppb) for two weeks. After two weeks of exposure the samples were removed from the exposure chambers. Some samples were leached in pure milli-Q water three times, each cleaning lasting for one minute. The exposures were then continued for two more weeks in either pure air or in air containing acetic acid.

Table 1. Exposures performed. Acetic acid (HAc) concentration was 170 ppb and relative humidity 95%.

No.	Exposure (2 weeks)	Water leaching	Exposure (2 weeks)
1.	HAc	No	HAc
2.	HAc	No	Pure air
3.	HAc	Yes	HAc
4.	HAc	Yes	Pure air

3. Results and Discussion

3.1 Corrosive factors found at the reference organs in the field study

The field measurements performed throughout Europe as a part of this study show that comparably high concentrations of organic acid vapours (e.g. acetic and formic acid) are present in the wind system of heavily corroded organs. Acetaldehyde (ethanal) and formaldehyde (methanal) were also found in smaller amounts. A comprehensive presentation of the field results is given elsewhere (Niklasson et al., 2004:2). As an example of the field measurements, results from the organ wind system in the Stellwagen organ in Lübeck are presented in Fig 3. High concentrations of acetic acid were found inside of the palletbox (700 ppb). In addition to acetic acid, formic acid, acetaldehyde, and formaldehyde were detected (50-250 ppb). It may be noted that the concentration of organic acid vapours is significantly lower (less than half) in organs less affected by corrosion. The concentration of organic acid vapours in indoor environments is typically in the range 0.05-40 ppb (Tétreault et al., 2003). Analysis of the metal coupons exposed in the Stellwagen organ for 3-12 months show that acetates, formiates and small amounts of chlorides and sulphates had accumulated on the sample surface. The presence of acetate and formiate indicates that the organic acid vapours react with the lead surface.

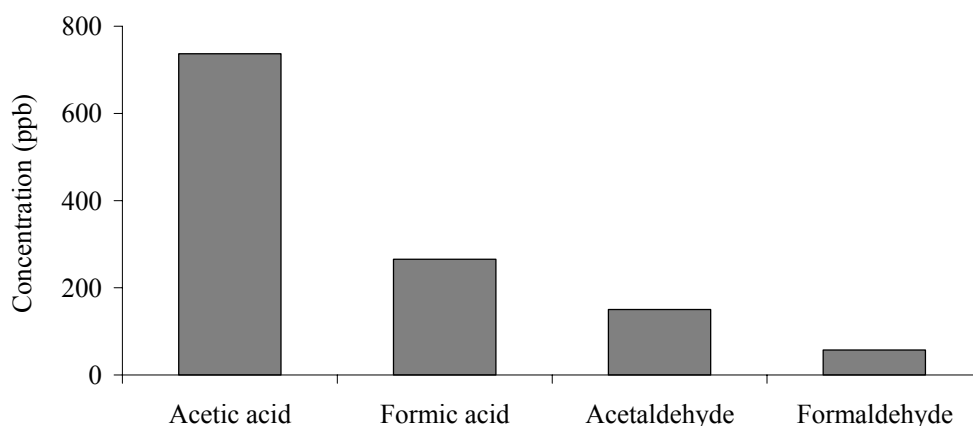


Figure. 3 Concentration of different organic gases in the pallet box in the Stellwagen organ in Lübeck.

3.2 Laboratory studies

3.2.1 Influence of organic acid vapours

The relatively high concentration of organic acid vapours in the organ environment and the accumulation of acetates and formiates on the lead coupons indicate that organic acids play a role in the corrosion of the organ pipes. To address this point, the effect of acetic and formic acid vapour on the atmospheric corrosion of lead was investigated in the laboratory. Figure 4 presents mass gain as a function of exposure time for lead samples exposed to 170 ppb acetic acid or 195 ppb formic acid vapour at 22.00 °C, RH 95 % and 350 ppm CO₂ for four weeks. The atmospheric corrosion of lead is strongly accelerated by traces of acetic acid, the mass gain being linear with time. While formic acid also accelerates lead corrosion, it appears to be slightly less corrosive than acetic acid.

By X-ray diffraction, plumbonacrite (Pb₁₀O(OH)₆(CO₃)₆), lead acetate oxide hydrate (Pb(CH₃COO)₂·2PbO·H₂O) and traces of massicot (β-PbO) were detected after exposure to acetic acid vapour, see Table 2. Lead formate hydroxide (Pb(HCOO)(OH)) and plumbonacrite were identified in the presence of formic acid vapour. Table 3 shows that the deposition of formic acid vapour is considerably faster compared to the corresponding figures for acetic acid. In contrast, corrosion is slower in the presence of formic acid. Consequently, the samples exposed to acetic acid form more carbonate and oxide than the samples exposed to formic acid. In the presence of acetic acid the corrosion product is made up from 50 % lead acetate oxide hydrate, 40 % plumbonacrite and 10 % massicot. In the case of formic acid about 90 % of the corrosion product mass consisted of lead formate hydroxide.

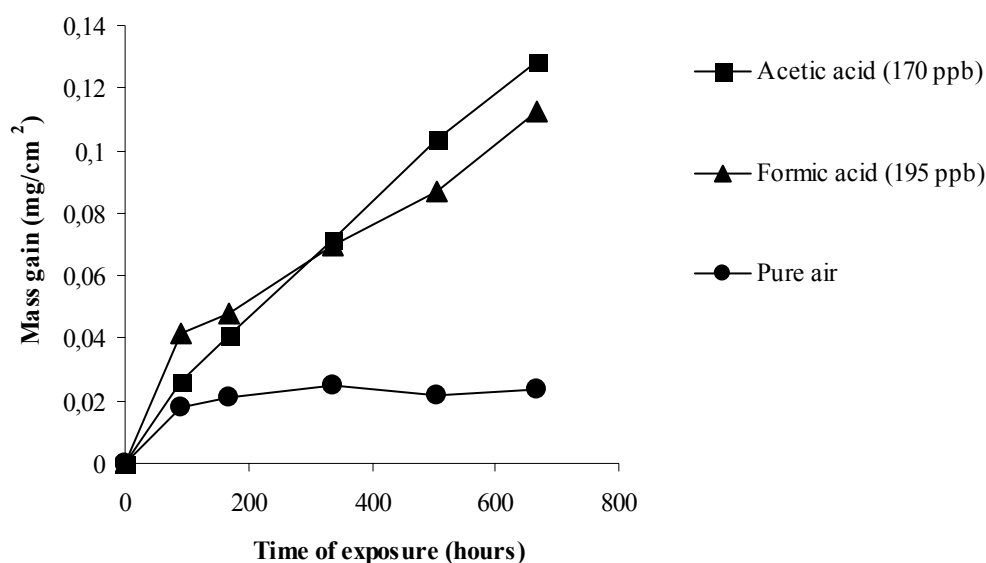


Figure 4. Mass gain vs. exposure time of lead samples exposed to 170 ppb acetic acid or 195 ppb formic acid vapour at 22.00°C, RH 95% and 350 ppm CO₂.

Table 2. Summary presentation of corrosion products identified by XRD.

Exposure environment	Corrosion product
Acetic acid vapour (170 ppb)	Plumbonacrite ($\text{Pb}_{10}\text{O}(\text{OH})_6(\text{CO}_3)_6$) Lead acetate oxide hydrate ($\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 2\text{PbO} \cdot \text{H}_2\text{O}$) Massicot ($\beta\text{-PbO}$)
Formic acid vapour (195 ppb)	Plumbonacrite Lead formate hydroxide ($\text{Pb}(\text{HCOO})(\text{OH})$)
Pure air	Plumbonacrite Litharge ($\alpha\text{-PbO}$)

It is suggested that the corrosivity of gaseous acetic acid towards lead is explained by its high solubility in water, its acidity, and by the solubility of lead acetate and lead acetate oxide hydrate. The acidification of the surface electrolyte by acetic acid results in the dissolution of the passive film, enhancing the anodic dissolution of lead. Lead acetate oxide hydrate is somewhat soluble because of the complexing of lead ions with acetate and hydroxide. Because the surface electrolyte is stable also at neutral and slightly alkaline pH, a corrosion cell is formed where the anodic and cathodic areas on the surface are connected by an electrolyte.

As noted above, formic acid is somewhat less corrosive towards lead in comparison to acetic acid even if formic acid deposits more rapidly on the surface. This implies that the surface electrolyte formed in the presence of formic acid is less corrosive in comparison to that formed in the presence of acetic acid. A comparison of the properties of formic and acetic acid shows, that while formic acid is a stronger acid than acetic acid, formate is a less efficient complexing agent for divalent lead.

Table 3. Wet and dry mass gain, amount of carbonates and the amount of water soluble anions found on lead exposed to 170 ppb acetic acid or 195 ppb formic acid vapour at 22.00 °C, RH 95 % and 350 ppm CO₂ for 4 weeks.

Exposure environment	Wet mass gain (mg/cm ²)	Dry mass gain (mg/cm ²)	Calculated contribution to mass gain by water soluble lead acetate oxide hydrate [#] (mg/cm ²)	Calculated contribution to mass gain by water soluble lead formate hydroxide ^{##} (mg/cm ²)	Calculated contribution to mass gain by plumbonacrite [*] (mg/cm ²)
Acetic acid vapour (170 ppb)	0.124	0.112	0.058		0.041
Formic acid vapour (195 ppb)	0.113	0.097		0.089	0.012
Pure air	0.024	0.012			

#) Assuming that all acetate found forms lead acetate oxide hydrate.

##) Assuming that all formiate found forms lead formate hydroxide.

*) Assuming that all carbonate found forms plumbonacrite.

3.2.2 Influence of water leaching

In order to investigate different possible measures to decrease the corrosion rate in organs, the effect of water leaching on corrosion was investigated. The results from several exposures with and without leaching are presented in Fig 5. Curve (1) shows mass gain in the presence of HAc with no water leaching. As was already mentioned, mass gain is linear in time in the presence of acetic acid. Curve (2) shows the mass gain of samples that were first exposed to HAc for two weeks. Then the supply of HAc was interrupted, resulting in a sudden decrease in the corrosion rate. The effect of water leaching after 2 weeks exposure to HAc is illustrated by curves (3) and (4), note that the mass gain after water leaching is put to zero (**). When the water leached samples are again exposed to HAc (curve (3)), the mass gain curve has the same slope as without leaching, indicating that water leaching does not affect the corrosion rate (compare the slope of the mass gain curves nos. (1) and (3)). Curve (4) shows the mass gain of samples that were exposed to pure air after water leaching. The flat mass gain curve indicates that the corrosion rate is very low in this case, being comparable to curve (2) and to the clean air run in Figure 4. To summarize, while the corrosion of lead is strongly dependent on the presence of acetic acid, water leaching has no apparent effect on corrosion rate.

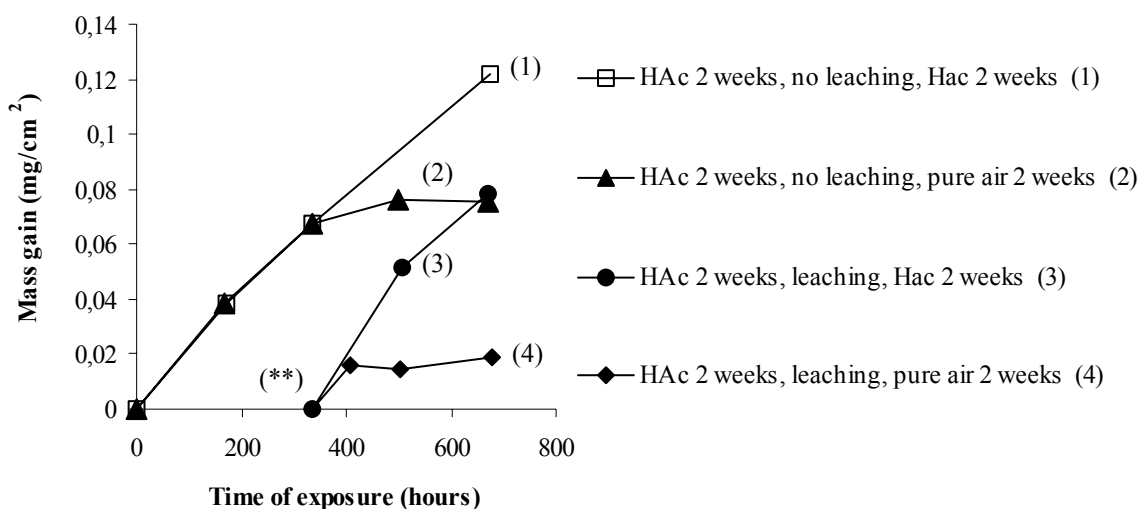


Figure 5. Mass gain as a function of exposure time for pure lead exposed in 95 % RH. Water leaching was performed on some samples after two weeks exposure.

The results of the quantitative analysis of the corrosion products are presented in Table 4. As expected, the amount of acetate on the samples is proportional to the time of exposure in the presence of HAc(g). It may be noted that the amount of acetate on the samples does not diminish upon exposure to pure humid air. This indicates that the conversion of lead acetate oxide hydrate to plumbonacrite must be slow. The results show that samples exposed to pure air during the last two weeks of exposure corrode very slowly even in the presence of ample amounts of acetate on the surface (see Figure 5 curve (2)). This implies that a continuous deposition of acetic acid is necessary to sustain a rapid corrosion process.

Table 4. Amount of acetate and carbonate found on lead exposed to 170 ppb acetic acid vapour at 22.00 °C, RH 95 % and 350 ppm CO₂.

No.	First Exposure (2 weeks)	Water leaching	Calculated contribution to mass gain by lead acetate oxide hydrate [#] (mg/cm ²).	Second Exposure (2 weeks)	Calculated contribution to mass gain by lead acetate oxide hydrate [#] (mg/cm ²)	Calculated contribution to mass gain by plumbonacrite [*] (mg/cm ²)
1.	HAc	No		HAc	0.06	0.04
2.	HAc	No		Pure air	0.04	0.04
3.	HAc	Yes	0.03	HAc	0.03	0.02
4.	HAc	Yes	0.04	Pure air	0.003	0.03

#) Assuming that all acetate found forms lead acetate oxide hydrate.

*) Assuming that all carbonate found forms plumbonacrite.

The samples that were leached in water and subsequently exposed to HAc-containing air produced qualitatively the same corrosion products as samples not leached in water. The only major change in corrosion product composition occurred for the samples exposed to pure humid air after water leaching. These samples formed the thermodynamically stable hydrocerussite rather than the metastable plumbonacrite.

This work deals with one important factor for the corrosion of lead pipes in historical organs namely the occurrence of organic acids in the organ wind system. However it must be emphasized that atmospheric corrosion of lead is influenced by a number of parameters including temperature, humidity, condensation in the pipe, emissions of other corrosive substances from materials inside and outside the organ etc. Combinations of the different corrosive factors should also be taken into account. Even so, the laboratory investigations have shown that the acetic and formic acid found can cause corrosion problems in the pipes all by themselves. It is assumed that the organic acids mainly originate in the wooden parts in the organ. This knowledge is important not only for the understanding of the existing corrosion problems but also to avoid creating a corrosive environment when restoring or repairing an historical organ.

4. Conclusions

Comparably high concentrations of acetic and formic acid vapour are present in the wind system of heavily corroded baroque organs in Europe. Laboratory studies show that the atmospheric corrosion of lead is strongly accelerated by traces of acetic acid, the deposition of acid and the mass gain being linear in time. The results imply that acetic acid vapour is a very important corrosive agent in the deterioration of lead pipes in historical organs. While formic acid also accelerates lead corrosion, it appears to be slightly less corrosive than acetic acid. The results show that a continuous deposition of acetic acid is necessary to sustain a rapid corrosion process. Water leaching has no apparent effect on the corrosion rate of lead in the presence of acetic acid vapour. The results imply that the rate of corrosion of lead pipes in historical organs can be effectively decreased by removing gaseous acetic acid from the wind system.

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