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Application of pH sensors for preventive preservation in storerooms at the Museo Nacional de Ciencias Naturales (Madrid)

Aplicação de sensores pH para conservação preventiva nas reservas do Museo Nacional de Ciencias Naturales (Madrid)

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Abstract

Environmental monitoring is essential for the proper preservation of natural materials in museums, both in exhibition halls and storerooms. Deterioration and degradation of natural materials occur when deviations from neutral pH conditions take place as a consequence of pollution, visitors, non-professional interventions, unsuitable storage conditions, catastrophes, or vandalism. Simple techniques to measure the extent of acidic or alkaline gasses in the museum atmosphere are therefore important, especially in storerooms where objects are placed for long periods. Sol-gel pH sensors have been synthesized and applied for monitoring storerooms of the Museo Nacional de Ciencias Naturales of Madrid (Spain). pH monitoring was carried out for one year under different meteorological seasons. Most of the storage systems monitored maintained a neutral pH, while some of them were slightly acidic. These acidic conditions could favour chemical deterioration on organic structures of naturalized animals, and cause acidic corrosion in minerals and inorganic parts of the objects.

KEYWORDS
Museum collections
Preventive conservation
Environment
Sol-gel sensors
Optical response
Acid pollution

Resumo

A monitorização ambiental é essencial para a preservação adequada dos materiais naturais nos museus, tanto em salas de exposição como em reserva. Os materiais naturais deterioram-se quando ocorrem desvios das condições neutras de pH, decorrentes de poluição, visitantes, intervenções não profissionais, condições inadequadas de armazenamento, catástrofes ou vandalismo. Desta forma, é importante existirem técnicas simples para medir a quantidade de compostos ácidos ou alcalinos na atmosfera de um museu, especialmente nas reservas, onde os objetos são mantidos por longos períodos. No presente estudo, foram sintetizados e aplicados sensores de pH sol-gel para monitorização das reservas do Museo Nacional de Ciencias Naturales de Madrid (Espanha), ao longo de um ano. A maioria dos sistemas de acondicionamento monitorizados mantiveram um pH neutro, no entanto alguns apresentaram-se ligeiramente ácidos. Estas condições ácidas podem favorecer reações de deterioração química nos materiais orgânicos dos animais naturalizados, bem como causar corrosão ácida em minerais e componentes inorgânicos dos objetos.

PALAVRAS-CHAVE
Coleções museológicas
Conservação preventiva
Ambiente
Sensores sol-gel
Resposta ótica
Poluição ácida

Introduction

Proper preservation of natural heritage needs a preventive conservation strategy [1-2] which includes monitoring and control of key environmental conditions: temperature, relative humidity, light and pollutants among others [3-5]. There is another parameter neither measured nor estimated but directly connected to the deterioration or even degradation of museum collections: the acidity of the surrounding air (environmental pH). Evaluating environmental pollution in a museum is important because most of the materials alterations and degradations [6-8] take place when neutral conditions deviate towards acidic or basic pH as previous research work has demonstrated [9-11]. Under acidic or basic pH, chemical reactions that promote alteration of materials, such as hydrolysis, proceed faster. Acidic pollutants in the air (both indoor and outdoor) are a dangerous risk to the preservation of natural materials [12]. Consequently, air quality control by measuring pH arises as an optimal and direct strategy for preventive preservation [13-17].

Acidic pollutants from external sources are generated during the burning of fossil fuels by cars, heating systems, industries, among others. These are SO_2 and NO_x mainly, and when combined with air humidity they generate inorganic sulphuric and nitric acids, respectively [18-19]. Inside showcases, drawers, or storage places, air quality and acidity risk depend on the nature and chemical composition of materials with which such containers were made, as well as on materials or natural substances forming the stored or exhibited objects. Other parameters that affect acidity risk are the dimensions and the tightness degree of storage containers, i.e. their volume and air exchange rate [20].

Since no commercial sensors and devices are available to measure quantitatively the acidity of the air, in the present work environmental pH sensors synthesized by the sol-gel method [21] have been applied in storage spaces of the Museo Nacional de Ciencias Naturales of Madrid (MNCN). These are chemical sensors with optical response in the visible range of the spectrum. Therefore, they are able to change their colour when the pH of the air changes. The measurement of the sensor's visible absorption is correlated with a calibration curve that gives the air pH value to which the sensors were exposed. pH is a useful measure of acidity (and basicity) in water, defined as minus the logarithm of the hydrogen ion concentration (in moles/litre). It ranges from 1 to 14. Water is neutral with a pH of 7. A pH below 7 is acidic and above 7 is basic. This type of sensor can be doped with different sensitive phases depending on its application [22-26]. For the present purpose, the pH range near neutral conditions between 5 and 8 is optimal for evaluating air quality in the MNCN storage spaces. Chlorophenol red (CR) is the sensitive phase selected since its change of colour occurs between pH=4.8 (yellow) and pH=7.0 (purple) being able to detect deviations from acidic to neutral conditions. CR has two tautomeric forms characterized by visible absorption bands at 430 and 570 nm approximately [27]. The sensor's optical response depends on the concentration of acidic and/or basic substances in the air, as well as on the relative humidity and temperature, which can affect the moisture content of the sensor. Dust deposits and dirt also affect the sensor's response and they have a finite lifetime. These pH sensors have been previously applied in other environmental monitoring oriented to cultural heritage protection and conservation [28-31]. Useful and promising results were obtained which contribute to enhancing preventive conservation tasks.

The main objective of this work was the monitoring of environmental pH in the MNCN storage spaces during the meteorological seasons all year round. The final purpose derived from the main objective was to get enough knowledge to take preventive preservation actions that improve the whole conservation of the museum's natural collections.

Materials and methods

Environmental pH sensors

Environmental pH sensors were synthesized by the sol-gel method to obtain porous thin coatings upon common glass slides (soda lime silicate glass). Glass substrates used were from Thermo Scientific Menzel-Gläser SuperfrostPlus, prewashed, ready to use, with frosted edges. The CR sensitive phase is immobilized into the pores of the pseudo glassy network formed by the sol-gel precursors. This sensitive phase will react with the air's acidic or basic species taking the corresponding tautomeric form responsible for the changes of colour that will be correlated with pH changes.

The sol (precursor of thin coatings) was prepared from 0.046 mol tetraethoxysilane ($Si(OC_2H_5)_4$, TEOS), 0.18 mol absolute ethanol (EtOH), 0.04 mol concentrated hydrochloric acid (37 wt. % HCl) and 1.96×10^{-4} mol CR (3',3''-dichlorophenolsulfonaphthalein) dissolved in 0.18 mol EtOH. All reagents used were of analytical grade purity. The molar ratio TEOS:HCl:EtOH was 1:4:8, and the CR concentration was calculated to be 3 wt. % added with respect to 100 wt. % pure silica gel once dried to complete the theoretical densification. During sol preparation acid hydrolysis of TEOS takes place to form H_4SiO_4 as a homogeneous colloidal suspension with particle size below the light wavelength (i.e. has a transparent appearance). After 20 min of continuous stirring, CR disssolved in EtOH is added to the prehydrolized silica suspension and a homogeneous and transparent deep red suspension is thus obtained.

Deposition of thin coatings upon glass slides was done by dipping, using a homemade dip-coater. Chemically clean glass slides were immersed into the prepared sol and drawn out at 1.35 mm × s^{-1}. After drying for 10 min at room temperature (23 °C), coated slides thus obtained were partially densified at 60 °C for three days in a forced air stove. This soft heat treatment allows an adequate pore size in the coatings to be obtained that favours the exchange of H^+/OH^- with the immobilized CR molecules. The conditioning of sensors consisted of cutting and polishing slide's edges to obtain the appropriate size and shape (4.0 cm × 2.5 cm × 0.1 cm). A Silberschnitt diamond cutter model 100 was used for cutting slides. Likewise, a Buehler micro cutter model Isomet 1000 Precision Saw was also used with Buehler diamond disks model Diamond Wafering Blade. Polishing of the slide's edges was carried out with a Buehler rotary polishing machine model Metaserv 2000 Grinder/Polisher, provided with silicon carbide polishing papers (120 grit).

Then, sensors were individually validated and calibrated following the methodology explained in [27]. For calibration, several pH buffered solutions within the pH range 5.0-8.0 were used. Buffered solutions were prepared from Buffer Hydrion Salt (Sigma Aldrich). Each sensor was previously hydrated in distilled water for 10 min and then immersed into the buffer pH 5.0 for 10 min and its visible spectrum was recorded; after washing in distilled water for 10 min, the sensor was dipped into the buffer pH 6.0 for 10 min and its visible spectrum was recorded. This procedure is repeated 5 times for each sensor at each pH and the corresponding average values were used for calibration purposes. Visible spectra were recorded with an Ocean Optics spectrophotometer model HR 4000 CG within the 380-750 nm wavelength range. For instance visible spectra recorded for some different pH values display the pattern of absorption bands shown in Figure 1.

The calibration curve for each sensor is built from data of its visible absorption intensity at 575.4 nm for each pH. Once calibration curves were built (Figure 2) sensors' accuracy was checked to be ± 0.1 units of the pH scale, and their response time was at about a maximum of 24 h depending on environmental conditions (relative humidity, mainly) [27]. According to previous field research, the sensors' lifetime was proved to be at about 9 months for indoor use, and about 3-4 months for outdoor use [21]. For field use, sensors could be protected by a perforated polyethylene bag since perforation allows direct contact between air and sensor surface. These perforated bags containing the sensors are used during the exposure to the environment to be evaluated. Their purpose is merely protection against breakage and handling.

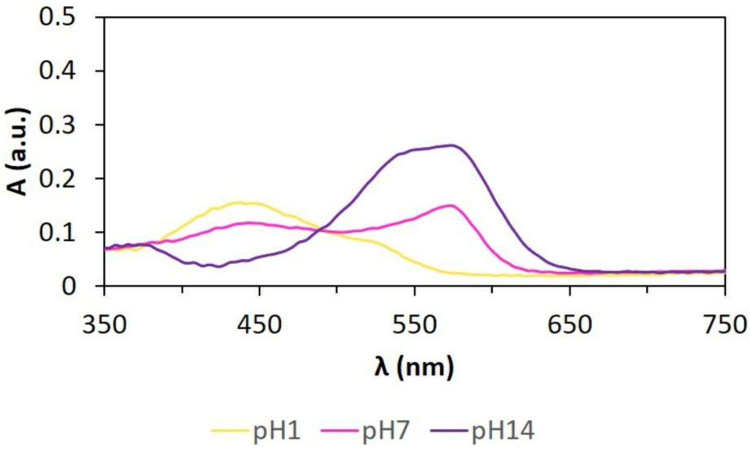

Figure 1. Visible spectra of sensors under three different pH buffered solutions.

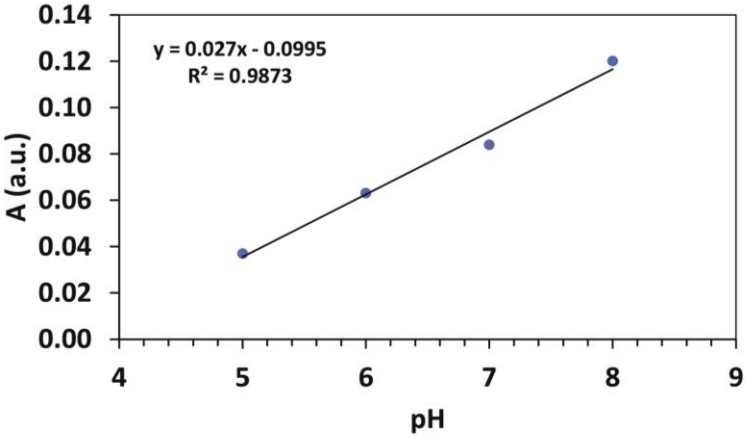

Figure 2. Example of calibration for a CR doped pH sensor (sensor nr. 1 calibrated in August 2019).

Among the sensors' properties, reversibility can be highlighted (previous regeneration by dipping into pH buffered solutions), reusing, good chemical resistance against water, reagents and solvents, low production cost, resizing ability, wireless and battery-free working [27]. The sensor's optical response was recorded in situ by using a portable measurement unit connected to a laptop [32-33] (Figure 3). The specific management software, which was conceived, programmed and patented including the corresponding calibration curves for the sensors [32], provides direct environmental pH values detected by each sensor once sensitized in their corresponding position in a museum storage space.

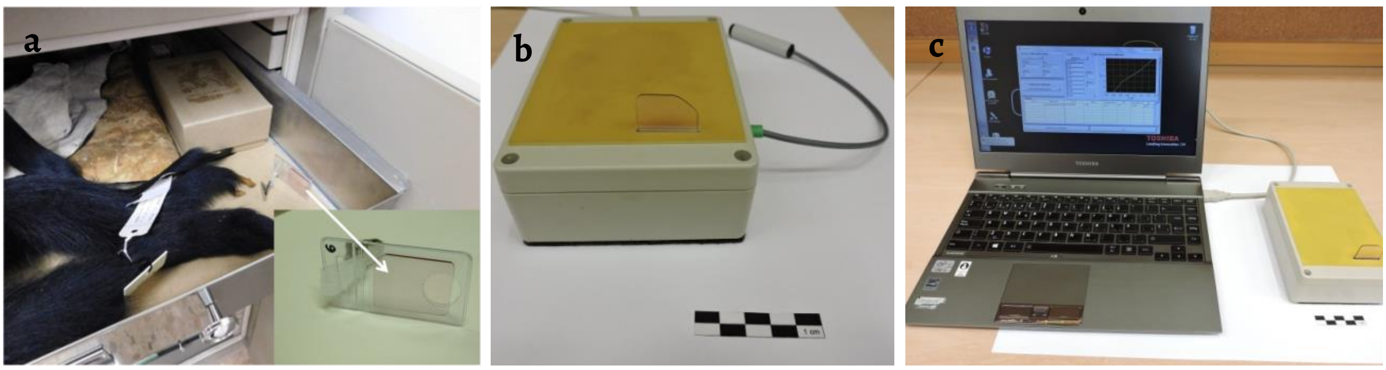

Figure 3. *a)* Sensor installed in a preserved mammals' M1 drawer provided with drying paper in the bottom; *b)* Sensor attached to the portable measurement unit; *c)* Portable measurement unit connected to a laptop.

Table 1. Positions of sensors during the monitoring (December 2018).

Sensor No.	General location	Particular position
1	Cylinder store	Free environment
2	Cylinder store	Birds 9 (showcase passerines)
3	C12 store	Free environment
4	C12 store	C1 (chamber) environment
5	C12 store	M1 (mammals) environment
6	C12 store	M1 (mammals) C12/M1/A04/04
7	C12 store	A1 (birds) environment left
8	C12 store	A1 (birds) environment right
9	C12 store	A1 (birds) vultures tray C12/A1/A24/02
10	C12 store	A1 (birds) nests tray A48/02/02

Sensor installation in the MNCN

A one-year monitoring, from December 2018 to December 2019, was carried out to detect the influence of different climatic conditions on the environmental pH of natural collections at MNCN [34-35]. MNCN storerooms are covered by an air-conditioning system, which maintains the average temperature and relative humidity at 20.8 °C and 29 %, respectively. Environmental pH monitoring was done during spring, summer, fall and winter in two different storage spaces: the C12 store and the so-called Cylinder (a store provided with showcases that can be visited). Sensors were placed both in the hall's free environment of storerooms and inside showcases and drawers (Table 1). The total number of different positions evaluated was 14 and the total number of pH recordings taken was 190. For reference purposes, two sensors were installed outdoor the MNCN, in the front façade (West orientation) and in the rear façade (East orientation), for every monitoring carried out throughout the meteorological seasons. It must be highlighted that MNCN is located in downtown Madrid near the Paseo de la Castellana, with heavy road traffic and, consequently, a high potential for environmental pollution.

Results

First monitoring – December 2018

Sensors were installed on December 10th, 2018 (Table 1). Four measurements were recorded for each sensor from December 11th to December 17th. The average temperature and relative humidity during this period were 19.5 °C and 29 %, respectively. As can be seen in Figure 4 the results obtained after 24 h show data that in most cases are corroborated by further recordings. The pH drop after the first 24 h is due to the sensitization of sensors once exposed to the environment to be monitored and corresponds to the sensors' response time, which is estimated to be between 24-48 h [27].

Second monitoring – May 2019

Sensors were monitored from May 6th 2019 to May 13th 2019 (Figure 5). The average temperature and relative humidity during this period were 20.2 °C and 29 %, respectively. The sensors' positions were the same as in the former monitoring except for sensor 9, which was installed in the same hall but in another position near the hummingbirds' tray. This change of position was made under the advice of the museum conservators since the initial position of sensor 9 (in C12 store, A1 (birds) vultures tray C12/A1/A24/02) proved to be very stable concerning pH. Hence that sensor was used for monitoring another position.

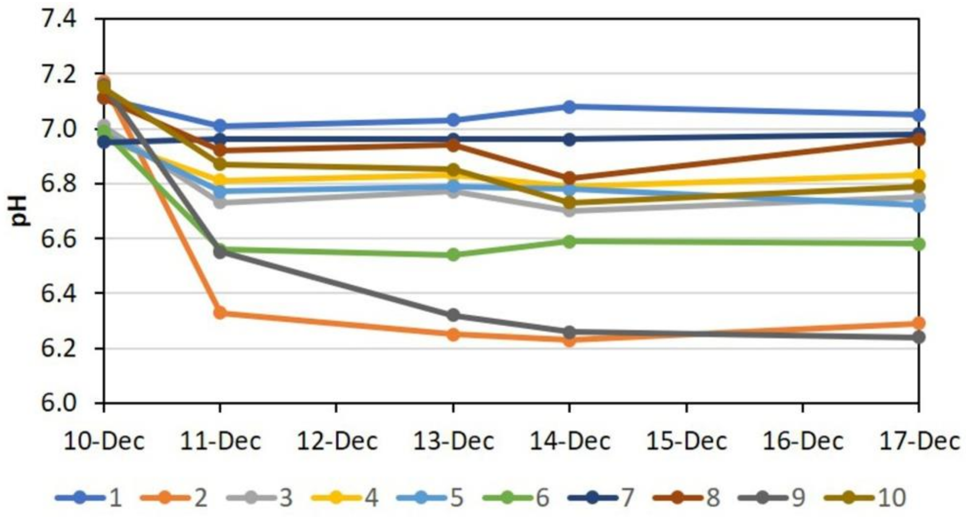

Figure 4. Evolution of pH values during the December 2018 monitoring.

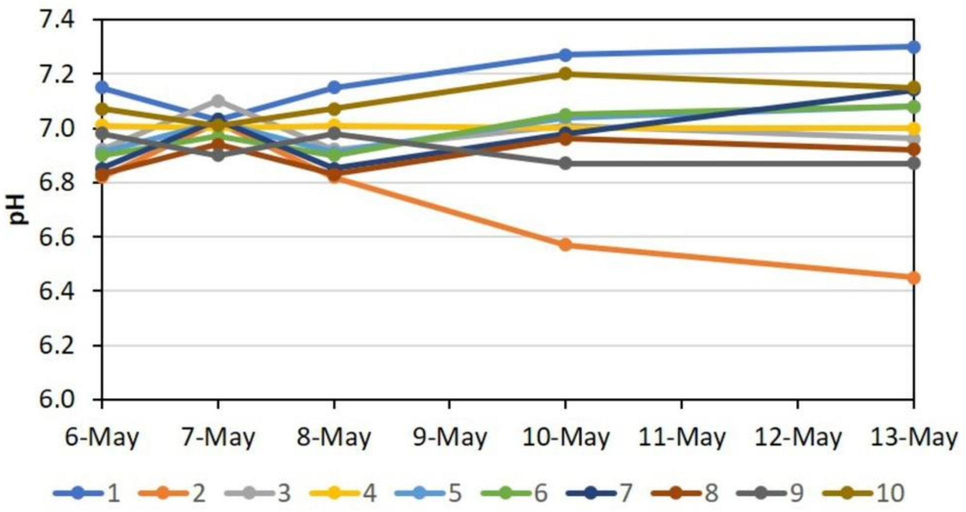

Figure 5. Evolution of pH values during the May 2019 monitoring.

Third monitoring – August 2019

Sensors were monitored from August 20th 2019 to August 28th 2019 (Figure 6). The average temperature and relative humidity during this period were 23.6 °C and 28 %, respectively. The position of two sensors was changed: sensor 2 from the Cylinder was now installed in the mammals' showcase 3, and sensor 6 was now installed in the primates' area. The reason for this change of sensors' position was the same as in the former monitoring.

Fourth monitoring – December 2019

Sensors were monitored from December 16th 2019 to December 20th 2019 (Figure 7). The average temperature and relative humidity during this period were 19.8 °C and 31 %, respectively. One of the sensors (sensor 6) was maintained in the same hall but was now installed inside a box containing drying paper to check the neutral conditions of this material.

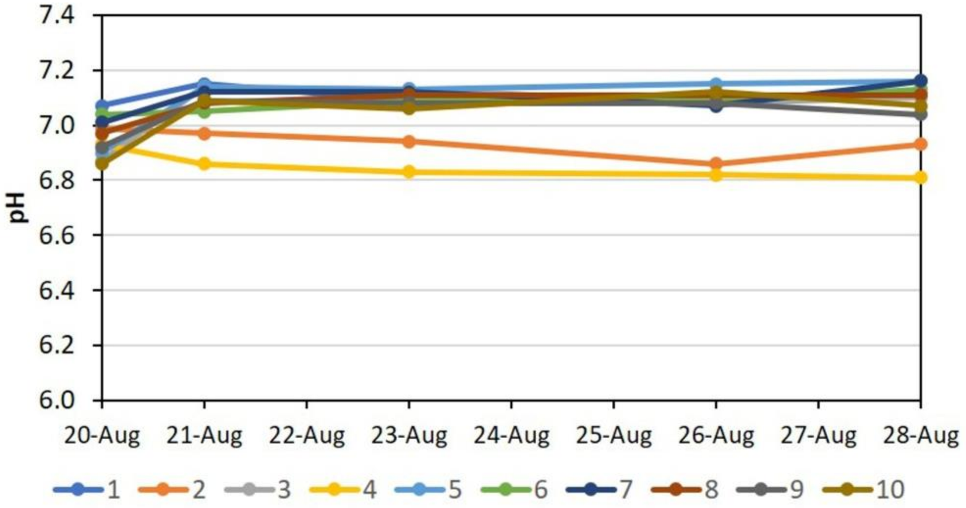

Figure 6. Evolution of pH values during the August 2019 monitoring.

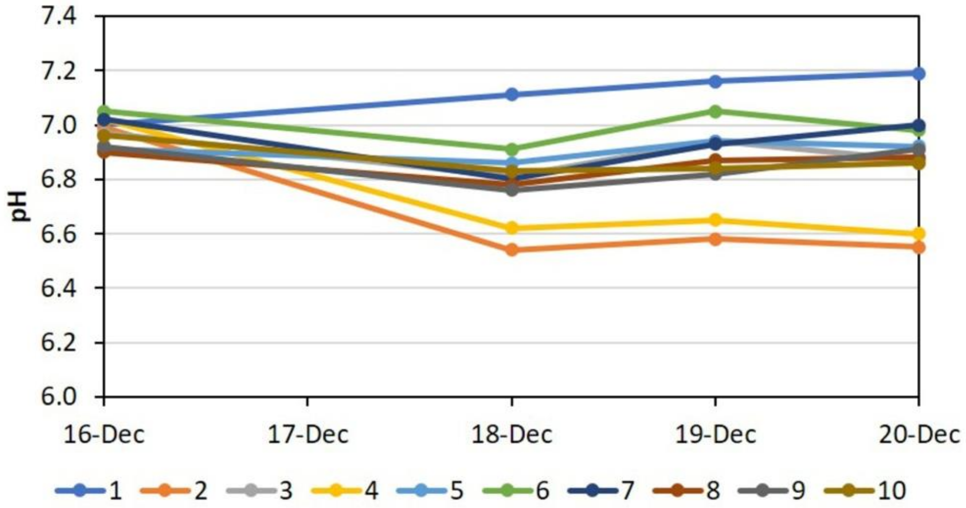

Figure 7. Evolution of pH values during the December 2019 monitoring.

Average pH values recorded throughout the evaluated year (December 2018-December 2019) are summarized in Table 2.

Since the position of several sensors was changed from one monitoring to another (namely sensors 2, 6 and 9), their corresponding pH average values have been presented separately.

As far as the response of the sensors installed outdoor is concerned, the environmental pH recorded is acidic since the MNCN is located very near the Paseo de la Castellana with heavy road traffic. Average pH values recorded in the main façade are 4.6 in the warm season (May-August) and 6.0 in the cold season (December), while in the rear façade are 5.5 in the warm season and 6.5 in the cold season. pH data recorded outdoor during the warm season are very acidic – those corresponding to the front façade are the most acidic ones – while the backyard of the building is partly protected from road traffic emissions.

Table 2. Comparison of average pH values recorded during the evaluated year.

Sensor Nr.	Objects/Materials	Dec-18	May-19	Aug-19	Dec-19	Average pH	Standard deviation
1		7.0	7.2	7.1	7.2	7.1	0.1
2a	Passerines	6.3	6.7			6.5	0.3
2b	Mammals 3			6.9	6.6	6.8	0.2
3		6.7	7.0	7.1	6.9	6.9	0.2
4		6.8	7.0	6.8	6.6	6.8	0.2
5		6.8	7.0	7.2	6.9	7.0	0.2
6a	Mammals	6.6	7.0			6.8	0.3
6b	Primates			7.1		7.1	---
6c	Drying paper				7.0	7.0	---
7		7.0	7.0	7.1	6.9	7.0	0.1
8		6.9	6.9	7.1	6.8	6.9	0.1
9a	Vultures	6.3				6.3	---
9b	Hummingbirds		6.9	7.1	6.8	6.9	0.2
10		6.8	7.1	7.1	6.8	7.0	0.2
Outdoors	Main façade	5.2			6.8	6.0	---
Outdoors	Rear façade	6.1			6.9	6.5	---
Outdoors	Main façade		5.3	3.9		4.6	---
Outdoors	Rear façade		5.8	5.2		5.5	---

--- Standard deviation is not calculated since there is only one value (two for outdoors recordings).

Discussion

Most of the pH values recorded in the MNCN storage spaces are neutral or slightly acidic. These results indicate that preservation conditions, as far as environmental pH (i.e. neutral conditions level) is concerned, are adequate. Regarding the sensors installed in the hall's free environment, pH values are neutral or very slightly acidic (between 6.8 for sensor 4 and 7.1 for sensor 1 installed in the Cylinder). The value of 6.8 recorded by sensor 4 could be due to the high number of naturalized animals stored in this hall and the scarce ventilation to which they are subjected. Under these conditions the concentration of acidic species in a small and confined space increases and promotes a microenvironment. Although nowadays the Cylinder store is not visited, the MNCN plans that it could be visited in the near future. Therefore, when the content of CO_2 and humidity will increase due to visitors, environmental conditions should be re-evaluated to check their impact on the current neutral conditions of such halls.

Sensors installed inside showcases and drawers recorded variable pH values compared to those recorded in the hall's free environment. Average values vary from neutral pH (sensors 6b, 6c, 9b and 10) up to acidic pH=6.3 on sensor 9a installed in the vultures drawer. Other positions of sensors 2a, 2b and 6a recorded slightly acidic average pH values – between 6.5 and 6.8. Showcases of the Cylinder (sensors 2a and 2b) were made on glass and metal that do not emit any acidic substances. Thus, the acidic environment detected would be due to the material of the objects exhibited, i.e. abundant naturalized animals. Such showcases have an almost hermetic closure by using silicone or similar sealants that hinders gaseous exchange with the hall's free environment, which is neutral and should be beneficial, provided there are no serious internal sources of pollution. Nevertheless, silicone used as a sealant could contain some components able to emit acetic acid or other acidic compounds [20]. In the birds' showcase (sensor 2a in passerines) the pH recorded was 6.5, while in the mammals' one the pH was 6.7.

Some sensors installed in drawers recorded a neutral pH (sensors 6b, 6c, 9b and 10). Sensor 6a recorded a slightly acidic pH (6.8) and sensor 9a a moderately acidic pH (6.3). Some corrective action should be taken in the latter case, for instance, periodic ventilation or the use of a specific absorbent for volatile acidic substances [36-37]. Drawers and lockers where sensors were installed are made of metal and they do not emit acidic compounds. Once again, the origin of the acidic pH recorded could be found in the naturalized animals stored. Moreover, some drawers have paper at the bottom that, when degraded after years could contribute to generating acidic emissions [38]. During the last monitoring, sensor 6c was installed inside a drawer provided with drying paper and the pH then recorded was neutral. Therefore, acidic emissions are not connected to this kind of protective paper. Previous results obtained by checking with optical pH sensors in special storage materials for museum objects indicated that they maintain neutral conditions in their surroundings for a long time [39].

Installation of sensors in the same positions throughout the four meteorological seasons of the year allows a comparison of the pH values recorded. As the results demonstrate, there is no noticeable pH variation that could be attributed to the change in meteorological seasons and the respective pH values measured outdoors. This can be explained by the location of the storage rooms inside the museum with limited ventilation, in such a way that pH variation outdoor has little or no influence on the pH values recorded.

Regarding pH values recorded by the sensors installed outdoors, the location of the MNCN in downtown Madrid favours the dry acid deposition phenomenon that has been detected [40]. This phenomenon takes place when pollutant concentration in the air is high and no rain has occurred, which would have removed pollution from the environment. For instance, the average pH values recorded outside, in the main façade, during the warm seasons (May-August) are lower (4.6) than during the cold season (December) (6.0), which can be explained by the almost absence of rain in downtown Madrid in summer. Similar behaviour of air pollutants and their impact on environmental pH has been previously detected in other locations [21, 27].

The main acidic pollutants are SO_2 and NO_x generated by fossils fuels burning in cars and heating systems. They form strong acids when combined with atmospheric humidity (i.e. H_2SO_4 and HNO_3) [18]. Therefore humidity seems to be another important factor to promote acidic pollutants [41]. Competition between this later mechanism and the dry acid deposition [40] will determine the whole concentration of acid species in the air and the corresponding environmental pH.

Conclusions

In the halls of the storage spaces of the MNCN, environmental pH is essentially neutral. In showcases and drawers, the recorded pH varies from neutral to moderate acidic values. The acidity detected is mainly generated by the natural materials contained in showcases and drawers and is possibly connected to the nature of naturalized animals (their organic components such as hair, skin, feathers, etc.) and the chemicals and materials needed for the taxidermy process.

Bearing in mind these results, proper preventive preservation of collections stored in the MNCN of Madrid should include an increase of ventilation in showcases and drawers in which a slightly acidic pH was detected. Likewise, in showcases and drawers where a moderately acidic pH has been detected, ventilation increase and installation of absorbents such as active carbon would be beneficial. In all cases ventilation should be carried out with pollutants' free air.

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