Indoor air pollution impact on cultural heritage in an urban and a rural location in Romania: the National military museum in Bucharest and the Tismana monastery in Gorj County

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Abstract
Assessment was performed of the air quality related risk to the conservation of cultural heritage objects in one urban and one rural indoor location in Romania, with expected different air quality related conservation challenges: the National military museum in Bucharest and the Tismana monastery in Gorj County. The work was performed within and subsequent to the EU-Memori project by applying Memori methodology, Memori®-EWO (Early warning organic) dosimeters and passive pollution badge samplers for acetic and formic acids. The measurements in the National military museum were performed in three rooms with different exposure situations, and inside protective enclosures in the rooms. The rooms had organic and inorganic objects on exhibition and in store. The observed risks were associated with photo-oxidizing impact probably due to traffic pollutants entering from outdoor, and/or light exposure and temperature. The risks were found to be moderate, generally comparable to typical European purpose built museum locations. The highest risk was observed in a more open exhibition room in the main museum building. It was indicated that some observable change might happen to sensitive pigments and paper within 3 years, and to lead, copper and sensitive glass within 30 years in this location. Risk for observable change to sensitive pigments, paper, lead and sensitive glass within 30 years, was indicated in the other locations. The lowest risk was observed in a warehouse. A reduction in photo-oxidizing risk was measured in two of the enclosures, but a slightly higher acidic impact was measured in all the three enclosures, as compared to the respective rooms. In the Tismana monastery, a high level of acetic plus formic acid was observed in the air in the storerooms for icons and textiles, and books. Damage risk within 3 years was indicated for lead objects and sensitive glass, and within 30 years for iron and varnish (Laropal A81, resin mastic and dammar). As organic acid attack increases significantly at higher air humidity (≥ 60%), this would be especially important to avoid. Risk for photo-oxidizing damage to paper and sensitive pigments within 30 years was indicated.

Keywords: Air pollution, Conservation, National Military Museum in Bucharest, Tismana monastery in Gorj County, Memori

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**Introduction**

This study assesses the main general air quality related risk for damage to cultural heritage objects in custody of the National Military Museum, Bucharest, and the Tismana monastery, Gorj County, in Romania. The Military Museum is located in the centre of Bucharest where air pollution, especially from local combustion sources in the city (“traffic and house heating pollutants”) is a health issue, with transgression of recommended outdoor levels [1] such as the EU 2008 Air Quality Directive (AQD) presently in force [2]. This indicates possible transgression of levels suggested for exposure of cultural heritage objects located indoor [3, 4]. The Tismana monastery is located in a forested part of the countryside with generally much less traffic pollutants than in Bucharest. A possible damage risk and preservation challenge for objects stored indoor in relatively closed rooms in the monastery, partly constructed with and containing organic materials, may be due to off-gassing of acidic components.

Air pollution measurements were implemented in this work to evaluate these possible risks.

The measurements were performed within the EU-Memori project [5]. Air quality was measured in selected indoor locations at the sites, and the evaluation system and results reporting developed in Memori was applied. Memori® air quality measurements and risk evaluation system for cultural heritage is described on the Memori technology web pages, where measurement results are also reported to users on assigned pages [6]. A Memori assessment takes into account the most common photo-oxidizing and acidic damage risks to cultural heritage materials observed indoor due to exposure to gaseous air pollutants.

The most prevalent and aggressive gaseous air pollutants, coming from the outdoors, and commonly observed indoors, are the oxidants nitrogen dioxide (NO₂) and ozone (O₃). NO₂ can react to form nitric acid (HNO₃). NO₂ and O₃ are usually emitted from outdoor combustion sources, mostly traffic, house heating and industry. Indoor sources for these pollutants, which could be for example kitchens with gas stoves, open fireplaces, or electrical appliances that produce ozone, are uncommon in cultural heritage buildings. Many building and object materials do however emit volatile organic compounds (VOCs). The types and manufacturing processes of building materials are very diverse. It is therefore not surprising that very many different species of VOCs have been observed in indoor air [7–9]. This includes the low molecular mass formic and acetic acids, which can damage some materials [10–14]. Damage due to exposure to formaldehyde has been reported, with the additional information that this effect may be due to oxidation to formic acid [4, 15]. In addition, various organic pesticides have historically been used in many collections [16–18]. Damage to cultural heritage objects due to exposure to heavier (than formic and acetic acid) weight VOCs seems to be uncommon. Such compounds could be involved in the degradation mechanisms of polymeric materials [19]. Retained and emitted organic solvents may have damaging effects on materials such as varnishes [20].

Air pollution is only one of many risk factors, and it is often a lesser one. Heritage objects can be threatened by dramatic events such as war, fire, earthquakes or flooding. Exposure to water in its different phases is often a serious risk. This includes effects of indoor air humidity and its fluctuations [21]. Ongoing climate change is affecting degradation rates and risks [22]. Damage due to air pollution typically develops in synergy with light and humidity exposure, which is easier to observe [23, 24]. Air pollution can be a critical factor in some situations. A typical example is the outdoor formation of black crusts on calcareous stone due to acidic-sulfuric impact and soot deposition [25, 26]. Tarnishing and corrosion of metal surfaces and accumulation of dust are commonly observed indoor [27–30]. Damage to objects from oxidizing and acidic air pollutants may be less obvious. Typical damage effects are fading of dyes and colour changes, and loss of strength in paper and textiles. Sensitive wooden objects such as musical instruments or inlays can be affected [6, 27, 28].

A general risk evaluation should be performed before implementing environmental measurements. The evaluation should consider possible air pollution species that could be present in damaging concentrations. Many different techniques can be applied to measure air pollution. It has been most common to measure single parameters. Passive sampling with subsequent analysis in the laboratory and continuous online monitoring are two main general methods. Several dosimeter methods have been developed to measure generic effects of the air pollution on materials. Passive sampling, either of single parameters or with dosimeters, is usually much less expensive and thus more accessible to most cultural heritage users [31]. Application of Memori dosimeters gives values for the most common indoor photo-oxidizing and acidic air pollution risks. Other air pollutants that may have a damaging presence in some situations, such as sulfur dioxide (SO₂), hydrogen sulfide (H₂S), dust and particles including chloride [27], must be measured with different methods.

Memori measurements have been performed in many studies in many indoor locations to assess and compare air quality for cultural heritage [32–34]. It is a well-suited method for general assessment of the main common damage risks related to gaseous air pollution. Diagnosis is performed by the separation between photo-oxidizing
impact (which is usually due to outdoor sources) and the acidic impact (which is usually due to indoor sources). This allows determination of the probable reason(s) for observed air quality related damage risk, and to suggest mitigation measures, which could be implemented to protect vulnerable objects against the exposure.

**Methods/experimental**

**Measurement locations**

To perform the air quality risk assessment, related to the preventive conservation of the objects in the National military museum and the Tismana monastery, air quality measurements were carried out over a 3 months period, from July to October in the year 2012, in locations of interest at the two sites. The measurements were performed in locations with significant objects on exhibit or in store, and which were expected to offer different degrees of protection against external and internally emitted air pollutants.

The measurements in the National military museum were performed in three rooms and inside a protective enclosure in each room: (1a) In the warehouse for foreign uniforms, and (1b) in a melamine fibreboard storage wardrobe in the warehouse; (2a) in the probative objects storage room, and (2b) in a wooden historic storage chest in the storage room; and (3a) in a contemporary history room in the main museum building, and (3b) in a display showcase in this room. Figure 1 shows five of the six locations. A photo of the measurement samplers located outside of the wooden chest in the probative objects storage room was not available.

Cultural heritage objects on exhibit or in store at these locations were woollen blankets, silk dresses, different types of military uniforms made from wool and cotton, swords, medals, military decorations, rifles, a binocular, a military casket, and different types of weapons and metals. The majority of the objects were composite objects consisting of inorganic and organic materials, some with specific coatings. Figure 1 shows some of the objects.

In the Tismana monastery, (Fig. 2) the measurements were performed in an icons and textile storeroom and in a book store room, and just outside of the rooms in a corridor. Figure 2 shows the Tismana monastery, and its iconostasis. Photos of the exact measurement locations were not available.

**Measurement methods**

A Memori risk evaluation can be based either on measurements with generic dosimeters and/or on parameter measurements of the considered photo-oxidizing (NO₂ and O₃) and acidic (acetic and formic acid) pollutant gases. Memori was developed with the use of Memori-EWO (PPO) (Early Warning Organic (Polyphenylenoxide)) synthetic polymer dosimeters to measure photo-oxidizing impact, and a specially designed sensitive glass dosimeter (GSD) to measure acidic impact [6]. The translucent dosimeter materials react with the atmosphere and become more opaque due to exposure in the heritage locations.

When dosimeters are used for the air quality measurements, the results are reported as change in light absorption due to the exposures, as “delta absorption values”, for the relevant wavelengths in the ultraviolet (the Memori-EWO) and the infrared (the GSD) region. This change observed in the dosimeter material due to the exposure, corresponds with the air pollution load and thus with the risk. In The EU-Propaint project [9, 23] dose-response equations were developed, which correlated the values for the influencing environmental parameters and the dosimeter responses, based on statistical treatment of a large database of measurements. In the indoor museum locations, the concentrations in air of NO₂ and O₃ (“traffic pollutants”), and the uv (ultraviolet)-light exposure were found to influence the EWO response at rates depending on the temperature, whereas the concentration in air of acetic acid was found to influence to GSD response.

It was a major task in the EU-Memori project to further correlate the dosimeter response with the expected impact on different cultural heritage materials [6], for the application in risk assessment, as reported below. The
dose-response equations from the EU-Propaint project and additional available information about the sensitivity of cultural heritage materials to photo-oxidizing and acidic air pollutants, was the basic information used for this assessment. As a strong statistical correlation was found between the GSD response and the measured concentration of acetic acid indoor in museums [23], the GSD absorption values reported by default in Memori evaluations, can also be approximated by calculation from measured concentration values of acetic acid. The applied correlation equation is [23]:

\[
\text{GSD(app)} = 0.2 \cdot \frac{[\text{HAc} + \text{FA}]}{1000}
\]

where GSD (app) = Approximated Memori-GSD value (absorption units). [HAc+FA] = the sum of measured concentrations of acetic and formic acids (µg/m³). This equation was used for the reporting in this work of the acidic effects as GSD values, or the concentration values of acetic plus formic acid are reported. Similarly, a dose-response equation for the influence of NO₂ and O₃ on the EWO dosimeter has been developed [23]. Thus, the photo-oxidizing impact can optionally be reported as EWO values calculated from measured concentration values of NO₂ and O₃ on the EWO dosimeter has been developed [23]. The results evaluation of the dosimeters is calibrated for a typical museum indoor temperature of 20 °C and relative humidity (RH) of 50%. The dosimeter is normally mounted in upright position. The holder then gives some sheltering against dust deposition. In indoor cultural heritage locations, the effect of dust during the recommended 3 months exposure has been found to be low. The explanatory power of the dose-response equation, which does not include dust impact, was about \( R^2 = 0.7 \) [23]. If the presence of dust is high or the dosimeter is exposed in horizontal position, lying down, dust can however accumulate on the dosimeter and affect the response.

In an indoor situation with a temperature (T) significantly different from 20 °C or RH significantly different from 50%, or with much dust, the dosimeter will respond to these factors and measure a higher risk value, and/or the object sensitivity may be different from that applied for the Memori traffic light evaluation (see below). The materials damage risk assessment was not calibrated towards these impacts. Thus, the occurrence and influence of such variations in environmental factors (T, RH and dust) on the dosimeter response, and on the risk evaluation, must be evaluated separately.

The acetic and formic acids were measured with passive pollution badge samplers. The gases diffuse through the net into the badge sampler (Fig. 3) and are absorbed.
from the air on an alkaline filter located at its base. Subsequent laboratory analysis gave the values for the concentrations of the acids in air. The detection limit has been found to be 0.5 µg/m³ [23].

The Memori assessment includes a “traffic light evaluation” of the measurement results, with indication of risk for degradation of 22 cultural heritage materials. The risk is described as the probable time before observable damage occurs and conservation is needed, with: “red” = within 3 years, “yellow” = from 3 to 30 years, and “green” = more than 30 years. General risk levels for cultural heritage, given as response values from measurements with the EWO and GSD, which are unrelated to the MEMORI “traffic light evaluation”, exist from pre MEMORI work. For the EWO these are described as different typical European indoor museum environments [23, 28]. For the GSD they are based on overall evaluation of results from dosimeter development and application [36]. These GSD levels can be approximated as acetic plus formic acid concentrations by Eq. (1).

Results
The values for the air quality measured in the locations in the National military museum and Tismana monastery are given in Table 1.

Much higher values of photo-oxidizing impact was measured in the contemporary history room in the main museum building of the National military museum than in the other locations. Much higher values of acetic and formic acids were measured in the storage rooms with the organic objects (icons and textiles, and books) in the Tismana monastery, than in the corridor outside of these rooms and in all the measurement locations in the National military museum. This is seen in Figs. 4 and 5.

A summary of the risk indications shown in the diagrams in Figs. 4 and 5, as provided by the Memori evaluation (see “Methods” section), for the measurement locations in the National military museum and the Tismana monastery are given in Table 2.

A comparison was then made in Fig. 6 with values measured in four seasons in 20 indoor museum locations (80 data points) over 1 year in the EU MASTER project, and arranged as “typical locations” in five categories (1 to 5) with decreasing air quality. For further description of the basis for this comparison, see [23].

The air quality risks in the National military museum were found to be moderate, generally comparable to typical European purpose built museum locations. The highest damage risk, more comparable to a historic house museum, was observed in the more open contemporary history exhibition room in the main museum building. The best situation was observed in a wardrobe in the warehouse for foreign uniforms, similar to a typical archive, storeroom or enclosure. A reduction in photo-oxidizing risk was measured in two of the enclosures, but a slightly higher level of acetic plus formic acidic was measured in all the three enclosures, as compared to the respective rooms. It was indicated that some observable change might happen to sensitive pigments and paper within 3 years, and to lead, copper and sensitive glass within 30 years, in the contemporary history exhibition room and showcase. Risk for observable change within 30 years, was indicated for lead, sensitive glass, sensitive pigments and...
paper in the other locations in the National military museum.

Relatively high concentrations of acetic and formic acids were measured in the air in the store rooms for icons and textiles, and books, in the Tismana monastery. The highest damage risk was found in the icons and textile room, where it was indicated that observable damage, which would require active conservation, was likely to occur to lead and sensitive glass within 3 years (“red”). For iron objects, sensitive pigments, varnish (Laropal A81, resin mastic and dammar) and paper, it was indicated that observable damage would take longer to develop in both locations, between three and about 30 years (“yellow”). The risk to paper and sensitive pigments was due to photo-oxidation rather than acidic impact. No lower threshold was identified by Memori for photo-oxidative impact on sensitive pigments, so this risk could probably not be totally avoided [6].

Discussion
Memori reporting based on dosimeter and/or parameter measurement methods
Differently from Eq. (1), the original statistical dose-response equation for the GSD dosimeter does not, include formic acid [23]. Formic acid is however a stronger acid than acetic acid and is known to have degrading impacts [4, 37]. In museum locations the presence of formic acid typically correlates with that of acetic acid, with a concentration of about 25% that of acetic acid, but with large variation [9, 11, 12]. Thus, in statistical treatments it is a risk that the formic acid effect is hidden by that of acetic acid, by co-correlation. The optional reporting in this work of Memori results with GSD values calculated from measured concentration values by Eq. (1), or directly with concentration values of acetic plus formic acid, rather than by the measured GSD dosimeter values, should give a closely similar evaluation, but it is not a direct parallel. Dosimetry of generic pollutant effects and parameter measurements are different.
approaches to risk assessment, with different qualities. The choice of measurement method could influence results, for example in situations with high temperature, humidity or dust levels. Dosimetry has the advantage of simultaneously assessing the combined impact of several environmental factors, whereas parameter measurements provide values for the concentrations in air of single air pollutants. The environmental degradation of complex objects is usually complex, and the sensitivities of the object and its materials are often uncertain. A Memori risk evaluation is therefore a risk indication, which usually needs further evaluation, specification and diagnosis if risk is identified (i.e. indicated).

Risk evaluation for the National Military museum and the Tismana monastery
The EWO-Memori dosimeter results indicated some damage risks to objects in the National military museum

Fig. 5 The measurement results for the locations in the National military museum and the Tismana monastery presented in the three remaining of seven (out of 22) Memori material risk evaluation diagrams, where some risk (red or yellow) were indicated (see the Fig. 4 caption)
in Bucharest, due to exposure to combustion pollutants, most likely NO₂ and O₃ ventilated indoor from traffic, and/or uv-light exposure and high temperature. This is very typical for central European city locations, as for example identified in a recent study with Memori measurements in cultural heritage locations centrally in London [32].

Still, all the measurement locations in the National military museum were found to be similar or better than typical European “historic house museums”. The observed reduction in the photo-oxidizing load and risk inside the enclosures in the Warehouse for foreign uniforms (1) and the contemporary history room in the main museum building (3) was an expected protective effect of the enclosures. The higher measured photo-oxidizing impact inside the wooden chest in the probative storage room (2) than in this room itself was thus surprising. This could be due to some unidentified oxidation impact, but probably more likely due to dust accumulation on the dosimeter glass, as the dosimeter was positioned horizontally besides rough textile materials (see Fig. 1, position 2b). Although dust accumulation was probably not a risk for the objects in this case, this points to the possible damage risks that may occur when co-locating sensitive objects with objects or materials which off-gas or release harmful substances. The slightly higher acidic impact measured inside all the enclosures than in the respective rooms in the National military museum is typical. It is well known that the levels of gaseous organic compounds are usually higher inside than outside of enclosures [9, 12, 38]. This is due to the larger emitting surfaces as compared to the volumes and usually lower ventilation rates of enclosures as compared to rooms. The small differences between the measured acidic impact in the enclosures and the rooms in the National military museum indicated little risk related to organic acid off gassing in the enclosures. This may be due to relatively low emitting materials and/or ventilation effects in the enclosures. The emission from materials is typically reduced as they age, and the aging of enclosures contribute to lower internal off gassing.

It seems that the most likely damages to develop in the National military museum in the short term (a few years) would be fading and colour change of pigments and surfaces, and embrittlement of paper. In the longer term (more than a few years), surface corrosion of metals could be expected. In this evaluation, it should be considered that surface corrosion of metal is very humidity dependent and that corrosion damage could appear

| Location | Risk indication (see also “Methods” chapter) |
|----------|---------------------------------------------|
| National military museum | Material damage |
| 1. Warehouse for foreign uniforms, room and wardrobe, and 2. storage room and wooden chest | Lead (A) |
| | Sensitive glass (A) |
| | Sensitive pigments (PO) |
| | Paper (PO) |
| 3. Main museum building, contemporary history room, in showcase and room | Sensitive pigments (PO) |
| | Paper (PO) |

Tismana monastery

| Location | Risk indication (see also “Methods” chapter) |
|----------|---------------------------------------------|
| Icons and textile room | Lead (A) |
| | Sensitive glass (A) |
| Book room | Lead (A) |
| | Sensitive glass (A) |
| Outside of rooms | Lead (A) |
| | Sensitive glass (A) |

Based on Figs. 4 and 5. “Red” indicates that damage is likely to occur to objects within 3 years and that the damage will require active conservation. “Yellow” indicates a situation in between “Red” and “Green” (“Green” indicates that within the constraints of present knowledge, it is unlikely that the materials will change significantly within a period of perhaps 30 years)

- A: acetic and formic acid; PO: photo-oxidation (Ozone, nitrogen dioxide and/or uv-light and temperature)
- Laropal A81, resin mastic, dammar
- Cotton linters, historical rag paper, lignin containing paper
faster at higher than 50% relative humidity. The museum
has many objects with such materials in exhibition and
in store. Improved protection from exposure to air from
outdoor and the consequent photo-oxidation could
potentially extend conservation intervals and reduce con-
servation costs for such objects. The present use of show-
cases and enclosures has this protective purpose, which
effect was verified by the measurements. Generally, some
possible mitigation measures to reduce this exposure risk
are: the moving of sensitive objects away from locations
most influenced by the outdoors such as entrances and
windows; avoiding exposure to light from outdoor; using
showcases for sensitive objects; keeping sensitive objects
in well closed and possibly conditioned store rooms; and
avoiding high and fluctuating temperature and humidity
conditions.

The indicated risk for acidic damage to metallic mate-
rials and sensitive (medieval) glass, and moderate risk
for varnishes, in rooms in the Tismana monastery, due
to exposure to acetic and formic acids, is expected in
relatively closed rooms with low ventilation and signifi-
cant emission especially from wood. The acidic atmos-
pheres could initiate and accelerate surface corrosion
on for example glass paintings and metallic objects. One
could consider if such objects should be moved from the
rooms. It would be beneficial to keep the rooms cool, and
ventilate the rooms under good (dry, cool) outdoor condi-
tions without producing dramatic climatic fluctuations.
As organic acid attack increases significantly at higher air
humidity (> ~ 60%), this would be especially important
to avoid [37, 39–41]. To most organic objects the acidic
atmospheres would be of little risk [6, 14]. A moderate
photo-oxidation risk was indicated for paper and sensi-
tive pigments. Such materials would be present in objects
in the icons and textile and the bookstore rooms. For
preservation in the long term additional protection of
such objects against exposure to light and outdoor air
would be beneficial, by similar methods as suggested
for the National military museum, for example by using
showcase or protective enclosures.

It is important to note that, in many cases, the sensi-
tivity of specific cultural heritage materials and objects
would be different from that applied in the MEMORI
assessment. Objects and surfaces are often complex
mixtures of materials that have already been subject to
change by environmental exposure. The exposure may
have produced damages and additional vulnerability, or
protective surface patinas. MEMORI is a tool, which sup-
plies an evaluation and ranking of air pollution risks. It
can give added information to conservators and assist in
efforts to improve the preventive protection of objects
in the most efficient way. Air quality measurements and
risk evaluation can lead the attention to situations of concern where further investigation of damages and damage processes should be performed. They do not replace the essential understanding of single objects, their materials and their vulnerability, which the conservators needs to apply.

**Conclusions**

Air quality measurements and risk assessment for cultural heritage materials were performed in the National military museum and the Tismana monastery in Gorj County in Romania, by applying Memori® methodology, dosimetry and passive pollution parameter sampling. Some risk was indicated for photo-oxidising damage to some types of sensitive materials in the National military museum in Bucharest. The highest risk for observable damage, which would need active conservation within 3 years, was found in a contemporary history exhibition room in the main museum building. The photo-oxidising damage risk in the room was evaluated to be similar to a typical European historic house. A moderate risk for observable damage, which would need active conservation within 30 years, was found in a warehouse, a storeroom and inside enclosures used in the museum, comparable to typical European purpose built museum locations. The materials most at risk were found to be sensitive pigments and paper. Some risk for damage to copper, lead, and sensitive glass was indicated. The risk could be reduced by measures to protect the objects against exposure to outdoor city air ventilated into the building, and against possible excessive light exposure and high and fluctuating temperature and humidity. The present use of protective enclosures has these functions. Significant risk for damage to some types of sensitive materials, due to exposure to an acidic atmosphere, was observed in the icons and textile room and book store room in the Tismana monastery. Materials at risk were found to be especially lead and sensitive glass, with some risk also for iron objects and varnish (Laropal A81, resin mastic, dammar). Some risk for photo-oxidation of paper and sensitive pigments was found. Sensitive objects could be moved out of rooms with high acid emissions, probably mostly from wood materials. It would be especially important to avoid high humidity situations with RH above ~ 60%, which accelerate corrosion. It would be beneficial to keep rooms cool. Rooms could be ventilated when the outdoor air is good (clean, dry and cool). Paper and objects with sensitive pigments could be moved into showcases or protective enclosures, or moved away from exposure to outdoor air and light.

**Abbreviations**

A: acidic; AQD: Air Quality Directive; EWO: early warning organic dosimeter; FA: formic acid; GSD: glass slide dosimeter; HAc: acetic acid; M: national military museum; PO: photo oxidizing; PPO: polyphenylenoxide; RH: relative humidity; T: Tismana monastery; VOC: volatile organic compound.

**Authors’ contributions**

OM did the measurement work, reporting from location and initial description of measurement locations. TG did the laboratory dosimeter preparation, laboratory measurements, organizing of the delivery of passive samplers and their analysis from the NILU laboratory, results data analysis, interpretation and development of the manuscript. Both authors contributed to finalizing the manuscript. Both authors read and approved the final manuscript.

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**Competing interests**

The authors declare that they have no competing interests.

**Availability of data and materials**

All equations and data necessary to calculate the model are given either in the text or in the cited references.

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