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Interpretation of climatic temperature variations for accelerated ageing models

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Using materials in new applications (in particular the built environment) requires that durability predictions be made. Often, the only way this can be done within economically favourable timescales is to use accelerated ageing tests. Extrapolating these tests to in-service temperatures requires that some average of the climatic temperature be used. The normally published mean temperature for a location does not in general adequately represent the time-temperature envelope and its use in calculations based on Arrhenius type relationships may lead to serious underestimation of degradation rates. This paper shows how an equivalent temperature, T^*, can be calculated from the numerical integration of a single annual temperature cycle, accounting for both daily and monthly temperature variations. The difference between the average temperature and T^* is shown to be strongly correlated to the daily and monthly temperature ranges, to be significant for most locations and sometimes as high as 10°C. © *2004 Kluwer Academic Publishers*

1. Introduction

As the pace of materials development increases and previously 'hi-tech' materials find wider applications, increasing use is being made of accelerated ageing rationales to estimate service lifetimes from relatively short tests. This is particularly true for relatively modern materials that are beginning to find uses in the built environment. In these applications, service lives of several decades are usually specified, thus accelerated tests which take as little time as possible to perform—but still provide user confidence—are required in order that time-to-market is minimised. Also, most built environment applications will be in the open air and thus exposed to relatively hostile conditions: high humidity and moisture, sunlight, cyclic temperature and so on. Use of materials in conjunction with cementitious composites (e.g., concrete, mortar) poses particular problems given their high alkalinity.

Accelerated ageing tests fall into two broad categories: 'Deemed-to-Satisfy' (DS) testing and predictive testing.

1.1. Accelerated ageing-DS testing

DS testing essentially involves subjecting samples of a material to a relatively harsh regime for a given time and subsequently testing the degradation of a certain property, usually strength. If the property has fallen by less than some pre-determined percentage, or retains the property above some specified level the material is deemed to have 'passed' and be fit for use. No estimation of likely service life is generally attached to the tests, which are for quality control. Examples of such tests include:

- application of dry heat (70, 100, 125 or 140°C) for up to 240 h and 100% relative humidity (RH) at 85, 105 or 120°C for up to 20 h (cellular polymeric materials) [1].
- ageing at elevated temperature (up to 300°C) in an air-circulating oven and in an oxygen pressure chamber at 70°C and 2.1 MPa, normally for up to 168 h (rubber) [2].
- Cyclic ageing, where each cycle involves 24 h immersion in water at 20°C, 30 minutes of forced drying in air at 70°C and 1 m s^{-1} airflow, 23 h in air at 70°C and 30 minutes of forced cooling in air at 20°C and 1 m s^{-1} airflow, for 10, 25 and 50 cycles (glass-fibre reinforced concrete) [3].

1.2. Accelerated ageing-predictive testing

Predictive testing rationales involve equating short periods of exposure to high 'load' (stress, temperature, pressure, acidity etc.) with longer periods of lower, in-service load. For example, regression analysis of log [pressure] vs. log [time to rupture] charts are used to predict maximum service pressures for oilfield pipelines [4]. However, by far the most common driver used in predictive accelerated ageing is temperature; short periods of exposure to high temperatures are equated to longer periods at lower, in-service temperatures e.g. room temperature or climatic temperature. Simple empirical relationships are sometimes used with materials that develop strength at a temperature dependent rate. Strength development in concrete at unusual temperatures is predicted using 'maturity', the product of time and the number of degrees Celsius above a datum temperature of −10°C [5] e.g., concrete cured for

28 days at 15°C should reach the same strength at 40°C after only 14 days. Another widely used 'chemist's rule-of-thumb' is that a change in temperature of 10°C effects a factor of two change in the rate of a process; thus the life of a lubricant might be expected to double if used in an operating environment 10°C lower than usual [6]. Other investigators use an equivalence factor α, usually expressed in decades per °C, to account for temperature. For rupture of polyethylene pipes, $\alpha = 0.11$ decades $^\circ\mathrm{C}^{-1}$ is used, meaning that a pipe intended to last 50 years must survive an accelerated test for $50/(10^{[20\times 0.11]}) = 0.315$ years (2764 h) at 20°C above its intended operating temperature [4]. This is sometimes called the time-temperature superposition method.

1.3. The Arrhenius relationship

All these methods are simplifications of a more general relationship between the rate of a process and temperature known as the Arrhenius relationship, which assumes that the rate of change of a given property x is related to temperature T by activation energy E, expressed in kJ mol^{-1}, such that;

$$\frac{\mathrm{d}x}{\mathrm{d}t} = Ae^{[\frac{-E}{RT}]} \tag{1a}$$

$$x = Ae^{[\frac{-E}{RT}]}t + x_0 \tag{1b}$$

where A is a constant, R is the universal gas constant (8.3145 kJ kmol^{-1} K^{-1}) and x_0 some initial value of x. For example, at temperatures of between −50°C and +100°C, the 'chemist's rule-of-thumb' actually corresponds to an activation energy of about 48 kJ mol^{-1}; the $\alpha = 0.11$ decades $^\circ\mathrm{C}^{-1}$ used in pipe rupture studies [4] corresponds to about 170 kJ mol^{-1}.

The Arrhenius relationship has been used to predict temperature-accelerated degradation in many fields including pharmaceuticals, insulation, adhesives and batteries and a summary of sources was given by Nelson [7]. The key assumptions in simple application of the Arrhenius model are that the same process controls degradation at both elevated and in-service temperatures, and that this single process continues to control degradation throughout the service life of the material. If these assumptions hold, then a value of E can be determined from experiments and/or service data over a range of temperatures and used to predict degradation or service life at a 'new' temperature.

The normal way that time-temperature degradation data is treated is to form Arrhenius plots or 'thermal endurance graphs' [8] which have the reciprocal of the absolute exposure temperature plotted as the abscissa and a rate parameter as the ordinate. The rate parameter may be derived in various ways. For ageing of unreinforced plastics, the rate parameter used is the time taken to reach an 'end-point criterion', usually half the original property value. Activation energies are not reported directly, but in terms of temperature indices, defined as the temperature that would cause a sample to reach the end-point criterion in 2×10^4 h, and halving intervals, the temperature increase required to halve the time taken to reach the endpoint criteria [8].

Some authors have proposed that this approach should be adopted as a standard protocol for predictions of long term properties of fibre-reinforced plastics (FRP) used in built environment applications [9]. They note that the property chosen as a degradation metric will reflect a particular degradation mechanism. Longitudinal tensile strength (LTS) is a primary degradation indicator for the fibres (with some contribution from the interface) while the longitudinal short beam shear strength (LSBSS) is a primary degradation indicator for the interface (with some contribution from the matrix). As well as LTS and LSBSS, it is suggested that the variation of longitudinal tensile modulus and glass transition temperature with time and temperature are a minimum subset of properties that should be included in accelerated ageing testing. Ageing—immersion in hot deionised water—is carried out for between 7 and 224 days at temperatures dependent on the glass transition temperature of the polymer matrix. It is suggested that property retention as a percentage is reported for projected lifetimes of 1, 10, 25, 50 and 75 years at 23°C, or lifetimes predicted for property retention of 50, 60, 75 and 90%. Arrhenius extrapolation, from 40, 55 and 75°C tests to a service temperature of 25°C, has also been used to predict the degradation of FRP recycled plastic components used underground [10]. There is some evidence [11] that although Arrhenius extrapolation is valid for short-term tests, in certain environments the rate of degradation can increase with time after an apparent induction period of around 200 days. This was attributed to leaching of alkaline components from the glass increasing the pH of the interfacial region and accelerating its breakdown. In general, such a phenomenon is described by modifying Equations 1a and b thus;

$$\frac{\mathrm{d}x}{\mathrm{d}t} = Ae^{[\frac{-E}{RT}]}t^{\beta} \tag{2a}$$

$$x = \frac{A}{\beta + 1}e^{[\frac{-E}{RT}]}t^{\beta+1} + x_0 \tag{2b}$$

In this case, $\beta > 0$; for $\beta < 0$, degradation slows down with time (e.g., due to the formation of a protective layer as with aluminium in air).

The use of accelerated ageing has become widely accepted for use with glass-fibre reinforced concrete (grc); it was recognised very early in its development that some degradation of strength and toughness was inevitable given the alkaline nature of the matrix and that credible predictive models were required. Early models [12, 13] were similar to those above with the rate parameter being defined as the ratio between the time taken for a fixed degree of degradation to occur at a given temperature and the time taken to observe a similar degree of degradation at a reference temperature of 50°C. Ageing was carried out in hot water at various temperatures. Results from bending tests on coupons and 'SIC' tests (strand-in-cement, where a single strand or tow of fibre, encased in a cement plug, is tested in tension to failure), having proved to be very similar, were pooled. Data from a number of natural weathering sites were also included. Results were presented and applied in terms of acceleration factors rather than service life predictions, e.g., 1 day of immersion in water at 50°C induced a strength loss equivalent to that induced by ≈100 days of weathering in UK climatic conditions. An activation energy for the strength loss process was also derived (89–93 kJ mol^{-1}).

A more recent model [14] differs slightly in that degradation of strength is modelled as being caused by slow, sub-critical growth of surface flaws on the fibres. By assuming that the growth rate of these flaws remains constant for a given temperature and combining standard expressions governing flaw size, fibre strength and composite strength, a relationship for normalised composite strength (i.e., strength as a fraction of original strength) S vs. time was derived;

$$S = \frac{1}{\sqrt{1 + kt}} \tag{3}$$

This was then fitted to a wide range of new and existing strength vs. time—temperature data. To derive service lives, the proportionality constant k was used as the rate parameter i.e., S was expressed as Equation 4

$$S = \frac{1}{\sqrt{1 + k_0 e^{[\frac{-E}{RT}]} t}} \tag{4}$$

(note k_0 is analogous to A in Equation 1) and an activation energy similar to those derived previously [12, 13] was found to apply. Differences in the durability characteristics of grcs with first- and second-generation alkali resistant fibres were attributed to changes in the pre-exponential term k_0. Current work [15] is further investigating the degradation characteristics of modern grc formulations with modified matrices, for which the acceleration factors previously advanced [12, 13] and still in use [e.g., 15] may not be valid.

Some attempts have been made to unify models for FRP and grc [16] and investigations continue. Their success will depend on whether fibre or matrix deterioration proves to be the dominant degradation mechanism in FRP used in built environment applications and whether the model can be modified to encompass FRP-specific effects e.g., those embodied in Equation 2. A more rigorous treatment of the application of Arrhenius relationships to accelerated testing and stochastic reliability of components was advanced by Meeker and co-workers [17].

2. Climatic ageing

All the approaches above assume that the temperature remains constant with time. Although this is generally the case during accelerated ageing tests, the in-service temperature for a component (particularly in built environment or infrastructure applications) will very often vary with climatic conditions. Previously, most investigators have simply used the average temperature at the site of interest in calculations [e.g., 12, 13], specified a constant service temperature [e.g., 9, 10] or implied that service temperature would be constant. The purpose of this study is to assess the likely magnitude of the error in such an assumption and how such inaccuracies might be avoided.

In general, an equivalent temperature T^* can be derived to better represent the temperature profile of a given location. Recognising that $T = f(t)$, we can amend Equations 1a and b thus;

$$\frac{\mathrm{d}x}{\mathrm{d}t} = Ae^{\frac{-E}{R \cdot T(t)}} \tag{5a}$$

$$x = \int Ae^{\frac{-E}{R \cdot T(t)}} \cdot \mathrm{d}t + x_0 \tag{5b}$$

Thus we see that for a constant temperature to have effected a similar level of degradation as a varying temperature regime after any given time t, Equation 6 must be satisfied;

$$e^{[-E/RT^*]}t = \int_0^t e^{[-E/R \cdot T(t)]} \cdot \mathrm{d}t \tag{6}$$

A relationship of slightly different form (expressed with T as the independent variable and involving a temperature frequency function) has previously been suggested for assessing degradation of solar absorber coatings [19].

Rearranging, for a given temperature regime $T(t)$,

$$T^*(t) = \frac{-E}{R \cdot \ln\left(\frac{1}{t} \cdot \int_0^t e^{[-E/R \cdot T(t)]} \cdot \mathrm{d}t\right)} \tag{7}$$

Equations of this sort are awkward to solve analytically, but given that $T(t)$ for most locations, whilst difficult to model continuously, is explicitly known in terms of monthly maximum, average and minimum temperatures, numerical solutions are appropriate and straightforward to apply. Fig. 1 plots T^*_m (T^* calculated using monthly temperature data to formulate $T(t)$ i.e., a numerical integration of $e^{-E/RT(t)}$ using a 1-month timestep over 20 years) vs. time, using typical climate data [18] for Osaka, Japan as an example. It is clear that the difference between T_a and T^*_m is a potentially significant

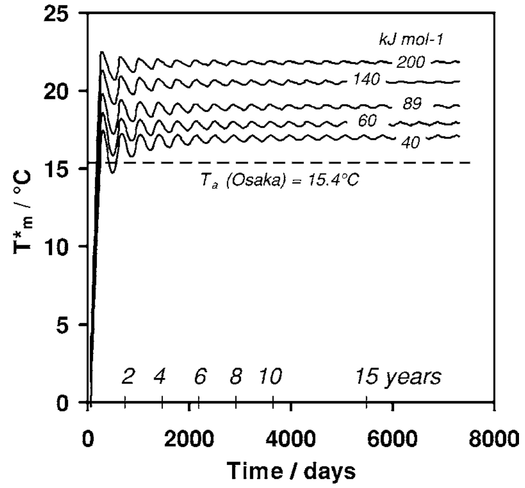

Figure 1 Variation of equivalent temperature (calculated using monthly data) T^*_m vs. time and activation energy for Osaka, Japan.

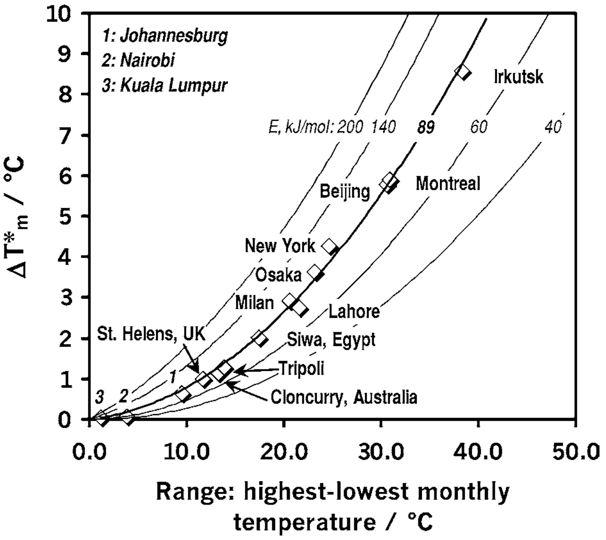

Figure 2 Temperature correction caused solely by monthly temperature variation ΔT^*_m vs. range.

source of error, which increases with activation energy. After about two years, T^*_m essentially stabilises to a single value. We can derive the equivalent stable value of T^* without integrating over long time periods. Recognising that $T(t)$ is periodic, with period L, it follows that $e^{[-E/R\cdot T(t)]}$ must have an identical period and thus at $t = nL$ (where $n = 1, 2, 3\ldots$) it can be shown that

$$T^* = \frac{-E}{R\cdot\ln(I_0/L)};\quad I_0 = \int_0^\mathrm{L} e^{[-E/R\cdot T(t)]}\cdot \mathrm{d}t \qquad (8)$$

Thus $T(t)$ need only be integrated over a single cycle to obtain I_0 (the area under a single cycle i.e., year of the time-temperature graph), rather than over a long period, to derive T^*.

The main factor that affects T^*_m, or more importantly the difference ΔT^*_m between T^*_m and the climatic average T_a, is the extent of variation in temperature throughout the year. Clearly, if the temperature varied very little throughout the year then Equation 5 would be closely approximated by Equation 1 and ΔT^*_m would be small. Fig. 2 shows, for various localities, the strong correlation between ΔT^*_m and the *range* (difference between the highest and lowest average monthly temperatures, an easily obtainable measure of the extent of local temperature variation). The relationship is well represented by a 2nd-order polynomial although for practical purposes a linear relationship with an appropriate intercept on the X-axis would probably suffice. The points were calculated using an activation energy of 89 kJ mol^{-1} (i.e., that for grc ageing) but the variation of the relationship with activation energy is also shown.

2.1. Daily temperature variations

Daily temperature variations would also be expected to affect the discrepancy between T_a and T^*. Although specific daily temperature predictions are not feasible, monthly average maximum (i.e., 'midday') and minimum (i.e., 'midnight') temperatures [18] are reasonably accurate and can be used to superimpose a daily cycle on the monthly temperature variation. The approach given above was modified by changing the time-step from 1 month to 0.1 days and assuming a sinusoidal daily variation between the minimum and maximum temperature for each month as shown for the first 60 days of such a model, using the data for Milan, in Fig. 3. The parameter ΔT^*_d was derived such that $T^* = T_\mathrm{a} + \Delta T^*_\mathrm{m} + \Delta T^*_\mathrm{d}$ i.e., equivalent temperature equals the climatic average plus the monthly correction plus the daily correction. It is plotted in Fig. 4, with activation energy as Fig. 2, vs. the daily range (average maximum temperature minus average minimum temperature). The correlation is poorer than for ΔT^*_m (Fig. 2) but the trend remains; the correction increases with increased range of temperature. The daily range correction ΔT^*_d is smaller than the monthly correction, since its sensitivity to range is smaller and the daily range variation is smaller (up to 15°C cf. 50°C). It does appear to be more sensitive to changes in activation energy. For the majority of climates, ΔT^*_d is less than 1°C over a wide range of activation energies.

2.2. Combined correction

Fig. 5 shows the combination of the monthly and daily corrections, T^*, vs. a 0.33:0.67 weighted average of the daily:monthly ranges (since the monthly correction is about twice the daily for a given range). The correlation to a 2-degree polynomial is reasonable although not as good as that for T^*_m. The variation of T^* with activation energy for a given range is approximately linear, i.e., doubling E will double T^* (although over a larger scale of E the relationship is logarithmic).

To test whether the error in using T_a is appreciable in practice, the Arrhenius plot for the largest data set in the current investigations [14, 15] into grc ageing (i.e., that for second-generation fibre/ordinary Portland cement matrix grc) was reformulated using T^*. The squared Pearson correlation coefficient R^2 was computed for

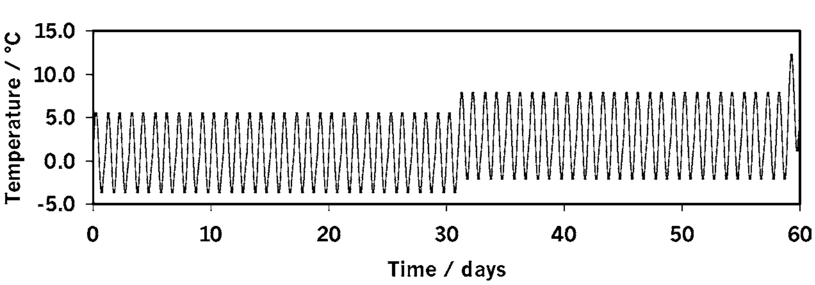

Figure 3 Superimposition of daily and monthly temperature variations; data for Milan, Italy.

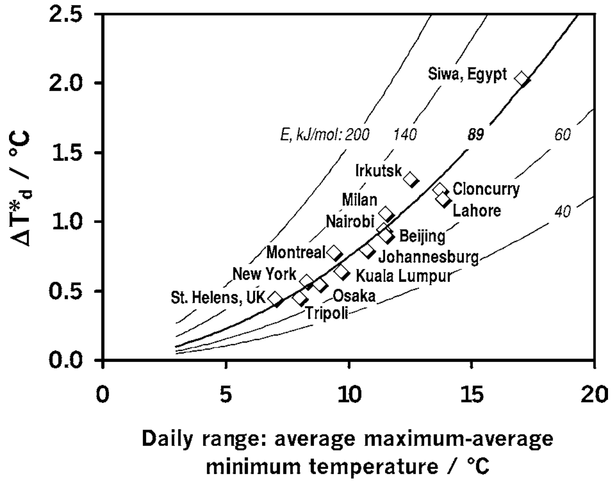

Figure 4 Temperature correction caused solely by daily temperature variation $\Delta T_{\mathrm{d}}^{*}$ vs. daily range.

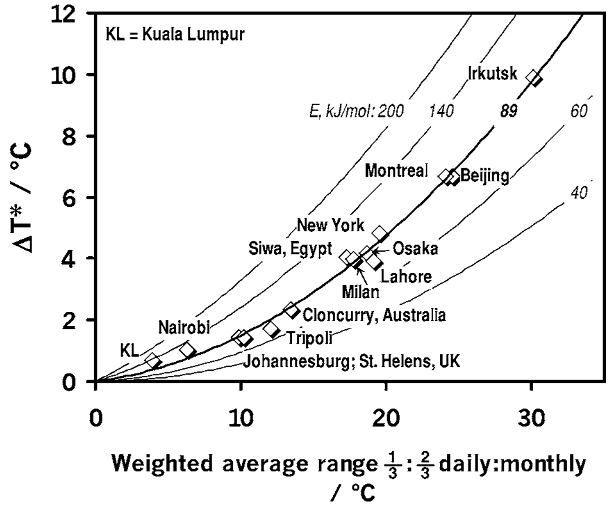

Figure 5 Combined temperature correction ΔT^{*} vs. weighted average of daily range and range.

the best least-squares fit straight line to the ln k vs. $1/T$ data and was slightly improved by using T^{*} instead of T_{a}. This suggests that using T^{*} at least equally well represents the natural weathering data. The values returned for activation energy and pre-exponential term were both increased by around 5%.

3. Discussion

It is clear that interpreting climatic ageing (or indeed any other process in which the temperature varies with the climate) by simply using an average temperature in calculations could lead to significant errors depending on the location in question. The locations shown on Figs 2 and 5 were chosen to represent the spread of daily and monthly temperature ranges rather than for geopolitical importance e.g., Siwa in Egypt has the largest daily temperature range and Irkutsk in Russia the largest monthly range, while in Nairobi both measures are small. The discrepancy between T_{a} and T^{*} can be as large as 10°C in extreme climates; returning to the 'chemist's rule of thumb', this would mean that a degradation process might well proceed twice as fast as predicted.

For example, in Beijing $T_{\mathrm{a}} = 11.8°\mathrm{C}$ yet $T^{*} = 18.5°\mathrm{C}$. The predicted service life of a grc component (assuming a critical strength of 50% i.e., $S = 0.5$ in Equation 4 and $E = 89$ kJ mol^{-1}) calculated using 11.8°C would be about 90 years, while using 18.5°C it would only be about 40 years. In the pipe rupture service life test [4], for a location where ΔT^{*} is 3°C, a reasonable value for a North European climate, using T_{a} instead of T^{*} would underestimate the test time required to validate service life by a factor of 2, with possible serious consequences.

Perhaps more importantly, the discrepancy is significant (i.e., $> 1°\mathrm{C}$) for all climates except in some tropical or equatorial regions. Thus virtually all studies which seek to simplify their analysis by collapsing a climatic temperature envelope onto a single temperature value need to consider evaluation of T^{*} or a similar parameter for accurate work. Although such a parameter can be estimated with reasonable accuracy from Fig. 5, for critical work it should be directly calculated from Equation 9 for the location in question. The integral of the combined daily/monthly temperature envelope can be computed to sufficient accuracy using any commercial spreadsheet package. The ease with which this can be accomplished and the ready availability of the requisite climatic data, is such that more complex approaches, e.g., analysing the Fourier series components of $T(t)$, is not warranted.

Equation 9 can also be used to assess the accuracy of accelerated ageing or other data obtained under less-than-perfect temperature control. Most ageing standards or procedures specify the tolerance to which temperature must be controlled, frequently ±2°C [e.g., 1, 3] but sometimes up to ±5°C. A sinusoidal variation of ±2°C superimposed on a 20°C baseline, applied to a 89 kJ/mol process, will cause it to be accelerated by 2% cf. a constant 20°C; at $60 \pm 5°\mathrm{C}$, the acceleration is over 5%. In the context of the relevant standards, this is not often a problem since the times involved are relatively short (typically thousands of hours). Cause for concern is generated when these temperature regimes are, by analogy with existing standards, used as the basis for longer-term tests.

4. Conclusions

Using average temperature values to represent climatic exposure conditions within models that extrapolate from accelerated ageing data using Arrhenius relationships can lead to serious errors, in particular underestimation of degradation rates. An 'equivalent temperature' T^{*}, derived from the integral of a single cycle of the periodic temperature-time curve, can be computed that more accurately represents the temperature envelope for a given location. The difference ΔT^{*} between T^{*} and the average temperature correlates well with a weighted average of the daily and monthly temperature ranges, being more sensitive to the latter. Depending on the activation energy of the process under study, ΔT^{*}

is significant (>1°C) for most climates and can be as high as 10°C.

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