Natural Weathering of Polymers – Dose-Response-Functions of Air-Pollution Effects for Service Life Prediction

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Goals

The mapping of air pollution effects on materials shall depict the deterioration potential of air pollution and the resulting economic damage. Therefore the dose-response functions for the deterioration caused by environmental effects have to be determined.

On the basis of the mapping results effective and cost efficient decreasing and diminishing strategies for air pollution could be developed and concluded.

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Method for economic damage evaluation

Air pollution concentrations, acid rain, dose-response-functions

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Climatic Data ➡ **Damage ΔZ**

↓

Critical Damage Z_{krit} ➡ **Surface Fraction**
Δa = ΔZ / Zkrit = 1 / t

↓

Material Surface O ➡ **Additional Restoration Areas O * a**

↓

Area Specific Restoration Costs ➡ **Economic Damages**

Investigated Materials

1. **Polyurethane PUR (car spoiler)**
2. **Polyvinylchloride PVC (window frames)**
3. **Fiber Reinforced Polyester PES-GFK (roofs, boats)**
4. **Alkyd resin based Lacquer (metal protections)**

Criteria for Investigation:

1. Long using time
2. Application in urban areas
3. Large economic relevance
4. Different application areas and branches

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Polyurethane PUR (Car spoiler)

Two component polyurethane lacquer; The PUR-specimen is designed with a black substrate material (PUR) and a painted white PUR-lacquer. The lacquer system is a light-grey base lacquer and a alpine white, high glossy finishing lacquer.

Polyvinylchloride PVC (window frames)

Additional to the base polymer a lot of additives are added: stabilizers, emulators, fillers, pigments, UV-absorber and modifiers.

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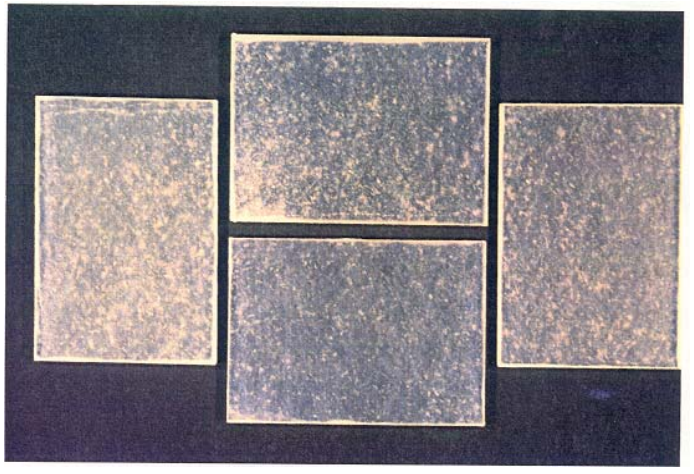
Fiber Reinforced Polyester
PES-GFK (roofs, boats)



A low viscose, middle reactive polyester resin (Basis Palatal 5).
With tailored additives the material get good optical and mechanical properties.
The specimen have seven fiber fleece layers.

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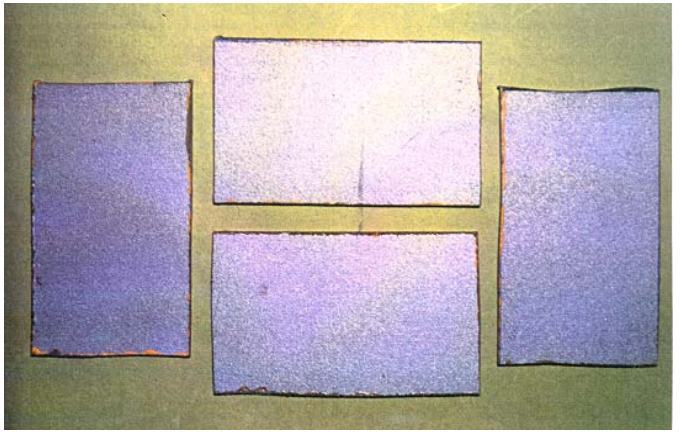
Alkyd resin based lacquer (metal protection)

Corrosion protection lacquer for metal surfaces.
The specimen have a 2 mm thick steel plate with a ground layer and a alkyd resin based lacquer.



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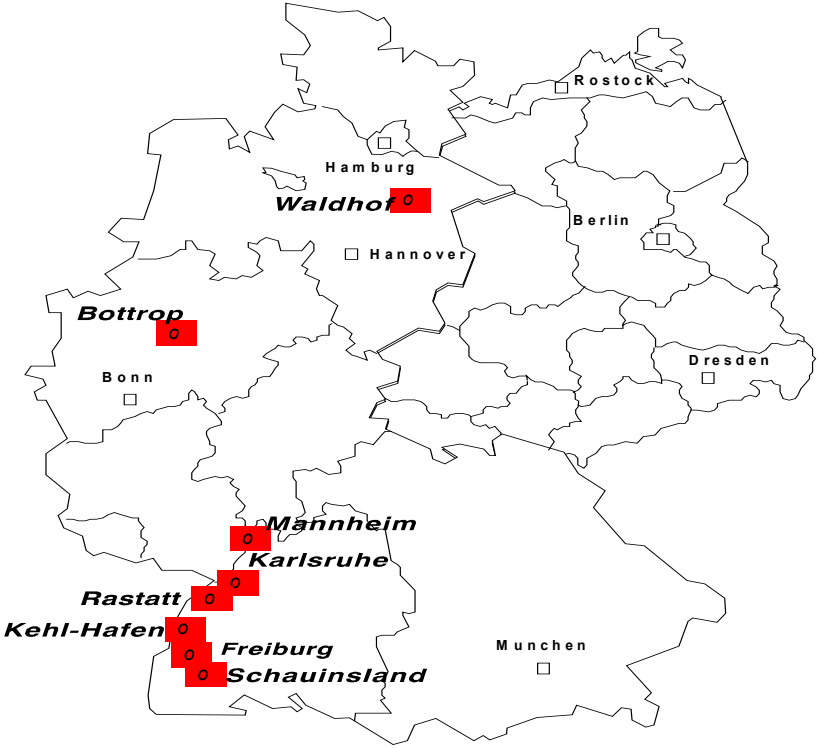
Natural weathering station with test rack and air pollution and climatic measurement station (Rhine harbor Kehl)

Locations of the natural weathering stations



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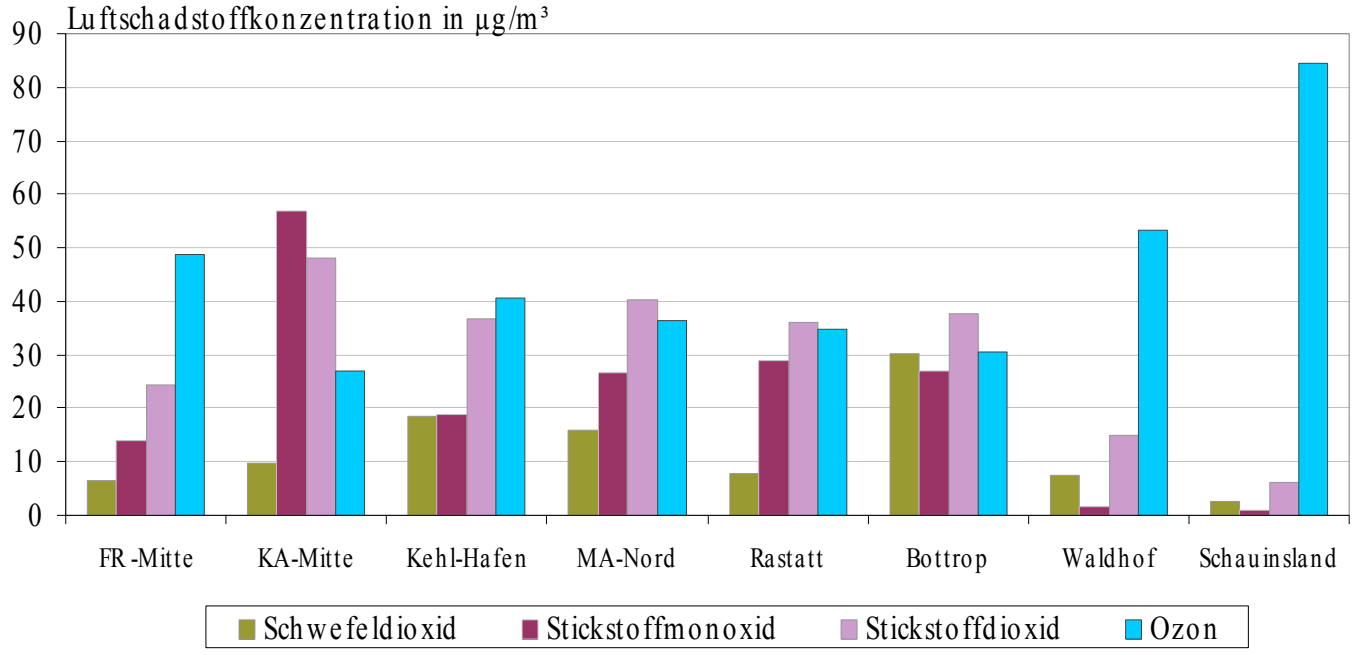
Averaged Air Pollution Concentration (05.92-04.00) at the Natural Weathering Locations



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Dose-Response-Functions of Air-Pollution Effects for Service Life Prediction

Morphological
- Microscopy on Cuts and Grindings
- Scanning Electron Microscopy

Mechanical
- Surface Hardness
- Tear Resistance
- Elongation at Break

Optical
- Visual Inspection
- Color Change
- Surface Roughness

Analytical
- FT-IR-Spectroscopy
- Mol-Mass-Distribution

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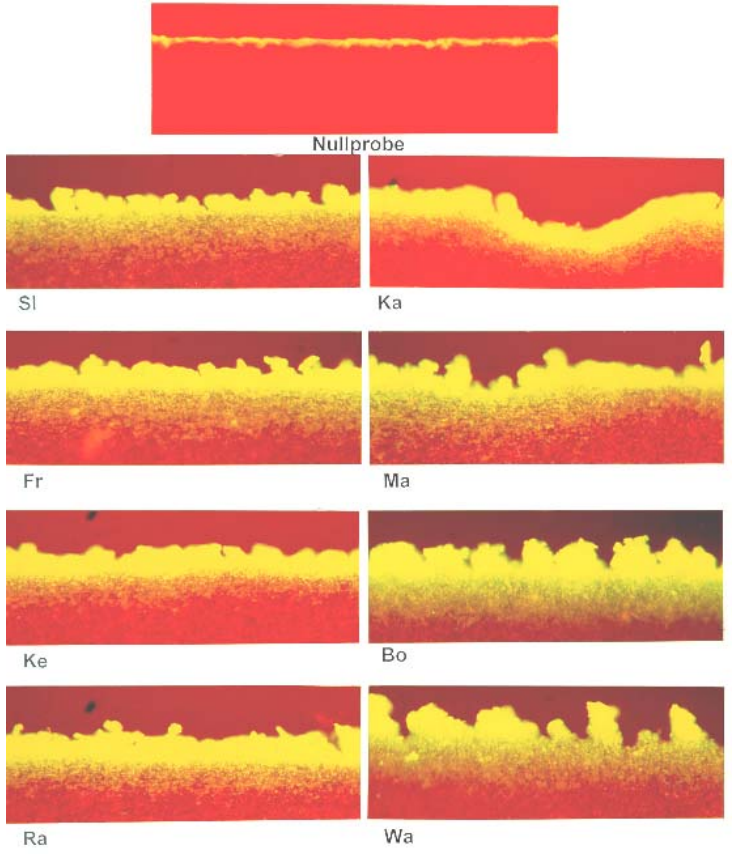
Dose-Response-Functions of Air-Pollution Effects for Service Life Prediction

Microtome cuttings of 8 years natural weathered PVC – specimen

(after a dying process with acridine orange)

(Enlargement 520:1)



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Dose-Response-Functions ?

Material Property = Fkt (t, Hglob, U, T, $[SO_2]$, $[NO_X]$, $[O_3]$, N ...)

t	**= Exposition time**
Hglob	**= Radiance**
U	**= Relative humidity**
T	**= Temperature**
$[SO_2]$	**= Concentration of sulphur dioxide**
$[NO_2]$	**= Concentration of nitrogen dioxide**
$[O_3]$	**= Concentration of ozone**
N	**= Amount of rain (acid rain)**

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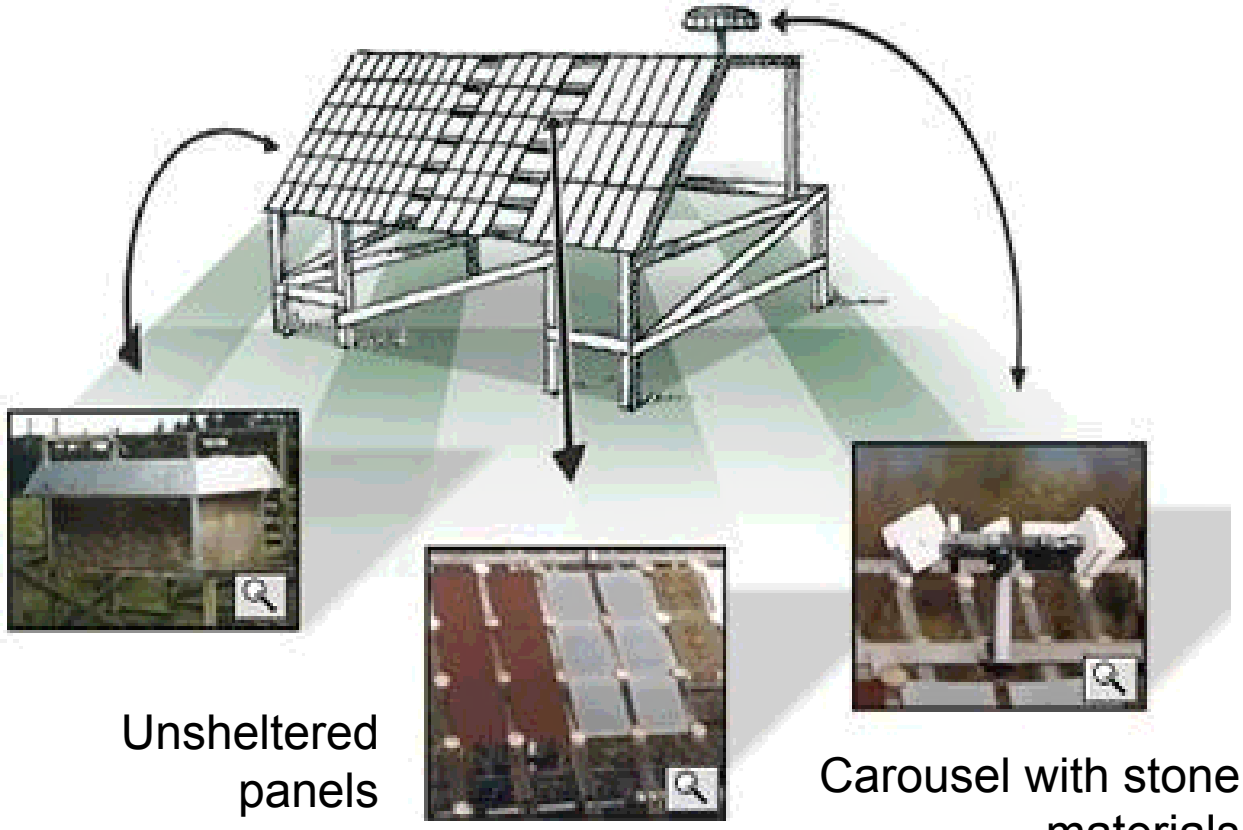
UN ECE ICP Materials

Sheltering box containing panels, carousels with stone materials and aluminium box with the electric contact materials



Unsheltered panels

Carousel with stone materials

Quelle: Tidblad

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Dose-Response-Functions for Metals

K = dry (T, Rh, [SO2], [NO2], [O3], t) + wet (Rain, [H^+], t)

Where K is the corrosion rate,

T is the temperature in degree C,
Rh is the relative humidity in %,
[Gas] is the concentration in µg/m^3 (SO2, NO2 and O3),
t is the weathering time in years,
Rain is the amount of rain and precipitation in mm and
[H^+] is the measured value correlated to the acid rain mg/l.

(Source: Tidblad et. al)

Dose-Response-Functions for Polymers

1. Step:
According Guillet et. al. /Rabek/ it is possible to assume for the surface material properties of a polymer a proportional effect to the incoming global radiation, cause the possibility of a chain scission is proportional to the amount of incoming photons.

$$MP \sim P1 \cdot G \cdot t^{P2}$$

G = radiance [W/m²]
t = exposition time
MP = Material Property
P1, P2 = Parameters

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Dose-Response-Functions for Polymers

2. Step:
Additional to the photo-inducted ageing the influence of the humidity, precipitation and air pollution lead to a damage of the polymer. During the life cycle the polymer product takes up water vapor and gases till the saturation level is reached by constant environmental conditions. In alternating environmental conditions the penetration depth PD of gases and water vapor is dependent from the periodicity Tp of the parameter and the temperature dependent diffusion coefficients $D_i(T)$

$$PD \sim (D_i(T) \cdot Tp/\pi)^{1/2}$$

$$MP \sim P_1[Gas_1]t^{P1}(D_1(T)T_1/\pi)^{1/2} + \ldots + P_N[Gas_N]t^{PN}(D_N(T)T_N/\pi)^{1/2}$$

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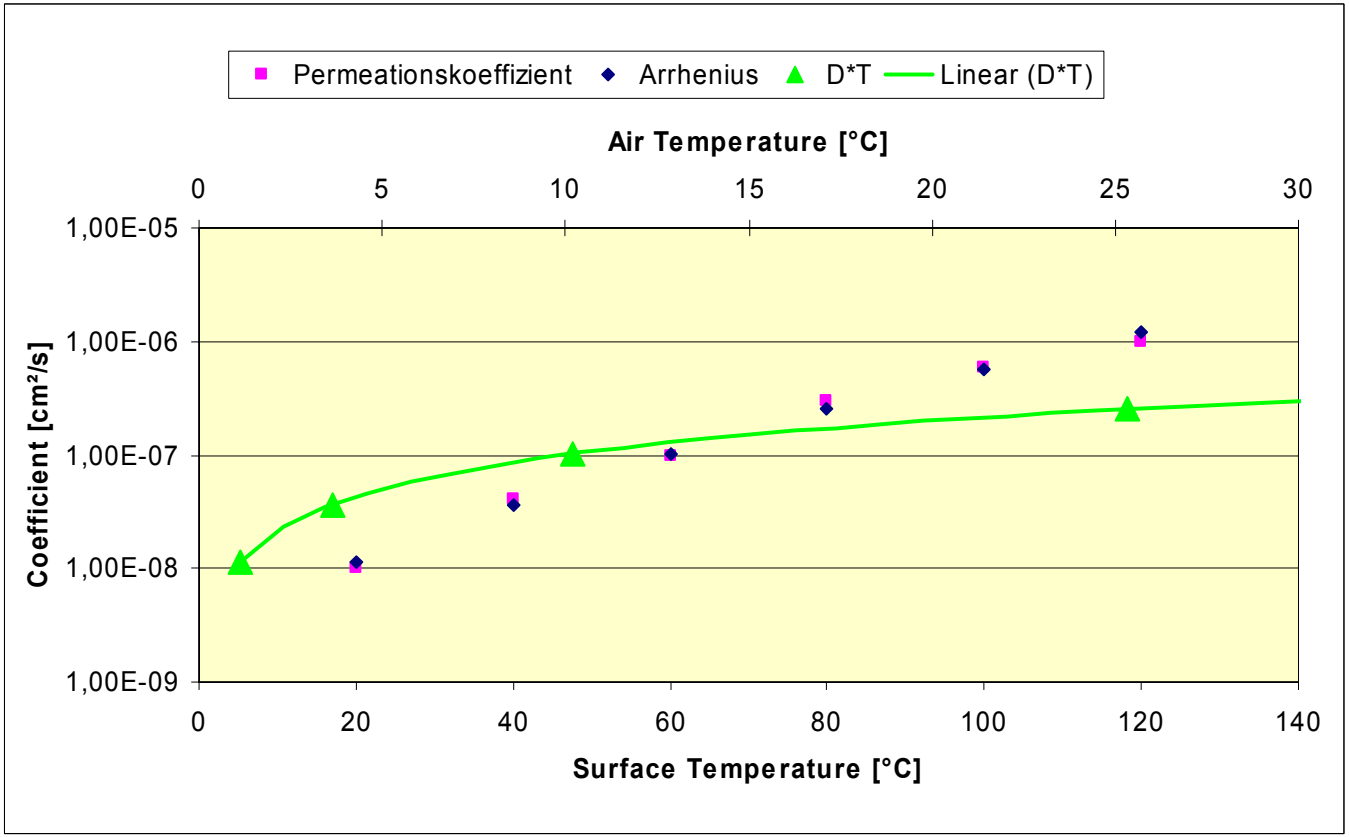
Dose-Response-Functions of Air-Pollution Effects for Service Life Prediction



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Damage depth of PUR

$$\text{Penetration depth in PUR} = 0{,}5777 + 0{,}4900 \cdot (G \cdot t)^{1/2} + 0{,}0253 \cdot (10^{-9} \cdot T \cdot 10^{8}/\pi)^{1/2} \cdot rH \cdot t + 0{,}0184 \cdot (10^{-9} \cdot T \cdot 10^{8}/\pi)^{1/2} \cdot [NO_2] \cdot t + 0{,}0122 \cdot (10^{-9} \cdot T \cdot 10^{8}/\pi)^{1/2} \cdot [O_3] \cdot t$$

With: Penetration depth in PUR in µm

G =	radiance (averaged annual value in W/m²)
t =	exposition time in years
T =	averaged annual air temperature at location (in °C)
rH =	averaged annual relative humidity at location (in %)
$[NO_2]$ =	averaged annual concentration for NO2 in µg/m³
$[O_3]$ =	averaged annual concentration for Ozone in µg/m³

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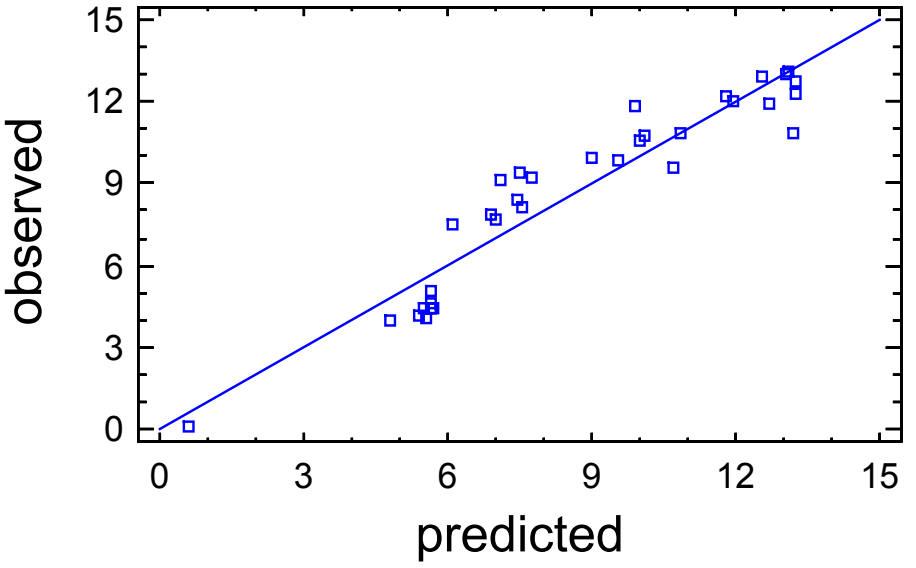
Damage depth of PUR



R^2 = 89,60 %

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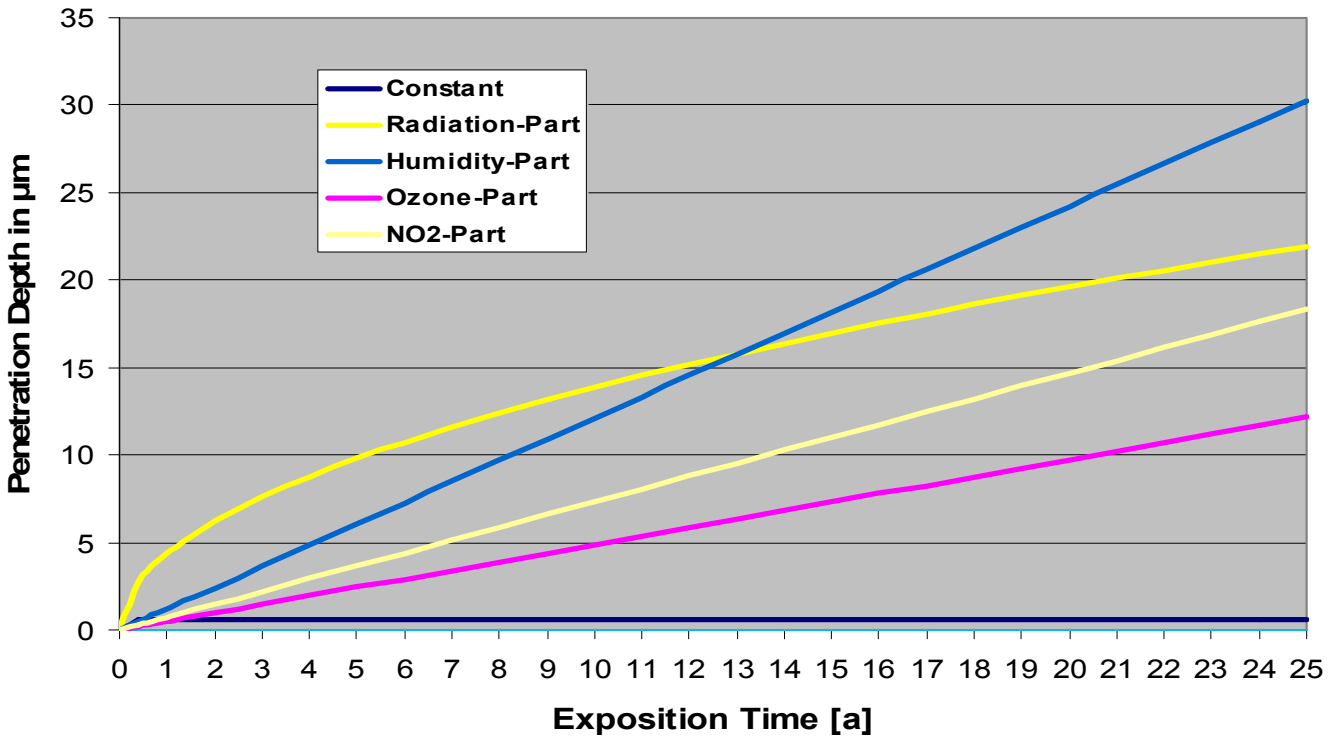
Damage depth of PUR



T = 20°C
rH = 60%
NO_2=50 µg/m³
SO_2=40 µg/m³
O_3 =50 µg/m³

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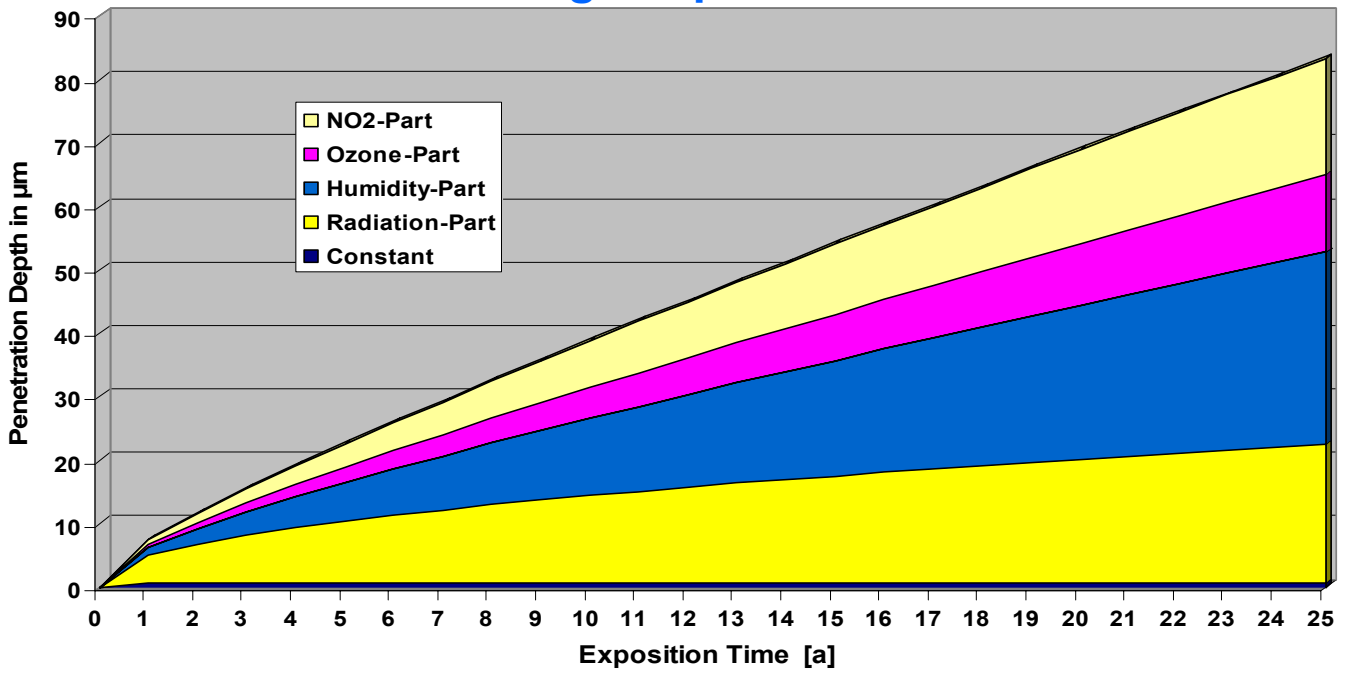
Dose-Response-Functions of Air-Pollution Effects for Service Life Prediction

Damage depth of PUR



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Color Change of Polyester GFK

$$\text{Delta E} = 0{,}4383 + 0{,}5979 \cdot (G \cdot t^{0{,}4})^{1/2} + 0{,}0354 \cdot (10^{-9} \cdot T \cdot 10^{8}/\pi)^{1/2} \cdot rH \cdot t^{0{,}65} + 0{,}0064 \cdot (10^{-9} \cdot T \cdot 10^{8}/\pi)^{1/2} \cdot [SO_2] \cdot t^{0{,}65} + 0{,}0195 \cdot (10^{-9} \cdot T \cdot 10^{8}/\pi)^{1/2} \cdot [O_3] \cdot t^{0{,}65}$$

With: Delta E (without dimension)

G =	radiance (averaged annual value in W/m²)
t =	exposition time in years
T =	averaged annual air temperature at location (in °C)
rH =	averaged annual relative humidity at location (in %)
$[SO_2]$ =	averaged annual concentration for SO2 in µg/m³
$[O_3]$ =	averaged annual concentration for Ozone in µg/m³

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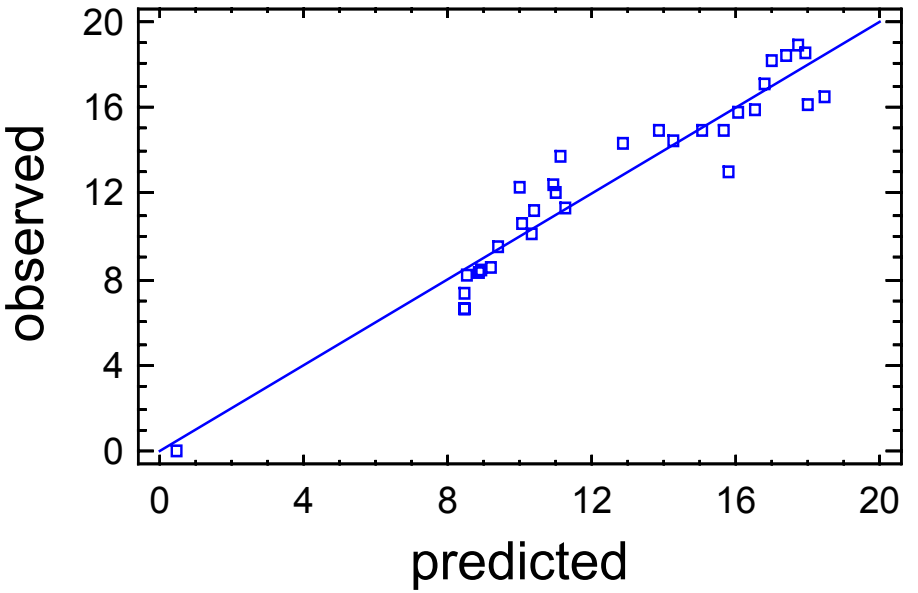
Color Change of Polyester GFK



R^2 = 91,68 %

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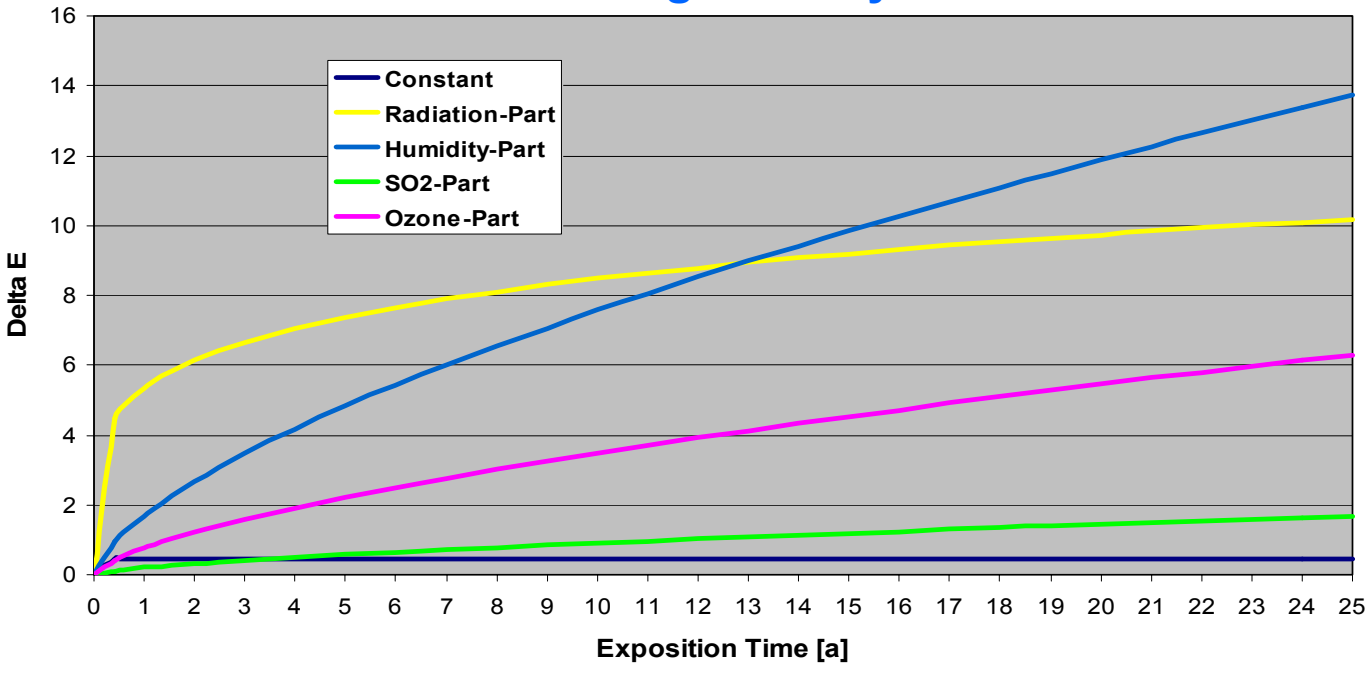

T = 20°C
rH = 60%
NO_2=50 µg/m³
SO_2=40 µg/m³
O_3 =50 µg/m³

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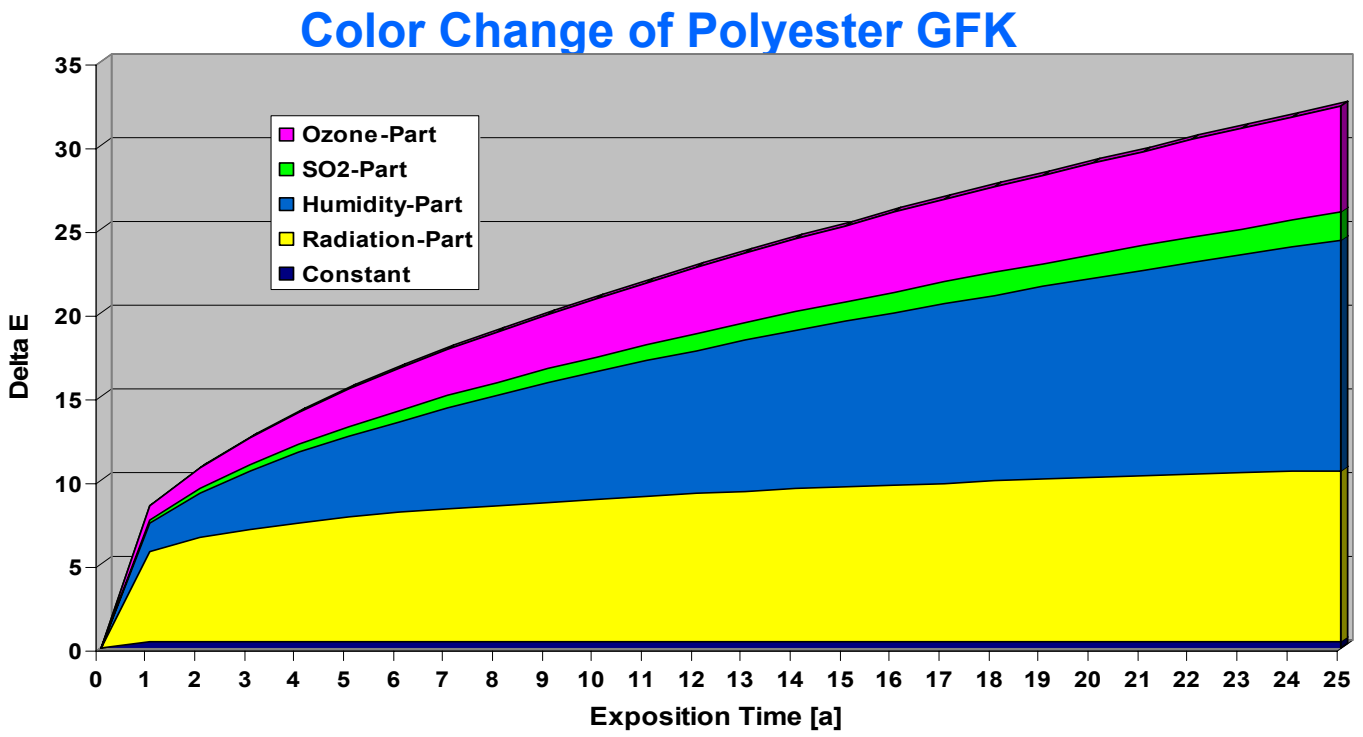

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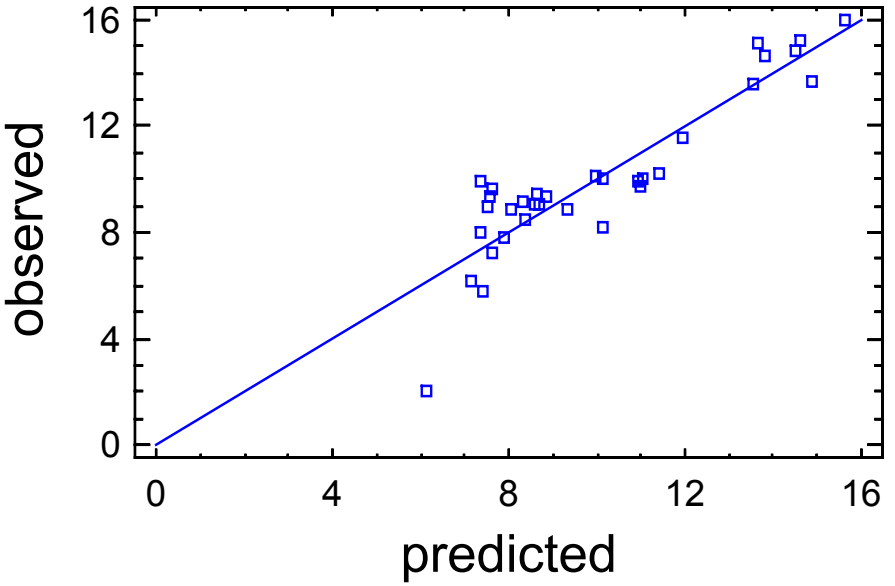
Damage Depth of PVC



R^2 = 81,43 %

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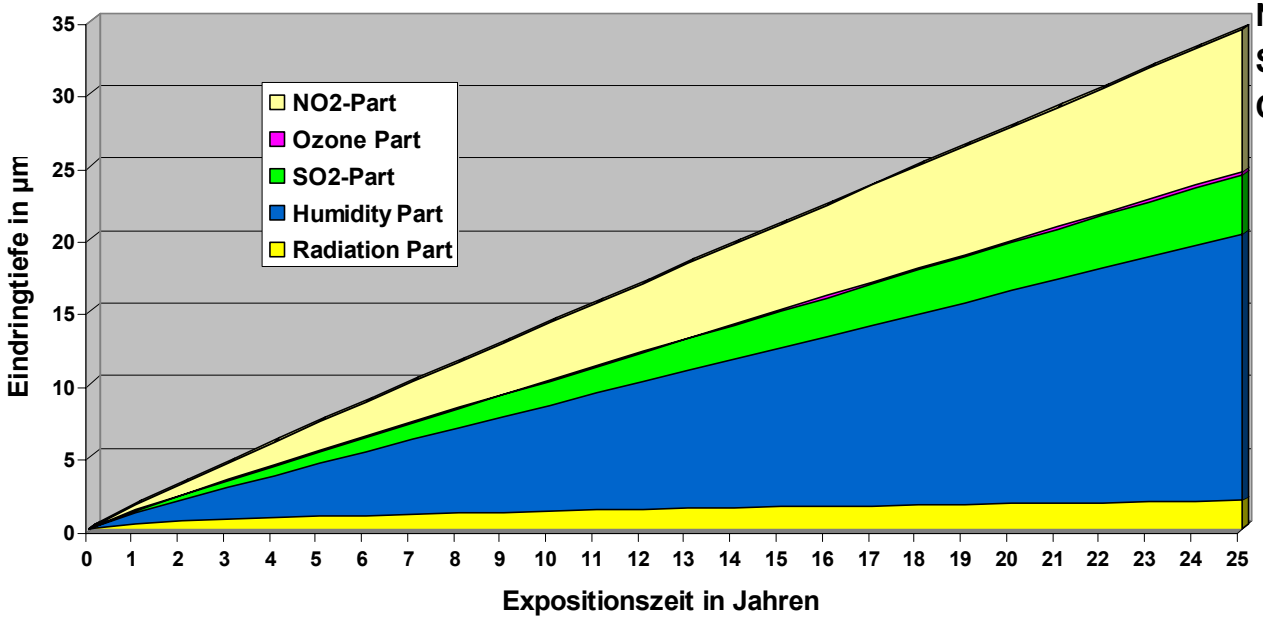
Dose-Response-Functions of Air-Pollution Effects for Service Life Prediction

Damage Depth of PVC

T = 20°C
rH = 60%
NO_2=50 µg/m³
SO_2=40 µg/m³
O_3 =50 µg/m³



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Conclusion

Dose-Response-Functions for Material Properties changed by climatic effects (solar radiation, humidity, temperature, air pollutants) have been developed.

Calculations of material damage and the different quantities from each environmental parameter are possible.

Comparisons of different climatic situations are possible.

With the aid of a lifetime criteria an estimation of the lifetime of the material is possible.

The application to other polymer materials should be proved.

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Thank you for your attention !

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