Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Supplementary Information

Heavy rainfall following a summer drought stimulates soil redox dynamics and facilitates rapid and deep translocation of glyphosate in floodplain soils

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S1 Soil profile and core photos

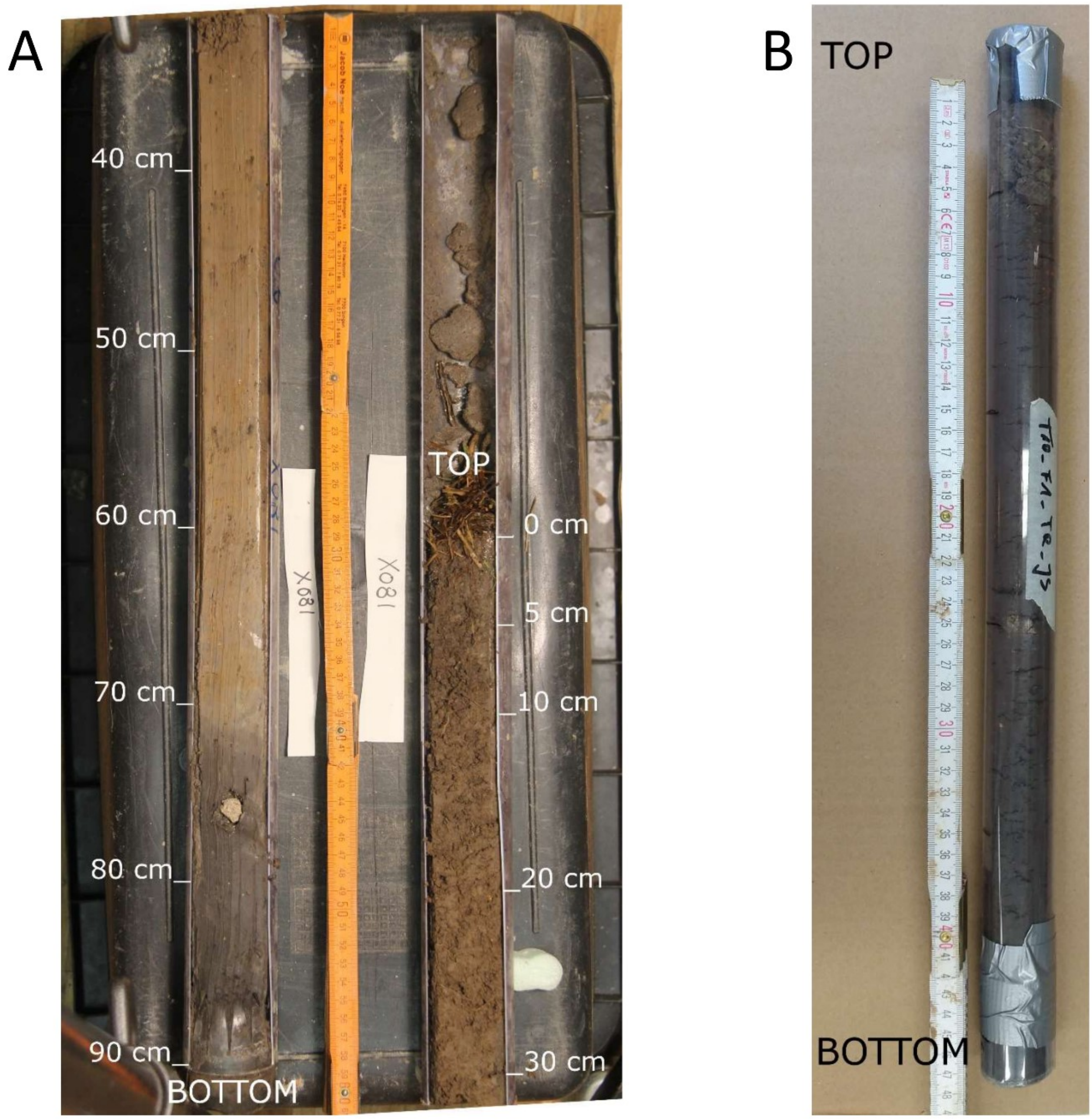

***Figure S1**: A. Soil profile from a location 100 m NW' of the experimental site. A 1.20 m core was taken with a direct push unit (6610 DT, Geoprobe, Salina, Kansas, US), the missing 30 cm can be explained by core loss at the bottom of the core. The core liner was cut at 0.6 m for taking the photo. Depth in cm below ground level is depicted besides the core. The top 70 cm of the soil have a red-brown color and comprise the oxidized Go horizon. A color shift towards grey is visible around 71 cm depth and marks the start of the reduced Gr horizon. Sampling depth in the presented study was 50 cm and thus within the Go horizon. (The photo is courtesy of S. Klingler and S. Martin) B. Photo of a 50 cm soil core taken from the Plot D1 at the experimental site of the presented study. The continuous red-brown color in the upper 50 cm is visible through the plastic liner.*

S2 Soil texture

Determination of soil texture

The cores taken for grain size analysis were cut with an oscillating saw into sections from 0 – 5 cm, 5 - 15 cm, 15 – 25 cm, 25 – 35 cm, 35 – 45 cm and 45 – 50 cm. For each section grain size analysis was performed according to German Standard DIN EN ISO 17892-4[1]. In brief, a representative subsample (50g) was sieved wet trough 2 mm, 1mm and 125 µm sieves to separate the fine-grained fraction below 125 µm. The fraction bigger than 125 µm was dried and sieved dry through 1mm, 500 µm, 250 µm and 125 µm sieves. Dry mass of all fractions was determined by weighting. The fraction smaller than 125 µm was further analyzed by sedimentation analysis using the integral suspension pressure method (ISP)[2] using a PARIO device (Meter Group, Munich, Germany).

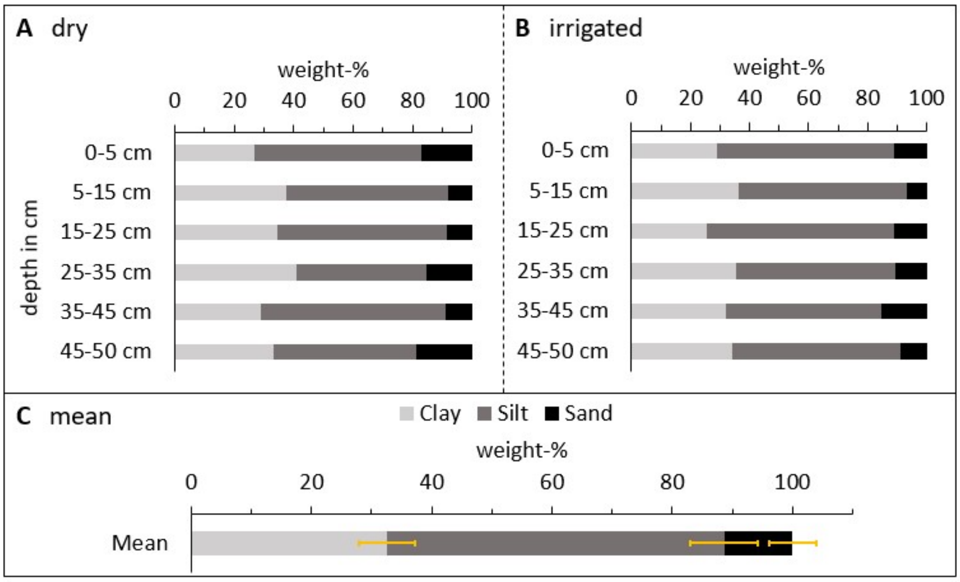

Figure S2: *A and B. Grain size distribution for cores from dry (D) (panel A) and irrigated (W) plots (B) are shown for six different depth intervals each. C. Shows soil texture as weight-% of clay (light gray), silt (dark gray) and sand (black). Mean grain size distribution and standard deviations (yellow bars) were calculated from all samples (n = 12). The soil is a silty clay loam.*

S3 Soil organic matter (SOM) quantified as total organic carbon (TOC)

Determination of total organic carbon (TOC)

To analyze total organic carbon (TOC), soil cores (DcT10 and WcT14) were cut with an oscillating saw into sections of 5 or 10 cm length (0 – 5 cm, 5 - 15 cm, 15 – 25 cm, 25 – 35 cm, 35 – 45 cm and 45 – 50 cm). Correlating depth segments each from the three replicate D and W cores, were combined to obtain representative samples. An aliquot of 10 g was freeze-dried (CHRIST ALPHA 1-4, CHRIST, Germany) and ground with a planetary mill to a grain size < 63 µm.
For each analysis, 1 g of dry, ground soil was used. Inorganic carbon was removed by decalcification with 16% aqueous HCl. Afterwards, samples were washed with ultrapure water until reaching a minimum pH of 5. The amount of inorganic carbon was estimated by weight loss after drying and independently determined by acid titration of a second subsample.
TOC was analyzed from the dried, decalcified sample by elemental analysis in an elemental analyzer (Elementar vario EL, Elementar, Hanau, Germany), with four replicate measurements for each sample. TOC was normalized to the initial dry weight of the soil and expressed as weight-%.

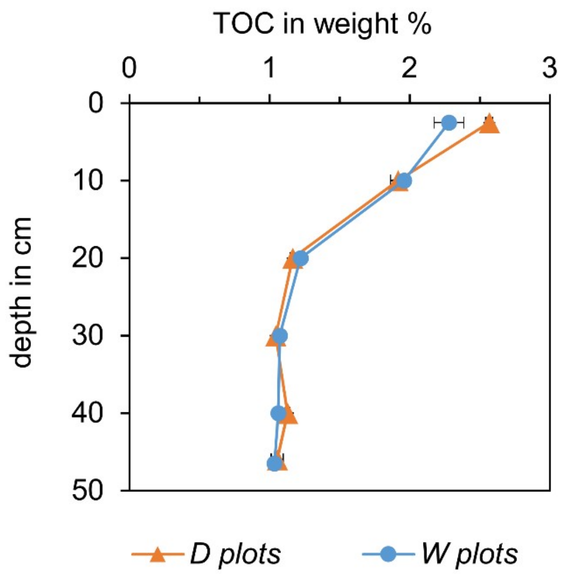

Figure S3: *Organic carbon content as TOC from dry (D, orange triangles) and irrigated plots (W, blue circles) are shown. Mean values and standard deviations were calculated from replicate measurements from the same sample (n = 4).*

S4 Weather data

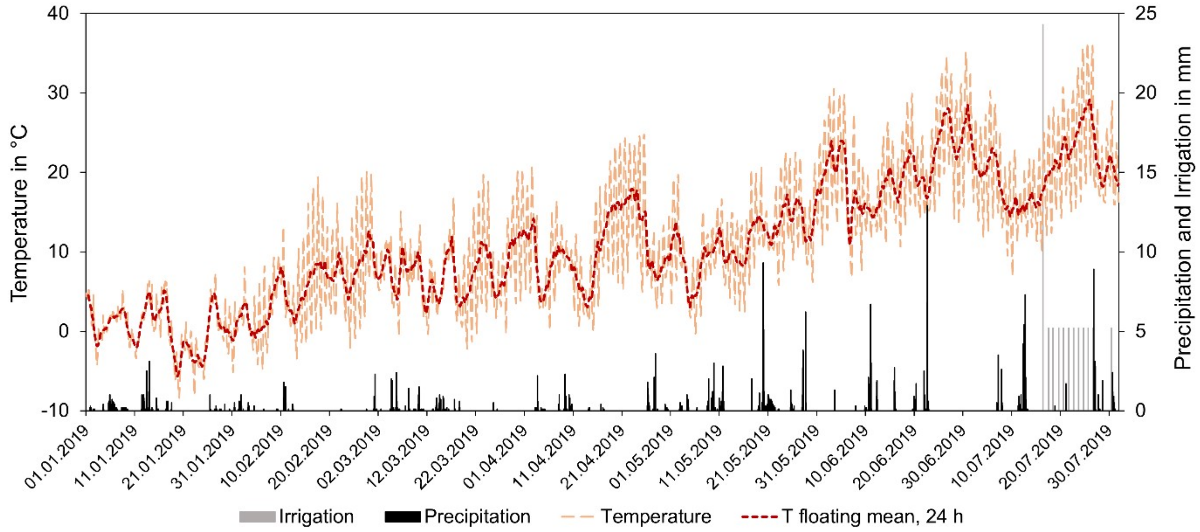

Figure S4: *Hourly data on irrigation (grey bars) and natural precipitation (black bars) in mm as well as temperature (T) in °C from 01.01.2019 until 31.07.2019 (experiment duration 16.07.2019 – 30.07.2019).*

S5 Calculation of reference evapotranspiration ETo according to FAO Irrigation and Drainage Paper No. 56 (REF)

Table S1: Data on temperature (T), relative humidity (RH) and global radiation (Rs) from the weather station in TÜ-Unterjesingen used for the calculation of the reference evapotranspiration ETo for the period 1st to 31st July 2019

Parameter	**Measured value**
T_{max} in °C	36.3
T_{mean} in °C	20.4
T_{min} in °C	6.9
RH_{max} in %	100.0
RH_{mean} in %	68.7
RH_{min} in %	26.0
Rs in W m^{-2}	236.0
ETo in mm day^{-1}	4.2

S6 Water balances

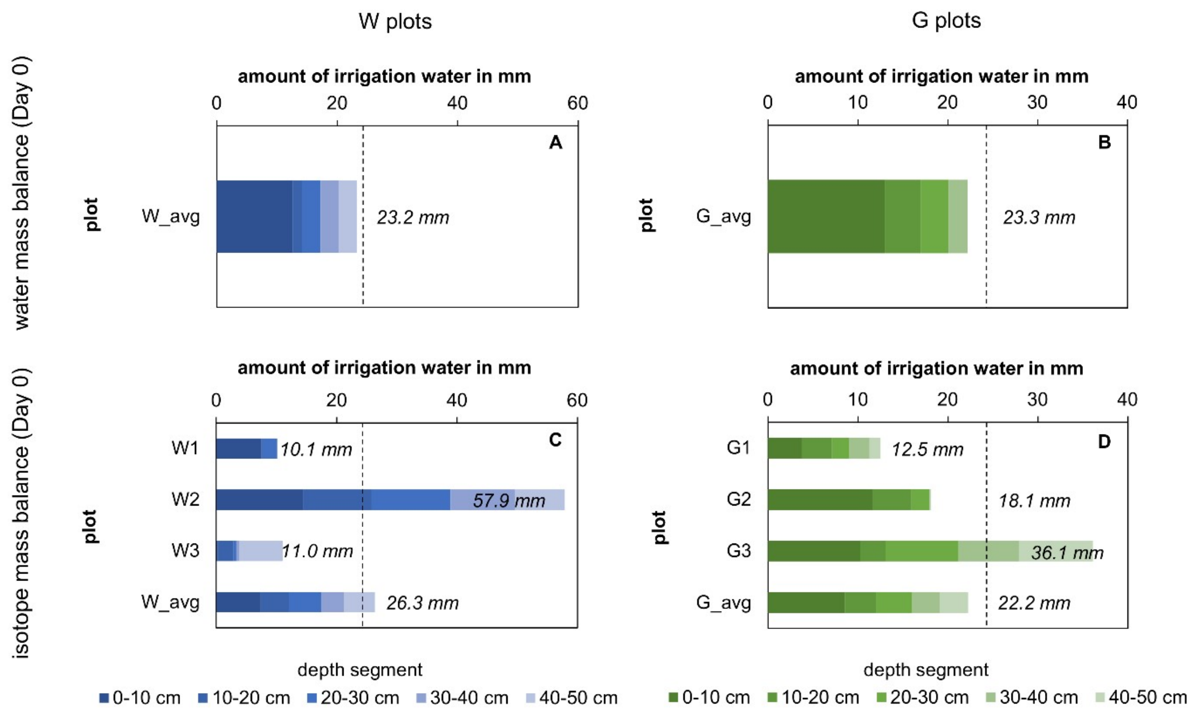

Figure S5: *The amount of irrigation water recovered in the cores right after the simulated heavy rain event (Day 0) is shown for all 10 cm depth segments (color gradient) and the sum of 0 - 50 cm depth is displayed close to the bar. The dashed line indicates the 24.3 mm (= 100 %) of irrigation water applied in the heavy rain event.* ***A.*** *The water mass balance was calculated from the difference between the mean gravimetric water content on W plots and D plots on Day 0.* ***B and C.*** *The isotope mass balances were calculated from the percentage of D_2O-labeled water (Figure 6 in the main article) and the gravimetric water content for W (blue, panel B) and G plots (green, panel C). Water balances from individual cores (W1 – 3 and G1 – 3) and the mean values are displayed (W_avg, G_avg).*

S7 Glyphosate concentration vs. percentage of irrigation water in soil water

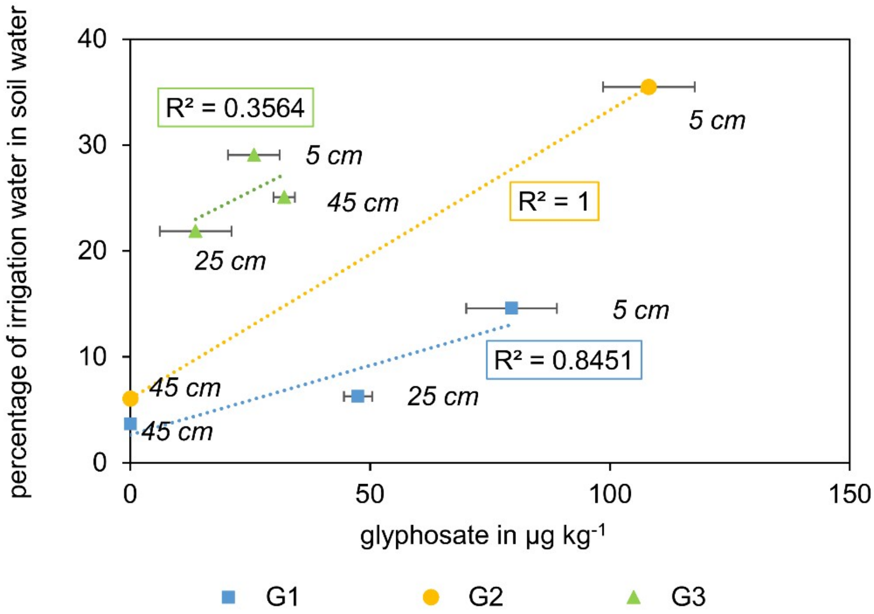

***Figure S6**: Correlation of glyphosate concentrations in the soil (µg kg^{-1}) and percentage of irrigation water in individual cores from plots G1 (blue squares), G2 (yellow circles) and G3 (green triangles). Trend lines and R^2 are shown in respective colors. Depth below ground level is displayed close to the data points (e.g., “5cm” corresponds to depth segment of 0 – 10 cm).*

S8 Redox potentials G plots

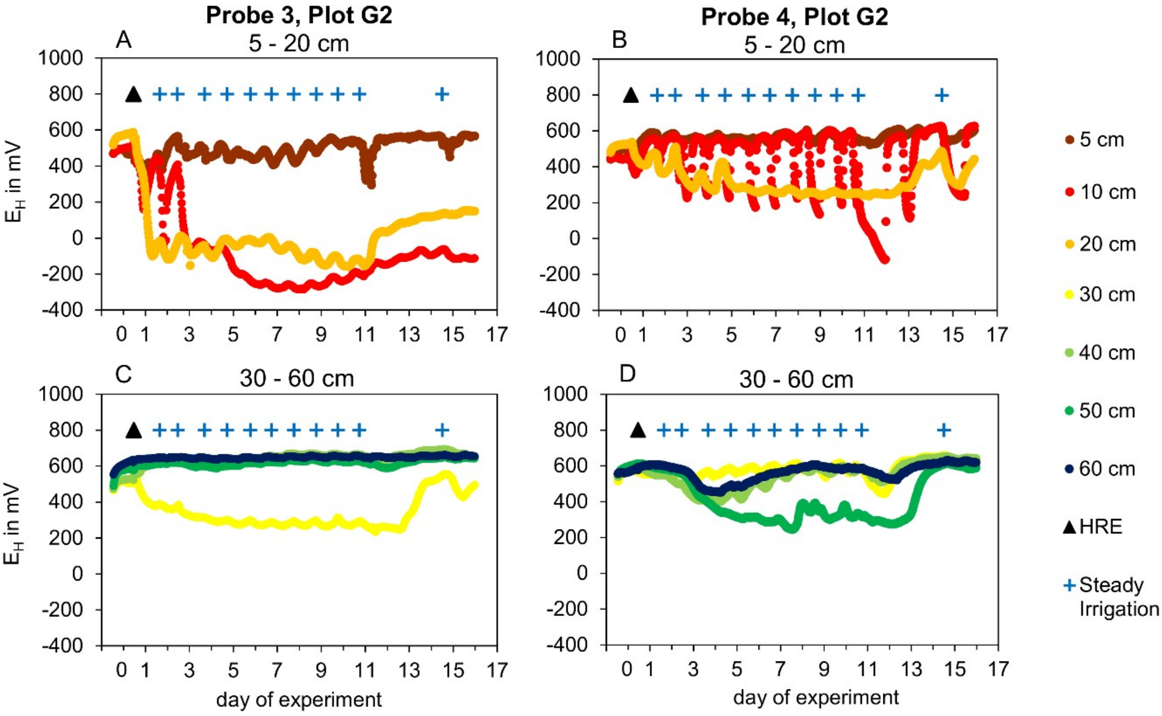

***Figure S7**: In situ redox potentials at ph7 reported in mV vs. SHE from the two redox probes installed on a plot (G2) treated with water and glyphosate. Panels A and B show potentials in the topsoil at depths of 5 cm (brown), 10 cm (light red), and 20 cm (orange). Panels C and D show potentials in the subsoil at depths of 30 cm (yellow), 40 cm (light green), 50 cm (dark green) and 60 cm (blue). The time point of the heavy rain event (HRE) is labelled with a black triangle and the times of the steady (daily) irrigation are labelled with dark blue crosses. The redox conditions are characterized as follows: oxidizing (> 400 mV vs. standard hydrogen electrode), weakly reducing (400 – 200 mV), moderately reducing (200 – 100 mV) and strongly reducing (< 100 mV)[3].*

S9 Elemental composition of the soil

Table S2: Elemental composition (Al, Ca, Cu, Fe, K, Mg, Mn, P, Zn) of the soil. Element concentrations are given in g kg^{-1}.

depth in cm	**Al** g kg^{-1}	**Ca** g kg^{-1}	**Cu** g kg^{-1}	**Fe** g kg^{-1}	**K** g kg^{-1}
0-10	33.6 ± 0.2	11 ± 1	0.03 ± 0	26.8 ± 0.1	31.5 ± 0.1
10-20	34.4 ± 0.5	12.9 ± 0.5	0.03 ± 0	27.3 ± 0.1	25 ± 12
20-30	35.4 ± 0.3	17 ± 3	0.027 ± 0.006	27.38 ± 0.09	32.2 ± 0.1
30-40	34 ± 2	29 ± 17	0.027 ± 0.006	27 ± 2	31 ± 2
40-50	34.3 ± 0.8	33 ± 16	0.027 ± 0.006	26 ± 1	31 ± 1

depth in cm	**Mg** g kg^{-1}	**Mn** g kg^{-1}	**P** g kg^{-1}	**Zn** g kg^{-1}
0-10	16.8 ± 0.2	0.27 ± 0.01	1.06 ± 0.05	0.07 ± 0
10-20	17.2 ± 0.2	0.73 ± 0.03	0.9 ± 0.1	0.07 ± 0
20-30	17 ± 1	0.69 ± 0.06	0.71 ± 0.08	0.063 ± 0.006
30-40	15 ± 2	0.62 ± 0.06	0.61 ± 0.07	0.06 ± 0
40-50	14 ± 1	0.60 ± 0.08	0.60 ± 0.05	0.06 ± 0

References

1. DIN Deutsches Institut für Normung e. V., *DIN EN ISO 17892-4 Geotechnical investigation and testing - Laboratory testing of soil - Part 4: Determination of particle size distribution*, Beuth, Berlin, 2017.
2. W. Durner, S. C. Iden and G. von Unold, The integral suspension pressure method (ISP) for precise particle-size analysis by gravitational sedimentation, *Water Resources Research*, 2017, **53**, 33-48 DOI: https://doi.org/10.1002/2016WR019830.
3. T. Mansfeldt, In situ long-term redox potential measurements in a dyked marsh soil, *Journal of Plant Nutrition and Soil Science*, 2003, **166**, 210-219 DOI: https://doi.org/10.1002/jpln.200390031.