Supporting Infomation

Effect of Radial Directional Dependences and Rainwater Influence on CVOC Concentrations in Tree Core and Birch Sap Samples Taken for Phytoscreening using HS-SPME-GC/MS

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Total Pages: 8

Site Description. The former military base Potsdam-Krampnitz lies south of the nature reserve "Döberitzer Heide" to the west of the German City of Berlin on the main B2 road on high ground of morphologically insular form. The site is bordered on the south east by Krampnitzer lake, on the south west by meadowland leading out to the Fahrlander lake and to the north by the lowland of the "Großen Luch", which drains via the "Großen Graben" into the Krampnitzer lake. Agricultural land lies to the west . Owing to the morphological high ground character, the site shows no particular direction of groundwater flow.

Two sections were available for its geological characterization. The first geological section begins to the southwest of tree 09, passes north of the dry cleaning building and the storage tanks and ends near groundwater well 19 in the east. The second section extends to the border with the wetland, passes tree 07, and the ground water wells 21, 22 and 23. Based on these two sections the subsurface of the contamination area (see Fig. S1 and S3) can described as followed. The section 1 showed a nearly constant aquifuge between 30 and 31 m NHN. The ground level is affected of earthworks and varying about two meters from the west to the east. The aquifer had an average thickness of 4 meters where the earthwork is between 0.5 and 2.5 m thick. To the ground water well 19 the aquifer becomes abrupt narrow and is only one meter thick. The section 2 showed the same aquifuge in the western part at 31 m NHN but the ground level is only 4 meter above. Aquifer and earthwork are both 2 meters in thickness. The eastern part of the section is influenced by the wetland and showed a peat clay nearby ground water well 22. The aquifer subsided here until 28 m NHN with 0.5 m thickness and is ending before ground water well 23. Overall the geology on the base is predominantly simple with a fixed top of the aquifuge. The ground level is varying a lot but for the ground water flow this might be not so important. In the north east of the base the geology is more complex and it is suggested that the situation in the wetlands is complex as well.

A dry cleaning plant in the north west area of the base has caused considerable ground water contamination, which (as a result of the locally uniform groundwater flow) flows into the bordering wetlands. This site is dominated by two tree species: in the wetland almost exclusively by white willow (Salix alba), and on the base by white birch (Betula alba).

There are also solitary poplars (Populus) outside the wetland area, oaks (Quercus), limes (Tilia) and other tree species. Because the former buildings have long been in a state of serious dilapidation, these trees are also partly to be found within the ruins of buildings without basements.

The contaminant plume of the volatile chlorinated hydrocarbons (CVOC) was already known before the start of the described investigation. Based on direct-push groundwater screening, the concentrations of CVOC reached a maximum of 122 mg CVOC/L in the outflow from the contamination source at the location of the dry cleaning plant (see Figure S2). In the ground water well 22 (see Table S2) the reached concentrations of 174 mg CVOC/L. Main components are trichloroethene (TCE) near the source, and both TCE and cis-1,2-dichloroethene (cDCE) in the plume. Also detected in relevant concentrations were chloroethene (vinylchloride, VC), 1,1-dichloroethene (1,1-DCE), and trans-1,2-dichloroethene (tDCE).

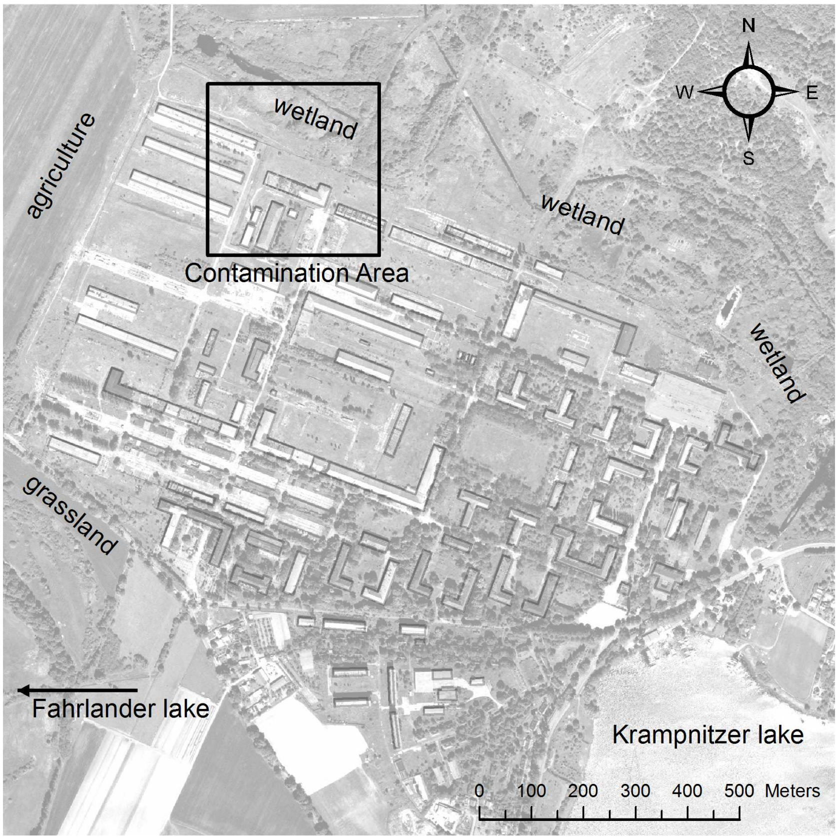

FIGURE S1: Former military base Potsdam-Krampnitz

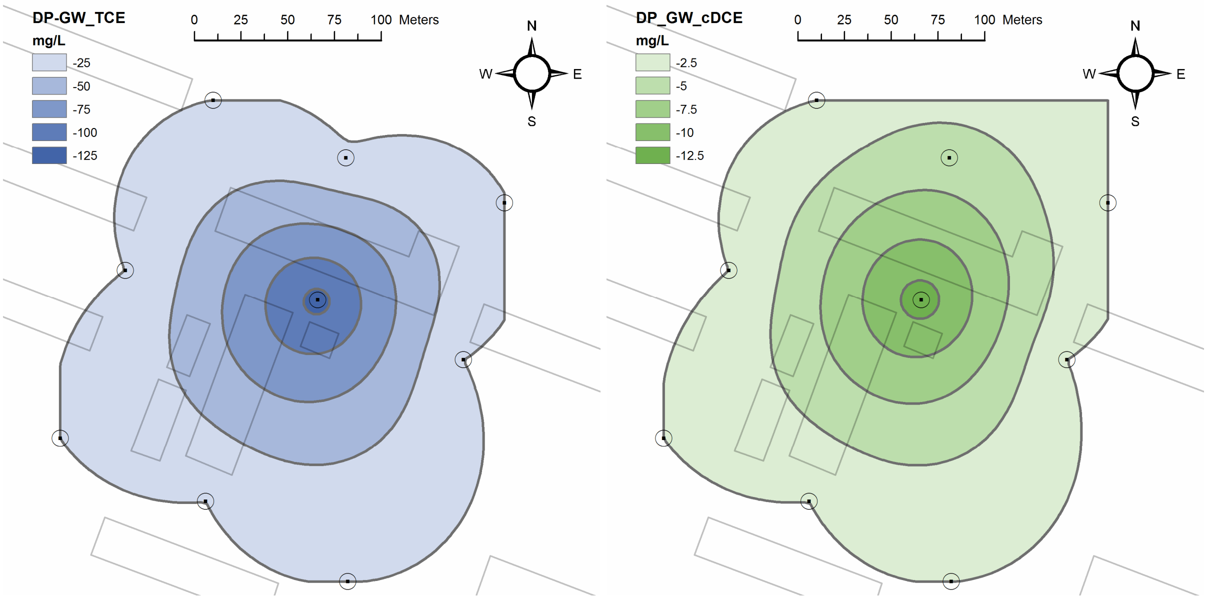

FIGURE S2: Interpolated (in kriging mode) TCE (left) and cDCE (right) concencentrations based on direct push ground water samples in month of August 2007; the circles depicts the points for direct push

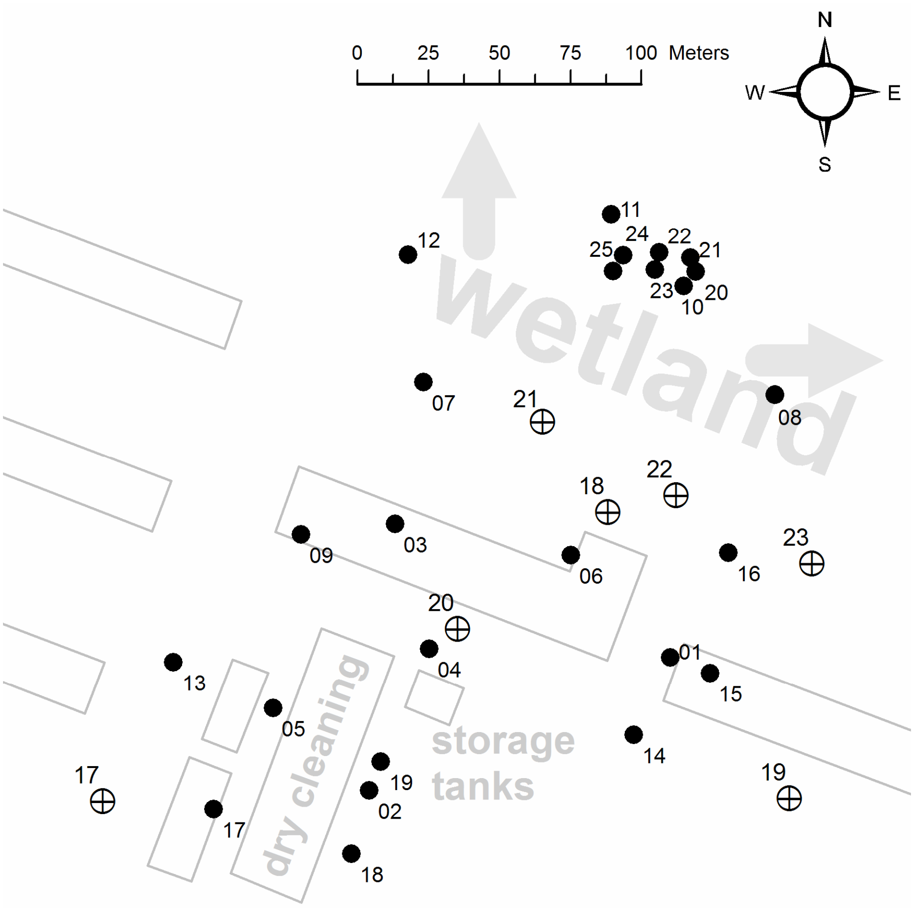

FIGURE S3: Contamination area and tree locations (solid points) with labels and ground water wells (circles with crosses) with labels.

TABLE S1: Ground water levels in the contamination area for the month March 2007 until September 2008

	Ground Water Level in m Below Ground Level						
Well - Label	**03/2007**	**06/2007**	**09/2007**	**12/2007**	**03/2008**	**07/2008**	**09/2008**
B17	4.45	4.06	3.72	3.83	3.74	3.79	4.27
B18	1.70	1.60	1.49	1.37	1.32	1.86	2.16
B19	1.15	1.04	1.04	0.87	0.85	1.67	2.13
B20	1.94	1.68	1.52	1.44	1.32	1.82	2.20
B21	2.10	2.03	1.89	1.78	1.70	2.15	2.40
B22	1.58	1.49	1.38	1.25	1.25	1.78	2.06
B23	1.34	1.36	1.29	1.17	1.10	1.66	1.88

TABLE S2: TCE and cDCE concentrations in the ground water wells

	TCE [µg/L]		cDCE [µg/L]	
Well - Label	**03/2007**	**03/2008**	**03/2007**	**03/2008**
B17	0.10	nd	0.30	nd
B18	70412	26700	6985	5613
B19	nd	nd	nd	nd
B20	112123	115574	7403	5465
B21	63088	75501	9404	11054
B22	152099	149723	21708	19816
B23	22.2	nd	6.9	3.2

TABLE S3: Summary of sampling data for the trees used in the study

Label	Tree	Perimeter in cm*	Date	Time	Weather	Sample	Motive
01	Betula alba	149	07/19/07 ; 03/20/08	- / 13:30	28°C, dry / 6°C, dry	Core / Sap	Radial Differences
02	Betula alba	150	07/19/07	-	28°C, dry	Core	Radial Differences
03	Betula alba	98	07/19/07	-	28°C, dry	Core	Radial Differences
04	Betula alba	165	07/12 - 07/19/07	daily 12:00	described**	Core	Weather Change
05	Betula alba	90	04/10/08	13:30	7°C, rainy	Sap	Radial Differences
06	Betula alba	103	04/04/08	18:00	13°C, dry	Sap	Radial Differences
07	Salix alba	110	05/22/08	15:00	21°C, dry slightly clouded	Core	Radial Differences
08	Salix alba	150	05/29/08	14:00	26°C, dry, sunny	Core	Radial Differences
09	Populus tremula	85		14:30		Core	Radial Differences
10	Salix alba	130	06/05/08	14:00	25°C, dry sunny	Core	Radial Differences
11	Salix alba	260		14:30		Core	Radial Differences
12	Salix alba	320		15:00		Core	Radial Differences
13	Quercus robur	70		15:30		Core	Radial Differences
14	Betula alba	75	06/19/08	11:00	26°C, dry slightly clouded	Core	Radial Differences
15	Betula alba	87		11:45		Core	Radial Differences
16	Malus spec.	56		12:15		Core	Radial Differences
17	Betula alba	110		13:00		Core	Radial Differences
18	Betula alba	105		13:30		Core	Radial Differences
19	Betula alba	75	06/26/08	11:30	25°C, dry clouded	Core	Radial Differences
20	Salix alba	106		12:30		Core	Radial Differences
21	Salix alba	90		12:45		Core	Radial Differences
22	Salix alba	180		13:00		Core	Radial Differences
23	Salix alba	140		13:15		Core	Radial Differences
24	Salix alba	198	07/10/08	14:00	18°C, dry clouded	Core	Radial Differences***
25	Salix alba	88		15:00		Core	Radial Differences***

* 50 cm above ground ** see text *** five samples from four directions

Solid-Phase-Microextraction (SPME). Temperature and time series were recorded under otherwise constant parameters to determine the best conditions for measurement using SPME. Optimization also included static headspace analysis. It emerged that the optimal temperature for TCE and cDCE measurement by SPME with the carboxen/ PDMS fiber was probably lower than the minimum agitator setting of 30°C. Because of high temperature variations in the laboratory, measurements were nevertheless made at 35°C. In general, cDCE und TCE behave similarly with respect to measurement parameters. It was therefore possible to set the best possible measurement conditions simultaneously for both analytes. The extraction conditions are summarized in Table 2.

TABLE S4: SPME measurement conditions

Step	Temperature	Time
Fiber bake out before series of measurements	300 °C	90 min
Conditioning of the sample	35 °C	30 min
Fiber bake out between each measurement	300 °C	15 min
Extraction	35 °C	30 min
Desorption at injector	250 °C	1 min

GC/MS measurements. GC separations were performed using a DB624 column or GS-Gaspro column (GC-System: HP 6980). The EPA Standard 624 Calibration Mix A (Supelco) was purchased, and spiked additionally with cDCE for calibration. Measurements were made partly in scan mode and partly in Selected Ion Monitoring (SIM) mode. Therefore a time window was defined for each substance using its retention time, within which the two most intense mass to charge ratios were measured with the mass spectrometer (Agilent 5973) in electron impact mode. Peak areas were measured for both of these masses, also when scan mode was used. The relation of the main mass (Quantifier) to the second mass (Qualifier) was used in SIM mode, along with the retention time, to identify the substances.

Calibration and Applicability. Aqueous samples were used for calibration to estimate the tree core concentrations. The results of the calibration for TCE und cDCE are given in Table 1. Directly comparing concentrations in tree cores and in aqueous samples is arguable, because there is a basic lack of a meaningful relation for stating concentration or content. Nevertheless, for unified sampling, semi-quantitative assessments related to different parameters, e.g. tree core volume or dry weight, deliver almost identical results.

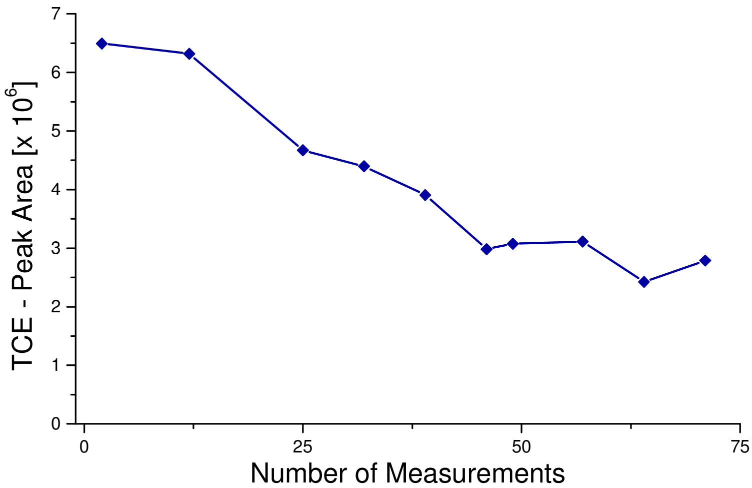

FIGURE S4: Measured sensitivity loss of a Carboxen^{TM}/ PDMS-fiber on the basis of TCE standards in aqueous solution

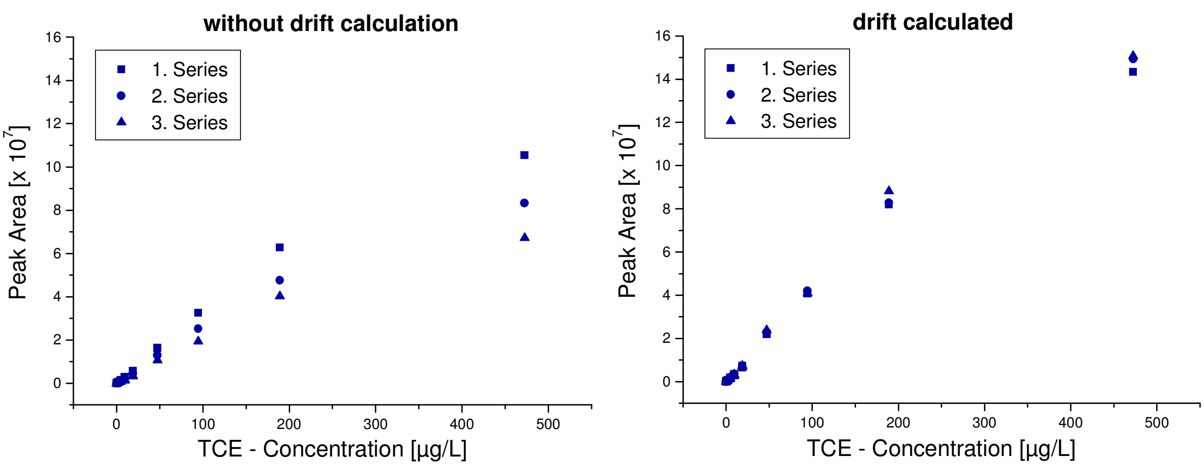

FIGURE S5: TCE calibration data without drift calculation (left) and drift calculated (right)

TABLE S5: Maximum concentrations in sap samples and in tree core samples for the trees used in this study; nd – not detected

Label	Tree	Sap - Max. Concentration µg/L		Tree Core - Max. Concentration µg/kg	
		TCE	cDCE	TCE	cDCE
01	Betula alba	3.12	0.52	155	54.2
02	Betula alba			66.1	0.31
03	Betula alba			91.4	0.56
04	Betula alba			2730	14.4
05	Betula alba	46.7	0.22		
06	Betula alba	0.18	0.01		
07	Salix alba			841	1419
08	Salix alba			3.7	3.11
09	Populus tremula			2059	43.2
10	Salix alba			0.17	9.75
11	Salix alba			20.9	43040
12	Salix alba			10.5	9261
13	Quercus robur			37.1	nd
14	Betula alba			14.4	nd
15	Betula alba			0.31	nd
16	Malus spec.			0.78	1.09
17	Betula alba			661	0.06
18	Betula alba			21.5	0.26
19	Betula alba			4181	0.44
20	Salix alba			1.77	721
21	Salix alba			5.67	2698
22	Salix alba			55.2	14497
23	Salix alba			11.1	4819
24	Salix alba			32.8	11022
25	Salix alba			21.8	24038

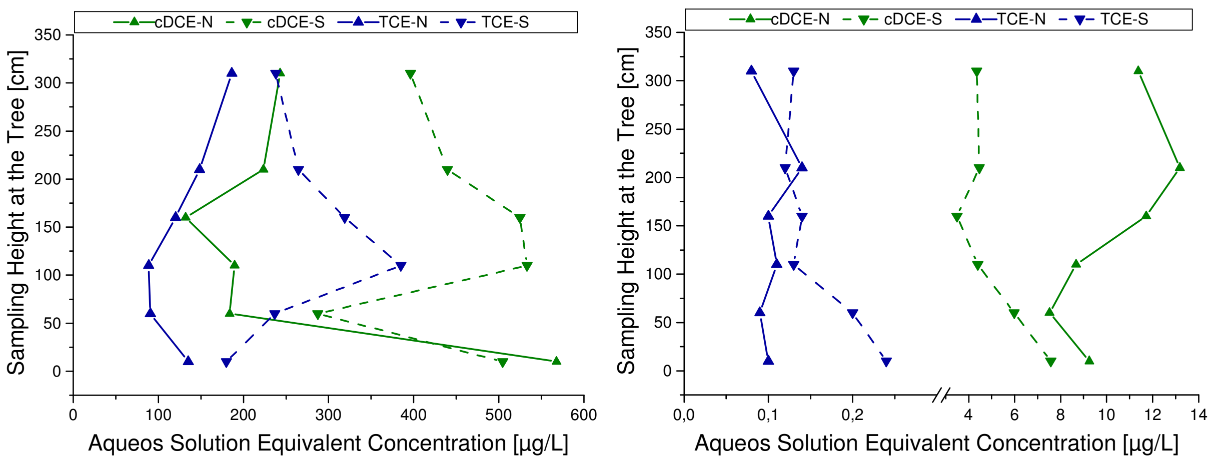

FIGURE S6: TCE and cDCE aqueous solution equivalent concentrations in tree cores depending on the sampling height from northside (continuous line) and from the southside (dashed line) of two different trees (left and right)

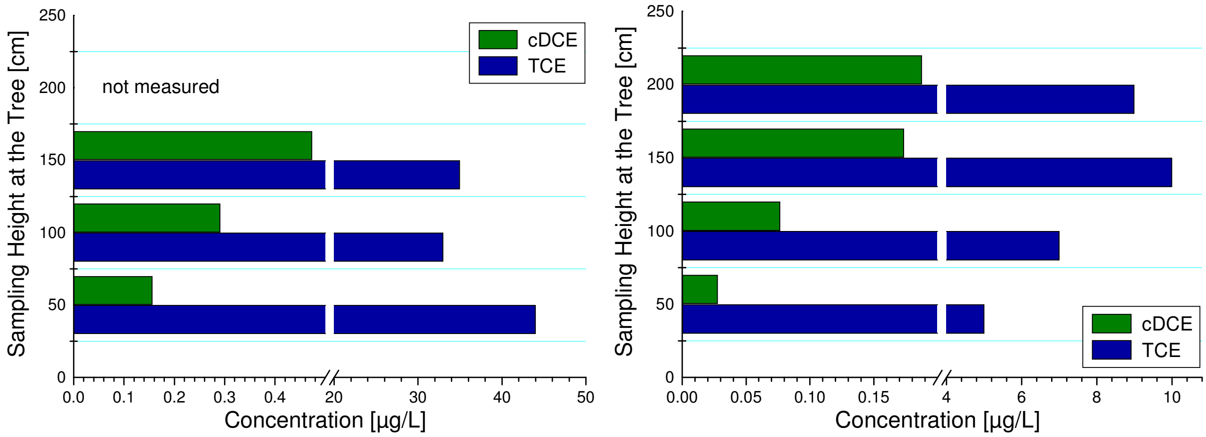

FIGURE S7: TCE and cDCE concentrations in sap depending on the sampling height from north side (left) and from the south side (right) of one birch tree

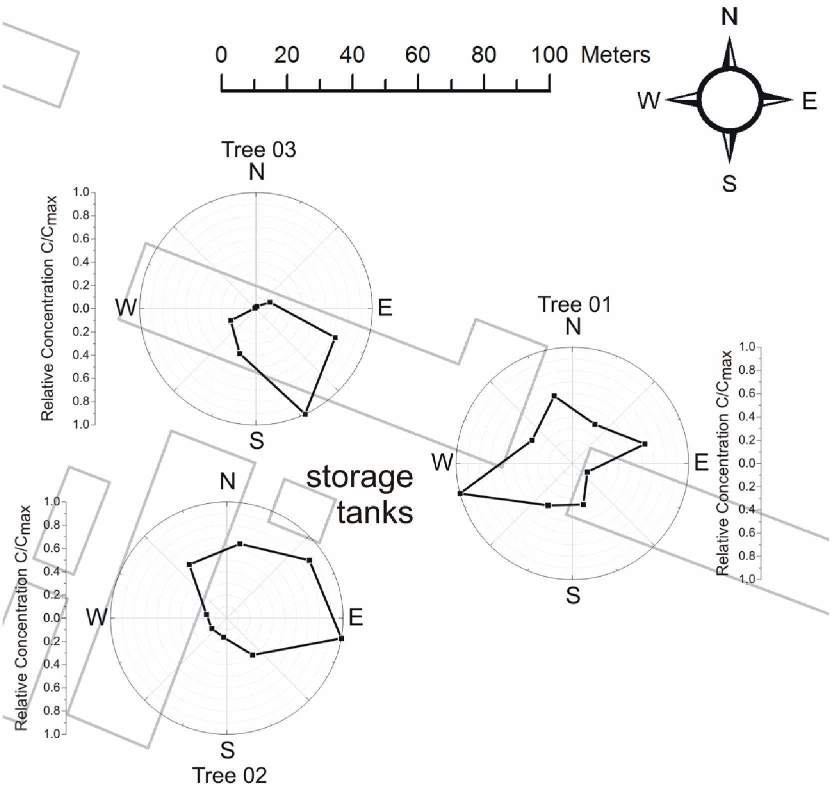

FIGURE S8: Relative concentrations related to the maximal value for the particular tree and positions of the trees from the radial sampling of tree cores 2007