Supporting Information – *Environmental Science and Technology*

MODIFIED POLYTOPIC VECTOR ANALYSIS TO IDENTIFY AND QUANTIFY A DIOXIN DECHLORINATION SIGNATURE IN SEDIMENTS - 1. THEORY

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FIGURE S1. Conceptual model of contaminant mixing system. The bar graphs represent the concentration contribution of a contaminant in the profile.

FIGURE S2. Graphical illustration of rotation procedure from principal components to end-members. Negative values in last bar graph are due to 5% error tolerance specified in program (t_1, see Note S1).

NOTE S1. Sensitivity of PVA to the parameters t_1 and t_2.

TABLE S1. Variance-covariance matrices and means used to generate randomly the loading matrices A for X_1 (a) and X_2 (b). The resulting means and covariances are slightly different because of elimination of samples with negative values in A and X.

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FIGURE S7. T-PVA results for X_1 (with dechlorination). Percentages in subfigures refer to the percent contribution to the total variability by the end-member.

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FIGURE S9. M-PVA results for X_2' (without dechlorination). Negative (grey) components in end-member 1 highlight the effect of relaxation. Percentages in subfigures refer to the percent contribution to the total variability by the end-member.

FIGURE S10. M-PVA results for X_1 (with dechlorination). Percentages in subfigures refer to the percent contribution to the total variability by the end-member.

FIGURE S11. M-PVA results for X_2 (with dechlorination). Percentages in subfigures refer to the percent contribution to the total variability by the end-member.

TABLE S3. Results for combinations of model and dechlorination.

Symbols:

T: 2,3,7,8 - tetraCDD

Pe: 1,2,3,7,8 - pentaCDD

Hx4: 1,2,3,4,7,8 - hexaCDD

Hx6: 1,2,3,6,7,8 - hexaCDD

Hx9: 1,2,3,7,8,9 - hexaCDD

Hp: 1,2,3,4,6,7,8 - heptaCDD

TF: 2,3,7,8 - tetraCDF

OF: 1,2,3,4,6,7,8,9 - octaCDF

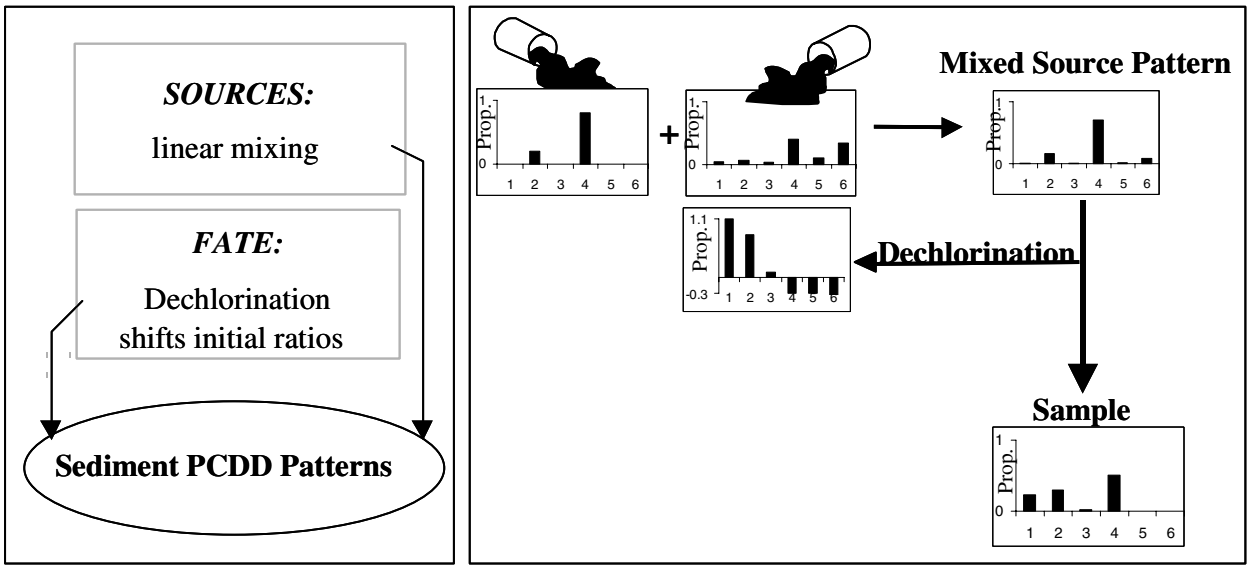

FIGURE S1. Conceptual model of contaminant mixing system. The bargraphs represent the concentration contribution of a contaminant in the profile.

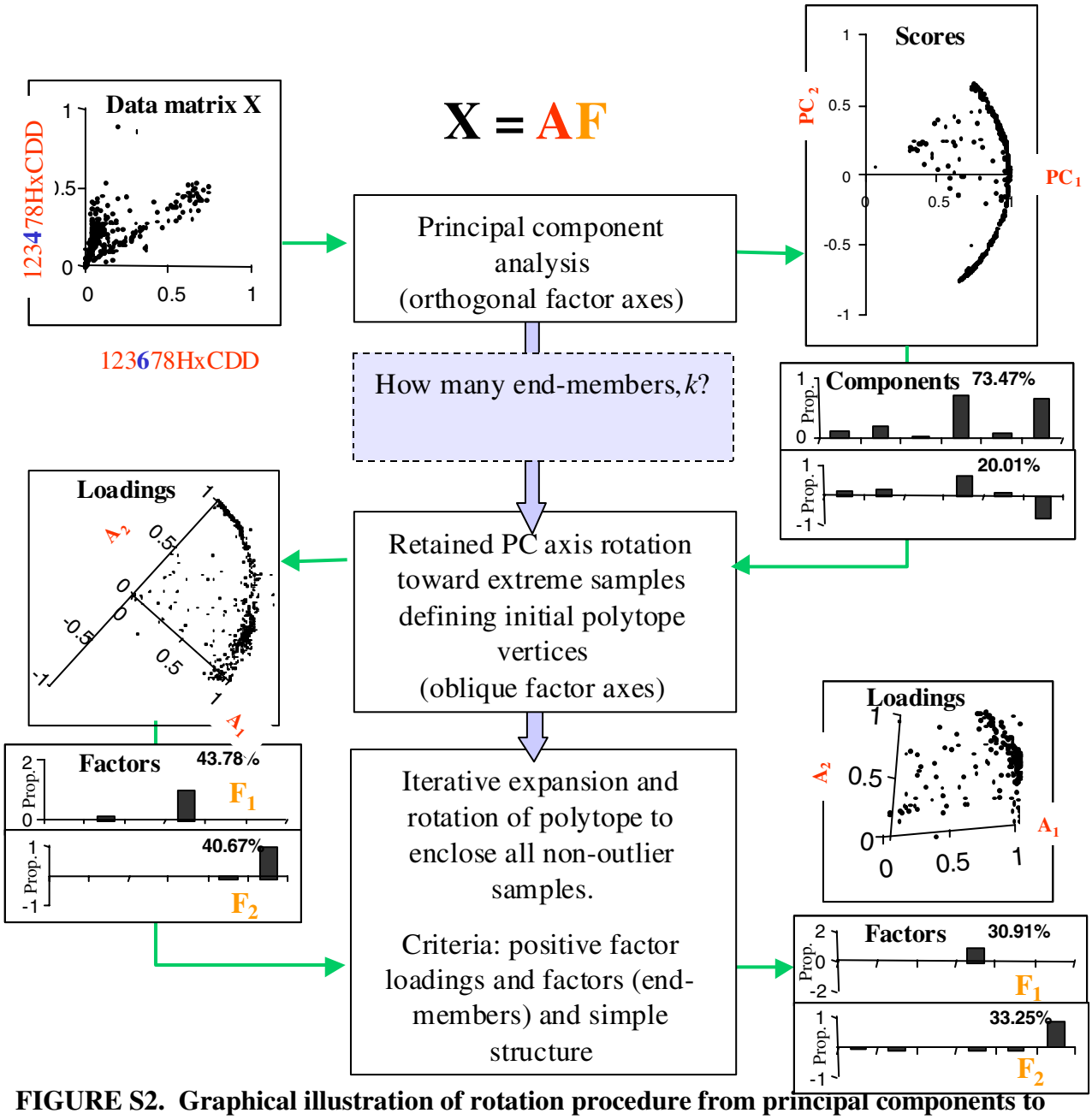

FIGURE S2. Graphical illustration of rotation procedure from principal components to end-members. Negative values in last bar graph are due to 5% error tolerance specified in program (t_1, see Note S1).

NOTE S1. Sensitivity of PVA to the parameters t_1 and t_2.

Although not part of the objectives of this paper, it is briefly noted that PVA is sensitive to two parameters t_1 and t_2, in Step 7. The error tolerance, t_1, is set to a default of 5% meaning that negative values up to -0.05 are accepted in matrix $\boldsymbol{A}$. The second parameter, t_2, specifies the highest negative value that is considered to be adjustable in $\boldsymbol{A}$. The default for t_2 is -0.25, but it is important to understand that this value should be varied by the modeler to be as negative as necessary for convergence to occur within a reasonable number of iterations. This setting may be too stringent and results inaccurate, while a slight decrease, for example to -1, could still lead to convergence and to accurate results (relative to an artificial data set). Thus, after each run, the minimum of all loadings should be inspected. If there are values lower than t_2, then this threshold should be decreased and the run repeated. Convergence will also be aided by slightly increasing the error tolerance.

TABLE S1. Variance-covariance matrices and means used to generate randomly the loading matrices *A* for X_1 (a) and X_2 (b). The resulting means and covariances are slightly different because of elimination of samples with negative values in *A* and *X*.

(a.) Variance-covariance matrix for X_1	0.0326	-0.0068	-0.0075	-0.0030	-0.0041
	-0.0068	0.0064	-0.0023	-0.0002	0.0007
	-0.0075	-0.0023	0.0088	0.0001	0.0021
	-0.0030	-0.0002	0.0001	0.0024	-0.0010
	-0.0041	0.0007	0.0021	-0.0010	0.0017
Means	0.223	0.157	0.101	0.146	0.077

(b.) Variance-covariance matrix for X_2	0.0264	0.0016	-0.0085	-0.0177	-0.0006
	0.0016	0.0030	0.0009	-0.0054	0.0002
	-0.0085	0.0009	0.0325	-0.0213	-0.0018
	-0.0177	-0.0054	-0.0213	0.0425	0.0015
	-0.0006	0.0002	-0.0018	0.0015	0.0006
Means	0.231	0.247	0.149	0.329	0.038

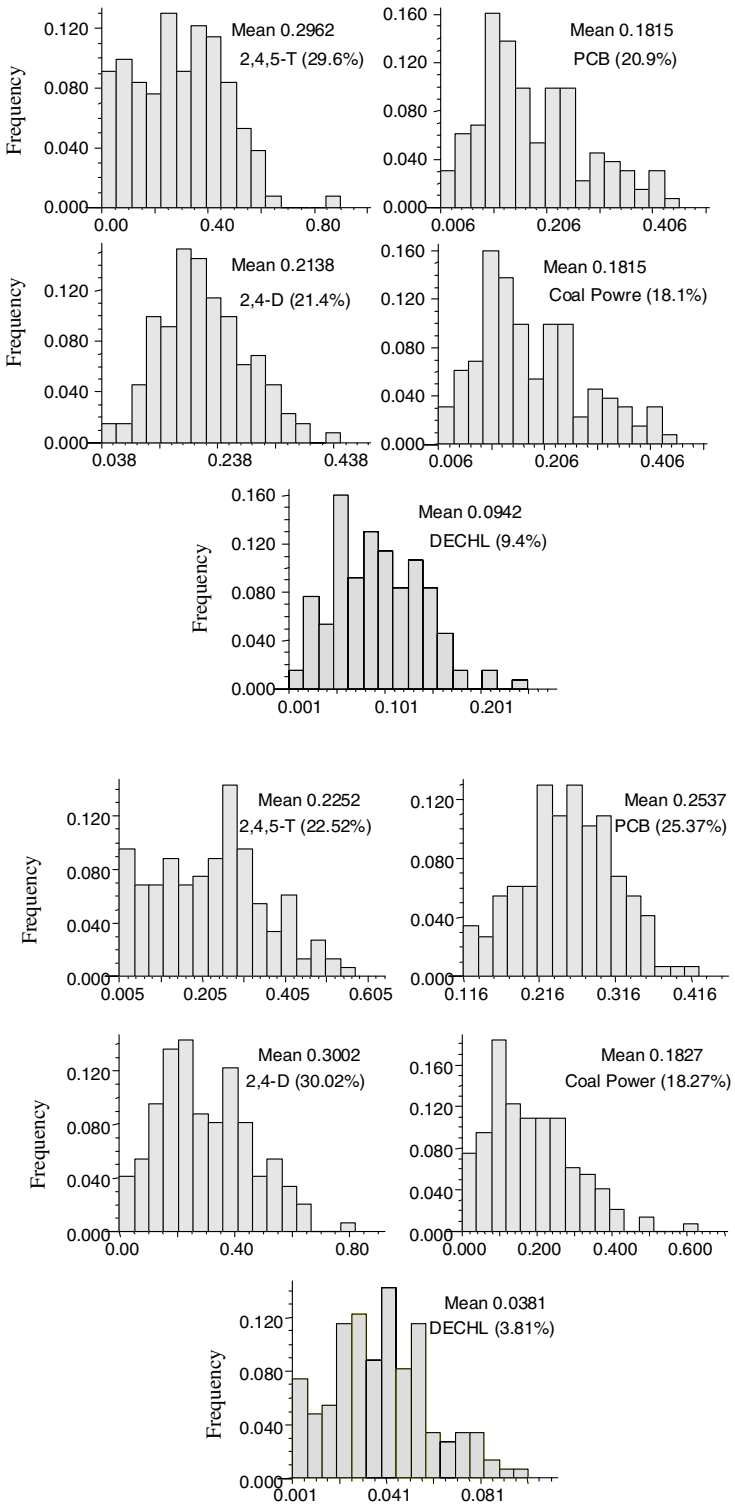

FIGURE S3. Histograms of the loadings for artificial data sets X_1 (top) and X_2 (bottom).

TABLE S2. Comparison of correlation patterns for loadings of X_1 and X_2.

X_1	PCB	Coal Power	2,4-D	DECHL
2,4,5-T	-0.55	-0.48	-0.44	-0.65
PCB		-0.37	0.16	0.25
Coal Power			-0.05	0.54
2,4-D				-0.22

X_2	PCB	Coal Power	2,4-D	DECHL
2,4,5-T	0.04	-0.34	-0.60	-0.06
PCB		0.10	-0.52	0.24
Coal Power			-0.43	-0.30
2,4-D				0.05

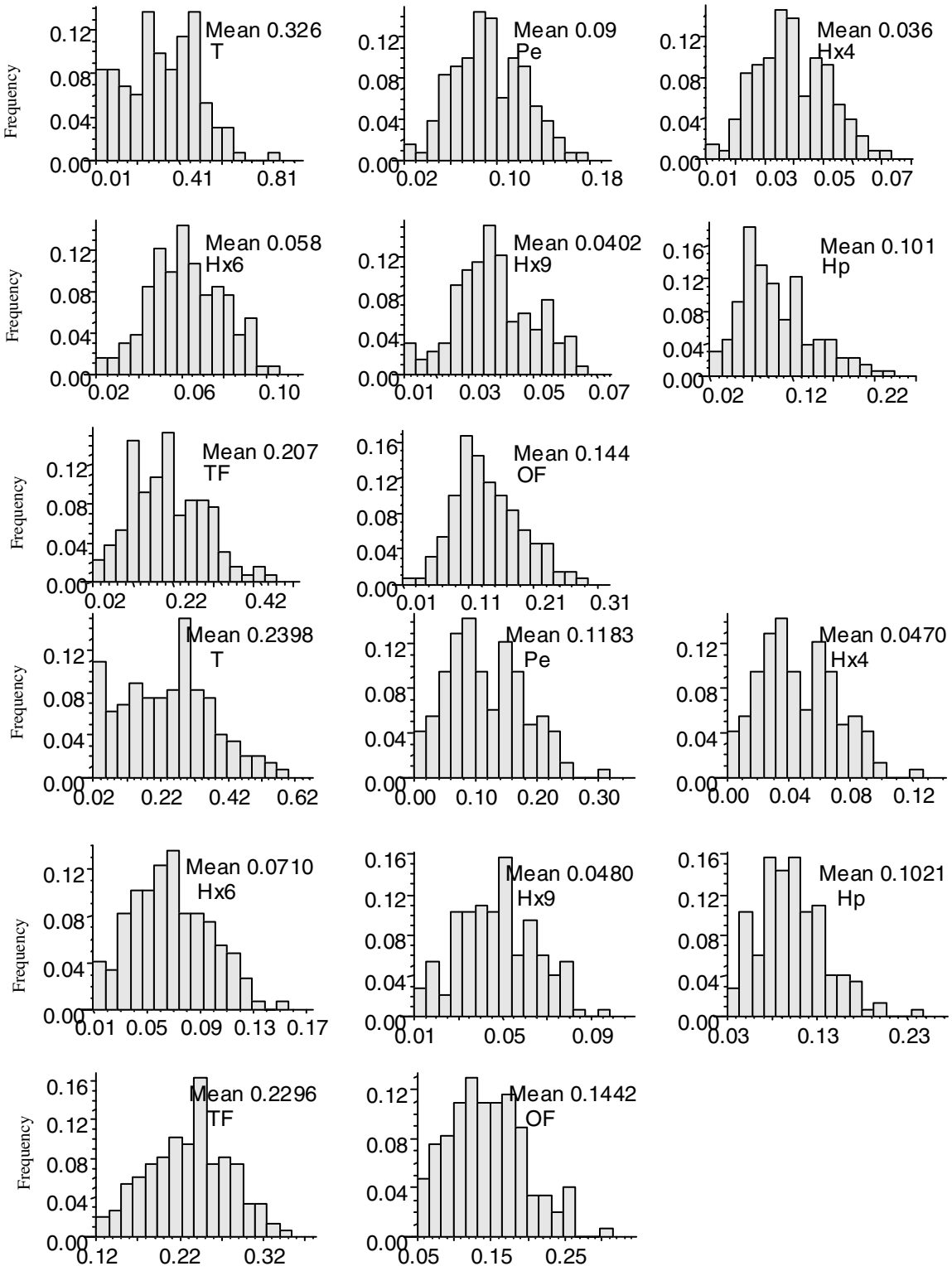

FIGURE S4. Histograms for artificial data X_1 (first three rows) and X_2 (last three rows).

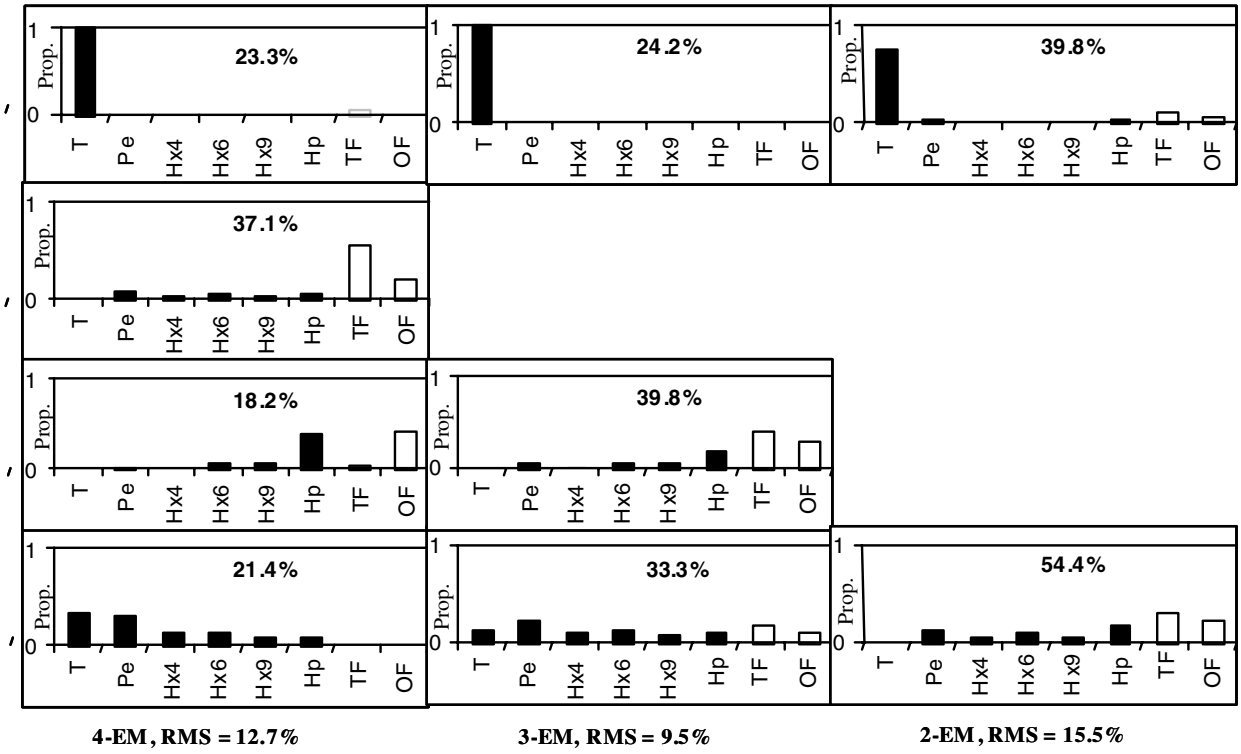

FIGURE S5. T-PVA results for X_1' (control case). Percentages in subfigures refer to the percent contribution to the total variability by the end-member.

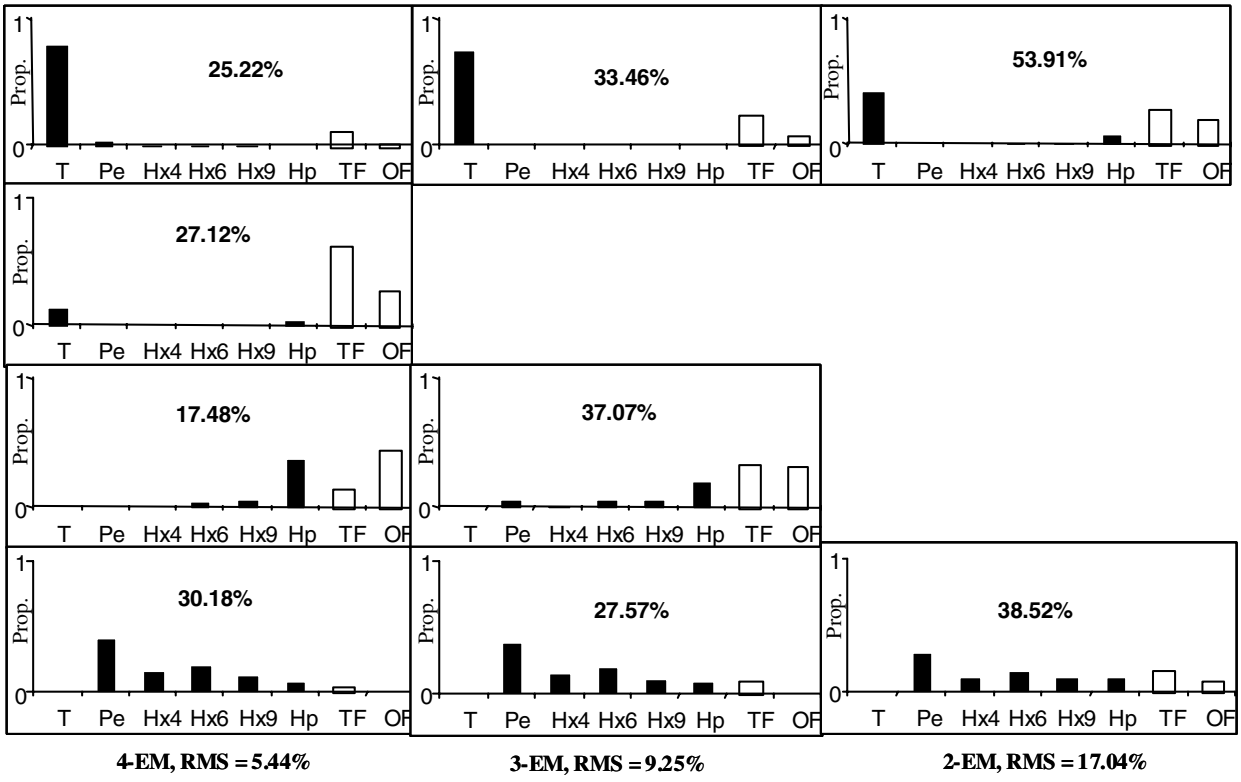

FIGURE S6. T-PVA results for X_2' (control case). Percentages in subfigures refer to the percent contribution to the total variability by the end-member.

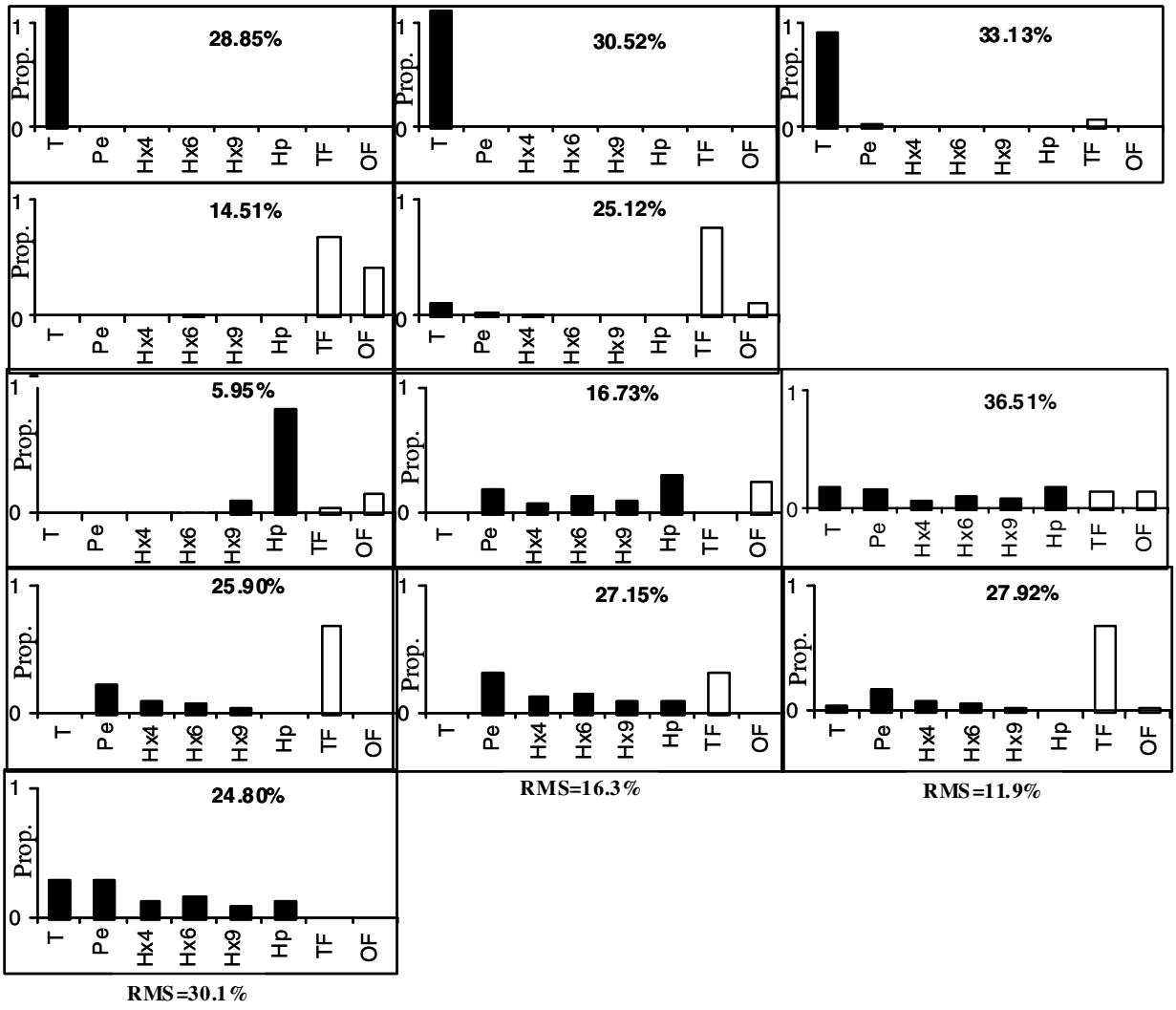

FIGURE S7. T-PVA results for X_1 (with dechlorination). Percentages in subfigures refer to the percent contribution to the total variability by the end-member.

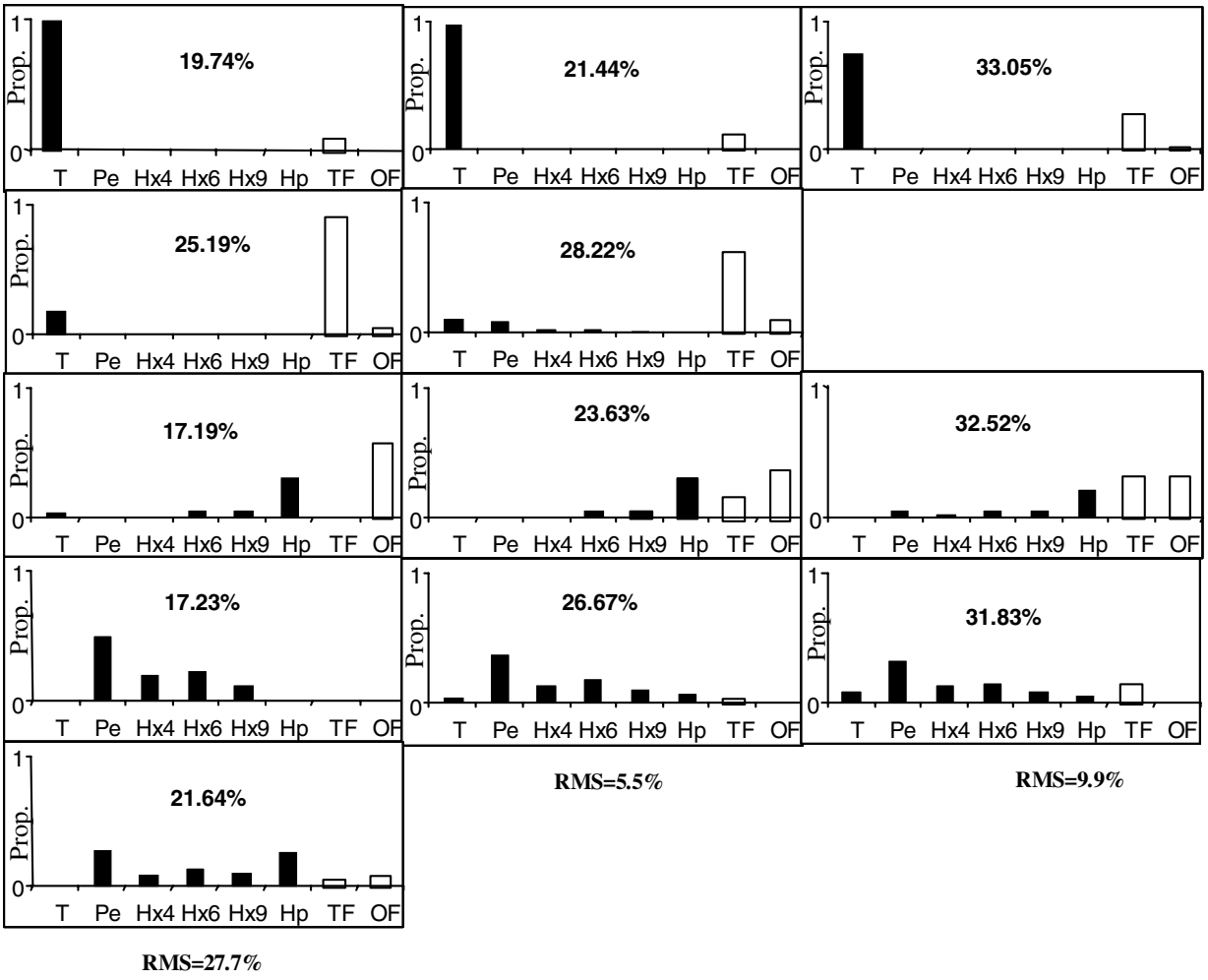

FIGURE S8. T-PVA results for X_2 (with dechlorination). Percentages in subfigures refer to the percent contribution to the total variability by the end-member.

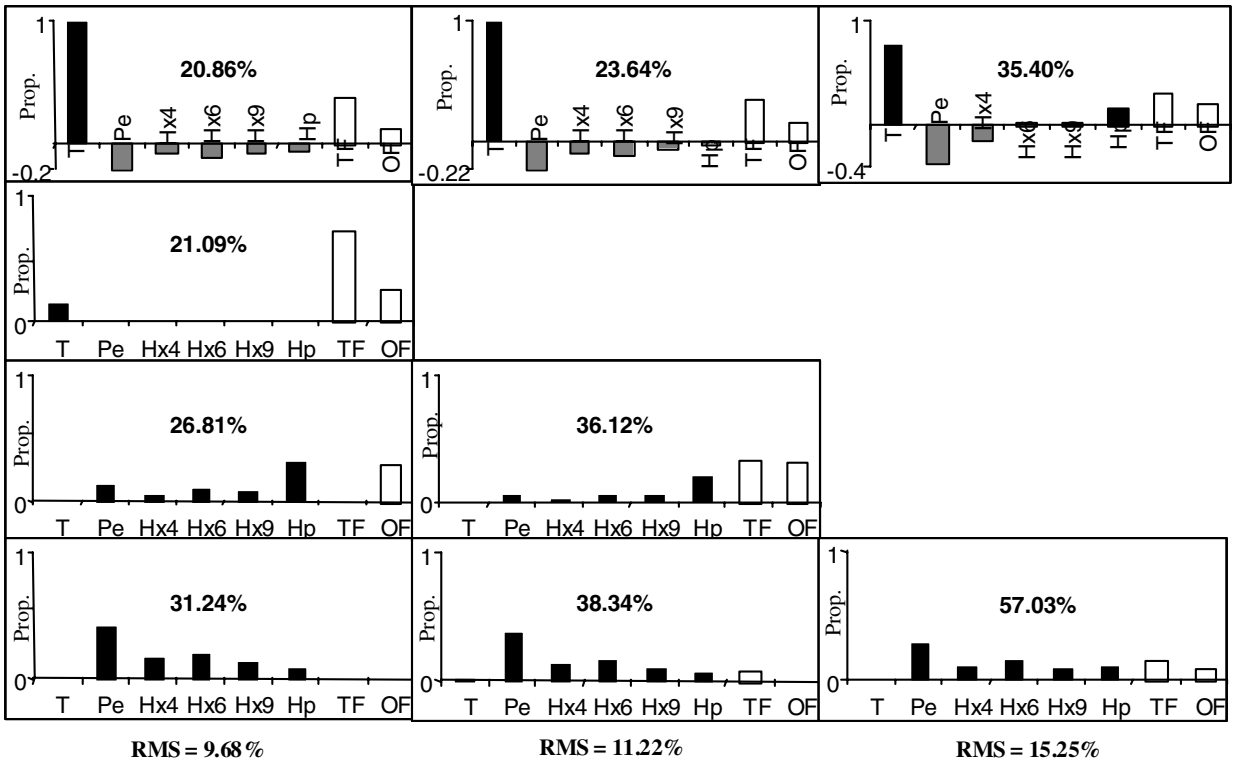

FIGURE S9. M-PVA results for X_2' (without dechlorination). Negative (grey) components in end-member 1 highlight the effect of relaxation. Percentages in subfigures refer to the percent contribution to the total variability by the end-member.

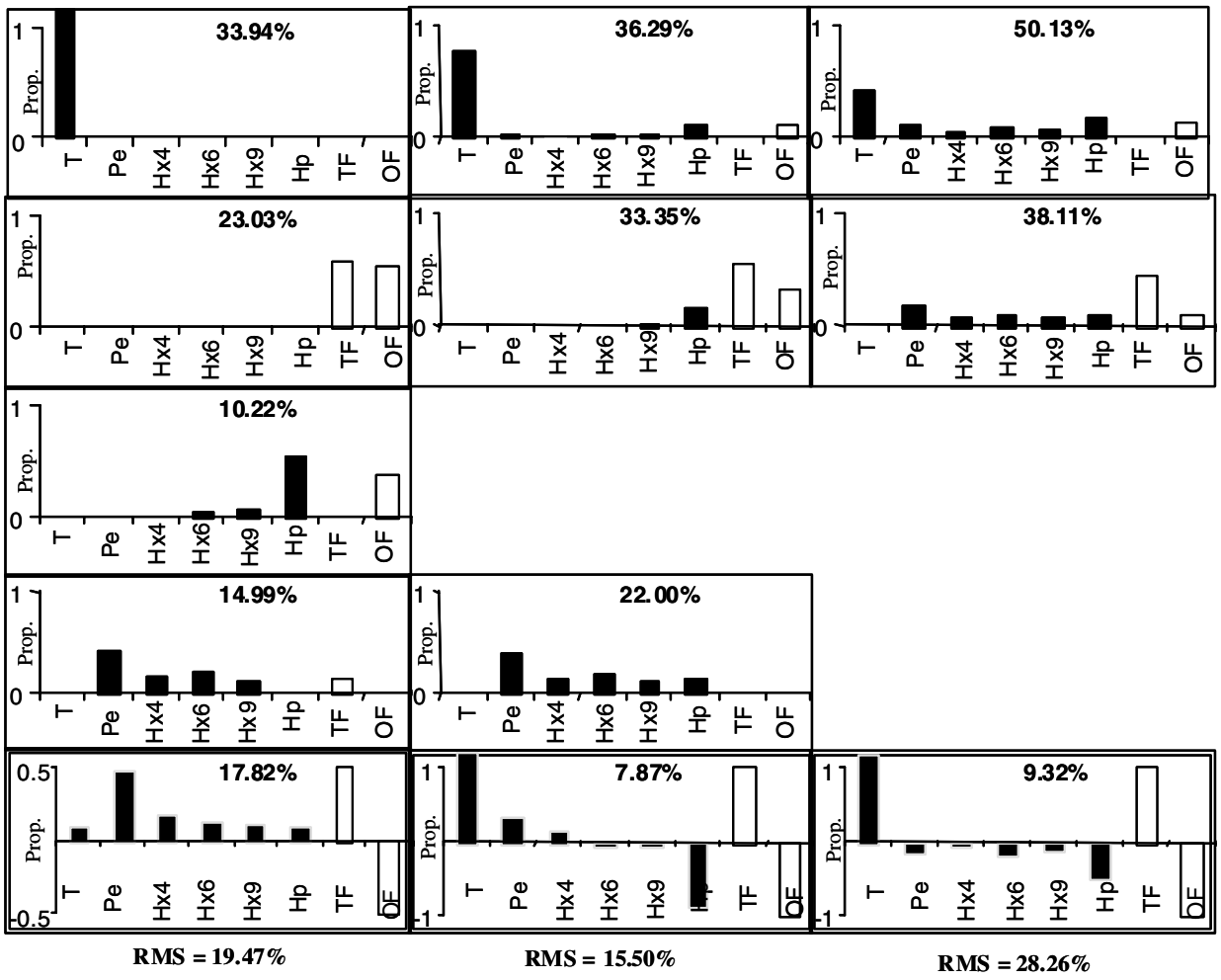

FIGURE S10. M-PVA results for X_1 (with dechlorination). Percentages in subfigures refer to the percent contribution to the total variability by the end-member.

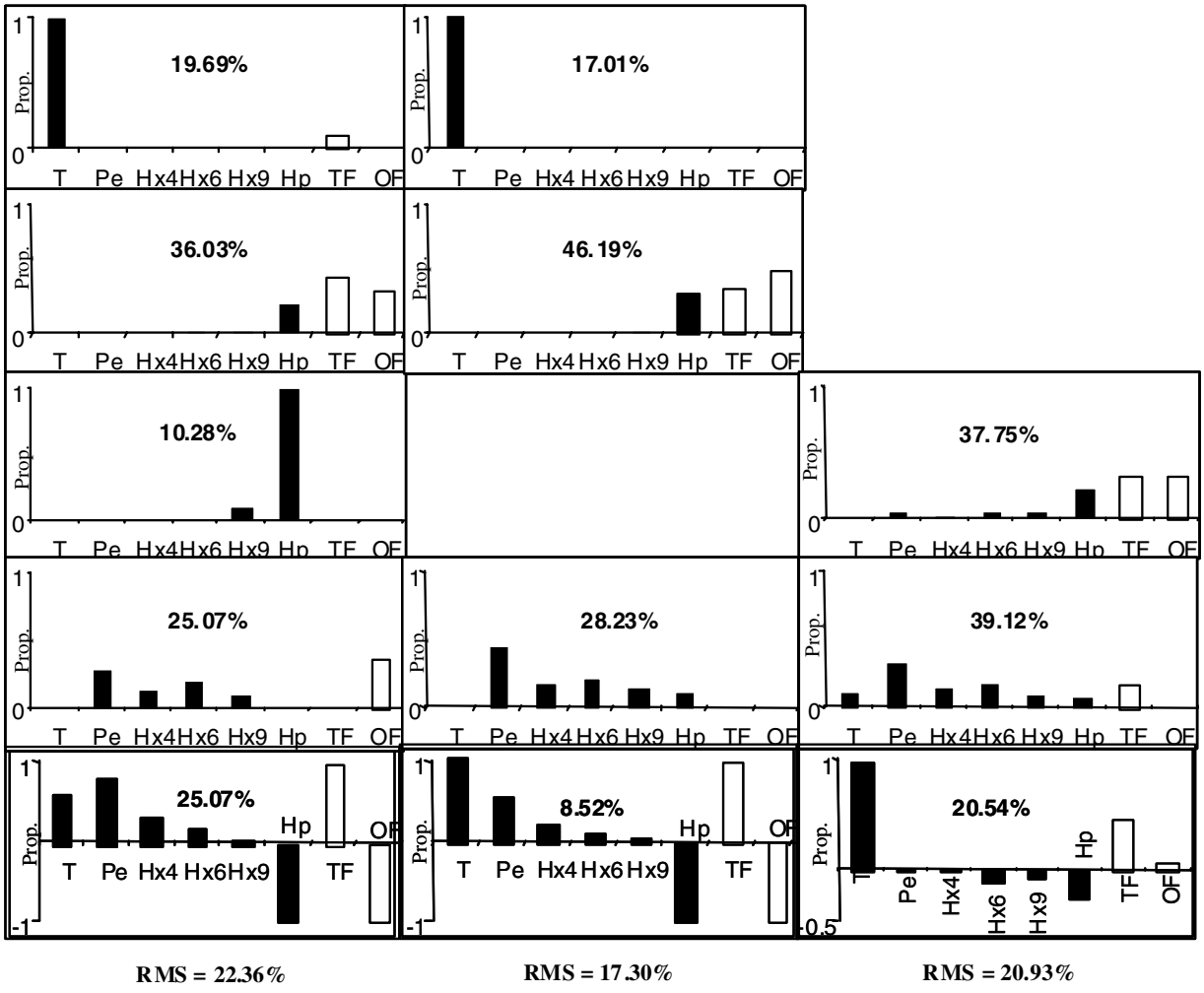

FIGURE S11. M-PVA results for X_2 (with dechlorination). Percentages in subfigures refer to the percent contribution to the total variability by the end-member.

TABLE S3. Results for combinations of model and dechlorination.

	Model without dechlorination: T-PVA	**Model with dechlorination: M-PVA**
Data set without dechlorination	**RMS X_1':** 9.5-15.5% **Var. error X_1':** 0.7-2.3 **Best model X_1':** 3 EMs **RMS X_2':** 5.4-17.0% **Var. error X_2':** 0.9-2.3 **Best model X_2':** 4EMs	**RMS X_1':** 18% **Var. error X_1':** 0.8-1.3 **Best model X_1':** 4 EMs **RMS X_2':** 9.7-15.3% **Var. error X_2':** 0.8-1.9 **Best model X_2':** 4 EMs
Data set with dechlorination	**RMS X_1:** 11.9-30.1% **Var. error X_1:** 0.3-2 **Best model X_1:** 3 EMs **RMS X_2:** 5.5-27.7% **Var. error X_2:** 0.6-1.5 **Best model X_2:** 4 EMs	***SOURCE EMs*** **RMS X_1:** 7.7-18.9% **Var. error X_1:** 0.6-1.9 **RMS X_2:** 8.0-17.0% **Var. error X_2:** 0.6-1.3 ***EM_{dechl}*** **RMS X_1:** 28-41% **Var. error X_1:** 1.0-1.9 **Best model X_1:** 4 EMs **RMS X_2:** 27.8-36.5% **Var. error X_2:** 2.2-5.4 **Best model X_2:** 3 EMs