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

Supporting information

An alternative clean-up column for determination of polychlorinated biphenyls in solid matrices

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1. Experimental

1.1 Preparation of sulphuric acid and silver nitrate impregnated silica gel

Silica gel 60 for column chromatography 0.063-0.200 mm (70-230 mesh) was activated by baking at 130 °C for 12 hrs. It was cooled in a desiccator and 44 g of concentrated sulphuric acid (96%) added to 56 g of the activated silica to make (44% H_2SO_4 on silica) then shaken until there were no more lumps and left for 2 hrs to equilibrate. Soil and sediment samples normally contain sulfur which is extracted with the analytes and presents challenges in the GC-ECD analysis. Therefore both activated copper and silver nitrate impregnated silica gel (SIO_2-$AgNO_3$) were applied to ensure total removal of sulfur. Copper was activated using dilute hydrochloric acid (1:3) and rinsed 3 times with methanol then stored in cyclohexane. $AgNO_3$ impregnated silica gel was prepared by adding 0.2 g silver nitrate in 1 mL water dropwise to 2 g silica gel to make a 10% $AgNO_3$ on silica gel. It was then shaken and dried in an oven for 1 hr at 80 °C.

1.2 Sulfur removal

Soil and sediment samples contain sulfur which is sensitive to ECD detection method, and interferes with PCBs quantification,[1] so after the clean-up step using specific columns, the extracts were subjected to a sulfur removal step. Approximately 250 mg of activated copper powder was added to the 1 mL eluate and allowed to equilibrate for a few minutes. To ensure that no traces of sulfur were left and to remove the copper sulfide (CuS) formed, the eluate was then passed through a column packed with 500 mg of silver nitrate impregnated silica gel (SiO_2-$AgNO_3$), and eluted with 4 mL hexane: DCM (9:1,v/v) followed by blow down and GC-µECD determination.

1.3 Sampling protocol for soil and sediment

Soil and sediment were collected using a shovel from at least three points within a radius of 50 m around the sampling site, homogenised on aluminium foil, and placed in zip-lock bags for transportation to the laboratory where they were kept in a freezer at -20 °C.

1.4 Kinetics and adsorption isotherms

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \qquad \text{Pseudo-first-order (1)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$ Pseudo-first-order (2)

q_e is amount adsorbed at equilibrium, q_t is the amount adsorbed at any given time (t, min), k_1 is rate constant for the pseudo-first-order (min^{-1}), and k_2 is rate constant for the pseudo-second-order (min^{-1} g μg^{-1}).

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$ Langmuir isotherm (3)

$$q_e = K_f C_e^n$$ Freundlich isotherm (4)

q_e is the bound analyte at equilibrium (µg g^{-1}), C_e is the equilibrium concentration in µg mL^{-1}, q_m represents the monolayer coverage or maximum adsorption capacity (µg g_{-1}), and K_L is a constant related to the adsorption energy (mL μg^{-1}), K_f and n are Freundlich constants representing the adsorption capacity and heterogeneity index.

1.5 Selectivity studies

Selectivity of the imprinted polymer was determined by competitive batch rebinding assays using PCB 14 and hexachlorobenzene (HCB) as the structural analogues of PCB 15. The three analytes each at a concentration of 0.88 µg mL^{-1} were treated as described in the section 2.5.

1.6 Results on the kinetic data

To understand the mechanism of adsorption, the kinetic data was applied on the pseudo-first-order (2) and pseudo-second-order kinetic models (3). Adsorption of PCB 15 followed the pseudo-second-order kinetic model as was indicated by high correlation coefficient (R^2) of 0.9918 for the MIP and 0.9897 for the NIP. The values for the equilibrium concentration (q_e) 7.23 and 6.41 µg g^{-1} for the MIP and NIP in the pseudo-second-order were also near the experimental 8.54 and 7.63 µg g^{-1}, thus confirming that the adsorption involved sharing or exchange of electrons,[2,3] which is consistent with the expected π-π interaction between the template and the polymer.

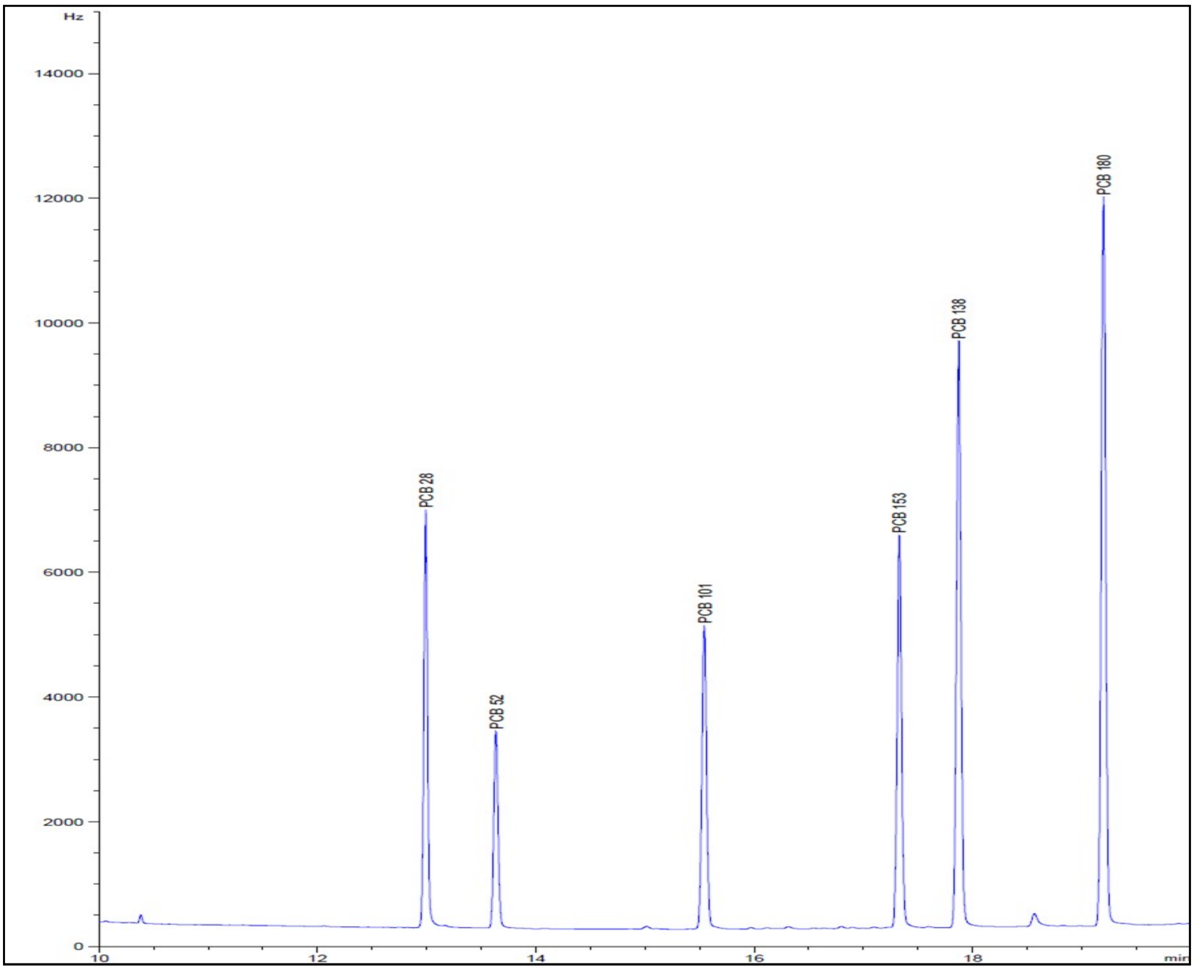

Fig. S1 Chromatogram of 100 ng mL^{-1} PCBs standard mixture with PCB 209 as the internal standard

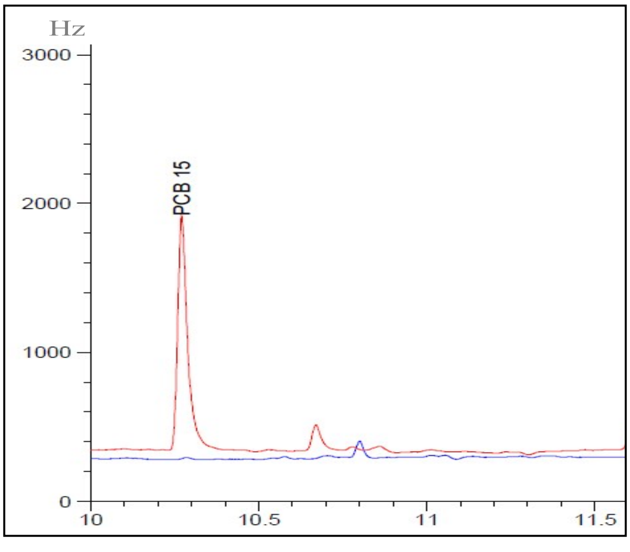

Fig. S2 Chromatogram of cleaned MIP (blue) and PCB 15 standard (red) using GC-µECD and Nitrogen as both the carrier and make-up gas at 2 mL min^{-1} and 30 mL min^{-1}, respectively

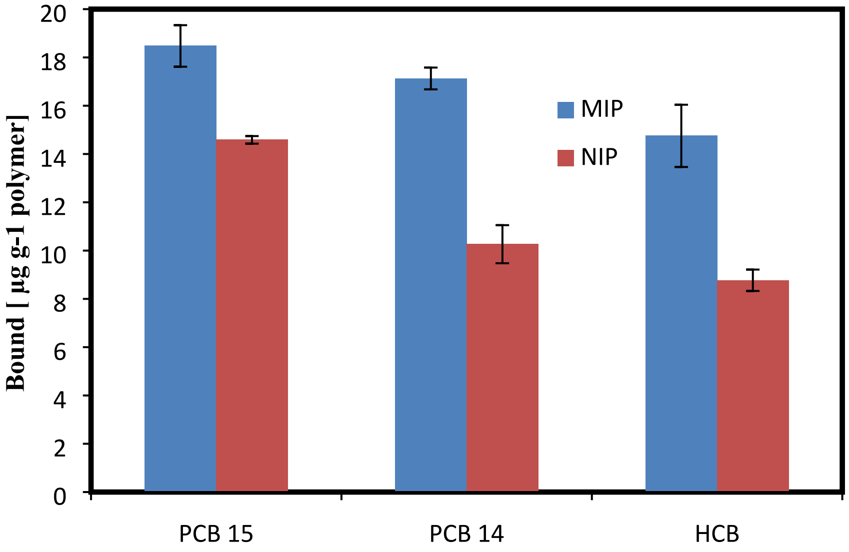

Fig. S3 Selectivity studies using PCB 15 and structurally similar PCB 14 and HCB

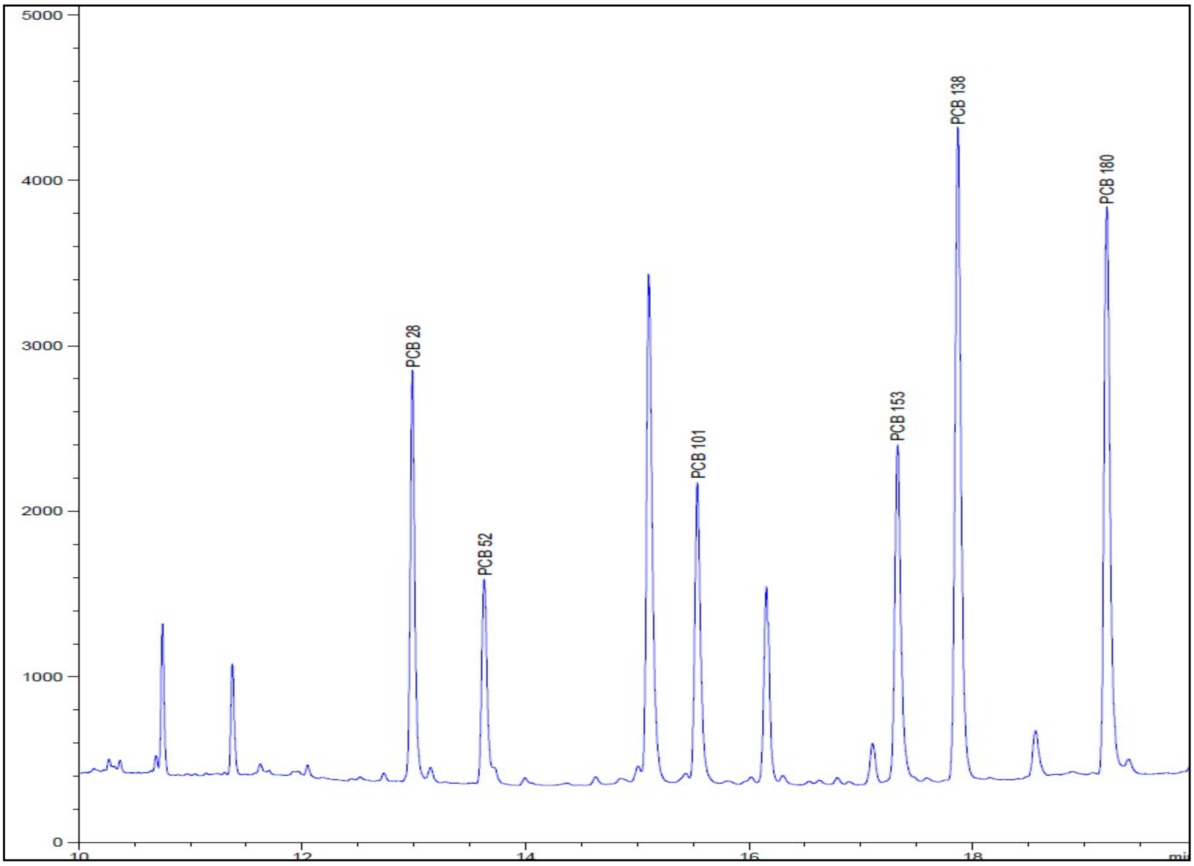

Fig. S4 Chromatogram of Mt. Kenya soil sample spiked at 4 μg kg^{-1} with PCB standard mixture and cleaned using MISPE

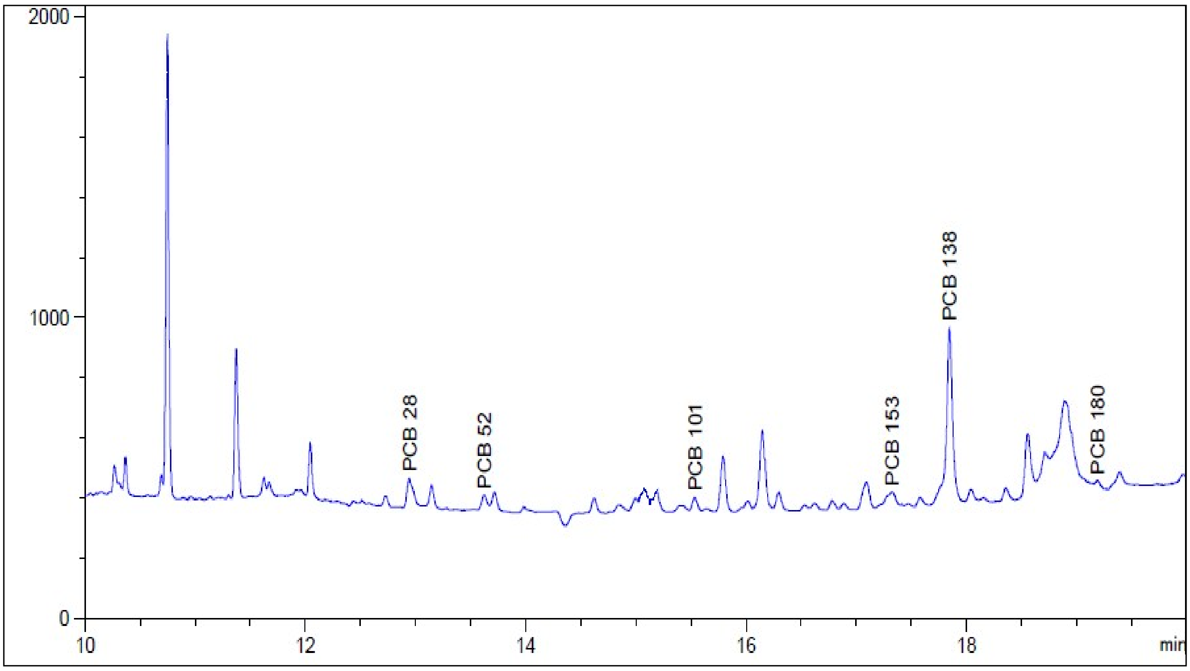

Fig. S5 Chromatogram of a soil sample from Dandora cleaned using MISPE

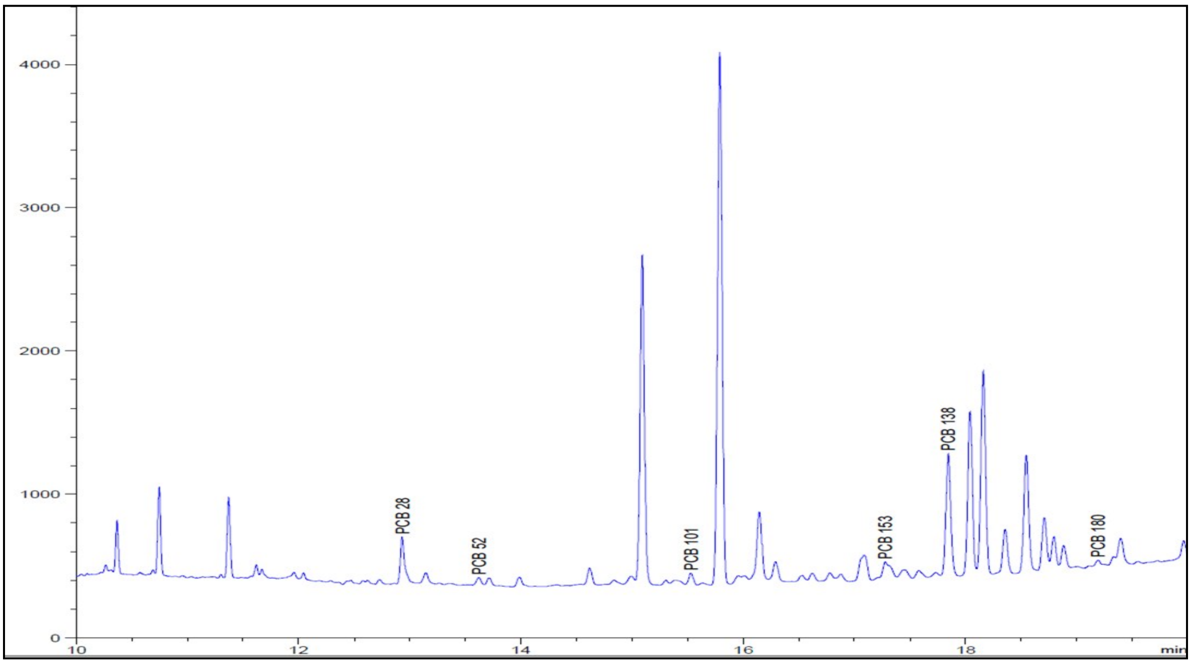

Fig. S6 Chromatogram of a sediment sample from Kijabe cleaned using MISPE

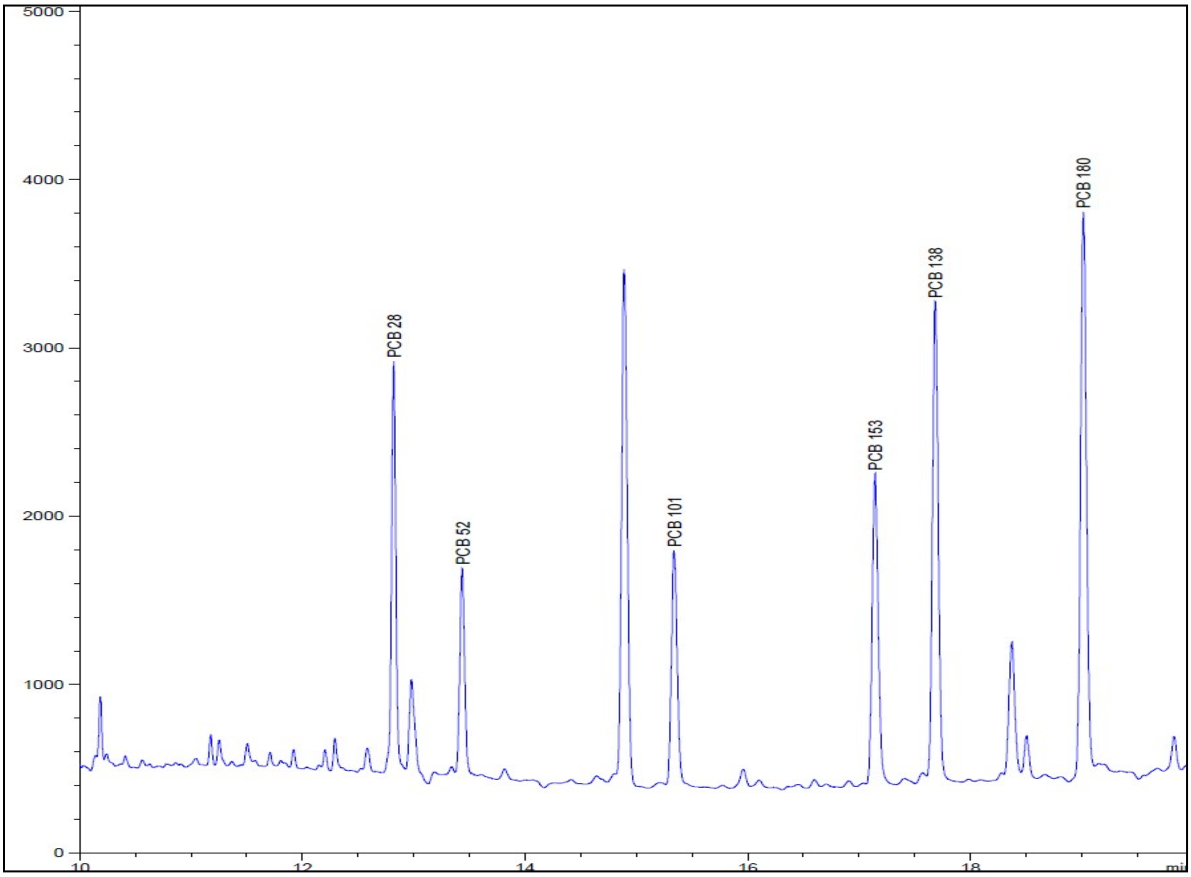

Fig. S7 Chromatogram of Mt. Kenya soil sample spiked at 4 µg kg^{-1} with PCB standard mixture and cleaned using acidified silica gel

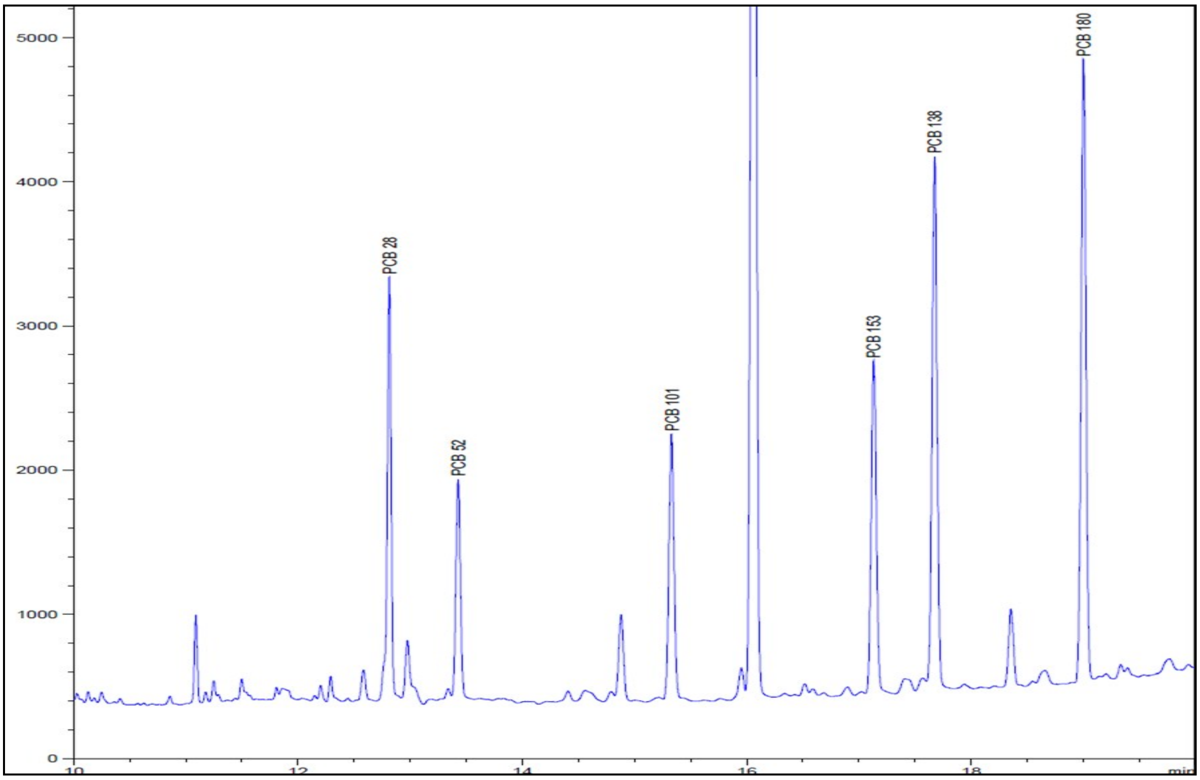

Fig. S8 Chromatogram of Mt. Kenya soil sample spiked at 4 µg kg^{-1} with PCB standard mixture and cleaned using sulfoxide modified silica

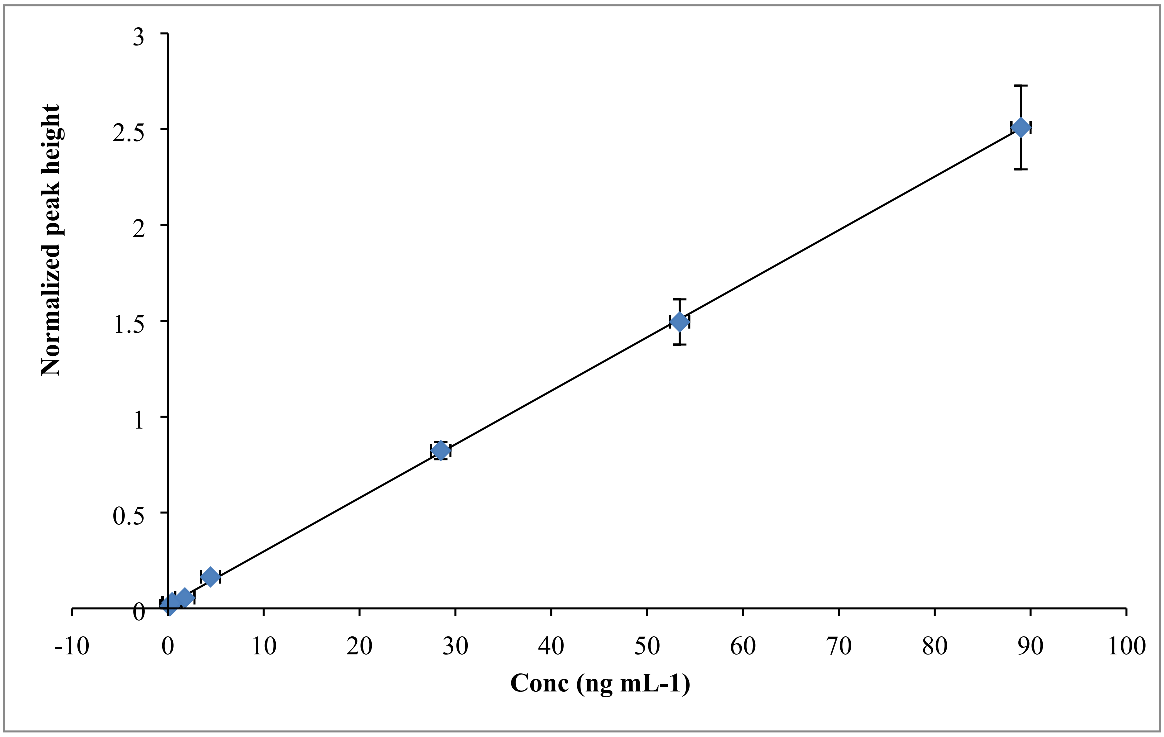

Fig. S9 Exemplary calibration curve of PCB 180 for the concentration range 0.22-89 ng mL^{-1} with PCB 209 as the internal standard. The error bars represent the standard deviation of 3 replicates.

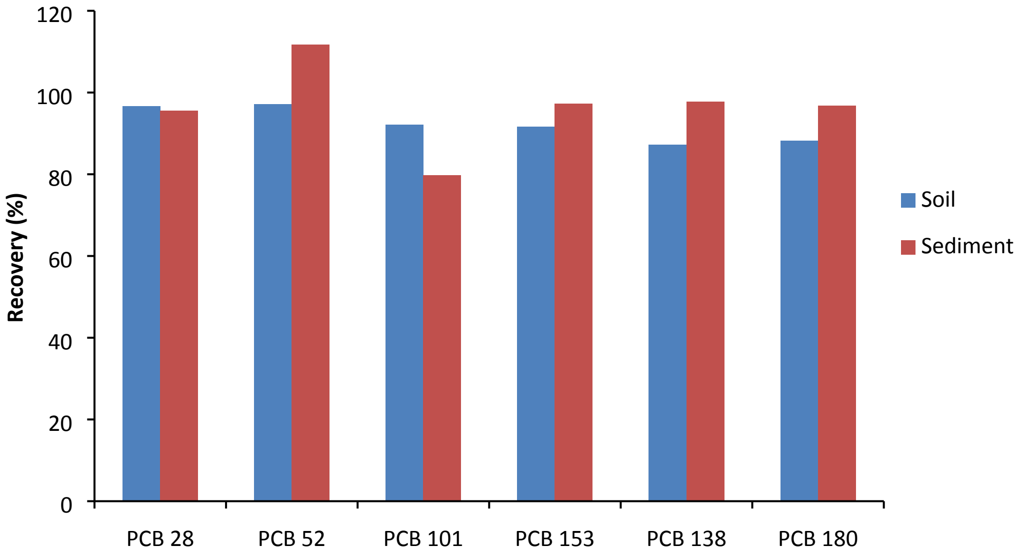

Fig. S10 Recoveries of PCBs on spiked soil and sediment on specific clean-up columns after 30 cycles of usage.

Table S1 Recoveries and losses (% ± SD) of PCBs on MISPE, NISPE, C18, Sulfoxide silica columns using PCBs standards in hexane at a concentration of 20 ng mL^{-1} and elution with *n*-hexane: DCM (9:1; v:v)

	Recovery (%)				Losses (%)			
	MISPE	NISPE	C18	Sulfoxide modified silica	MISPE	NISPE	C18	Sulfoxide modified silica
PCB 28	99.0 ± 0.64	91.7 ± 3.96	72.5 ± 2.83	83.8 ± 2.62	1.20 ± 0.14	0.80 ± 0.0	26.1 ± 5.30	7.10 ± 0.37
PCB 52	96.6 ± 0.78	90.4 ± 2.19	78.9 ± 7.64	88.0 ± 0.35	4.05 ± 1.20	7.90 ± 0.84	32.4 ± 1.98	5.03 ± 1.71
PCB 101	95.0 ± 8.41	93.6 ± 0.49	72.5 ± 1.98	90.2 ± 0.78	1.70 ± 0.14	2.60 ± 0.57	31.0 ± 3.18	4.97 ± 0.85
PCB 153	94.9 ± 2.16	98.9 ± 0.42	69.2 ± 8.49	84.3 ± 1.27	0.70 ± 0.0	0.70 ± 0.0	32.8 ± 4.10	5.00 ± 0.32
PCB 138	96.1 ± 5.16	95.3 ± 6.79	71.4 ± 0.85	85.8 ± 0.21	0.75 ± 0.07	0.55 ±0.07	30.1 ± 0.92	3.44 ± 0.33
PCB 180	96.3 ± 5.15	94.0 ± 4.88	71.5 ± 2.33	87.6 ± 0.85	1.25 ± 0.07	0.0	31.1 ± 2.40	0.0

SD = standard deviation of replicate analysis

References

(1) Smedes, F.; de Boer, J. Determination of chlorobiphenyls sediments -analytical methods. *trends Anal. Chem.* **1997**, *16*, 503–517.

(2) Ho, Y.-S. Review of second-order models for adsorption systems. *J. Hazard. Mater.* **2006**, *136*, 681–689.

(3) Ho, Y.; McKay, G. Pseudo-second order model for sorption processes. *Process Biochem.* **1999**, *34*, 451–465.

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