Supplementary information

Evidence of chlordecone resurrection by glyphosate in French West indies

Pierre Sabatier [†,], Charles Mottes [‡,§], Nathalie Cottin [||], Olivier Evrard [|], Irina Comte [§,#], Christine Piot [||], Bastien Gay[†,||], Fabien Arnaud[†], Irène Lefevre [|], Anne-Lise Develle [†], Landry Deffontaines[‡,§], Joanne Plet[‡,§], Magalie Lesueur-Jannoyer[‡,§], Jérôme Poulenard [†]*

[†]: Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, EDYTEM, LE Bourget du lac, France

[‡] : Cirad, UPR HortSys, F-97285 Le Lamentin, Martinique, France

[§] : HortSys, Geco, Univ Montpellier, CIRAD, Montpellier, France

|| : Univ. Savoie Mont-Blanc, LCME, Le Bourget du Lac, France

| : Univ. Paris-Saclay, UVSQ, CEA, CNRS, LSCE/IPSL, F-91191, Gif-sur-Yvette, France

: Cirad, UPR GECO, F-97130 Capesterre-Belle-Eau, Guadeloupe, France

18 pages: 5 supplementary figures 1 3 supplementary tables and a detailed pesticide analysis protocols:

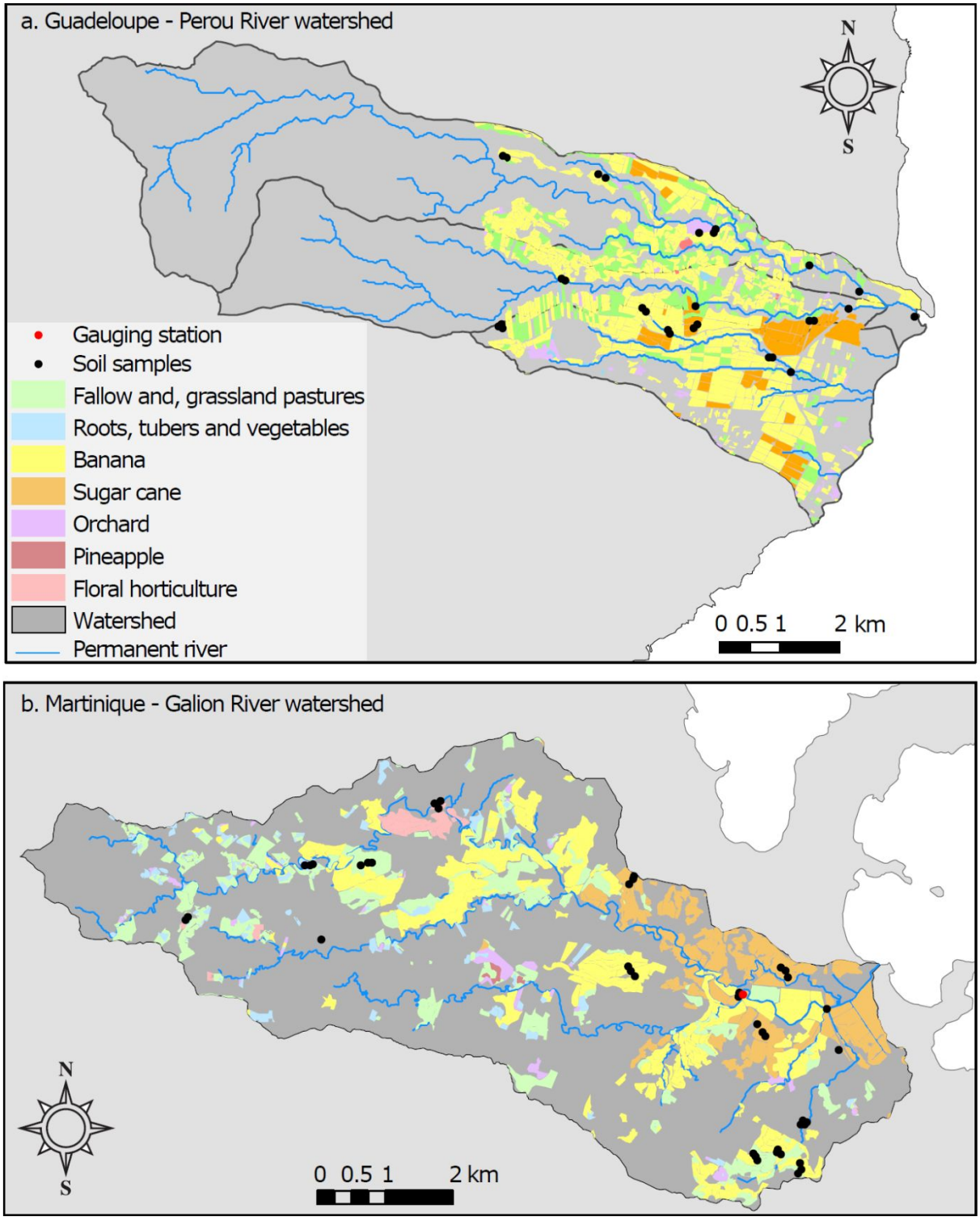


Fig. S1: Land use in the investigated watersheds. a, b, Pérou (Guadeloupe) and Galion (Martinique) river watersheds (dark gray) with land uses; different colors indicate the types of

crops, and bananas are in yellow. Black circles indicate surface soil samples under different land use conditions. The red circle (**b**) indicates the location of the gauging station for the data displayed in Fig. S3. These two watersheds are a part of the OPALE observatory (Observatoire des Pollutions Agricoles aux Antilles - Observatory for Agricultural Pollution in Antilles). The Pérou River watershed (**a**) is located on the volcanic island of Basse-Terre, Guadeloupe, in the FWI and is described in Carbit et al. (2016)(20). It is located on the eastern windward coast and covers an area of 12.6 km², ranging from 0 to 1400 m above mean sea level. The climate is a humid tropical climate with a marine influence and an important altitudinal rainfall gradient from 2400 $mm.yr^{-1}$ downstream to 6000 $mm.yr^{-1}$ upstream. The hydrological system is mainly linear with one major watercourse, the Pérou River, which is a tributary of the Great River of Capesterre. The upstream portion of the catchment is characterized by steep slopes (100-295%) and steep banks several meters high along the river. This area is also characterized by considerable forest coverage (55% of the catchment area) by Andosols, Ferralsols and young soils. The intermediate area is characterized by a short plateau and medium slopes (20-40%) and has been cultivated principally with banana (*Musa* spp.) on Andosols. The downstream part of the watershed is characterized by low slopes (0-20%), sugarcane and banana plantations installed on Nitisols and urban settlements. The other watershed, located on the eastern windward coast between the municipalities of Sainte-Marie and Petit-Bourg, is composed of older Ferralsols. It has similar climatic and topographic conditions as the Pérou catchment. The land uses are similar, although with lower proportions of the catchment areas occupied by banana fields. A larger proportion of fallows and pastures is found instead. The Galion River watershed (**b**) is located on the East coast of Martinique, a volcanic island in the FWI, and is described in Mottes et al. (2019)(45). The watershed covers 44.5 km^2, ranging from 0 to 694 m above sea level. The climate is humid tropical with oceanic influence, and rainfall ranges from 1500 $mm.y^{-1}$ downstream to 4000 $mm.y^{-1}$ upstream. The hydrological system is composed of 4 major permanent rivers and a very dense network of intermittent gullies. The upper watershed is characterized by steep slopes (>80%) and dominated by Andosols characterized by both high infiltration rates and a high organic matter content under tropical forest and agricultural land for livestock and traditional food production. The intermediate zone is characterized by lower slopes (~35%) cultivated with banana or occupied by mixed farming on intergrade soils between Andosols and compact Ferralsols. The floodplain

found in the lower watershed is underlain by Ferralsols and dominated by industrial crop production, including banana and sugar cane.

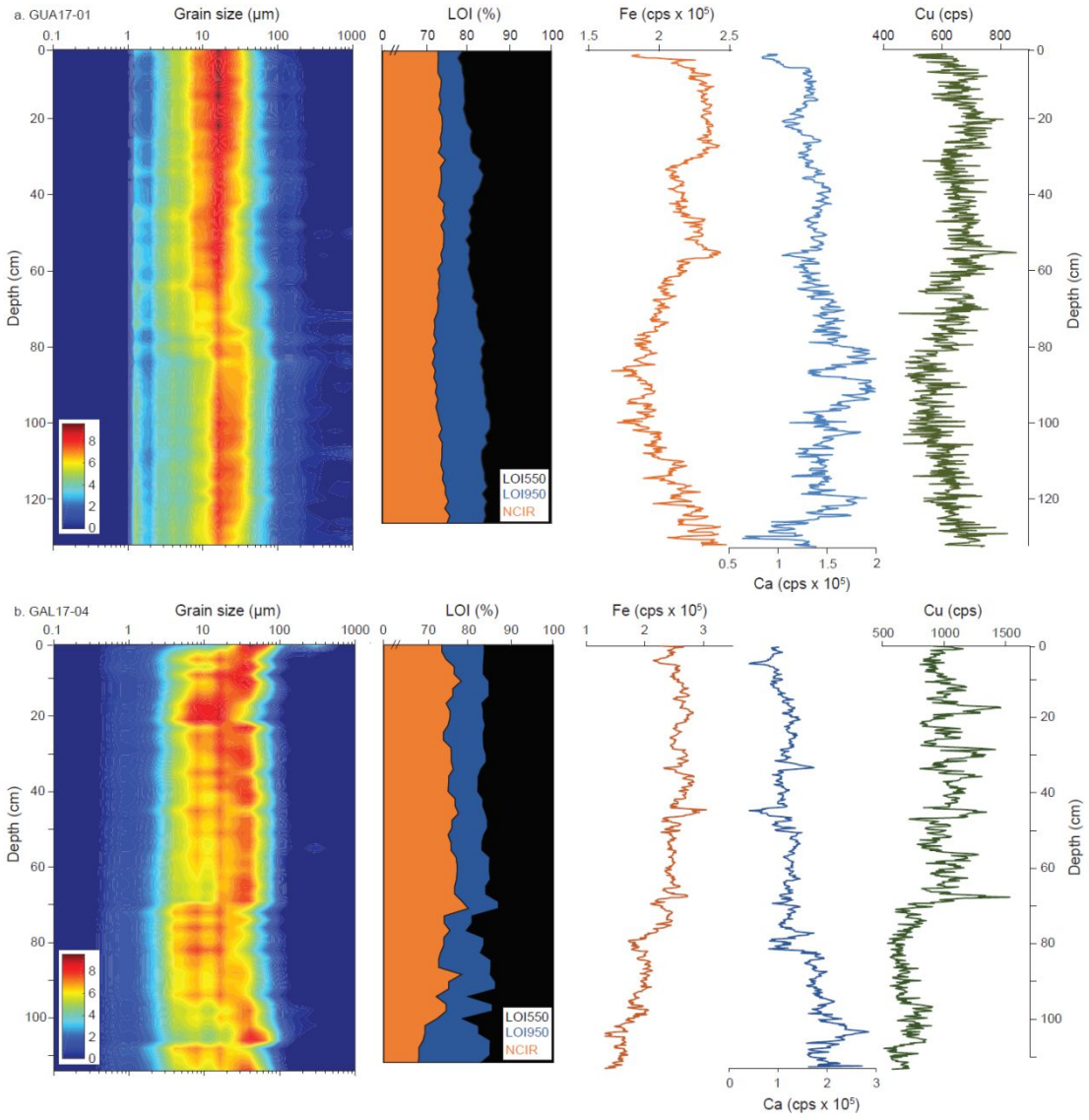


Fig. S2: Sedimentological and geochemical data in marine cores. a, b, from left to right in the grain size contour plot, LOI, Fe, Ca and Cu for the GUA17-01 and GAL17-04 cores. Above 80 cm in GUA17-01 (**a**) and along the whole core in GAL17-04 (**b**), NCIR and Fe both decrease with depth, and LOI950 and Ca both increase with depth. The grain size dramatically shifted at approximately 76 cm in GUA17-01 (**a**) and at 70 cm associated with an increase in Cu in GAL17-04 (**b**). In both cores, the carbonate fraction (LOI950) increased with depth, the organic fraction (LOI550) remained almost constant, and the terrigenous content (NCIR) decreased with depth. The grain size distribution was relatively homogeneous, with median values of 9.5 µm and 11.25 µm in GUA17601 and GAL17-04, respectively.

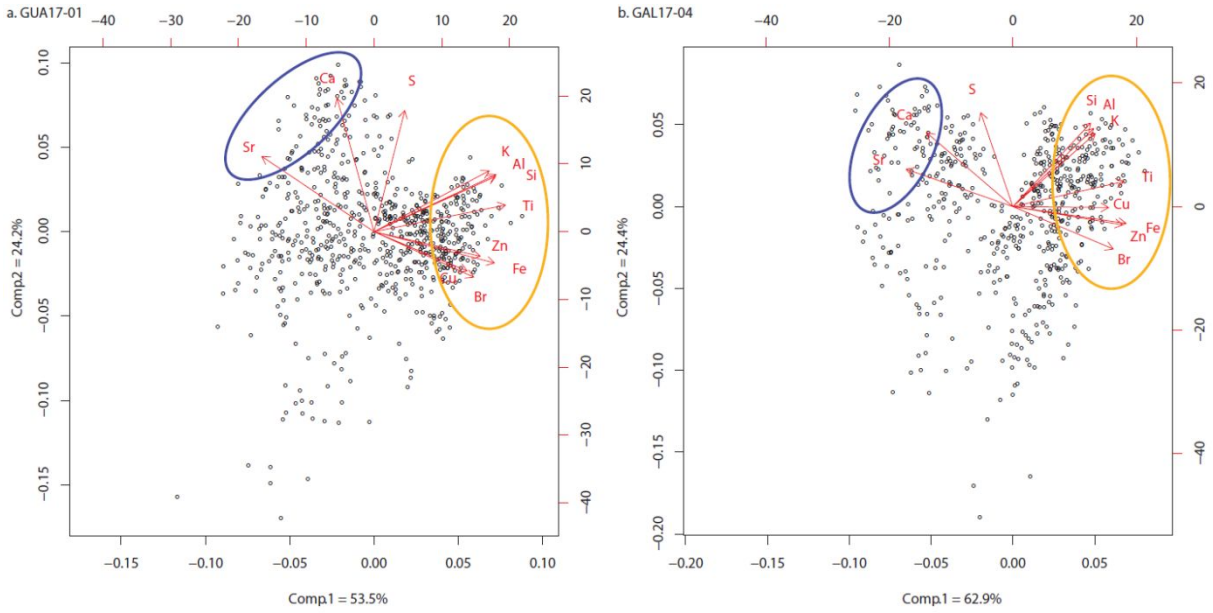


Fig. S3: Biplot of the principal component analysis (PCA) of XRF geochemical data. a, PCA for GUA17-01; Comp1 and Comp2 explained 77.7% of the total variability. **b**, PCA for GAL17-04; Comp1 and Comp2 explained 87.7% of the total variability. The two PCAs show a similar structure with high positive loadings of K, Al, Si, Ti, Fe, Zn, Br and Cu on comp1 and negative loadings of Ca and Sr on Comp1 with S in the intermediate position. Comp2 shows positive loadings of Ca, Sr, S, SI, Al and K. This PCA of the bulk sediment of the two cores provides the same result and allows identification of two geochemical endmembers: 1) inputs from the watershed with aluminosilicates (K, Al, Si, Ti, Fe), organic matter (Br) and metallic pollutants (Cu, Zn) in orange and 2) marine carbonate productivity (Ca and Sr) in blue. The geochemical data are in good agreement with the LOI data, indicating an upward increase in terrigenous inputs from the watershed and simultaneous decrease in carbonate productivity (Fe and Ca in Fig. S3). Accordingly, the Fe/Ca ratio is used as a high-resolution proxy for the terrigenous fraction.

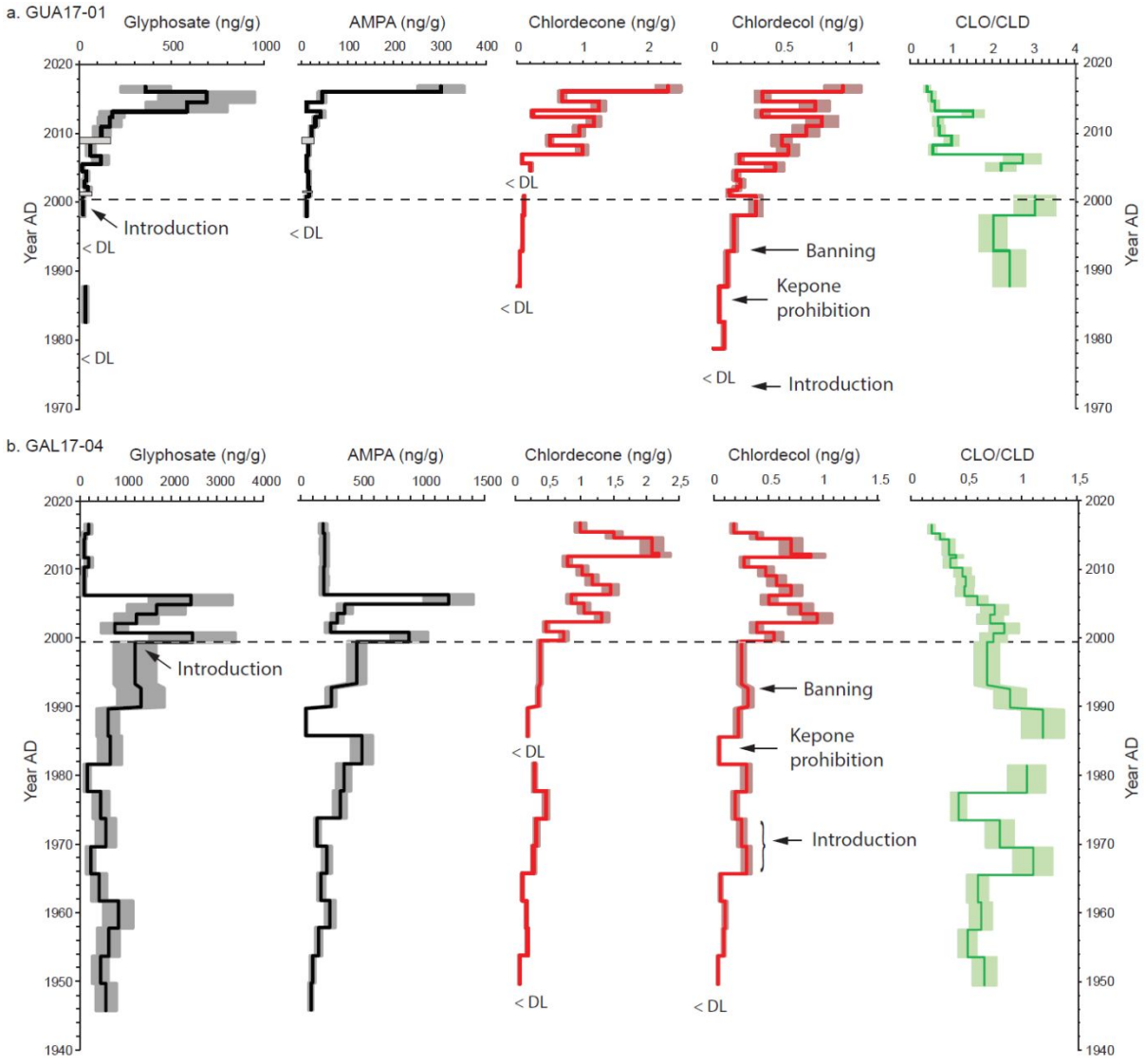
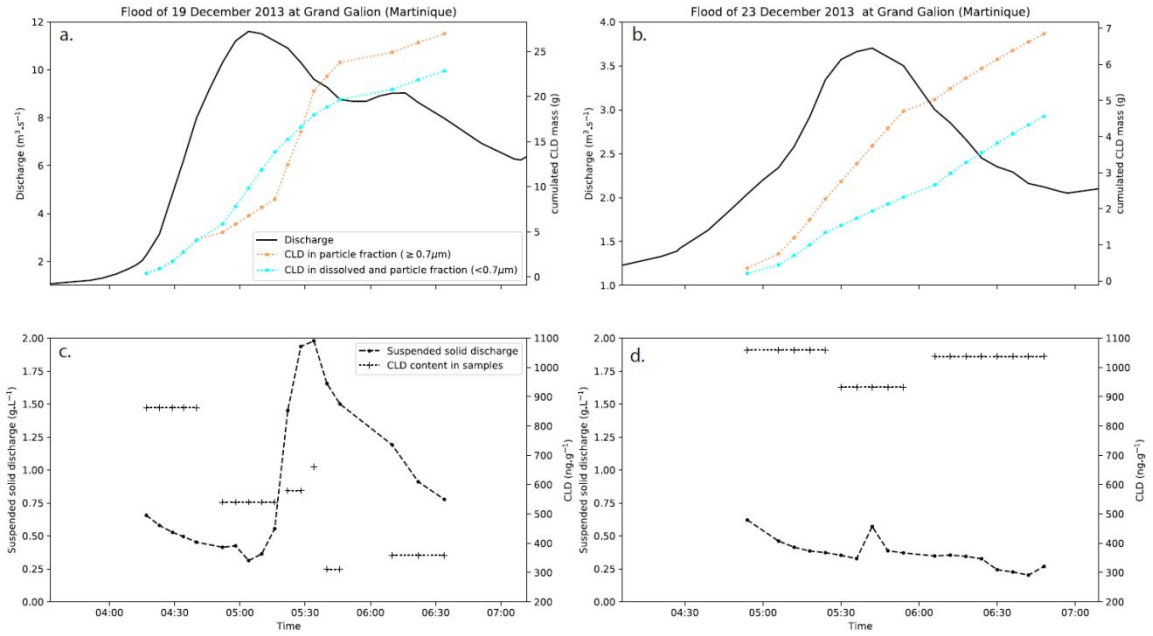


Fig. S4: Pesticide chronology expressed in concentration. **a, b**, from right to left: glyphosate and its degradation product AMPA, CLD and one of its degradation products CLD and the CLO/CLD ratio (CLO/CLD) in GUA17-01 and GAL17-04. <DL indicates below the detection limit. The grey rectangle in **a** indicates a lack of data at this depth. Horizontal dashed lines indicate the main change in sedimentation rate in both cores. Above the two dashed lines, increases in glyphosate and AMPA synchronous with increases in CLO and CLD are observed. The glyphosate and AMPA chronologies present downward diffusive transport in the sediment column, as these molecules appear before their introduction in the FWI in GAL17-04 (**b**). Even if the first increases in CLD and CLO correspond to the introduction period (1972 or later, within dating uncertainties), these

molecules also undergo downward diffusive transport in GAL17-04 (**b**), although more limited than observed for glyphosate. The CLO/CLD ratio in both cores presents the same increase with depth. These observations indicate that the CLD transformation into CLO is more favored in anaerobic conditions (in marine sediment) than in aerobic conditions (in soils of the watershed) if the CLD observed in the upper sediment sections has approximatively the same age (1972-1993) as that in the deeper part of the core.



100 **Fig. S5: Gauging station data during two flood events in the Galion watershed. a, b,** Water discharge and cumulative chlordecone mass in fractions below (blue) and above (orange) 0.7 µm during two flood events on 19.12.2013 and 23.12.2013 of medium and low intensity, respectively. Note that the fraction below 0.7 µm could contain colloids. **c, d**, Suspended soil discharge (dashed line) and chlordecone content (dotted line) in individual samples for the two floods. These data
105 indicate that during the two floods, chlordecone mass transfer is higher in suspended matter than in the dissolved fraction.

Sample	Flood of 19 December 2013		Flood of 23 December 2013	
	Filtrated	Integrated in composite sample n°	Filtrated	Integrated in composite sample n°
1	x	1	x	1
2	x	1		
3	x	1	x	1
4	x	1	x	1
5	x	1	x	1
6			x	1
7	x	2	x	2
8	x	2	x	2
9	x	2	x	2
10	x	2	x	2
11	x	2	x	2
12	x	3		
13	x	3	x	3
14	x	4	x	3
15	x	5	x	3
16	x	5	x	3
17			x	3
18			x	3
19			x	3
20	x	6	x	3
21				
22	x	6		
23				
24	x	6		

Table S1: Selected samples for filtration and composite sample composition for the two sampled floods at the Grand Galion outlet.

depth_top (mm)	depth_bottom (mm)	density (g/cm3)	Pbxs (Bq/g)	Pbxs_er (Bq/g)
0	20	1.32	89.67	6.51
40	60	1.31	67.56	6.26
80	100	1.34	77.68	7.34
160	180	1.29	77.63	6.10
240	260	1.38	78.14	4.29
320	340	1.41	74.58	4.61
400	420	1.34	83.84	5.13
440	460	1.37	62.45	6.20
480	500	1.35	73.52	4.17
520	540	1.26	87.27	5.85
560	580	1.36	62.59	4.23
600	620	1.35	64.66	3.37
640	660	1.39	50.02	2.68
680	700	1.39	59.60	3.79
720	740	1.51	50.16	3.91
760	780	1.50	51.05	3.11
800	820	1.54	32.56	3.75
840	860	1.61	23.64	4.57
880	900	1.53	21.49	3.37
920	940	1.54	20.91	4.15
960	980	1.59	10.47	2.84
1000	1020	1.47	8.04	2.97

Table S2 : Depth, density and ^{210}Pbxs and uncertainties data for core GUA17-01.

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depth_top (mm)	depth_bottom (mm)	density (g/cm3)	Pbxs (Bq/g)	Pbxs_er (Bq/g)
0	20	0.97	73.8	8.0
20	40	0.92125	NA	NA
40	60	1.07125	NA	NA
60	80	1.155	79.2	7.7
80	100	1.08125	NA	NA
100	120	0.94875	NA	NA
120	140	1.10875	71.6	7.2
140	160	1.1	NA	NA
160	180	1.12125	NA	NA
180	200	1	80.4	13.2
200	220	1.0275	NA	NA
220	240	1.075	NA	NA
240	260	1.07875	63.2	10.9
260	280	0.90375	NA	NA
280	300	1.07625	NA	NA
300	320	1.01875	58.2	8.2
320	340	1.12375	NA	NA
340	360	1.0275	NA	NA
360	380	1.04625	52.1	7.1
380	400	1.04625	NA	NA
400	420	0.80125	51.3	5.6
420	440	0.97625	31.0	11.0
440	460	0.95625	43.3	6.2
460	480	0.92875	39.3	4.0
480	500	0.72375	41.3	9.4
500	520	1.0225	NA	NA
520	540	0.97	NA	NA
540	560	0.94625	31.4	7.3
560	580	1.16125	NA	NA
580	600	1.035	NA	NA
600	620	0.96625	20.4	8.7
620	640	1.14	NA	NA
640	660	1.145	NA	NA
660	680	1.14	13.7	8.1

Table S3: Depth, density and ^{210}Pbxs and uncertainties data for core GAL17-04.

Detailed pesticide analysis protocols

Chemicals and standards

Chlordecone (CLD, CAS: 143-50-0) and chlordecone-alcohol (CLO, CAS: 1034-41-9) each at 10 $\mu g.mL^{-1}$ in acetonitrile were purchased from A2S.

Glyphosate (CAS: 1071:-83-6), AMPA (CAS: 1066-51-9), GLYPHOSATE-2-13C15N (CAS: 285978-24-7) and AMPA-13C15N each at 100 $\mu g.mL^{-1}$ in water were purchased from HPC Standard GmbH.

LCMS-grade acetonitrile was obtained from Carlo Erba, and ultrapure water (18.2 MΩ) was prepared by a purification system.

Other chemicals and solvents were HPLC grade.

Sample preparation for CLD and CLO analysis

A stock standard solution of CLD and CLO was prepared in acetonitrile, stored at 4°C for 1 month and diluted with acetonitrile to a concentration of 0.5 to 200 $ng.mL^{-1}$ (7 concentrations) for working standards. Calibration standard curve was obtained from 5 injections of each standard realized during analysis runs. Calibration was validated for each run of samples in order to evaluate the derive of instrument.

Sediment samples were lyophilized (Buchi Lyovapor L200) before extraction to remove water.

Three grams of dry sediment was extracted using an accelerated solvent extraction system (ASE200, Dionex) with a methanol and dichloromethane mixture (50:50 v/v) at 100°C and 100 bar for 3 cycles.

The organic extract was evaporated using an accelerated solvent extractor (ASE 200, Dionex) to a volume of 10 mL and purified using an Oasis HLB Prime 100 mg cartridge (Waters). The cartridge was conditioned with 6 mL of dichloromethane followed by 6 mL of methanol. The organic extract was added to the top of the cartridge and eluted, and the cartridge was rinsed with 1 mL of methanol. The mixture was evaporated under a nitrogen stream, and the volume was adjusted to

1 mL with methanol. The purified extract was filtered through a 0.2 µm PTFE filter before LCMS analysis. Samples extract were analyzed in triplicates to evaluate the analytical precision.

To evaluate the recovery of the sample preparation method, 3 g of dry sediment (in triplicates) was fortified with CLD and CLO at a concentration of 10 $ng.g^{-1}$ DM.

The matrix effect was evaluated by the extraction of sediment sample coming from the bottom of GUA and GAL marine core where concentration of pollutants were below the limit of detection. After extraction and purification, CLD and CLDOH were added to the extract at different concentration. The results indicated a positive matrix effect and the signal were augmented of 30% and 20% for CLD and CLDOH respectively.

Blanks were obtained by the extraction of solvent without sample. The procedure of extraction and purification applied to blanks was the same that the procedure with the sample core and no contamination was observed.

LCMS analysis of CLD and CLO

The analysis was performed on an ALTHUS 30 UPLC system (Perkin Elmer, USA) coupled in tandem to a triple quadrupole mass spectrometer equipped with an electrospray ionization (ESI) source (Perkin Elmer QSigth 200).

The desolvation and nebulizer gases were nitrogen. The desolvation gas flow was 300 $L.h^{-1}$, and the drying gas flow was 120 $L.h^{-1}$. The hot surface-induced desolvation (HSID) temperature was 320°C, and the source temperature was 400°C.

ESI-MS was performed in negative ion mode with multiple reaction monitoring (MRM). The transitions of m/z 506.5 to 426.5 (collision energy = 25 eV) and m/z 492.7 to 35 (collision energy = 131 eV) were employed for CLD and CLO determination, respectively.

UPLC was performed on a Brownlee SPP-phenyl hexyl column (100*4.6 mm, 2.7 µm) from Perkin Elmer, compatible with highly aqueous mobile phases to facilitate the retention and separation of polar compounds.

The mobile phase consisted of water supplemented with 2 $mmol.L^{-1}$ aqueous NH_3 (A) and acetonitrile (B) at a flow rate of 0.5 $mL.min^{-1}$, and the column was maintained at 40°C. The mobile

phase was maintained at 95% solvent A from 0 to 1 min, changed linearly to 100% B over 10 min, maintained at 100% B for 10 min, changed to 95% A over 2 min and maintained at 95% A for 3 min before the next analysis.

CLD and CLO had retention times of 10.95 and 11.72 min, respectively.

The calibration curve (7 points of calibration injected at each run of samples) was linear between 0.5 and 200 $ng.mL^{-1}$. Calibration was stable over time and deviation was low (<5%). The LOD (corresponding to a signal-to-noise ratio of 3) and LOQ (corresponding to a signal-to-noise ratio of 10) were 0.22 $ng.mL^{-1}$ and 0.67 $ng.mL^{-1}$ for CLD and 0.1 $ng.mL^{-1}$ and 0.3 $ng.mL^{-1}$ for CLO, respectively.

The recoveries of CLD and CLO from sediment were investigated to assess the efficiency of the method. The developed method had good recoveries of 77.75% ± 2.5% for CLD and 70.61% ± 8.6% for CLO.

LC CONDITIONS				
LC column	Brownlee SPP-phenyl hexyl			
	100*4.6mm	2.7µm		
mobil phase A	water + 2mmol.L^{-1}aqueous NH_3			
mobil phase B	ACN			
mobil phase gradient	time (min)	flow rate ($mL.min^{-1}$)	A	B
	initial	0.5	95	5
	1	0.5	95	5
	10	0.5	0	100
	20	0.5	0	100
	22	0.5	95	5
	25	0.5	95	5
column oven temperature	40°C			
autosampler temperature	5 °C			
injection volume	10µL			

MS SOURCE CONDITIONS				
ESI voltage	-4500V			
drying gas	120			
nebuliser gas	300			
source temperature	400°C			
HSID temperature	320°C			
detection mode	Time-managed MRM			

Sample preparation for glyphosate and AMPA analysis

Glyphosate and AMPA standard solutions were prepared in a concentration gradient of 10 to 400 $ng.mL^{-1}$ (5 concentrations) in ultrapure water in polypropylene (PP) or polyethylene (PE) bottles and analyzed immediately after preparation. Solutions were spiked with GLYPHOSATE-2-13C15N, and AMPA-13C15N was used as an internal standard at a final concentration of 100 $ng.mL^{-1}$. Calibration is conducted for each run of samples.

Sediment samples were lyophilized to remove water before extraction.

One gram of dry sediment was added to 10 mL of 0.5 M KOH and vortexed for 1 min.

GLYPHOSATE-2-13C15N and AMPA-13C15N standard solutions were added as internal standards at final concentrations of 100 $ng.mL^{-1}$. The extract was centrifuged at 5000 rpm for 5 min. The water extract was filtered through a 0.2 µm nylon filter and analyzed immediately after preparation.

To evaluate the recovery of the sample preparation method, 1 g of dry sediment (in triplicates) was fortified with glyphosate and AMPA at concentrations of 200 $ng.g^{-1}$ DM.

Blanks were obtained by the extraction of solvent without sample. The procedure of extraction and purification applied to blanks was the same that the procedure with the sample core.

LCMS analysis of glyphosate and AMPA

The analysis was performed on an ALTHUS 30 UPLC system (Perkin Elmer, USA) coupled in tandem to a triple quadrupole mass spectrometer equipped with an ESI source (Perkin Elmer QSigth 200). The desolvation and nebulizer gases were nitrogen. The desolvation gas flow was 300 $L.h^{-1}$, and the drying gas flow was 120 $L.h^{-1}$. The HSID temperature was 320°C, and the source temperature was 400°C.

ESI-MS was performed in negative ion mode with MRM. The transitions of m/z 168 to 63 (collision energy = 29 eV) and m/z 110 to 63 (collision energy = 32 eV) were employed for glyphosate and AMPA determination, respectively.

UPLC was performed on a universal NH2 column (100*2.1 mm, 3 µm) from Perkin Elmer.

The mobile phase consisted of water supplemented with 5 mM ammonium acetate adjusted to pH 11 with NH_4OH (A) and acetonitrile (B) at a flow of 0.25 $mL.min^{-1}$, and the column was maintained at a temperature of 35°C. The mobile phase was maintained at 20% A from 0 to 2 min, changed to 80% A and maintained at 80% A for 6 min before taking 4 min to return to the initial conditions. After the analysis of every ten samples, the column was regenerated with water and acetonitrile to remove NH4OH.

Glyphosate and AMPA had retention times of 5.73 and 5.77 min, respectively.

The calibration curve was linear between 50 and 400 $ng.mL^{-1}$. The LOD (corresponding to a signal-to-noise ratio of 3) and LOQ (corresponding to a signal-to-noise ratio of 10) were 2 $ng.mL^{-1}$ and 6 $ng.mL^{-1}$ for glyphosate and 1 $ng.mL^{-1}$ and 3 $ng.mL^{-1}$ for AMPA, respectively.

The recoveries of glyphosate and AMPA from sediment were investigated to assess the efficiency of the method. The developed method had good recoveries of 69.3% ± 32.4% for glyphosate and 86.5% ± 7.6% for AMPA.

LC CONDITIONS				
LC column	column NH2 100*2.1mm			
	Pré-colonne NH2	10*2.1 mm		
mobil phase A	5mM ammonium acetate in water adjusted at pH=11 with NH_4OH 30%			
mobil phase B	acetonitrile			
mobil phase gradient	time (min)	flow rate ($mL.min^{-1}$)	A	B
	initial	0.25	20	80
	2	0.25	20	80

	2.01	0.25	80	20
	8	0.25	80	20
	8.01	0.25	20	80
	12	0.25	20	80
column oven temperature	35°C			
autosampler temperature	10°C			
injection volume	20µL			
MS SOURCE CONDITIONS				
ESI voltage	-4500V			
drying gas	150			
nebuliser gas	200			
source temperature	400			
HSID temperature	320			
detection mode	Time-managed MRM			

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