Electronic supplementary information (ESI)

Impact of abiotic and biogeochemical processes on halogen concentrations (Cl, Br, F, I) in mineral soil along a climatic gradient

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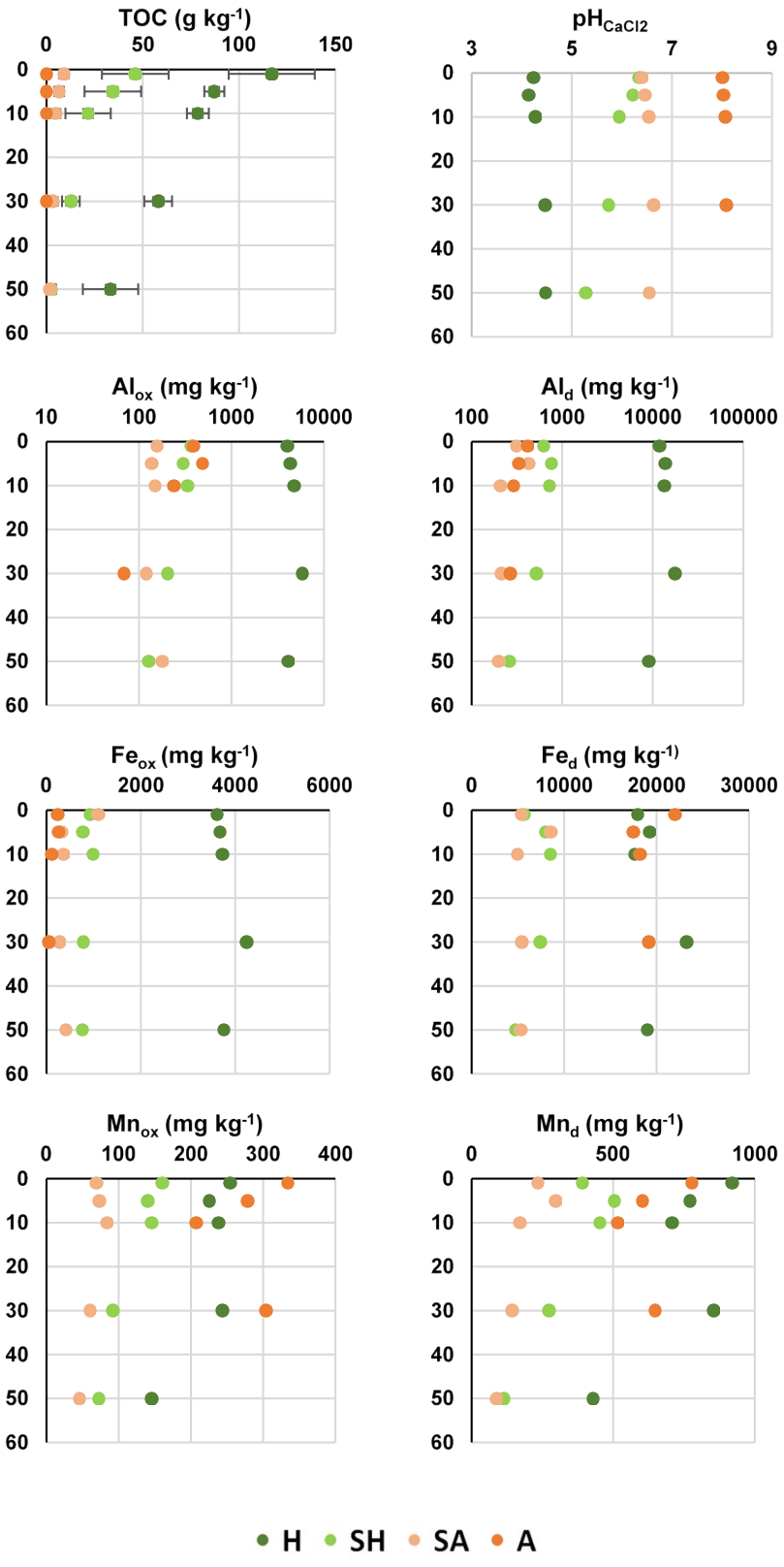

Figure S1: Depth profiles of soil variables measured at the humid (H), semi-humid (SH), semi-arid (SA) and arid (A) site. TOC values representing averages and standard deviations (SD) of triplicate analyses; other data depicted representing single analyses.

Table S1: Brief description of soil profiles (obtained from [1]) located on a south-facing mid slope at each study site. Three replicate soil profiles were excavated in a parallel line at distances of 15 to 20 m next to the mid slope soil profiles of the EarthShape project [1]. Abbreviations texture: SL = sandy loam, LS = loamy sand, SCL: sandy clay loam. Soil description and classification after [2] and [3].

Study site; Soil profile	Depth (cm)	Horizon	Texture	Munsell color (moist)
Arid: Pan de Azúcar; AZPED 50, south-facing mid slope, 40°, '-70.54920, -26.11020, Regosol				
	0 - 5	Aycz	SL	10YR 5/4
	5 - 20	Bycz	SL	10YR 5/6
	20 - 50	BCycz	SL	-
Semi-arid: Santa Gracia; SGPED40, south-facing mid slope, 25°, '-71.16637,- 29.75740, Cambisol				
	0 - 10	Ah	LS	10YR 3/4
	10 - 30	Bw	LS	10YR 3/4
	30 - 50	BCw	SL	10YR 4/4
Semi-humid: La Campana LCPED20, south-facing mid slope, 23°, '-71.06349, -32.95588, Cambisol				
	0 - 7	Ah1	SL	10YR 2/2
	7 - 35	Ah2	SL	10YR 2/2
	35 - 42	Ah3	SL	10YR 3/2
	40 - 60	Bw	SL	10YR 3/3
Humid: (Nahuelbuta) NAPED20, south-facing mid slope, 15°,'-73.01353, -37.80765, orthodystric Umbrisol				
	0 - 8	Ah1	SCL	10YR 3/4
	8 - 20	Ah2	SCL	10YR 3/4
	20 - 50	Ah3	SCL	10YR 3/4

Table S2: Sample overview. Horizon assignments obtained from [1].

Study site; Soil profile	Depth interval (cm)	Horizon[1)]	ISGN
Arid, Pan de Azúcar			
Replicate a	0 - 1	Aycz	GFOTN000A
	2 – 5	Aycz	GFOTN000N
	5 – 10	Bycz	GFOTN001J
	20 - 30	BCycz	GFOTN001M
Replicate b	0 - 1	Aycz	GFOTN000B
	2 – 5	Aycz	GFOTN000P
	5 – 10	Bycz	GFOTN001K
	20 - 30	BCycz	GFOTN001N
Replicate c	0 - 1	Aycz	GFOTN000C
	2 – 5	Aycz	GFOTN000Q
	5 – 10	Bycz	GFOTN001L
	20 - 30	BCycz	GFOTN001P
Semi-arid, Santa Gracia			
Replicate a	0 - 1	Ah	GFOTN0007
	1 – 5	Ah	GFOTN000K
	5 – 10	Ah	GFOTN0019
	20 - 30	Bw	GFOTN001C
	40 - 50	BCw	GFOTN001F
Replicate b	0 - 1	Ah	GFOTN0008
	1 – 5	Ah	GFOTN000L
	5 – 10	Ah	GFOTN001A
	20 - 30	Bw	GFOTN001D
	40 - 50	BCw	GFOTN001G
Replicate c	0 - 1	Ah	GFOTN0009
	1 – 5	Ah	GFOTN000M
	5 – 10	Ah	GFOTN001B
	20 - 30	Bw	GFOTN001E
	40 - 50	BCw	GFOTN001H
Semi-humid, La Campana			
Replicate a	0 - 1	Ah1	GFOTN0004
	1 – 5	Ah1	GFOTN000G
	5 – 10	Ah1Ah2	GFOTN0010
	20 - 30	Ah2	GFOTN0013
	40 - 50	Bw	GFOTN0016
Replicate b	0 - 1	Ah1	GFOTN0005
	1 – 5	Ah1	GFOTN000H
	5 – 10	Ah1Ah2	GFOTN0011
	20 - 30	Ah2	GFOTN0014
	40 - 50	Bw	GFOTN0017
Replicate c	0 - 1	Ah1	GFOTN0006
	1 – 5	Ah1	GFOTN000J

	5 – 10	Ah1Ah2	GFOTN0012
	20 - 30	Ah2	GFOTN0015
	40 - 50	Bw	GFOTN0018
Humid, Nahuelbuta			
Replicate a	0 - 1	Ah1	GFOTN0001
	1 – 5	Ah1	GFOTN000D
	5 – 10	A1Ah2	GFOTN000R
	20 - 30	Ah3	GFOTN000U
	40 - 50	Ah3	GFOTN000X
Replicate b	0 - 1	Ah1	GFOTN0002
	1 – 5	Ah1	GFOTN000E
	5 – 10	A1Ah2	GFOTN000S
	20 - 30	Ah3	GFOTN000V
	40 - 50	Ah3	GFOTN000Y
Replicate c	0 - 1	Ah1	GFOTN0003
	1 – 5	Ah1	GFOTN000F
	5 – 10	Ah1Ah2	GFOTN000T
	20 - 30	Ah3	GFOTN000W
	40 - 50	Ah3	GFOTN000Z

Table S3: Summary of average total halogens concentrations and proportion of labile inorganic halides relative to total concentrations at the study sites. Values as average concentrations including standard deviations (±).

average values	**arid** (n=11)	**semi-arid** (n=15)	**semi-humid** (n=12)	**humid** (n=15)
$\mathbf{F_{tot}}$ (mg kg^{-1})	897 ± 77	163 ± 15	210 ± 63	348 ± 99
$\mathbf{F^-_{H2O}}$ (%)	0.1 ± 0.1	0.3 ± 0.3	0.1 ± 0.1	0.1 ± 0.0
$\mathbf{Cl_{tot}}$ (mg kg^{-1})	4,270 ± 2,910	60 ± 12	129 ± 19	237 ± 40
$\mathbf{Cl^-_{H2O}}$ (%)	94.2 ± 14.8	2.6 ± 2.8	1.8 ± 1.1	12.0 ± 5.8
$\mathbf{Br_{tot}}$ (mg kg^{-1})	5.5 ± 3.7	2.3 ± 1.0	2.4 ± 0.7	42.6 ± 19.2
$\mathbf{Br^-_{H2O}}$ (%)	100	1.0 ± 0.5	0.5 ± 0.6	2.3 ± 1.1
$\mathbf{I_{tot}}$ (mg kg^{-1})	3.1 ± 2.2	0.2 ± 0.2	0.1 ± 0.1	9.8 ± 4.8
$\mathbf{I^-_{H2O}}$ (%)	2.0 ± 2.5	<dl	<dl	0.6

Table S4: Summary of soil properties at the four study sites. NaOH-P data from [4], CIA values calculated from major elemental concentrations as described by [5] for the same sites, grain size data from [1].

Location	depth (cm)	NaOH-P (mg kg^{-1})	CIA	sand (wt%)	silt (wt%)	clay (wt%)
Humid	0 - 1	552	78	56	20	25
	1 - 5	552	78	56	20	25
	5- 10	444	79	54	20	27
	20 - 30	416	79	51	21	27
	40 - 50	286	75	52	21	27
Semi-humid	0 - 1	136	61	73	17	10
	1 - 5	136	61	73	17	10
	5- 10	102	62	75	17	9
	20 - 30	122	63	76	14	11
	40 - 50	88	63	77	15	9
Semi-arid	0 - 1	34	60	77	18	6
	1 - 5	34	60	77	18	6
	5- 10	27	60	79	15	6
	20 - 30	24	60	78	14	8
	40 - 50	16	60	77	14	10
Arid	0 - 1	12	58	69	22	9
	1 - 5	12	58	69	22	9
	5- 10	0	53	64	23	14
	20 - 30	0	46	44	44	12

Table S5: Correlation analysis along the gradient (n=53 for correlations between respective total halogens, water-extractable halides and TOC; n=19 for the comparisons including other soil variables). Spearman rank correlation, significant at **p*<0.05, ***p*<0.01. Note: for correlation analysis with TOC, the arid site has been excluded (n= 42).

		F_{tot} (mg kg^{-1})	Cl_{tot} (mg kg^{-1})	Br_{tot} (mg kg^{-1})	I_{tot} (mg kg^{-1})	F^-_{H2O} (mg kg^{-1})	Cl^-_{H2O} (mg kg^{-1})	Br^-_{H2O} (mg kg^{-1})	I^-_{H2O} (mg kg^{-1})	TOC (g kg^{-1})	pH	NaOH-P (mg kg^{-1})	CIA	Al_{ox} (mg kg^{-1})	Fe_{ox} (mg kg^{-1})	Mn_{ox} (mg kg^{-1})	Al_d (mg kg^{-1})	Fe_d (mg kg^{-1})	Mn_d (mg kg^{-1})	sand (wt%)	silt (wt%)	clay (wt%)
F_{tot} (mg kg^{-1})	r_S	**1.00**	**.91****	**.54****	**.65****	**.41****	**.81****	**.87****	**.75****	**.54****	0.10	-0.16	-0.07	0.40	-0.18	**.71****	0.20	**.68****	**.60****	**-.74****	**.76****	**.59****
Cl_{tot} (mg kg^{-1})	r_S		**1.00**	**.52****	**.65****	**.27***	**.89****	**.80****	**.76****	**.80****	0.07	-0.06	-0.08	0.41	-0.11	**.85****	0.30	**.74****	**.74****	**-.84****	**.86****	**.61****
Br_{tot} (mg kg^{-1})	r_S			**1.00**	**.79****	-0.05	**.54****	**.58****	**.68****	**.58****	-0.35	0.38	**.46***	**.58****	0.38	0.45	**.49***	**.60****	**.54***	**-.79****	**.48***	**.88****
I_{tot} (mg kg^{-1})	r_S				**1.00**	0.05	**.65****	**.75****	**.76****	**.50****	-0.26	0.24	0.32	**.64****	0.33	**.54***	0.42	**.69****	**.59****	**-.73****	**.61****	**.71****
F^-_{H2O} (mg kg^{-1})	r_S					**1.00**	**.39****	**.50****	0.16	**-.35***	**.59****	**-.69****	-0.45	-0.26	**-.68****	0.16	-.57*	0.02	-0.02	0.09	0.11	-0.07
Cl^-_{H2O} (mg kg^{-1})	r_S						**1.00**	**.80****	**.72****	**.81****	0.13	-0.09	-0.17	**.47***	-0.07	**.84****	0.33	**.77****	**.79****	**-.82****	**.90****	**.57***
Br^-_{H2O} (mg kg^{-1})	r_S							**1.00**	**.75****	**.39****	0.21	-0.28	-0.16	0.28	-0.20	**.65****	0.02	**.65****	**.54***	**-.67****	**.77****	**.54***
I^-_{H2O} (mg kg^{-1})	r_S								**1.00**	**.58****	-0.29	0.29	0.30	**.65****	0.32	**.72****	**.56***	**.87****	**.77****	**-.90****	**.77****	**.79****
TOC (g kg^{-1})	r_S									**1.00**	**-.89****	**.97****	**.84****	**.61****	**.88****	0.07	**.82****	0.16	0.34	-0.29	-0.12	**.47***
pH	r_S										**1.00**	**-.96****	**-.95****	**-.59****	**-.91****	-0.01	**-.76****	-0.13	-0.26	0.28	0.17	**-.48***
NaOH-P (mg kg^{-1})	r_S											**1.00**	**.92****	**.64****	**.91****	0.07	**.83****	0.17	0.32	-0.32	-0.13	**.51***
CIA	r_S												1.00	**.61****	**.89****	-0.01	**.70****	0.11	0.21	-0.28	-0.23	**.55***
Al_{ox} (mg kg^{-1})	r_S													**1.00**	**.66****	**.56***	**.83****	**.61****	**.70****	-.63**	0.42	**.70****
Fe_{ox} (mg kg^{-1})	r_S														**1.00**	-0.02	**.75****	0.14	0.22	-0.30	-0.11	**.48***
Mn_{ox} (mg kg^{-1})	r_S															**1.00**	**.48***	**.81****	**.91****	**-.81****	**.83****	**.56***
Al_d (mg kg^{-1})	r_S																**1.00**	**.61****	**.70****	-.65**	0.33	**.66****
Fe_d (mg kg^{-1})	r_S																	**1.00**	**.88****	**-.86****	**.83****	**.67****
Mn_d (mg kg^{-1})	r_S																		1.00	**-.83****	**.78****	**.65****
sand (wt%)	r_S																			**1.00**	**-.80****	**-.85****
silt (wt%)	r_S																				1.00	**.48***
clay (wt%)	r_S																					1.00

Table S6: Outcome of Wilcoxon signed rank tests (significant at *p<0.05) for comparing halogen concentrations in the top and bottom of the sampled soil profiles.

Site / Halogen	Arid -top (0-1 and 1-5 cm, n=6) -bottom (5-10, 20-30 cm, n=5)	Semi-arid -top (1-5 and 5-10 cm, n=6) -bottom (20-30 and 40-50 cm, n=6)	Semi-humid -top (0-1 and 1-5 cm, n=6) -bottom (20-30 and 40-50 cm, n=5)	Humid -top (1-5 and 5-10 cm, n=6) -bottom (20-30 and 40-50 cm, n=6)
F_{tot}	not significant	not significant	top < bottom*	top < bottom*
Cl_{tot}	top < bottom*	not significant	not significant	not significant
Br_{tot}	top < bottom*	top < bottom*	not significant	top < bottom*
I_{tot}	top > bottom*	top < bottom*	not significant	top < bottom*

Supplemental Literature

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