

Use of reflectance infrared spectroscopy for monitoring the metal content of the estuarine sediments of the Nerbioi-Ibaizabal River (Metropolitan Bilbao, Bay of Biscay, Basque Country)

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Table S1 - State-of-the-art of previously published papers about the determination of metals in soil and sediment samples using vibrational procedures.

Sample	Metals	Chemometric technique	Number of factors	Spectral range (nm)	Spectral Data	Total number of samples	Validation procedure	RPD values	Ref.
North-western Ontario (Canada) sediments	Cd, Cu, Fe, Mn, Ni, Pb and Zn	Partial Least Squares Regression (PLS)	3 for Cu, Fe, Mn, Ni, Pb and Zn 10 for Cd	1100-2500	First derivative	169	odd-numbered spectra as calibration set and even-numbered spectra as prediction set	1.74; 3.35 2.64; 3.66 2.96; 2.45 3.80	(8)
Uruguay soils	Cu, Fe and Mg	Modified PLS (MPLS)	-----	400-2500 (Vis-NIR)	First derivative	332	Cross-Validation	-----	(9)
Tarnowskie Gory (Poland) soils	Cd, Cu, Fe, Ni, Pb and Zn	PLS	5/4 for Cd (*) 7/10 for Cu (*) 9/6 for Fe (*) 4/5 for Ni (*) 5/7 for Pb (*) 6/3 for Zn (*)	400-2500 (NIR) 2500-25000 (MIR)	Raw data	70	Cross-Validation	-----	(10)
Aznalcollar (Spain) soils	As, Cu, Pb and Zn	MPLS	-----	400-2500	First derivative	100	70 samples for calibration and 30 for an external validation	2.25; 1.59 2.13; 1.96	(11)
Krakowsko-Częstochowska (Poland) soils	Pb and Zn	MPLS	3 for Pb 3 for Zn	400-2500	Second derivative	74	Group Cross-validation	1.3 1.1	(12)
Baguazhou Island (China) soils	As, Cd, Co, Cr, Cu, Ni, Pb and Zn	PLS	-----	400-2500	Raw and first derivative data	61	Cross-validation	1.90; 1.23 2.18; 2.50 1.74; 2.35 1.49; 1.45	(13)
United States soils	Cu, Fe, Mg, Mn and Zn	PCR	14 for Cu 9 for Fe 14 for Mg 12 for Mn 9 for Zn	1300-2500	First derivative	802	Cross-validation	0.92 1.66 1.78 1.79 1.07	(14)
Ria de Arousa (Spain) sediments	As, Cd, Cr, Pb and Sn	PLS	1 for As 6 for Cd 2 for Cr 3 for Pb 5 for Sn	833-2976	First derivative	81	31 samples for calibration and 50 samples for validation	1.4 1.3 1.6 1.2 1.7	(15)
Murcia (Spain) soils	As, Cd, Co, Cr, Cu, Ni, Se, Tl and Zn	PLS	1 for As 2 for Cd 4 for Co 2 for Cr 1 for Cu 5 for Ni 3 for Se 2 for Tl 2 for Zn	800-2600	First derivative	148	39 for calibration and 109 for validation	1.3 1.4 1.4 1.1 1.0 1.2 1.1	(16)

Note: For critical comparison, only data which belong to those metals evaluated in the present study were summarized. (*) The number of PLS factors indicated correspond to NIR/MIR measurements.

Table S2A - Characteristics of estuarine sediment samples classified into clusters after dendrographic treatment of reflectance data.

Sampling technique			NIR					
Cluster index			1	2	3	4	5	6
Number of samples			19	5	36	16	31	10
Metals	[Al]	mean ± s	6537 ± 3311	4189 ± 1418	4354 ± 1780	4610 ± 1581	3566 ± 1936	2350 ± 1158
	[As]	mean ± s	64 ± 59	144 ± 85	31 ± 31	79 ± 47	17 ± 20	13 ± 27
	[Cd]	mean ± s	5 ± 4	6 ± 5	3 ± 3	4 ± 3	1.6 ± 2.5	0.4 ± 1.3
	[Co]	mean ± s	8 ± 3	9 ± 2	7 ± 2	9 ± 6	6 ± 3	5 ± 2
	[Cr]	mean ± s	54 ± 19	65 ± 17	42 ± 23	56 ± 33	30 ± 13	18 ± 9
	[Cu]	mean ± s	184 ± 112	297 ± 59	113 ± 98	259 ± 167	84 ± 100	77 ± 92
	[Fe]	mean ± s	18886 ± 7844	26194 ± 7837	12298 ± 3288	19985 ± 6877	11157 ± 6119	8658 ± 3207
	[Mg]	mean ± s	3633 ± 2140	2247 ± 1382	3065 ± 1693	3559 ± 1799	2471 ± 1379	2305 ± 2759
	[Mn]	mean ± s	488 ± 262	302 ± 200	299 ± 59	403 ± 215	256 ± 149	217 ± 51
	[Ni]	mean ± s	31 ± 24	25 ± 7	27 ± 17	50 ± 77	25 ± 21	14 ± 7
	[Pb]	mean ± s	206 ± 95	338 ± 75	143 ± 87	251 ± 77	107 ± 93	72 ± 86
	[Sn]	mean ± s	24 ± 11	42 ± 13	15 ± 8	31 ± 13	10 ± 8	6 ± 6
	[V]	mean ± s	16 ± 11	27 ± 10	9 ± 7	18 ± 7	6 ± 7	4 ± 8
	[Zn]	mean ± s	890 ± 438	1087 ± 360	523 ± 270	858 ± 336	397 ± 355	358 ± 390
Samples					AR_0512,			
					AR_0610,			
					AR_0701,		AS_0610,	
					AR_0704,		AS_0704,	
					AR_0710,		AS_0710,	
					AR_0801,		AS_0801,	
					AR_0810,		AS_0804,	
					AS_0501,		AS_0807,	
					AS_0509,		AZ_0509,	
		AR_0505,			AS_0512,		AZ_0512,	
		AR_0509,			AS_0603,	AR_0804,	AZ_0603,	
		AR_0603,			AS_0607,	GA_0607,	AZ_0707,	
		AR_0607,			AS_0701,	GA_0704,	AZ_0807,	
		AR_0707,			AS_0707,	GA_0804,	AZ_0810,	
		AR_0807,			AS_0810,	GA_0810,	GA_0509,	AZ_0505,
		AS_0505,			AZ_0501,	GO_0501,	GA_0710,	AZ_0704,
		GA_0501,	GA_0505,		AZ_0610,	GO_0505,	GA_0801,	AZ_0804,
		GA_0512,	GO_0801,		AZ_0701,	GO_0509,	GO_0610,	GO_0810,
		GA_0603,	UD_0501,		AZ_0710,	GO_0701,	GO_0704,	KA_0505,
		GA_0610,	UD_0505,		AZ_0801,	GO_0707,	GO_0710,	KA_0603,
		GA_0707,	UD_0509		GA_0701,	UD_0603,	KA_0501,	KA_0607,
		GO_0512,			GA_0807,	UD_0701,	KA_0509,	KA_0810,
		GO_0603,			GO_0607,	UD_0710,	KA_0512,	ZO_0704
		KA_0707,			GO_0804,	UD_0801,	KA_0610,	
		UD_0512,			GO_0807,	UD_0810,	KA_0704,	
		UD_0607,			KA_0701,	ZO_0801	KA_0807,	
		UD_0610,			KA_0710,		ZO_0505,	
		UD_0707			KA_0801,		ZO_0509,	
					KA_0804,		ZO_0603,	
					UD_0704,		ZO_0607,	
					UD_0804,		ZO_0707,	
					UD_0807,		ZO_0710,	
				ZO_0501,		ZO_0804,		
				ZO_0512,		ZO_0807,		
				ZO_0610,		ZO_0810		
				ZO_0701				

Note: $\pm$ s refers to the standard deviation of the mean.

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All metal concentration values are expressed in $\mu\text{g g}^{-1}$ units. Code for samples belongs to sampling station year/month

Table S2B - Characteristics of estuarine sediment samples classified into clusters after dendrographic treatment of reflectance data.

Sampling technique			MIR											
Cluster index			1	2	3	4	5	6	7	8	9	10	11	
Number of samples			9	7	5	28	10	13	12	15	12	4	2	
Metals	[Al]	mean ± s	4642 ± 4216	2003 ± 667	8814 ± 4691	4336 ± 1615	4488 ± 1998	6401 ± 2600	5075 ± 1120	2403 ± 1535	3833 ± 1297	3863 ± 1082	1106 ± 274	
	[As]	mean ± s	15 ± 16	4 ± 3	32 ± 16	59 ± 68	25 ± 51	46 ± 39	74 ± 60	30 ± 38	27 ± 32	9 ± 10	40 ± 54	
	[Cd]	mean ± s	0,7 ± 1,1	0,1 ± 0,2	1.5 ± 1.5	4 ± 4	0.9 ± 1.5	3 ± 4	5 ± 3	2.2 ± 1.6	2 ± 3	0.6 ± 1.1	3 ± 4	
	[Co]	mean ± s	5 ± 3	4,1 ± 1,4	7 ± 3	8 ± 3	4.5 ± 1.3	6 ± 3	7 ± 3	11 ± 6	8 ± 3	4.5 ± 1.8	7 ± 4	
	[Cr]	mean ± s	22 ± 10	20 ± 10	28 ± 11	52 ± 19	32 ± 12	34 ± 19	52 ± 12	43 ± 38	43 ± 31	20 ± 11	34 ± 10	
	[Cu]	mean ± s	76 ± 53	86 ± 77	71 ± 28	148 ± 93	64 ± 54	214 ± 193	224 ± 131	104 ± 89	107 ± 102	34 ± 19	94 ± 103	
	[Fe]	mean ± s	9125 ± 3652	8624 ± 2232	12005 ± 2751	16388 ± 7895	10146 ± 3471	13691 ± 4909	18418 ± 6020	12424 ± 6490	12474 ± 3916	7811 ± 729	11021 ± 3491	
	[Mg]	mean ± s	2811 ± 2691	1002 ± 814	5577 ± 2673	2429 ± 1270	1579 ± 477	3114 ± 1014	2962 ± 690	5068 ± 2135	3131 ± 2049	960 ± 230	2493 ± 2182	
	[Mn]	mean ± s	326 ± 213	218 ± 64	527 ± 249	290 ± 170	159 ± 55	310 ± 165	366 ± 253	315 ± 172	329 ± 163	282 ± 131	194 ± 81	
	[Ni]	mean ± s	12 ± 6	12 ± 7	13 ± 3	34 ± 28	20 ± 4	20 ± 9	29 ± 16	56 ± 77	29 ± 17	13 ± 6	20 ± 3	
	[Pb]	mean ± s	68 ± 49	37 ± 17	125 ± 28	208 ± 117	82 ± 77	164 ± 91	250 ± 79	153 ± 108	109 ± 68	67 ± 67	97 ± 107	
	[Sn]	mean ± s	8 ± 6	4 ± 3	15 ± 4	23 ± 14	11 ± 9	17 ± 11	28 ± 10	16 ± 16	13 ± 7	3.0 ± 0.5	14 ± 13	
[V]	mean ± s	6 ± 6	2 ± 3	11 ± 6	13 ± 12	5 ± 10	15 ± 10	17 ± 10	10 ± 7	10 ± 8	1 ± 2	9 ± 13		
[Zn]	mean ± s	388 ± 394	140 ± 67	760 ± 467	707 ± 441	524 ± 455	597 ± 453	927 ± 362	479 ± 295	458 ± 257	341 ± 300	430 ± 448		
Samples						AR_0704, AS_0505, AS_0509, AS_0512, AS_0704, AS_0710, AS_0810, AZ_0501, AZ_0701, AZ_0710, GA_0501, GA_0505, GA_0701, GA_0704, GA_0707, GA_0710, KA_0701, UD_0501, UD_0505, UD_0509, UD_0512, UD_0701, UD_0707, UD_0710, ZO_0501, ZO_0512, ZO_0701, ZO_0710		AS_0707, AZ_0607, AZ_0610, AZ_0704, AZ_0707, UD_0610, ZO_0607, ZO_0610, ZO_0704, ZO_0707	AR_0707, AR_0710, GO_0607, GO_0610, GO_0701, GO_0704, GO_0707, GO_0710, KA_0610, KA_0704, KA_0707, KA_0710, UD_0704	AR_0801, AS_0607, AS_0610, GA_0603, GA_0607, GA_0801, GO_0501, GO_0603, GO_0801, UD_0603, UD_0607, UD_0801	AR_0810, AS_0701, AS_0807, AZ_0807, AZ_0810, GA_0610, GA_0804, GA_0807, GA_0810, GO_0810, KA_0807, KA_0810, UD_0810, ZO_0807, ZO_0810	AR_0804, AR_0807, AS_0801, AS_0804, AZ_0801, GO_0804, GO_0807, KA_0801, KA_0804, UD_0804, ZO_0801, ZO_0804	AS_0603, AZ_0603, KA_0603, ZO_0603	AZ_0804, UD_0807

Note: $\pm s$ refers to the standard deviation of the mean.

All metal concentration values are expressed in $\mu\text{g g}^{-1}$ units. Code for samples belongs to sampling station_year/month.

Figure S1: Dendrographic classification of sediment samples from their NIR (A) and MIR (B) reflectance spectra. The Euclidean distance on the vector normalized spectra and the Ward linkage methods were used. For details about cluster group composition see data in Table S2 (Supporting information). Samples are identified with two letters (corresponding to the sampling point) and 4 numbers (the first two numbers for the year and the last ones corresponding to the month).

