EDA Ashfield Sediment Data 2019-2022

This document describes exploratory and some detailed data analysis

Sample map

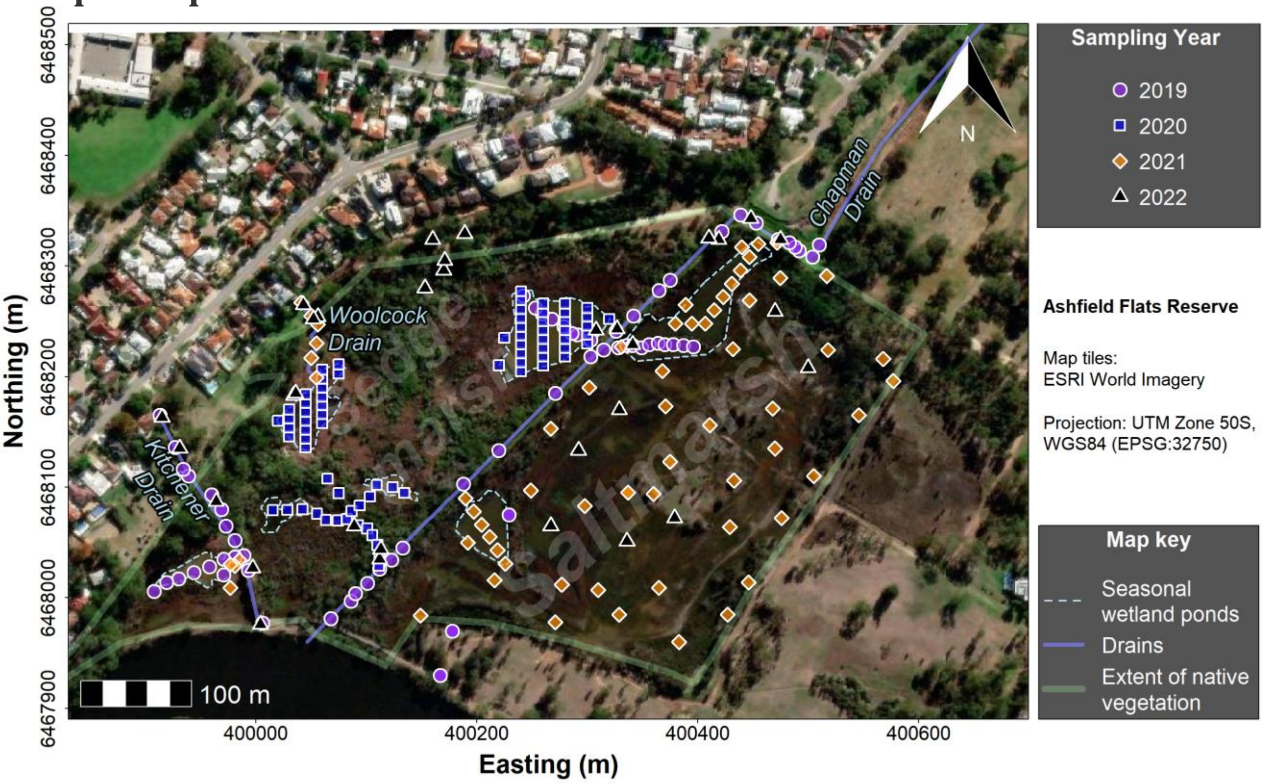


Figure 1: Map of sediment sample locations at Ashfield Flats for all sampling years 2019-2022.

Samples were taken each year from 2019 to 2022 (Figure *1*). Different sampling designs were implemented each year depending on the perceived gaps in understanding of the site and the learning objectives desired for the students involved. Apart from three soil/sediment depth profiles in 2019, all samples were subaqueous or subaerial surface sediments (0-10cm) from stormwater drains, wetland ponds (with or without water), saltmarsh, or seasonally flooded woodland.

Data summaries

pH, EC, Al-Cu

Table 1: First block of elements

Stat	pH	EC	Al	As	Ba	Ca	Cd	Ce	Co	Cr	Cu
mean	5.974	9.814	30160	8.445	59.51	3677	0.203	91.72	14.59	4940	124.5
sd	0.874	2.11	13430	8.48	30	4638	0.236	61.7	12.7	2.09	130
rsd	14.6%	215.2%	44.5%	100.4%	50.7%	126.1%	116.1%	67.2%	86.9%	42.6%	104.6%
0%	3.16	0.014	888	0.4	4.6	470	015	2.2	1.800	1.8	2
50%	6	6.590	31810	6.605	57	2317	0.12	82.45	12	54.3	79
100%	8.36	280	64430	62	191	48460	1.602	271	110	84	1008
NAs	32	33	1	13	1	1	98	1	1	1	8

Fe-Ni

Table 2: Second block of elements

Stat	Fe	Ga	Gd	K	La	Li	Mg	Mn	Mo	Na	Nd	Ni

mean	40980	17.37	6.526	2485	45.2	27.9	3845	153.1	2.771	11570	35.1	19.430
sd	20480	7.527	3.630	1341	28.6	15.54	2330	345.7	2.104	11040	21.7	8.309
rsd	50%	43.3%	55.6%	54%	63.3%	55.7%	60.6%	225.8%	75.9%	95.4%	61.8%	42.8%
0%	1562	-2.0	0.2	59	1	0.5	106	6.0	0.1	61	0.8	2.0
50%	38610	17.6	6.285	2718	41.35	30	3722	80.95	2.000	10450	34	19.700
100%	135500	40.7	18.0	5265	126.	80	20740	3503	13.0	95760	98.0	50.0
NAs	1	17	7	1	1	1	1	1	4	1	1	8

P-Zn

Table 3: Third block of elements

Stat	P	Pb	Rb	S	Sc	Sr	Th	Ti	V	Y	Zn
mean	649.6	60.66	37.57	5548	6.962	60.25	13.410	211.200	63.3	21.22	550.1
sd	724.3	94.62	24.79	9151	3.493	50.24	6.512	81.710	24.49	15.00	1138
rsd	111.5%	156%	66%	164.9%	50.2%	83.4%	48.6%	38.7%	38.7%	70.7%	206.9%
0%	26	3.3	0.6	225	0.1	2.3	0.4	47.2	2.3	0.4	11.2
50%	454	40.0	41.2	2969	8.00	52.8	14.70	218.90	70.95	19.35	246
100%	7020	831	88	76630	12.4	512	26.9	395.2	117.5	67.0	7556
NAs	1	1	174	1	170	1	3	167	1	1	5

The elements of primary interest in this study are the rare-earth (*REE* or lanthanide) elements La, Ce, Nd, and Gd; Y (often considered together with the REE); major elements considered to be useful proxies for sediment parameters expected to affect geochemical reactions of REE: Al, Ca, Fe, P and S. Aluminium (Al) is a proxy for clay minerals (although pXRD data show that other aluminosilicates are present, such as feldspars and micas, these are resistant and less likely than the phyllosilicate clays to report Al to an *aqua regia* digest). Calcium (Ca) is a proxy for carbonate minerals (since silicate-bound Ca would also be resistant to dissolution in *aqua regia*). Iron (Fe) concentrations are a proxy for iron oxide (and possibly iron sulfide) minerals. Phosphorus (P) is included since secondary REE phosphates such as rhabdophane may be a REE sink. Sulfur (S) most likely represents sulfate and sulfide minerals, would be expected to accumulate in wet, reducing environments, and is strongly linked to acid sulfate soils.

Sediment pH and EC have numerous but not excessive missing observations and are included due to their substantial effects on sediment geochemical processes.

The trace elements As, Cu, Pb, and Zn are included as common inorganic contaminants. In addition, Pb may be immobilised in environments receiving acid sulfate soil drainage due to the insolubility of $PbSO_4$. Thorium (Th) may be depleted in oxidised acid sulfate soils.

Note that several elements have too many missing observations to be useful: Cd, Ga, Rb, Sc, and Ti.

Drain sediment

Table 4: Basic statistics for Drain Sediment

Stat	pH	EC	Al	Ca	Fe	P	S	La	Ce	Nd	Gd	Y
mean	6.35	8.55	18000	3700	33300	589	6390	20.3	39.6	15.9	3.33	9.22
sd	1.13	41.1	13000	4000	22500	601	7840	17.7	39.3	15	2.63	9.57
0%	3.49	0.014	888	470	1560	26	225	1	2.2	0.8	0.2	0.4
50%	6.64	0.985	14100	2200	32700	389	3910	13.4	24.8	10.6	2.22	4.8
100%	8.27	280	64400	21600	88000	2800	40900	87	183	70	12	45

Lake sediment

Table 5: Basic statistics for Lake Sediment

Stat	pH	EC	Al	Ca	Fe	P	S	La	Ce	Nd	Gd	Y
mean	6.090	8.94	36,000	4,550	41,400	600	7,530	60.6	124.0	45.0	8.23	29.1
sd	0.808	6.20	11,500	5,430	16,700	428	12,200	30.7	65.9	22.3	3.76	16.4
0%	3.160	0.17	2,860	961	8,220	81	380	3.0	3.0	2.0	1.00	2.0
50%	6.170	8.20	36,900	3,770	38,300	502	3,650	65.0	129.0	47.0	8.60	29.6
100%	8.360	32.90	59,800	48,500	135,000	2,390	76,600	126.0	271.0	98.0	18.00	67.0

Saltmarsh

Table 6: Basic statistics for Saltmarsh

Stat	pH	EC	Al	Ca	Fe	P	S	La	Ce	Nd	Gd	Y
mean	5.67	15.3	30,900	3,120	48,600	961	3,860	47.2	94.7	38.4	6.88	21.7
sd	0.69	18.2	11,500	4,250	23,600	1,120	5,510	20.3	47.1	17.7	2.72	10.8
0%	4.35	0.12	6,070	584	11,900	85	281	6.2	6.0	5.9	2	3.2
50%	5.70	11.5	31,900	1,960	41,400	540	2,780	52.0	107.0	42.0	7	22.8
100%	7.24	135	53,800	31,400	130,000	7,020	42,300	93.4	218.0	95.7	16.8	53.4

Distribution tests

Table 7: Shapiro-Wilk statistics and p-values for untransformed (_orig) and transformed (_log, _pow) variables, power terms, and dip test of multimodality of log-transformed variable, from soil and sediment analysis at Ashfield Flats Reserve 2019-2022.

Variable	W orig	p orig	W log	p log	W pow	p pow	PowEst	PowRnd	D diptest	p diptest
pH	0.991	0.195	0.963	9.45e-06	0.994	0.545	1.47	1	0.0161	0.98
EC	0.301	1.1e-28	0.934	1.09e-08	0.964	1.52e-05	0.18	0.18	0.023	0.574
Al	0.974	0.00011	0.828	2.36e-16	0.975	0.000157	1.03	1	0.0175	0.889
As	0.701	7.9e-21	0.986	0.0179	0.987	0.0255	0.0468	0	0.032	0.0706
Ba	0.967	9.2e-06	0.934	1.96e-09	0.994	0.323	0.563	0.5	0.0234	0.424
Ca	0.516	3.1e-26	0.982	0.00197	0.995	0.632	-0.206	-0.33	0.0115	0.996
Ce	0.956	4.2e-07	0.907	1.08e-11	0.982	0.00197	0.501	0.5	0.018	0.858
Co	0.659	1.3e-22	0.98	0.000842	0.98	0.000863	-0.0092	0	0.0203	0.687
Cr	0.945	2.6e-08	0.766	4.73e-19	0.954	2.49e-07	1.2	1	0.0165	0.937
Cu	0.774	1.9e-18	0.978	0.000521	0.982	0.00228	0.103	0	0.0144	0.991
Fe	0.886	3.8e-13	0.827	2.07e-16	0.941	9.69e-09	0.579	0.5	0.0132	0.993
Gd	0.972	6.2e-05	0.928	7.51e-10	0.988	0.0313	0.565	0.5	0.0252	0.314
K	0.965	5.3e-06	0.821	1.04e-16	0.962	1.9e-06	0.815	0.815	0.0232	0.442
La	0.962	2e-06	0.906	9.75e-12	0.987	0.0202	0.526	0.5	0.0171	0.913
Li	0.968	1.6e-05	0.814	5.16e-17	0.961	1.73e-06	0.8	0.8	0.0289	0.133
Mg	0.903	5.9e-12	0.874	7.02e-14	0.971	3.66e-05	0.558	0.5	0.0234	0.426
Mn	0.283	1.2e-30	0.913	3.23e-11	0.935	2.52e-09	-0.167	-0.167	0.0128	0.994
Mo	0.85	4.1e-15	0.966	8.38e-06	0.989	0.039	0.229	0.33	0.0485	0.000151
Na	0.788	3.8e-18	0.879	1.55e-13	0.971	3.21e-05	0.366	0.33	0.0324	0.0492
Nd	0.968	1.3e-05	0.887	4.67e-13	0.983	0.00295	0.58	0.5	0.0263	0.239
Ni	0.981	0.0015	0.89	1.18e-12	0.98	0.0012	0.909	1	0.0286	0.157
P	0.618	9.5e-24	0.971	4.19e-05	0.973	6.1e-05	0.0438	0	0.0133	0.993
Pb	0.404	1.6e-28	0.952	1.28e-07	0.959	9.91e-07	-0.0991	-0.0991	0.0153	0.976
S	0.49	8.5e-27	0.984	0.00506	0.987	0.0172	-0.0664	0	0.0191	0.782
Sr	0.712	5.6e-21	0.964	4.15e-06	0.983	0.00336	0.222	0.33	0.0185	0.824
Th	0.963	3.5e-06	0.79	5.63e-18	0.964	3.63e-06	1	1	0.0272	0.196
V	0.914	4.2e-11	0.723	1.39e-20	0.943	1.39e-08	1.44	1.44	0.0203	0.68
Y	0.944	1.9e-08	0.923	1.97e-10	0.984	0.00602	0.444	0.5	0.0174	0.897
Zn	0.428	7.1e-28	0.967	1.19e-05	0.967	1.23e-05	-0.0097	0	0.0243	0.372

Most variables except pH are not normally distributed (Table 7). No variables have normal distributions when log_{10}-transformed. A few variables have normal distributions when power-transformed: pH, Ba, & Ca. The non-normal distributions of variables, even when transformed, suggest non-parametric tests are required *e.g*. for means comparisons).

check Na bimodality

This is worth doing to see if there is more than one population of samples based on salinity (assuming the main source of Na to *aqua regia* digests is halite).

The resulting map (Figure 2) shows a smaller population of low-Na locations, corresponding with where low salinity would be expected (*i.e*. away from tidal influence, and/or where evaporative concentration of Na salts is unlikely).

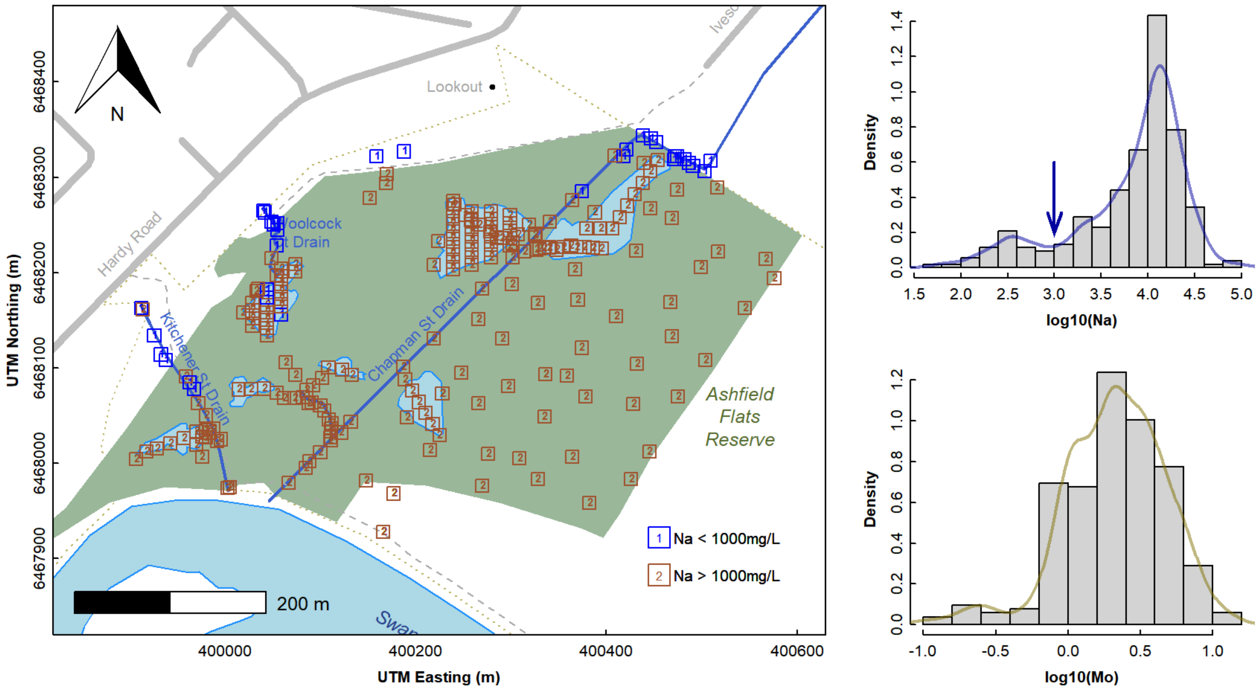


Figure 2: Density histograms for potentially multi-modal variables.

Additional explanatory maps

Surface water wetland naming

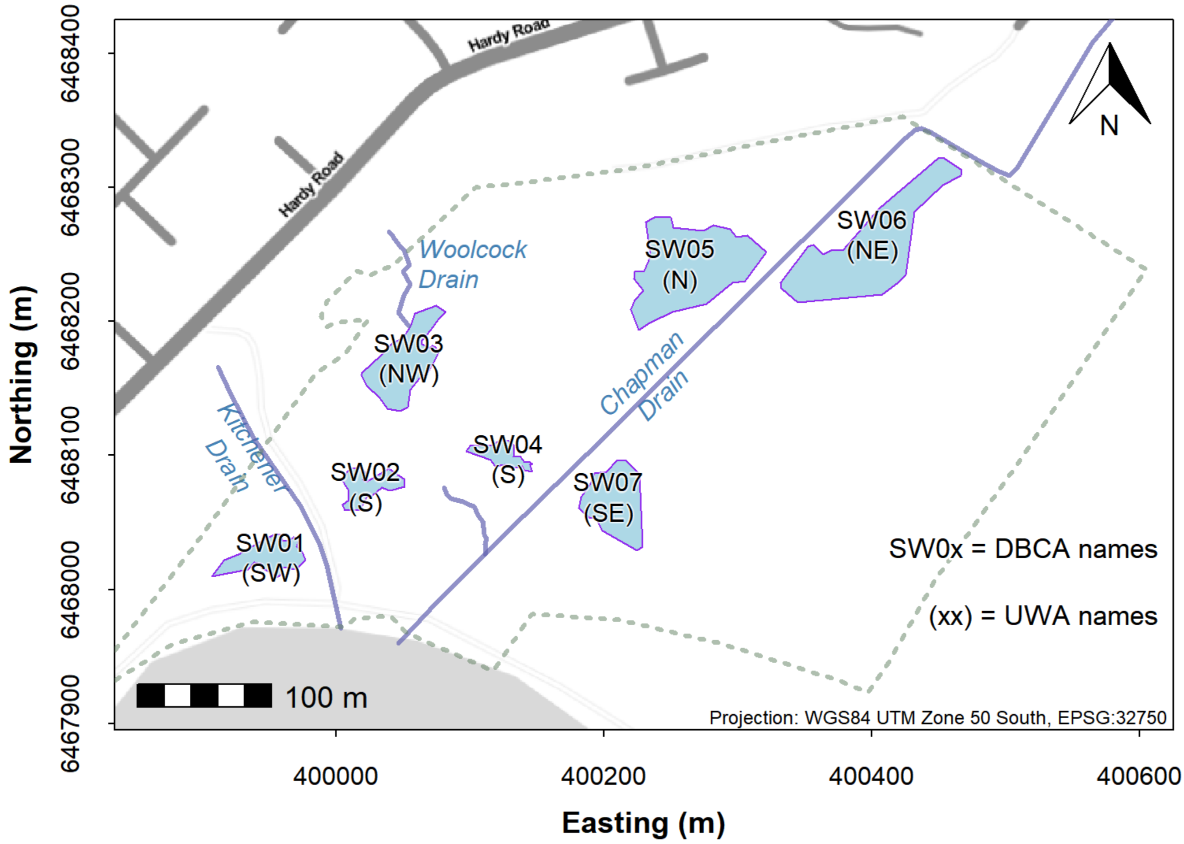


Figure 3: Map of wetland pond locations at Ashfield Flats comparing naming systems.

Sampling zones

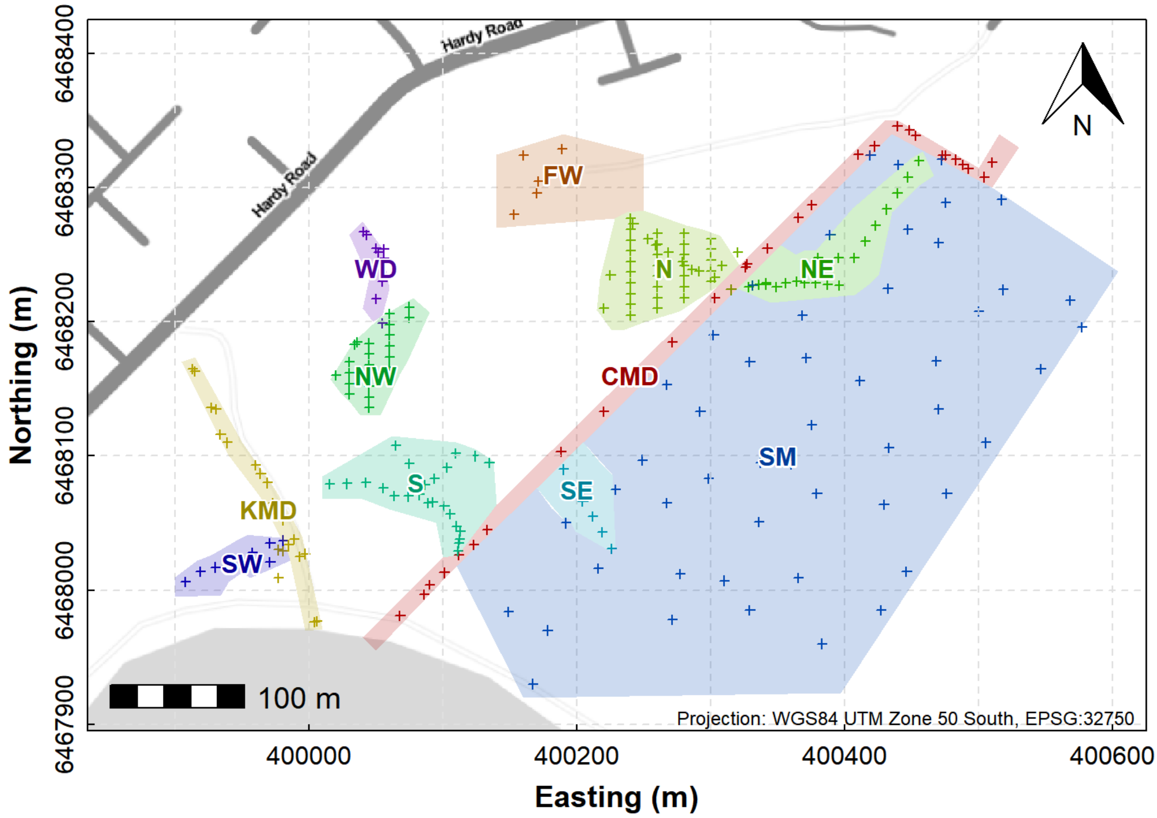


Figure 4: Map of sampling zones at Ashfield Flats 2019-2022

Means by Kruskal-Wallis

Comparing means (strictly mean rank sums) between sampling zones (the factor `ZoneSimp`) as this seems most appropriate. As shown in Table **8**, all overall effects are significant at p<0.001. Some post-hoc pairwise comparisons show significant differences (P≤0.05), differing for each variable.

Table 8: Mean comparisons and pairwise letter comparisons from Kruskal-Wallis and pairwise Conover test for selected elements including REEs (REE = ∑REE), by simplified sampling zone, at Ashfield Flats 2019-2022.

Variable	KW χ^2	KW p	CMD	KMD	LP	N	NE	NW	S	SE	SM	SW	WD
Al	119.6	6.21e-21	abc	abcd	a	e	d	bcd	d	bde	d	bcd	ac
Ca	117.7	1.52e-20	ab	abcde	cde	c	ad	ade	ce	abd	b	cde	cde
Fe	66.56	2.03e-10	ab	ac	c	ab	abd	ac	d	abcd	ab	bd	ac
K	139.6	4.99e-25	a	ab	a	c	bd	a	cd	c	bd	bcd	a
Na	155.1	3.25e-28	a	abc	bcd	e	de	ab	f	cde	cd	f	a
S	107.4	1.81e-18	ab	cd	ae	abc	d	ae	ae	abcd	d	e	bcd
P	69.1	6.62e-11	ab	a	bcd	cd	cd	ab	c	bcd	ab	bcd	abd
As	83.97	8.34e-14	a	abc	b	a	abc	ac	d	abc	b	abc	bc
Co	70.05	4.34e-11	abc	a	bcde	de	abc	bcde	d	bcde	ab	abce	cde
Cr	128.6	9.13e-23	ab	abc	a	d	ce	ab	ce	de	ce	bcde	a
Cu	127.6	1.41e-22	ab	cd	acd	e	be	c	e	be	ad	abcd	c
Ni	124.6	5.89e-22	ab	a	a	c	d	ab	d	cd	d	bd	a
Pb	71.35	2.43e-11	abc	abcd	d	a	a	bd	a	ac	bc	abcd	bd
Th	103.4	1.12e-17	abc	abde	c	de	de	ac	bd	e	de	abde	c
Zn	150.4	3.15e-27	a	ab	cd	e	a	cd	cde	acde	b	ace	d
La	139.2	6.06e-25	abc	abcd	a	e	ef	abc	bd	bcdf	d	bcd	ac
Ce	143.4	8.27e-26	abc	abcde	a	f	df	abc	bc	bde	e	bce	ac
Nd	141.1	2.47e-25	ab	abc	a	d	cd	ab	b	bcd	c	bc	a
Gd	133.1	1.06e-23	abc	abcd	a	e	ef	abc	bd	bdf	d	bcdf	ac
Y	140.6	3.19e-25	ab	abc	a	d	de	ab	bc	bce	c	bce	a
REE	132.3	1.58e-23	ab	abcd	a	e	ce	ab	bd	bcd	d	abd	ab

REE boxplot by Zone

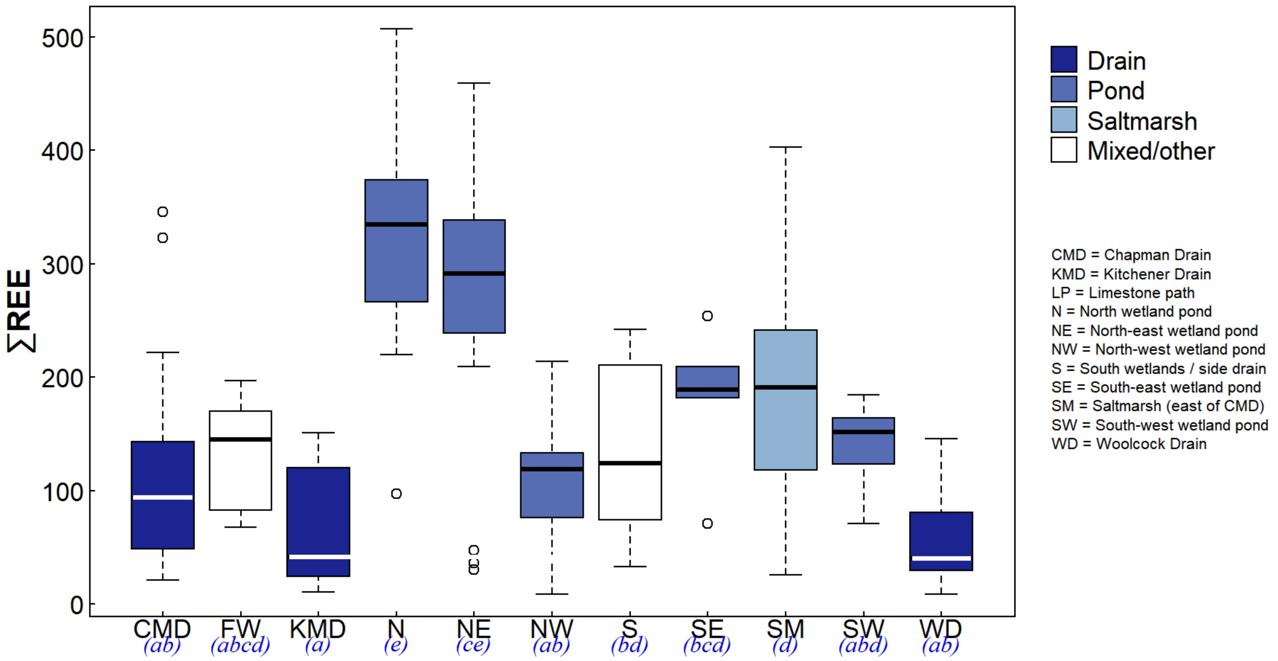


Figure 5: Sum of REE concentrations by sampling zone at Ashfield Flats for all sampling years. Different colours show environment sub-types, and means are different (p<0.05, Kruskal-Wallis) if italic text below x-axis labels has no common letters.

The greatest concentrations of ∑REE are in the north and northeast wetland pond sediments (SW05 (N) and SW06 (NE) in McGrath 2021, see Figure 5). The pattern of ∑REE means across zones is similar to that for Al in Figure 6.

Aluminium boxplot by Zone

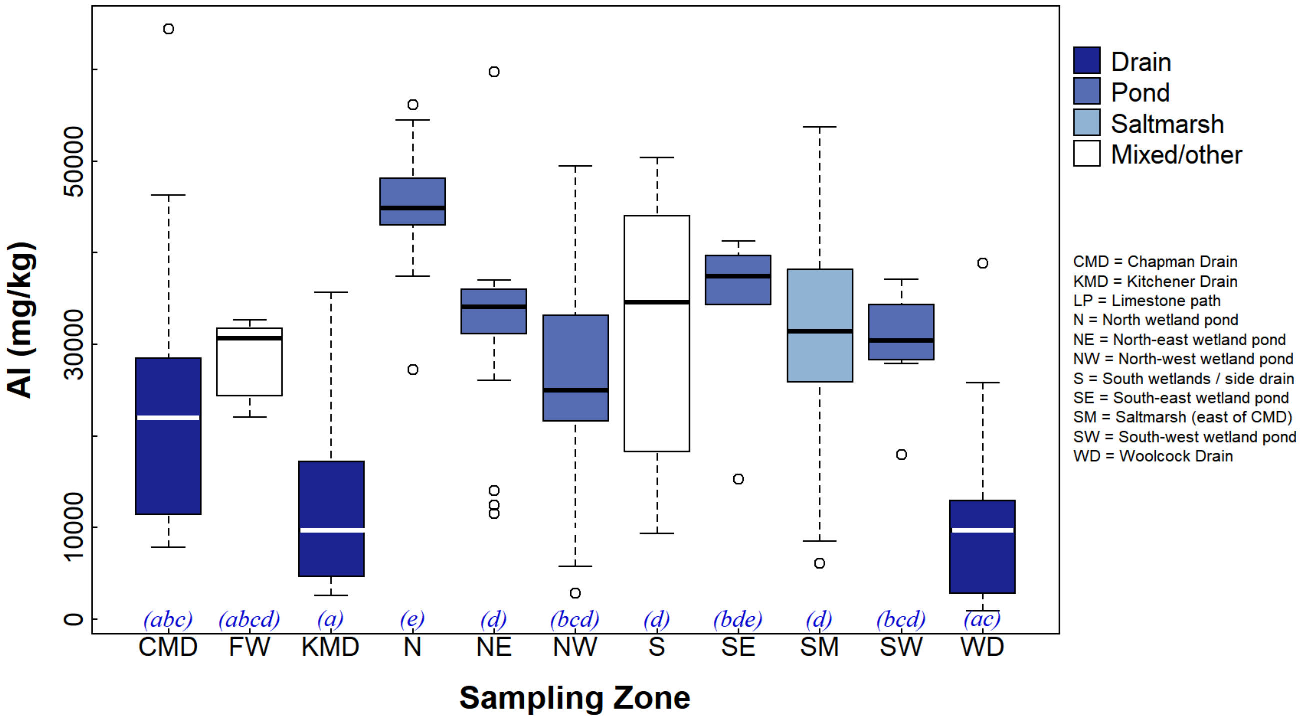


Figure 6: Al concentrations by sampling zone at Ashfield Flats for all sampling years. Different colours show environment sub-types, and means are different ($p<0.05$, Kruskal-Wallis) if italic text below x-axis labels has no common letters.

Bubble maps

∑REE

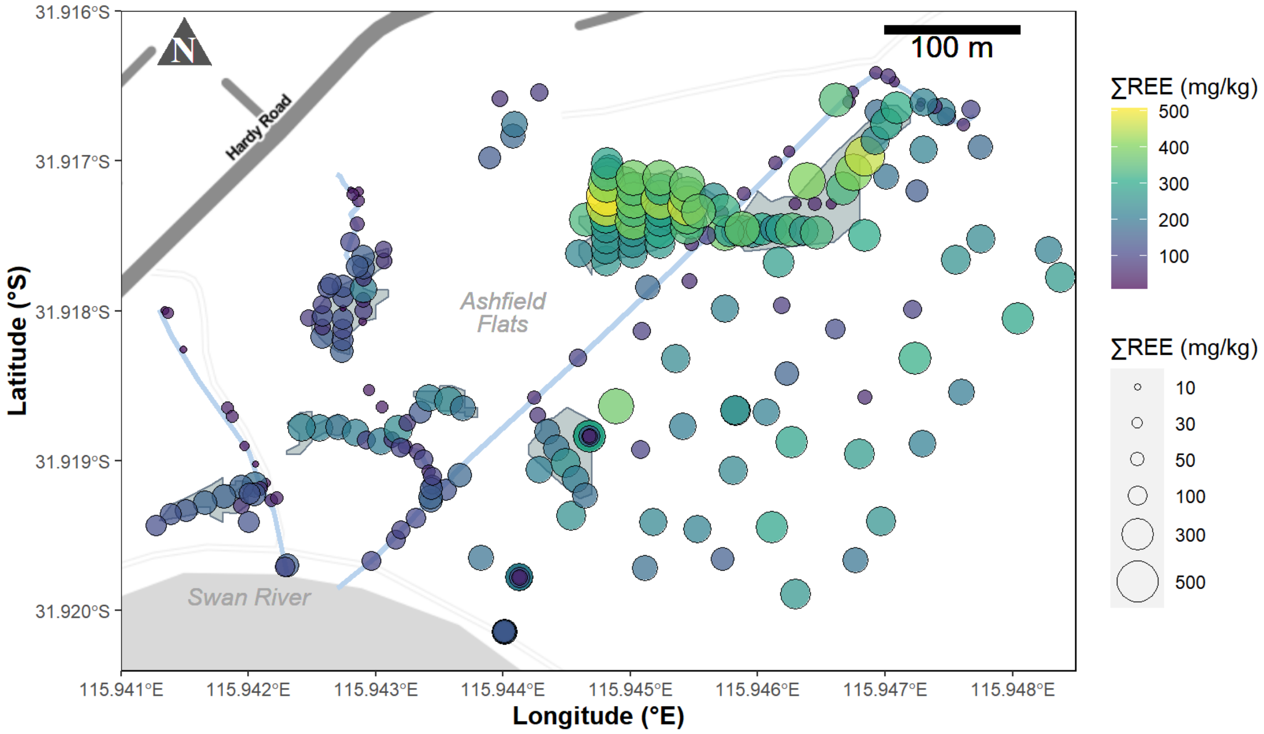


Figure 7: Map of REE concentrations by location at Ashfield Flats for all sampling years.

Al

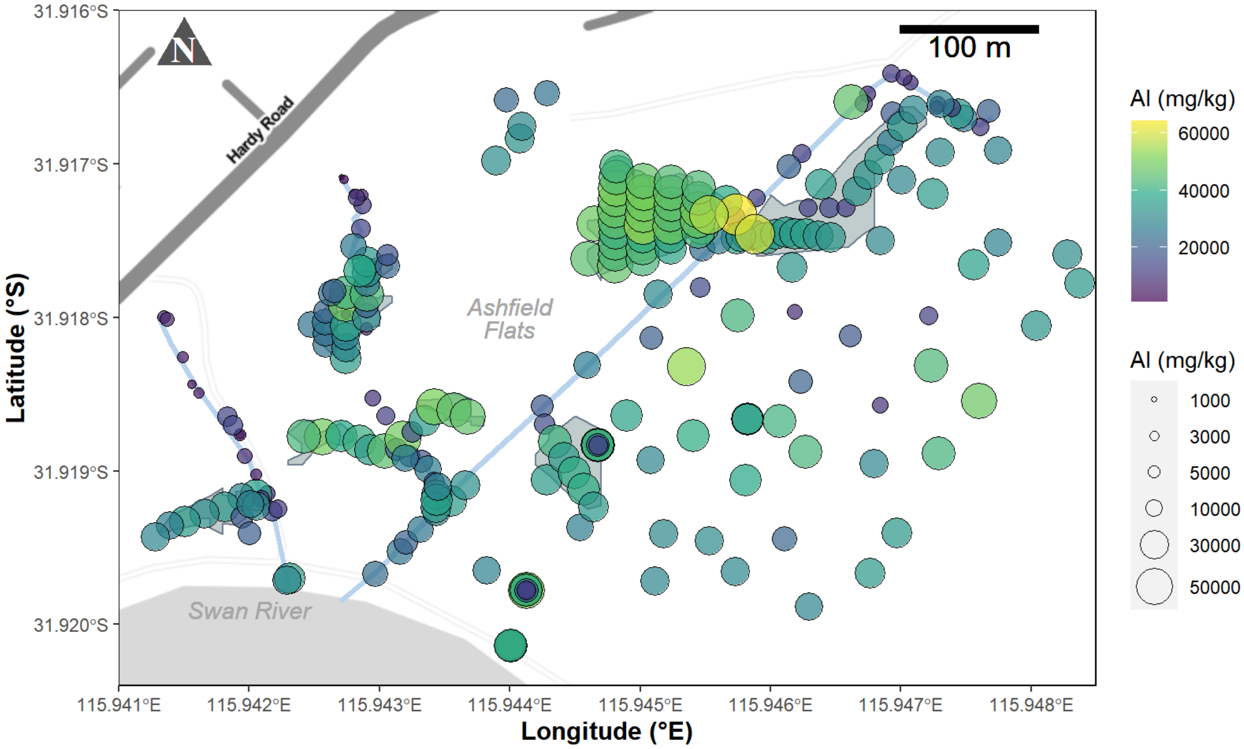


Figure 8: Map of Al concentrations by location at Ashfield Flats for all sampling years.

Boxplots by Type

∑REE and Al, Ca, Fe, S

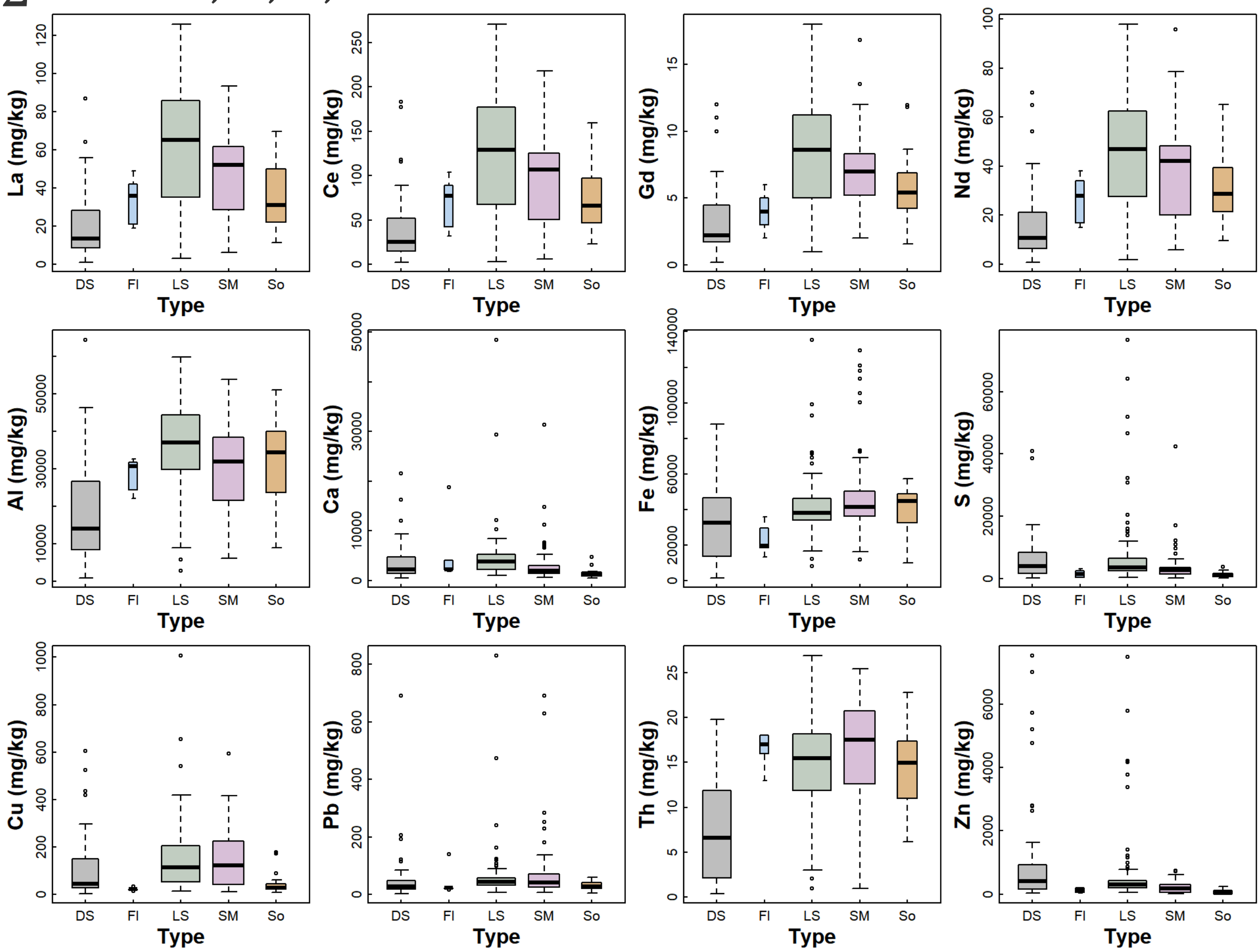


Figure 9: Boxplots of REEs and selected major and trace elements by sample type at Ashfield Flats for all sampling years (DS = Drain sediment; Fl = Flooded; LS = Lake Sediment; SM = Saltmarsh; So = Soil).

Boxplots by Zone

Ce, La, Nd, Gd

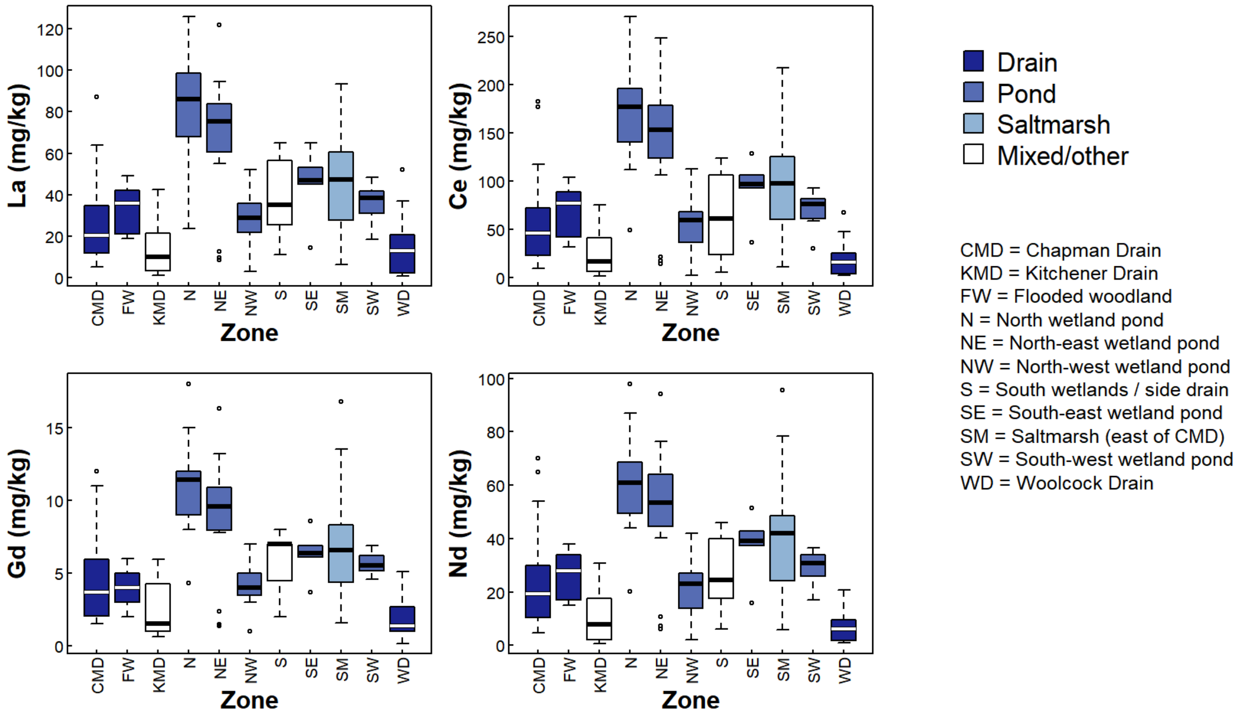


Figure 10: Boxplots of REEs by sampling Zone at Ashfield Flats for all sampling years (DS = Drain sediment; Fl = Flooded; LS = Lake Sediment; SM = Saltmarsh; So = Soil).

Al, Ca, Fe, S

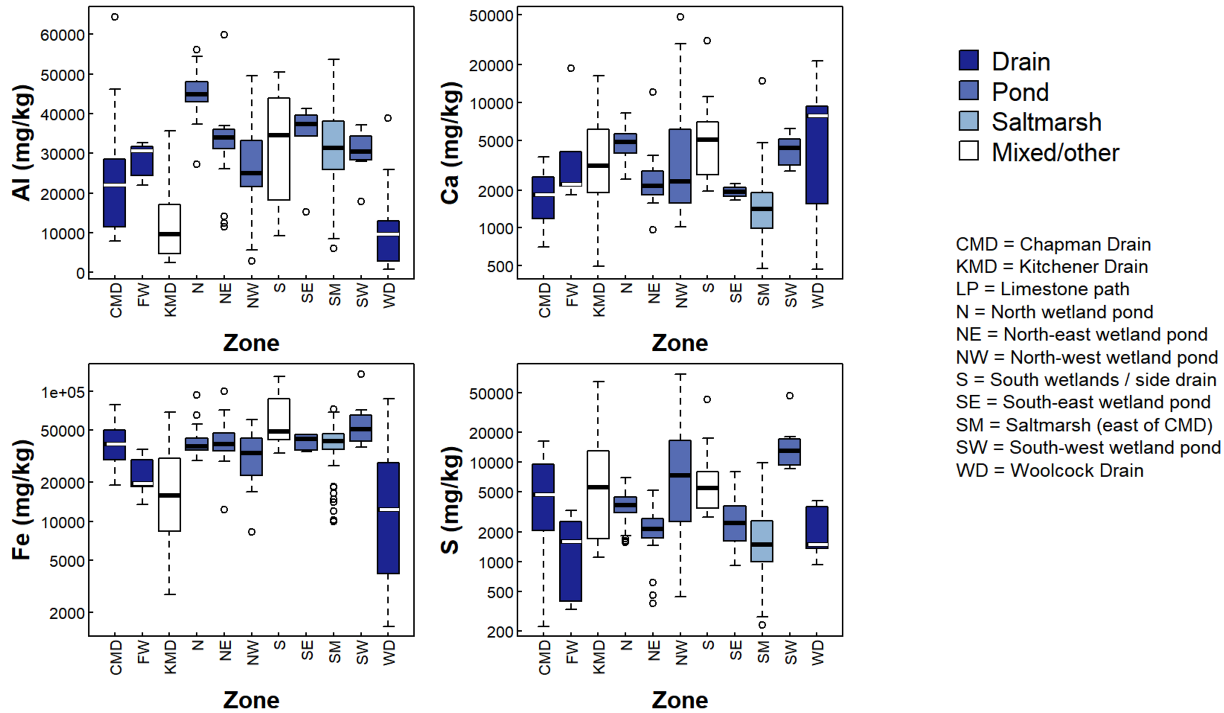


Figure 11: Boxplots of selected major elements by sampling Zone at Ashfield Flats for all sampling years.

Co, Cr, Cu, Ni, Pb, Zn

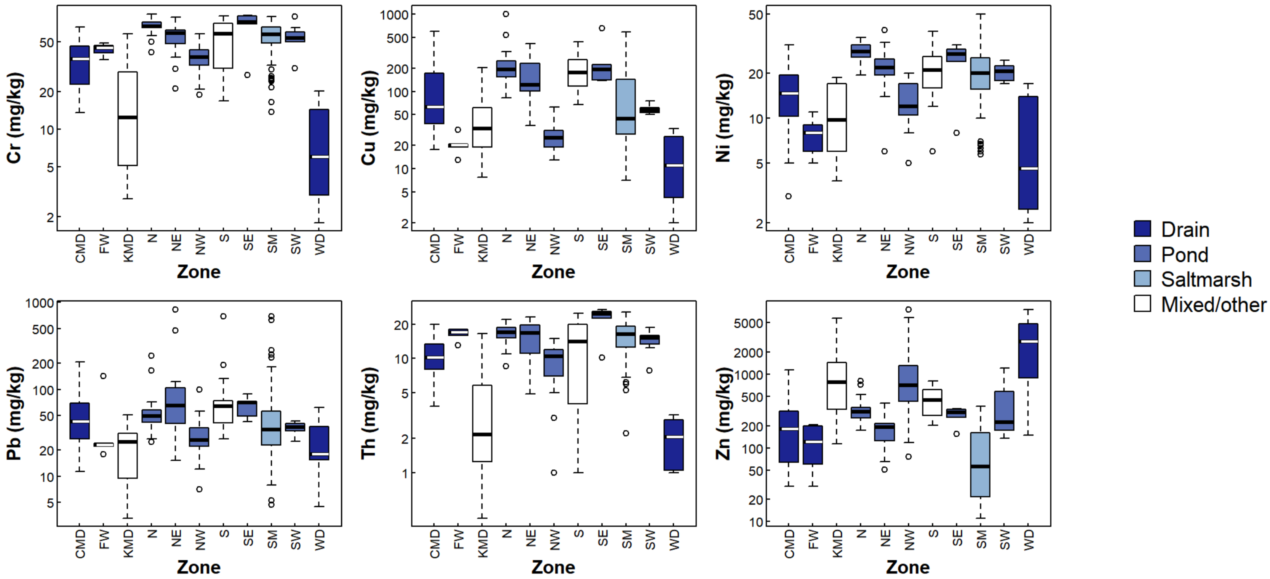


Figure 12: Boxplots of selected trace elements by sampling Zone at Ashfield Flats 2019-2022 (CMD = Chapman Drain, KMD = Kitchener Drain, LP = Limestone path, N = North wetland pond, NE = North-east wetland pond, NW = North-west wetland pond, S = South wetlands / side drain, SE = South-east wetland pond, SM = Saltmarsh (east of CMD), SW = South-west wetland pond, WD = Woolcock Drain).

Scatter plot matrix majors & REEs raw

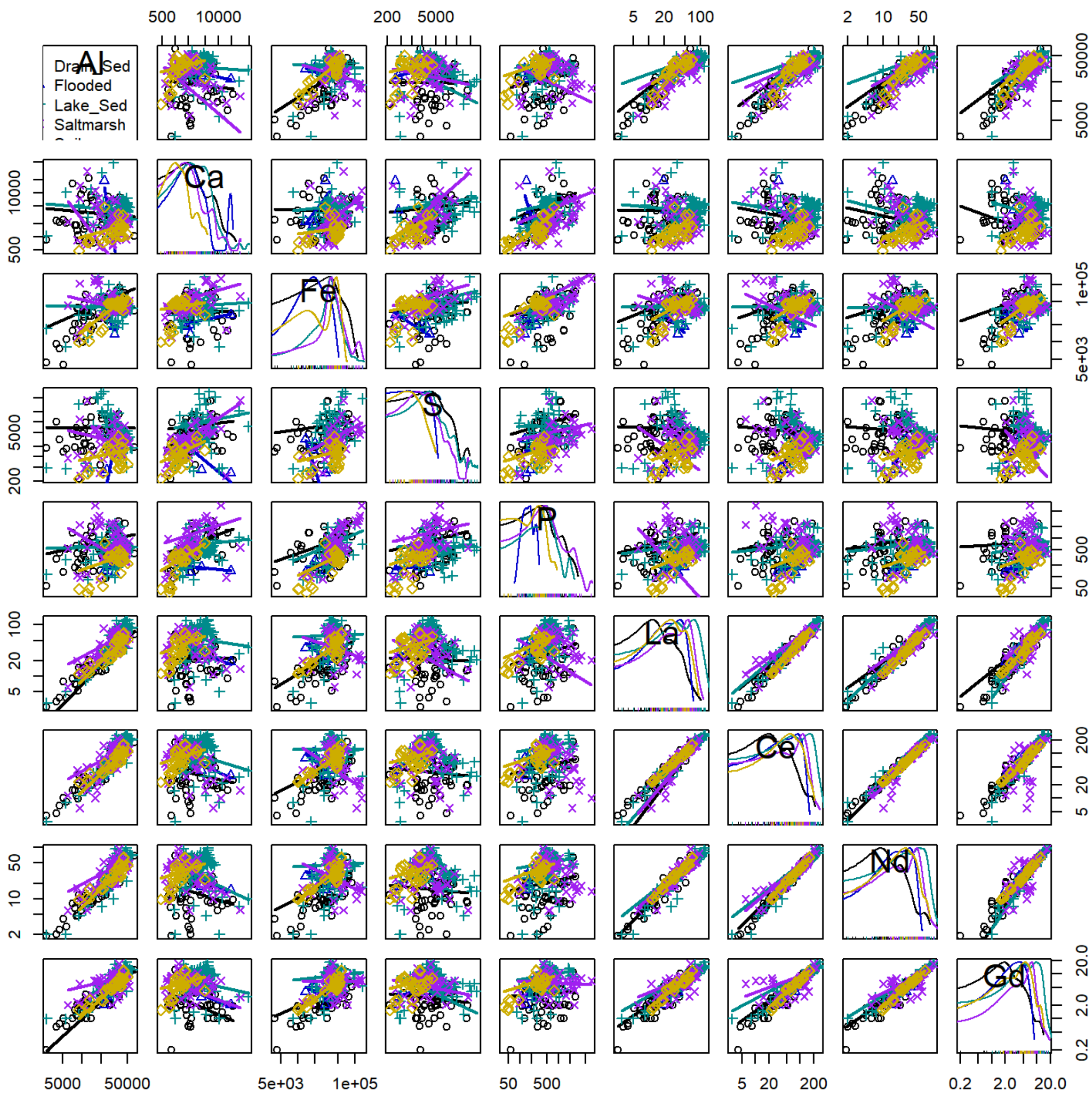


Figure 13: Scatter plot matrix for log10-transformed elements at Ashfield Flats for all sampling years.

Scatter plots

Ce, La, Nd, Gd *vs*. Al

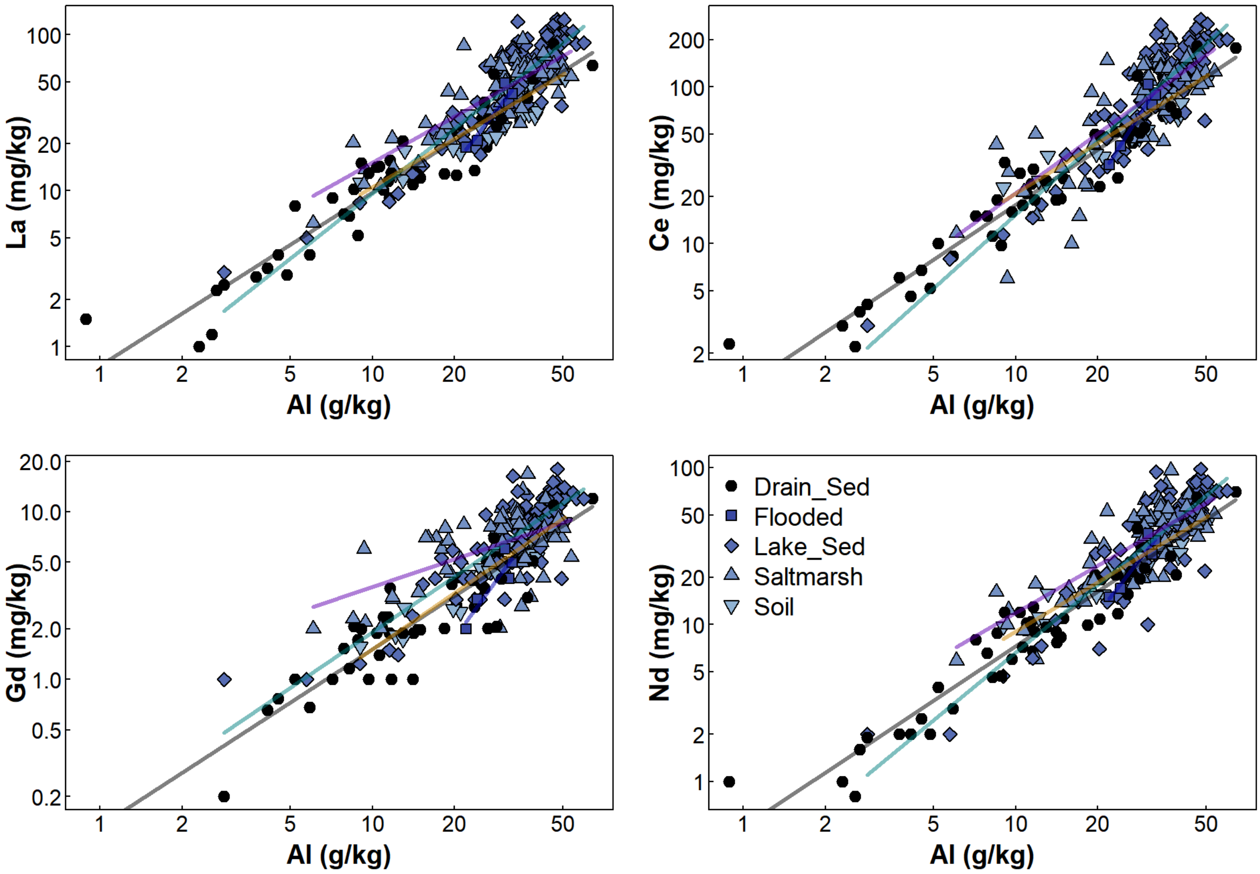


Figure 14: REE-Al relationships at Ashfield Flats for all sampling years.

Ce, La, Nd, Gd *vs.* Fe

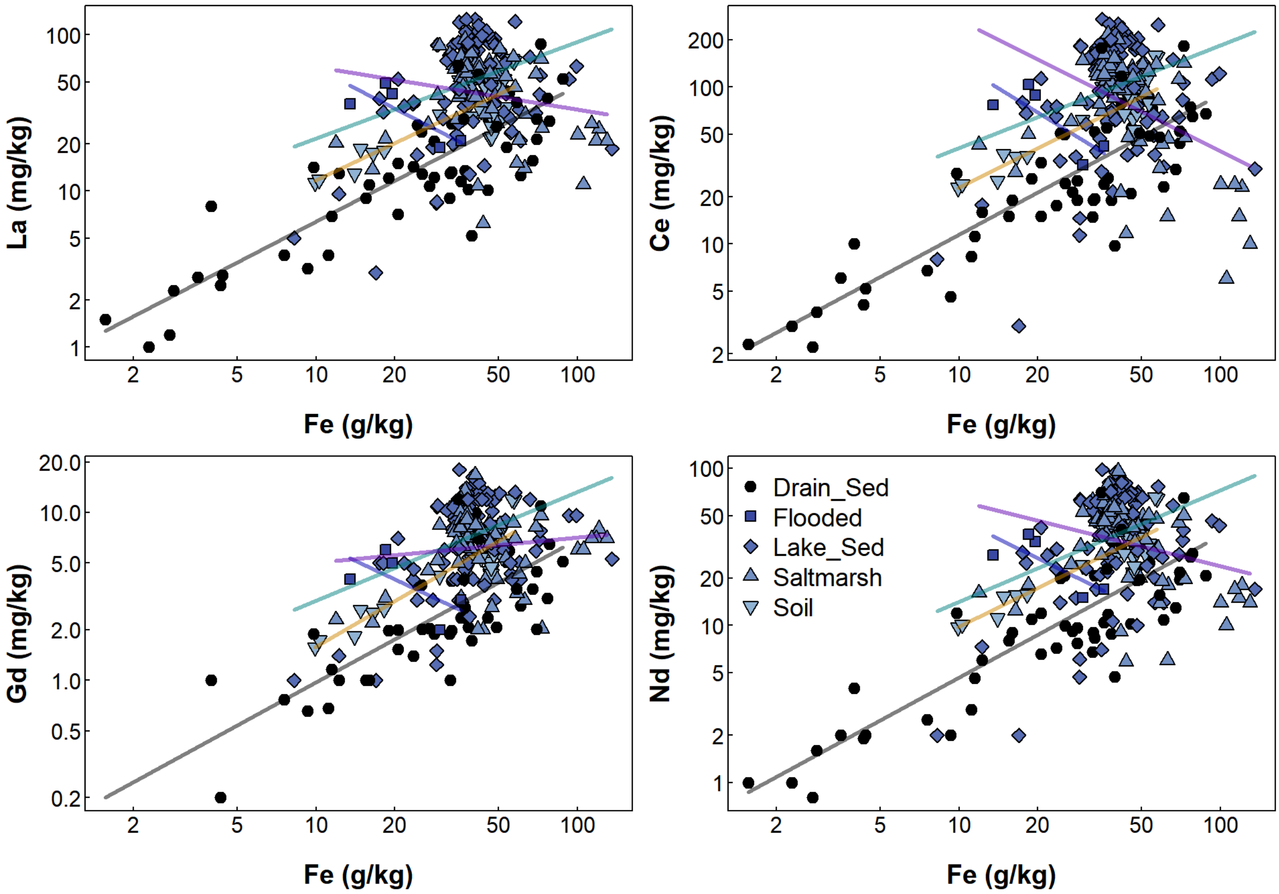


Figure 15: REE-Fe relationships at Ashfield Flats for all sampling years.

Ce, La, Nd, Gd *vs.* P

z

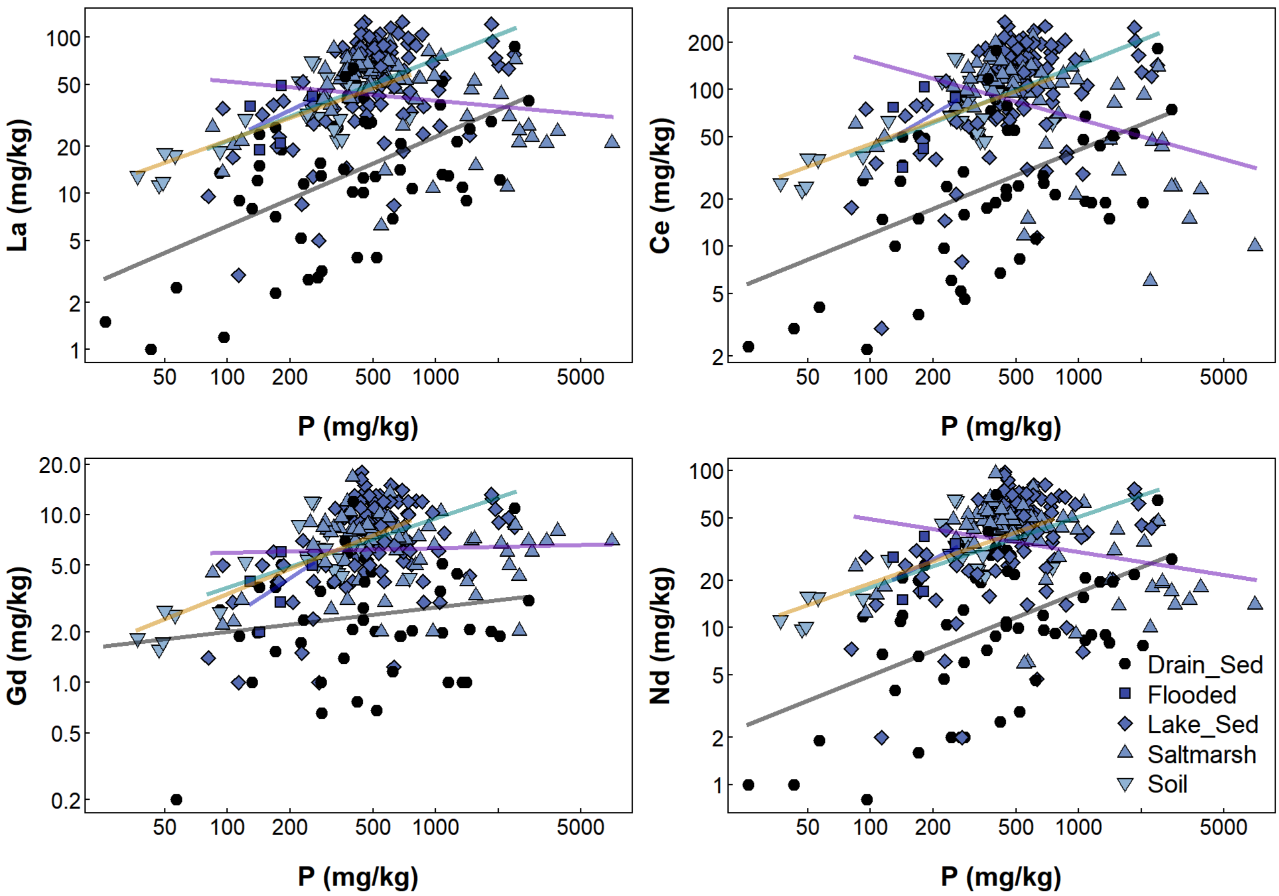


Figure 16: REE-P relationships at Ashfield Flats for all sampling years.

```
afs1922clr <- afs1922[,c(1:27,29:33,35:46,48,50:51,53:55)]
afs1922clr[,24:50] <- t(apply(afs1922clr[,24:50], MARGIN = 1,
                        FUN = function(x){log(x) - mean(log(x),na.rm=T)}))
cat("Untransformed:\n")
head(signif(afs1922[,c("Al","Ca","Fe","P","S","La","Ce","Nd","Gd","Cu","Pb","Th","Zn")],3))
cat("\nCLR-transformed:\n")
head(signif(afs1922clr[,c("Al","Ca","Fe","P","S","La","Ce","Nd","Gd","Cu","Pb","Th","Zn")],3))
```

```
## Untransformed:
##      Al   Ca    Fe   P     S   La   Ce   Nd   Gd   Cu   Pb   Th   Zn
## 1  9000 5180 28800 630 32400  8.4 11.4  4.7 1.24 19.0 31.1  2.1 4180
## 2 37100 3280 44700 544 17900 48.6 93.0 36.6 6.51 75.8 43.2 15.7 1220
## 3 28700 4430 48600 419 13900 41.5 81.6 32.5 5.73 54.7 32.0 15.3  418
## 4 33900 2840 53100 533  9880 41.9 81.0 33.1 5.90 62.9 41.8 18.6  270
## 5 31200 3050 71500 744  8540 41.5 82.9 34.9 6.90 50.5 34.7 12.4  173
## 6 34800 4220 38400 465  8910 35.4 72.5 29.0 5.39 58.3 36.9 16.0  176
##
## CLR-transformed:
##     Al   Ca   Fe     P    S    La     Ce    Nd    Gd     Cu     Pb    Th    Zn
## 1 4.70 4.15 5.86 2.040 5.98 -2.28 -1.970 -2.86 -4.19 -1.460 -0.969 -3.66 3.930
## 2 5.28 2.86 5.47 1.060 4.55 -1.36 -0.708 -1.64 -3.37 -0.913 -1.480 -2.49 1.860
## 3 5.20 3.34 5.73 0.978 4.48 -1.33 -0.658 -1.58 -3.31 -1.060 -1.590 -2.33 0.976
## 4 5.23 2.75 5.68 1.080 4.00 -1.47 -0.806 -1.70 -3.43 -1.060 -1.470 -2.28 0.396
## 5 5.31 2.99 6.14 1.580 4.02 -1.31 -0.619 -1.48 -3.10 -1.110 -1.490 -2.52 0.116
## 6 5.47 3.36 5.57 1.160 4.11 -1.42 -0.702 -1.62 -3.30 -0.920 -1.380 -2.21 0.186
```

Scatter plot matrix majors-REEs CLR-transformed

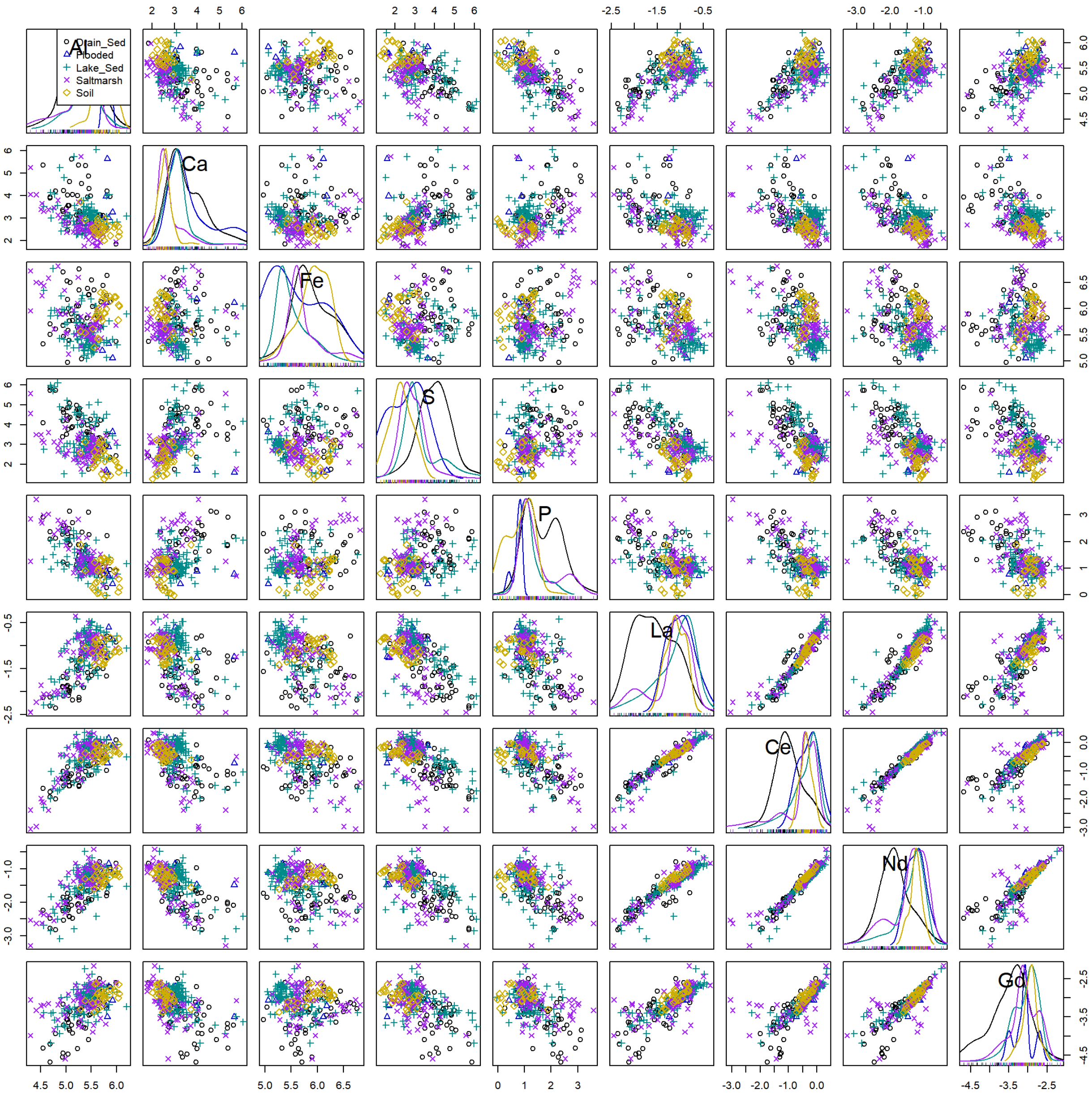


Figure 17: Scatter plot matrix of CLR-transformed elements at Ashfield Flats for all sampling years.

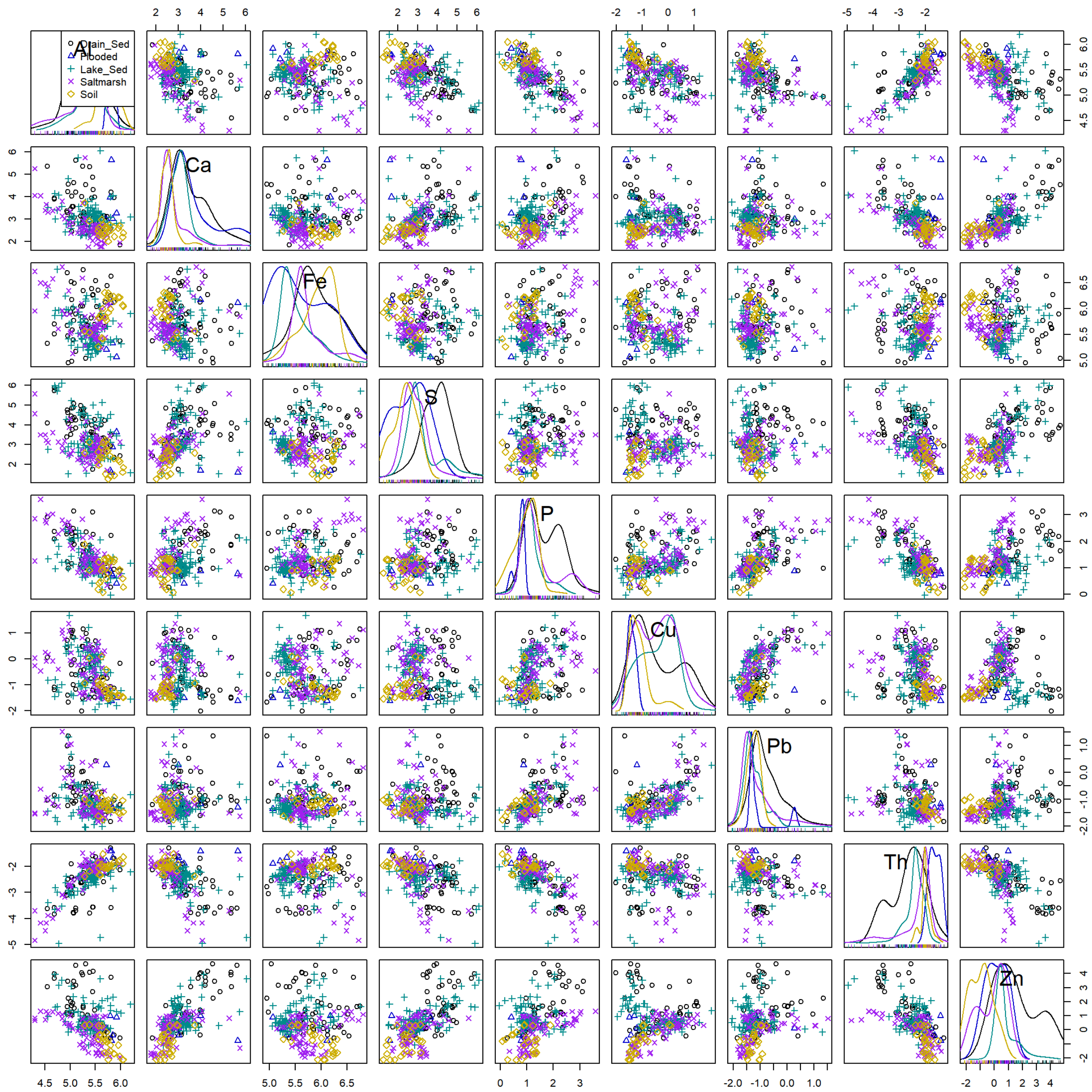


Figure 18: Scatter plot matrix of CLR-transformed elements at Ashfield Flats for all sampling years.

Scatter Plots for CLR-transformed variables

Ce, La, Nd, Gd *vs.* Al

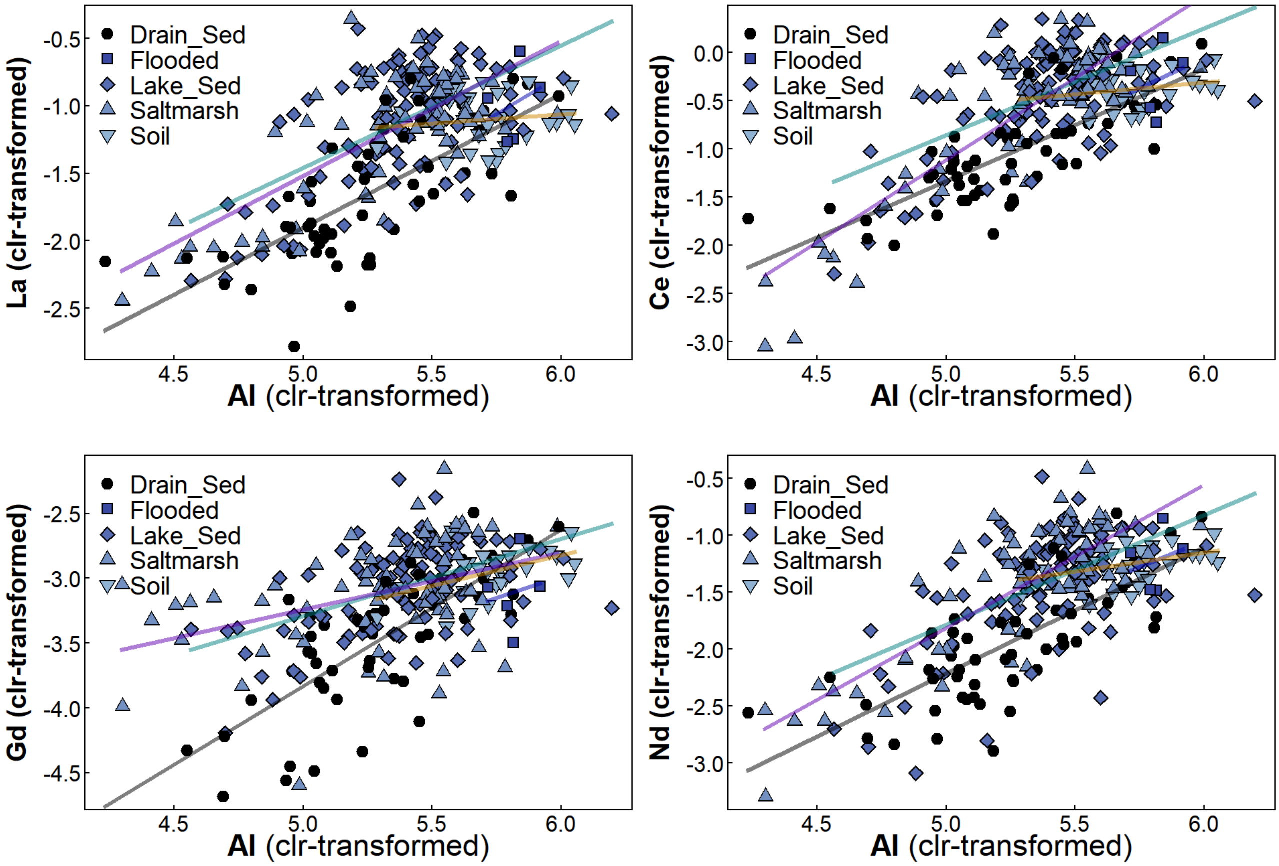


Figure 19: REE-Al relationships (concentrations CLR-transformed) at Ashfield Flats for all sampling years.

Fit linear models: ungrouped and grouped

Now we fit linear models for each REE *vs.* Al.
Maybe only Gd has significantly different slopes due to anthropogenic addition?

La-Al

```
data0 <- na.omit(afs1922clr[,c("Type","Al","La")])
lmLaAl0 <- with(data0, lm(La ~ Al)) ; summary(lmLaAl0)
cat(rep("-=-",20),sep="");lmLaAl1 <- with(data0, lm(La ~ Al * Type)) ; summary(lmLaAl1)
cat(rep("-=-",9),"\n");aovLaAlmods <- anova(lmLaAl0,lmLaAl1); print(aovLaAlmods, type="te
xt")
##
## Call:
## lm(formula = La ~ Al)
##
## Residuals:
##      Min       1Q  Median       3Q      Max
## -1.1511 -0.2809  0.0059  0.2520  1.0735
##
## Coefficients:
##             Estimate Std. Error t value Pr(>|t|)
## (Intercept) -6.19611    0.36301  -17.07   <2e-16 ***
## Al           0.91933    0.06736   13.65   <2e-16 ***
## ---
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
##
## Residual standard error: 0.3726 on 259 degrees of freedom
## Multiple R-squared:  0.4183, Adjusted R-squared:  0.416
```

```
## F-statistic: 186.2 on 1 and 259 DF,  p-value: < 2.2e-16
##
## -=--=-=--=-=---=----=-=--=-=-------=--=--=-------=-
## Call:
## lm(formula = La ~ Al * Type)
##
## Residuals:
##      Min       1Q   Median       3Q      Max
## -0.84567 -0.22780 -0.00319  0.23156  0.97653
##
## Coefficients:
##                  Estimate Std. Error t value Pr(>|t|)
## (Intercept)      -6.86475    0.68680  -9.995  < 2e-16 ***
## Al                0.99251    0.13048   7.606 5.66e-13 ***
## TypeFlooded      -0.75044   13.02023  -0.058   0.9541
## TypeLake_Sed      0.87406    0.92289   0.947   0.3445
## TypeSaltmarsh     0.34512    0.89399   0.386   0.6998
## TypeSoil          4.96331    2.05443   2.416   0.0164 *
## Al:TypeFlooded    0.14791    2.23948   0.066   0.9474
## Al:TypeLake_Sed  -0.08633    0.17350  -0.498   0.6192
## Al:TypeSaltmarsh  0.00791    0.16921   0.047   0.9628
## Al:TypeSoil      -0.85250    0.36250  -2.352   0.0195 *
## ---
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
##
## Residual standard error: 0.3296 on 251 degrees of freedom
## Multiple R-squared:  0.5589, Adjusted R-squared:  0.5431
## F-statistic: 35.34 on 9 and 251 DF,  p-value: < 2.2e-16
##
## -=- -=- -=- -=- -=- -=- -=- -=- -=-
## Analysis of Variance Table
##
## Model 1: La ~ Al
## Model 2: La ~ Al * Type
##   Res.Df    RSS Df Sum of Sq      F    Pr(>F)
## 1    259 35.958
## 2    251 27.264  8    8.6943 10.005 4.314e-12 ***
## ---
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

Ce-Al

```
data0 <- na.omit(afs1922clr[,c("Type","Al","Ce")])
lmCeAl0 <- with(data0, lm(Ce ~ Al)) ; summary(lmCeAl0)
lmCeAl1 <- with(data0, lm(Ce ~ Al * Type)) ; summary(lmCeAl1)
anova(lmCeAl0,lmCeAl1)
##
## Call:
## lm(formula = Ce ~ Al)
##
## Residuals:
##      Min       1Q   Median       3Q      Max
## -1.14358 -0.31362  0.00762  0.31213  1.09640
##
## Coefficients:
##             Estimate Std. Error t value Pr(>|t|)
## (Intercept) -7.43647    0.42871  -17.35   <2e-16 ***
## Al           1.27175    0.07956   15.98   <2e-16 ***
## ---
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
##
## Residual standard error: 0.44 on 259 degrees of freedom
## Multiple R-squared:  0.4966, Adjusted R-squared:  0.4947
## F-statistic: 255.5 on 1 and 259 DF,  p-value: < 2.2e-16
##
##
## Call:
## lm(formula = Ce ~ Al * Type)
##
## Residuals:
```

```
##      Min       1Q  Median       3Q      Max
## -0.9719 -0.2464 -0.0003  0.2444  0.9963
##
## Coefficients:
##                  Estimate Std. Error t value Pr(>|t|)
## (Intercept)      -7.16933    0.80805  -8.872  < 2e-16 ***
## Al                1.16715    0.15352   7.603  5.8e-13 ***
## TypeFlooded      -0.51771   15.31905  -0.034  0.97307
## TypeLake_Sed      0.78319    1.08584   0.721  0.47141
## TypeSaltmarsh    -2.47936    1.05184  -2.357  0.01918 *
## TypeSoil          5.36626    2.41716   2.220  0.02731 *
## Al:TypeFlooded    0.10525    2.63487   0.040  0.96817
## Al:TypeLake_Sed  -0.06073    0.20414  -0.297  0.76633
## Al:TypeSaltmarsh  0.54001    0.19908   2.713  0.00714 **
## Al:TypeSoil      -0.91763    0.42650  -2.152  0.03239 *
## ---
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
##
## Residual standard error: 0.3878 on 251 degrees of freedom
## Multiple R-squared:  0.6212, Adjusted R-squared:  0.6076
## F-statistic: 45.73 on 9 and 251 DF,  p-value: < 2.2e-16
##
## Analysis of Variance Table
##
## Model 1: Ce ~ Al
## Model 2: Ce ~ Al * Type
##   Res.Df    RSS Df Sum of Sq      F  Pr(>F)
## 1    259 50.151
## 2    251 37.741  8     12.41 10.317 1.8e-12 ***
## ---
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

Nd-Al

```
data0 <- na.omit(afs1922clr[,c("Type","Al","Nd")])
lmNdAl0 <- with(data0, lm(Nd ~ Al)) ; summary(lmNdAl0)
lmNdAl1 <- with(data0, lm(Nd ~ Al * Type)) ; summary(lmNdAl1)
anova(lmNdAl0,lmNdAl1)
##
## Call:
## lm(formula = Nd ~ Al)
##
## Residuals:
##      Min       1Q   Median       3Q      Max
## -1.16952 -0.25495  0.00926  0.27641  1.03659
##
## Coefficients:
##             Estimate Std. Error t value Pr(>|t|)
## (Intercept) -7.31838    0.38249  -19.13   <2e-16 ***
## Al           1.07984    0.07098   15.21   <2e-16 ***
## ---
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
##
## Residual standard error: 0.3926 on 259 degrees of freedom
## Multiple R-squared:  0.4719, Adjusted R-squared:  0.4699
## F-statistic: 231.4 on 1 and 259 DF,  p-value: < 2.2e-16
##
##
## Call:
## lm(formula = Nd ~ Al * Type)
##
## Residuals:
##      Min       1Q   Median       3Q      Max
## -1.21598 -0.21714  0.00927  0.22164  0.94727
##
## Coefficients:
##                  Estimate Std. Error t value Pr(>|t|)
## (Intercept)       -7.7609     0.7373 -10.526  < 2e-16 ***
## Al                 1.1095     0.1401   7.920 7.68e-14 ***
## TypeFlooded        1.2757    13.9780   0.091   0.9274
```

```
## TypeLake_Sed       1.1598     0.9908   1.171   0.2429
## TypeSaltmarsh     -0.3435     0.9598  -0.358   0.7207
## TypeSoil           4.6282     2.2056   2.098   0.0369 *
## Al:TypeFlooded    -0.2034     2.4042  -0.085   0.9326
## Al:TypeLake_Sed   -0.1466     0.1863  -0.787   0.4321
## Al:TypeSaltmarsh   0.1482     0.1817   0.816   0.4154
## Al:TypeSoil       -0.7792     0.3892  -2.002   0.0463 *
## ---
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
##
## Residual standard error: 0.3538 on 251 degrees of freedom
## Multiple R-squared:  0.5843, Adjusted R-squared:  0.5694
## F-statistic: 39.21 on 9 and 251 DF,  p-value: < 2.2e-16
##
## Analysis of Variance Table
##
## Model 1: Nd ~ Al
## Model 2: Nd ~ Al * Type
##   Res.Df    RSS Df Sum of Sq      F    Pr(>F)
## 1    259 39.921
## 2    251 31.422  8    8.4986 8.4858 3.267e-10 ***
## ---
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

Gd-Al

```
data0 <- na.omit(afs1922clr[,c("Type","Al","Gd")])
lmGdAl0 <- with(data0, lm(Gd ~ Al)) ; summary(lmGdAl0)
lmGdAl1 <- with(data0, lm(Gd ~ Al * Type)) ; summary(lmGdAl1)
anova(lmGdAl0,lmGdAl1)
##
## Call:
## lm(formula = Gd ~ Al)
##
## Residuals:
##      Min       1Q   Median       3Q      Max
## -1.18254 -0.19238  0.03097  0.26627  0.92315
##
## Coefficients:
##             Estimate Std. Error t value Pr(>|t|)
## (Intercept) -6.71352    0.36674 -18.306   <2e-16 ***
## Al           0.66194    0.06794   9.743   <2e-16 ***
## ---
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
##
## Residual standard error: 0.3652 on 253 degrees of freedom
## Multiple R-squared:  0.2728, Adjusted R-squared:  0.2699
## F-statistic: 94.92 on 1 and 253 DF,  p-value: < 2.2e-16
##
##
## Call:
## lm(formula = Gd ~ Al * Type)
##
## Residuals:
##      Min       1Q   Median       3Q      Max
## -1.34908 -0.16556  0.03977  0.22193  0.84458
##
## Coefficients:
##                  Estimate Std. Error t value Pr(>|t|)
## (Intercept)       -9.8722     0.7623 -12.951  < 2e-16 ***
## Al                 1.2077     0.1439   8.390 3.89e-15 ***
## TypeFlooded        2.9176    12.9167   0.226 0.821483
## TypeLake_Sed       3.5975     0.9772   3.682 0.000285 ***
## TypeSaltmarsh      4.4365     0.9504   4.668 5.01e-06 ***
## TypeSoil           4.1950     2.0660   2.031 0.043383 *
## Al:TypeFlooded    -0.5462     2.2218  -0.246 0.806010
## Al:TypeLake_Sed   -0.6110     0.1833  -3.334 0.000989 ***
## Al:TypeSaltmarsh  -0.7687     0.1793  -4.288 2.59e-05 ***
## Al:TypeSoil       -0.7316     0.3650  -2.005 0.046104 *
## ---
```

```
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
##
## Residual standard error: 0.3268 on 245 degrees of freedom
## Multiple R-squared:  0.4359, Adjusted R-squared:  0.4152
## F-statistic: 21.04 on 9 and 245 DF,  p-value: < 2.2e-16
##
## Analysis of Variance Table
##
## Model 1: Gd ~ Al
## Model 2: Gd ~ Al * Type
##   Res.Df    RSS Df Sum of Sq      F    Pr(>F)
## 1    253 33.740
## 2    245 26.172  8    7.5682 8.8558 1.213e-10 ***
## ---
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

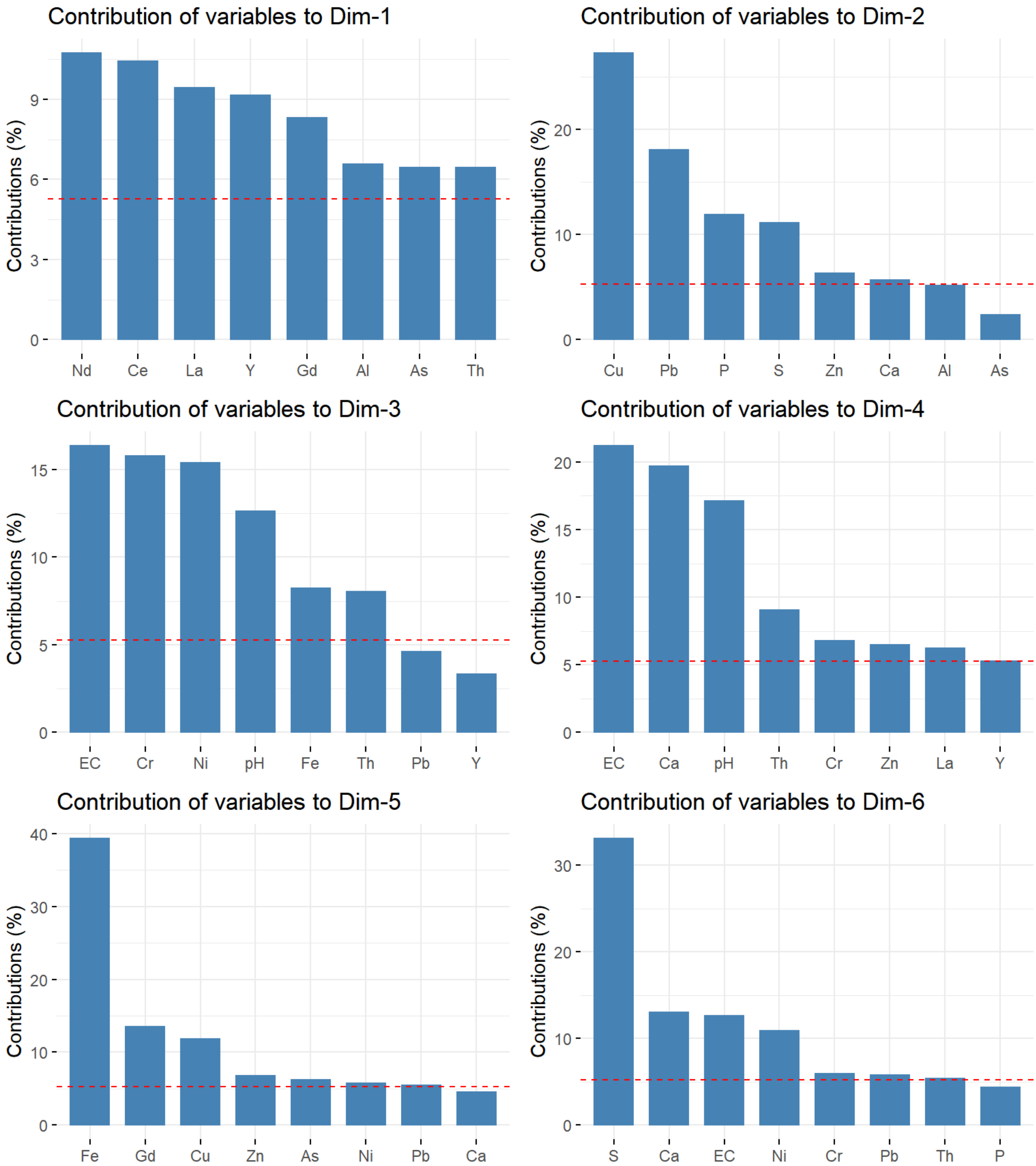
From the output

Principal components analysis

PCA Summary

```
## Importance of components:
##                           PC1    PC2    PC3     PC4     PC5    PC6     PC7
## Standard deviation     2.8922 1.4590 1.4110 1.19798 1.02381 0.9101 0.82625
## Proportion of Variance 0.4403 0.1120 0.1048 0.07554 0.05517 0.0436 0.03593
## Cumulative Proportion  0.4403 0.5523 0.6571 0.73263 0.78780 0.8314 0.86733
##                            PC8     PC9    PC10    PC11    PC12    PC13    PC14
## Standard deviation     0.72077 0.71313 0.67446 0.51658 0.44520 0.41887 0.36647
## Proportion of Variance 0.02734 0.02677 0.02394 0.01405 0.01043 0.00923 0.00707
## Cumulative Proportion  0.89467 0.92144 0.94538 0.95942 0.96986 0.97909 0.98616
##                          PC15    PC16    PC17    PC18    PC19
## Standard deviation     0.3515 0.24809 0.18308 0.17264 0.12075
## Proportion of Variance 0.0065 0.00324 0.00176 0.00157 0.00077
## Cumulative Proportion  0.9927 0.99590 0.99766 0.99923 1.00000
```

Contribution of variables to principal components



PCA Biplots by Type

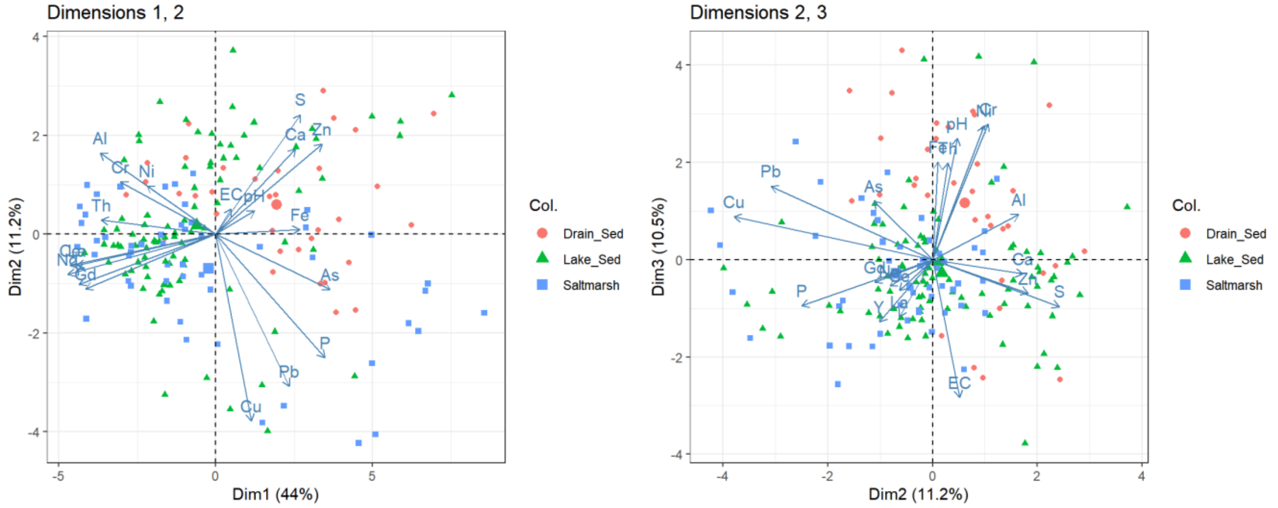


Figure 20: Principal components biplot for 2019-2022 Ashfield data grouped by sample Type.

PCA Biplots by Zone

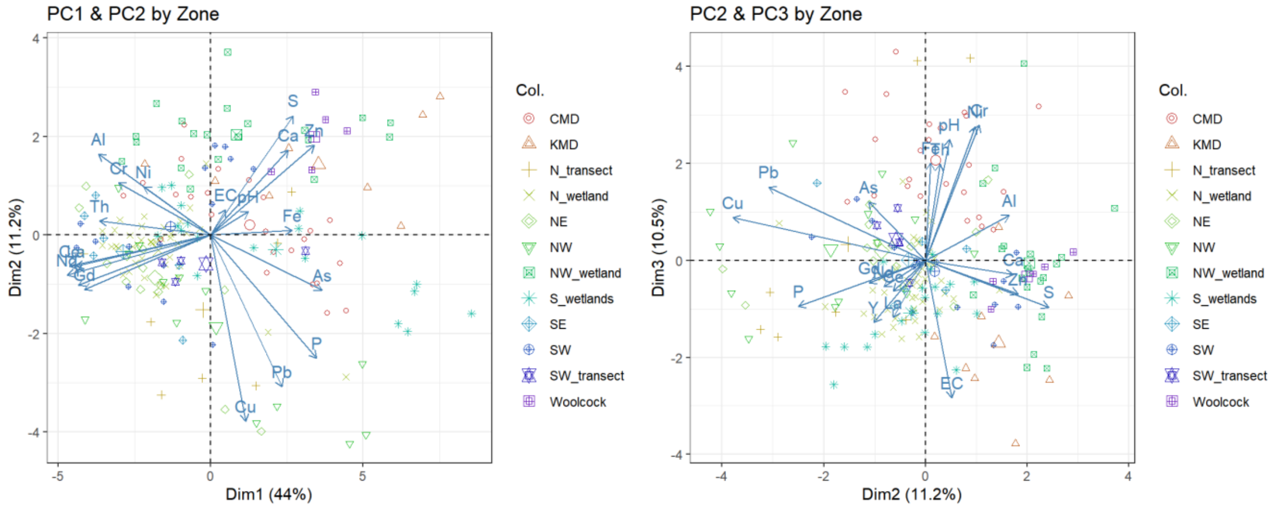


Figure 21: Principal components biplot for 2019-2022 Ashfield data grouped by sampling Zone.

PCA Biplots by ZoneSimp

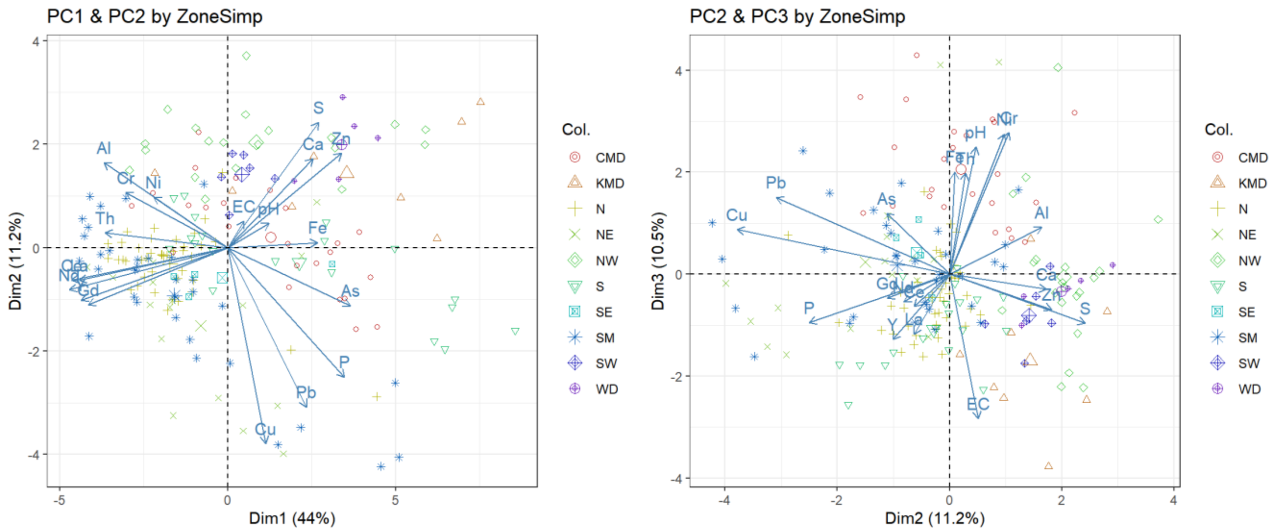


Figure 22: Principal components biplot for 2019-2022 Ashfield data grouped by simplified sampling Zone.

Water analyses to support acid sulfate

Read and curate water data

```
afwater1922 <- read.csv(paste0(git,"afw1922.csv"), stringsAsFactors = TRUE)
afwater1922$Year <- as.factor(afwater1922$Year)
afwater1922$Sample <- as.character(afwater1922$Sample)
afwater1922$Sample_Code <- as.character(afwater1922$Sample_Code)
afwater1922fresh <- droplevels(subset(afwater1922,afwater1922$salinity=="Fresh"))
```

Estimate sulfate/chloride ratios in fresh water samples

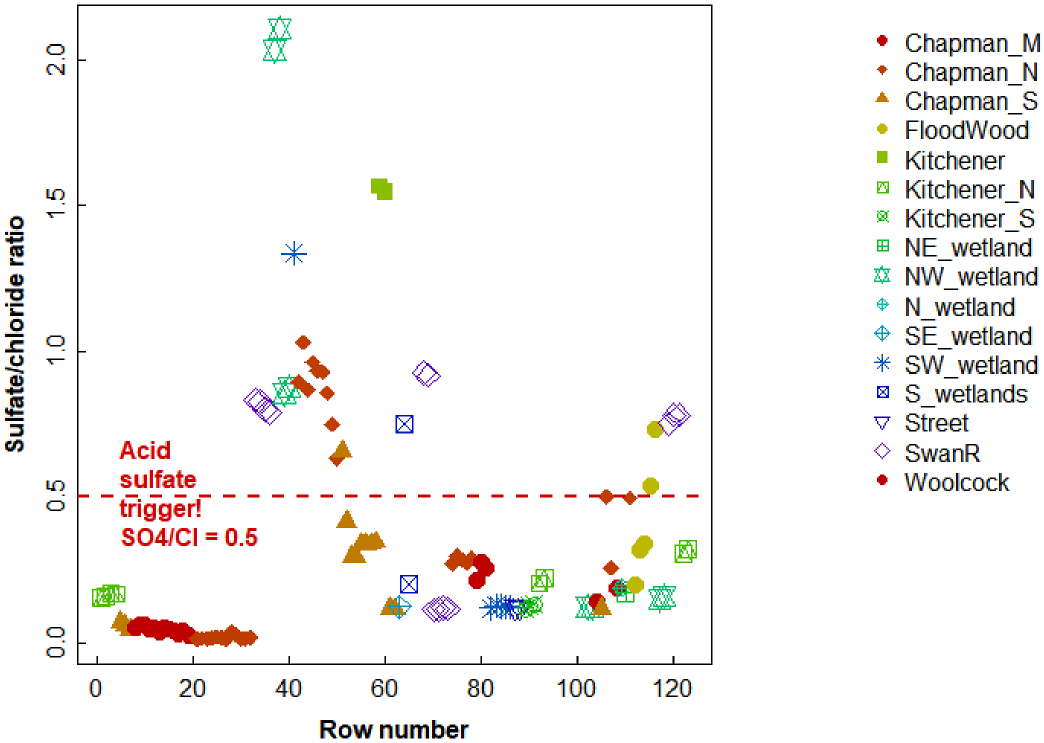


Figure 23: Sulfate to chloride ratios in Ashfield Flats fresh water samples 2019-2022, categorized by Zone.

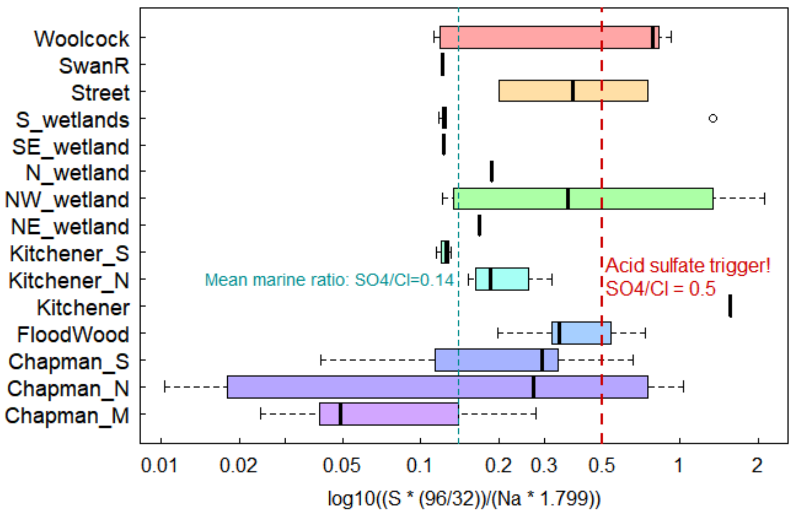


Figure 24: Sulfate to chloride ratios in Ashfield Flats fresh water samples 2019-2022 showing threshold values.

Figures 23 and 24 suggest that acid sulfate oxidation has contributed SO_4^{2-} to the Woolcock Drain, NW wetland (SW03), and Kitchener Drain, possibly due to contributions from the Yelland Way pyritic containment cell. The incidences of SO_4/Cl > 0.5 in the Chapman drain (Table 9) more likely reflect on-site acid sulfate oxidation.

Table 9: Identity and ASS-related properties of Ashfield Flats water samples with SO4/Cl > 0.5

Year	Sample	Drain	Zone	SO4_Cl	pH
2019	1	Woolcock	Woolcock	0.834	5.50
2019	2	Woolcock	Woolcock	0.826	5.67
2019	3	Woolcock	Woolcock	0.800	5.71
2019	4	Woolcock	Woolcock	0.789	5.71
2020	W_1		NW_wetland	2.030	5.70
2020	W_2		NW_wetland	2.110	6.11
2020	W_5		NW_wetland	0.855	8.73
2020	W_6		NW_wetland	0.875	8.30
2020	W_9		S_wetlands	1.340	
2020	W_13	Chapman	Chapman_N	0.896	7.38
2020	W_14	Chapman	Chapman_N	1.030	7.29
2020	W_15	Chapman	Chapman_N	0.867	6.84
2020	W_16	Chapman	Chapman_N	0.963	7.06
2020	W_17	Chapman	Chapman_N	0.933	6.87
2020	W_18	Chapman	Chapman_N	0.930	7.23
2020	W_19	Chapman	Chapman_N	0.855	6.98
2020	W_20	Chapman	Chapman_N	0.749	6.73
2020	W_21	Chapman	Chapman_N	0.631	6.98
2020	W_23	Chapman	Chapman_S	0.654	6.83
2020	W_40	Kitchener	Kitchener	1.560	7.49
2020	W_41	Kitchener	Kitchener	1.550	7.71
2021	AF21_23	Street	Street	0.749	7.09
2021	AF21_31	Woolcock	Woolcock	0.926	6.04
2021	AF21_32	Woolcock	Woolcock	0.917	6.49
2022	2022_W23	Chapman	Chapman_N	0.500	7.42
2022	2022_W31		FloodWood	0.537	7.69
2022	2022_W32		FloodWood	0.733	7.46
2022	2022_W35	Woolcock	Woolcock	0.751	6.82
2022	2022_W36	Woolcock	Woolcock	0.782	6.96
2022	2022_W37	Woolcock	Woolcock	0.782	6.47

References

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Scott, B., Taplin, R., & Loos, C. (2009). Classification and acid sulfate soil detection at Ashfield, Western Australia. *Environmental Health*, **9**(3/4), 72-86.

Xu, N., Rate, A. W., & Morgan, B. (2018). From source to sink: Rare-earth elements trace the legacy of sulfuric dredge spoils on estuarine sediments. *Science of The Total Environment*, **637-638**, 1537-1549. *https://doi.org/10.1016/j.scitotenv.2018.04.398*

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