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DESCRIPTION AND ANALYSIS OF NAFAP BRIQUETTE SURFACE CHEMISTRY FILES (Comprising data from 1984 to 1995)

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1. EXECUTIVE SUMMARY

From 1984 to 1995, NAPAP researchers exposed limestone and marble briquettes to weathering for months to years at several different sites. They sampled the briquettes and analyzed multiple layers for anion content (sulfate SO4, nitrate NO3, chlorine Cl, and fluorine F). In the first four years, they analyzed a subset of samples for fifteen cations (Mg, Al, Cd, Mn, Ba, Be, Ni, Pb, Co, Cr, Cu, Fe, Sr. V. and Zn). They compiled the results into several BSC (briquette surface chemistry) data files and documented the data—field formats thereof both in table headers and in separate files.

In July of 1998 I received nineteen BSC files as email attachments: three format files (and two duplicates) describing the fields in the data files, twelve anion data files (four material types times three project cycles) , and two cation data files (from the first cycle, and which were re-sent separately in September). In examining these files, I have verified and extended their format descriptions, transformed all to a common physical format, combined the fourteen date files into two master files, slightly modified (recoded) and reordered identification data, and done preliminary analyses of the measured data.

For this study, the outdoor treatment units are the briquettes while the laboratory analytical. Units are the layers sampled from each briquette. The data files reflect this hierarchical structure. Each line, representing a layer, has a briquette and layer id; treatment fields describing the rock type and condition, exposure site and rack slot, and exposure period; and analytical fields giving values for either the four anions or fifteen cations and indicating which are below detection limits. The briquette treatment fields are duplicated for each layer of a given briquette.

Proper statistical analysis must also reflect this two-level structure. This is impeded in this study by the diversity of layers sampled for different briquettes. (There are sixteen different patterns, not counting some of the control blocks). On the other hand, there are essentially no missing data. Overall, the data are in good shape for statistical analysis after the few changes I made. The disk accompanying this report contains the ready-to-analyze anion and cation files. There are three versions to meet the differing input needs of different programs.

Lacking existing analyses to review, I performed *some* myself. The report text and tables tabulate the briquette treatment variables and the below-detection indicators for layers for both the anion and cation files. Histograms, plots, and analyses of covariance show the following about the overall relationship between treatment and anion content: rock type (limestone versus marble), exposure time, and layer selected all affect each of the anions; condition (fresh versus weathered) affects SO4 and Fluorine.

There are two directions to go for further analyses. One is to examine Subsets of data to answer specific questions. The other is to augment the current data with other information.

2. DATA FIELDS AND RECORDS

From a user viewpoint, a data table comprises a set (or sequence) of records, each with the same sequence of fields. The logical format and content remains the same regardless of how the table is stored and displayed and whether the medium is paper or electromagnetics. From this viewpoint, all the BSC tables (data files) have the same format for the record identification and treatment fields, which come first, and analogous formats for the measurement data, which are the same for all anion and cation files respectively. Therefore, once the physical format differences are removed (as described in the next section) it is easy to combine files as appropriate for various analyses.

2.1 Format files

The five format files include two duplicates I slighted edited the three distinct files and gave them the following descriptive names (the original names are given in parentheses).

formcat.txt (docm_icp.txt, docm_icp.wp)
forman88.txt (docum_ic.txt, docum_ic.wp)
forman92.doc (!docsurf.che)

Suffixes ‘cat’ and ‘an’ refer to cation and anion data files Suffixes ‘88’ and ‘92’ refer to presumed year of creation. The later anion format file is a lightly edited version of the earlier one; the main change is the addition of codes for exposure periods longer than four years. Extensions ‘txt’ and ‘doc’ indicate ASCII text and MS-Word file formats. The original wp/txt files were apparently intended to be WordPerfect and ASCII text versions of the same file, but they are identical and not quite either format. Instead, they are mostly plain text with the addition of a few junk characters that were easily deleted.

2.2 Identification and treatment fields

The initial fields in the BSC records identify each briquette and layer thereof and describe how it was created and treated.

1. Rock Type: L,M = limestone, marble.
2. Condition: F,W = fresh, weathered (new, old).
   In the files as received, Condition and Rock Type are combined (in that order, into one Material Type field with four codes: FL,WL,FM,WM (but also see note after 4 Spray). The order is somewhat arbitrary, but it makes slightly more sense to me to think of Condition as modifying Rock. Type than the opposite, so I have reversed the order in accordance with the standard general-to-specific ordering of database fields. As for combining the two fields into one with two subfields: if fields are designated by column position, it does not make any difference since two adjacent columns can be regarded as desired as either one two-column field or two one—column fields. If fields are separated by tabs or some other character, it is more difficult to switch back and forth. Combination is probably better for entry and display; separation is probably better, overall, for analysis.

3. Site (of exposure): CB,DC,NC,NJ,NY,OH,OS = characterization block (control with no exposure), Washington DC, North Carolina, New Jersey, New York, Ohio, and Ohio (movable) shelter.
   In the files as received, ‘OS’ is ‘OHM’, but a third character is neither necessary nor convenient. Also, Site is first, before Material Type. While this may have been convenient for entry and display, given that the data were split into separate files for each Material Type, it also contradicts the implication of that division, which is that Material Type is a more ‘important’ grouping variable than Site. In addition, the exposure regime and slot variables which follow logically complete exposure place. All three are followed in turn by the exposure time variables. For the CE samples, these following fields are not applicable and are entered as NA.
4. Spray (at Site OS): ‘ ’, -, + = <not applicable>, absent (dry), present (wet). In the files as received, this is prefixed to Material Type and coded

‘ ‘, D, S = <none>, dry, sprayed. The coding is a matter of preference but the (mis)placement is a double design error. First, making a variable that is possibly null (and here it usually is so) a prefix unnecessarily complicates the logic of extracting the rest of the information from the combined fields. In the files as received, for instance, the rule for extracting Rock Type would be “second character of Material Type, unless the first character is ‘D’ or ‘S’, in which case it is the third”. Second, this (sub)variable is logically a modifier of Site OS, designating the dry and sprayed subareas thereof, which were used simultaneously. It could be eliminated by replacing OS (OHM) with, for instance, SD (shelter-dry) and SS (shelter-wet).

5. Slot (in exposure rack) three digit number (or NA = not applicable). In the files as received, Slot is field 10, after the time variables. However, Site and Slot jointly say specifically where the briquette was exposed; they belong together Slot numbers are 1## for most limestone, 2## for most marble, and 3## for both at site OS. They run independently at each site. The leading digit is somewhat redundant with Rock Type and Site. It could be deleted or made unique for each site (and thereby replace Site). Given information for each site about the structure and setting of its rack and the correspondence between slot number and position, analysis for position effects might be possible and useful. Otherwise, slot serves as an administrative variable only. (In the files as received, Slot was sometimes coded N1 or N1, N2, N3 when not applicable I changed all such codes to NA.)

6. Exposure Period: two subcodes for nominal exposure length and period number.

6a. Exposure Length: ‘,A,B,T,Q,C,S,H,O,N,D= 25,1,2,3,4,5,6,7,8,9,10 years. Blank is quarter, A is annual, B etc are bi-, tri-, quadr-, quinqu-, sex-, sept-, oct-, non-, and dec-ennials (C and H(ept) substitute for duplicate Q and S). The length is nominal in that the exact number of days depends on the Site and Period Number (next).

6b. Period Number: 1,2,3,4, = sequence number for exposure length. Period numbers are sequence numbers that run separately for each exposure length and, at least for some, each site. T1s and Qls start in 1984. T2s and Q2s start in 1986, not 1985, because no T or Q periods were started in 1985. T3s start in 1988 but Q3s in 1989. Fall 1994 is quarter 2 at NC and NJ (but with a two-week difference) and quarter 1 at DC. Or, to put it another way, quarter 1 is summer 1984 in NC and NJ (but with slightly different start and stop days) and fall 1984 in DC.

7. Start Year: 84—90 = 1984 to 1990.

8. Start JDay: 1-366 = Jan 1 to Dec 31.
This and End JDay below are Julian days within each year. The format files incorrectly label these as Julian dates, but the latter are the number of days from some arbitrary date and also encode the year.

9. End Year: 84-95

10. End JDay: 1-366

11. Briquette: XYZ-## (X,Y,X are always,mostly, seldom a letter; ## are digits)
These identifiers apply to one briquette and to the one sample (or set of samples, I am not sure which) taken therefrom. They obviously have a structure that is probably meaningful administratively but hopefully irrelevant for analysis (unless one wanted to check for systematic effects of analysis runs). (This field was originally called Sample. While this may be more accurate for the control samples, it seemed ambiguous, taken by itself, when applied to the treated material -- briquette, sample thereof (possibly multiple) , or layer?)

12. Layer: A,B,C …U,V,W,X,Y,Z from outermost top to outermost bottom. I infer that top means exposed to sun and direct precipitation and bottom means not. The particular set of layers analyzed and reported depends on the particular sample. However, sets of samples with the same exposure period were often treated the same. The number of layers ranges from one to seven, being generally higher for longer exposures There is no layer

that is reported for all samples. (Exception: the layers for weathered CB controls are numbered instead of lettered, and number as many as nine.

2.3 Measurement fields

The anion files report measurements of four anions: sulfate SO4, nitrate NO3, chlorine Cl, and fluorine F. The cation files report, for a subset of early samples, 15 cations: Mg, Al, Cd, Mn, Ba, Be, Ni, Pb, Co, Cr, Cu, Fe, Sr, V, and Zn. The format files say nothing about the units of measurement and report. To do any analysis of a particular ion, we must assume that the same unit is used consistently for that ion (this seems to be so -- as discussed later). To compare ions, we must assume that they were reported with the same unit. While this must be true for some (unknown) subsets, its only a guess for all 19 species.

Concentration measurements always have a lower threshold of detection and sometime an upper limit (as in radioimmunoassay). Upper limits are usually overcome by accurately diluting samples that are known or suspected of being above the limit. For some types of work, it is possible to concentrate samples to raise them above the lower limit, but this tends to be difficult and expensive to impossible to do very accurately. The alternative is to simply report the low values as low.

There are two issues with low values; first is how they are recorded. The BSC files have two fields for each ion: a value field followed by a flag field. The flag field is blank for good values and ‘<‘ for values below the detection limit (low values), in which case the value entered is (appears to be) the detection limit. (The format files imply but do not quite State this last point.)

There are also one-field solutions that narrow the display width of the file. (This is mostly a concern with tabbed files.) Low values can be left blank (if there are no missing values) or entered as 0, with thresholds recorded elsewhere. Or, the detection limit and flag can be combined. (Since all concentrations are positive, a ‘-‘ will do.) Or, one can enter the compromise value to be used for analysis (see next paragraph).

Regardless of how low values are coded, the second issue is what to do with them in statistical analyses. Deleting them is bad; it discards information and introduces the worse problem of missing values. But to not delete them, they must be given some specific value. The detection threshold is too high; it overweighs the low values. Zero is similarly too low; it also results in missing values if one applies a log transform, as is common with concentration data. So a compromise is needed, such as half the detection limit.

2.4 Comments

As received, the anion files have 19 fields on each line: 10 experiment fields (1, 2, and 4 above are combined as one), 8 (4x2) measurement fields, and a comment field. Leaving aside the few sample or layer specific comments, the standard entries are the following:

(blank) This is the most common.

ICP (in anion file) The layer was also analyzed for cations.

ICP+ (in anion file) The layer sample was aggregated for cation analysis. (Changed from ICP* due to conflict with another use of *.)

BULK (new CB only) Replicates (3) of sample are from volumetric center of briquette (Layer is NA - not applicable).

AGG Analysis is of aggregate sample. Since Slot and Sample are entered as NA, I presume this means that multiple samples were combined for some reason. In order to differentiate between different aggregate samples, I gave them artificial sample identifiers AGG-0l to AGG-16.

##ml In the CB samples for weathered material, which had numbers instead of letters for the layer, the comment is of the form I-Jml, where I and J are numbers from 0 to 2000, with I < J. Some also have a letter prefix. The

meaning of all this is not clear.

2.5 Units, records, and statistical analysis

The experimental (manipulation) units for the BSC study are the briquettes. Each is carved from a particular material and placed in a particular site rack slot for a particular period. The analytical (measurement) units are the layers carved from each briquette (or core thereof -- as have no information as to the subsample protocol). They serve as repeated measurements characterizing the briquettes. There are, therefore, three ways of looking at the combined data.

The first view sees a file of layer records, one physical line per record. The second sees briquette records with a variable multiplicity of lines, one per layer subrecord, with treatment data redundantly duplicated on each. The third view is that the file is the relational join of two relational data tables. The first would be a briquette table with briquette id and the treatment data. The second would be a layer table with briquette and layer as the key followed by the measurements. Each would have the comments applying to that type of unit.

The two-level structure of units complicates statistical analysis. Analysis of layers is problematical because they are not independent units but spatial repeated measurement units nested within the treated briquettes. Analysis of briquettes is difficult because of the variation in the layer sets. What is needed is multiple analyses of different subsets.

3. DATA FILES

3.1 Anion data files

ESC researchers set out briquettes for exposure in summer 1984 and at various times up to fall 1990. They brought them back in for analysis at various times from fall 1984 to fall 1995. The analyses of briquettes whose exposure ended by summer 1988 were tabulated in four ASCII text files (one for each Material Type). Eriquettes whose exposure ended in fall 1988 to summer 1992 were later tabulated in four old-version Mac Word files attributed to Bill Ellingson. The remainder were finally tabulated in four Word 6 (Mac) files attributed to J. Scott Steckenrider.

To more easily keep track of and manipulate the resulting twelve files, I assigned them new names based on the Rock Type, Condition, and latest exposure ending year of the briquettes tabulated within, with an extension matching their physical file format. These are listed below, along with the names they came to me with (which, for the -90 to -95 files, appear to be DOS 8 3 condensations of longer Mac names).

limnew88.txt	lms.ic.tab
limnew92.doc	!limeche.m88
limnew95.doc	!limeche.m92
limold88..txt	pels_icp.tab
limold90.doc	!wthlime.88-
limold95.doc	!wthlime.92-
marnew88.txt	mar_ic.tab
marnew92.doc	!mrblche.m88
marnew95.doc	!mrblche.m92
marold88.txt	pemb_icp.tab
marold90.doc	!wthmrbl.88-
marold95.doc	!wthmrbl 92-

3.2 Merging the files

The division of the data into three groups of files by date appears to be an

artifact of the grant/project cycle and without scientific basis. Merger is necessary for any analysis crossing the time boundaries. The separation of material types is fine for analyses confined to just one of them, but it inhibits or prevents direct comparison of limestone to marble or fresh to weathered material. It also inhibits making global changes to the record format and field coding (and any such change should be global). I therefore reduced all twelve files to a common format suitable for merging into a master anion data file.

The format I chose for merging is one line per layer with no space characters and with tab characters separating the fields. I chose the extension ‘tab’ to designate a file exactly in this format (which is why I changed .tab to .txt for the 1998 files as received). Converting the 1998 files (xxxyyy88.txt) only required deletion of three file and field header lines at the top and the blank lines scattered below to separate lines for the various sites. The reduced versions, produced with the Win95 NotePad program, were saved as xxxyyy88.tab.

The Word files were more challenging. The data within each file is contained within a single Word table, as distinct from a series of lines with tab or space separated text. Moreover, the older 1990/92 table format is distinctly different from the newer Word 6 format used in 1995.

Under Windows 95, MS Word Viewer and Word 7 both read and convert each of the older format xxxyyy9#.doc Mac Word files. Word Viewer creates a nicely spaced text form which can be viewed on the screen and printed but not saved. Word 7 creates a version 7 table. From this, producing the desired tabbed text file took four tries For each table:

1. Save the table as a text file Problem: Word puts each field on a separate line. Although a program could be written to gather the fields of each record back onto one line, I tried something else.
2. Save the table in DOS WordPerfect (WP) 5 1 format, read it in with WP, and have WP save it as a text file. Problem: WP puts all fields of all records on one line, with Ctrl-G as a field separator. Although a program could be written to split this one mega-line into records, I again tried something else.
3. Find and delete the Table code (using Reveal Codes); delete the header and blank lines, and delete all spaces (by globally replacing them with nothing). When this is done after maximizing the declared line length (via landscape mode and minimal margins), WP converts the tables to the desired format of text lines with tab-separated fields.

3A. Save the properly formatted file as ASCII text by the normal means: Text In/Out (Ctrl-F5) / Dos Text / Save. Problem: WP converts the tabs to spaces.

3B. Save the file by the alternative path: Ctrl-F5 / Save As / Generic Result: success.

Two of the newer Word 6 files (limold95 doc, marold95 doe) have a different problem: as read by Word Viewer and Word 7, some table columns have a defined display width too narrow for their data. Consequently, each table cell (data field) is wrapped onto two display lines. Attempts to fix the tables by widening the too-narrow columns froze Word, so that it had to be externally canceled (via Ctrl-Alt-Del).

The Windows 95 WordPad program, which can read and write text, RTF, and Word 6 files, and in the process convert from one format to another, does better. Somewhat ironically, this is because it is a limited editor that cannot create or edit tables as tables. So it automatically converts them on input to a sequence of text lines with tab-separated fields, exactly as here desired. This conversion makes column widths irrelevant, so it restored the two files to one line per layer. Moreover, it saves text files with tabs intact. (In retrospect, the 1990/92 files could probably have been converted easier by saving them as Word 6 files and then using WordPad.

The compatible tab versions of the twelve anion files easily combine into a

master data file with the DOS COPY command (copy * tab all.tab). (I have not yet found an equivalent facility in Windows 95). The result has 2019 lines (layer records). There was originally one more (L26-03 Z), but it had no measurements due to the vial breaking (said the comment). Being a useless nuisance for analysis, I removed it.

3.3 Treatment fields: checks, changes, and tabulations

As described in the previous section, the following changes were made to the treatment protocol fields:
1. Swap Site and Material Type (making the latter first).
2. Move Spray from a D/W Material Type prefix to a -/+ Site OS suffix.
3. Move Slot to just after Site/Spray. Recode N1, N2, N3 to NA.
4. Replace Briquette NA for aggregates with AGG-0l to AGG-16.

Material Type and Site/Spray were not yet split into separate fields.

Material Type and Site were checked for validity in the sense of having one of the prescribed categorical values. One OH was found to have been entered as <zero>H and corrected. Exposure Periods were checked for legal Exposure Length code and sensible Period Number. Briquettes with multiple layers were checked for treatment field consistency. Material Type to End JDay should be (and are) the same for each layer of a briquette.

A briquette table (briqan.tab) was produced with one line per briquette (or CB sample id). Each line contains the Material Type to Briquette fields plus a calculated field listing the layers analyzed for that briquette. The 64 ids with just one layer listed were considered to be possible entry errors. The corresponding layer line was found in all tab and checked against neighboring layers. Since two briquettes cannot be in the same slot at the same site at the same time, identicality of these variables between the suspect and a neighbor indicates an error. Three such matches were found, and in all three cases, the ids differed only in a single character, verifying that the difference was a single bad keystroke. The following changes were make to all.tab:

GU7-24 to GU7-04
G34-14 to G3l-l4
Kl4- 29 to K14-21

In addition, AC-l was changed to ACC-01 for consistency of format with all other ids.

A revised briqan.tab was regenerated from the revised all tab. It has 611 lines. Tables 1 to 5 tabulate he number of briquettes with the different Material Types, Sites, Exposure Periods, nominal exposure durations, and layer sets. The one briquette with layers AX was the one for which the layer Z vial broke.

On first examination of the data, the four date fields seem redundant with respect to Site and Exposure period in that they appear to determined by and predictable from the latter two. If this were true, they could be replaced with an auxiliary. Date table listing their values for each actual combination of Site and Exposure Period. Table 6 lists all 108 empirical combinations of Site, E.P. and the dates. It shows that this hypothesis is almost true, except that period A5 has two different starting days, for different batches of briquettes, at each site. There is also an anomaly at OS: A6 (a nominal year) is given as running from 90-9 to 93-152, nearly three and one half years. Some entry is not correct, but which is not obvious.

3.4 Measurements

Table 7 tabulates the anion values flagged with ‘<‘. The first version of this table showed that one briquette (found to be Fl5-12 layer A) had Cl listed as ‘81 <‘. Since 81 is clearly detectable and since the other two layers of F15-12 had Cl listed as ‘8 <, I changed 81 to 8 and modified the table accordingly. Two of the anions, 504 and Chlorine have relatively few low values (9% and 12%). The main problem for their analysis is to pick the replacement value. Should it be

a fraction of each threshold, or one value (such as the lowest threshold) for all layers? Fluorine, on the other hand, may best be collapsed to low versus high since nearly half the values were below detection NO3 is similarly problematical, though not as bad.

With the broken vial line deleted, all measurements are present -- none missing. With checks completed, the layer lines were written to a fixed format (column oriented) file all.txt. The CB ‘NA’S for inapplicable treatment variables and layer indicators were written as ‘*‘. This is the default missing value indicator for BMDP. With ‘ICP*’ changed to ‘ICP+’, these can easily be changed to anything else for any other program. (This was one reason for the change; the other is that aggregation is a ‘+‘ rather than '*' operation.)

3.5 Cation files

Fifteen cations were measured for 165 layers. My names and the originals are:

limcat88.tab	icp_lms.tab
marcat88.tab	icp_mar.tab

As with the other 1988 files, they only needed removal of the header lines (there were none blank) before being merged into cation data. As with the anion data, I swapped Material Type and Site and moved Slot. Since Site OS did not occur here, neither did Spray. There was also no need to change briquette ids.

The 165 layers come from 73 briquettes -- 42 limestone and 31 marble, all fresh. The distribution among sites is 6 CB, 15 DC, 22 NC, 15 NJ, and 15 NY (no OH or OS). The 67 non-CBs were exposed at the beginning of the study: 24 for a quarter, 7 for a year, and 36 for two years. Their layer patterns are as follows: ABC:28, A:20, XYZ:5, AZ,B,C:4, ABCXYZ:2 (total:67 non—CBs).

A visual scan of the combined layer data shows that all measurements are present for all layers included. It also reveals that eight cations -- Cd, Ba, Be, Ni, Pb, Co. Cr, and V -- -- are always below the threshold (or almost always, with just a few barely above). I removed their sixteen fields. Another four -- Mg, Mn, Fe, and Sr -- are always above the threshold, so I kept their values and removed their always-blank indicator fields. After these deletions there are ten (4 + 3*2) measurement fields in addition to the ten id and treatment fields. The last three cations -- Al, Cu, and Zn -- are mixed. Some values fall below detection and some above, with some too high to discard. However, I would not be surprised if further analysis (or some of the other four kept) fail to find much relationship with the treatment variables. The variation observed is small enough that it could just be mostly noise. Table 11 summarizes the seven cations kept.

4. STATISTICAL ANALYSES

Anions

Table 8 summarizes the four anion measurements and their log values. As is typical, the log values appear to have a much more symmetrical distribution. This is suggested 1) by the better balance of low and high values in relation to the means (the Z scores) and 2) by the standard deviation to mean ratios (less than 5 for logs and greater than 1 0 for raw measures).

Histograms 1 to 8 (produced by BMDP Statistical Software program 7D) give more direct evidence of the distributions. They show histograms for the four anions and their logs for each of the four material types. Not only are the log distributions more ‘normal’ (gaussian), but the standard deviations for the four groups are more nearly equal. The logarithms thus better satisfy the two basic assumptions of most analysis of variance calculations. I therefore conclude that they are the proper scaling for statistical analyses of the anion measurements.

The original BMDP output also had analysis of variance tables for the effect of Rock Type and Condition on each variable. They say that the difference between limestone and marble is significant for all anions. Condition appears to effect SO4 (logs thereof), Fluorine, and maybe NO3. There seems to be an interaction for Chlorine. However, I have not included these tables because they do not include the effects of exposure duration and layer measured, which are probably not balanced among the four groups.

Plots 1 to 4 show the effect of exposure duration. Points that do not overlap are labeled by a letter indicating the material type of the layer measurement plotted. Plots 5 to 8 do the same for layer, with A,B,C,U,V,W,X,Y,Z simply converted to 1 through 9. Both factors appear to affect all four anions.

Table 9 shows the results of analyses of covariance that examines the effect on anions of all four independent variables (simultaneously). It combines and mostly confirms the subanalyses that accompany the histograms and plots. Rock type, exposure duration (this time in years instead of days), and layers all affect each of the anions. Condition affects 504 and Fluorine. The only significant interaction is for SO4.

Technically speaking, the layer factor is and should be analyzed as a repeated measures factor within briquette rather than as an independent covariate. The layers are treated in groups as part of briquettes rather than independently, one by one. The degrees of freedom for the treatment effect error term should be about 600 instead of the 1971 that this analysis pretends. However, repeated measures analysis (at least as implemented by EMDP) requires complete repetition. So it can be used here only by selecting subsets of briquettes that are complete for a particular subset of layers. Fortunately, the results in Table 9 are clear enough that I would expect the general conclusions to be the same even if the study were designed differently (with the same layer set for all briquettes).

The similarity of results for the different anions suggests that they might be correlated. Table 10 shows that the correlations over the entire dataset range from .51 to .74. Plots 9 to 14 show the relationships of each pair in more detail. For instance, Plot 12 suggests that the correlation of NO3 and Chlorine is real even within the subgroups of limestone and marble layers, while Plots 13 and 14 suggest that Fluorine is not so much correlated with N03 and Chlorine for limestone while it is for marble.

Recommendations

The analyses reported above use all the anion data (or all except for some of the control blocks). Similar analyses should be done with the cation data, even though I suspect most will confirm null hypotheses of no effect. Additional analyses of the anion data should mostly focus on subsets of the data to answer specific questions. Although subject-matter specialists might think of more, the following list makes a start.

1. control blocks -- to characterize the material on entry to the study. I believe that this subset of the data could also be used to gain some indication of the consistency of replicate laboratory analyses.

2. briquettes with layer sets A, Z, AZ, or ABC, etcetera -- for repeated measures analyses of layer effects and for better characterization of the effects of other treatment factors. Though there are some obvious problems, it might be possible to fill in some missing layers by interpolation to expand the size of some subsets.

3. briquettes exposed for one quarter, with season added as a factor.

4. one year briquettes -- for year to year differences.

5. OS briquettes -- for differences between the dry and spray subareas.

6. layer and briquettes with cations measured -- for relationships between anions and cation.

Some additional analyses would require incorporating other data. These are more difficult and possibly not worth the effort. Possible sources and analyses include:

1. Environmental data to better relate site and exposure period to actual temperature and precipitation. Some of this might be extractable from the environmental and precipitation data.

2. The relation of slot to rack positions for possible position effects.

3. Information decoding ids which might help relate control blocks to exposed blocks or layers to analytical runs (depending on what the ids encode).

TABLES, HISTOGRAMS, PLOTS, AND ANALYSES OF COVARIANCE

Note: in tables 1 to 5 below, the numbers add to 611, the number of briquette (or CB) identifiers

1. Material Types

LF: 274	LW: 32
MF: 274	MW: 31

Table 2. Sites

CE: 12	NY: 172
DC: 172	OH: 75
NJ: 40	OS+: 30
NC: 90	OS-: 20

Table 3. Exposure Periods (47, counting NA for CBs)

1: 24	11: 4	Al: 24	Bl: 24	Q1: 18
2: 24	12: 6	A2: 16	B2: 6	Q2: 6
3: 24	13: 6	A3: 6	B3: 8	Q3: 12
4: 24	14: 6	A4: 32	B4: 6	Cl: 18
5: 2	15: 6	A5: 66	B5: 31	C2: 12
6: 2	16: 6	A6: 20	T1: 18	S1: 12
7: 2	17: 6	A7: 12	P2: 6	Hl: 12
8: 2	18: 6		P3: 12	O1: 12
9: 6	19: 6		T5: 12	N1: 12
10: 6	20: 6	NA: 12		Xl: 12

4. Expose Durations

yrs	N
0	12
.25	174
1	176
2	75
3	48
4	36
5	30
6	12
7	12
8	12
9	12
10	12

5.Layer Sets

Pattern	N
ABC :	85
ABC XYZ:	51
ABC Z:	18
AB YZ:	4
A CU X Z:	47
A UVWXYZ:	4
A U WXYZ:	1
A U X Z:	53
A U Z:	13
A XYZ:	45
A XZ:	101
A X :	1
A Z:	52
XYZ:	8

XZ: 55
Z: 61
<CB=none>: 12˘

Table 6. Exposure Sites, Periods, and Dates

St	EP	SY	SDy	Ey	EDy	N	St	EP	SY	SDy	Ey	EDy	N
CB	NA	NA	NA	NA	NA	12	NY	1	84	171	84	269	6
DC	1	84	224	84	320	6	NY	2	84	269	84	356	6
DC	2	84	320	85	45	6	NY	3	84	356	85	79	6
DC	3	85	45	85	133	6	NY	4	85	79	85	172	6
DC	4	85	133	85	224	6	NY	17	88	190	88	306	6
DC	13	87	231	87	318	6	NY	18	88	306	89	51	6
DC	14	87	318	88	48	6	NY	19	89	51	89	174	6
DC	15	88	48	88	160	6	NY	20	89	174	89	258	6
DC	16	88	180	88	258	6	NY	A1	84	171	85	172	6
DC	A1	84	224	85	224	6	NY	A2	85	172	86	177	4
DC	A2	85	224	86	226	4	NY	A4	87	176	88	190	6
DC	A4	87	223	88	258	6	NY	A5	88	162	89	202	6
DC	A5	88	160	89	222	6	NY	A5	88	190	89	202	6
DC	A5	88	258	89	222	6	NY	A6	89	202	90	193	6
DC	A6	89	222	90	243	6	NY	A7	90	269	91	206	6
DC	A7	90	243	91	346	6	NY	B1	84	171	86	177	6
DC	B1	84	224	86	226	6	NY	B5	88	162	95	13	6
DC	B5	88	160	95	73	6	NY	T1	84	171	87	176	6
DC	T1	84	224	87	223	6	NY	T3	87	176	90	193	6
DC	T3	87	223	90	243	6	NY	T5	90	269	93	221	6
DC	T5	90	243	93	244	6	NY	Q1	84	171	88	190	6
DC	Q1	84	224	88	258	6	NY	Q3	88	190	92	181	6
DC	Q3	88	258	92	246	6	NY	C1	84	171	89	202	6
DC	C1	84	224	89	222	6	NY	C2	89	202	95	13	6
DC	C2	89	222	95	73	6	NY	S1	84	171	90	193	6
DC	S1	84	224	90	243	6	NY	H1	84	171	91	206	5
DC	H1	84	224	91	346	6	NY	O1	84	171	92	181	6
DC	O1	84	224	92	246	6	NY	N1	84	171	93	221	6
DC	N1	84	224	93	244	6	NY	X1	84	171	95	13	6
DC	X1	84	224	95	73	6	OH	9	86	198	86	293	6
NC	1	84	146	84	237	6	OH	10	86	293	87	33	6
NC	2	84	237	84	331	6	OH	11	87	33	87	111	4
NC	3	84	331	85	60	6	OH	12	87	111	87	209	6
NC	4	85	60	85	136	6	OH	A3	86	198	87	209	6
NC	5	85	136	85	240	2	OH	A4	87	209	88	223	6
NC	6	85	240	85	331	2	OH	A5	88	152	90	9	6
NC	7	85	331	86	62	2	OH	A5	88	223	90	9	6
NC	8	86	62	86	155	2	OH	B2	86	198	88	223	6
NC	A1	84	146	85	136	6	OH	B4	88	223	90	283	6
NC	A2	85	136	86	155	4	OH	B5	88	152	95	32	5
NC	A4	87	160	88	188	6	OH	T2	86	198	90	9	6
NC	A5	88	161	89	143	12	OH	Q2	86	198	90	283	6
NC	A5	88	188	89	143	6	OS+	A4	87	209	88	223	4
NC	B1	84	146	86	155	6	OS+	A5	88	152	90	9	4
NC	T1	84	146	87	160	6	OS+	A5	88	223	90	9	4
NC	Q1	84	146	88	188	6	OS+	A6	90	9	93	152	4
NC	C1	84	146	89	143	6	OS+	B3	87	209	90	9	4
NJ	1	84	157	84	251	6	OS+	B5	88	152	93	152	6
NJ	2	84	251	84	349	6	OS+	B5	90	9	93	152	4
NJ	3	84	349	85	65	6	OS-	A4	87	209	88	223	4
NJ	4	85	65	85	158	6	OS-	A5	88	223	90	9	4
NJ	A1	84	157	85	158	6	OS-	A6	90	9	93	152	4
NJ	A2	85	158	86	169	4	OS-	B3	87	209	90	9	4
NJ	B1	84	157	86	169	6	OS-	B5	90	9	93	152	4

˘Table 7. Thresholds and Low Anion Values

SO4	N	NO3	N	Cl	N	Fl	N

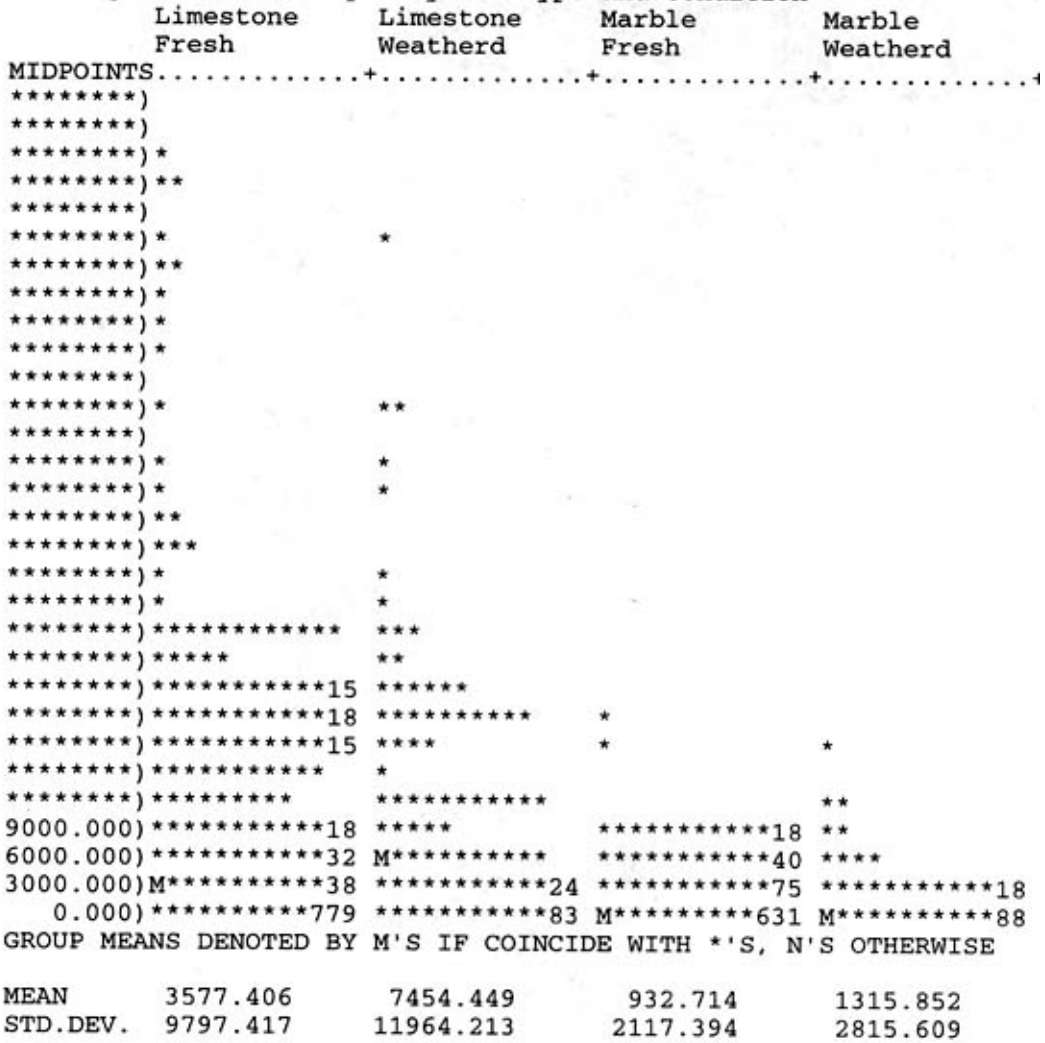
8	4	8	15	3	20	2	140
9	9	9	34	4	2	3	2
10	31	10	128	5	47	5	202
15	73	12	5	7	1	7	93
16	24	15	290	8	82	8	210
20	48	17	68	10	81	9	17
		20	81	15	2	10	305
all	189	all	621	all	235	all	969
	9%		31%		12%		48%

Table 8. Summary of Anion Values and Logarithms

Variable	Mean	StdDev	Low	Z	High	Z
SO4	2765.9	7974.5	4.0	-0.35	82300	9.97
NO3	46.3	84.9	4.0	-0.50	960	10.76
Chlorine	23.2	24.9	1.5	-0.87	202	7.17
Fluorine	11.0	15.7	1.0	-0.63	128	7.44
logSO4	2.4	1.0	0.60	-1.77	4.9	2.60
logNO3	1.3	0.5	0.60	-1.56	3.0	3.40
logChlor	1.2	0.4	0.18	-2.52	2.3	2.79
logFluor	0.8	0.4	0.00	-1.83	2.1	3.04

Z is number of standard deviations from mean

ˇHistogram 1. SO Grouped by RockType and Condition



GROUP MEANS DENOTED BY M'S IF COINCIDE WITH *'S, N'S OTHERWISE

MEAN	3577.406	7454.449	932.714	1315.852
STD.DEV.	9797.417	11964.213	2117.394	2815.609

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S. E. M.    314.414        925.819         76.505        262.557
MAXIMUM   82300.000      70700.000      19600.000      18700.000
MINIMUM      29.000         33.000          4.000          8.000
CASES INCL.    971            167            766            115
^Histogram 2. NO3 Grouped by RockType and Condition
          Limestone      Limestone      Marble         Marble
          Fresh          Weatherd       Fresh          Weatherd
MIDPOINTS.............+.............+.............+.............+
1015.000)
 980.000)
 945.000)*
 910.000)
 875.000)*
 840.000)*
 805.000)*
 770.000)**
 735.000)
 700.000)*
 665.000)**
 630.000)****
 595.000)****
 560.000)**
 525.000)*
 490.000)*
 455.000)
 420.000)*
 385.000)**
 350.000)*****          *
 315.000)*****
 280.000)*********
 245.000)***********18
 210.000)***********21 *              ***
 175.000)***********14 *              ***********
 140.000)***********39 ****           ***********19 *
 105.000)***********55 ************** ***********29 *******
  70.000)M**********73 ***********16  ***********44 ********
  35.000)**********282 M**********73  M*********290 M**********61
   0.000)**********426 ***********58  **********370 ***********38
GROUP MEANS DENOTED BY M'S IF COINCIDE WITH *'S, N'S OTHERWISE

MEAN         62.182         39.260         30.049         30.326
STD.DEV.    114.350         43.178         35.838         26.924
S. E. M.      3.670          3.341          1.295          2.511
MAXIMUM     960.000        355.000        220.000        149.000
MINIMUM       4.000          4.000          4.000          8.000
CASES INCL.     971            167            766            115
^Histogram 3. Chlorine Grouped by RockType and Condition
          Limestone      Limestone      Marble         Marble
          Fresh          Weatherd       Fresh          Weatherd
MIDPOINTS.............+.............+.............+.............+
 203.000)*
 196.000)
 189.000)***
 182.000)***
 175.000)**
 168.000)*
 161.000)***
 154.000)*
 147.000)****
 140.000)****
 133.000)*****
```

```
 126.000)****
 119.000)*******
 112.000)******
 105.000)*********                                *
  98.000)****
  91.000)*********
  84.000)***                        *
  77.000)***********15              **
  70.000)***********  *             *
  63.000)***********27 *            **
  56.000)***********15 *****        *              **
  49.000)***********34 ******       *****
  42.000)***********47 *********    *******        *
  35.000)M**********60 ***********24 ********      **
  28.000)**********168 M**********48 ***********25 ******
  21.000)**********335 ***********43 ***********52 *********
  14.000)**********148 ***********21 **********148 M**********22
   7.000)***********41 ********     M*********404 ***********72
   0.000)                           **********110
GROUP MEANS DENOTED BY M'S IF COINCIDE WITH *'S, N'S OTHERWISE

MEAN         33.988         27.293         10.283         11.991
STD.DEV.     30.085         11.410          9.960         13.227
S. E. M.      0.965          0.883          0.360          1.233
MAXIMUM     202.000         73.000         85.000        103.000
MINIMUM       5.000          4.000          1.500          4.000
CASES INCL.     971            167            766            115
ˇHistogram 4. Fluorine Grouped by RockType and Condition
          Limestone      Limestone      Marble         Marble
          Fresh          Weatherd       Fresh          Weatherd
MIDPOINTS.............+.............+.............+.............+
 145.000)
 140.000)
 135.000)
 130.000)*
 125.000)
 120.000)                           *
 115.000)                           *              *
 110.000)                           **
 105.000)               *           **
 100.000)               *           ***            *
  95.000)                           *
  90.000)               *           **
  85.000)               *           *******
  80.000)               *           *              *
  75.000)                                          *
  70.000)               **          ****           *
  65.000)*                          **
  60.000)*              ****        ****           *
  55.000)*              ***         **********
  50.000)*****          ******      ********       **
  45.000)*******        **********15 ********
  40.000)*****          *********   *****          **
  35.000)*********      *****       ****           *
  30.000)***********16  ********    ******         *
  25.000)***********19  M*********  ***********15  **
  20.000)***********62  ********    ***********14  *
  15.000)**********108  ***********20 ***********14 ******
  10.000)M*********208  **********  M**********26  M***********
   5.000)**********494  ***********62 **********285 ***********74
   0.000)***********34              **********341 ********
```

GROUP MEANS DENOTED BY M'S IF COINCIDE WITH *'S, N'S OTHERWISE

MEAN	9.845	22.934	9.613	12.117
STD.DEV.	9.219	21.397	18.776	19.724
S. E. M.	0.296	1.656	0.678	1.839
MAXIMUM	128.000	103.000	120.000	115.000
MINIMUM	2.500	3.500	1.000	2.500
CASES INCL.	971	167	766	115

˘Histogram 5. logSO4 Grouped by RockType and Condition

MIDPOINTS	Limestone Fresh	Limestone Weatherd	Marble Fresh	Marble Weatherd
4.950)	***			
4.800)	*******	**		
4.650)	*******	***		
4.500)	**********18	******		
4.350)	**********37	**********17	*	
4.200)	**********23	*****	*	**
4.050)	**********15	**********14	*****	*
3.900)	**********25	***	**********22	***
3.750)	**********18	**********	**********25	***
3.600)	********	******	**********20	*******
3.450)	**********16	*********	**********28	***
3.300)	**********	******	**********20	******
3.150)	**********22	M****	**********26	****
3.000)	**********31	*********	**********21	**
2.850)	**********39	***	**********19	***
2.700)	**********53	*****	**********17	*
2.550)	M**********57	****	**********19	*******
2.400)	**********61	**********	**********29	********
2.250)	**********71	**	**********21	M********
2.100)	**********85	**********	**********	******
1.950)	**********173	**********16	M**********33	******
1.800)	**********139	******	**********26	*
1.650)	**********47	*********	**********53	**********
1.500)	****	*****	**********74	********
1.350)			**********59	****
1.200)			**********33	*
1.050)			**********67	*******
0.900)			**********90	**********
0.750)			**********31	
0.600)			**********	

GROUP MEANS DENOTED BY M'S IF COINCIDE WITH *'S, N'S OTHERWISE

MEAN	2.560	3.101	1.938	2.255
STD.DEV.	0.843	0.985	0.987	0.948
S. E. M.	0.027	0.076	0.036	0.088
MAXIMUM	4.915	4.849	4.292	4.272
MINIMUM	1.462	1.519	0.602	0.903
CASES INCL.	971	167	766	115

˘Histogram 6. logNO3 Grouped by RockType and Condition

MIDPOINTS	Limestone Fresh	Limestone Weatherd	Marble Fresh	Marble Weatherd
3.300)				
3.200)				
3.100)				
3.000)	*			
2.900)	*****			
2.800)	**********			
2.700)	****			

```
   2.600)*****          *
   2.500)************
   2.400)***********25
   2.300)***********20 **             ********
   2.200)***********29 *              ************ *
   2.100)***********34 ******         ***********20 **
   2.000)***********43 ********       ***********20 ***
   1.900)***********30 *******        ************ *****
   1.800)***********35 ******         ***********26 ****
   1.700)***********35 ***********15 ***********39 ****
   1.600)***********45 ***********17 ***********41 ********
   1.500)***********60 ************ ***********68 ********
   1.400)M**********67 M**********14 ***********69 M**********19
   1.300)***********84 ***********19 M**********79 ***********23
   1.200)***********43 ******         ***********44 **
   1.100)***********46 ******         ***********23 *********
   1.000)***********57 ***********37 ***********42 ***********24
   0.900)**********186 *******        **********172 ***
   0.800)******                       **
   0.700)***********85                ***********77
   0.600)***           **             **********
   0.500)
   0.400)
GROUP MEANS DENOTED BY M'S IF COINCIDE WITH *'S, N'S OTHERWISE

MEAN          1.404          1.418          1.261          1.361
STD.DEV.      0.543          0.381          0.418          0.308
S. E. M.      0.017          0.029          0.015          0.029
MAXIMUM       2.982          2.550          2.342          2.173
MINIMUM       0.602          0.602          0.602          0.903
CASES INCL.     971            167            766            115
ˇHistogram 7. logChlorine Grouped  by RockType and Condition
          Limestone      Limestone      Marble         Marble
          Fresh          Weatherd       Fresh          Weatherd
MIDPOINTS.............+.............+.............+.............+
   2.400)
   2.320)**
   2.240)**********
   2.160)*************
   2.080)***********19
   2.000)***********14                                *
   1.920)***********19                ***
   1.840)***********28 *              **
   1.760)***********33 ******         **             **
   1.680)***********48 ********       *******
   1.600)***********40 ***********    ******         *
   1.520)***********60 ***********25  *********      ***
   1.440)M*********111 ***********35  ***********16 **
   1.360)**********179 M**********46  ***********24 *********
   1.280)**********206 ******         ***********35 ***
   1.200)**********112 *****          ***********63 *********
   1.120)***********26 ****           ***********37 ***********
   1.040)**********    ************   ***********48 **
   0.960)***********36 ****           **********102 M*********
   0.880)              ***            M**********38 ******
   0.800)                             ***********22
   0.720)*****                        **********140 ***********16
   0.640)              *              **********102 ***********40
   0.560)                             *
   0.480)                             ***********36
   0.400)                             ***********47
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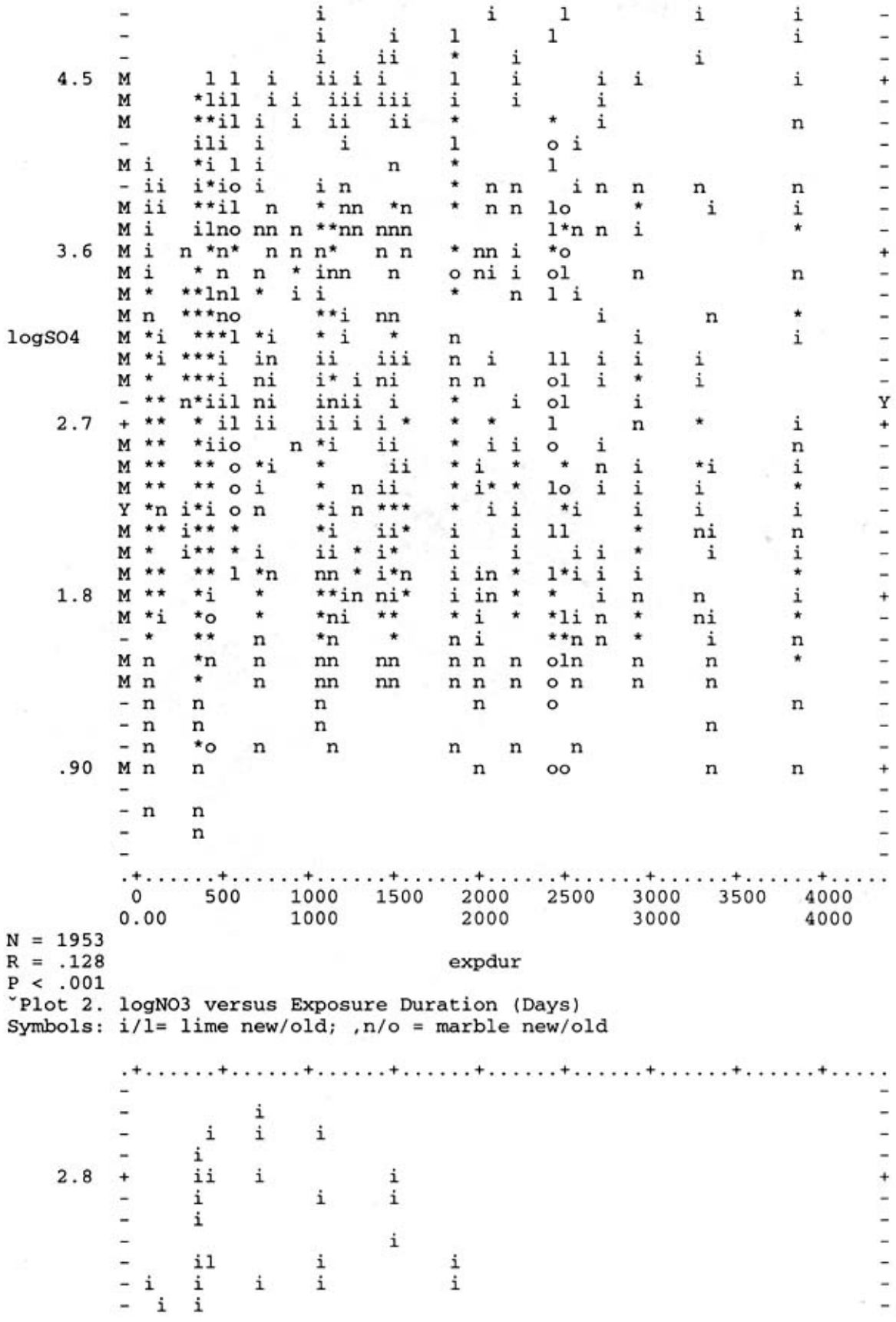
   0.320)                              ******
   0.240)
   0.160)                              ***********20
   0.080)
GROUP MEANS DENOTED BY M'S IF COINCIDE WITH *'S, N'S OTHERWISE

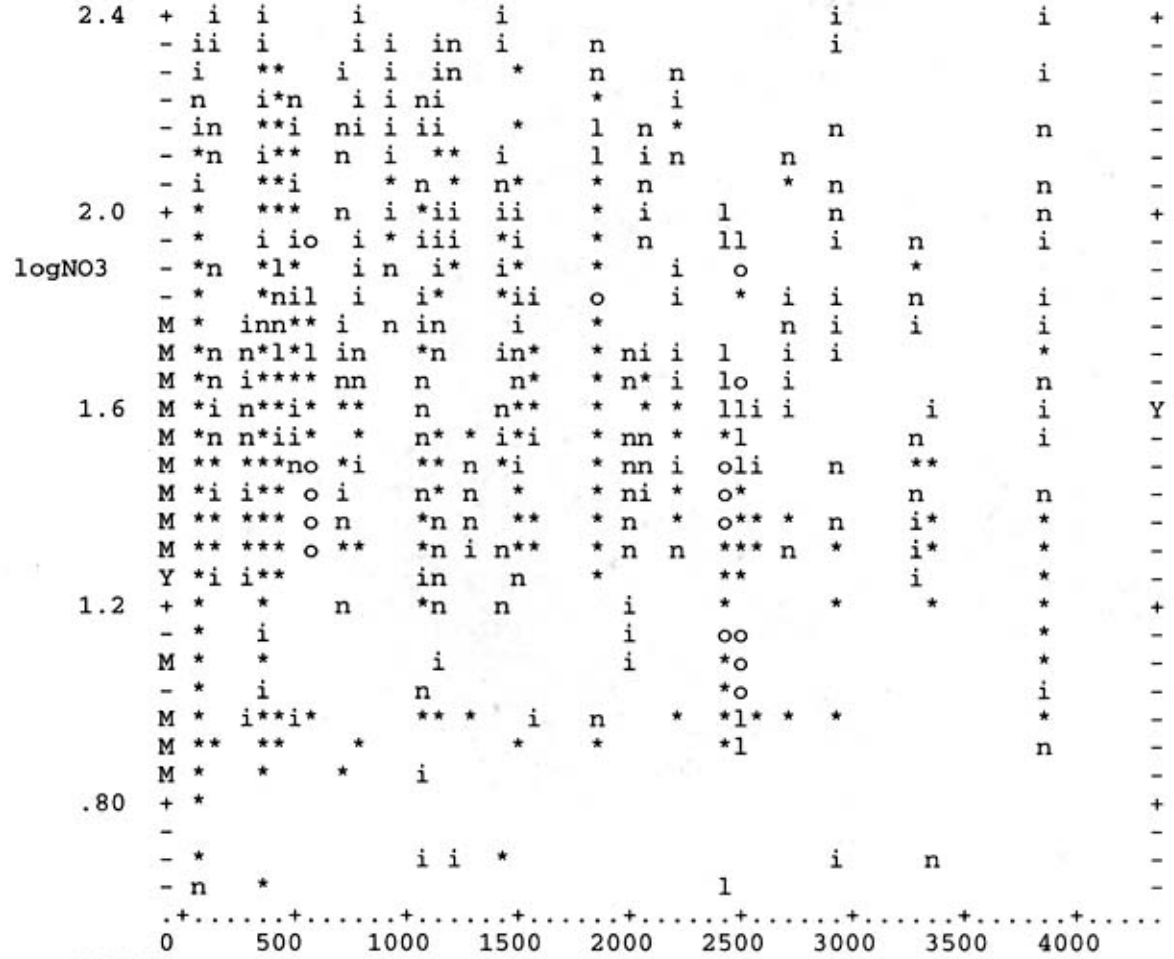
MEAN          1.431          1.395          0.874          0.928
STD.DEV.      0.268          0.198          0.338          0.337
S. E. M.      0.009          0.015          0.012          0.031
MAXIMUM       2.305          1.863          1.929          2.013
MINIMUM       0.699          0.602          0.176          0.602
CASES INCL.     971            167            766            115
ˇHistogram 8. logFluorine Grouped  by RockType and Condition
          Limestone      Limestone      Marble         Marble
          Fresh          Weatherd       Fresh          Weatherd
MIDPOINTS.............+.............+.............+.............+
   2.320)
   2.240)
   2.160)
   2.080)*                            ****           *
   2.000)              **             *******        *
   1.920)              ***            *********      **
   1.840)*             **             ******         *
   1.760)**            *******        ***********14  *
   1.680)*********     ***********20  ***********16  **
   1.600)********      **********     *****          ***
   1.520)************* *********     *****
   1.440)***********20 ********       *********      ***
   1.360)***********29 **********     ***********17  *
   1.280)***********44 ****           ********
   1.200)***********63 ************   ******         ***
   1.120)***********45 M*******       ********       ***
   1.040)***********24 ***            *****          *********
   0.960)**********147 **             ***********17  ***
   0.880)M**********59 ******         *****
   0.800)***********42                ********       M
   0.720)**********233 ***********31  **********121  ***********26
   0.640)**********150 ***********26  M**********92  ***********44
   0.560)***********45 ****           ***********41  ***
   0.480)**                           ***********22
   0.400)***********34                **********160  ********
   0.320)                             ***********34
   0.240)
   0.160)                             **
   0.080)
   0.000)                             **********145
GROUP MEANS DENOTED BY M'S IF COINCIDE WITH *'S, N'S OTHERWISE

MEAN          0.879          1.153          0.601          0.828
STD.DEV.      0.293          0.445          0.494          0.392
S. E. M.      0.009          0.034          0.018          0.037
MAXIMUM       2.107          2.013          2.079          2.061
MINIMUM       0.398          0.544          0.000          0.398
CASES INCL.     971            167            766            115
ˇPlot 1. logSO4 versus Exposure Duration (Days)
Symbols: i/l= lime new/old; ,n/o = marble new/old

         .+......+......+......+......+......+......+......+......+.....
         -                                                              -
         -                                                              -
         -                              i               i               -
```

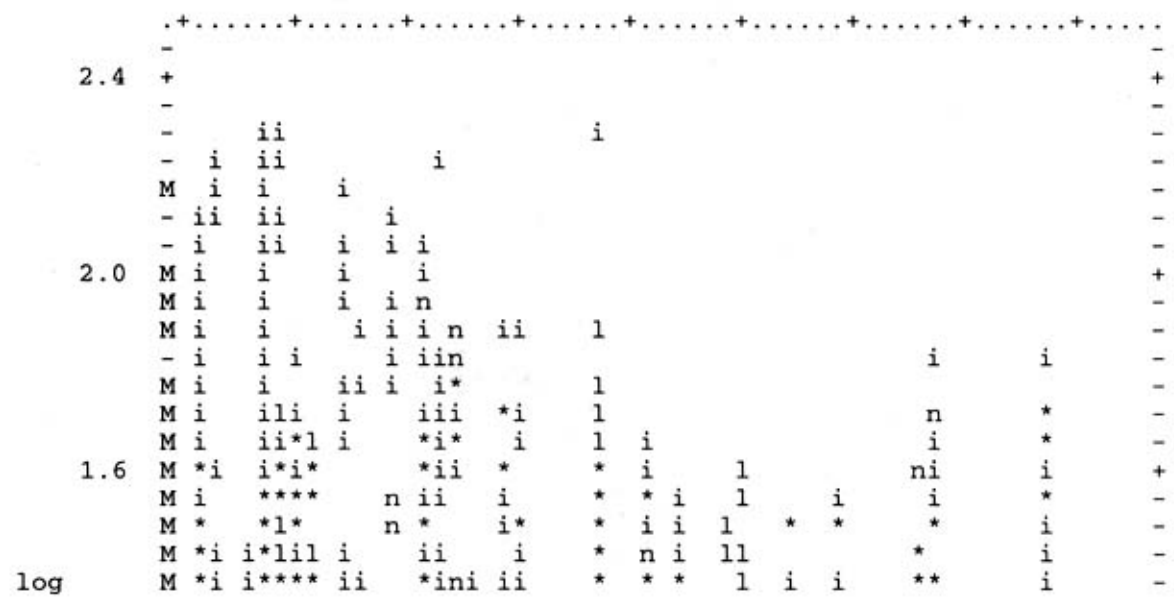


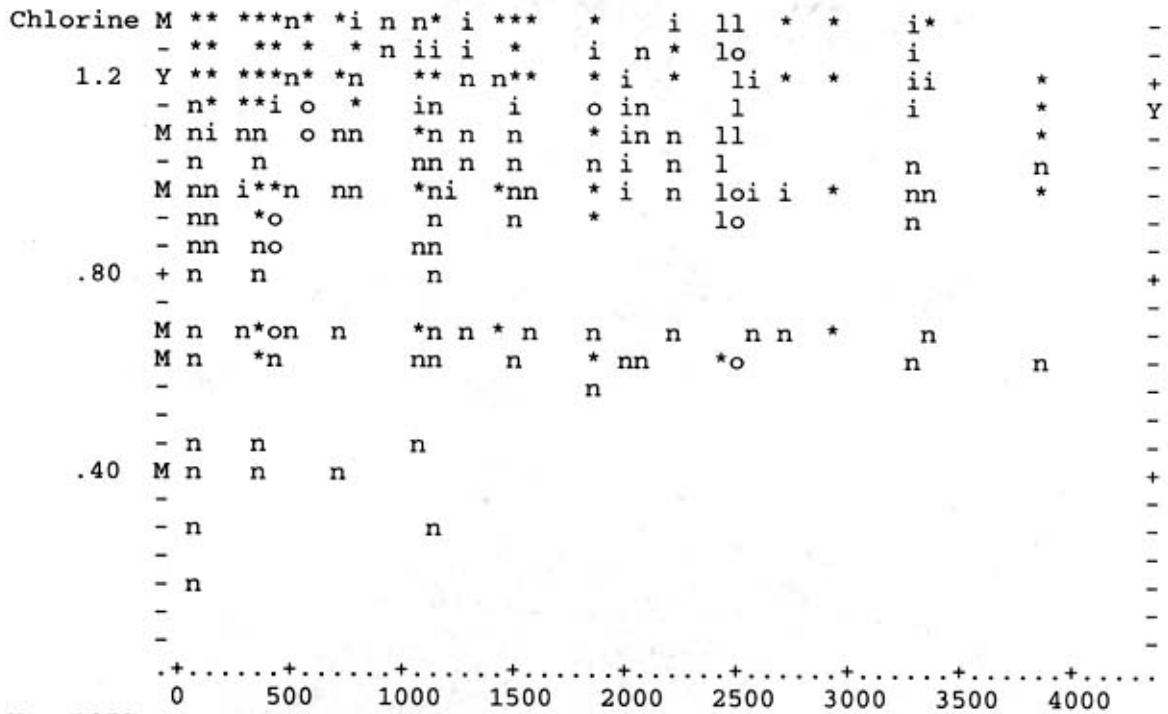
ˇPlot 2. logNO3 versus Exposure Duration (Days)
Symbols: i/l= lime new/old; ,n/o = marble new/old



N = 1953
R = .152
P < .001

ˇPlot 3. logChlorine versus Exposure Duration (Days)
Symbols: i/l= lime new/old; ,n/o = marble new/old

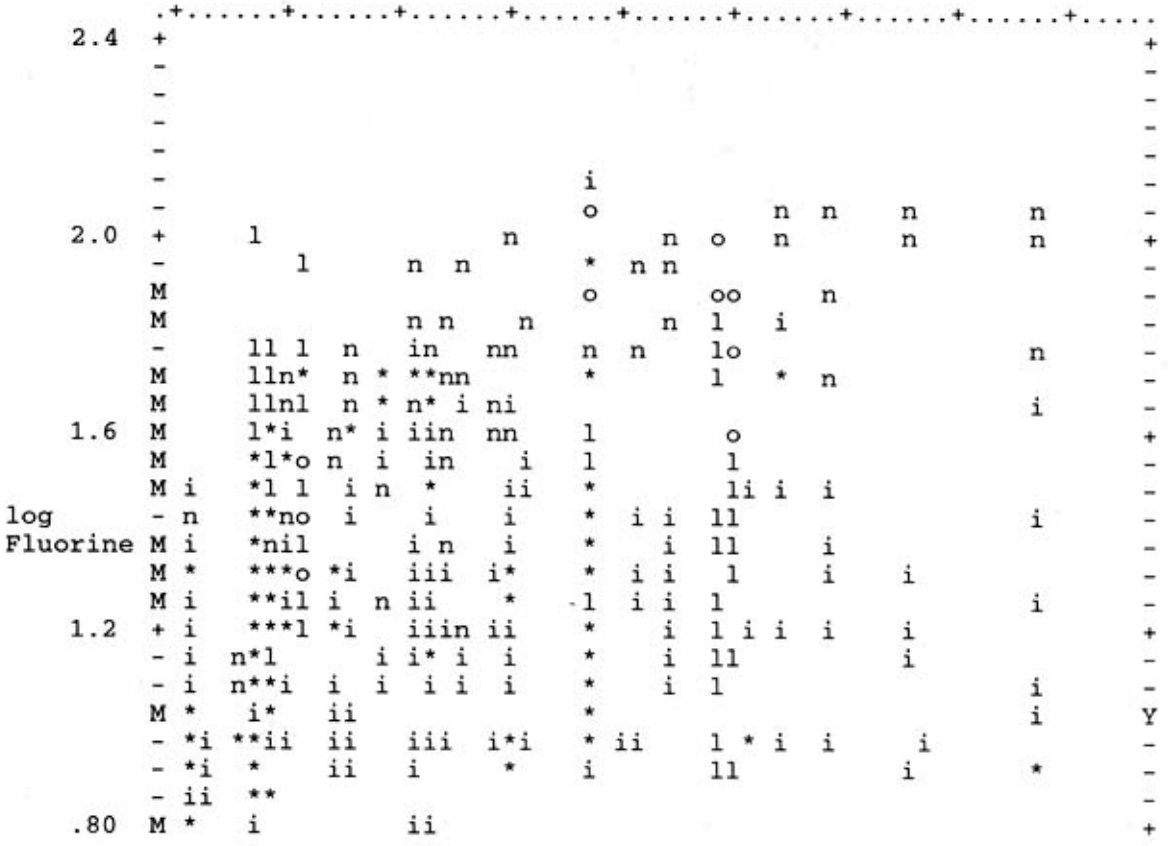


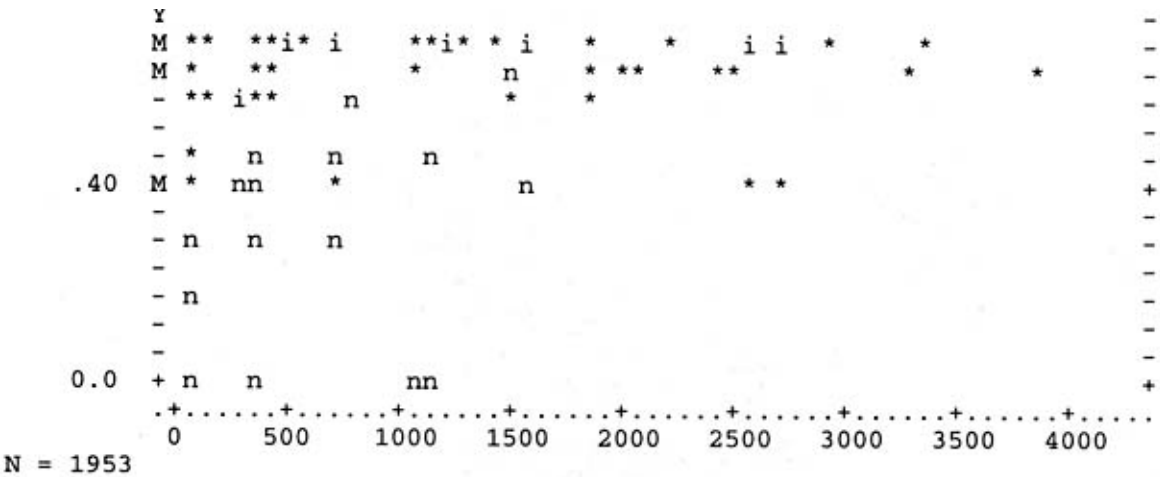


N = 1953
R =-.048
P = .035

expdur

˘Plot 4. logFluorine versus Exposure Duration (Days)
Symbols: i/l= lime new/old; ,n/o = marble new/old

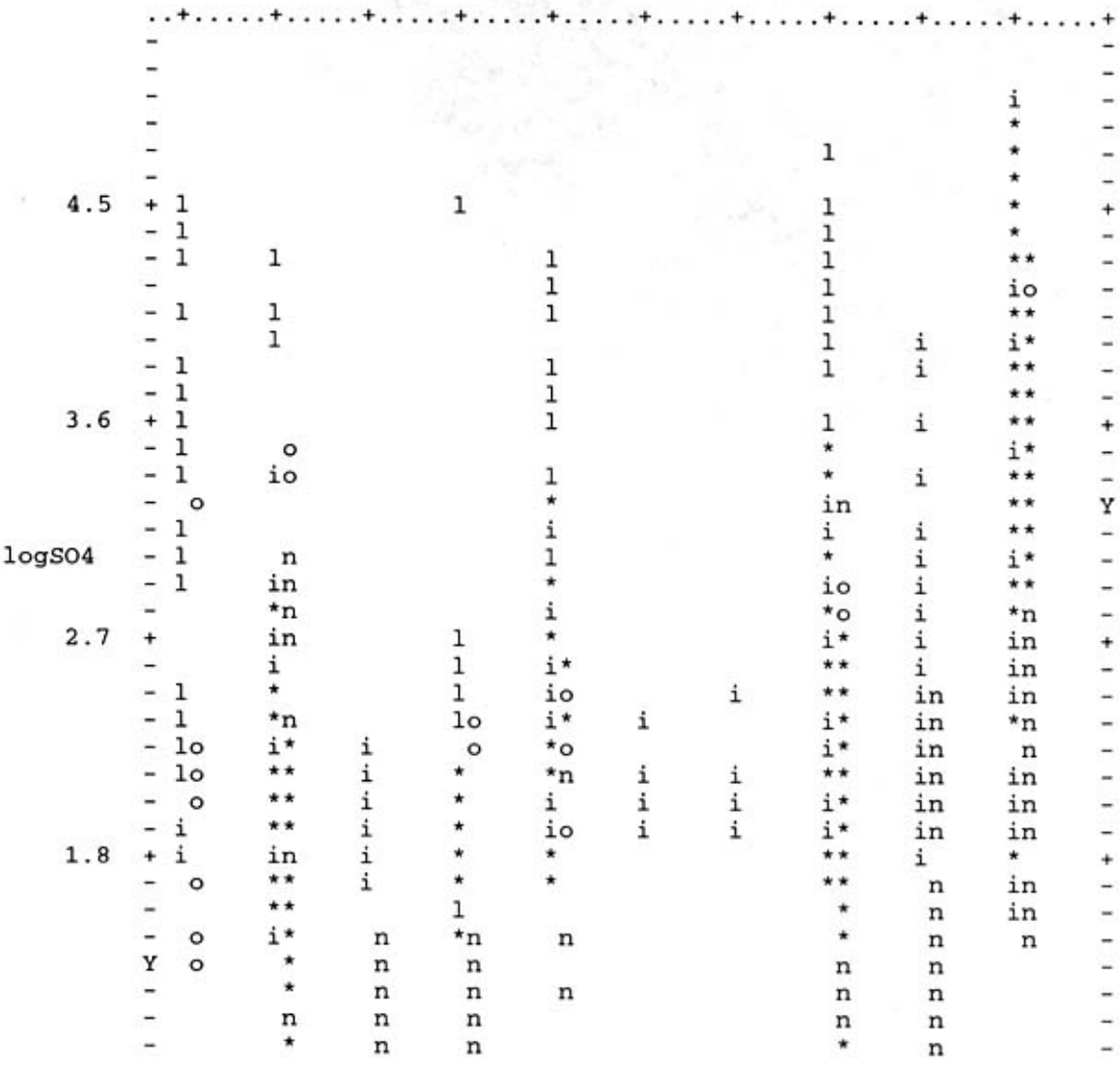


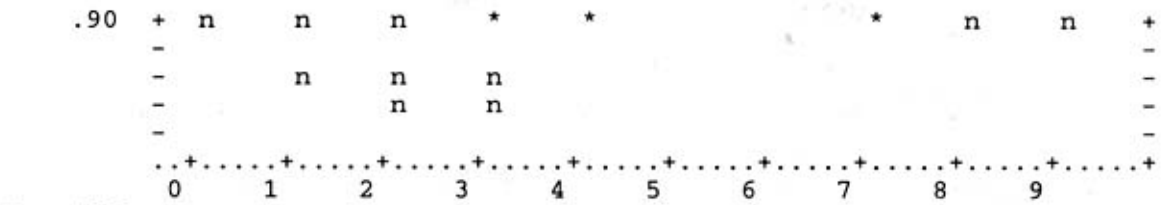


N = 1953
R = .176
P < .001

expdur

ˇPlot 5. logSO4 versus Layer (ABCUVWXYZ = 123456789)
Symbols: i/l= lime new/old; ,n/o = marble new/old

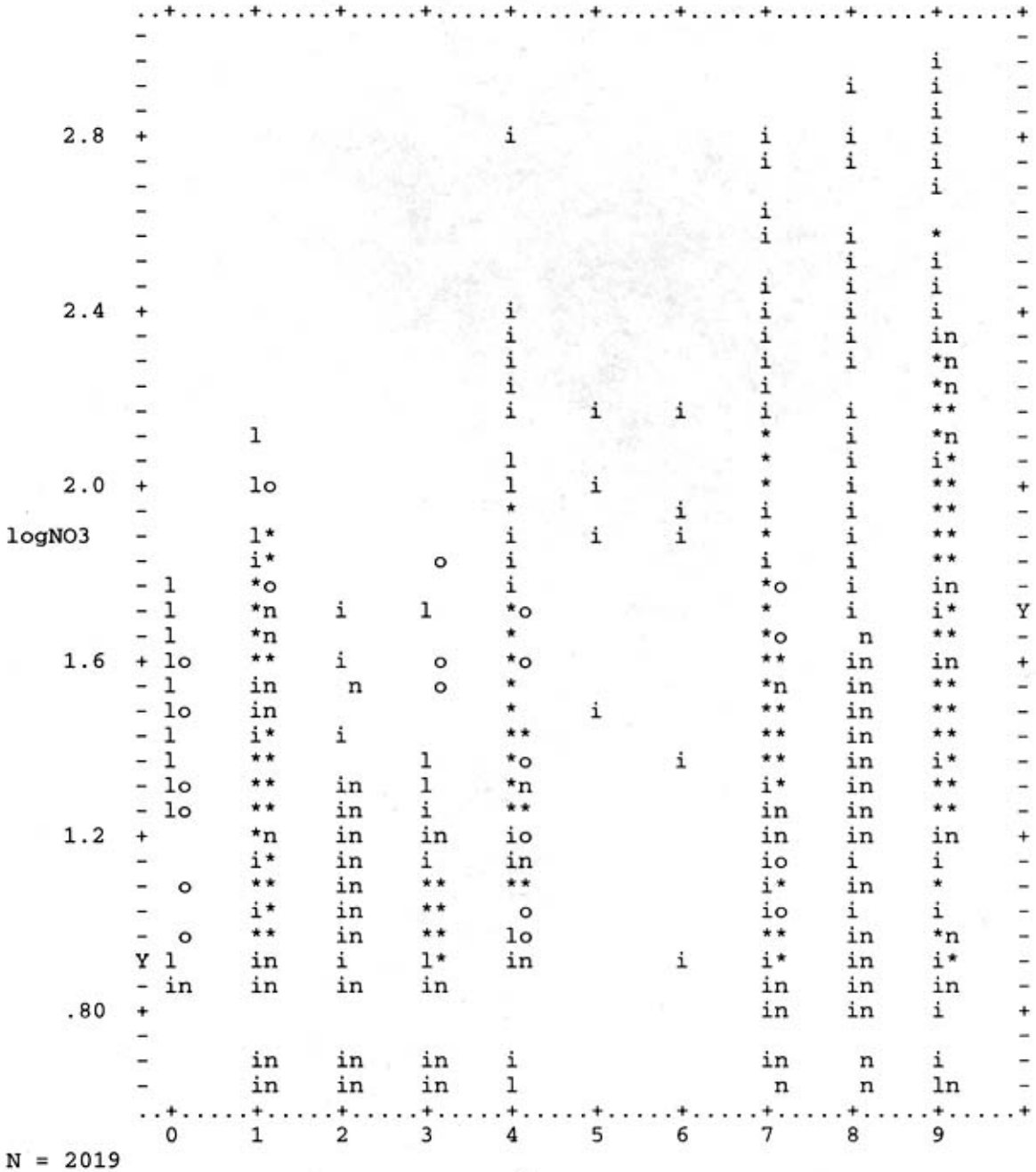




N = 2019
R = .609
P < .001

layer

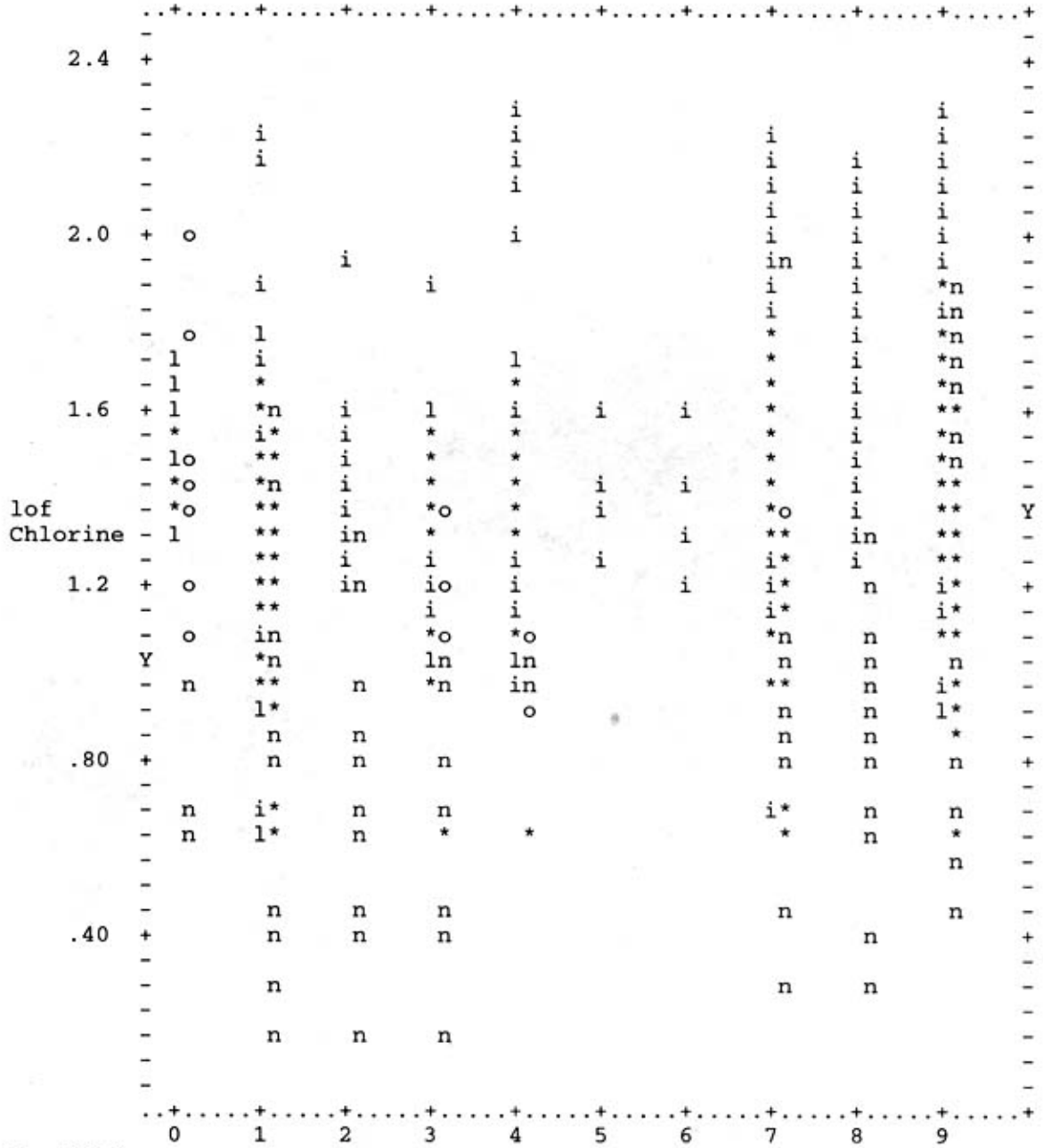
ˇPlot 6. logNO3 versus Layer (ABCUVWXYZ = 123456789)
Symbols: i/l= lime new/old; ,n/o = marble new/old



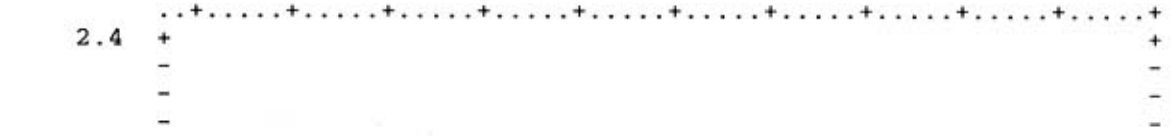
N = 2019
R = .531

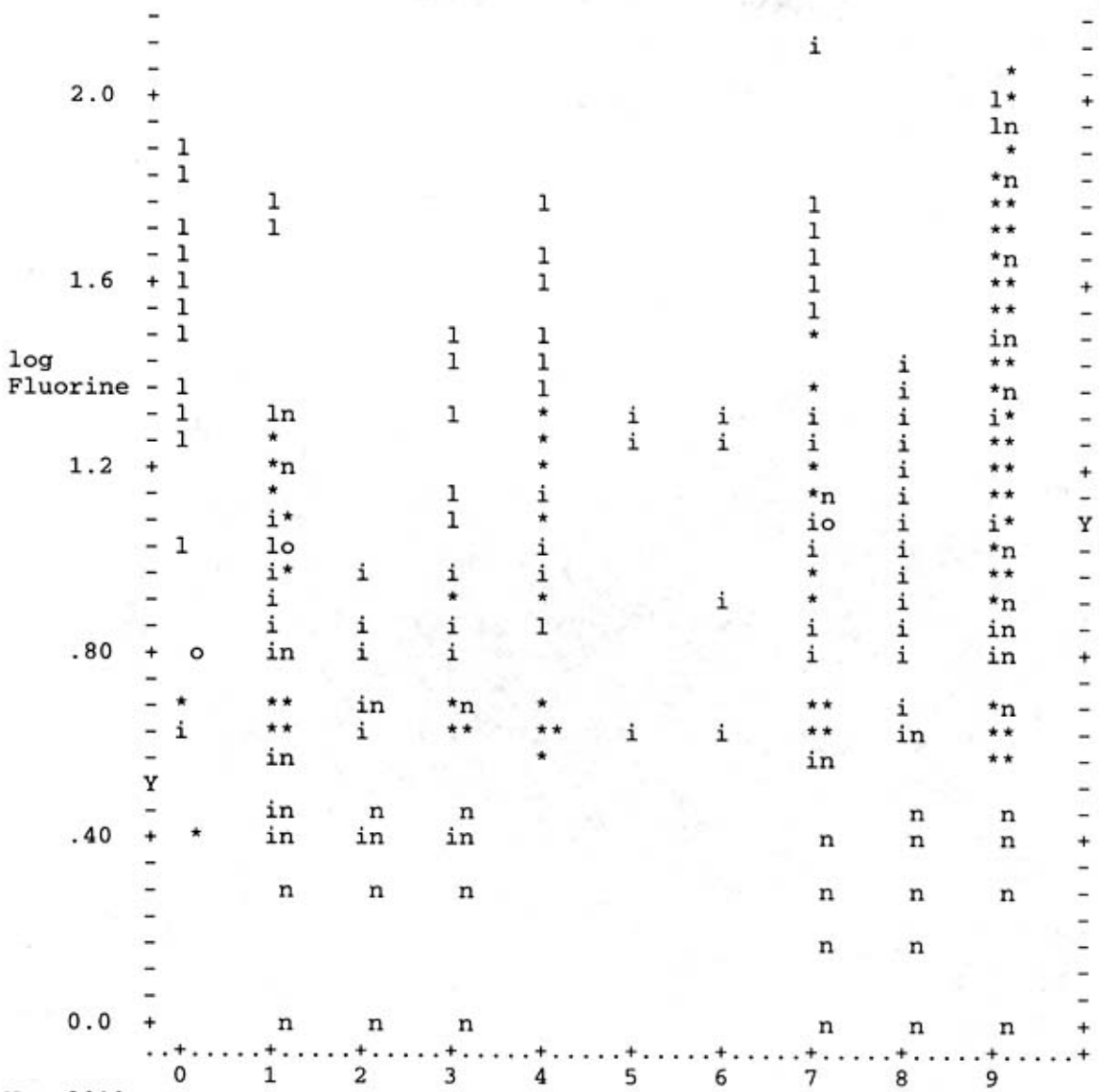
layer

P < .001
ˇPlot 7. logChloine versus Layer (ABCUVWXYZ = 123456789)
Symbols: i/l= lime new/old; ,n/o = marble new/old



N = 2019
R = .259
P < .001
ˇPlot 8. logFluorine versus Layer (ABCUVWXYZ = 123456789)
Symbols: i/l= lime new/old; ,n/o = marble new/old





N = 2019
R = .425
P < .001

˘Table 9. Analysis of Covariance for Anions

SOURCE	SUM SQUARES	DF	MEAN SQUARE	F	TAIL PROB	REGR COEF
log SO4						
rocktype	109.83454	1	109.83454	255.22	0.0000	
conditon	31.23378	1	31.23378	72.58	0.0000	
rc	4.44823	1	4.44823	10.34	0.0013	
expdur	14.36969	1	14.36969	33.39	0.0000	0.0309
layer	797.21355	1	797.21355	1852.47	0.0000	0.1960
ALL COVARIATES	827.07645	2	413.53822	960.93	0.0000	
ERROR	848.22279	1971	0.43035			
log NO3						
rocktype	2.66771	1	2.66771	17.04	0.0000	
conditon	0.42649	1	0.42649	2.72	0.0990	

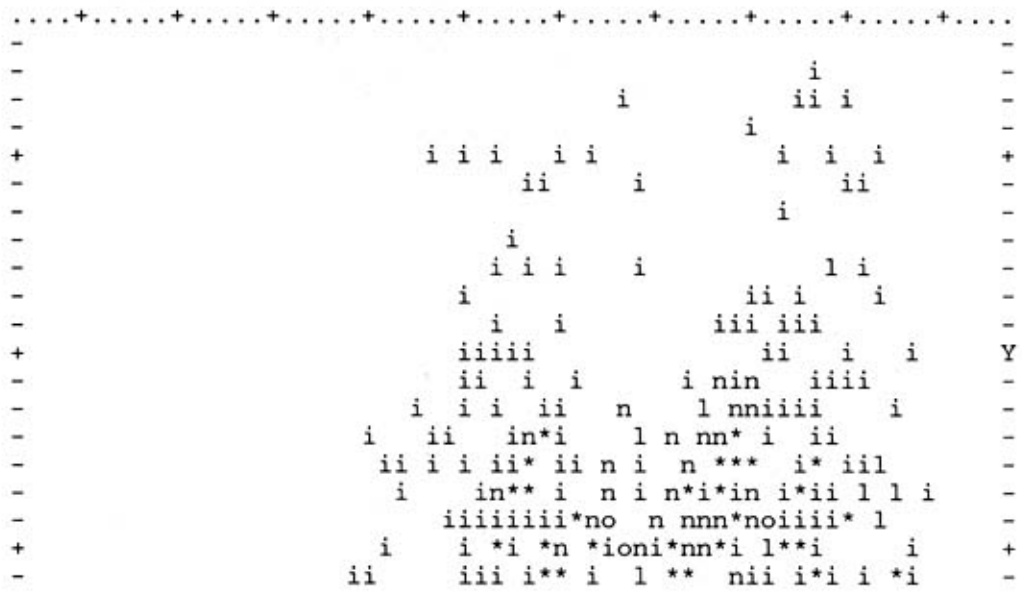
rc	0.03751	1	0.03751	0.24	0.6246
expdur	7.42606	1	7.42606	47.42	0.0000
0.0222					
layer	130.99377	1	130.99377	836.51	0.0000
0.0795					
ALL COVARIATES	142.59257	2	71.29629	455.29	0.0000
ERROR	308.64812	1971	0.15659		
log Chlorine					
rocktype	58.04502	1	58.04502	795.50	0.0000
conditon	0.05250	1	0.05250	0.72	0.3964
rc	0.12372	1	0.12372	1.70	0.1930
expdur	0.81101	1	0.81101	11.11	0.0009 -
0.0073					
layer	27.89851	1	27.89851	382.35	0.0000
0.0367					
ALL COVARIATES	28.24686	2	14.12343	193.56	0.0000
ERROR	143.81678	1971	0.07297		
log Fluorine					
rocktype	18.43261	1	18.43261	157.24	0.0000
conditon	12.85531	1	12.85531	109.67	0.0000
rc	0.20248	1	0.20248	1.73	0.1889
expdur	6.52570	1	6.52570	55.67	0.0000
0.0208					
layer	72.41672	1	72.41672	617.77	0.0000
0.0591					
ALL COVARIATES	81.78964	2	40.89482	348.86	0.0000
ERROR	231.04613	1971	0.11722		

Table 10. Correlations of Log Anions

	logSO4	logNO3	logChlor
logNO3	.71		
logChlor	.61	.60	
logFluor	.74	.55	.52

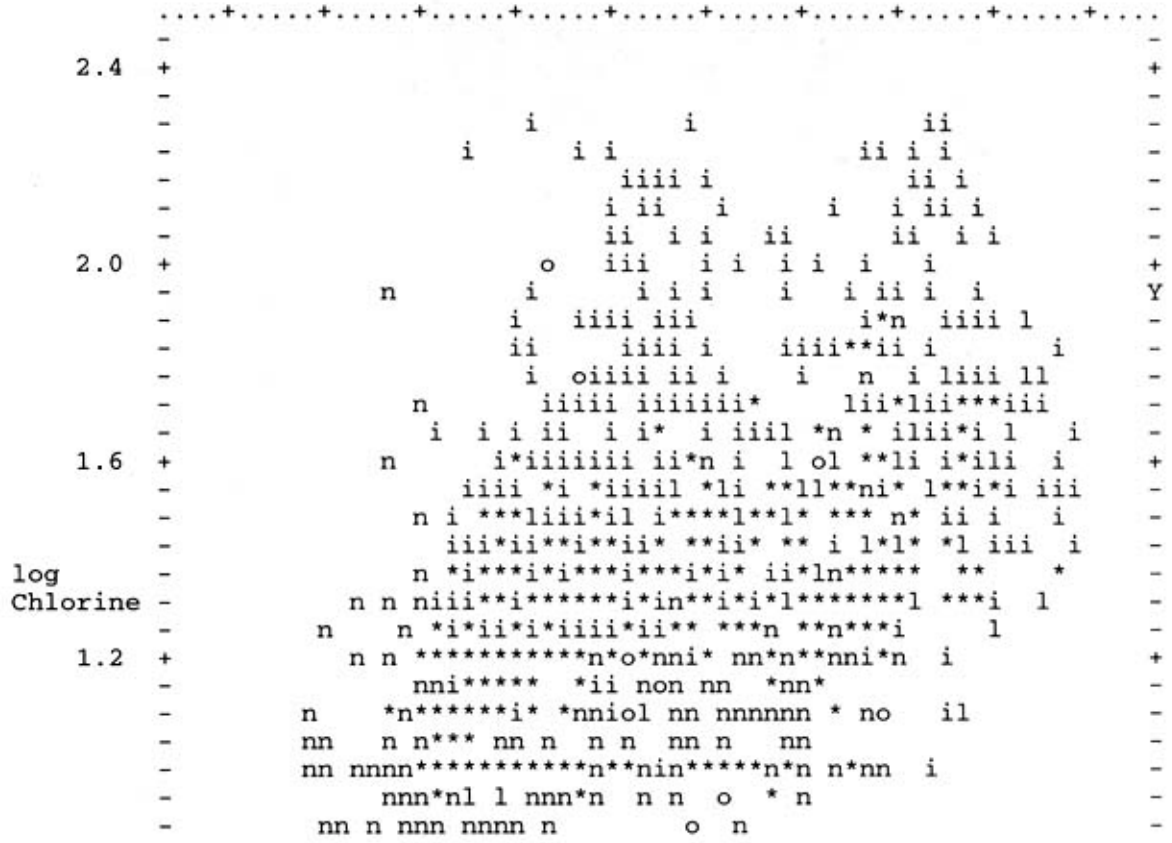
ˇPlot 9. logNO3 versus logSO$

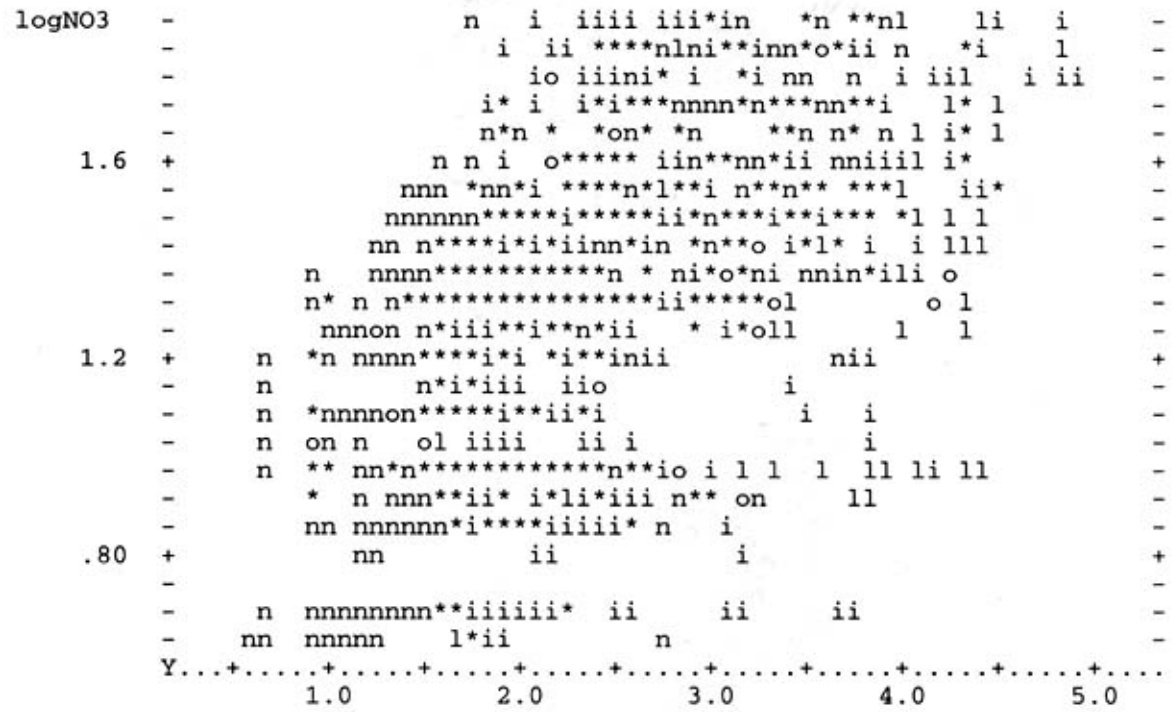
Symbols: i/1= lime new/old; ,n/o = marble new/old



N = 2019
R = .708
P < .001

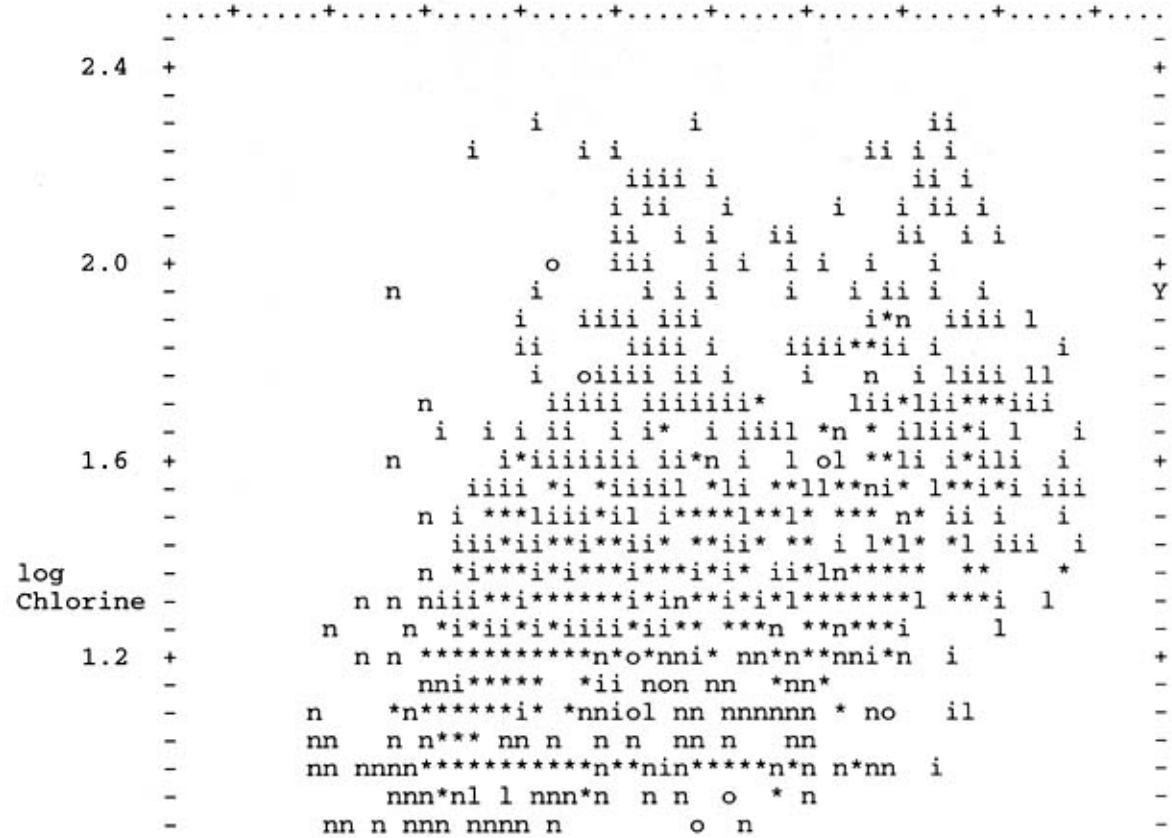
ˇPlot 10. logChlorine versus logSO4
Symbols: i/l= lime new/old; ,n/o = marble new/old

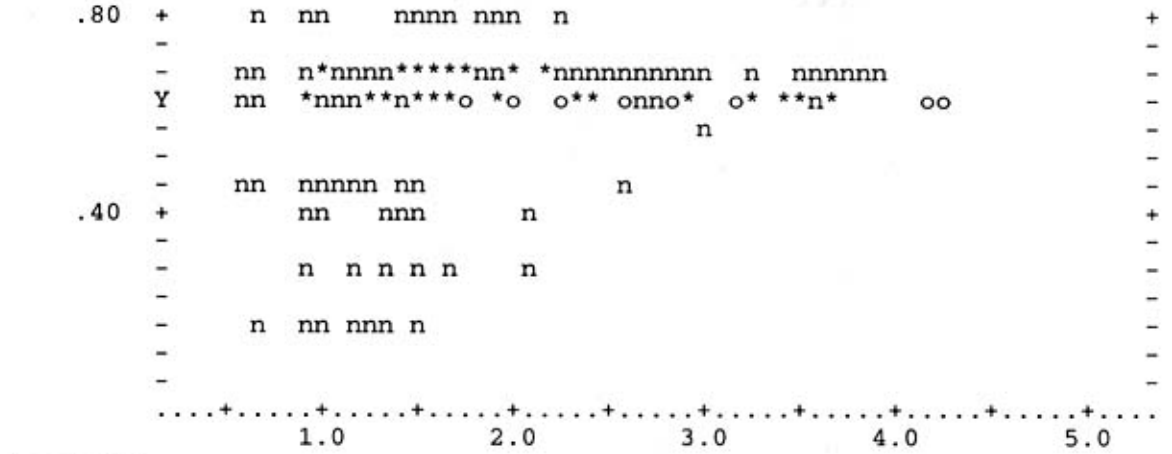




N = 2019
R = .708
P < .001

ˇPlot 10. logChlorine versus logSO4
Symbols: i/l= lime new/old; ,n/o = marble new/old

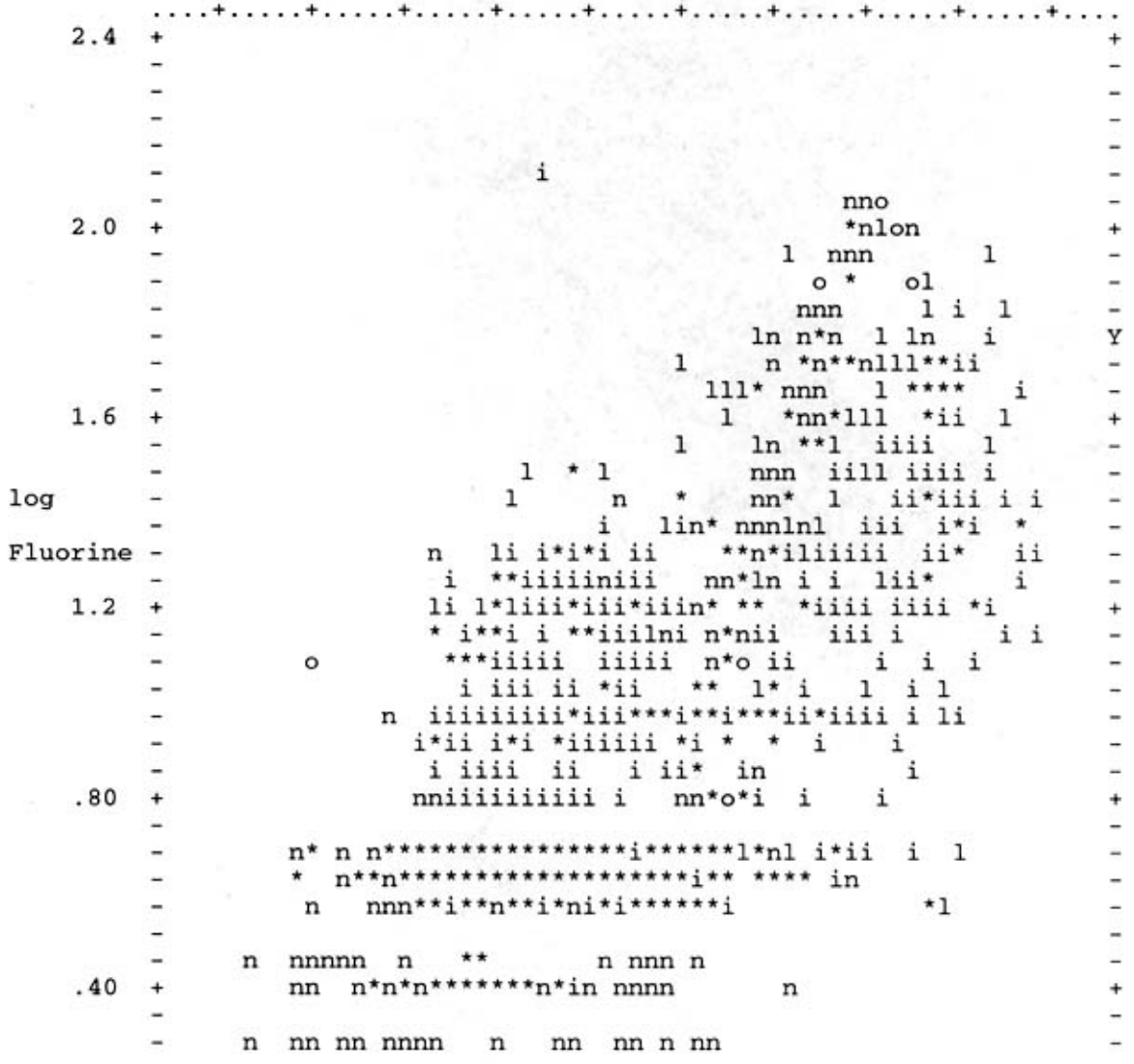


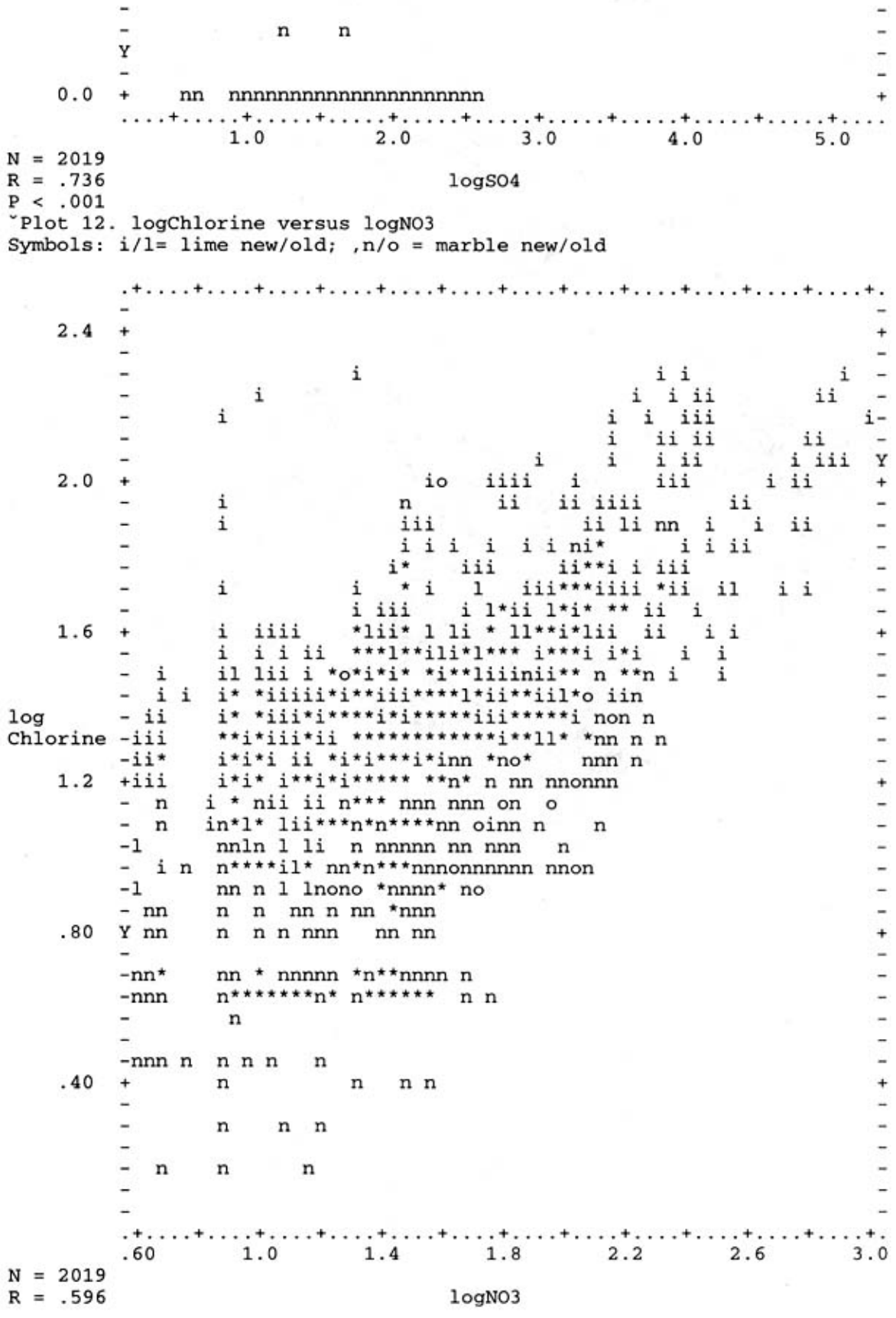


N = 2019
R = .608
P < .001

logSO4

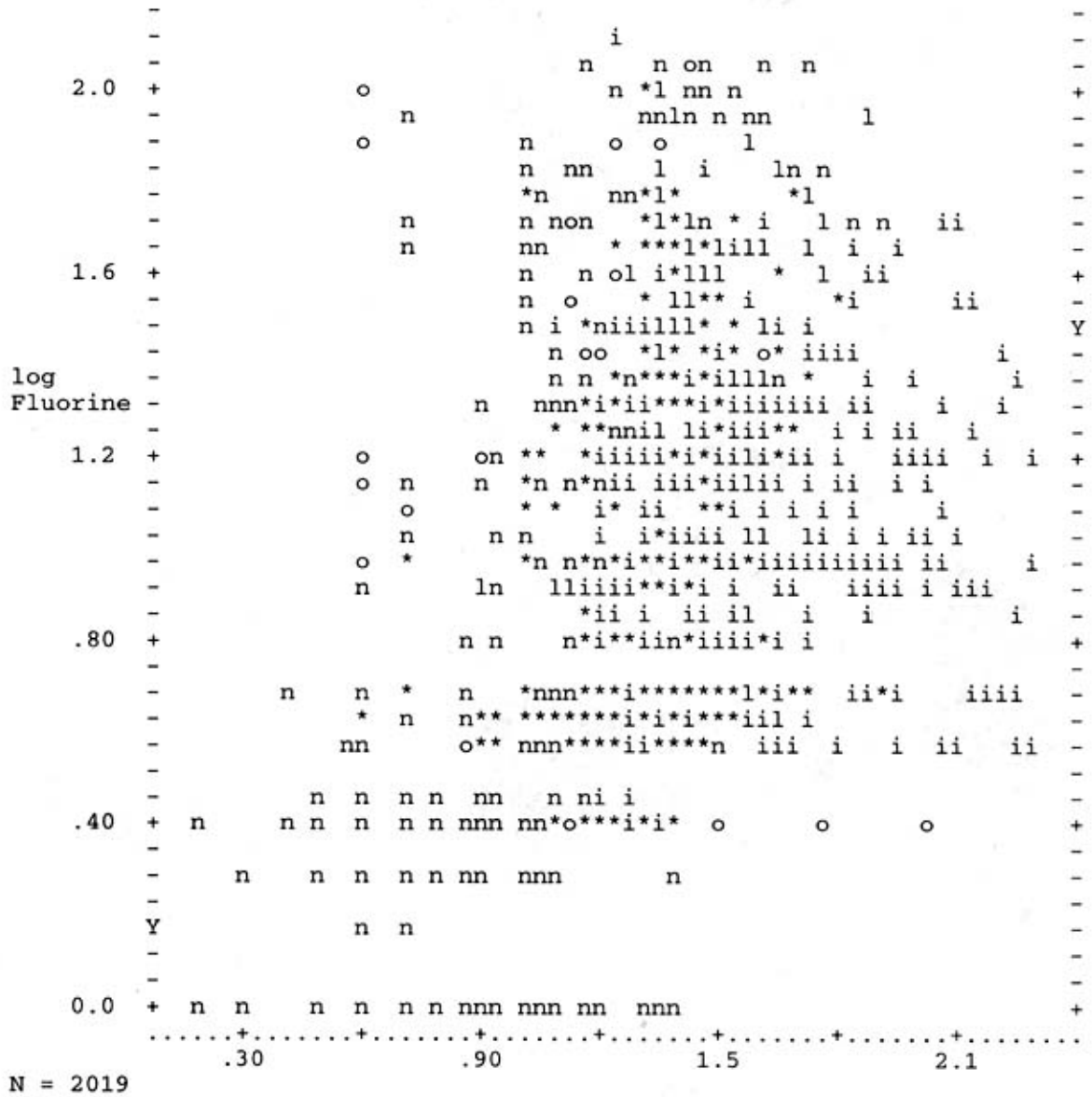
˘Plot 11. logFluorine versus logSO4
Symbols: i/l= lime new/old; ,n/o = marble new/old




0.0
1.0
2.0
3.0
4.0
5.0
N = 2019
R = .736
logSO4
P < .001
˘Plot 12. logChlorine versus logNO3
Symbols: i/l= lime new/old; ,n/o = marble new/old
2.4
2.0
1.6
1.2
.80
.40
log
Chlorine
.60
1.0
1.4
1.8
2.2
2.6
3.0
N = 2019
R = .596
logNO3

P < .001
ˇPlot 13. logFluorine versus logNO3
Symbols: i/l= lime new/old; ,n/o = marble new/old

N = 2019
R = .554
P < .001
ˇPlot 14. logFluorine versus logChlorine
Symbols: i/l= lime new/old; ,n/o = marble new/old



N = 2019
R = .520
P < .001

˘Table 11. Summary of Cation Values by RockType

Variable	Mean	StdDev	Low	Z	High	Z
Mg	2302	547	1160	-2.08	3550	2.28
Limestone	2671	101	2420	-2.48	2880	2.06
Marble	1836	525	1160	-1.29	3550	3.26
Al	39.8	34	10	-0.87	192	4.41
Limestone	38.8	22	10	-1.26	110	3.11
Marble	41.1	45	10	-0.69	192	3.34
Mn	42.6	22.6	15	-1.22	75	1.43
Limestone	62.5	4.4	55	-1.69	75	2.79
Marble	17.6	1.3	15	-1.97	21	2.57
Cu	4.7	3.2	1	-1.16	21	5.04
Limestone	4.6	3.1	1	-1.16	18	4.28
Marble	4.9	3.3	1	-1.16	21	4.79

Fe	285	78	190	-1.22	610	4.14
Limestone	277	76	190	-1.14	610	4.36
Marble	296	79	210	-1.09	610	3.93
Sr	191	29	109	-2.76	230	1.30
Limestone	213	15	109	-6.89	230	1.11
Marble	163	18	130	-1.81	230	3.58
Zn	6.6	5.3	1	-1.05	27	3.78
Limestone	10.1	4.3	5	-1.20	27	3.89
Marble	2.2	2.5	1	-0.48	21	7.50

Z is number of standard deviations from mean.

DESCRIPTION AND ANALYSIS OF NAPAP BRIQUETTE SURFACE CHEMISTRY FILES (Comprising data from 1984 to 1995)

Terry J. Reedy
Statistician/Consultant
October 1998

1. EXECUTIVE SUMMARY

From 1984 to 1995, NAPAP researchers exposed limestone and marble briquettes to weathering for months to years at several different Sites. They sampled the briquettes and analyzed multiple layers for anion content (sulfate SO4, nitrate NO3, chlorine Cl, and fluorine F). In the first four years. they analyzed a subset of samples for fifteen cations (Mg, Al, Cd, Mn, Ba, Be, Ni, Pb, Co, Cr, Cu, Fe, Sr. V. and Zn). They compiled the results into several BSC (briquette surface chemistry) data files and documented the data-field formats thereof both in table headers and in separate files.

In July of 1998 I received nineteen BSC files as email attachments: three format files (and two duplicates) describing the fields in the data files, twelve anion data files (four material types times three project cycles), and two cation data files (from the first cycle, and which were re-sent separately in September). In examining these files, I have verified and extended their format descriptions, transformed all to a common physical format, combined the fourteen date files into two master files, slightly modified (recoded) and reordered identification data, and done preliminary analyses of the measured data.

For this study, the outdoor treatment units are the briquettes while the laboratory analytical units are the layers sampled from each briquette. The data files reflect this hierarchical structure. Each line, representing a layer, has a briquette arid layer id; treatment fields describing the rock type and condition, exposure site and rack slot, and exposure period; and analytical fields giving values for either the four anions or fifteen cations and indicating which are below detection limits. The briquette treatment fields are duplicated for each layer of a given briquette.

Proper statistical analysis must also reflect this two-level structure. This is impeded in this study by the diversity of layers sampled for different briquettes. (There are sixteen different patterns, not counting some of the control blocks.) On the other hand, there are essentially no missing data. Overall, the data are in good shape for statistical analysis after the few changes I made. The disk accompanying this report contains the ready-to-analyze anion and cation files. There are three versions to meet the differing input needs of different programs.

Lacking existing analyses to review, I performed some myself. The report text and tables tabulate the briquette treatment variables and the below-detection indicators for layers for both the anion and cation files Histograms, plots. and analyses of covariance show the following about the overall relationship between treatment arid anion content: rock type (limestone versus marble), exposure time, and layer selected all affect each of the anions; condition (fresh versus weathered) affects S04 and Fluorine.

There are two directions to go for further analyses. One is to examine subsets of data to answer specific questions. The other is to augment the current data with other information.

2. DATA FIELDS AND RECORDS

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2 DATA FIELDS AND RECORDS