Journal of Environmental Protection and Ecology 17, No 1, 18–30 (2016)

Water pollution

APPLICATIONS OF THE MATHEMATICAL MODEL ANOVA IN THE AREA OF AN INDUSTRIAL PLATFORM FOR ASSESSMENT OF GROUNDWATER QUALITY

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Abstract. The purpose of this study was to evaluate the quality of ground water in the area of industrial platform, using statistical models for the interpretation of environmental analysis. Many researchers have pointed out the usefulness of statistical analysis in assessing environmental problems. Statistical models used in the present study were the ANOVA techniques. By applying these techniques was tracked the time evolution of ground water quality in the studied area, the interaction between drillings studied depending on their positioning to industrial platform and the influence of the investigation period on ground water quality.

Keywords: groundwater, ANOVA techniques, environmental assessments.

AIMS AND BACKGROUND

The statistical study has received much attention in the last years[1–12]. For an overview of some of the recent trends, one should see the special issue edited by González-Manteiga and Vieu[13], and for some very recent publications[14–16]. Methods for multiple criteria ranking[17–19] build a set of additive value functions compatible with the revealed preference information, which are piecewise defined (mostly piecewise linear). Hence, a mathematical approach based on differentiation does not possess the required generality. We, therefore, shift the background to the integral expansion of a multivariate function (*f*) generated by the high dimensional model representation (HDMR) theory (functional ANOVA) (Refs 20–24). For this expansion to hold, in fact, the sole easurability of *f* is required. Functional ANOVA is a fundamental tool in statistics and global sensitivity analysis[21,24,25]. This study describes the foundations of functional ANOVA and offers its interpretation, as

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a tool for expanding multivariate measurable functions. The origin of functional ANOVA is linked to the problem of decomposing the variance of a square integrable statistics generated by the seminal works of Hoeffding in the 1940s (Ref. 26). The 'jackknife' decomposition is proven by Efron and Stein[27]. The technique utilised by Efron and Stein[27] consists in the dissection of *f* via a sequence of nested conditional expectations in accordance with the Grahm–Schmidt orthogonalisation process.

Orthogonality is at the basis of the results by Takemura[28], where the orthogonal decomposition of any square integrable function is cast in the context of tensor analysis and multilinear algebra. Rabitz and Alis[21] introduced an alternative generalisation of functional ANOVA, called high dimensional model representation (HDMR) theory. Rabitz and Alis[21] proved the functional ANOVA decomposition through the dissection of the linear space to which the function belongs. A fourth and independent way of proving the functional ANOVA expansion is due to Sobol[29,30]. Sobol[29] developed the decomposition in the context of quadrature methods and called 'the decomposition into summands of different dimensions'[31]. Having decided on which effects to include as random and which as fixed, the question arises as to which approach of model selection to use. Model selection in general, and selection of regression and ANOVA type models[32–36]. A particular challenge for model selection of mixed-effects models is how to handle the two types of effects; random-effects and fixed-effects. If the random effects are not well chosen, this will affect the estimates and the hypothesis tests of the fixed-effects. Vice versa, variation in the response variable not modelled in terms of fixed-effects can partly end up in the random effects.

This paper presents a work done using the analysis of variance (ANOVA) to interpret experimental data. The objective of this study was to apply three techniques ANOVA (simple, with repeated measurements and factorial) in the interpretation of environmental assessments, in our case for environmental factor 'groundwater'.

EXPERIMENTAL

The present study aimed to apply ANOVA techniques for interpreting environmental analytical data obtained from groundwater of drillings and fountains, located in the industrial platform. Quality indicators that were followed were ammonium and sulphate.

Materials and methods. In the present study ammonium in groundwater samples was determined by spectrophotometric method according to SR ISO 7150-1:2001 (Ref. 37) and sulphates by turbidimetric method according to EPA 427 C (Ref. 38). The reagents used were of analytical quality.

Samples of groundwater. Groundwater samples were taken from drillings and fountains located in an industrial area (Fig. 1). To apply simple ANOVA statistical technique were studied three fountains (Stuparei, Stolniceni and Copacelu).

For these, ammonium quality indicator was determined quarterly for a period of three years 2012, 2013 and 2014. For ANOVA with repeated measurements were followed up six drillings located outside the industrial platform (points 1, 2, 3, 4, 5 and 6 on the map, Fig. 1). Groundwater samples were taken in 2011 in each quarter. For factorial ANOVA was followed ammonium quality indicator for two drillings located within the industrial platform (point 7 on the map, Fig. 1) and outside the industrial platform (point 3 on the map, Fig. 1), in three different periods.

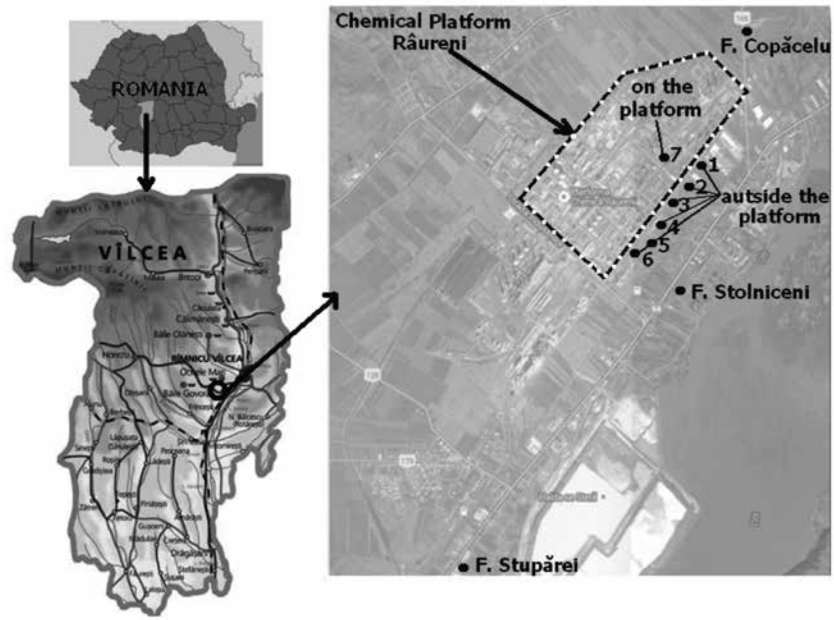

Fig. 1. Localisation points

Statistical analyses. All statistical analyses were conducted using EXCEL. In the present study were applied three ANOVA statistical techniques for assessing groundwater from the drillings and the fountains located in the industrial platform. To calculate the ratio F of ANOVA was used method called ABC (Refs 39–43).

ANOVA simple was used to determine the relationship between the concentration of ammonium and sampling period for three fountains located in the studied area. To calculate the ratio F of ANOVA simple was used the so-called ABC (Refs 39 and 40). A, B and C were calculated according to equations (1), (2) and (3):

$$\mathrm{A} = \sum X^2; \quad (1)$$

$$\mathrm{B} = (\sum X)^2/N; \quad (2)$$

$$C = (\sum X_1)^2/n_1 + (\sum X_2)^2/n_2 + \ldots + (\sum X_i)^2/n_i, \quad (3)$$

where A was obtained by squaring the results of each test and then summing them (regardless of the sampling point); B – by the sum of the results of all samples analysed (regardless of the sampling point), raising the amount to the square and then dividing the total number of determinations, and C – by the sum of determinations from a sampling point, squaring the value obtained by dividing followed by the total determinations for each sampling point. The process was repeated for all analytical determinations of all sampling points, finally all partial results have been gathered. ANOVA simple, represented as a table, was illustrated in Table 1.

Table 1. Representation of ANOVA simple

Dispersion	SS	df	MS	F
Intergroup	C–B	k–1	(C–B)/(k–1)	MS1/MS2
Intragroup	A–C	N–k	(A–C)/(N–k)	
Total	A–B	N–1		

Note: X is concentration of pollutants (mg/l) for groundwater samples; N – total number of samples analysed; k – number of the fountains; SS – sum of squares; df – number of degrees of freedom; MS – the square mean; F – ANOVA report.

ANOVA with repeated measurements was applied to see how influenced the passage of a certain time, the water quality of the drillings studied. In applying this technique was followed in time, sulphates quality indicator, from groundwater of drillings studied. The term, repeated measurements involves evaluating a sampling point two or more times in regarding the dependent variable (quality indicator analysed). In this case, the total sum of squares and thus the total dispersion are divided into three components: the dispersion of sampling points; dispersion due to the independent variable; and residual dispersion.

A, B, C and D were calculated according to equations (1), (2), (4) and (5):

$$C = \frac{(\sum X_{1n})^2 + (\sum X_{2n})^2 + ... + (\sum X_{kn})^2}{k}; \quad (4)$$

$$D = \frac{(\sum X_{1k})^2 + (\sum X_{2k})^2 + ... + (\sum X_{nk})^2}{n}, \quad (5)$$

where C is obtained by summing the results obtained from the first sampling point during all evaluations (k). The procedure is repeated for the other sampling points of the experiment. These partial results add up, and the resulting value is divided by the total assessments of each sampling point; D is obtained by summing the results of the determinations from a sampling point, squaring the value obtained. The process is repeated for the other sampling points and partial results add up, the proceeds shall be divided into the number of final determinations contained in a sampling point; k is the number of evaluations, the default sampling points; N – number of determinations from a sampling point.

Summary table for ANOVA with repeated measurements necessary for the calculation of F is represented in Table 2.

Table 2. Summary representation for ANOVA with repeated measurements

Source of dispersion	SS	df	MS	F
Individual	C–B	n–1	SS/df	
V independence	D–B	k–1	SS/df	F
Residual	(A–B) – [(C–B) + (D–B)]	(k–1)(n–1)	SS/df	
Total		N–1		

Individual SS = C–B; SS independent (true treatment) = D–B; The residual SS = (A–B) – [(C–B) + (D–B)]; SS total = A–B; n – the number of samples from a sampling point; N – number of samples analysed in the experiment, and k – the number of repetitions of testing; F is derived by taking the ratio of independent MS and MS residual.

Factorial ANOVA was applied to track quality indicator influence to the two studied drillings located inside and outside the industrial platform, the influence of the period enable the determinations and the influence of the place where drillings are located compared to chemical platform. Factorial ANOVA summary is represented in Table 3.

Table 3. Summary representation for factorial ANOVA

Source of dispersion	SS	df	MS	F
Line – A factor	C–B	l–1	SS/df	F
Column – B Factor	D–B	c–1	SS/df	F
interaction	(E–B) – (C–B)(D–B)	(l–1)(c–1)	SS/df	F
intracellular	(A–E) – (E–B)	(N–1) – rest	SS/df	
Total	A–B	N–1		

l is the number of lines (variable steps A); c – the number of columns (variable steps B) and degrees of freedom (df) for intracellular are calculated by subtracting the total df other degrees of freedom (lines, columns interaction).

A, B, C, D, and E were calculated according to equations (1), (2), (6), (7) and (8):

$$\mathrm{C} = \frac{(\sum X_{11})^2 + (\sum \mathrm{X}_{12})^2 + ... + (\sum X_{1n})^2}{n_{\mathrm{line}}}; \tag{6}$$

$$\mathrm{D} = \frac{(\sum X_{c1})^2 + (\sum \mathrm{X}_{c2})^2 + ... + (\sum X_{cn})^2}{n_{\mathrm{column}}}; \tag{7}$$

$$E = \frac{(\sum X_{cel1})^2 + (\sum X_{cel2})^2 + ... + (\sum X_{celn})^2}{n_{cel}}. \quad (8)$$

C is obtained by summing the results obtained by the presence on the front line, the result is squared. The procedure is repeated for the other lines. These partial results add up, resulting value is divided by the total number of determinations of a line, regardless of columns; D is obtained by summing the results of the determinations in column 1 and then squaring the value obtained. The process is repeated for the other columns and partial results add up and the sum is divided by the number of determinations contained in a column, regardless of the line; E is obtained by summing the results of the determinations of the first cell and then squaring the sum obtained. The process is repeated for all cells factorial design and partial results are added together. The result is divided by the number of measurements from a single cell.

RESULTS AND DISCUSSION

The present study was conducted to interpret the data analysed for the groundwater, in an industrial area, using three techniques ANOVA: simple, with repeated measurements and factorial. The results obtained from the experimental runs carried out, for groundwater are shown in Tables 1, 3 and 5 and the results of applying the three ANOVA techniques are summarised in Tables 2, 4 and 6. The calculations for the three types of ANOVA were carried out using equations (1)–(8). The applications of ANOVA techniques have allowed the emphasis of some additional information regarding the experimental data obtained and measure the influence of independent factors on the groundwater environmental factor.

ANOVA SIMPLE OR ONE-WAY ANOVA

To apply One-way ANOVA was followed ammonium quality indicator for three years for groundwater from three fountains, located in the area of the industrial platform. All this time, samples were collected quarterly. The dependent variable in the current example was ammonium quality indicator. The results are presented in Table 4. In Table 5 are reported the results obtained after applying statistical technique ANOVA simple, according to equations (1)–(3). The major interest in Table 5 is the reported value of *F*. This value comes[41] for significance levels of 0.05 or 0.1. *F* report has been obtained by dividing the mean square (MS) to media intergroup square (MS) intragroup. Each corresponding quadratic mean certain degrees of freedom. In the case ammonium indicator is seen as a MS intergroup has 2 df (2 degrees of freedom) and intragroup MS has 33 df.

The upper critical values of the *F* distribution[44] reads the corresponding value for intergroup degrees of freedom (on the second column because df = 2) and intragroup (df = 33, so line 33). Two values were passed at the intersection of column 2 line 33 (2.060 to $p < 0.05$ and respectively 2.471 for $p < 0.1$).

The value of F, obtained experimentally ($F = 3.066$), was compared with 'upper critical values of F distribution' and noted that F obtained experimentally is higher than the theoretical value, thus the null hypothesis is dismissed (2.060 to $p < 0.05$, 2.471 to $p < 0.1$). This means that the ratio F obtained is statistically significant, the null hypothesis is rejected, and then there are differences between the averages of the three groups.

Table 4. Results for ammonium quality indicator, from the groundwater of fountains Stuparei, Solniceni and Copacelul in the period 2012–2014

Sampling period		Stuparei		Stolniceni		Copacelu	
				NH_4^+ (mg/l)			
		X	X^2	X	X^2	X	X^2
2012	Quarter I	0.033	0.00109	0.018	0.00032	0.018	0.00032
	Quarter II	0.018	0.00032	0	0	0	0
	Quarter III	0.033	0.00109	0	0	0	0
	Quarter IV	0.063	0.00397	0	0	0	0
2013	Quarter I	0.099	0.0098	0.07	0.0049	0.07	0.0049
	Quarter II	0.09	0.0081	0	0	0	0
	Quarter III	0.07	0.0049	0.06	0.0036	0	0
	Quarter IV	0.056	0.00314	0.08	0.0064	0.056	0.00314
2014	Quarter I	0.014	0.0002	0.024	0.00058	0.02	0.0004
	Quarter II	0.013	0.00017	0.022	0.00048	0.018	0.00032
	Quarter III	0.013	0.00017	0.017	0.00029	0.013	0.00017
	Quarter IV	0.19	0.0361	0.09	0.0081	0.044	0.00194
	$\sum X$	0.692	0.06904	0.381	0.02467	0.239	0.01119
	Average	0.05767		0.03175		0.01992	

Table 5. Results obtained from ANOVA statistical technique of applying simple

Dispersion	SS	df	MS	F
Intergroup	0.008947	2	0.004473528	3.066489297
Intragroup	0.048142	33	0.001458843	
Total	0.048142	35		

Mathematically the result was written in the form $F(2,33) = 3.066$, $p < 0.05$ (read 'F with 2 and 33 degrees of freedom has value 3.066 and is significant at 0.05').

Rejection of the null hypothesis shows that these three fountains studied differ in terms of average results of the dependent variable, in this case ammonium quality indicator.

ANOVA WITH REPEATED MEASUREMENTS

ANOVA with repeated measurements technique was applied to track the time variation of quality indicator sulphates from the water of drillings studied. The hypothesis that was released in this problem was: drillings water quality indicator differs by as much as sulphates persist. Null hypothesis of the research was: M1 = M2 = M3 = M4.

Tables 6 and 7 show the values of the analytical determinations for the six drillings, obtained by the 'ANOVA with repeated measurements technique'.

Table 6. Results for the quality indicator sulphates in the groundwater drillings analysed in 4 quarters of 2011

No crt	Sample name	Year 2011							
		Quarter I		Quarter II		Quarter III		Quarter IV	
		SO_4^{2-} (mg/l)							
		x	x^2	x	x^2	x	x^2	x	x^2
1	F1	419.80	176232	436.21	190279.16	468	219024	457.1	208940.41
2	F2	33.64	1131.65	51.15	2616.322	58.6	3433.96	49.8	2480.04
3	F3	38.02	1445.52	46.77	2187.432	56.4	3180.96	54.2	2937.64
4	F4	105.99	11233.9	116.93	13672.624	135.5	18360.25	119.1	14184.81
5	H16	27.08	733.326	35.83	1283.788	36.7	1346.89	32.3	1043.29
6	H53	29.27	856.733	22.71	515.7441	38.8	1505.44	54.2	2937.64
∑		653.80	191633.1	709.60	210555.07	794	246851.5	766.7	232523.83
Average		108.96		118.26		132.33		127.78	

Table 7. Results of applying statistical technique ANOVA with repeated measurements

Source of dispersion	SS	df	MS	F	F, $p < 0.05$
Individual	3158032.225	5	631606.4451		
V. independence	1943.547917	3	647.8493056	9.2930999	3.287
Residual	1045.694083	15	69.71293889		
Total	525298.5231	23			

The value of F, obtained experimentally ($F = 9.29$) was higher than 'upper critical values of F distribution' at a threshold of 0.05 for 3 and 15 degrees of freedom ($F = 3.29$), thus, null hypothesis was dismissed. We found significant differences between the averages of four series of analytical determinations. Mathematically, the result can be written: F (3, 15) = 9.29, $p < 0.05$.

FACTORIAL ANOVA

Factorial ANOVA was applied to two drillings located outside and inside a chemical platform. In this study we were interested in the influence of two independent variables: quality indicator ammonium and where they are located drillings studied (drilling located inside the chemical platform – point 7 on the map in Fig. 1, and drilling located outside the chemical platform – point 3 on the map in Fig. 1). We have therefore a model of type 3×2 factorial ANOVA (three rows and two columns).

The hypothesis of this issue was: the two drillings were influenced by the quality indicator analysed, the period enable of the determinations, as well as where drillings were located compared to chemical platform, meaning that the drilling that is inside of the platform are more affected compared to the drilling that is outsite of the platform. The results obtained after applying factorial ANOVA are presented in Tables 8 and 9.

So, we see that of the three ratios *F*, two lines are statistically significant *F* (determined by factor B columns) and *F* interaction (determined by the joint action of factors A and B).

The graphical representation of the influence of factors A and B and their interaction on the dependent variable is shown in Fig. 2, where on the horizontal axis is one of the independent variables (quality indicator ammonium), while the dependent variable values are passed on the ordinate axis. Two independent variables which do not interact have a parallel graphical representation. But in the present study, the variables interact with each other, the two lines intersecting even in the two places.

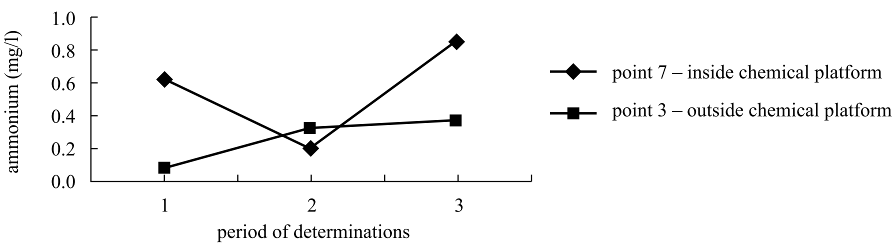

Fig. 2. Variation of ammonium quality indicator in 3 periods for the two drillings studied

Table 8. Results obtained for quality indicator ammonium in the groundwater for two drillings located inside (point 7) and outside (point 3) industrial platform in three different periods of time

Period	Analyte evaluated	Drilling from inside chemical platform point 7 X	Drilling from inside chemical platform point 7 X^2	Drilling from outside chemical platform point 3 X	Drilling from outside chemical platform point 3 X^2	Calculation	
1		0.55	0.3025	0.79	0.6241	A_1	5.820
		0.67	0.4489	0.21	0.0441	A_1^2	4.347
	NH_4^+ (mg/l)	0.8	0.64	1.1	1.21	average A_1	0.582
		0.8	0.64	0.18	0.0324		
		0.63	0.3969	0.09	0.0081		
	SUM	3.45	2.4283	2.37	1.9187		
	average	0.69		0.474			
	No. det.	5		5			
2		0.5	0.25	0.49	0.2401	A_2^2	4.4600
		0.15	0.0225	0.63	0.3969	A_2^2	2.3552
	NH_4^+ (mg/l)	0.5	0.25	0.69	0.4761	average A_2	0.4460
		0.71	0.5041	0.25	0.0625		
		0.21	0.0441	0.33	0.1089		
	SUM	2.07	1.0707	2.39	1.2845		
	average	0.414		0.478			
	No det.	5		5			
3		0.62	0.3844	0.31	0.0961	A_3^2	6.4500
		0.61	0.3721	0.63	0.3969	A_3^2	11.5465
	NH_4^+ (mg/l)	0.86	0.7396	0.48	0.2304	average A_3	0.6450
		0.86	0.7396	0.85	0.7225		
		0.85	0.7225	0.38	0.1444		
	SUM	3.80	9.9562	2.65	1.5903		
	average	0.76		0.53			
	no. det.	5		5			
B_1	9.32		B_2	7.41		$X_{tot.}$	16.7300
B_1^2	13.4552		B_2^2	4.7935		$X_{tot.}^2$	18.2487
Average B_1	0.62133		average B_2	1.984		average $X_{tot.}$	0.5576666

Table 9. Results of applying statistical techniques, factorial ANOVA

Source of dispersion	SS	df	MS	F experimental	F theoretical	Threshold p
Line – A factor	0.206886	2	0.103443	0.310838 (2,24)	3.403	>0.05
Column – B factor	4.271573	1	4.271573	12.83573 (1,24)	4.260	<0.05
Interaction	4.944476	2	2.472230	7.428876 (2,24)	3.403	<0.05
Intracellular	7.986903	24	0.332787			
Total	8.918936	29				

CONCLUSIONS

Three ANOVA models were applied in this study to interpret environmental data for the groundwater, from fountains and drillings, in an industrial area. Applications on real samples of groundwater, for the three types of ANOVA show that the statistical model used gives us supplemented information useful for interpreting environmental analysis for the environmental factor studied, and in this case for 'groundwater'. ANOVA models are easy to apply for the environmental factors studied. After analysing the results, after applying the ANOVA models for environmental factor 'groundwater, following general conclusions can be summarised: applied ANOVA model generated realistic indicative values for the environmental study, namely groundwater; the values obtained for section 'groundwater' are comparable and compatible with the values obtained by analytical measurements, which provides rapid indication on the assessment of pollution with the pollutant studied

Thus, applying these statistical models can quickly provide conclusive indications for a rapid risk assessment, which underpin the conclusions on actions/ future preventive measures for study area. In conclusion, we can say that ANOVA techniques are interesting tools that can be employed by engineers to approach real case studies with laboratory conclusions.

Acknowledgements. The authors acknowledge the financial support from the CORE Program (Environmental Research – priority in sustainable industrial development – MEDIND, PN 09-13.02.12), and the work done by L. R. Popescu has been supported by the Sectoral Operational Programme Human Resources Development (SOP HRD), financed from the European Social Fund and the Romanian Government under the contract number POSDRU/159/1.5/S/137390/.

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Received 19 October 2015
Revised 22 December 2015