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LOCAL VARIANCES IN BIOMONITORING

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Abstract:

The present study was undertaken to explore possibilities to judge survey quality on basis of a limited and restricted number of a-priori observations. Here, quality is defined as the ratio between survey and local variance (signal-to-noise ratio). The results indicate that the presented surveys do not permit such judgement; the discussion also suggests that the 5-fold local sampling strategies do not merit any sound judgement. As it stands, uncertainties in local determinations may largely obscure possibilities to judge survey quality.

The results further imply that surveys will benefit from procedures, controls and approaches in sampling and sample handling, to assess both average, variance and the nature of the distribution of elemental concentrations in local sites. This reasoning is compatible with the idea of the site as a basic homogeneous survey unit, which is implicitly and conceptually underlying any survey performed.

1. INTRODUCTION

The present paper deals with the (larger-scaled) biomonitoring survey and specifically focuses on the survey quality. In earlier work (Wolterbeek et al. 1996), the survey quality was proposed as measurable by analysis of the signal-to-noise ratio, which, in turn, can be determined by the ratio between survey and local variance. The inherent drawback of this analysis is of course that quality can only be judged afterwards: the assessment asks for the survey variance. The present study is concerned with possibilities to estimate the survey's quality before the start-up of the full survey. This implies an important prepositioning of thinking: the a-priori set-up of the survey should contain measurable information about it's quality. As a first collection of thoughts, both survey and local variances were studied in more detail. Here, the aims of the study make that attention should not only be focused on analytical (instrumental) variances (Wolterbeek et al. 1996, Wolterbeek and Bode 1995), but that especially the total local and survey variances (including biological and all further unspecified variances) should be investigated (Wolterbeek et al., 1996; Wolterbeek and Bode, 1995; Shantangeeva, 1994 1995; Wyttenbach et al., 1994).

In most surveys, the sampling site is simply selected or defined as a spot of (geographical) dimensions which is small relative to the dimensions of the total survey area. Implicitly it is assumed that the sampling site is essentially homogeneous relative to the variations in survey parameters. As such, the sampling site is mostly regarded as "the basic unit" of the survey. As a logical consequence, the local (sampling site) variance should also be seen as a basic and important characteristic of the survey. In the present study, work was carried out to gain more knowledge of the local variance. Multiple sampling was carried out at a specific site, multi-elemental analyses were carried out by NAA, and local variances were investigated by conventional statistics and bootstrapping (Hall, 1986; Efron and Tibshirani, 1986; Diciccio and Romano, 1988). The outcomes were set in the context of the total survey.

For the survey, the approach was essentially similar: outcomes from a limited number of sites, processed by bootstrapping, were used to estimate the true survey variance. The present paper addresses outcomes, differences between estimated and true variances and discusses possibilities for "a-priori" judgement of survey quality.

2. MATERIALS AND METHODS

2.1. Sampling, sample handling and elemental analysis

Multiple samples were taken from tree bark (local site at Delft, The Netherlands), and from mosses and soil (local site at Hattem, The Netherlands), all in the context of national biomonitoring surveys on trace element air pollution (Kuik and Wolterbeek, 1994 1995; Rühling and Steinnes, 1995). Tree bark and moss samples were handled as in (Kuik and Wolterbeek, 1994 1995), immersed in liquid N2, and milled in a FRITSCH (pulverisette 114) Rotor Speed Mill. Soil samples were dried at 40 oC after presieving through a 5 mm sieve (Linker Industrie-Technik); after drying sieving was repeated through a 2.8 mm sieve.

Elemental analyses were carried out by INAA, following instrumental methods as essentially described by Blaauw (1993). Quality control was performed by the regular analysis of standard reference materials (NBS-1572 "Citrus leaves", NIST SRM 2711 "Montana soil"). For the Hattem tree bark, separate from INAA on the initially taken samples, the rest of the sample masses were mixed thoroughly (a total of about 1000 g mass), after which 32 sub-samples were taken and also processed by INAA. The rest of the mass was analyzed as a bulk sample by the IRI BISNIS large volume facility (Bode and Overwater, 1993; Overwater et al., 1993).

2.2. Data processing

General and initial processing of data was by straightforward statistics. Bootstrap procedures (Hall, 1986; Efron and Tibshirani, 1986; Diciccio and Romano, 1988) were used to construct confidence regions for local and survey concentrations. In general terms, and wihout going into detailed mathematics, the bootstrap method is a computer-based method, used to assess the accuracy of an estimation of an unknown (statistical) parameter, thereby substituting considerable amounts of computation in place of theoretical analysis (Efron and Tibshirani, 1986). Thus, in the present study, the initial data were considered as estimates of the true populations of elemental concentrations: bootstrapping can be regarded as the use of simulation to approximate the true statistical distributions (Diciccio and Romano, 1988).

3. RESULTS AND DISCUSSION

Calculations were carried out on data obtained in moss and soil surveys, and in tree bark. Initial approaches were aimed at getting more insight into local data: the question asked here was whether the general survey set-up (5-fold local sampling, mixing before analysis) permits an adequate expression of local circumstances. Similar questions were addressed on survey level, since surveys are based on a series of local concentrations. The main underlying question was whether survey quality could be reasonably assessed by a restricted number of a-priori observations, that is, by a very limited number of sites, selected throughout the survey area of interest In the following paragraphs, the local problems are discussed, after which their consequences are indicated on survey level.

3.1. Local data

The determination of the local variance implies that all aspects of the survey are taken into account: biomonitor selection, definition of the sampling site, sampling, sample handling, elemental analysis etc. The local variance is suggested as not related to concentration levels (Wolterbeek et al., 1996; Sloof, 1993); furthermore, analytical uncertainties hardly contribute to local uncertainties (Wolterbeek et al., 1996). This means that in larger-scaled surveys any effort to improve analytical precision may be regarded as meaningless.

Considering the Delft 32-fold tree bark sampling, mixing of all initial samples, milling, and the elemental analysis of the then-taken 32 sub-samples did not invariably show increased homogeneity: success varied between elements (Table 1). This means that average local levels and uncertainties may only be obtained by analysis of a multitude of initially taken local samples. The IRI large volume facility (analysis of 1000 g mass) was used to avoid homogeneity problems. The results (Table 1) indicate differences in outcomes for a number of elements; furthermore, the single analysis approach makes that any information on distribution characteristics and local variance is lost. For Ba, bootstrapping resulted in strongly reduced variances, probably indicating differences from normal distributions.

Considering the sampling sites at Delft and Hattem for tree bark, moss and soil, repeated randomized n=5 trials were taken out of the total number of local samples (n=32, 25 and 25 for tree bark, moss and soil respectively). Table 2 gives results obtained after 500 trials, and presents the mean and maximal increment factors by which the trial local variance should be increased to ensure full compatibility with the actual local elemental concentration population (T-test threshold approach).

This testing implies a very strict verification of the local trial outcomes: although survey quality is using local variance only, the test compares both means and variance of the trial with the concentration population characteristics. Table 2 also presents the number of cases in which the factor value ^{1} 1.0. The data indicate that statistically speaking n=5 trials give reasonable results (agreement with local populations for all selected elements in > 90 % of the trails). However, the remaining up to 10 % of all selected cases, and both mean and maximal values also suggest effects from outlyers and/or from skewness and/or kurtosis of the local distributions. Here should also be noted that in the 25-32 fold local sampling, the repeated calculations on randomized n=5 trials undoubtly suffered from overlaps: the F and E values may strongly underestimate reality.

3.2. Survey data

The trial approach (Table 2 for local sites) was also followed with survey data: 500 trials, each comprising 5 randomized samples, and each T-tested to compare with survey characteristics, yielded results as given in Table 3. The data indicate that agreement between trial and survey was highly variable, probably due to skewed distributions for several elements. It should be noted here that the survey data in Table 3 inevitably comprise all local problems discussed sofar (Table 2). It may also be clear that the survey quality Q, defined as the ratio between survey and local variance, will suffer from both local and survey problems. This is illustrated in Table 4, where Q is expressed both on the direct survey data (Q1) and on the bootstrapped data (Q2), and is also calculated in repeated trials (N=500) of randomly selected 20 % and 40 % of the available local and survey data (Q3). The differences between Q1 and Q2 (suggesting skewed distributions) and the relatively large variances in sub-set Q3's all indicate the difficulties in reproducing survey behaviour in restricted randomized sub-sets. After devision of the moss survey into two sub-sets of 25 locations each, or into three sub-sets of 18 locations each, in all approaches ensuring comparable aera coverage, Q data were obtained as given in Table 5. Here, the calculations were simulating parallel surveys, with comparable area coverage although using different locations: the outcomes are comparable to those of Table 4, and underline the element-specific variability in Q values.

In a series of calculations, the Hattem local site (n=25) was taken for both moss and soil. Out of the total number of observations repeated (N=18) randomized n=5 trials were processed as if they represented a survey: this was performed three times, and the outcomes were compared to the actually performed moss and soil surveys, each in turn devided into three area-ensured sub-surveys. The results are presented in Table 6, for a number of selected elements. The data indicate that 5-fold local sampling could not be used to express the local population's elemental average and variance. The variability of the outcomes was expressed as a Qloc, which was about 0.3-0.4 in all cases.

This means that the local Hattem outcomes, build up from 5-fold sampling, may be seen as a low-quality survey, of which the variance is due to the fact that 5-fold sampling is inadequate in fully expressing the local circumstances. Here, as with the results presented in Table 2, should be noted that the real variance may be underestimated due to the fact that in initial 25 local samples the repeated (three times N=18) calculations on randomized n=5 trials may have led to overlaps.

4. CONCLUSIONS

The study was undertaken to gain more knowledge on local and survey variances, all ment to explore possibilities to judge survey quality on basis of a limited and restricted number of observations. The results indicate that the present survey data cannot be used to assess "a-priori judgement" possibilities. The present surveys comprise 5-fold local sampling, which, on basis of the data on Hattem and Delft multi-fold local sites, is not always adequate in expressing local averages and concentrations. This means that, strictly speaking, the present surveys do not permit sound judgement, it goes wrong in about 10 % of all cases. The discussion underlines the basic importance of the local sampling site in the total survey. In future set-ups, local sites and sampling strategies should be examined, aimed at the assessment of local (normal) distributions, and expressed in number of samples to be taken, sample handling and elemental analysis. Furthermore, in surveys, strict procedures and control should be agreed upon with respect to sample handling, in all cases where multiple samples are to be processed into single analysis procedures for the assessment of elemental concentrations.

5. FUTURE WORK

Future work will be focused on strategies in selecting local sites, and on local sampling; furthermore the use of clusters of nearby-sites and the effects and control of- and by (selected techniques in) interpolation will be studied.

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*TABLE 1. Element concentrations (mg/kg±SD) in tree bark (Delft, The Netherlands, n=32), in initial 32 samples, in the bootstrap-derived population, in 32 sub-samples after mixing, and in the 1 kg total mass (IRI BISNIS facility, single analysis, no SD, * = different from average after mixing)*

Element	*Bark, initial*	*Bark, bootstrap*	*Bark, mixed*	*Bark, BISNIS*
As	*0.29±0.06*	*0.29±0.05*	*0.30±0.02*	*0.21**
Ba	*527±1028*	*414±619*	*433±156*	*440*
Br	*13.3±2.6*	*13.2±2.6*	*12.6±0.3*	*12.8*
Cr	*13.1±7.3*	*13.2±6.5*	*13.9±0.8*	*14.5*
Cs	*0.06±0.02*	*0.06±0.02*	*0.06±0.01*	-
Cu	*32±5*	*32±5*	*31±5*	-
Fe	*850±220*	*850±210*	*860±23*	*808**
K	*1240±244*	*1230±277*	*1260±40*	*1300*
Mg	*666±91*	*665±93*	*675±88*	-
Zn	*60±11*	*60±10*	*61±1*	*84**

TABLE 2. Repeated (N=500) randomized sub-sampling (n=5) in local populations, and T-tests on trial with population. Outcomes are expressed in increment factors F (means and maxima) in the local variance necessary to maintain full compatibility between trial outcome and population. E= number of trials with $F \neq 1.0$. Initial local sampling was 32 for bark, and 25 both for moss and soil.

El.	F (Bark)			F(Moss)			F(Soil)		
	mean	max	E	mean	max	E	mean	max	E
As	1.34	32	33	1.20	11	42	1.13	9	25
Br	1.04	6	11	1.32	16	46	1.07	7	14
Cr	1.12	13	30	-	-	-	1.18	9	43
Cs	1.05	7	12	1.08	6	24	1.16	13	33
Cu	1.16	30	24	-	-	-	-	-	-
Fe	1.15	13	21	1.07	10	10	1.04	5	17
K	1.06	13	8	1.14	8	33	1.12	9	22
Mg	1.11	12	12	1.17	8	38	-	-	-
Zn	1.36	26	41	1.17	29	18	1.03	7	6

TABLE 3. Repeated (N=500) randomized sub-sampling (n=5 sites) in survey populations, and T-tests on trial with population. Outcomes are expressed in increment factors F (means and maxima) in the survey variance necessary to maintain full compatibility between trial outcome and population. E= number of trials with F ≠ 1.0. Initial number of sampling sites was 54 both for moss and soil.

El.	F(Moss)			F(Soil)		
	mean	max	E	mean	max	E
As	1.00	3	1	1.46	22	33
Br	1.00	1	0	1.82	16	130
Cr	1.34	7	88	1.00	1	0
Cs	1.00	1	0	1.77	56	77
Fe	1.38	10	101	1.00	1	0
K	1.56	17	70	1.34	20	50
Mg	1.00	1	0	-	-	-
Mn	1.44	9	135	1.02	5	4
Zn	1.01	3	3	1.20	6	66

TABLE 4. Signal-to-noise ratio's (Q) for moss and soil surveys (54 sites). Q_1 = Q on actual survey. Q_2 = Q on bootstrapped survey. Q_3 = Q based on a fraction of the survey's sampling sites (A= 20 % survey and 5-fold local; B = 40 % survey and 10-fold local). Q_3 determined in 500 trials. av = average, N = number of cases (out of 500 trials) that Q_3 is outside range of Q_1 ±50%.

El.	Moss survey					Soil survey				
	Q_1	Q_2	Q_3			Q_1	Q_2	Q_3		
			a / b	Av±SD	N			a / b	Av±SD	N
As	1.4	2.8	a	1.6±1.2	136	1.5	1.6	a	1.9±1.4	111
			b	1.5±0.5	78			b	1.6±0.4	34
Br	1.9	4.9	a	2.2±1.3	165	1.3	1.2	a	1.6±1.0	128
			b	2.0±0.7	76			b	1.4±0.4	56
Cr	-	-	a	-	-	2.9	6.3	a	5.2±5.3	266
			b	-	-			b	3.9±2.6	190
Cs	1.8	4.7	a	2.3±1.7	175	1.5	1.3	a	1.9±1.1	155
			b	2.1±0.9	117			b	1.6±0.6	57
Fe	4.7	3.3	a	6.4±6.8	233	2.8	4.4	a	3.8±2.9	152
			b	5.2±3.2	179			b	3.2±1.1	63
K	1.3	1.2	a	2.0±1.6	227	1.6	1.4	a	2.1±1.4	163
			b	1.5±0.7	127			b	1.8±0.8	102
Mg	1.1	2.9	a	1.4±1.2	118	-	-	a	-	-
			b	1.2±0.3	36			b	-	-
Mn	4.9	3.1	a	6.2±6.4	250	4.2	5.9	a	5.5±5.2	217
			b	5.3±2.8	147			b	4.8±2.2	136
Zn	4.2	8.3	a	4.9±3.4	105	4.6	11.6	a	8.4±13.8	247
			b	4.4±1.3	35			b	5.9±3.4	150

TABLE 5. Repeatibility calculations for moss and soil surveys. Quality Q determined for the total surveys (Q_1), for 50 % of the survey data, ensuring area coverage (Q_2, n=2), and for 30 % of the survey data, ensuring area coverage (Q_3, n=3). For Q_2, individual outcomes are presented. For Q_3, both the individual outcomes and the mean (Av) and variances (SD) are presented.

El.	Moss survey				Soil survey			
	Q_1	Q_2	Q_3	Q_3 Av±SD	Q_1	Q_2	Q_3	Q_3 Av±SD
As	1.4	1.7 1.1	1.8 1.1 1.3	1.4±0.4	1.5	1.5 1.5	1.7 1.7 1.1	1.5±0.4
Br	1.9	2.2 1.6	1.0 1.7 2.5	1.8±0.8	1.3	1.5 1.0	1.4 1.2 1.4	1.3±0.1
Cr	-	-	-	-	2.9	3.4 2.4	3.6 2.4 2.5	2.9±0.7
Cs	1.8	2.0 1.6	2.3 1.4 1.6	1.8±0.5	1.5	1.5 1.5	1.6 1.2 1.7	1.5±0.2
Fe	4.7	5.9 3.3	7.3 2.8 2.6	4.3±2.7	2.8	3.2 2.5	3.3 2.9 2.3	2.8±0.5
K	1.3	1.4 1.1	1.3 1.1 1.3	1.2±0.1	1.6	1.7 1.5	1.9 1.1 1.8	1.6±0.5
Mn	4.9	5.0 4.9	3.8 7.0 2.8	4.5±2.2	4.2	5.0 3.1	4.6 5.3 1.5	3.8±2.0
Zn	4.2	4.3 4.1	5.0 4.1 3.5	4.2±0.8	4.6	4.0 5.1	3.8 1.1 1.4	2.1±1.5

TABLE 6. Q_{sur}-values for moss and soil surveys in 30 % coverages (18 locations), expressed as Av.±SD (n=3), Q_{loc}-values, Av±SD (moss and soil) for the Hattem location (n=25 total), for which a "survey" (n=18) was three times simulated by randomly taking n=5 sub-samples, and the residual survey Q (Q_{res}, Av±SD), after correcting Q_{sur} for contributions from Q_{loc}. P-values denote outcomes of a Kolmogorov-Smirnov test on the local distributions ($P < 0.05$: the location does not have a normal distribution of elemental concentrations).

El.	*Moss survey*				*Soil survey*			
	Q_{sur}	Q_{loc}	Q_{res}	*P*	Q_{sur}	Q_{loc}	Q_{res}	*P*
Al	*3.65±2.33*	*0.37±0.03*	*3.29±2.34*	-	*0.16±0.05*	*0.41±0.04*	*-0.25±0.06*	*.00*
As	*1.38±0.39*	*0.49±0.10*	*0.89±0.41*	*.86*	*1.49±0.35*	*0.48±0.09*	*1.01±0.37*	*.51*
Au	-	-	-		*0.71±0.45*	*0.42±0.01*	*0.28±0.45*	*.01*
Cr	-	-	-		*2.86±0.66*	*0.41±0.05*	*2.45±0.66*	*.14*
Cs	*1.77±0.51*	*0.41±0.07*	*1.37±0.51*	*.61*	*1.51±0.25*	*0.47±0.13*	*1.04±0.28*	*.99*
Fe	*4.25±2.68*	*0.38±0.10*	*3.87±2.68*	*.29*	*2.82±0.52*	*0.41±0.12*	*2.41±0.53*	*.40*
K	*1.22±0.10*	*0.47±0.06*	*0.75±0.12*	*.44*	*1.61±0.44*	*0.37±0.05*	*1.24±0.44*	*.75*
Mg	*1.10±0.09*	*0.47±0.07*	*0.63±0.11*	*.99*	-	-	-	-
Mn	*4.53±2.24*	*0.44±0.03*	*4.09±2.23*	*.45*	*3.79±2.04*	*0.47±0.04*	*3.32±2.04*	*.52*
Tl	*4.44±3.65*	*0.44±0.08*	*4.00±3.65*	*.03*	-	-	-	-
V	*2.47±0.53*	*0.40±0.08*	*2.07±0.53*	*.84*	*0.24±0.04*	*0.41±0.16*	*-0.16±0.17*	*.00*
Zn	*4.19±0.75*	*0.45±0.09*	*3.75±0.76*	*.88*	*4.45±1.21*	*0.54±0.07*	*3.91±1.21*	*.18*