Arh hig rada toksikol 1999;50:31–36

REVIEW

WAGENINGEN EVALUATING PROGRAMMES FOR ANALYTICAL LABORATORIES (WEPAL)

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Received January 1998

The paper describes three of the Wageningen Evaluating Programmes for Analytical Laboratories (WEPAL). These include the analyses of numerous compounds and elements and different parameters such as inorganic chemical composition, organic matter, polycyclic hydrocarbons (PAH), polychlorinated biphenyls (PCB), organochlorine pesticides, some herbicides, heavy metals, particle size, and so on in soil, sediment, compost, manure, and sludge. One programme includes the analysis of inorganic chemical composition, nutritional values, and selected vitamins and amino acids in plant samples. Finally, the paper describes how the results are reported and statistically evaluated.

Key words:
compost, heavy metals, manure, organochlorine pesticides, plants, polychlorinated biphenyls, polycyclic hydrocarbons, sediments, sludge, soils

Quality control of analytical procedures for soils, plants, sediments, manure, compost, and sludge is of utmost importance for production of reliable and reproducible analytical data. Analytical laboratories take three levels of quality control measures. The first line control refers to certified reference materials (CRMs). However, the number and the matrix variation in CRMs for environmental analytical research are still very limited. The second line control often uses internal reference samples which, in their turn, yield questionable values for many element and parameter concentrations, as there is practically no possibility to check them with relevant CRMs. The third line control is recommended to involve laboratory-evaluating exchange programmes (ring tests). One of the reasons for the steady increase in the number of laboratory-evaluating programmes is that accredited laboratories are advised, and in some countries obliged, to participate in such programmes if available.

This paper describes the contribution of the Wageningen Evaluating Programmes for Analytical Laboratories (WEPAL) for plants, soils, sediments, manure, composts, and sludge.

Presented at the AOAC INTERNATIONAL Central Europe Subsection 5th International Symposium on Interpretation of Chemical, Microbiological and Biological Results and the Role of Proficiency Testing in Accreditation of Laboratories, Varaždin, Croatia, 21–23 October 1998.

ORGANISATION of WEPAL

As early as 1956 the Section of Soil Science and Plant Nutrition of the Wageningen University in the Netherlands started with the organisation of a worldwide laboratory-evaluating programme for determining inorganic chemical composition of dry plant materials. Since then, three other laboratory-evaluating programmes have started involving now as many as 800 laboratories in about 80 countries. Table 1 gives details about the four programmes.

The laboratories participating in the International Plant-analytical Exchange (IPE) periodically receive six and those participating in the International Soil-analytical Exchange (ISE), International Sediment Exchange for Tests on Organic Contaminants (SETOC), and International Manure and Refuse Sample Exchange Programme (MARSEP) four different dry samples for analysis. The laboratories are required to report results using report forms or special software programmes before a new period starts. The results are compiled every two or three months, just as a cycle is completed. The reports are based on the oven-dry material and a representative subsample should be used to determine the moisture content at 105 °C. Member laboratories can report results for as many parameters as they wish. The distributed samples are labelled with a number (sample 1, sample 2, etc.) and the corresponding reports identify these samples by their name and number.

Over the year, one of the distributed samples in each cycle is the same and is called *home reference sample*. Results obtained from these samples enable reproducibility ratings which are reported every year. Throughout the year, the participants receive at least 25 different plant samples and/or 10 different soil, sediment, or manure, compost, and sludge samples. This means that the distributed samples largely vary in the matrix, which is an extra advantage for the participating laboratories in the internal method evaluation.

The wide variation of distributed samples is attributed to different origins from various countries. The participating laboratories often have samples from their own country, or, on request, distribute their own internal reference samples to the schemes.

SAMPLE PREPARATION AND DISTRIBUTION

Samples are dried at 70 °C (IPE) or 40 °C (ISE, SETOC, MARSEP) and milled. The soil and sediment samples are milled until they pass a 0.5 mm sieve. The bulk samples are stored in 16-litre containers with WEPAL's automatic equipment and the content in the containers is tested for homogeneity of distribution. The container content is then distributed in sealed plastic bags containing 10 g (IPE) of the material or in sealed plastic flasks containing 20 g (MARSEP), 100 g (ISE) or 150 g (SETOC) of the sample material. The distribution process utilises a special sample divider (1) which mixes the bulk sample in a rotating drum which can contain about 60 kg of soil or sediment, or – in a separate mixer – about 5 kg of plant, manure, compost, or sludge sample. After mixing, the content of the drum is spread out on a belt in at

Table 1 *Wageningen Evaluating Programmes for Analytical Laboratories (WEPAL)*

Programme*	IPE	ISE	SETOC	MARSEP
Start (year)	1956	1988	1990	1994
Members**	220	287	104	54
Countries**	70	68	15	16
Material	Plant	Soil	Soil, sediment	Compost, manure, slugde
Pretreatment	dried at 70 °C, milled	dried at 40 °C, milled	dried at 40 °C, milled	dried at 40 °C, milled
Storage	at -20 °C	laboratory conditions; in the dark	laboratory conditions; in the dark	at -20 °C
Frequency and no. of samples	6 times a year 6 samples	4 times a year 4 samples	4 times a year 4 samples	4 times a year 4 samples
g/sample***	10 g/sample	100 g/sample	150 g/sample	20 g/sample
Fee/year******	850.00	850.00	1,500.00	1,200.00
Reported parameters	inorganic chemical composition; nutritional values (crude fibre, TDF, ADF, NDF, total ash, total fat, saccharides); Vitamin A, E, B1, B6 and D; 18 different amino acids.	total inorganic chemical composition; acid-extractable inorganic chemical composition; heavy metals after extraction with 2 M HNO_3; heavy metals after extraction with 0.1 M $NaNO_3$; heavy metals after extraction with 1 M NH_4NO_3; pH, nutrients, metals, etc. after extraction with 0.01 M $CaCl_2$; B, Ca, Cu, Fe, K, Mg, Mn, Na, P, Zn with Mehlich-3; CEC's + exchangeable cations; pH-H_2O, pH-KCl, EC, CN-total-free, CN-total-complex; particle sizes, F-total, F-water soluble, B-hot water; P-Bray, P-Olsen, loss-on-ignition, P and K with DL and CAL.	16 different polycyclic hydrocarbons (PAH); 12 different polychlorobiphenyls (PCB); 29 different organochlorine pesticides; some herbicides; AOX, EOX, CN-total-free, CN-total complex; organic matter, particle sizes; heavy metals in Aqua Regia digests; In one round per year also 8 different PCDD's and 10 different PCDF's.	total inorganic chemical composition; acid-extractable inorganic composition; loss-on-ignition; AOX.

* IPE – International Plant-analytical Exchange
ISE – International Soil-analytical Exchange
SETOC – International Sediment Exchange for Tests on Organic Contaminants
MARSEP – International Manure and Refuse Sample Exchange Programme
** Situation December 1998
*** A double portion of each sample can be ordered for an extra 70% of the fee.
**** Fee for the year 1999 (in Dutch guilders).

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least 10 rows and 10 layers. Portions of the sample are then weighed and collected in plastic bags or flasks, sealed, and labelled. The testing of every 50th sample has proved that the sample dividing process yields homogeneous subsamples (1). Concurrently, checks on the automatic equipment involved in the process are run at least 8 times a year.

REPORTS

The results are reported every two (IPE) or three months (ISE, SETOC, and MARSEP). A median and a Median of Absolute Deviations (MAD) are calculated from all received data. Data showing high deviation are marked by two asterisks (**). The calculation of the second median excludes the data marked by two asterisks. Data showing high deviation from the second MAD are marked with one asterisk (*). This MAD is an indication of the spread of the reported values; it is more resistant to outliers than the average (2). This allows every participating laboratory to compare results with other laboratories. Values marked by asterisks usually differ significantly from the values reported by others. Yet, the absence of (marked) significantly different results does not mean that the analytical process is perfect. The results may systematically lie above or below the mean or median. A »quality control chart« serves to check such possibility. This is why the Z-score of the participant's values is included in the periodic reports. The Z-scores are calculated as follows:

$$\text{Z-score} = \frac{X - X_{mean}}{\text{standard deviation}}$$

Standard deviation values may be those taken from the exchange programme, or those that are found acceptable. The latter may be stricter than the generally larger standard deviations that are characteristic of ring tests. The Z-values are usually assessed as follows:

$|Z| < 2$ – situation satisfactory
$2 < |Z| < 3$ – situation unsatisfactory
$|Z| > 3$ – situation critical

In addition to the periodic reports, year reports published data collected throughout a year and consist of four sections. The first section groups the data according to the element or parameter and organises them in columns. The first group of columns shows all results as received, the second group of columns shows results without outliers marked with two asterisks, and the third group of columns excludes all asterisk-marked outliers. In many cases, data in the last group of columns can be viewed as the best estimates of the true value. This last set of data enters the second part of the year report, in which all data are grouped per sample. The second part of the year report makes the basis of sample reference values. The third part of the year report gives median and MAD calculations of the so-called home reference sample for

each laboratory, element, or parameter, and gives an indication of the reproducibility of the individual analytical data. The report for last quarter of the year totals the score of deviations (marked by either one or two asterisks) for each laboratory and parameter.

WEPAL'S POTENTIAL IN TERMS OF NATIONAL AND INTERNATIONAL QUALITY CONTROL OF ANALYTICAL LABORATORIES

The potentials of the WEPAL can be summed up as follows:

- Participation of laboratories in one or more WEPAL programmes enables each individual laboratory to compare its analytical data with those of other laboratories worldwide;
- On request, WEPAL programmes may include special national and/or international standardised analytical procedures. Results collected through the WEPAL programmes are open to participant laboratories for discussion at regularly held meetings which may be attended by a WEPAL representative;
- Since all accredited laboratories shall have to participate in the round-robin tests in the near future, WEPAL offers that possibility for many matrices. Only with the permission of individual laboratories shall the data scored in the WEPAL be used by an accrediting body for regular evaluation of the laboratories' analytical performance;
- WEPAL has the possibility to produce or make available valuable reference materials of different origin, matrix, and composition.

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Sažetak

WAGENINGENSKI PROGRAMI ZA EVALUACIJU ANALITIČKIH LABORATORIJA

Opisana su četiri Wageningenska programa za evaluaciju analitičkih laboratorija (Wageningen Evaluating Programmes for Analytical Laboratories – WEPAL). Tri programa uključuju analize brojnih spojeva i elemenata i određivanje raznih parametara – na primjer sadržaj anorganskih komponenata, sadržaj organske tvari, policiklični aromatski ugljikovodici (PAH), poliklorirani bifenili (PCB), organoklorni pesticidi, neki herbicidi, teški metali, veličina čestica itd. – u tlu, sedimentu, kompostu, gnojivu i mulju. Jedan program obuhvaća analize sadržaja anorganskih komponenata, sadržaj nekih vitamina i aminokiselina te nekih nutritivnih vrijednosti u uzorcima biljaka. Opisan je način izvještavanja rezultata i statističke evaluacije rezultata.

Ključne riječi.
biljke, gnojivo, kompost, mulj, organoklorni pesticidi, policiklički ugljikovodici, poliklorirani bifenili, sedimenti, teški metali, tla

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