Environmental Sampling for Trace Analysis

Edited by Bernd Markert

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Editor:
Prof. Dr. Bernd Markert
Internationales Hochschulinstitut Zittau
Markt 23
D-02763 Zittau

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of trace substances on the "xerothermic hills" near Würzburg, F.R.G..

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Preface

Environmental analysis has entered a phase which is difficult to describe precisely because of its meteoric development. The advent of more and more modern systems of instrumental analysis now makes it possible to penetrate areas of ecology and ecotoxicology that would have been considered inaccessible a few years ago. Trace analysis and ultra-trace analysis of individual substances, in particular, have proved to be a useful dynamo for new scientific findings. One example is the development of possible concentration and action models for specific dioxin molecules which it would have been impossible to investigate without highly efficient analytical procedures. In addition to detecting lower and lower concentrations, such highly sophisticated measuring equipment has the important advantage of opening up totally new fields of work. Procedures such as multielement analysis, chemical fingerprinting and non-target screening are already familiar to many laboratories and will continue to pave the way for trendsetting research strategies.

But orientation towards more and more efficient analytical methods also involves a risk that is all too easily overlooked. Too little attention is often given to analytical steps before and after actual instrumental measurement – sampling and the preparation of specimens, for example – because the measuring work itself is the focus of interest. Representative sampling, especially, has not kept pace with the development of increasingly sensitive analytical systems. Today it has to be said that the greatest error in the overall result of the analytical process is usually caused by improper sampling.

This development becomes obvious when we compare the almost uncountable number of publications on the measurement of any arbitrary substance X in sample Y with the small number of scientific publications dealing with careful representative sampling suitable for trace and ultra-trace analysis. The ratio of publications is probably somewhere around 1000 : 1.

The reason for this development is clear. First of all, sampling is only a small step in the overall process of analysis and one that is unlikely to produce any "spectacular" data for a subsequent discussion of the overall result. This means that sampling is all too easily dismissed as uninteresting. Secondly, the equipment it requires is often less expensive than the apparatus needed for the instrumental measurement itself. In many cases a rigid PVC spade is all that is needed to acquire a soil specimen, so that manufacturers do not at once consider it lucrative to orient their product range towards sampling systems. Sampling as a field of work in its own right is therefore very quickly deemed unattractive from both the scientific and the commercial point of view. So it is not surprising that progress towards quality control in representative environmental sampling lags far behind that in actual instrumental measurement, where remarkable steps towards "true data" have

been made as a result of precise definition of the terms accuracy, reproducibility or concentration-dependence of the accuracy of the analytical results ("Horwitz Trumpet"), and the production of suitable reference materials. The results are serious: the data from individual study groups cannot be compared with each other; harmonization of research in the various fields, so often demanded, is difficult to achieve even at the stage where the data are generated.

A further problem is that the *first* principle of sampling, namely that "the sample taken from the system should have exactly the same chemical composition as the original material" cannot be followed even approximately in the field. It should never be forgotten that environmental processes are continuous in terms of space and time. Watercourses, for example, demonstrate most plainly that sampling has to be carried out in a time/space continuum if the findings are to be relevant. Many investigations, even recent ones, fail to take this into account sufficiently. In order to achieve meaningful and comparable results in respect of the current state of the environment it is necessary to develop standards for sampling similar to those that already exist in Germany for the water, sewage and sludge sector (German Standard Procedure for Water, Sewage and Sludge Analysis). By developing suitable guidelines at a national and, still more important, at an international level it must then be ensured that the *second* and *third* principles of sampling can be implemented. These are: "The probability of being selected from a total population must be equal for each individual", and "the amount of work required for sampling increases with the degree of dispersion of the individuals and the number of such individuals".

One must, however, bear in mind that practical difficulties during the actual sampling process make it virtually impossible to follow the first two principles. A sample taken out in the field can never have exactly the same chemical composition as the original material; at best it will be very similar. One of the reasons is that often only a tiny fraction of the original material is actually analyzed (e.g., 100 mg of 100 kg of leaves from a forest ecosystem). The initial content of the material can be altered by contamination or volatilization of individual constituents while the sample is being taken and during transportation. Moreover, it is scarcely possible to give each individual the same likelihood of being selected when such individuals are diffusely distributed over the ecosystem. The objective must rather be to come as close as possible to the first two principles by means of a carefully prepared sampling strategy. Some practical, basic rules may be helpful here:

- Avoid contaminating the sample in any way with the equipment used, the containers, or by the person taking the sample.
- Avoid any volatilization of chemical compounds as a result of microbial activity, absorption by the walls of the vessels in which the samples are kept or overheating of the samples during transportation and storage.
- Take reasonably large samples, provided that there is enough material in the system and this is not subject to the nature conservation laws.
- Take account of seasonal fluctuations in the composition of the original material and other parameters affecting its overall composition such as temperature, humidity, light etc.

The aim of this book is to provide an overview of the techniques commonly used at present for taking many different kinds of environmental samples. Because of the host of different environmental samples a selection had to be made, which was painful in some cases but unavoidable in view of the limited printing capacity. The subject of human samples has been left out completely, for it is a domain of the medical profession and analysts with the relevant training. In water sampling emphasis has been put on fresh water; the sampling of "wet depositions" such as rain and snow has not been included, for excellent monographs already exist in this field. Most animals have also had to be excluded. Only ants are used as an example of how sampling might be conducted. The editor was not authorized by the Federal Office of the Environment to publish even an extract from the sampling guidelines of the "Environmental Specimen Programme" of the Federal Ministry for Research and Technology. This is a pity, especially with respect to long-term investigations, for the results are important and valuable. It remains to be hoped that these Standard Operating Procedures of the Federal Office of the Environment will soon be made accessible to a wide circle of readers in the form of a monograph.

No attempt has been made to standardize the terminology used in sampling. The reason is that there is still a great need to establish unequivocal technical terms, especially in German and American English.

In spite of the deficiencies of this book the editor and the authors agree that together they have been able to reflect the state of the art in a field which will have to undergo much more intensive development in the future.

Again, this book would not have been come about if friends and associates had not created the scope necessary for its realization, from the initial idea to the finished product. The central figures were of course the authors, who once again succeeded in submitting, amending and improving the manuscripts within a year in spite of their numerous other commitments. The suggestions for improvements came from a multitude of associates in Germany and abroad and from my employees and associates at the GKSS Research Centre, Geesthacht. I was motivated not least by Mrs Vera Weckert of the study group on systems research at the University of Osnabrück, who missed no opportunity of urging me on and encouraging me in difficult phases. I also wish to thank VCH Publishers, especially Dr. Kraus, and Wirt.-Ing. Hans-Jochen Schmitt, for their generous and friendly assistance.

The editor and the authors hope that the book will be disseminated widely and that the problems it discusses will be examined closely; they themselves will be pleased to listen to constructive criticism.

Magdeburg, January 1994 Bernd Markert

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Outline

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List of Contributors

Dr. Sarolta Büttner
Department of Botany and Plant Physiology
Agricultural University
Páter Karoly u. 1
H-2103 Gödöllö
Hungary

Prof. Dr. Judith C. Chow
Desert Research Institute
University of Nevada System
Energy and Environmental Engineering Center
5625 Fox Avenue
P.O. Box 60220
Reno, NV 89506
U.S.A.

Dr. Ursula M. Cowgill
Department of Environmental,
Population and Organismic Biology
University of Colorado at Boulder
P.O. Box 1327
Carbonale, CO 81623
U.S.A.

Dr. Gerd Crößmann
Landwirtschaftliche Untersuchungs- und
Forschungsanstalt
Postfach 5480
Nevinghoff 40
D-48147 Münster
F.R.G.

Dr. Zsolt Csintalan
Plant Physiology Section
Department of Botany and Plant Physiology
Agricultural University
H-2103 Gödöllö
Hungary

Dr. Elie M. Dick
ISCO Environmental Division
531 Westgate Boulevard
Lincoln NE 68528-1586
U.S.A.

Dr. Rumiana Djingova
Faculty of Chemistry
University of Sofia
1, J. Bouchier Blvd.
BG-1126 Sofia
Bulgaria

Prof. Dr. W. H. O. Ernst
Department of Ecology and Ecotoxicology
Faculty of Biology
Vrije Universiteit
De Boelelaan 1087
NL-1081 HV Amsterdam
The Netherlands

Prof. Dr. Otto Fränzle
Geographisches Institut der
Christian-Albrechts-Universität zu Kiel
Ludewig-Mayn-Str. 14
D-24118 Kiel
F.R.G.

Dr. Ernô Führer
Forest Research Institute
Paprét 17
H-9400 Sopron
Hungary

Dr. Eric Fujita
University of Nevada System
Energy and Environmental Engineering Center
5625 Fox Avenue
P.O. Box 60220
Reno, NV 89506
U.S.A.

Dr. Helmut Guhr
Institute for Inland Water Research
GKSS Research Centre
Am Biederitzer Busch 12
D-39114 Magdeburg
F.R.G.

Mrs. Susanne Hannappel
Department of Analytical Chemistry
Institute for Inland Water Research
GKSS Research Centre
Gouvernementsberg 1
D-39104 Magdeburg
F.R.G.

Dr. Peter Hoffmann
Fachgebiet Chemische Analytik
Fachbereich Materialwissenschaft
Technische Hochschule Darmstadt
Hilpertstr. 31
D-64295 Darmstadt
F.R.G.

Dr. Ranjith Jayasekera
Department of Botany
University of Kelaniya
Kelaniya
Sri Lanka

Dr. László Kaszab
Department of Botany and Plant Physiology
Agricultural University
Páter Karoly u. 1
H-2103 Gödöllö
Hungary

Prof. Dr. Helmut Klapper
Institute for Inland Water Research
GKSS Research Centre
Am Biederitzer Busch 12
D-39114 Magdeburg
F.R.G.

Prof. Dr. Margit Kovács
Department of Botany and Plant Physiology
Agricultural University
Páter Karoly u. 1
H-2103 Gödöllö
Hungary

Prof. Dr. Günther Kraft
Hans-Thoma-Str. 6
D-61476 Kronberg/TS 1
F.R.G.

Dr. Ivelin Kuleff
Faculty of Chemistry
University of Sofia
1, J. Bouchier Blvd.
BG-1126 Sofia
Bulgaria

Dr. Vambola Maavara
Institute of Plant Protection
Estonian Agricultural University
Riia 12
EE-2400 Tartu
Estonia

Prof. Dr. Bernd Markert
Lehrstuhl für Umweltverfahrenstechnik
Internationales Hochschulinstitut Zittau
Markt 23
D-02763 Zittau
F.R.G.

Dr. Ants Martin
Institute of Plant Protection
Estonian Agricultural University
Riia 12
EE-2400 Tartu
Estonia

Dr. Theodor W. May
Gesellschaft für Organisation und Entscheidung
Apfelstraße 119
D-33613 Bielefeld
F.R.G.

Mr. Zoltan Nagy
Plant Physiology Section
Department of Botany and Plant Physiology
Agricultural University of Gödöllö
H-2103 Gödöllö
Hungary

Dr. James E. Norris
BCM Engineers Inc.
P.O. Box 1784
Mobile, AL 36633-1784
U.S.A.

Dr. Norbert Nothbaum
Institut für Didaktik der Mathematik
Universität Bielefeld
Universitätsstraße
D-33615 Bielefeld
F.R.G.

Prof. Dr. Pekka Nuorteva
Department of Environmental Protection
University of Helsinki
Caloniuksenkatu 6 C 64
SF-00100 Helsinki
Finland

Mr. Ahto Oja
Department of Environmental Protection
University of Helsinki
PB 27
SF-00014 Helsinki
Finland

Mr. Andreas Paetz
Deutsches Institut für Normung
Burggrafenstr. 6
D-10772 Berlin
F.R.G.