REGIONAL SEAS

UNITED NATIONS ENVIRONMENT PROGRAMME OCTOBER 1988

Guidelines for the determination of selected trace metals in aerosols and in wet precipitation

Reference Methods For Marine Pollution Studies
No. 42 (draft)

Prepared in co-operation with

WMO IAEA

UNEP 1988

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PREFACE

The Regional Seas Programme was initiated by UNEP in 1974. Since then the Governing Council of UNEP has repeatedly endorsed a regional approach to the control of marine pollution and the management of marine and coastal resources and has requested the development of regional action plans. The Regional Seas Programme at present includes ten regions and has over 120 coastal States participating in it. (1), (2)

One of the basic components of the action plans sponsored by UNEP in the framework of the Regional Seas Programme is the assessment of the state of the marine environment and of its resources, and of the sources and trends of the pollution, and the impact of pollution on human health, marine ecosystems and amenities. In order to assist those participating in this activity and to ensure that the data obtained through this assessment can be compared on a world wide basis and thus contribute to the Global Environment Monitoring System (GEMS) of UNEP, a set of Reference Methods and Guidelines for marine pollution studies are being developed and are recommended to be adopted by Governments participating in the Regional Seas Programme.

The methods and guidelines are prepared in co-operation with the relevant specialized bodies of the United Nations system as well as other organizations and are tested by a number of experts competent in the field relevant to the methods described.

In the description of the methods and guidelines the style used by the International Organization for Standardization (ISO) is followed as closely as possible.

The methods and guidelines, as published in UNEP's series of Reference Methods for Marine Pollution Studies, are not considered as final. They are planned to be periodically revised taking into account the development of our understanding of the problems, of analytical instrumentation and the actual need of the users. In order to facilitate these revisions the users are invited to convey their comments and suggestions to:

Marine Environmental Studies Laboratory
International Laboratory of Marine Radioactivity
International Atomic Energy Agency
c/o Musee Oceanographique
MC98000 MONACO

which is responsible for the technical co-ordination of the development, testing and intercalibration of Reference Methods.

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(1) UNEP: Achievements and planned development of the UNEP's Regional Seas Programme and comparable programmes sponsored by other bodies. UNEP Regional Seas Reports and Studies No. 1 UNEP, 1982.

(2) P. HULM: A Strategy for the Seas. The Regional Seas Programme: Past and Future UNEP, 1983.

This draft issue of the Reference Method for Marine Pollution Studies No. 42 was prepared in co-operation with the World Meteorological Organisation (WMO) and the International Atomic Energy Agency (IAEA). It includes comments received from a number of scientists who reviewed and tested the method. The assistance of all those who contributed to the preparation of the draft issue of this reference method is gratefully acknowledged.

CONTENTS

1. SCOPE AND FIELD OF APPLICATION

This publication describes sampling and analytical procedures suitable for the collection and analysis of representative samples of atmospheric aerosols and wet precipitation for selected trace metals.

2. REFERENCES

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3. PRINCIPLES

Most trace metals exist in the atmosphere associated with very fine particulate matter. Mercury is an important exception, being present in the atmosphere mainly in a gaseous form. The particulate matter in the atmosphere ranges in size from 0.1 μm to about 10 μm, though particles larger than 2 μm tend to settle out rapidly under gravity and hence are rare away from immediate sources. Many of the trace metals of interest (e.g., Pb, Zn, Cu, Cd) are found predominantly associated with the finer fractions of aerosols except very close to sources. Crustal material such as clays tends to be associated with somewhat coarser particles as is also the case for sea-salt.

Particles are removed from the atmosphere by wet and dry deposition. For large dense particles, dry deposition is the dominant removal process, and hence dominates close to sources. Away from sources the relative importance of wet deposition increases due to the slow gravitational settling (and hence inefficient dry deposition) of fine particles. Dry deposition rates are usually estimated from the atmospheric particulate concentrations and a term called the dry deposition velocity. Wet deposition rates are measured directly via sampling of precipitation. This precipitation includes particles scavenged from the atmosphere both in clouds and below clouds. Some of the particles, such as sea-salt, are readily soluble while others, such as clay particles, are relatively insoluble. In practice there will be a range of particles and solubilities with factors such as rainwater acidity and mode of formation controlling the balance. In this method, the presence of particulates in precipitation is recognised, though the samples are generally analysed without separation of particulate and dissolved components.

Sampling of precipitation may be achieved both manually and automatically. Manual collection equipment consists essentially of a funnel and collection bottle. An automatic precipitation collector includes a cover which covers the sample container during dry periods but which moves away automatically during precipitation to allow sample collection. Rigorous precautions are necessary for the preparation and deployment of sampling equipment to prevent contamination of the sample. Collection periods vary with the aims and scale of a survey together with the resources available, though daily sampling is preferable.

Suspended particulate matter is sampled by passing volumes of air through a filter. Sampling systems divide into high and low volumes with the choice being governed by ambient concentrations, sampling times and resources. As for precipitation, great care is necessary to avoid contamination of the samples. After collection, samples are dissolved by acid digestion. Both precipitation and digested particulates are generally analysed by graphite furnace atomic absorption spectrophotometry (GFAAS). In areas with unusually high atmospheric trace metal concentrations, a flame atomic absorption spectrophotometer may have sufficient sensitivity for the analysis. Increasing the volume of air sampled or pre concentration of the rainwater sample may also allow a flame atomic absorption spectrophotometer to be used. Alternative measurement methods are available (see section 8).

The methods presented here are applicable to most trace metals. Minor modifications are required for the analysis of mercury and these are noted. However, this method is concerned with atmospheric particulates and precipitation, and it should be noted that the bulk of the mercury in the atmosphere is present as a gas.

As noted above, the concentrations of trace metals in precipitation and aerosols in areas away from major sources are low requiring considerable care in collection and analysis of samples. To illustrate this, Tables 1 and 2 present a compilation of some recently reported aerosol and precipitation data for some trace metals. These samples have been collected with great care and probably are representative of the range of values likely to be encountered. In these tables the distinction between rural and remote is arbitrary but is generally between populated areas away from urban centres and essentially unpopulated areas.

Table 1: Trace metal concentrations in precipitation from rural and remote area ($\mu g\ l^{-1}$)*

	rural	remote
Cd	0.04-0.7	0.002-0.093
Cu	1.4-24	0.013-1.8
Pb	3.0-15	<0.04.-2.4
Mn	1.3-6.8	0.01-5.4
Ni	0.8-17	0.2-0.7
V	0.4-1.0	0.02-1.0
Zn	4-50	0.05-12

*Adapted from Barrie et al., 1987.

Table 2: Trace metal concentrations in aerosols from rural and remote areas (ng/m^3)*

	rural	remote
Cd	0.1-22	0.005-0.4
Cu	0.5-110	0.014-3.3