Abstract  In view of its intended use as a sample for proficiency testing or as a reference material the stability of the extractable trace element contents of a soil from an irrigation field was tested using the extraction with 1 mol/L ammonium nitrate solution according to DIN 19730. Therefore, changes of the extractability of sterilized and non sterilized soil samples stored at different temperatures were evaluated over a period of 18 months. Sets of bottles were kept at –20 °C, +4 °C, about +20 °C and +40 °C, respectively. The NH₄NO₃ extractable contents of Cd, Cr, Cu, Ni, Pb and Zn were determined immediately after bottling and then after 3, 6, 12 and 18 months with ICP-AES or ETAAS. Appropriate storage conditions are of utmost importance to prevent deterioration of soil samples prepared for the determination of NH₄NO₃ extractable trace element contents. Temperatures above +20 °C must be avoided. The observed changes in the extractability of the metals (especially for Cr and Cu) most likely could be related to thermal degradation of the organic matter of the soil. There is no need to sterilize dry soil samples, because microbiological activity in soils with a low moisture content appears to be negligible with regard to trace element mobilization.

Introduction

The German Federal Soil Protection Act (BBodSchG) [1] establishes conditions for effective soil protection and remediation of contaminated sites in Germany. Risk assessment criteria and methods for the determination of environmentally harmful substances are fixed in the German Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV) [2]. The extraction with 1 mol/L ammonium nitrate solution (German standard DIN 19730) [3] is one of the requested extraction procedures.

The use of (certified) reference materials is a widely recognized tool to verify the accuracy of analytical techniques. Together with the participation in proficiency testing schemes it represents an essential element of quality control systems used, e.g. in accreditation schemes. Because of the lack of suitable reference materials (RMs) for the extraction with ammonium nitrate solution the analytical laboratories applying this procedure have problems to assess their performance.

In the preparation of RMs, several requirements have to be taken into consideration [4–6]. They include the representativeness of the samples, their homogeneity and stability. Stability studies described by Houba et al. [7] and Quevauviller et al. [8] showed that soil samples for certification purposes using extractants like 0.01 mol/L CaCl₂, 0.05 mol/L EDTA or 0.005 mol/L DTPA should be stored at low temperatures. The observed changes in the extractability of trace elements with storage time and increasing temperature appear to be caused by changes in the status of the organic matter.

The aim of our investigation was to evaluate changes of the NH₄NO₃ extractable trace element contents of soil samples stored under different conditions. Some samples of the test material were exposed to elevated temperatures (e.g. +40 °C) that are expected to accelerate any process of modification or degradation.

Besides thermal degradation, microbiological action is the most likely mechanism for alteration of soil samples. For materials that are to be utilized for element determination, the sterilization by γ-irradiation is widely used to destroy microorganisms like bacteria and fungi. In this study, storage of sterilized and non sterilized samples under extreme conditions is compared to storage at lower temperatures for a period of 18 months. Inductively coupled plasma atomic emission spectrometry (ICP-AES) and electrothermal atomic absorption spectrometry (ETAAS) were used for the determination of the trace elements in the extracts. Moreover, measurements of the microbiological activity of the soil samples were performed.
Experimental

Sample preparation

A sandy soil with a very high content of organic matter (total organic carbon content: 20%; loss on ignition at 550 °C: 46%) was used. The soil was taken from the A-horizon of an irrigation field near Berlin. The material was air-dried at ambient temperature (about 20 °C) involving the manual crushing of lumps and removal of stones and plant or wood pieces. Subsequently, the material was passed through a 2 mm sieve discarding the fraction > 2 mm. The soil fraction ≤ 2 mm was blended and split into two sub-batches. One batch was sterilized by γ-irradiation (60Co source, dose: 27.9 kGy) to destroy the microorganisms, the other part remained untreated. Both batches were separately homogenized by cross-riffing [9] using a spinning riffer. The soil was bottled in portions of approximately 20 g in brown glass bottles with tightly closing screw caps for single use. The content of dry matter was determined at 105 °C according to DIN ISO 11465 [10] to be 93.8%. The homogeneity of the prepared samples between individual units (between-bottle homogeneity) was verified and was found to be satisfactory for the intended use.

Stability study

Equal numbers of bottles with sterilized and non-sterilized soil samples were stored at –20 °C (freezer), +4 °C (refrigerator), room temperature (about 20 °C) and +40 °C (laboratory drying oven). From each of these batches four soil samples were extracted with 1 mol/L ammonium nitrate solution immediately after bottling (storage time = 0) and then after 3, 6, 12 and 18 months, respectively.

Extraction procedure

According to DIN 19730 a 20 g sample of soil was extracted with 50 mL 1 mol/L ammonium nitrate solution for 2 h on a mechanical end-over-end type shaker rotating at about 20 rpm. After settling of the undissolved residue the supernatant solution was filtered through a 0.45 µm cellulose acetate membrane filter. The filtrate was acidified with 500 µL nitric acid (Merck Suprapur, Darmstadt, Germany) and used for analysis. Blank extractions without soil were carried out for each set of analysis.

Ammonium nitrate (p.a.) was obtained from Merck. All apparatus was washed with acid and deionised water, and reagents were checked for purity.

Analytical techniques

ICP-AES. For the determination of Cd, Cu, Ni, and Zn a Perkin-Elmer (Überlingen, Germany) Optima 3000 instrument with an Echelle spectrometer and a segmented-array, charge-coupled device detector (SCD) was applied. The Perkin-Elmer AS-90 autosampler was used for automated sample handling. The instrument was operated under normal conditions with a plasma argon flow of 15 L/min, an auxiliary gas flow of 0.5 L/min and a nebulizer gas flow of 0.8 L/min. The RF-power was set to 1300 W and the observation height was 15 mm above the load coil. The plasma conditions can be characterized as being ‘robust’ to minimize interference effects [11]. The sample uptake rate through the GemTip Cross-Flow nebulizer was set to 1.0 mL/min. The integration time varied automatically between 5 s and 10 s. All data intensities read from the detector were processed in the peak area mode. Yttrium was used as internal standard.

The following spectral lines were used: Cd 214.438 nm, 226.502 nm; Cu 327.396 nm; Ni 231.604 nm; Zn 202.548 nm, 206.200 nm; Y 371.030 nm.