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CHEMICAL ASPECTS OF THE COLLECTION AND EVALUATION OF DATA ON THE QUALITY OF GROUNDWATER

D.L. MILES and J.M. COOK

Hydrogeology Unit, Institute of Geological Sciences, Wallingford, Oxon OX10 8BB, UK

ABSTRACT

The operations typically involved in the acquisition and evaluation of data on the chemical composition of groundwater are critically reviewed. They are grouped into four main interdependent stages: on-site measurement and sample collection; sample storage; laboratory analysis; and data interpretation. Factors which can affect the accuracy and precision of chemical data are highlighted.

INTRODUCTION

Data on the chemical composition of groundwater may be collected for many purposes, including: water quality monitoring, pollution studies, resource evaluation and fundamental hydrogeochemical investigations. Thus the type and quantity of chemical data required in groundwater investigations will vary widely. However, certain unifying principles can be identified within the overall philosophy of data acquisition and interpretation. Four interdependent stages may be defined: sample collection and on-site measurement, sample storage, laboratory analysis, and data interpretation. These are illustrated in Figure 1 with reference to the collection of data on the inorganic chemical composition of groundwater. This paper aims to highlight factors which, during the first three stages, may contribute to, or detract from, the precision and accuracy of those data.

SAMPLE COLLECTION AND ON-SITE MEASUREMENT

Strategy

Throughout all the stages involved in data acquisition, the overall aims of the particular project within which the data will be utilised should be actively considered. Chemical data should rarely be collected in isolation and full account should be taken at a very early stage in any investigation of all relevant hydrogeological information. In addition to the obvious constraints imposed by spatial and temporal considerations on sampling frequency, factors such as the logistics of sample collection and storage and, in particular, the requirements of the analytical methods which will be applied to the samples subsequently should play a major role in determining the overall sampling strategy.

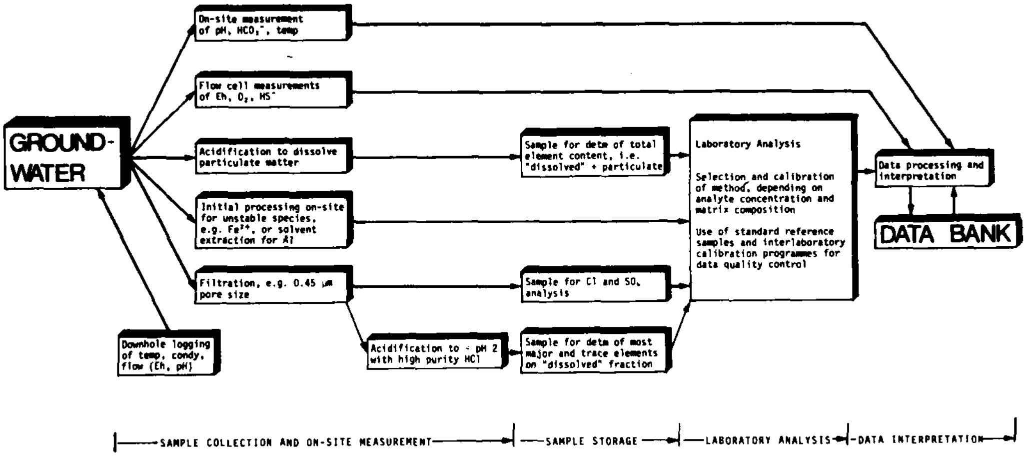

Fig. 1. Flowchart showing the operations typically involved in the collection of inorganic chemical data on groundwater. These are grouped into the four main stages of: sample collection and on-site measurement, sample storage, laboratory analysis,data interpretation.

On-site measurement

Parameters such as pH, Eh, alkalinity and dissolved oxygen, which may be prone to rapid change when groundwater is subjected to alterations in its physicochemical environment, are typically measured on-site using portable equipment (Ref. 1). The limitations of these data are those associated more with practical execution than theoretical concepts. Both precision and accuracy may suffer as a result of the very real difficulties encountered in carrying out, under field rather than laboratory conditions, even the very simple manipulations involved. Rigorous evaluation of equipment reliability under realistic conditions is vital and should be undertaken prior to any major investigation to identify those systems which, contrary to their manufacturers' claims, do not function satisfactorily. Accuracy may be further degraded by the lack of stability of calibration solutions or their inadvertant contamination under adverse working conditions. Wherever possible, some form of quality control should always be instituted for on-site measurements.

Sample collection

Painstaking implementation of a carefully planned sampling strategy is of paramount importance. Data from the most extensive and accurate analyses are worthless if the samples do not represent the waters under investigation. In addition, sample collection techniques must be reconciled with the requirements of the analytical methods used subsequently.

The potential influences of sampling procedures *per se* on sample collection are broadly those of: contamination from collection apparatus, modification of the chemical form of some constituents, and loss by adsorption. Different procedures are usually required for different groups of constituents, e.g. collection techniques and equipment suitable for waters to be analysed for, say, Na or SO_4 at a level of 10-1000 mg l^{-1} may not be appropriate for samples where Cu is to be determined at a concentration of 1-10 µg l^{-1}, or for low Eh waters on which ferrous iron is to be measured.

A fundamental decision to be taken is whether filtered or unfiltered samples are to be collected. Filtration introduces the possibility of contamination from equipment or loss of some ions by adsorption, and raises the question of the physicochemical interpretation of terms "dissolved" and "particulate". It is common practice in groundwater investigations to pass samples through a filter with pores having a nominal diameter of 0.45 µm, but it must be stressed that the choice of this particular pore size is arbitrary and reference to that material passing through it as "dissolved", purely convention. The data of Kennedy *et al* (Ref. 2) have particular implications for the investigation of groundwaters from unconsolidated sediments, upon which this Symposium is focussed. Concentrations of Al, Fe, Mn and Ti were found to vary by up to an order of magnitude, depending on whether 0.45 µm or 0.1 µm filters were used in the filtration of samples containing suspended clay minerals. In addition, levels of metal in the filtrates were affected markedly by the degree of clogging as filtration proceeded. Filters of different types but nominally the same pore size have been shown to produce filtrates in which metal levels differed significantly (Refs 3-4). Clearly, data on the concentration of various species "in solution" in groundwater which are based on an operational distinction between dissolved and colloidally dispersed or particulate matter may be useful and acceptable for some applications, but are of limited value in, for example, thermodynamic calculations.

The use of metal filtration apparatus should be avoided where trace elements are to be determined (Ref. 5). Contamination may be further minimised by leaching filters and equipment with dilute, high purity acid (Refs 6-9). Losses by adsorption during filtration have been recognised for several elements (Refs 10-11).

Where data on potentially unstable species are required, immediate partial processing of the water on-site is necessary to convert the analyte to a form in which it may be stored for a limited period prior to laboratory analysis. This is essential in the measurement of ferrous iron (Ref. 12); solvent extraction on-site has been used in the determination of mononuclear aluminium (Refs 13-14).

The process of sample collection can thus influence significantly the reliability and applicability of data on the chemical composition of groundwater. Although guidance from the literature should be sought, the precise sampling procedures and equipment to be used for a particular investigation should, wherever possible, be tested in detail so that any effects can be minimised or quantified.

SAMPLE STORAGE

The potential effects on chemical data of contamination or loss of analyte by adsorption onto equipment surfaces apply as much to sample storage as sample collection. The main areas of concern are the materials from which the sample containers are constructed, the purity of any reagents added to samples, and the pH conditions under which samples are stored. Further problems arise for those species, such as nitrate and phosphate, which are biologically labile (Refs 15-18).

For most major constituents of groundwater (>1 mg l^{-1}) well washed and rinsed containers should be used and the pH adjusted to $\simeq$pH 1-2 by the addition of high purity HCl or HNO_3. Separate samples for NO_3, Cl and SO_4 determination may be stored unacidified depending on the requirements of the analytical method used subsequently.

However, where trace element data are sought, sample storage is much more critical. Glass should be avoided, except where Hg analysis is involved, and only plastic containers used. These must be thoroughly cleaned by leaching with acid before being brought into use; levels of contamination to be expected from different types of plastic together with appropriate cleaning procedures have been reported (Ref. 19). Polycarbonate should be avoided for long-term storage because of its high permeability to water vapour (Ref. 20).

Adsorption effects depend very much on the particular ion under investigation, the precise nature of the container material and any treatment it has received prior to coming into contact with the sample. Detailed examination of specific storage conditions is therefore recommended (Refs 10, 21-28).

LABORATORY ANALYSIS

The aim of the laboratory analysis should be to generate data which reflect accurately and precisely the chemical composition of the groundwater samples. Points to be considered are: individual analyte concentration relative to overall sample composition; laboratory environment with respect to sample handling and possible contamination; selection of analytical method; and data quality control.

Contamination from the laboratory atmosphere can be a significant hazard, particularly in trace metal analysis, but may be minimised by good laboratory design and the use of clean-room facilities (Refs 20, 29-31). Certain common items of equipment, such as pH electrodes (Ref. 32), and plastic micropipette tips (Refs 33-35), are potential sources of contamination. All solutions should be prepared with high purity water (Ref 36) and, at regular intervals, reagent blanks should be carried through the complete analytical procedure.

The selection of a particular analytical technique from the wide choice of methods applicable to groundwater (Refs 12, 37-41) will be governed by several factors, including. the physicochemical form and approximate concentration of each analyte; the concentration of other ions; the quality and quantity of data required, and the available analytical facilities and personnel. For a given element, the exact

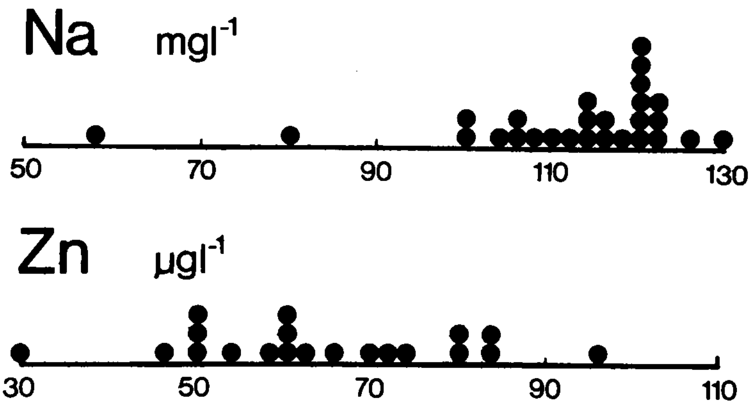

Fig. 2. Values for Na and Zn in a Triassic Sandstone groundwater reported by laboratories participating in a collaborative analysis programme. The mean values and RSDs are: Na 112.6 mg/l, 13.7%; Zn 64.8 μg/l, 24.7%.

chemical species that an analytical method will detect has a direct bearing on the data ultimately generated. For example, colorimetric methods for the analysis of silicon will tend to respond to reactive Si only, whereas atomic spectroscopic methods will detect total Si. The preconcentration techniques typically used in trace element analysis can strongly influence the final measured values by selectively concentrating certain analyte fractions relative to others (Refs 42-43). Potential interferences from other components of the sample must be assessed for each method. Reliable calibration standards are an essential prerequisite for accurate analysis and their composition should be checked regularly (Ref. 44).

Certain straightforward tests should be applied to analytical data routinely within a laboratory to act as preliminary indicators of potential sources of error. The calculation of ionic charge balance is a simple example. For groundwaters of moderate TDS, the difference between the sums of the major cations and anions expressed as a percentage of the total ionic concentration should typically be less than ±3%; higher values may indicate a systematic bias in one or more of the measured concentrations. In studies of groundwater chemistry, data quality control is of prime importance and the operation and staffing of laboratories should be such that 10-20% of the total effort may be devoted to it (Ref. 45).

The accuracy of chemical data may be checked by analysing reference samples of known composition, such as those prepared by the US National Bureau of Standards and the Environment Protection Agency; interlaboratory studies are an alternative approach (Refs 46-50). Typical data from an interlaboratory collaborative analysis programme for groundwater, currently being conducted by the Hydrogeology Unit of IGS and involving over 30 laboratories worldwide are plotted in Figure 2. Considerable variation exists in the values reported for major elements such as sodium, and an even greater scatter is shown in the trace element data, exemplified by that of zinc.

Valid estimates of the precision of an analytical method are vital in any realistic utilisation of the data generated, to prevent over-interpretation of the results. It is important that these estimates should be related specifically to the particular concentration of analyte in the type of sample under consideration. Precision should be estimated within a laboratory by analysis of replicate samples spread between many batches over several days; however, other techniques relying solely on the measurement of duplicate samples have been described (Ref. 51).

Detection limit figures should similarly reflect the performance of a method under realistic operating conditions; published values need to be viewed with some circumspection and not taken out of context. A performance figure of greater utility for data quality evaluation in environmental chemistry (Ref. 52) is the LQDC (Lowest Quantitatively Determinable Concentration).

CONCLUSION

On-site measurement, sample collection, sample storage and laboratory analysis have all been shown to influence the reliability of data on the chemical composition of groundwater. An awareness of the mechanisms through which these influences operate enables steps to be taken throughout an investigation to minimise and quantify their effects, but it is most unlikely that they will be totally eliminated. Thus, in the interpretation of chemical data it is of paramount importance that the magnitudes of the residual uncertainties are borne in mind. In this way, real features of the groundwater chemistry may be distinguished from spurious fluctuations in the data.

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