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Constraints on the use of “in situ distribution coefficients (K_d)” values in contaminant transport modelling

W. RUSSELL ALEXANDER¹ & IAN G. MCKINLEY²

Key words: Contaminant, retardation, in situ, non-conservative

Extended abstract

In models of solute transport in natural waters, the interactions of the solute with solid phases are usually bulked together into a simple distribution coefficient. In the simplest case, a distribution constant is assumed, i.e.

$$C_r = K_d \cdot C_w$$

where

C_w = the solute concentration in the aqueous phase (mol m^{-3})

C_r = the concentration sorbed on the solid phase (mol kg^{-1})

K_d = the distribution coefficient ($\text{m}^3 \text{kg}^{-1}$).

In a simple system, such a K_d may be thermodynamically based, but the value used in transport models is usually an empirical representation of kinetically fast, concentration independent, reversible sorption (see McKinley & Alexander 1992, for a detailed discussion).

K_d values are normally measured in the laboratory by simple batch sorption experiments where a rock-water slurry is spiked with the tracer of interest and, following some period of equilibration, the water and rock are separated and the distribution of the tracer between the two phases is defined (see Sibley & Myttenaere 1986, for detailed discussion of batch sorption techniques etc.). Recently, production of “in situ K_d values” has become very fashionable and the geochemical and waste management literature is full of examples. This is partly due to a desire to produce site relevant retardation data for toxic and radioactive waste management and partly because of the mistaken belief that evaluation of in situ K_d values is somehow easier than measuring sorption in the laboratory. This is patently simplistic, but has not prevented the (mis)measurement of such data and the subsequent misapplication of the results by the geochemical and waste management communities. All reported in situ K_d data should be treated with great care as most can be shown to be “non-conservative”, leading to an under-prediction of contaminant transport.

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Proper assessment of in situ retardation is very difficult and rigorous quantification of in situ distribution coefficients is almost impossible (McKinley & Alexander 1992). This is, to a large extent, due to the constraints inherent in correct application of the K_d concept. Several points must be taken into account when deriving K_d data (see fig. 1):

- 1 In situ K_d values are applicable only if the operational retardation mechanism can be shown to distribute a species between the aqueous (groundwater) and solid (rock) phase in such a manner that the equilibrium solid phase concentration is directly (linearly) related to that in the aqueous phase (see fig. 1). In most transport modelling applications, such uptake is also assumed to be fast and reversible.
- 2 Where the relationship is non-linear (i.e. sorption is a function of solute concentration), an isotherm is required to describe retardation, that is a series of groundwater/rock pairs must be analysed over a range of groundwater concentrations appropriate to the application envisaged. Such isotherms are usually completely empirical and hence cannot be extrapolated beyond the conditions examined.
- 3 Precipitation cannot be included with sorption in a K_d value or sorption isotherm. Here, there is no direct relationship between the amount of species in the precipitated phase and the solution concentration.
- 4 The number of sites for sorption on a solid phase is limited and, after these have been filled, there is again no direct relationship between aqueous and solid phase concentrations.

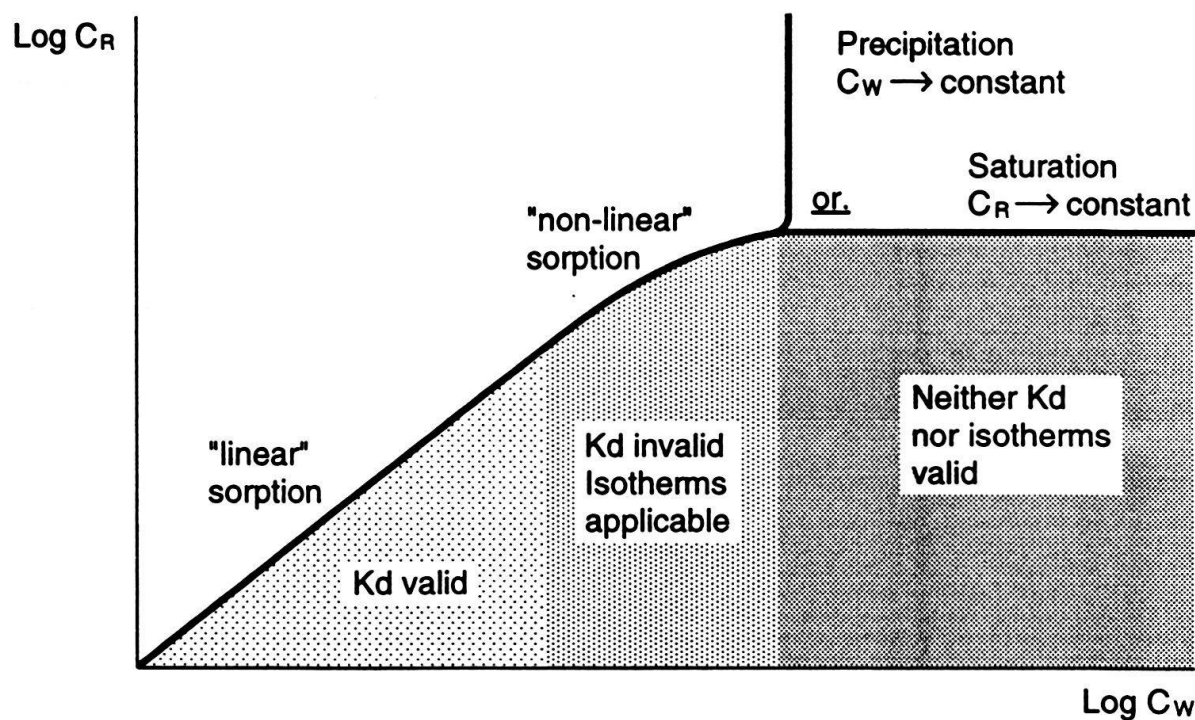


Fig. 1. Schematic representation of the variation of contaminant concentration in the rock (C_R) with the contaminant concentration in the water (C_W) for a general isotherm. The effects of precipitation and saturation are also shown (from McKinley & Alexander 1992).

Regardless of the above problems, the waste disposal and soil science literature is full of examples of supposed in situ Kd values. The data are produced in three main ways (McKinley & Alexander 1993 a, b):

- i) by measuring the concentration of a “contaminant” in the rock and in the water from an appropriate source (the rock/water concentration method);
- ii) by measuring a concentration profile;
- iii) by use of models interpreting natural decay series disequilibria (Krishnaswami et al. 1982).

All of these techniques have major problems, which are generally ignored by the producers of in situ Kd values. In the case of the rock/water concentration method, the major criticism is that the wet chemistry leaching techniques used to define the various “sorbed”, “exchanged” or “complexed” phases simply cannot do what they are claimed to do (see Alexander & McKinley 1992, for discussion). Appropriate information could be collected by the additional use of various surface analytical techniques, but to date this has been pursued only rarely (e.g. Nightingale 1988).

The concentration profile method is more promising in that laboratory based data can be fit to the observed profiles and some form of retardation can be defined. The principle here is that the redistribution of a well-defined and dated geochemical anomaly can be interpreted in terms of a retardation factor, R , where

$$V_n = V_w/R$$

where

V_n = the mean velocity of the solute (m s^{-1})

V_w = the mean velocity of the water (m s^{-1}).

However, there is absolutely no indication that the so defined retardation coefficients (not in situ Kd values!) are applicable beyond the precise system studied. It should also be noted that the retardation factor is only a constant for cases where sorption is ‘linear’ and that mean velocities of water movement are extremely difficult to measure in most of the environments considered – especially bearing in mind that these ‘mean values’ may be averages over geological time periods.

The limitations of the isotope ratio method of Krishnaswami et al. (1982) and examples of its missapplication have been discussed elsewhere (McKinley & Alexander 1992; 1993 a). A more recent model (Ku et al. 1992) is even more problematic as, in its fundamental mass balance equation, it explicitly includes precipitation as a first order process which allows sorption and precipitation to be included together in a type of retardation factor. Such an approach appears to be chemically nonsensical as, even if precipitation was a first order process, it would be related to the difference between concentration and a solubility limit and not absolute concentration, as in the Ku et al. (1992) model. Following a series of gross oversimplifications (such as ignoring Th transport by colloids and assuming that “the adsorbed (sic) pool resides in a surface layer which provides the sites for reversible ion exchange”), a set of equations is derived which allow an entire range of element / rock interaction parameters to be defined based on measurement of activities of a number of Th isotopes on a single sample.

The problems with this model are more easily seen from a direct example of its (mis)application (Ivanovich et al. 1993). For U, the model produces partial (sic) retardation factors (i. e. sorption only, no precipitation component) for the isotopes ^{238}U and ^{234}U which vary by factors of 5 to 350 on particular samples! Further, detailed analysis of the model application is complicated by cryptic nomenclature, for example, giving "time in solution before irreversible sorption" of Th of <1 s, even though a fundamental assumption of the model is that sorption is reversible (indeed a desorption rate constant is reported!). Such observations clearly indicate that the approach used is invalid and the paper epitomises the GIGO principle (garbage in, garbage out) when mathematical models are blindly used without consideration of either their fundamental correctness or their applicability to the system considered.

In summary, no studies of in situ Kd values have unambiguously shown that the data either conform with the points 1–4 listed above or that the analytical (and sampling) techniques have unambiguously identified "sorbed" phases. In other cases, the reported in situ Kd values would anyway be applicable only to the specific environment studied. As such, all reported data should be approached with great caution as use of such values in contaminant transport models may not only lead to conclusions that are incorrect, but which are dangerously "non-conservative" – predicting less contaminant migration than would actually occur.

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Characterization of groundwater and polluted water by ultra trace element analysis, using High Resolution Plasma Source Mass Spectrometry

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Key words: High resolution, Plasma, Mass spectrometry

ABSTRACT

Characterization of groundwater and polluted waters using trace element analysis is presented. Molecular interference complications using a unit resolution Plasma Source Mass Spectrometer (ICP-MS) are described. Unambiguous identification and quantification at ultratrace levels of elements is necessary to characterize the origin of similar groundwaters or the source of water pollution. This has been achieved thanks to the High Resolution Plasma Source Mass Spectrometry (HR-ICP-MS) technique which allows to resolve the molecular interferences from the elements of interest.

RESUME

Détermination de l'origine d'eaux souterraines et caractérisation d'eaux polluées grâce à la technique utilisant la spectrométrie de masse à haute résolution couplée à une source à plasma (HR-ICP-MS). La technique HR-ICP-MS permet de résoudre les interférences moléculaires des éléments en trace à analyser et d'améliorer ainsi leurs seuils de détection.

1. Introduction

The water resources study, especially that of groundwater, is a principal research field in our laboratory. Our hydrogeological research group involved in the characterization of a water by its chemical composition in order to determine its origin (Parriaux et al. 1990). The mineral composition characterizes also the water quality and allows to define the possible anthropogeneous elements in polluted water. The Plasma Source Mass Spectrometry (ICP-MS) seems to be today the most suitable analytical technique to study trace elemental analysis. The advantages of this new technique, such as high sensitivity, simple interpretation and low detection limits across essentially the entire periodic table, have quickly established this powerful technique in a number of diverse applications (Date & Gray 1989, Holland & Eaton 1991).

However, depending on the matrix, some polyatomic ions, especially metal oxide ions MO^+ , are formed in the plasma and then can interfere, on the mass spectrum, with ana-

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lyte ions at the same nominal mass (Reed et al. 1993). In practice, these interference problems decrease the detection limits for some elements since the resolution of the quadrupole mass analyser typically used in ICP-MS is not sufficient to resolve isobaric ions.

A number of methods have been used to attenuate such interferences. These include blank correction, chemical pre-treatment to reduce the matrix effect etc However, there is an alternative approach to solve this problem using the powerful capabilities of mass spectrometry: the increase of the instrumental resolution. This idea has been achieved by VG-Elemental, by coupling a Plasma Source to a High Resolution double focusing mass analyser (HR-ICP-MS), to allow the separation and resolution of poly-atomic ions and analyte ions at the same nominal mass.

2. Methods

A schematic diagram of the VG Plasma Trace instrument is shown in Figure 1. It consists of a torch, through which argon flows at atmospheric pressure, surrounded by a load coil. (Table 1) A power of 1.5 kW at a stabilized frequency of 27 MHz is applied to the load coil to maintain the plasma at an effective temperature of about 7,000 K. Under such conditions, the most predominant sample species in the plasma are singly charged ions

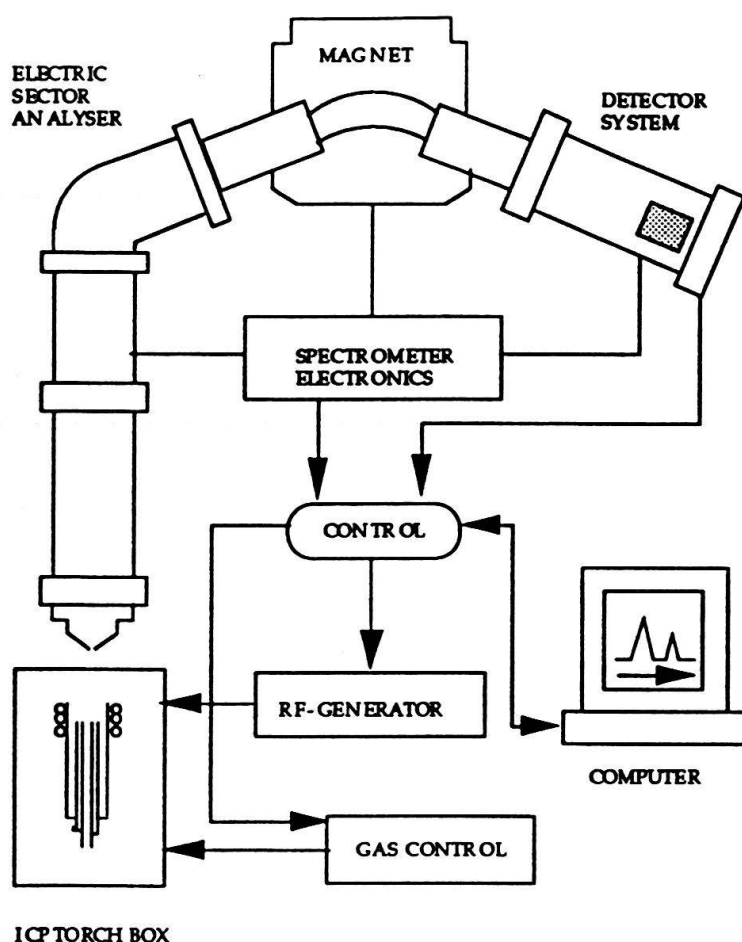


Fig. 1. Schematic diagram of the HR-ICP-MS instrument.

ICP source	Typical operating parameters
Gas	Ar at 1 atm.
Coolant gas flow	15 Lmin ⁻¹
Auxiliary gas flow	0.8 Lmin ⁻¹
Nebulizer gas flow	0.75 Lmin ⁻¹
rf power	1.5 kW

Tab. 1. Typical operating parameters for the Plasma Source.

(Houk 1986) with a degree of ionization of over 80% for the majority of all elements (Horlick et al. 1987). The ions are then transported through successive pumping stages into the mass spectrometer at low pressure (around 10^{-7} mbar). The ion beam is extracted from the plasma through the sampling interface and accelerated into the mass analyser which consists of an electric sector followed by a magnetic analyser. The collector assembly is dual detector system using a Faraday cup for high ion beam currents together with electron multiplier for low level signals.

3. Results and discussions

Analysis of groundwaters and waste waters requires the determination of transition metals and pollutants (Purves 1985). The ultra trace transition element analysis using a unit mass resolution quadrupole ICP-MS system can be difficult, especially for waters containing high level concentrations of elements such as: C, Na, Si, K, Cl and S. These elements react in the plasma with the argon or the oxygen and then form polyatomic ions which interfere with the elements of interest and affect their detection limits. Table 2 shows some known matrix interferences and also the resolution required to separate the species (Reed et al. 1993).

Some precautions can be taken for known molecular interferences, to minimize their effect on the analytical performance with unit mass resolution system. However, the problem remains for unknown interferences: if the presence on the mass spectrum of an interference is not identified, it is difficult to suspect it and estimate its effect on the element of interest. This will probably compromise the analytical results. Indeed, in recent work we have observed an ion current signal at $m/z = 45$, using a unit mass resolution system, in typical groundwater samples [8]. Naturally this has been identified as Scandium.

This result was at the beginning exciting and then became suspect when we found a good correlation between Sc and Silicon concentrations. We concluded that these water samples could not contain Sc, and that the presence of a peak at mass 45 could be an artefact due to a molecular interference from Si corresponding to SiOH or SiO. This assumption has been confirmed by analysing a standard solution of Si and checked the presence of a signal at mass 45. In order to quantify the contribution from the SiOH molecular interference at mass 45, we measured the ion current signal generated at mass

Element	accurate mass	interference	Accurate mass	Resolution
^{45}Sc	44.9559	$^{28}\text{Si}^{16}\text{O}^1\text{H}$ $^{14}\text{C}^{16}\text{O}_2^1\text{H}$ $^{14}\text{N}_2^{16}\text{O}^1\text{H}$	44.9796 44.9976 45.0088	1895 1080 850
^{48}Ti	47.9479	$^{32}\text{S}^{16}\text{O}$ $^{16}\text{O}_3$	47.9669 47.9847	2521 1305
^{51}V	50.9405	$^{16}\text{O}^{35}\text{Cl}$	50.9637	2580
^{52}Cr	51.9405	$^{38}\text{Ar}^{14}\text{N}$ $^{40}\text{Ar}^{12}\text{C}$	51.9658 51.9629	2054 2375
^{63}Cu	62.9295	$^{40}\text{Ar}^{23}\text{Na}$	62.9521	2778
^{64}Zn	63.9291	$^{32}\text{S}_2$ $^{32}\text{S}^{16}\text{O}_2$	63.9441 63.9619	4268 1960
^{65}Cu	64.9277	$^{32}\text{S}^{16}\text{O}_2^1\text{H}$ $^{32}\text{S}_2^1\text{H}$	64.9697 64.9519	1550 2675
^{75}As	74.9216	$^{40}\text{Ar}^{35}\text{Cl}$	74.9312	7775

Tab. 2. Known molecular interferences and the resolution required to separate the species.

45 with Si standard solutions within a concentration range between 1 and 20 mg/l, which is a typical range of water samples. Then, the signals obtained were integrated and calculated as Sc, from Sc standard curve calibration. The results are presented in Figure 2 where we can see that 1 mg/l of Si generates a signal at mass 45 which nearly corresponds to 1 µg/l of Sc solution.

Under these conditions, the determination of Sc or other trace elements with similar interference effects will be difficult with an ICP-MS system having a unit mass resolution.

In order to overcome all these molecular interference analytical problems, we have opted for the trivial solution which consists of increasing the instrumental resolution to resolve most interferences from the elements of interest. The VG Plasma Trace instrument offers this powerful capability. Using these techniques we can fix the resolution between 400 and 8,000.

Table 3 shows a multielemental analysis at a resolution of around 3,500. At this resolution the HR-ICP-MS technique allows unambiguous identification and quantitation at ultra trace levels.

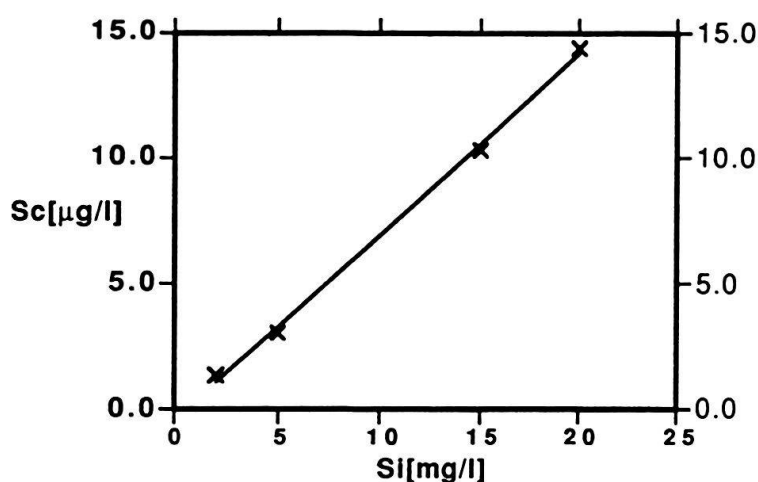


Fig. 2. Silicon effect at m/z 45 expressed as equivalent concentration of Sc.

Figure 3 demonstrates the power of high resolution ICP-MS technique. Elements of interest have been resolved from molecular interferences in groundwater and waste water samples. These results show that the ion currents from the molecular interferences at mass 52, 58 and 59 are respectively comparable to ion current of Cr, Ni and Co, elements of interest. At mass 45 and 56, the interference signal intensities are much higher than the signals of Sc and Fe. A unit mass resolution spectrometer would not have resolved these isobaric ions but would have integrated them as one peak which compromises both accuracy and limits of detection for these elements. We conclude from these

Element	Groundwater	Polluted water	Waste water
Li	9.65	3.60	73.30
B	13.76	18.9	3731.70
Al	0.27	0.13	56.90
Sc	0.01	0.03	n.d.
V	n.d.	0.06	0.70
Cr	0.39	3.27	15.30
Fe	4.19	194.80	120.60
Mn	0.51	12.60	309.50
Ni	0.03	4.01	35.00
Co	n.d.	0.12	2.10
Cu	n.d.	2.60	109.30
Zn	0.22	163.10	365.20
Br	10.32	22.0	4828.20
Rb	1.47	1.30	77.08
Mo	1.34	n.d.	17.50
Cd	0.01	0.01	2.34
I	63.21	2.0	2928
Ba	22.15	18.40	182.75
Hg	n.d.	303.20	n.d.
Pb	0.08	0.20	2.91
U	0.14	2.41	2.20

Tab. 3. Multielemental analysis at medium resolution mode for different water samples. (n. d. = not detected). The results are expressed in $\mu\text{g/l}$.

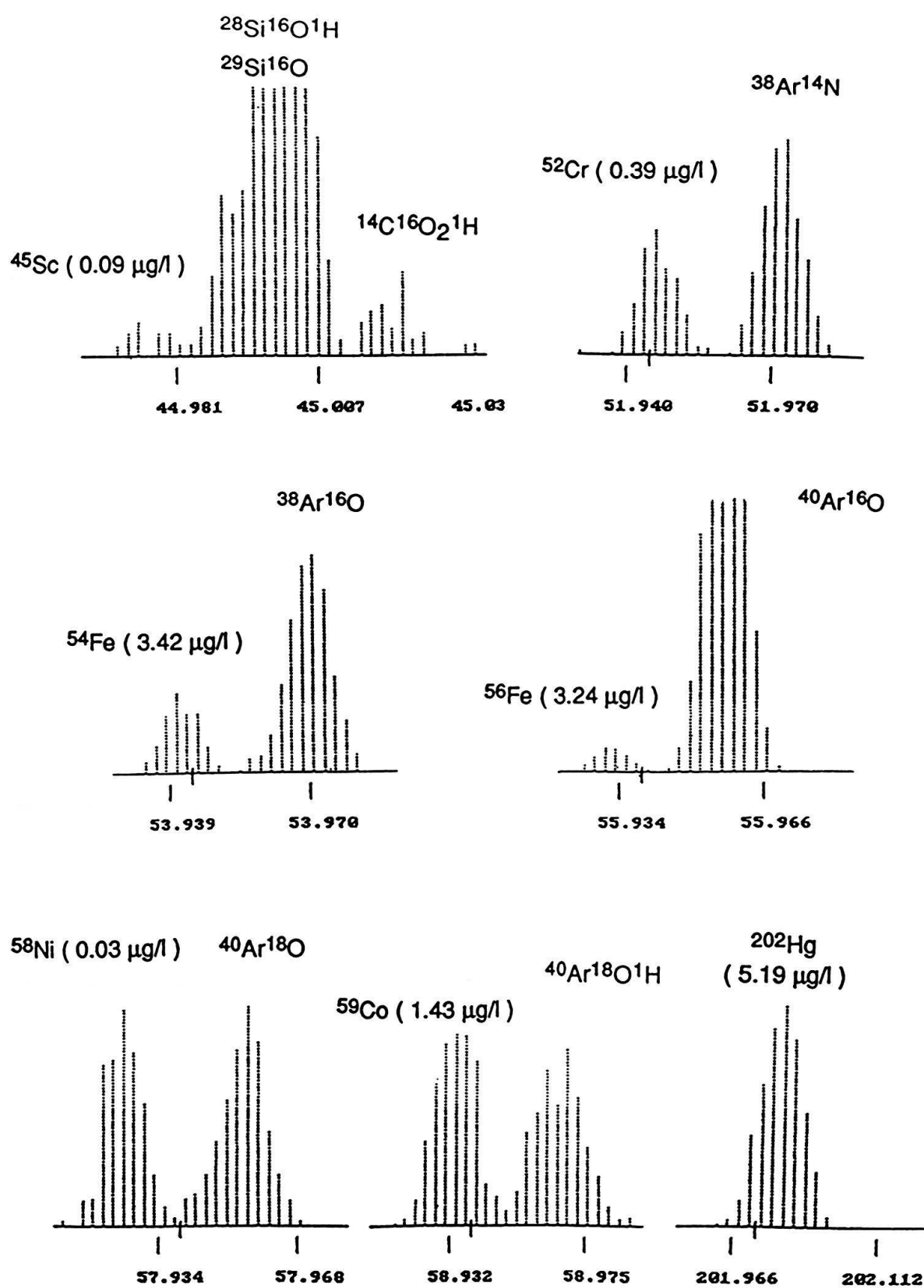


Fig. 3. Examples of molecular interferences observed in groundwater and polluted water samples using the HR-ICP-MS instrument.

results that, even in low mineralized groundwater samples, the contribution of molecular interferences generated from major elements (Na, Mg, Si, K, Ca etc ...) are important and must not be neglected in the calculation procedure to achieve very low detection limits.

4. Applications

Groundwater

The next step in this study was the characterization of natural waters using the ICP-MS technique to measure the trace elements present in four natural waters. Indeed, the analysis of the chemical composition is a technique which is currently used by hydrologists to distinguish waters from different origins (Bensimon et al. 1991).

Traditionally, this study is achieved by measuring the concentration of the major elements such as Ca, Na and K. However, systematic field observations show that this characterization is not sufficient to discriminate different types of aquifers. Samples of different origins can show similar general composition, thus preventing their identification with classical methods.

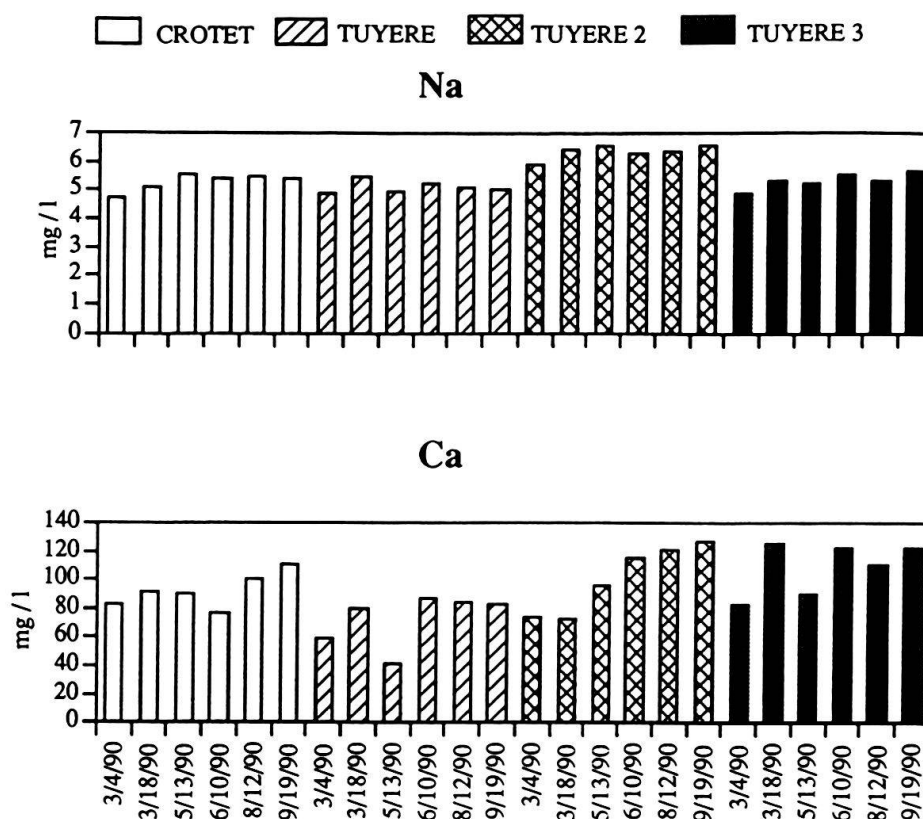


Fig. 4. Concentration measurements of Na and Ca as a function of time for the water samples of CROTET, TUYERE, TUYERE2 and TUYERE3 springs.

In order to solve this problem, the AQUITYP project was created to set a new technique using trace element analysis. To explore this idea, four water samples issued of a tertiary aquifer of the molassic Swiss Plateau have been studied. The concentration variations as a function of time have been measured for some elements. As an example, Na and Ca concentration levels are shown in Figure 4 and those of Li, Cr and U are given in Figure 5. The plots in Figure 4 do not permit to distinguish between these water samples. On the contrary, the concentration levels of Li, Cr and U given in Figure 5 show clearly that the TUYERE water has a different behaviour compared to the others.

Polluted waters

Multielemental trace analysis is also used to detect and characterize a water pollution even at very low level after the pollution has been spread and diluted with other non contaminated waters. In this case, the HR-ICP-MS technique is necessary to resolve molecular interferences from analyte ions to achieve unambiguous identification and quantification at ultratrace levels. As an illustration, we have taken 2 samples up-stream and downstream of an old urban waste site (Looser et al. 1993).

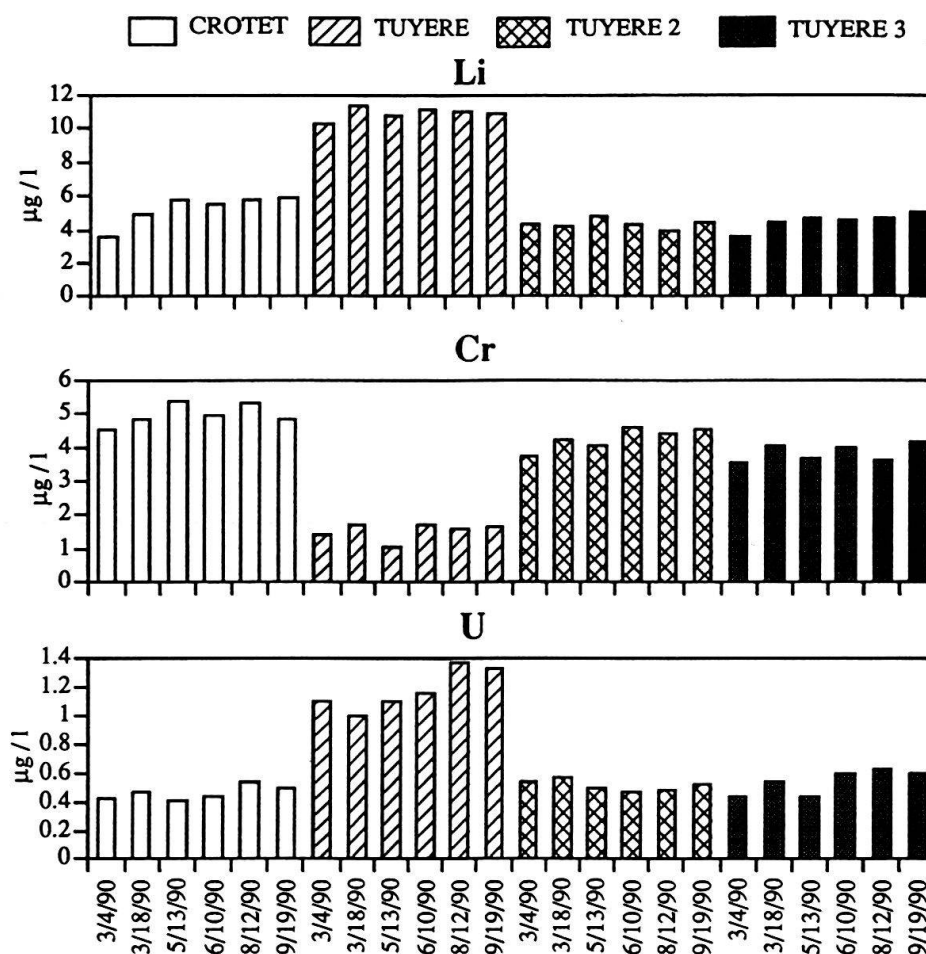


Fig. 5. Concentration measurements of Li, Cr and U as a function of time for the water samples of CROTET, TUYERE, TUYERE2 and TUYERE3 springs.

The stream, which drains the alluvial ground water, receives diffuse contaminations issued from the non-confined waste.

The trace element analysis of these samples is displayed in Figure 6. For comparison with natural waters, Figure 6 shows also the typical composition of a groundwater sample taken in this region.

Figure 7 displays the difference in contamination between down- and up-stream. Despite the high dilution by the stream, this clearly shows that the down-stream sample is contaminated by the waste site characterized by high values for B, Ba, Br, Cu, I, Mo, Ni and Rb elements.

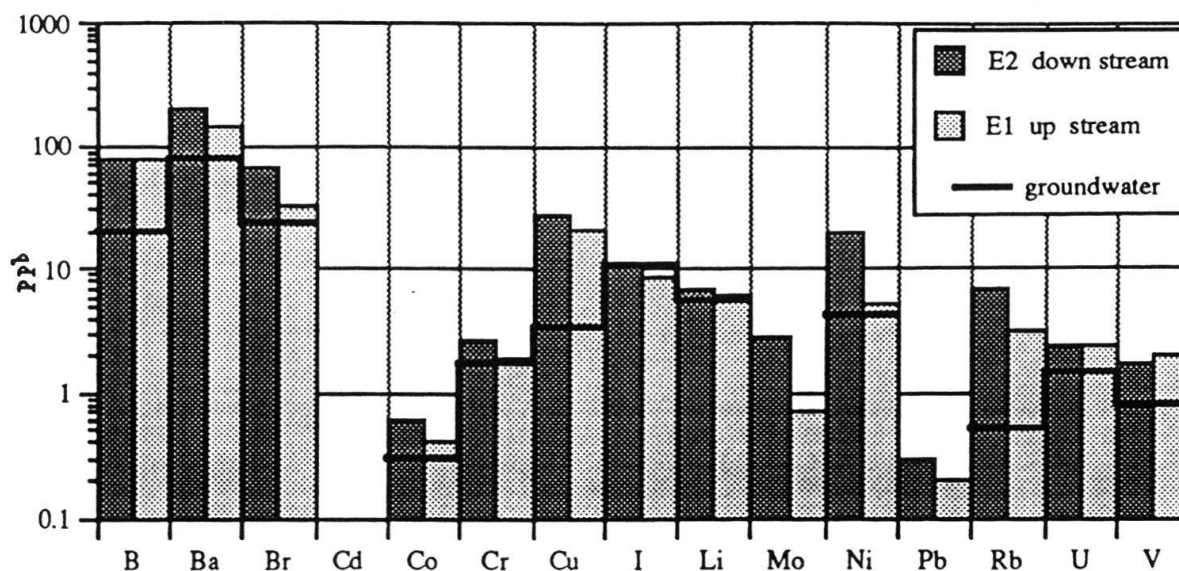


Fig. 6 Multi-elemental analysis for down-stream and up-stream near an old waste site compared to groundwater sample.

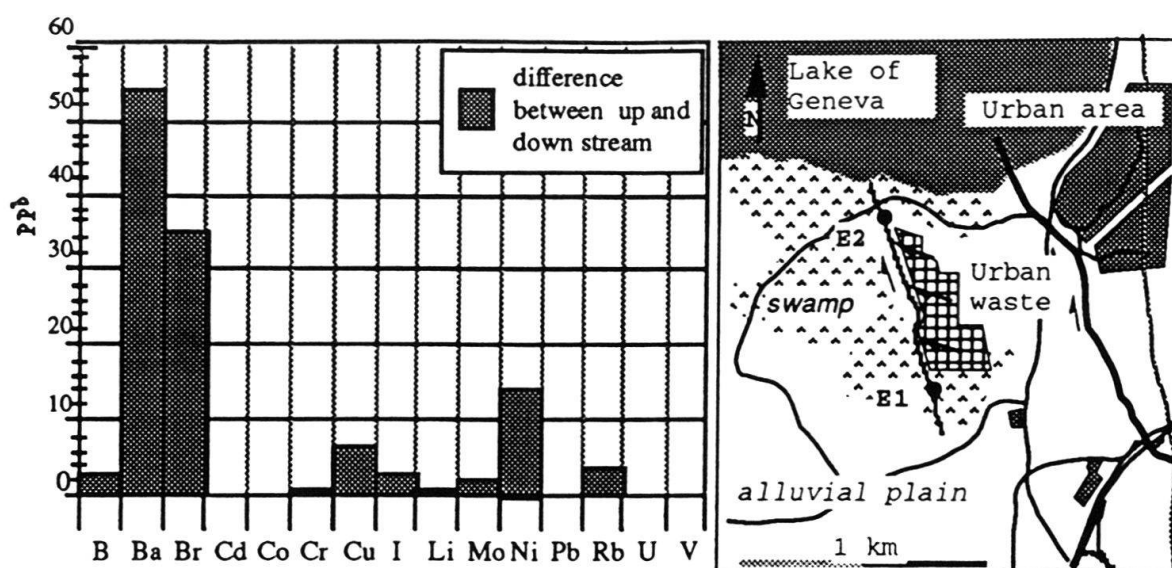


Fig. 7. Concentrations difference between the up- and down-stream samples and their situations.

5. Conclusions

The coupling of the ICP ion source with a double focusing mass spectrometer is the most easy and elegant way to overcome the molecular interference problems at very low detection limits.

A resolution of 4,000 will resolve most interferences from elements of interest, except for arsenic which requires a resolution of about 8,000 which is available in the high resolution mode.

High resolution determination of elements at very low levels (ng/l) extends considerably the number of geochemical tracers over the whole mass range to characterize the geological origin of a groundwater or to detect the source of a water pollution.

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