U – salinity relationships in the Mediterranean: implications for $^{234}Th:^{238}U$ particle flux studies

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Abstract

Knowledge of the ^{238}U concentration in seawater is important for ^{234}Th:^{238}U disequilibrium studies of particle fluxes. However, these concentration data are normally obtained through a standard relationship between ^{238}U and salinity, which has been determined for the open ocean. This study examines ^{238}U data from both the open Mediterranean and the coastal Thermaikos Gulf, Greece, and compares it to the open ocean. No deviation from the open ocean ^{238}U – salinity relationship was found for the Thermaikos Gulf, but some enhancement was noted close to Thessaloniki in the vicinity of a phosphate fertiliser plant. The open Mediterranean data showed a small enhancement relative to the open ocean. Although an analytical bias could not be ruled out, a review of ^{238}U and salinity data in the literature shows that the standard relationship may not be as robust as is often assumed and the 1 % uncertainty typically used is not justified at the present time. Nevertheless, salinity-based derivations continue to be the most appropriate means of determining ^{238}U concentrations for routine applications. We propose a new relationship that accounts for the uncertainties observed, *i.e.* ^{238}U (dpm l^{-1}) = $(0.0713 \pm 0.0012) \times$ salinity.

Keywords: uranium; thorium; salinity; uranium-234/uranium-238 ratio; thorium-234; Trans-Mediterranean Cruise; Mediterranean Sea; Greece, Thermaikos Gulf

1. Introduction

^{238}U is a long-lived ($t_{1/2} = 4.68 \times 10^9$ y) naturally-occurring radionuclide, which occurs in the oxic marine environment as the soluble uranyl carbonate species $UO_2(CO_3)_3^{4-}$. It decays to the particle-reactive nuclide ^{234}Th ($t_{1/2}$ = 24.1 d), which is removed from solution in the presence of settling particulate material. The resulting disequilibrium is widely exploited to determine particle fluxes in the water column, with one of the most common applications being the determination of particle export from the euphotic zone and associated organic carbon cycling (Cochran and Masqué, 2003). In this type of study, particularly in the open ocean, the ^{238}U activity is usually determined from its relationship with salinity as established by Chen *et al.* (1986), namely ^{238}U (ng g^{-1}) = (0.0919 ± 0.0005) × salinity, where the uncertainty quoted is the 99% confidence limits of the mean.

The estimation of the ^{238}U activity from salinity is not unreasonable given our knowledge of its marine geochemistry. Dunk *et al.* (2002) have reviewed in detail the oceanic U budget, and found that, within uncertainties, the global ocean is at steady state with respect to U concentrations and that the oceanic residence time is $3.2 – 5.6 \times 10^5$ years. The large magnitude of this oceanic residence time, compared to the mixing time of water, indicates that the U concentration should be near constant. Indeed, Chen *et al.* (1986) calculated that the relative difference between the surface ocean (where all the inputs occur) and deep ocean U concentrations should be no more than 3 ‰, based on a uranium residence time of 3×10^5 years. Using Dunk *et al.*'s upper limit reduces this difference further. Thus, given the ease and accuracy with which salinity can de determined, inference of ^{238}U activity from salinity seems wholly appropriate in the open ocean.

There are two main areas in which the global ocean ^{238}U – salinity relationship may break down. Firstly, areas of low salinity, such as estuaries and enclosed seas, may show non-conservative behaviour. Secondly, due to the redox sensitivity of U, regions experiencing prolonged anoxia, such as the Black Sea, can show U depletion (Anderson, 1982; Anderson *et al.*, 1989; Wei and Murray, 1991). For example, the Baltic shows small deviations from a linear ^{238}U – salinity relationship due to influence from rivers with variable ^{238}U concentrations, and also depletion in places due to anoxia (Andersson *et al.*, 1995). Other estuaries, such as the Hudson (Feng *et al.*, 1999), show conservative behaviour and Gustafsson *et al.* (1998) found that ^{238}U activities had an open ocean signature at their study site in the coastal Gulf of Maine, for salinities as low as 30.

Although, for the most part, questions have been raised about ^{238}U – salinity relationships for low salinity and anoxic environments, the Mediterranean is also an unusual, semi-enclosed basin. The salinity is relatively high (~ 38) and exchange with the open ocean is restricted. Several major rivers flow into the basin (*e.g.* the Ebro, the Rhône, the Po and the Nile), and exchange occurs with the Atlantic at Gibraltar and the Black Sea through the Bosphorus. Although many studies of ^{234}Th:^{238}U disequilibrium in the Mediterranean have assumed an open ocean relationship with salinity (*e.g.* Frignani *et al.*, 2002; Radakovitch *et al.*, 2003), the unusual characteristics of the Mediterranean indicate that there is value in examining the ^{238}U – salinity relationship of this basin. Two small-scale studies have been carried out on this relationship previously (Schmidt and Reyss, 1991; Delanghe *et al.*, 2002), but both were of relatively few samples, collected only from the western basin. Therefore, the first aim of this study is to examine the distribution of ^{238}U with respect to salinity across the entire Mediterranean, but focussing on the eastern basin. We will examine both a coastal area and the open Mediterranean, and assess the degree to which the ^{238}U – salinity relationship of Chen *et al.* (1986) holds.

One of the key uses for ^{238}U concentrations is in determining particle fluxes or export through its disequilibrium with its daughter ^{234}Th. As methods for ^{234}Th determination become more precise, uncertainty in ^{238}U concentrations becomes more important in ^{234}Th:^{238}U disequilibrium studies (van der Loeff *et al.*, 2006). Thus, the second aim of this work is to review the available literature on ^{238}U – salinity relationships and evaluate sources of uncertainty in derived ^{238}U concentrations.

2. Methods

Samples for this paper were collected during two EU projects, MATER (MAss Transfer and Ecosystem Response) and INTERPOL (Impact of Natural and Trawling events on the Resuspension, dispersion and fate of POLlutants), over a 5 year period from March 1997 to February 2002. The INTERPOL project was based in the Thermaikos Gulf, in northern Greece, whereas MATER encompassed the open Mediterranean. A summary of the sampling stations is given in Figures 1 and 2.

2.1 INTERPOL samples (Thermaikos Gulf)

Samples were collected during 3 cruises of the *R/V Aegaeo* to the Thermaikos Gulf in September and October 2001 and February 2002 (IP/1-01, IP/2-01 and IP3-02 respectively). On each occasion, a series of 8 stations was visited (Figure 1). Water samples (10-litres) were collected from a range of depths from surface to near bottom using Go-flo bottles, and were immediately filtered through 142 mm diameter, 0.45 μm pore-size cellulose nitrate membrane filters. The filters were retained for ^{234}Th analysis. Each sample filtrate was split into 2 aliquots; 5 litres were used for ^{238}U analysis and the remainder for ^{234}Th analysis. The ^{234}Th data have been published elsewhere (Muir *et al.*, 2005). Between samples, the filtration equipment and sample containers were rinsed in 10% nitric acid and de-ionised water.

After filtration, the samples were acidified to pH < 2, iron carrier added and the samples spiked with ~ 0.2 Bq ^{232}U. After a period of equilibration, the pH was raised to ~ 9 by adding NaOH solution to precipitate $Fe(OH)_3$. Ammonia is more commonly used for pH adjustment than NaOH, but in this instance safety considerations prevented its use. The precipitate was allowed to flocculate and settle and was then separated by filtration onto GF/F filters.

Upon return to the laboratory, the Fe precipitate was dissolved in 9M HCl. The solution was passed through an anion exchange column (Bio-Rad AG1X8, 100-200 mesh, Cl^- form), which retained U and the Fe carrier. Fe was eluted by first reducing it to Fe(II) with 1M NH_4I, then rinsing the column with 9M HCl. U was then eluted using 1.2M HCl. The U fraction was taken to dryness and treated with concentrated HNO_3 to convert any iodide present to iodine, which was then removed by heating. This step was repeated until addition of HNO_3 resulted in a clear solution. The solution was dried down in a clean beaker, and re-dissolved in 9M HCl. Slight traces of Fe could usually be detected at this stage, in the form of a faint orange coloration. Therefore, all samples were further purified by solvent extraction. The sample was extracted with di-isopropyl ether (DIPE); U was retained in the aqueous layer while any remaining traces of Fe were extracted into the solvent. U was then purified using a second, smaller ion exchange column, similar to that described above, but excluding the Fe reduction step.

The samples were then prepared for counting using electrodeposition. The sample was dissolved in a 2% $(NH_4)_2SO_4$ solution at pH 2.5. The samples were plated onto stainless steel planchettes using a platinum wire anode, and a current of 0.8 A for 1.5-2 hours. Samples were counted using an Ortec silicon-surface barrier detector system for 1-3 days until at least 1000 counts were accumulated in the main peaks. Backgrounds were collected for up to 1,000,000 seconds at least once every 2 months.

2.2 MATER samples (open Mediterranean)

Samples were collected during 3 cruises of the *N/O Urania* to the southern Adriatic and northern Ionian Seas in March and August 1997 and March 1999 (MAI/1-97, MAI/2-97 and MAI/8-99 respectively). Further samples from across the Mediterranean basin were collected during the Trans-Mediterranean Cruise (TMC) onboard the *R/V Aegaeo* in June 1999. In all cases, 30 litre water samples were collected in Go-Flo bottles from a range of depths. The water was immediately filtered through a 142 mm diameter, 0.45 µm pore-size cellulose nitrate membrane filter, and a 60 ml sub-sample taken for uranium analysis, which was stored, unacidified, at 4 ºC until analysis.

On return to the laboratory, the samples were brought up to room temperature before a 50 ml aliquot was taken, which was spiked with ~ 200 ng ^{236}U. The tracer was allowed to equilibrate with the sample for 24 hours, and the sample was taken slowly to near dryness, taking care to avoid bumping during the latter stages. The sample was then taken up in 9M HCl. In order to remove sea-salt, U was purified on a Cl^- form anion exchange column (Bio-Rad AG 1X8) as described above, excluding the Fe reduction step. The sample was then taken to dryness, and re-dissolved in 5 % nitric acid. Samples from each cruise were analysed separately, within 6 months of collection.

Procedural blanks were run with each batch of samples. For the MAI/1-97 and MAI/2-97 samples, 5 blanks were spiked with ^{236}U and then treated as samples. For the MAI/8-99 and TMC samples, a combination of spiked and unspiked blanks were run, in order to check for any contribution of ^{238}U from the tracer solution as well as assessing the ^{236}U blank. The blank count rate from ^{236}U was very low, equating to no more than 0.01 % of the ^{236}U peak. There was no detectable contribution of ^{238}U from the ^{236}U tracer. The total blank contribution to the ^{238}U peak equated to no more than 0.5 % of the signal from the sample. The appropriate blank count rates were subtracted from the raw sample count rates before any fractionation correction was performed.

Samples were analysed on a VG Elemental PQ2 plus (VG Elemental, Cheshire, UK) fitted with a Meinhard nebulizer and a water cooled glass Scott double pass spray chamber at the Scottish Universities Environmental Research Centre, East Kilbride. Data were collected in peak jumping mode, with 5 measurements made for each sample. Instrument sensitivity was optimised to 3.5×10^5 cps for a 10 ng g^{-1} ^{115}In solution and the response curve was tuned to provide enhanced sensitivity in the heavy mass range.

Mass bias or mass fractionation was accounted for in the MAI/8-99 and TMC samples using an NBS U500 standard, which is certified to have a ^{235}U:^{238}U ratio of 0.9997. The U500 standard was analysed at the start of the run to correct the mass bias, and then run again after every 5 samples to monitor and correct any drift from the initial settings over the course of the analyses. The ^{236}U:^{238}U ratio was corrected for fractionation by applying 2/3 the fractionation determined for the ^{235}U:^{238}U ratio. Samples from the MAI/1-97 and MAI/2-97 cruises were not corrected for fractionation, which will have resulted in some deviation from the true value. The implications of this are discussed below.

3. Results and discussion

3.1 Data treatment

One of the major constraints in comparing U data across the literature is the diverse range of dimensions employed. Studies based on α-spectrometry tend to present data as activities, whereas mass-spectrometric studies use either mass or molar concentrations. Furthermore, there is a lack of consistency between the use of mass (or activity) per unit volume or per unit mass seawater.

Chen *et al.* (1986) determined the mean total U concentration (^{238}U + ^{235}U) of 21 Pacific and Atlantic samples, normalised to a salinity of 35, to be 3.238 ± 0.018 ng g^{-1}. Using the published ^{235}U:^{238}U isotope ratios, these data were converted to a mean salinity normalised ^{238}U concentration (U* = 3.215 ± 0.018 ng g^{-1}), where the uncertainties are the 99 % confidence limits of the mean. By normalising to a salinity of 35, variability in the ^{238}U concentration due to salinity effects can be removed. This salinity normalised ^{238}U concentration is termed U* throughout the present work.

In order to compare our α-spectrometric data with Chen *et al.*'s relationship, we have used equation 1 to convert from mass to activity:

$$M = \frac{t_{1/2}}{\ln 2} \times \frac{238}{N_A} \times A \qquad (1)$$

where M is the mass of ^{238}U in grams, $t_{1/2} = 4.468 \times 10^9$ years (expressed in seconds) (Jaffey *et al.*, 1971), N_A is Avogadro's constant = 6.022×10^{23} mol^{-1}, and A is the activity in Bq.

To convert from concentrations per unit mass to per unit volume, it was necessary to consider the potential variations in seawater densities. An approximation to the full UNESCO equations of state (Knauss, 1997), that is accurate to within ± 0.05 %, was used to calculate the density of each sample based on its published salinity and a temperature of 20 °C (masses were determined in the laboratory and room temperature was assumed). Following this procedure results in Chen *et al.*'s U* = 2.458 ± 0.014 dpm l^{-1} (where the uncertainties are 99 % confidence limits of the mean).

In order to minimise the number of conversions between units, and the inherent uncertainties associated with these conversions, data derived from mass spectrometric studies have all been presented with units of ng g^{-1}, including the open Mediterranean data from this study.

It should be noted that throughout the discussion, wherever mean data are referred to, the associated uncertainties are the 99 % confidence limits of the means, in order to facilitate comparison between groups of data.

3.2 Thermaikos Gulf

The results from the Thermaikos Gulf are presented in Table 1. The 1 sigma uncertainty in the data points varies between 2.1 and 4.8%, with the mean uncertainty being 3.4%. These values are typical for data derived by α-spectrometry, and are due principally to counting statistics. In some instances, problems were found in re-dissolving the Fe precipitates. These samples tended to have extremely low recoveries (< 1%) and were excluded from further consideration.

Although no formal replicate samples were taken, the proximity in the water column of some samples means that they can be treated as such. The criteria used were that samples should be < 5 m apart in the water column and that the salinity should differ by no more than 0.005. Samples that were considered as replicates in this way are shaded in Table 1. To assess reproducibility, the difference between pairs of replicate samples was determined. Where three or more samples were considered replicates, this difference was calculated for each possible pair of samples. The differences were then normalised to the mean ^{238}U concentration for that group of replicates. The mean of these normalised differences (expressed as a percentage) is termed the "reproducibility error" from here on.

For the Thermiakos Gulf samples, the reproducibility varies considerably, but the overall reproducibility error is 5.6%. This value is slightly higher than the uncertainty in the individual data points, and could be considered as being more representative of the true measurement uncertainty.

3.2.1 Variation with salinity

The salinity range found for the Thermaikos Gulf varied between 36.4 and 38.6. Although 3 major rivers discharge into the Thermaikos Gulf (the Axios, Aliakmon and Pinios Rivers) their influence on salinity is restricted to the area immediately adjacent to their mouths (Zervakis *et al.*, 2005). The salinities clustered around two points, ~ 37 and ~ 38.4, with the lower salinities representing water above the thermocline during the September and October 2001 cruises and the higher salinities representing deeper water. The lower salinity surface waters are not entirely attributable to riverine discharges, as stations in the eastern part of the Gulf experienced lower salinities than those in the western area (Zervakis *et al.*, 2005). Instead, with the exceptions of stations 1 and 10, they can be attributed to lower salinity surface water from the Aegean Sea, which is influenced by the Black Sea discharges through the Dardanelles. The thermocline had broken down before the February 2002 cruise, and the lower salinity cluster had disappeared.

Figure 3 shows the data divided into the three hydrographic zones identified by Zervakis *et al.* (2005), namely the northern (stations 1 and 10), western (stations 17, 27, 38 and 41) and eastern (stations 18 and 30) areas. The northern area is influenced by discharge from the Axios and Aliakmon Rivers); the western area represents the western coastal shelf area and is influenced in the south by the Pinios River; and the eastern area is the deeper part of the Gulf, and is isolated from riverine influences (Figure 1).

The data from the western and eastern parts of the Gulf are somewhat scattered with a mean U* of 2.48 ± 0.04 dpm l^{-1}, but are not significantly different from the Chen relationship (U* = 2.458 ± 0.014 dpm l^{-1}). However, the northern area shows elevated ^{238}U concentrations relative to open ocean seawater, with a mean U* of 2.58 ± 0.05 dpm l^{-1}. Furthermore, the difference between the northern area and the rest of the Gulf is statistically significant, despite the scatter in the data. Given that the majority of the data points in the northern group are derived from station 1, which lies in front of the mouth of the River Axios (Figure 1), the most likely source of the excess ^{238}U is the river. However, despite its proximity to the river outflow, the salinity is not greatly reduced for most of the samples, indicating a maximum contribution of about 5 % river water. For this to result in the observed elevation in seawater ^{238}U concentrations, the river water would need to have a ^{238}U concentration of 4.5 dpm l^{-1}. By way of comparison, the world mean river concentration is approximately 1 – 1.2 nmol kg^{-1}, which equates to approximately 0.2 dpm l^{-1} (Dunk *et al.*, 2002).

No data on the radionuclide concentrations of the Axios River are available. However, U in rivers comes primarily from two sources, the natural dissolution of rocks (weathering) and phosphate fertilisers (Dunk *et al.*, 2002). The U concentrations of "typical" world rivers are related to the total dissolved solids (TDS), as the U concentration is a function of weathering. TDS and electrical conductivity data for the Axios and adjacent Aliakmon River give ranges of around 200-400 mg l^{-1}

TDS (Lazaridou-Dimitriadou *et al.*, 2000; Simeonov *et al.*, 2003), which can be equated to approximately 2 – 4 nmol kg^{-1} U or 0.5 dpm l^{-1} ^{238}U (Dunk *et al.*, 2002). While some rivers depart dramatically from the typical relationship due to intense weathering of U-rich rocks in the catchment (*e.g.* the Ganga-Brahmaputra system), the maximum U concentrations observed are around 35 nmol kg^{-1} or 6.3 dpm l^{-1} (Sarin *et al.*, 1990). Although the geology of the Axios catchment is diverse (Karageorgis *et al.*, 2005) none of the rock types found in the catchment is likely to result in such high U concentrations.

Enhanced U activities have been observed in some rivers (up to 5.2 dpm l^{-1}) that have been attributed to normal, if prolonged, use of phosphate fertilisers (Barišić *et al.*, 1992). However, other studies have found that the enhancement is due to natural weathering processes (Zielinski *et al.*, 1997). Thus, heavy usage of phosphate fertilisers could be contributing to the observed elevation. Indeed, the catchment is intensively farmed (Karageorgis *et al.*, 2005) and phosphorus discharges from the Axios are significant at 2.7 kt P y^{-1}, representing 38 % of Greek P discharges despite having only 10 % of the runoff (Karageorgis *et al.*, 2003).

However, perhaps a more likely explanation is related to the two phosphate fertiliser plants on or close to the river. One is in the town of Veles in the Former Yugoslavian Republic of Macedonia (FYROM), on the Axios River, and the other is in Thessaloniki. Both plants process imported phosphorites from Morocco (Papastefanou, 2001; Karageorgis *et al.*, 2005), which are known to contain high concentrations of natural decay series nuclides (Barišić *et al.*, 1992; Azouazi *et al.*, 2001; Papastefanou, 2001), and could well discharge waste products into the Axios River or the sea close to Thessaloniki. Although there is no firm evidence to support this hypothesis, other phosphate ore processing plants are known to discharge elevated levels of natural decay series radionuclides into the environment (*e.g.* Periáñez and Martínez-Aguirre, 1997; McCartney *et al.*, 2000). In addition, waste phophogypsum from the Thessaloniki plant has been used for soil amendment in the surrounding agricultural areas (Papastefanou *et al.*, 2006). ^{234}U:^{238}U isotope ratios can be used to identify inputs from phosphate fertilisers (Zielinski *et al.*, 1997), given that phosphate ores and their resulting fertilisers tend to have an isotope ratio of 1.00, compared with 1.14 in seawater. Unfortunately, in this case, the precision of the measurements is not sufficiently good to detect the small difference this would induce. ^{210}Po enhancement is also indicative of phosphate fertiliser contamination, but no water column data are available from this area. Sediment cores from station IP01 have been analysed separately for ^{210}Po (Karageorgis *et al.*, 2005), but without ^{210}Pb data, it is not possible to say whether they show ^{210}Po enhancement. Thus fertiliser production and / or its waste products are a likely, but unproven, source of U enrichment in the northern Thermaikos Gulf.

Another sub-group of the data that may not be expected to conform to the standard open ocean U – salinity relationship are the lower salinity, Black Sea influenced samples (Fig 3B). Surface water in the Black Sea is relatively fresh and strongly influenced by the characters of the major rivers which flow into it. Additionally waters below the thermocline are anoxic leading to the reduction of U and its subsequent loss from the water column (Anderson *et al.*, 1989). The Black Sea outflow will primarily originate with water above the halocline (< 50 m deep), which has a U: salinity ratio of 0.0811 dpm l^{-1} ‰$^{-1}$ (Wei and Murray, 1991; Gulin, 2000). This ratio is higher than that found for the open ocean, *i.e.* 0.0702 dpm l^{-1} ‰$^{-1}$ (Chen *et al.*, 1986). These shallow waters are clearly not affected by the loss of U from the anoxic deeper water.

Assuming that the Black Sea influenced water comprises a simple mixture of Black Sea surface water with a salinity of 18.6 and Mediterranean water with a salinity of 38.5, a salinity of 37.1 is achieved by mixing 93 % Mediterranean water with 7 % Black Sea water. If the Mediterranean water has the open ocean U:salinity ratio defined by Chen *et al.* (1986), this Black Sea influenced water is expected to have a ^{238}U concentration of 2.62 dpm l^{-1}, or 2.47 dpm l^{-1} when normalised to a salinity of 35, compared to 2.458 dpm l^{-1} for the open ocean (Chen *et al.*, 1986). This difference is relatively small, given the uncertainties in the data set, and no significant difference is observable in U* between the lower salinity Black Sea influenced waters and the deeper Mediterranean waters.

3.3 Open Mediterranean

The results from the open Mediterranean are presented in Tables 2 and 3. The measurement uncertainties are small, ranging between 0.2 % and 1.4 %, the mean being 0.6 %. Replication was also good; the 8 pairs of duplicate samples from the cruises MAI/1-97 and MAI/2-97 have a mean difference of 0.7 %, with the maximum difference being 1.8 %. This reproducibility error is consistent with the analytical uncertainty on individual data points. The greater precision of these analyses compared to the Thermaikos Gulf is due to the use of ICP-MS and the simpler clean-up procedure.

3.3.1 Variation with salinity

Figure 4 shows the open Mediterranean data normalised to a salinity of 35. The open Mediterranean data set results in a mean U* that is statistically greater (at the 1 % significance level) than the Chen *et al.* (1986) value, the former being 3.266 ± 0.014 ng g^{-1} and the latter 3.215 ± 0.018 ng g^{-1}. However, if the data from each cruise is considered separately some differences emerge. Data from the MAI/1-97 and MAI/2-97 cruises have a combined mean U* = 3.235 ± 0.013 ng g^{-1}, which is not significantly different from the Chen *et al.* value at the 1 % significance level, whereas data from the MAI/8-99 and the TMC cruises have a combined mean U* of 3.297 ± 0.016 ng g^{-1} and are significantly different. Given that the former data were not corrected for mass fractionation, there is some additional uncertainty in the MAI/1-97 and MAI/2-97 data, and it is not unreasonable to assume that the MAI/8-99 and TMC data were the more accurate. Thus, we have some initial evidence that the standard relationship may not hold in the Mediterranean.

There are several possible reasons for this potential offset between the ^{238}U – salinity relationship determined for this Mediterranean data set and Chen *et al.*'s relationship derived for the Atlantic and Pacific Oceans. Firstly, there could be a real difference in the Mediterranean Sea; exchange with the open ocean is restricted, which could lead to variations in its character. Secondly, there could be an analytical bias in the current data set. These possibilities are discussed further below.

First we examine literature evidence for U enrichment in the Mediterranean. Two studies have looked previously at the ^{238}U – salinity relationship for the Mediterranean. Schmidt and Reyss (1991) examined ^{238}U data from the western Mediterranean (principally from the Ligurian Sea and one sample from the Alboran Sea) and the eastern Atlantic. Some additional Atlantic ^{238}U data from the same period were later published in Schmidt (2006), and these have been included in this discussion for comparison with the Mediterranean data. Schmidt and Reyss (1991) concluded that the Mediterranean was enriched in ^{238}U relative to the open ocean relationship of Ku *et al.* (1977) by around 4 %. They hypothesised that either the ^{238}U – salinity relationship does not hold at higher salinities or that the Mediterranean is specifically enriched in ^{238}U. An enrichment mechanism connected with increasing use of phosphate fertilisers was discussed, but no isotope ratio data were available to support this suggestion. However, when their data are examined more closely (Table 4, Figure 5) it can be seen that there is only a small difference between their mean salinity normalised ^{238}U concentration for the Mediterranean ($U^* = 2.59 \pm 0.05$ dpm l^{-1}) and the Atlantic ($U^* = 2.57 \pm 0.05$ dpm l^{-1}). This difference is not statistically significant. Thus it is impossible to conclude from this evidence that the Mediterranean is enriched with respect to U. Given the magnitude of the offset from both the Chen *et al.* and Ku *et al.* data sets, and the fact that both oceans show an offset, it seems more likely that all the data from Schmidt and Reyss (1991) and Schmidt (2006) suffer a systematic analytical bias.

Ten years later, Delanghe *et al.* (2002) analysed an additional 5 samples from the north-western Mediterranean in a higher precision TIMS study, that included both ^{238}U and isotope ratio data. They concluded that there was no evidence of U enrichment in Mediterranean relative to the open ocean, from either ^{238}U concentrations or the ^{234}U:^{238}U isotope ratio (Table 4, Figure 5), although it should be remembered that this is a very small data set from a single location. Indeed the mean U* for the Mediterranean and Atlantic data are slightly lower than that of Chen *et al.* (1986) (Chen *et al.*, U* = 3.215 ± 0.018 ng g^{-1}; Delanghe *et al.*, Mediterranean U* = 3.201 ± 0.043 ng g^{-1}; Delanghe *et al.*, Atlantic U* = 3.190 ± 0.065 ng g^{-1}), but the difference is not significant. This data set is discussed more fully below in the context of the global ocean data set. However, it can be concluded that there is no compelling evidence in the literature for U enrichment in the open Mediterranean.

The possibility of analytical bias in the current data set needs to be acknowledged; either all the data could be systematically biased with respect to the Chen *et al.* relationship or a group of the data could be biased compared to the rest. One potential source of bias is that the Mediterranean data presented here are derived from filtered water samples, whereas the majority of other data are from unfiltered samples. Anderson (1982) is one of the few published studies of ^{238}U concentrations in suspended particulate material (SPM) in the open ocean, which were found to range between 2.3 and 24 dpm 10^6 l^{-1} (equivalent to 3.17×10^{-6} and 3.30×10^{-5} ng g^{-1}, assuming a seawater density of 1.027 kg l^{-1}). Thus, the presence or absence of SPM does not appear to be capable of producing the observed offset.

The samples were collected on 4 separate campaigns over a 2 year period, so the only likely persistent source of bias is the ^{236}U tracer solution. The ^{236}U tracer solution was purchased immediately prior to the first campaign, and, following dilution was stored at 4 °C throughout this work. No additional calibrations were carried out on this tracer, so the possibility of an initial inaccuracy in the published concentration or of some drift during the work cannot be eliminated, particularly given the small size of the offset observed.

To conclude, we have observed a small offset from the Chen *et al.* relationship in some of our open Mediterranean data. We cannot rule out an analytical source of this offset and there is no evidence in other (limited) published data sets for a Mediterranean U enrichment. If, however, this offset is real, any U enhancement in the Mediterranean is unlikely to be of phosphate origin, as has been postulated in the past. A more credible source is the Black Sea (section 3.2.1), however there is little direct evidence to strong support this hypothesis. These possibilities require further consideration in the light of the wider global data set.

3.4 ^{238}U - salinity relationships in the global ocean

Chen *et al.* (1986) was a pivotal study, being the first to use high-precision mass spectrometric techniques to examine U and Th systematics in the world's oceans. The uncertainty is small (1 % standard deviation), and certainly better than can routinely be obtained by measuring ^{238}U by α-spectrometry. Until recently, no study (including those using mass-spectrometric techniques) has achieved the same degree of measurement precision, and therefore there was no reason to question their results. However, the data presented here and by Robinson *et al.* (2004) (Table 4) are at odds with the Chen *et al.* (1986) relationship. Therefore, if we are to continue using an uncertainty of 1 % in ^{234}Th:^{238}U disequilibrium studies, we must carefully examine the evidence for doing so.

In its simplest form the flux of particulate ^{234}Th (P) can be calculated using equation 2:

$$P = \lambda(A_U - A_{Th}) \qquad (2)$$

where A_u and A_{Th} are the activities of ^{238}U and ^{234}Th respectively, and λ is the decay constant for ^{234}Th. The uncertainty in the flux of particulate ^{234}Th (σ(P)) is calculated from equation 3:

$$\sigma(P) = \lambda\sqrt{\sigma^2_{A_U} + \sigma^2_{A_{Th}}} \qquad (3)$$

where σ_{AU} and σ_{ATh} are the uncertainties on the ^{238}U and ^{234}Th activities respectively (Savoye *et al.*, 2006). Using the ^{238}U – salinity relationship of Chen *et al.* (1986) with its quoted uncertainty of 1 %, it can be argued that any uncertainty in P is dominated by the uncertainty in A_{Th}. The short half-life of ^{234}Th and the difficulty in gaining good measurements have often produced data with uncertainties of the order of 5 %. However, if small deviations from equilibrium are to be quantified accurately, the uncertainty in the ^{234}Th determination has to be minimised.

Precision in the ^{234}Th determination is coming under greater scrutiny with the introduction of the small volume MnO_2 precipitation technique (Benitez-Nelson *et al.*, 2001; Buesseler *et al.*, 2001) and more precise data is being generated as the method is gradually refined (Pike *et al.*, 2005; Rodriguez y Baena *et al.*, 2006; van der Loeff *et al.*, 2006). For example, Bidigare *et al.* (2003) achieved precisions of approximately 4 % for data collected in 2000, and Savoye *et al.* (2004) reported mean precisions of 2 % a year later in 2001. However, as ^{234}Th measurements improve so there is a greater need to know exactly what the ^{238}U concentration is in a body of seawater, especially for low particle environments, where the depletion of ^{234}Th is small. Figure 6 illustrates the effect of the uncertainty in A_{Th} and A_U on the uncertainty in P. It can be seen that, even for a fairly standard depletion of 0.5 dpm l^{-1}, an improvement in the uncertainty in A_U would be beneficial even for an uncertainty in A_{Th} of 1 %.

In order to assess the validity of the Chen *et al.* relationship, the published data on ^{238}U and salinity has been collated here (Table 4, Figures 5 and 7), together with the open Mediterranean data presented in this study. The α-spectrometry data from the present work has not been included due to the sample location, and the evidence discussed in section 3.2.1 regarding U enrichment.

While the Chen *et al.* study is embraced as representing the best estimate we have of open-ocean ^{238}U concentrations it is not without problems. Firstly, although the samples used do cover a range of salinities, it is a rather narrow range (34.14 – 36.08) and the sampling locations were not geographically extensive. Secondly, as noted by Chen *et al.*, there is a small but significant difference between the mean values obtained for the two oceans (Atlantic U* = 3.189 ± 0.023 ng g^{-1}; Pacific U* = 3.238 ± 0.089 ng g^{-1}). Finally, Chen *et al*. noted a discrepancy between the spread of data obtained and models of U distribution in the oceans. Due to the long residence time of U with respect to water it is predicted that the surface and deep reservoirs should have virtually identical U concentrations. This prediction was not born out by their data, which exhibited a range an order of magnitude greater than predicted by the model. Two possibilities can account for this anomaly: either the estimated residence time of U in the ocean is too large or there is an analytical artefact in the data, perhaps that U is lost to the container walls during transit or that there is a greater uncertainty in individual measurements than is acknowledged. These options are systematically evaluated below.

Dunk *et al.* (2002) carried out a comprehensive review of the uranium budget for the Holocene ocean. They considered in detail the uncertainties associated with all U sources and sinks to the world ocean, and produced a net input to the oceans of 41.9 ± 17.8 Mmol y^{-1} and an output of 47.9 ± 13.8 Mmol y^{-1}. Taking the extremes of these values, along with an oceanic reservoir of (19 ± 1.2) × 10^6 Mmol (based on Chen *et al.*'s mean U*), gives a range in oceanic residence times of 2.9 - 8.4 × 10^5 years. The lowest of these values is still an order of magnitude too high to explain the variation in Chen *et al.*'s data. Given the conservative approach that Dunk *et al.* adopted in their determination of uncertainties, it seems unlikely that the residence time of U in the oceans lies outside this range.

The final possibility is analytical. In order to fully discuss this possibility, other studies need to be considered (Table 4, Figures 5 and 7). Three other studies result in a mean U* equal, within statistical uncertainty, to Chen *et al.*'s value, namely Ku *et al.* (1977), Delanghe *et al.* (2002) and

Gustafsson *et al.* (1998). Ku *et al.* (1977) is a low precision alpha spectrometry study, but it covers a wide range of salinity and 4 oceans (Atlantic, Pacific, Arctic and Antarctic). Indeed, this study is the only published collection of data from the polar oceans. However, it contains a large spread of data and, although the replicates agree extremely well (0.01 % replication error), the precision of individual measurements is not good compared to mass-spectrometric data (1.9 %). Delanghe *et al.* (2002) is a high-precision TIMS study of 21 samples from 3 oceans (Atlantic, Indian and Mediterranean) covering a good range of salinities (34.72 – 38.56). They observed significant variations between the oceans, in particular between the Atlantic and Mediterranean, which were in close agreement as discussed above, and the Indian Ocean (Table 4, Figure 5). Although their precision for individual measurements was excellent (0.1 %), they had a limited set of replicate samples, which were not in particularly close agreement (1.6 %). Finally, Gustafsson *et al.* (1998) looked at a limited data set (2 sets of triplicate samples) at a low salinity site in the Gulf of Maine. Although they achieved high precision measurements (0.3 % for individual samples), again there was a relatively large scatter in the data.

In general, these studies have all concluded that Chen *et al.*'s ^{238}U – salinity relationship is supported by their data. No attempt has been made to explain the scatter seen in the data with one exception. Delanghe *et al.* (2002) observed two points from the Atlantic that fell significantly below the Chen *et al.* relationship, which were hypothesised to be influenced by Mediterranean Outflow Water (MOW). During its transit out of the Mediterranean, water is forced deep and into contact with relatively organic rich sediments, which could deplete U. However, Schmidt (2006) studied MOW in samples from either side of the Gibraltar Strait and in Meddies in the eastern Atlantic. Although this data set seems to suffer a systematic bias, as discussed in section 3.3.1, there is no evidence of depletion of ^{238}U in MOW relative to other Atlantic samples within the same study.

Now, however, Robinson *et al.* (2004) have completed another high-precision study in the Atlantic. Only one station was studied, but due to its location in the Bahamas the samples encompass a wider range of salinity than Chen *et al.*'s work (approximately 35.4 – 37.3, Table 4). This study is the only one to match Chen *et al.* for precision in both individual measurements *and* in replication, but more importantly there is virtually no scatter in the data. The correlation between ^{238}U and salinity gives an $R^2 = 0.92$, compared to 0.53 for Chen *et al.*'s data. Consequently, this is the first study that provides ^{238}U concentration data that is as constant as the models predict. However, the mean U* determined by Robinson *et al.* is significantly different from that of Chen *et al.* (3.33 ng g^{-1} compared to 3.215 ± 0.032 ng g^{-1}). There are various explanations for this discrepancy: (i) Robinson *et al.* have a systematic bias in their data; (ii) the ^{238}U – salinity relationship is not as simple as supposed and there is much more scatter in the data than can be accounted for by the models; or (iii) Robinson *et al.* have determined the correct value for U* and the community needs to re-evaluate its use of the Chen *et al.* relation.

At the present time, the lack of any other high precision data precludes choosing between these options, although option (ii) seems unlikely given our knowledge of U biogeochemistry at the current time. The data evaluated in this study for the Mediterranean lie between the mean U* for Chen *et al.* and Robinson *et al.*, and could therefore be used to argue for either study. However, there is a mounting body of evidence that we cannot be as confident in our evaluation of the ^{238}U – salinity relationship as has previously been supposed. Although the offset between the Chen *et al.* and Robinson *et al.* relations is small in absolute terms (approximately 3 %), if it is treated as an additional uncertainty in the ^{238}U concentration, there is a large impact in the resulting uncertainties in particulate ^{234}Th fluxes calculated from the ^{234}Th deficit.

Taking only the mass spectrometric data presented in Table 4 and Figures 5 and 7, a new mean U* has been determined for the world ocean, *i.e.* 3.257 ± 0.057 ng g^{-1} or 2.496 ± 0.043 dpm l^{-1} (where the uncertainties are 1 standard deviation of the means, and assuming a seawater density of 1.027 kg l^{-1}). Thus, ^{238}U can be determined by equations (4) and (5):

$$A_U\left(ng\,g^{-1}\right) = (0.0931 \pm 0.0016) \times S \qquad (4)$$

$$A_U\left(dpm\,l^{-1}\right) = (0.0713 \pm 0.0012) \times S \qquad (5)$$

where S is the salinity. Although the difference between this relation and that of Chen *et al.* in terms of the absolute ^{238}U concentration is small, the uncertainty has been doubled. Until such a time as the ^{238}U can be determined with greater precision and accuracy and its relationship with salinity better defined, this larger uncertainty should be used when determining ^{238}U concentrations by this method.

4. Conclusions

This work has examined ^{238}U – salinity data from a coastal region (the Thermaikos Gulf) and the open Mediterranean. The Thermaikos Gulf data are somewhat scattered, but in general support the use of the Chen *et al.* ^{238}U – salinity relation. However, evidence of U enrichment in the northern part of the Gulf, close to Thessaloniki, could be the result of phosphate fertiliser plants in the catchment. The data for the open Mediterranean is slightly offset from the Chen *et al.* relation. When the open Mediterranean data set is put into the context of all known literature values for ^{238}U – salinity, it becomes apparent that the tight constraints normally placed on U* are not justified by the data, in particular when the current study and recent work by Robinson *et al.* (2004) is taken into account.

The only way to eliminate analytical artefacts as a cause of scatter within data sets and the offset between Chen *et al.* (1986) and the current work and Robinson *et al.* (2004) is to carry out a wide-ranging study, using the best analytical techniques available, including as many geographic regions as possible, and crucially including a high degree of replication, which is the only means of completely eliminating the possibility of real scatter in the data. In particular, more samples must be collected from the polar oceans from which no samples have been studied since the 1970s (Ku *et al.*, 1977). Additional consideration needs to be given to the role of particulate U, as previous studies have all been on unfiltered water.

In the meantime thought must be given to how ^{238}U – salinity relationships are applied in ^{234}Th disequilibrium studies. Given that few laboratories world-wide can routinely achieve the necessary analytical precision in ^{238}U determinations, the best strategy is to continue using salinity-derived data. However, the new relation proposed here should be used, and the larger uncertainty taken into account.

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Figure captions

Figure 1: Sampling stations in the Thermaikos Gulf. The position of the Thermaikos Gulf in relation to the Mediterranean is shown in Figure 2.

Figure 1: Approximate positions of the sampling stations in the open Mediterranean (MATER and Trans-Mediterranean cruises). The A, O and S transects referred to in Table 2 run through the principal stations (A1, O2 and I1 respectively), perpendicular to the coastline. The box indicates the Thermaikos Gulf.

Figure 3: ^{238}U concentration normalised to a salinity of 35 (U*) for the Thermaikos Gulf, NW Aegean Sea: (A) northern area; (B) eastern and western areas as defined by Zervakis *et al.* (2005). Error bars on the data points are the 1 sigma uncertainties, based on counting statistics. The solid lines represent the mean U* for the Chen *et al.* (1986) data set and the Thermaikos Gulf data sets as indicated on the figure. The shaded areas are the 99 % confidence intervals of each mean, with the Chen *et al.* interval being bounded by dashed lines.

Figure 4: ^{238}U concentration normalised to a salinity of 35 (U*) for the open Mediterranean (see Tables 2 and 3 for collection details). The solid lines represent the mean U* for the Chen *et al.* (1986) relationship, the MAI/1 and MAI/2 data and the TMC and MAI/8-99 data as indicated on the figure. The shaded areas are the 99% confidence intervals of each mean, with the Chen *et al.* interval being bounded by dashed lines.

Figure 5: Mean ^{238}U activities normalised to a salinity of 35 for each of the published ^{238}U – salinity data sets. The number in each column is the total number of samples analysed in each study. The solid and dotted lines represent the mean ± 99% confidence interval U* found by Chen *et al.* (1986). The error bars represent the range of the data and symbols are mean values for each studied ocean, except for the "all" data point, which is the mean ± 99% confidence interval of all the mass spectrometric studies collated here. A) Alpha spectrometric studies, together with the Chen *et al.* (1986) study converted to dpm l^{-1} (see text for details); B) mass spectrometric studies.

Figure 6: The uncertainty in the flux of particulate ^{234}Th (P) as a function of the uncertainty in the ^{234}Th activity (A_{Th}) for different ^{238}U activity (A_U) uncertainties between 1% and 5%. In all cases, the ^{234}Th depletion is 0.5 dpm l^{-1}, where ^{234}Th depletion is defined as $A_U - A_{Th}$.

Figure 7: ^{238}U concentrations as a function of salinity for all mass spectrometric studies. The solid line is the mean salinity normalized ^{238}U for Chen *et al.* (1986), extrapolated to the range of salinities shown, together with the 99 % confidence interval. The data from Robinson *et al.* (2004) have been extrapolated from the published mean ^{238}U concentration, over the range of salinities studied.

Table 1: ^{238}U concentrations and salinity data from the Thermaikos Gulf: cruises IP/1-01, IP/2-01 and IP/3-02. The locations of the stations are given in Figure 1. Shaded data were treated as replicates. The uncertainties are 1σ errors, based on propagated counting statistics.

Cruise (Date)	*IP/1-01 (Sept. 2001)*		*IP/2-01 (Oct. 2001)*		*IP/3-02 (Feb. 2002)*	
Depth (m)	**^{238}U (dpm l^{-1})**	**Salinity**	**^{238}U (dpm l^{-1})**	**Salinity**	**^{238}U (dpm l^{-1})**	**Salinity**
Station IP01 (Water column depth = 29 m)						
2	2.81 ± 0.08	36.423	2.82 ± 0.11	37.036	2.76 ± 0.09	37.510
10	--	--	2.67 ± 0.09	37.039	2.80 ± 0.08	37.856
20	--	--	2.65 ± 0.11	37.045	2.83 ± 0.09	38.419
25	--	--	2.78 ± 0.10	37.091	2.96 ± 0.10	38.383
28	--	--	2.65 ± 0.11	37.102	2.84 ± 0.07	38.378
Station IP10 (Water column depth = 40 m)						
30	2.72 ± 0.10	37.838	--	--	--	--
39	--	--	--	--	2.73 ± 0.07	38.236
Station IP17 (Water column depth = 55 m)						
2	--	--	2.52 ± 0.09	36.999	2.86 ±0.13	38.610
10	--	--	--	--	2.98 ± 0.12	38.608
20	2.62 ± 0.07	37.130	--	--	--	--
45	2.73 ± 0.08	28.207	2.63 ±0.12	38.233	--	--
53	2.88 ± 0.10	38.363	2.78 ± 0.08	38.523	2.78 ± 0.13	38.467
53.5	2.57 ± 0.10	38.363	--	--	--	--
54	2.80 ± 0.12	38.363	--	--	2.77 ± 0.12	38.465
54.5	2.56 ± 0.07	38.363	--	--	2.85 ± 0.13	38.465
Station IP18 (Water column depth = 59 m)						
2	2.80 ± 0.10	36.973	--	--	--	--
20	2.52 ± 0.09	37.128	--	--	--	--
50	2.87 ± 0.09	28.527	--	--	--	--
55	2.62 ± 0.09	38.540	--	--	--	--
58	2.67 ± 0.09	38.538	--	--	--	--
Station IP27 (Water column depth = 63 m)						
2	2.68 ± 0.09	37.070	2.56 ± 0.12	37.016	2.76 ± 0.10	38.601
10	--	--	--	--	2.60 ± 0.13	38.598
20	2.51 ± 0.09	37.199	--	--	2.60 ± 0.08	38.586
50	--	--	--	--	2.65 ± 0.07	38.384
54	2.88 ± 0.10	38.322	2.69 ± 0.10	38.539	--	--
59	2.72 ± 0.12	38.326	2.44 ± 0.11	38.555	--	--
62	2.67 ± 0.10	38.311	2.58 ± 0.08	38.547	--	--
Station IP30 (Water column depth = 84 m)						
2	2.72 ± 0.07	37.097	--	--	--	--
20	2.93 ± 0.08	37.112	--	--	--	--
50	2.79 ± 0.07	38.475	--	--	--	--
70	3.07 ± 0.08	38.539	2.86 ± 0.12	38.550	--	--
76	3.06 ± 0.08	38.537	--	--	--	--
Station IP38 (Water column depth = 50 m)						
2	2.63 ± 0.10	37.094	2.54 ± 0.10	37.025	2.72 ± 0.10	38.536
10	2.68 ± 0.09	37.100	--	--	2.73 ± 0.09	38.609
20	2.66 ± 0.08	37.115	--	--	2.59 ± 0.09	38.509
41	2.59 ± 0.07	38.100	2.60 ± 0.10	38.232	2.48 ± 0.11	38.580
46	2.91 ± 0.10	38.109	2.55 ± 0.11	38.299	2.58 ± 0.10	38.565
49	--	--	2.87 ± 0.13	38.297	2.47 ± 0.10	38.551
Station IP41 (Water column depth = 79 m)						
2	--	--	--	--	2.80 ± 0.14	38.633
10	2.72 ± 0.08	37.085	2.57 ± 0.12	37.137	--	--
20	2.62 ± 0.07	37.113	--	--	2.84 ± 0.11	38.627
50	2.73 ± 0.08	38.209	--	--	--	--
70	2.74 ± 0.08	38.289	--	--	--	--

Table 2: ^{238}U concentrations and salinity data from the open Mediterranean: Adriatic and Ionian Seas. The locations of the stations are given in Figure 2. A and B indicate replicate samples. Samples from each cruise were analysed separately. Samples from MAI/1-97 and MAI/2-97 were not corrected for mass fractionation, whereas samples from the MAI/8-99 cruise were (see text for details). The uncertainties are 1σ errors.

Station	Position	Depth	^{238}U (ng g^{-1})	Salinity
Cruise: MAI/1-97 (March 1997)				
A1	41º 48´N 17º 48´E	5A	3.532 ± 0.022	38.502
		5B	3.566 ± 0.034	38.502
		200	3.592 ± 0.025	38.700
		500	3.588 ± 0.023	38.652
		1054	3.556 ± 0.029	38.595
O2	39º 49´N 18º 56´E	5A	3.585 ± 0.031	38.486
		5B	3.548 ± 0.027	38.486
		60	3.575 ± 0.035	38.462
		150	3.580 ± 0.029	38.782
		500A	3.595 ± 0.029	38.735
		500B	3.587 ± 0.027	38.735
		650	3.553 ± 0.029	38.721
I1	38º 30´N 18º 00´E	5	3.529 ± 0.029	38.044
		80A	3.545 ± 0.027	37.969
		80B	3.572 ± 0.021	37.969
		150	3.599 ± 0.018	38.713
		500	3.599 ± 0.023	38.751
		2200A	3.566 ± 0.019	38.748
		2200B	3.558 ± 0.016	38.748
Cruise: MAI/2-97 (August 1997)				
A1	41º 50´N 17º 47´E	5A	3.621 ± 0.029	38.778
		5B	3.556 ± 0.021	38.778
		50	3.531 ± 0.033	38.674
		150A	3.571 ± 0.051	37.717
		150B	3.548 ± 0.031	37.717
		350	3.588 ± 0.027	38.683
		1000A	3.549 ± 0.031	38.601
		1000B	3.541 ± 0.021	38.601
O2	39º 51´N 18º 59´E	5	3.563 ± 0.027	38.638
		60	3.563 ± 0.035	38.607
		200	3.554 ± 0.033	38.883
I1	38º 29´N 18º 06´E	5	3.513 ± 0.049	38.452
		200	3.534 ± 0.046	38.754
		1000	3.557 ± 0.035	38.713
		2200	3.590 ± 0.035	38.754
Cruise: MAI/8-99 (March 1999)				
P1	42º 50´N 14º 54´E	2	3.586 ± 0.009	38.540
A2	41º 12´N 16º 56´E	5	3.595 ± 0.018	38.296
A6	41º 26´N 17º 15´E	5	3.607 ± 0.010	38.693
A8	41º 40´N 17º 34´E	5	3.607 ± 0.010	38.706
A10	42º 02´N 18º 04´E	5	3.694 ± 0.018	38.716
A12	42º 09´N 18º 12´E	5	3.674 ± 0.015	38.708
O0	39º 50´N 18º 36´E	5	3.519 ± 0.014	38.656
O2	39º 50´N 18º 57´E	5	3.590 ± 0.020	38.786
O3	39º 50´N 19º 06´E	5	3.591 ± 0.022	38.618
S4	38º 30´N 18º 30´E	5	3.727 ± 0.017	38.766
S5	38º 30´N 19º 00´E	5	3.660 ± 0.012	38.700

Table 3: ^{238}U concentrations and salinity data from the open Mediterranean: Trans-Mediterranean Cruise, June 1999. The locations of the stations are given in Figure 2. The uncertainties are 1σ errors.

Station	Position	Depth	^{238}U (ng g^{-1})	Salinity
TM-01	35º 48´N 28º 41´E	3	3.654 ± 0.008	39.008
		100	3.679 ± 0.016	39.055
TM-02	34º 09´N 32º 46´E	3	3.701 ± 0.010	38.943
		100	3.725 ± 0.009	38.930
		200	3.652 ± 0.018	39.017
TM-03	33º 23´N 28º 19´E	100	3.725 ± 0.017	38.905
		350	3.691 ± 0.009	38.926
TM-04	34º 53´N 22º 32´E	100	3.697 ± 0.013	38.844
		200	3.649 ± 0.013	38.910
TM-05	35º 43´N 20º 08´E	3	3.687 ± 0.010	38.595
		100	3.636 ± 0.016	38.650
		200	3.675 ± 0.010	38.941
TM-06	35º 37´N 17º 23´E	100	3.616 ± 0.009	38.530
		200	3.651 ± 0.009	38.631
TM-07	36º 19´N 12º 15´E	3	3.548 ± 0.012	37.278
		100	3.556 ± 0.007	37.768
		200	3.663 ± 0.016	38.469
TM-08	38º 24´N 06º 53´E	3	3.521 ± 0.010	37.436
		100	3.567 ± 0.011	38.031
		200	3.614 ± 0.010	38.360
TM-10	40º 35´N 04º 55´E	3	3.522 ± 0.016	37.464
		100	3.590 ± 0.011	38.148
		200	3.615 ± 0.008	38.234

Table 4: Summary of published ^{238}U – salinity relationships. U* is the mean ^{238}U concentration normalised to a salinity of 35. The units of U* are those given in the study, and converted to dpm l^{-1} (alpha spectrometry studies) or ng g^{-1} (mass spectrometry studies) as described in the text. Measurement uncertainties are the mean errors quoted for individual data points; replication uncertainties are the mean differences between replicate samples, as described in the text. The quoted errors are 1 standard deviation of the mean.

Study	**Method**	**Mean Uncertainties**		**N**	**U***		**Salinity range**
					Published	**Converted**	
Ku *et al.* (1977)	Alpha spectrometry	Measurement	Replication		µg l^{-1}	dpm l^{-1}	
Overall		1.9 %	0.01 %	67 (4)	3.34 ± 0.10	2.50 ± 0.10	3.30 – 36.140
Arctic				13 (0)	3.42 ± 0.04	2.56 ± 0.03	30.30 – 34.93
Antarctic				19 (0)	3.27 ± 0.05	2.44 ± 0.04	33.492 – 34.965
Atlantic				28 (4)	3.35 ± 0.10	2.50 ± 0.08	34.513 – 36.140
Pacific				7 (0)	3.37 ± 0.13	2.51 ± 0.10	34.590 – 35.173
Schmidt & Reyss (1991); Schmidt (2006)	Alpha spectrometry	Measurement	Replication		dpm l^{-1}		
Overall		4.9 %	--	32 (0)	2.58 ± 0.08		35.21 – 39.18
Atlantic				14 (0)	2.57 ± 0.07		35.21 – 36.45
Mediterranean				18 (0)	2.59 ± 0.08		38.14 – 39.18
Rengarajan *et al.* (2003)	Alpha spectrometry	Measurement	Replication		µg l^{-1}	dpm l^{-1}	
Overall (Arabian Sea)		2.6 %	--	61 (0)	3.210 ± 0.107	2.396 ± 0.080	34.892 – 36.557
Chen *et al.* (1986)	Mass spectrometry	Measurement	Replication		ng g^{-1}	dpm l^{-1}	
Overall		0.5 %	0.3 %	21 (5)	3.215 ± 0.032	2.458 ± 0.024	34.140 – 36.080
Atlantic				10 (2)	3.189 ± 0.028	2.440 ± 0.022	34.611 – 36.080
Pacific				11 (3)	3.238 ± 0.011	2.476 ± 0.009	34.140 – 35.275
Gustafsson *et al.* (1998)	ICP-MS	Measurement	Replication		dpm kg^{-1}	ng g^{-1}	
Overall (Gulf of Maine)		0.3 %	3.6 %	6 (2)$	2.413 ± 0.058	3.233 ± 0.077	31.267 – 31.705
Delanghe *et al.* (2002)	TIMS	Measurement	Replication		pmol g^{-1}	ng g^{-1}	
Overall		0.1 %	1.6 %	21 (1)	13.562 ± 0.281	3.228 ± 0.067	34.72 – 38.56
Atlantic				8 (1)	13.405 ± 0.298	3.190 ± 0.071	34.94 – 35.92
Indian				8 (0)	13.789 ± 0.164	3.282 ± 0.039	34.72 – 35.28
Mediterranean				5 (0)	13.451 ± 0.157	3.201 ± 0.037	38.44 – 38.56
Robinson *et al.* (2004)	MC-ICP-MS	Measurement	Replication		µg kg^{-1}	ng g^{-1}	
Overall (Atlantic)		0.2 %	0.3 %	14 (3)	3.33†	3.33†	35.4 – 37.3 ‡
This study	ICP-MS	Measurement	Replication			ng g^{-1}	
Overall (Mediterranean)		0.6 %	0.7 %	68 (8)		3.266 ± 0.045	37.278 – 39.055

$ Two sets of triplicate samples.; † No uncertainty quoted. ‡ No salinity data quoted in paper, approximate values taken from graph.

Figure 1: Sampling stations in the Thermaikos Gulf. The position of the Thermaikos Gulf in relation to the Mediterranean is shown in Figure 2.

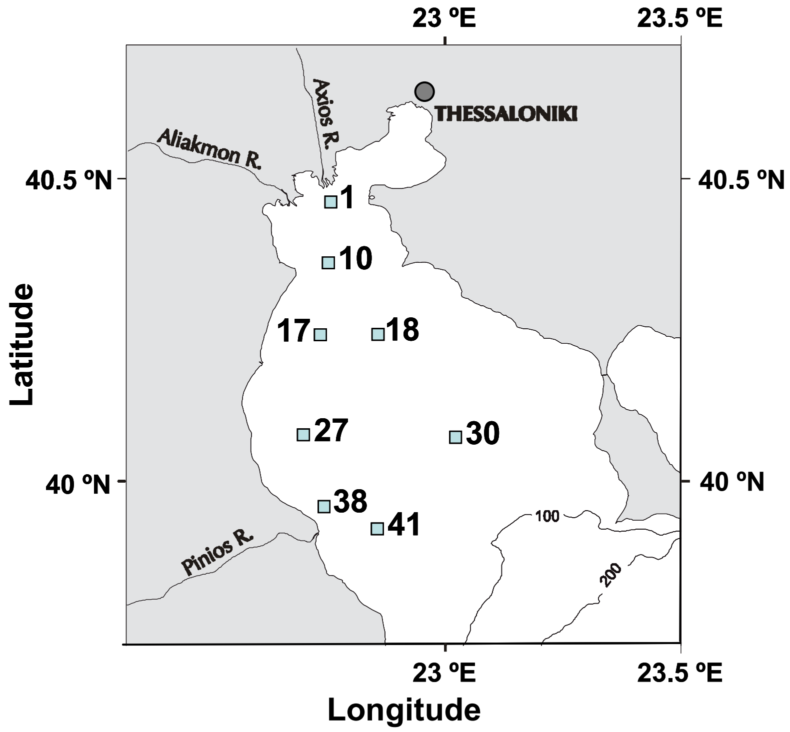

Figure 2: Approximate positions of the sampling stations in the open Mediterranean (MATER and Trans-Mediterranean cruises). The A, O and S transects referred to in Table 2 run through the principal stations (A1, O2 and I1 respectively), perpendicular to the coastline. The box indicates the Thermaikos Gulf.

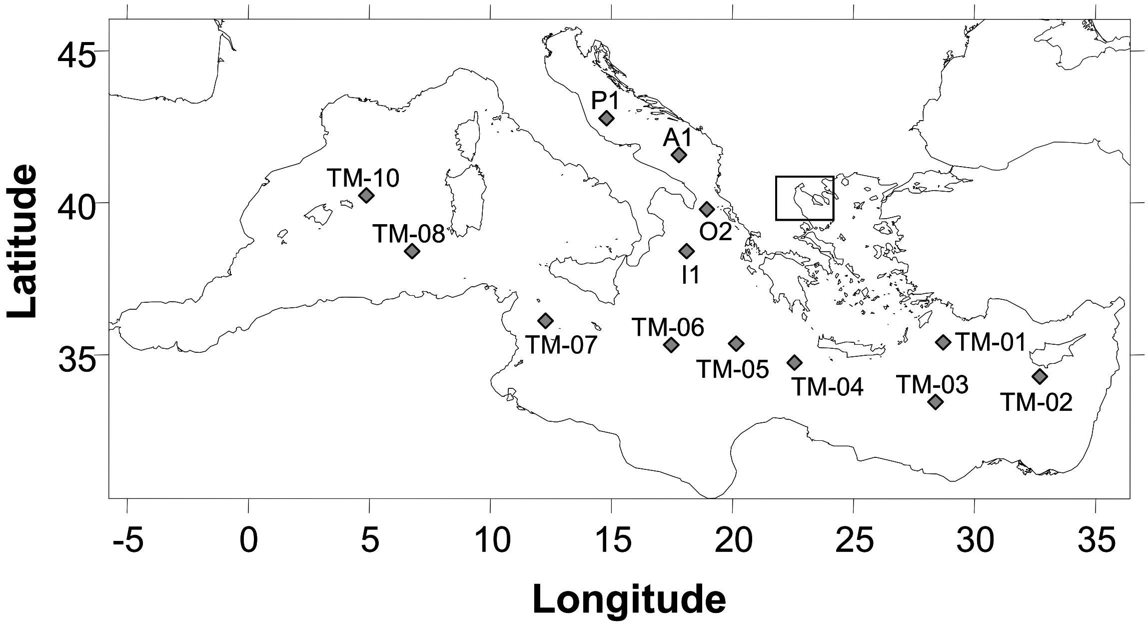

Figure 3: ^{238}U concentration normalised to a salinity of 35 (U*) for the Thermaikos Gulf, NW Aegean Sea: (A) northern area; (B) eastern and western areas as defined by Zervakis *et al.* (2005). Error bars on the data points are the 1 sigma uncertainties, based on counting statistics. The solid lines represent the mean U* for the Chen *et al.* (1986) data set and the Thermaikos Gulf data sets as indicated on the figure. The shaded areas are the 99 % confidence intervals of each mean, with the Chen *et al.* interval being bounded by dashed lines.

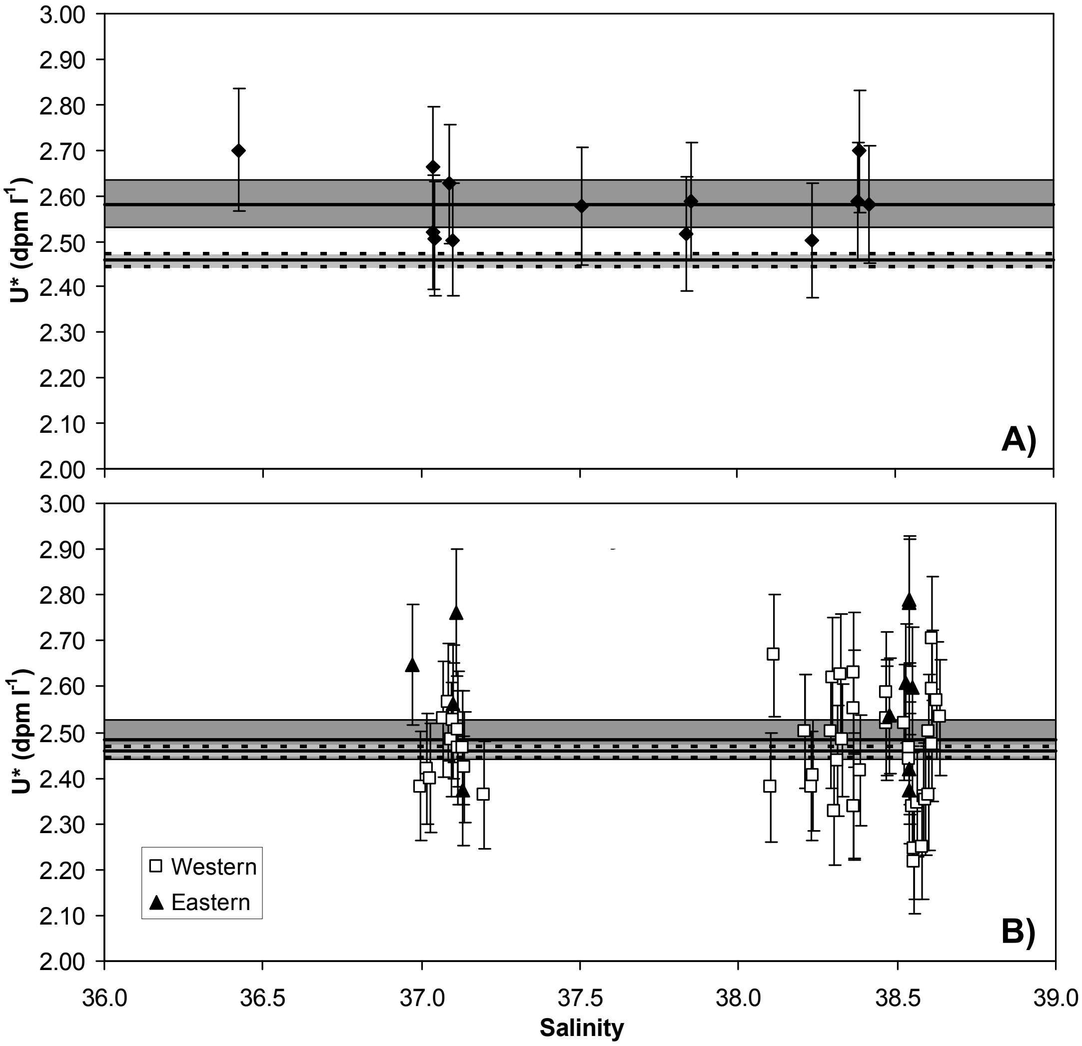

Figure 4: ^{238}U concentration normalised to a salinity of 35 (U*) for the open Mediterranean (see Tables 2 and 3 for collection details). The solid lines represent the mean U* for the Chen *et al.* (1986) relationship, the MAI/1 and MAI/2 data and the TMC and MAI/8-99 data as indicated on the figure. The shaded areas are the 99% confidence intervals of each mean, with the Chen *et al.* interval being bounded by dashed lines.

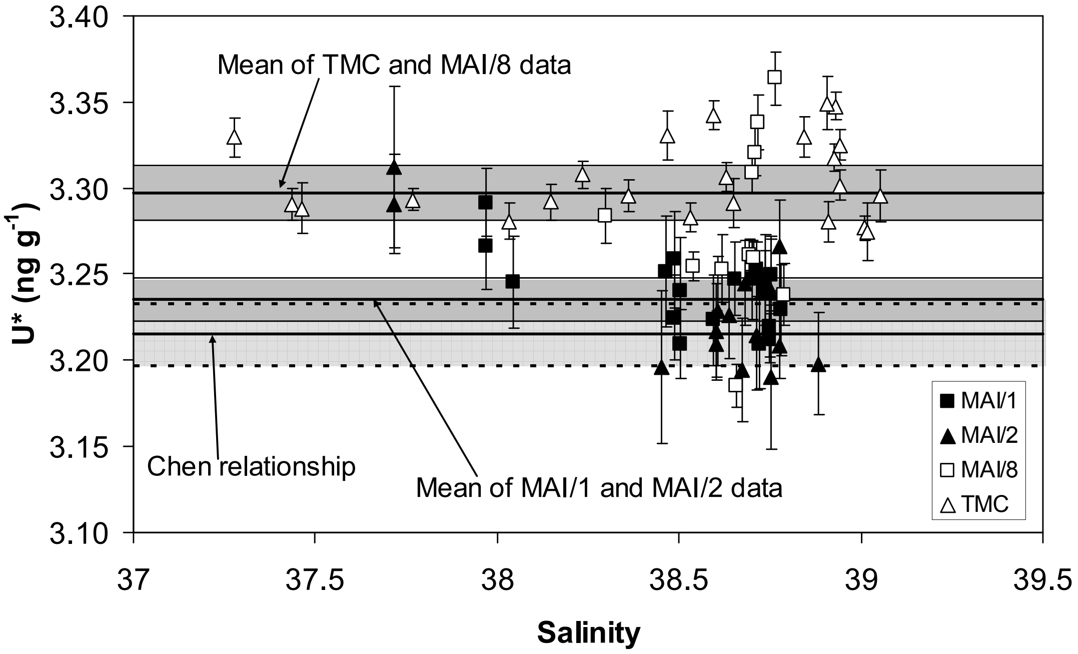

Figure 5: Mean ^{238}U activities normalised to a salinity of 35 for each of the published ^{238}U – salinity data sets. The number in each column is the total number of samples analysed in each study. The solid and dotted lines represent the mean ± 99% confidence interval U* found by Chen *et al.* (1986). The error bars represent the range of the data and symbols are mean values for each studied ocean, except for the "all" data point, which is the mean ± 99% confidence interval of all the mass spectrometric studies collated here. A) Alpha spectrometric studies, together with the Chen *et al.* (1986) study converted to dpm l^{-1} (see text for details); B) mass spectrometric studies.

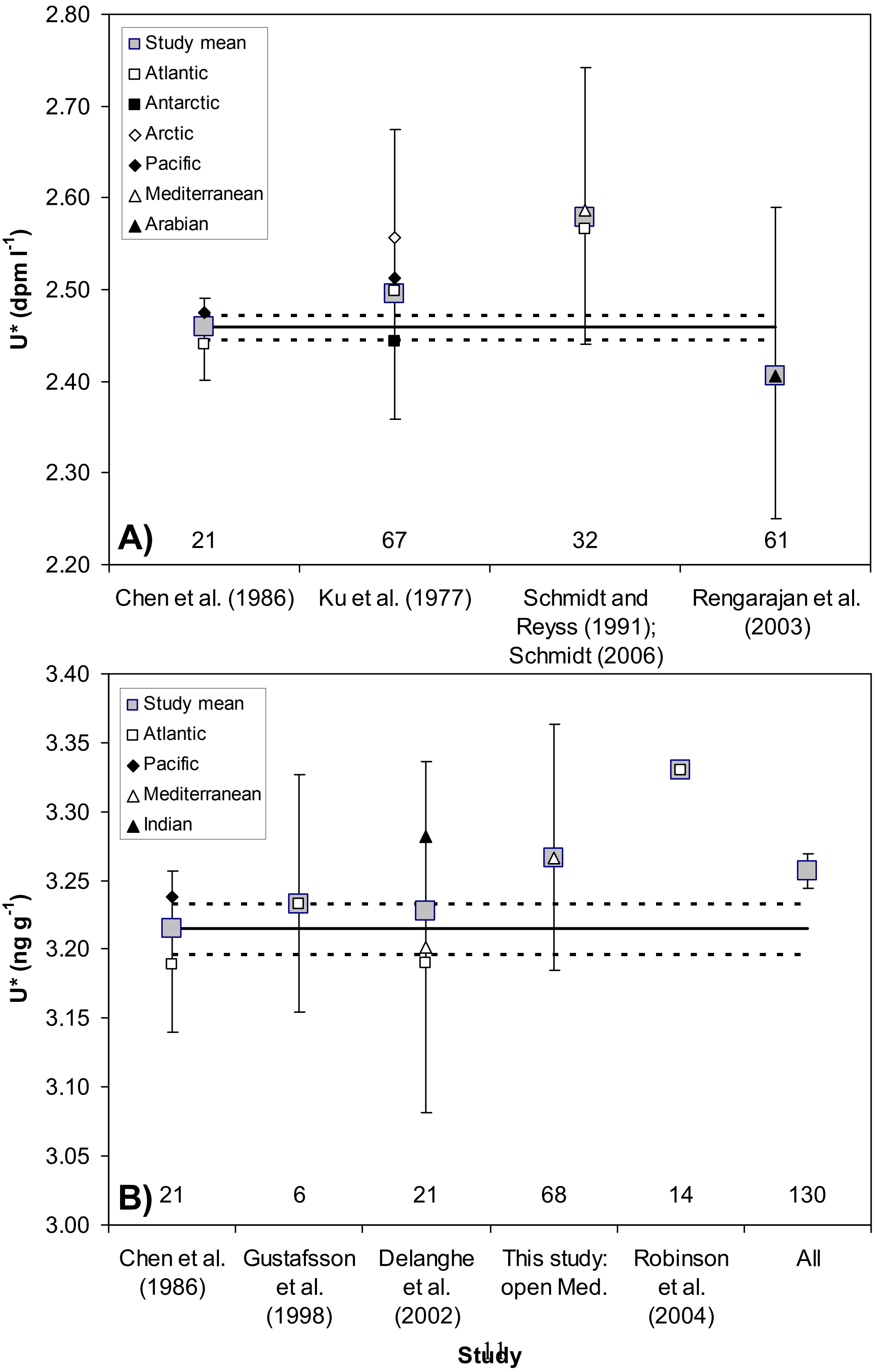

Figure 6: The uncertainty in the flux of particulate ^{234}Th (P) as a function of the uncertainty in the ^{234}Th activity (A_{Th}) for different ^{238}U activity (A_U) uncertainties between 1% and 5%. In all cases, the ^{234}Th depletion is 0.5 dpm l^{-1}, where ^{234}Th depletion is defined as $A_U - A_{Th}$.

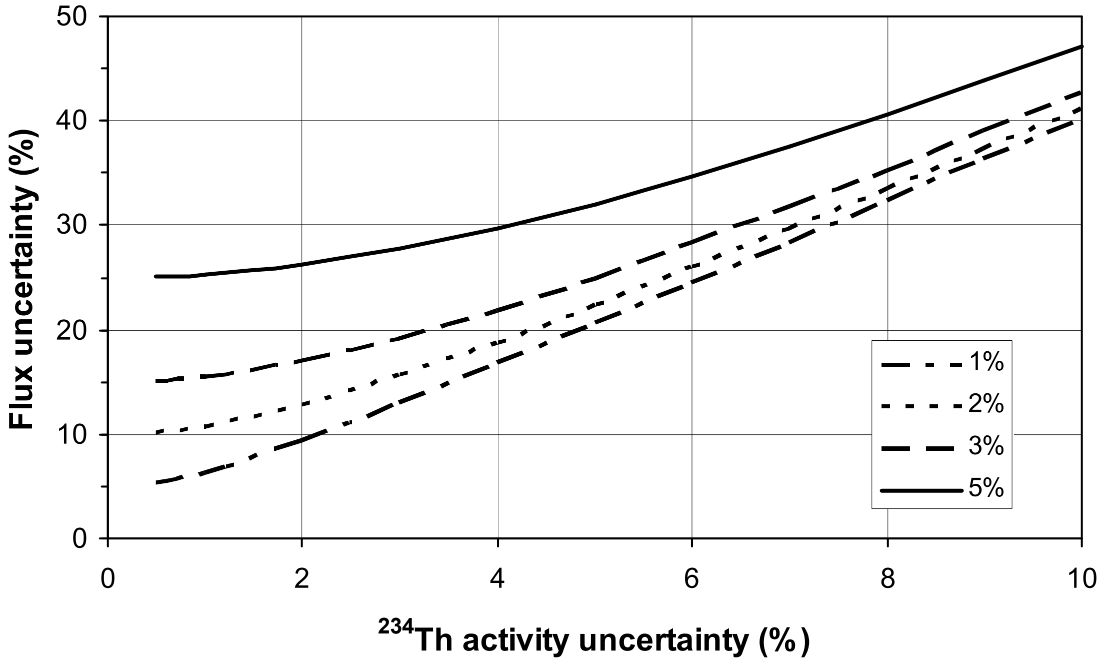

Figure 7: ^{238}U concentrations as a function of salinity for all mass spectrometric studies. The solid line is the mean salinity normalized ^{238}U for Chen *et al.* (1986), extrapolated to the range of salinities shown, together with the 99 % confidence interval. The data from Robinson *et al.* (2004) have been extrapolated from the published mean ^{238}U concentration, over the range of salinities studied.