A DECADE OF QUASIMEME Z SCORES

by Bryn Jones

Introduction

In Early 1993 Quasimeme held its first quality control intercomparison, which included 6 trace metals in marine sediments. A decade later our participation in Quasimeme has increased to include 13 metals in marine sediments and 10 metals in marine biota. We can now review our participation in the Quasimeme scheme by observing the Z scores obtained for each intercalibration.

During the past decade most of the staff employed on trace metal methods have changed, as has most of the instrumentation. Methods have been continually updated to improve the quality of data and many new staff trained. This discontinuity of methods and staff lends itself to poor analytical quality control. Throughout this period Z scores from Quasimeme have been used to identify problems at a point in time. It would take a number of years to spot trends using Quasimeme Z scores; so usual QC procedures are used to identify long-term trends. With 10 years of Z scores from Quasimeme we can look back at how successful or otherwise we have been. To observe these trends the Quasimeme decade has been split in half depending on the start date of the first intercomparison. The averages of the Z scores for each trace element measured are then given in Table 1 for sediments and Table 2 for biota.

Sediment Results

Arsenic, Mercury and Zinc are three examples where an improvement over the period can easily be identified. Arsenic had a small positive bias in the first half of the decade. For mercury a strong improvement has been made in the second half of the decade. The early years showed a positive bias with 9 results greater than +2, followed by an even bias with all z scores below +-1. Cadmium shows a dramatic improvement, a series of very high positive results in the early years are followed by a sudden improvement in the latter half. There are however a number of cadmium results with less than values or without assigned values. Where a Z score is not derived from the dataset this does decrease the overall numbers of data available for comparison.

Table 1: Mean Z scores

	As	Cd	Cr	Cu	Fe	Pb
1992-1997	0.98	8.96	0.72	1.58		1.08
1997-2001	0.46	0.33	1.33	0.66	0.34	0.81
	Li	**Mn**	**Hg**	**Ni**	**Zn**	**Al**
1992-1997			2.67	4.33	0.72	0.71
1997-2001	0.45	0.60	0.65	1.75	0.30	0.92

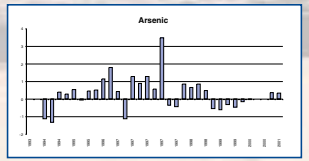
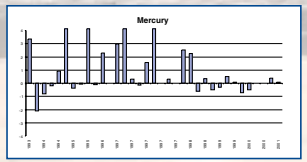


Figure 1:



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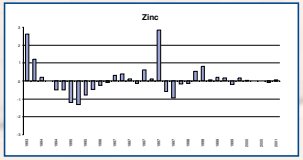

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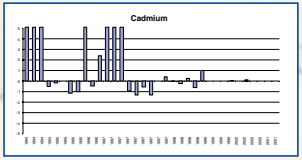

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Biota Results

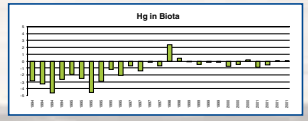
In 1994 we changed our method from an open beaker digestion to a closed vessel microwave digestion. We noticed immediately that our mercury analysis on the QC material indicated a negative bias. Surprisingly the sediments using an identical method, instrumentation and standards was producing a positive bias. The reason was traced to nitrous oxide being retained in the digest and subsequently interfering in the stannous chloride reduction step. The problem was discussed at the Quasimeme Hamburg workshop, resulting in a reliable improvement. Since then a new high pressure microwave and a different mercury analyser have overcome this problem with Z scores now less than +-1.

Table 2: Mean Z scores

	As	Cd	Cr	Cu	Pb
1994-1998	0.60	2.19	23.97	1.28	3.16
1998-2001	0.44	1.57	4.00	0.86	0.72
	Hg	**Ni**	**Zn**	**Se**	**Ag**
1994-1998	2.27	1.38	0.80	2.50	
1998-2001	0.64	0.99	0.86	1.36	0.35

All arsenic results to date have had Z scores less than 2 although a positive bias is present. In the period 1997-1998, slightly more variable Z scores were achieved, at this time staff turnover was high. This shows how even the most robust methods can be affected.

Zinc and copper are little changed with contamination from laboratory sources being a continual problem. Of the other trace metals Lead and Chromium are improved. Lead again was poorer during 1997. Our Chromium results have shown a very positive bias in the first period. Investigations into this problem have shown that it is likely due to two reasons, contamination and carbon interference on the Cr 52 isotope (C12 + Ar 40). It is also apparent that the effect is small and reasonably constant, affecting only low concentration samples. Attempts to measure this and subtract the interference have so far been unsuccessful. Improvement has been made in the latter years mainly by reducing contamination.



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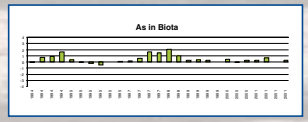

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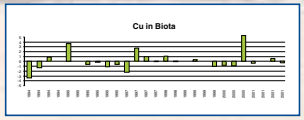

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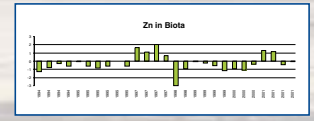

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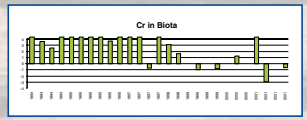

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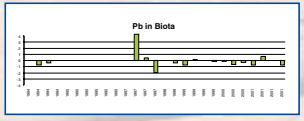

Figure 10:

Conclusion

Overall the Quasimeme scheme has helped the quality control procedures by providing marine derived material for its intercalibration exercises. It is often the case that normal QC materials show the methods to be in control, only to find the marine based Quasimeme samples fail. This can occur for a number of reasons, the most common of these include: The method is not as robust as believed for use with marine samples. Concentration levels in the intercomparison samples are lower than the normal QC materials used. Reporting and transcription errors, these often occur when reporting results in non- routine units.

The Quasimeme programme of intercalibration samples and workshops have undoubtedly helped improve the quality of the trace element data produced at this laboratory.

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