The relationship of Calcium loss with trace element concentrations in seawater life systems

Relation entre perte de Calcium et concentration en éléments traces dans l'eau de mer des aquariums

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ABSTRACT

Trace element analysis in seawater in aquarium situations was examined by ICP-OES and ICP-MS techniques.

In our traditional low-flowbed biofilter circulation seawater systems we are not losing calcium-ions, but in our invertebrate system, with a protein skimmer, however, we lose small amounts of calcium. The efficiency of protein skimmers differs according to bioload and there is evidence that relatively more calcium disappears in the foam fraction than other elements, although the reason is not yet understood.

Addition of supplements to life systems may cause strange effects. Iodide rises to very high levels after several dosages of potassium iodide in our systems.

RESUME

Une analyse des oligo-éléments dans l'eau de mer de nos aquariums a été réalisée par les techniques ICP-OES et ICP-MS.

Ces analyses nous ont indiqué que, dans notre système de filtration biologique, nous ne perdons pas d'ions calcium. Dans la section des invertébrés marins, dans laquelle un écumeur de protéines est installé, nous perdons par contre des quantités minimes de calcium. L'efficacité des écumeurs dépend largement de la charge en matières organiques et il semble que la perte en calcium soit relativement plus importante que la perte d'autres éléments. La cause de cette perte n'est pas encore comprise.

L'addition de certains suppléments dans le système de circulation peut causer des effets bizarres. Après un nombre important de dosages de potassium iodure, il apparaît que la teneur en iodure p.e. peut atteindre un niveau très élevé dans notre système.

INTRODUCTION

In the Artis Zoo Aquarium in Amsterdam there are seven closed-circulation systems in a 118-year-old building: five seawater systems and two freshwater systems. The seawater part consists of a 10°-Celsius seawater system with a volume of 70,000 litres, an 18°-Celsius seawater system with a volume of 120,000 litres, a tropical 24°-Celsius system with a volume of 120,000 litres, our largest seawater system of 400,000 litres and, last but not least, an invertebrate seawater system. The invertebrate system with a total volume of 60,000 litres consists of 4,300 litres of display aquaria and 55,000 litres in the reservoir. This system is equipped with a small protein skimmer with a capacity of 12,000 litres/hr. The building and all the equipment were almost totally renovated in 1996.

Over the years the loss of calcium in seawater life systems became much more important in relation with attempts to keep corals in good condition (Brockman, 1995.) The growth and health of living corals in aquaria is not always successful, and the shortage of minerals seems to be the main reason (Richter, 1999). Few of us have the possibility of measuring those minerals.

We asked ourselves the following questions:

Does an effective detection methods for trace elements in seawater exist?
Can our calcium detection method be optimised?
Do we have a calcium problem?

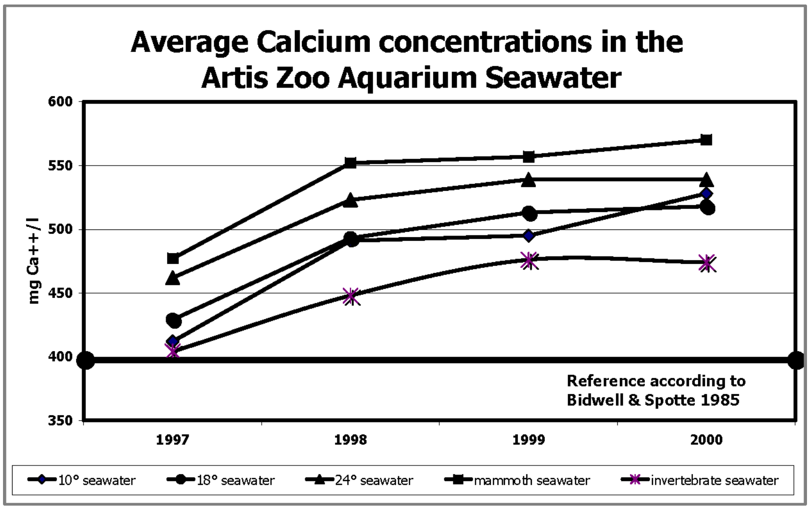
The answers were sought through analytical and chemical detection methods and the use of the analytical results to understand what is occurring in aquarium situations.

DETERMINATION OF CALCIUM IN SEAWATER IN THE ARTIS ZOO AQUARIUM

Routinely calcium is measured in seawater by a titrimetric method using EGTA and zincon as indicators (Vogel, 1978). This method is inexpensive, well suited but, to an extent, subjective.

For that reason we sought a more objective method and found spectrophotometry to be useful for seawater investigation (Merck, 1994). This method, the Merck spectroquant calcium test 14815, is based on the colour change of Glyoxalbis-(2-hydroxianil) with calcium to a red-violet complex.

This method was investigated and compared with the EGTA method. The results of both methods were comparable, but the advantage of the new method is that it is simpler.



Graph.1: Average calcium concentrations in the Artis Zoo Aquarium Seawater compared with a reference value

In the 20 years of measuring calcium in our seawater, we never found concentrations lower than natural levels. With our invertebrate system, however, the only circulation system with a protein skimmer, we have found a small decrease in calcium concentrations.

The high levels of calcium and magnesium from our mammoth system are due to the concrete material in the tank.

There is an indication that the calcium concentration is declining in our invertebrate seawater system, the only circulation system adapted with a protein skimmer.

We collected foam from the protein skimmer and analysed it. Because there is no regular sampling method for protein skimmer foam we calculated the amount of calcium as a percentage of the sodium concentration, which we considered constant.

The relative amount of calcium in the foam fraction was 30% higher than in natural seawater, hinting at selective removal of the calcium.

DETERMINATION OF TRACE ELEMENTS IN SEAWATER

Last year at the yearly meeting of the “Aquagroup”, a group of Dutch and Belgian aquarium and zoo co-workers involved in water-quality management in their institutions, the difficulties in detecting trace elements in seawater were discussed.

An investigation program was set up with three Zoos to measure trace elements in seawater samples by Inducted Coupled Plasma - Optical Electron Spectroscopy (ICP-OES) and Inducted Coupled Plasma - Mass Spectroscopy (ICP-MS).

Together both methods can deal with concentrations from 1 g/l of ions to 0.001 µg/l. They are very accurate thanks to the absence of interference due to the high salt concentration of seawater.

NATURAL SEAWATER FOR THE ARTIS ZOO AQUARIUM

The Artis Zoo Aquarium obtains its seawater from the middle of the Atlantic Ocean on the co-ordinates within small ranges from 45°41'N, 24°42'W. This area lies on the route of the large Hual Benelux b.v. Automobile carriers that travel regularly from Amsterdam to Halifax (NS, Canada) and New York (NY, USA). The seawater is taken in from a depth of 9 metres and remains no longer than 4 days in the ballast tanks. In Amsterdam, 160,000 litres of that seawater is brought by a vessel through the canals near the aquarium building and pumped into the aquarium reservoirs.

Element analysis in natural seawater
From the location 45° 46'N. 21°30' W.

Element	Reference	Average Range	Element	Reference	Average Range
	ppm			**ppb**	
Ca	400	422	Mo	10,33	2
K	383	393	Ru	?	<0.1
Mg	1319	1312	Rh	?	0
Na	10590	10731	Pd	?	<0.1
S	878	945	Ag	0,21	0
B	4,53	4	Cd	0,1	0
Fe	0,01	1	In	10	0
P	0,067	0	Sn	1,27	0
Sr	8	7	Sb	0,28	0
Br *	60*	69	I	59	50
			Cs	0,37	0
	ppb		Ba	24	6
Li	176	119	La	0,0034	<0.1
Al	10	26	Ce	0,14	<0.1
Ti	0,67	13	Pr	?	<0.1
Cr	0,6	1	W	0,11	<0.1
Mn	1,4	28	Pt	?	<0.1
Co	0,1	1	Au	0,005	<0.1
Ni	4,29	9	Hg	0,05	<0.1
Cu	2,07	30	Tl	0,1	0
Zn	6,68	353	Pb	0,03	2
Rb	121	126	Bi	0,02	<0.1
Y	0,11	0			

Table1: Elements in natural seawater for the Artis Zoo Aquarium measured by ICP-OES and ICP-MS. The results are compared with the references from Bidwell and Spotte (1985)

The constituents of seawater can be divided into major elements, minor trace elements and essential trace elements.

Table 2 shows the results of the detection of major elements in our circulation systems. It is very difficult to interpret the results only from the reference point of view. All these elements are important but some are of greater interest and give an idea of the quality of our systems.

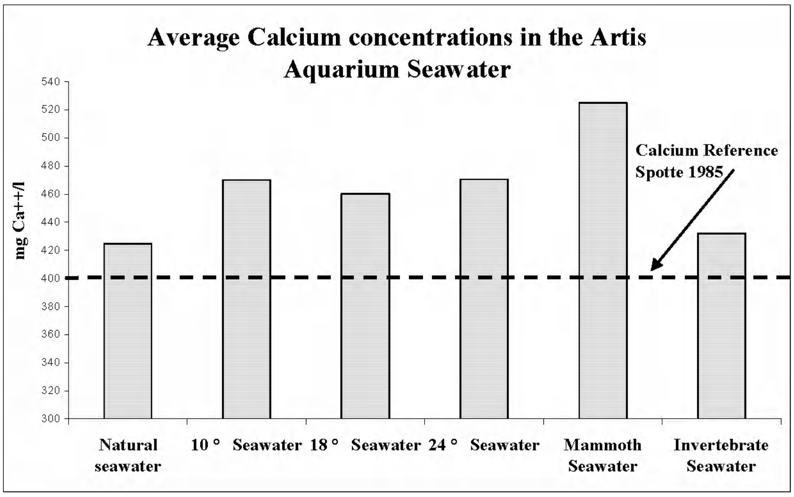
Ranges of Major Elements in Seawater from the Artis Aquarium

ppm	Natural Seawater	10 ° Seawater	18 ° Seawater	24 ° Seawater	Mammoth Seawater	Invertebrate Seawater
Calcium	425	487	460	471	523	433
Potassium	396	391	383	381	398	378
Magnesium	1314	1227	1226	1227	1236	1222
Sodium	10753	10280	10026	10080	10668	10221
Sulphur	936	872	908	907	920	873
Boron	3,89	3,96	3,86	3,87	3,46	3,61
Phosphorus	0,02	2,68	4,29	1,38	1,42	0,17
Strontium	7,14	7,15	7,04	7,00	7,74	7,22

Table 2. Major elements in natural and system seawater from the Artis Zoo Aquarium

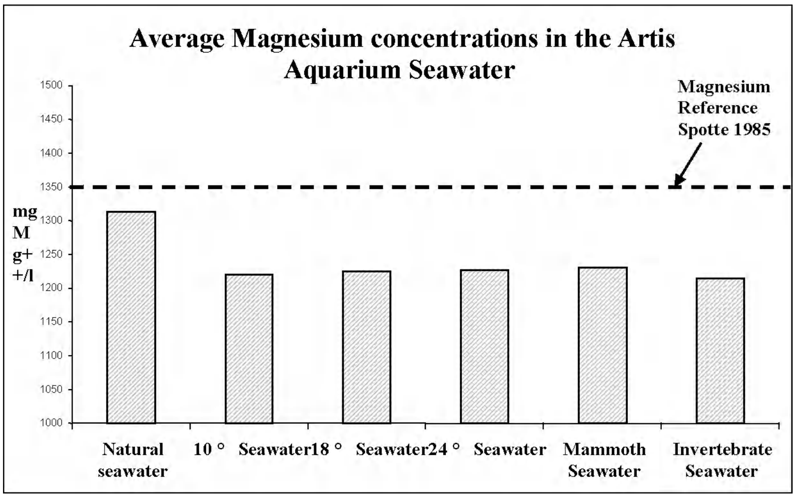
SOME ESSENTIAL TRACE ELEMENTS

Now able to measure the elements necessary for good invertebrate growth, we paid special attention to some of them. Magnesium and calcium are responsible for the p*H* and buffering capacity of seawater and are of considerable importance in the solubility of other elements (Spotte, 1992).



Graph. 2: Calcium concentrations in Artis Aquarium seawater

In graph 2, calcium concentration in natural seawater is almost as in the references, just as in our invertebrate seawater system. The high calcium levels in the other circulation systems are due to slightly higher salinity, but in the mammoth system the concrete material of the decoration material is responsible.



Graph. 3: Magnesium concentrations in Artis Aquarium seawater

Magnesium concentration shows the opposite pattern: the amount of magnesium in all systems is lower than the natural and reference values.

It is not clearly understood what kind of influence this may have on the health of fishes and invertebrates. The difference in the p*H* of these systems gives no explanation of this behaviour of elemental calcium and magnesium (the p*H* of the 10° system and the 18° system are close to 7.8; the other systems have a p*H* of 8.1 - 8.4)

MINOR TRACE ELEMENTS IN SEAWATER

It was always thought that the way we obtained our seawater was perfectly safe and sound, so there were no direct indications for changes. The concentration of some metals (zinc, titanium, manganese) in this natural seawater was surprising compared to the reference values, and due presumably to the influence of the ballast-tank, paints or pump materials.

Though the subsequent disappearance of these high concentrations in the circulation systems is not always explainable, it is rather welcome since the effect on our animals is unclear.

Some minor elements in the Artis Aquarium seawater

Reference ppb		Average natural seawater	Average circulation syst.	Average Invertebrate syst.
10	Aluminium	25	20,6	18,4
1	Titanium	10	26,7	9,6
0,05	Chromium	1	1,0	1,6
2	Manganese	35	1,1	1,1
0,4	Cobalt	1	0,8	0,7
7	Nickel	8	16,4	4,7
3	Copper	25	13,8	8,3
10	Zinc	440	39,5	51,5
10	Molybdenum	2	1,7	0,7
0,11	Cadmium	0	0,4	0,2
0,004	Indium	0	0,1	0,0
0,8	Tin	0	0,3	0,3
60	Iodide	54	316,7	140,3
0,3	Caesium	0	2,6	1,1
30	Barium	7	43,2	20,6
0,03	Lead	3	1,0	0,6
65 ppm*	Bromium ppm*	69	65,6	58,4

Table 3. Minor trace elements in Artis Zoo Aquarium seawater

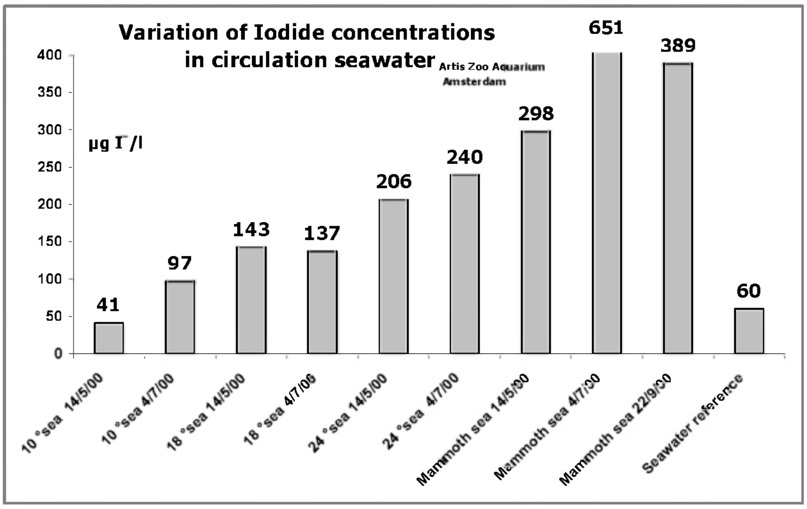
MEASURING IODIDE IN SEAWATER FROM THE ARTIS AQUARIUM

Our method for measuring iodide in seawater (Emaus, 1988) is very time-consuming and yielded only semi-quantitative results. But these results indicate that, when potassium iodide was supplied to seawater, it was first adsorbed, but after doubling the dosage, the concentration became constant and even increased after further supplementation (Sondervan, 1992). Potassium iodide was dosed in a calculated concentration of 100 µg I-/l, while suspending the activated carbon filters.

Graph 7 details the results of our circulation systems. On the 17th of May a calculated amount of 100 µg I-/l (as potassium iodide) was dosed to our regular circulation systems. We did not yet have the results of the samples taken on the 14th of May.

After May 17th no potassium iodide was supplied to our circulation systems. This did not explain the high concentrations and definitely not the super-high concentration in the mammoth system on July 4th.

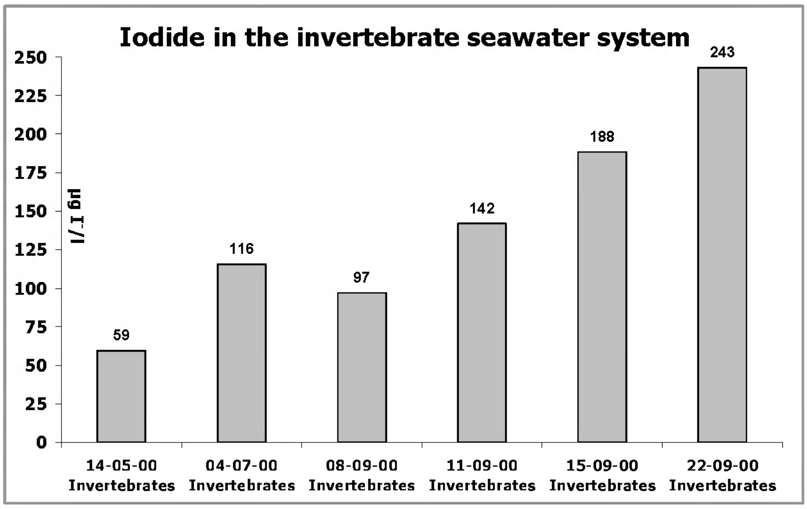
Supplementation of trace elements is not risk-free; it requires great caution until the mechanism of these high amounts of iodide is explained.



Graph 4. Variation of iodide concentrations in circulation seawater

IODIDE IN THE INVERTEBRATE SEAWATER SYSTEM

We looked at our Invertebrate seawater system separately; no potassium iodide had been dosed before. On the 17th of May, a calculated amount of 100 µg I-/l was dosed. We obtained our data after the 14th of May, but the concentration peaked nonetheless even in July and lowered until September.



Graph 5. Iodide in the invertebrate system after adding a mixture of trace elements

On the 8th of September we started dosing a mixture of trace elements to our invertebrate system, using a standard commercial product, with known concentrations of elements. This calculated amount of elements for 60,000 litres of seawater was dosed in three weekly portions starting on the 8th of September.

It is interesting to see that iodide concentration rises to more than four times the natural amount by adding this mixture of trace elements.

Most of the dosed iodide was found in our results, even a concentration of more than four times the natural concentration seems of no harm for the animals in this system, but how high can we go?

DISCUSSION

Measuring water quality parameters in marine aquariology systems is extremely important, salinity and some major elements can be easily tested by test kits. But these results do not take enough into consideration the special demands in terms of quality required by more sensitive animals. Measuring trace elements in seawater can be of great help but is complicated.

There are some good calcium testing methods; we found a small decline in calcium concentration in our only system with a protein foam skimmer. Finding relatively more calcium in the foam fraction could be an indication that the activity and efficiency of the protein skimmer relates to this calcium loss. But measuring the decline of one element can only be seen as a warning of a structural problem in a life support system.

Some of the results in the trace element analyses were surprising, and the high amount of some metals in our basic natural seawater can only be explained by the equipment used to obtain this seawater. These high metal levels were not found when the seawater was being recirculated in the aquarium.

The rise in iodide levels in our systems, after addition of potassium iodide, indicates that a system will adsorb this element to a certain extend. Levels more than six times the natural concentration seem of no direct harm for the animals, but should be avoided anyway.

The high amount of iodide after addition a mixture of trace elements to our seawater was not surprising but should be a warning signal.

Adding chemical mixtures to seawater-recirculation life systems can be of great help; the results confirm the need for caution for all supplementation, whatever its nature, because little is still known about long-term additions.

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