KINETICS SORPTION OF METAL RADIOTRACERS IN THE WATER-SEDIMENT INTERFACE OF A HIGHLY CONTAMINATED COASTAL AREA (SEPETIBA BAY, RIO DE JANEIRO, BRAZIL)

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Kinetic Sorption: Radiotracer Study

- Laboratory experiments with radiotracer studies improved the evaluation of trace metals transfer in the sediment-water interface and contributed to determine the sediments capacity to maintain these elements (Santschi, 1988; Hall et al., 1989; Schaanning et al. 1996; Ligero et al., 2006; Machado et al., 2008);

- Radiotracer experiments with mangrove sediment columns have showed the efficiency of metal removal from the water column to the underlying sediment (Machado et al., 2001);
Objective

Radiotracer technique (\(^{65}\)Zn and \(^{109}\)Cd) was used in a mangrove sediment at Sepetiba Bay, Rio de Janeiro Brazil to:

- Determine the removal kinetics of \(^{65}\)Zn and \(^{109}\)Cd from tidal water to sediments;
- Evaluate the efficiency of bacterial biofilm Cd and Zn resistance as an environmental compartment that amplify metal removal in the sediment-water interface;
- Compare biological activity on the sediment sorption capacity by submitting some cores to a formaldehyde solution treatment.
Study Area

BRAZIL

RIO DE JANEIRO

SEPETIBA BAY
Study Area

Saco do Engenho, Sepetiba Bay - RJ
Study Area

Cia. Ingá Mercantil (1962-1998)

- In 1962, Cia. Inga Mercantile began its industrial activity by processing high purity zinc in Sepetiba Bay, Rio de Janeiro;

- The Industrial wastes were deposited in open-air storage areas of the company, without any environmental management.

- The company was declared bankrupt in 1998 and left a large environmental liability in Sepetiba Bay.

Ferreira, 2010
Study Area

Saco do Engenho, Sepetiba Bay - RJ
Study Area

Saco do Engenho, Sepetiba Bay - RJ

Itaguai Harbor

22°55'11,0'' S, 43°49'05,98'' W
Materials and Methods

Sediment + Tidal Water

Water: Physico-chemical Parameters

<table>
<thead>
<tr>
<th>pH</th>
<th>T °C</th>
<th>atm</th>
<th>Salinity</th>
<th>DO%</th>
<th>tss ppt</th>
</tr>
</thead>
<tbody>
<tr>
<td>8,23</td>
<td>27,760</td>
<td>0,998</td>
<td>31,450</td>
<td>88,70</td>
<td>24,14</td>
</tr>
</tbody>
</table>
Materials and Methods

10 sediment cores

6 sediment cores

4 sediment cores

Bacterial Biofilm Cd and Zn resistance

16 ml Formaldehyde solution (Formal P.A. 4%) – 2 hours

Natural Biofilm without treatment process

Bacterial Biofilm without treatment process
Materials and Methods

Bacterial Biofilm

Bacteria with Cd and Zn resistance were cultivated in the Laboratory of Bacterial Ecology (UFF). pH= 8,0

Bacterial biofilm (2 ml) were inoculated in 4 sediment surface cores for 2 days.
Materials and Methods

150 ml of seawater spiked with $^{65}\text{Zn}$ and $^{109}\text{Cd}$ were added to each core.

**Initial activity:**

$^{65}\text{Zn} : 7.4 \times 10^5 \text{Bq} \ (20 \mu \text{Ci})$

$^{109}\text{Cd} : 1.1 \times 10^6 \text{ Bq} \ (30 \mu \text{Ci})$

Radiotracers Supplier: PerkinElmer Inc.
Materials and Methods

Water samples were taken at regular intervals to measure the activity of radiotracers $^{65}$Zn and $^{109}$Cd (Suzuki et al, 2012).
**Materials and Methods**

Gamma-ray Spectroscopy

**Genie 2000 Software**

<table>
<thead>
<tr>
<th>Radiotracer</th>
<th>Half-life (day)</th>
<th>Energy (KeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{65}\text{Zn}$</td>
<td>244.01</td>
<td>1115</td>
</tr>
<tr>
<td>$^{109}\text{Cd}$</td>
<td>461.4</td>
<td>88</td>
</tr>
</tbody>
</table>

GX1518 multichannel acquisition system
Kinetics removal: First-order kinetics

Concentration of reagents decreases in time exponentially. The process depends on the initial concentration.

\[
\ln [A] = -kt + \ln [A]_0
\]

Half-life time estimate:

\[
t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}
\]
Results and Discussion

1) Zn - 65
2) Cd - 109

First-order kinetics with two half-life times
Results and Discussion

1) Zn - 65

First-order kinetics with two half-life times

2) Cd - 109

$22.77 \pm 3.28$ h
Results and Discussion

1) Zn - 65

2) Cd - 109

First-order kinetics with two half-life times

<table>
<thead>
<tr>
<th></th>
<th>Zn (First t1/2)</th>
<th>Zn (Second t1/2)</th>
<th>Cd (First t1/2)</th>
<th>Cd (Second t1/2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NB</td>
<td>0.86 ± 0.02h</td>
<td>1.85 ± 0.13h</td>
<td>0.86 ± 0.02h</td>
<td>1.85 ± 0.13h</td>
</tr>
<tr>
<td>BB (Formal)</td>
<td>0.86 ± 0.02h</td>
<td>1.85 ± 0.13h</td>
<td>0.86 ± 0.02h</td>
<td>1.85 ± 0.13h</td>
</tr>
</tbody>
</table>

0.86 ± 0.02h

1.85 ± 0.13h
Results and Discussion

1) Zn - 65

2) Cd - 109

First-order kinetics with two half-life times

9.49 ± 2.05h

11.39 ± 1.26h
Conclusion

• Bacterial biofilm (Cd and Zn resistant) can be more efficient than natural biofilm in metal removal.

$^{65}\text{Zn}$ $t\frac{1}{2}$ faster: $1,24 \pm 0,02h$; $6,49\pm 0,42h$; $t\frac{1}{2}$ longer: $2,24\pm 0,13h$; $6,93 \pm 0,48h$.

$^{109}\text{Cd}$ $t\frac{1}{2}$ faster: $0,86\pm 0,02h$; $6,47\pm 0,68h$; $t\frac{1}{2}$ longer: $1,85\pm 0,13h$; $6,94\pm 0,01h$.

• Zn is a element that in lower concentrations acts like micronutrients and is essential for the growth of certain organisms, although at higher levels they can be toxic (Fisher 1986). Therefore, the half-live time of $^{65}\text{Zn}$ is longer than $^{109}\text{Cd}$ in every experiment treatment.

• Formaldehyde solution treatment used in the cores shows an efficient method to inhibit the biological activity.
Acknowledgement

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Scholarship grade 10, No. 01/2014 - Protocol: E – 26/100.373/2014
References


References


Thank you!!

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