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Mathematical description of the relation between water and sea organism pollution

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Dedicated to Acad. Ivan Juchnovski on the occasion of his 80th birthday

Urban and industrial activities introduce large amounts of pollutants into the marine environment, causing significant and permanent disturbances in marine systems and, consequently, environmental and ecological degradation. The present paper explores the heavy metals as contaminants. Our purpose is to develop a mathematical description of the relation between marine water and sediments and sea organism pollution.

Key words: pollutants; heavy metals; sea organisms; sea water

INTRODUCTION

Urban and industrial activities introduce large amounts of pollutants into the marine environment, causing significant and permanent disturbances in marine systems and, consequently, environmental and ecological degradation. This phenomenon is especially significant in coastal zones, as these are the main sinks of almost all anthropogenic pollutants. It has long been recognized that metals in the marine environment are particularly significant in the ecotoxicology, since they are highly persistent and can be toxic in traces. Certain kinds of contaminants, such as heavy metals, occur naturally in the environment and it is important to be able to distinguish between anthropogenic contamination and background or natural levels so as to enable accurate evaluation of the degree of contamination in a particular area [1].

The use of marine organisms as bioindicators for trace metal pollution is currently very common. Algae, molluscs and fishes are among the organisms most used for this purpose [2]. Fishes are able to accumulate trace metals, reaching concentration values that are thousands of times higher than the corresponding concentrations in sea water.

The use of biological species in the monitoring of marine environment quality permits the evaluation of the biologically available levels of contaminants in the ecosystem or the effects of contaminants on living organisms. The analysis of environmental matrices such as water or sediment provides a picture of the total contaminant load rather than of that fraction of direct ecotoxicological relevance. Thus, the use of biomonitors eliminates the need for complex studies on the chemical speciation of aquatic contaminants.

Because the metal pollution in aquatic environments can be harmful to human health, it is necessary to understand and control the hazard levels of pollution in seafood. Therefore, it is of great importance to determine the levels of As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in the marine water, sediments and muscles of the different fish species from Black Sea, Bulgaria.

The purpose of this paper is to develop some qualitative measures for an estimate of the transfer of heavy metals from water to some marine species.

NUMERIC ESTIMATIONS

Here, our efforts were directed to create some numeric estimates of the transfer of pollution from the sea water and sediments to fish and other sea organisms. This development will focus further on the development of an engine which will be a part of a warehouse consisting of a database and software attached to it.

First, some correlations between marine pollution with heavy metals and as a result, pollution of the marine organisms, fish, shellfish, etc., (biota) were proposed. As a first step some statistical indicators on the percentage of pollution of the marine biota Xfw (from water)and Xfs (from sediments) as a percentage of water pollution (Xfw%) and as a percentage of contamination of sediments (Xfs%) were introduced. They have the following expressions:

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Xfw =1.0-(Wx-Fx)/Xw (1)

Xfw%=Xw . 100 (1')

Xfs = 1.0-(Sx-Fx)/Xs (2)

Xfs%=Xs .100 (2')

Wx and Sx are the amounts of a pollutant (heavy metal element) in water and sediment and Fx is the amount of a contamination (heavy metal element) in fish or mollusc. Xw and Xs are the contaminations from water and sediments respectively from 0 to 1.0, Xw% and Xs% are the same values expressed as percentages, from 0% to 100%.

If the entire amount of pollutant passes in fish or mollusks, then the expressions (1) and (2) provide either 1.0 or in percentage 100%. Figure 1 shows some results of these values for 3 fishes in any water and sediments (.Xfw%, Xfs%,).

Since fish do not stay in one the same water area we made an average between the numerical values of the waters and sediments of all areas using average values obtained by the following expressions:

XavfW=1.0-(avrgWx-Fx)/avrgXw (3)

XavfW%=Xav x 100 (3')

XavfS=1.0-(avrgSx-Fx)/avrgXs (4)

XavfS%= XavS x 100 (4')

Here XavfW where the degree of contamination of fish by the average amount of a pollutant in all waters avrgXw, and XavfS degree of contamination of fish by the average amount of a pollutant in all sediments avrgXs. It should be noted that we do not know how long the fish stay in either one or another marine area, so we average the waters and sediments. Further, we shall attempt to draw a conclusion about the fish stay. Some results of our calculations are presented in Figure 1 with XavfW%, XavfS%.

But we noticed that the use of separate water and sediments in some cases produce results greater than 100% (see the discussions bellow). This is the case with the element Cu. Clearly, we must use both factors together. So we obtained the following expressions for the pollution:

Xws=1.0-(Wx+Sx-Fx)/(Wx+Sx) (9)

Xws%=Xws x100 (10)

as well as by using the averaged values for sediments and water we obtain the following experession:

XavWS=1.0-(avSx+avWx-Fx)/(avSx+avWx) (11)

XavWS% = XavWS x 100 (12)

Now we attempted to determine the average time that sea organisms stay in both water and sediments. The expressions for calculation of these values are the following:

$$fSum = \sum_{allelements} Xf \quad (13)$$

Here Xf is the contamination of the fish from all heavy metal elements.

$$wSum = \sum_{allelements} Xw \quad (14)$$

wSum is the pollutions of fish from all waters.

$$wsSum = \sum_{allelements} Xws \quad (15)$$

wsSum is the pollution of the fish from sediments and waters.

So that the accumulation of all the elements for a fish to water Wall, for sediment

Sall, WSall, is calculated by following statements:

Accumulation of water:

$$Wall = 1 - \frac{(wSum - fSum)}{wSum} \quad (16)$$

Accumulation of sediments:

$$Sall = 1 - \frac{(sSum - fSum)}{sSum} \quad (17)$$

Accumulation of water and sediment:

$$WSall = 1 - \frac{(wsSum - fSum)}{wsSum} \quad (18)$$

Based on these expressions attempt was made to calculate the duration of stay of each fish in water (Tw) and sediment (Ts) in percentages.

This was accomplished with the decision of the two equations:

wsSum = Ts . sSum + Tw . wSum (19)

Tw = (1-Ts) (20)

And here we get:

$$Ts = \frac{(wsSum - wSum)}{(sSum - wSum)} \quad (21)$$

as *Tw = (1-Ts)* (22)

Here *Tw* and *Ts* are the times which the fish stay in water and in sediments, respectively.

DISCUSSION

The program for calculating the degree of accumulation of toxic metals in fish from sea water and sediments ***fish-water.jar*** was developed by Prof. Bangov, by using the Java computer platform (Oracle). Data on fish, surface sediment values and sea water from the Black Sea (see the Supporting data) are given initially in an Excel file format. Then, the file is converted into text (txt) tabbed file format, and the program reads this data and calculates the degree of accumulated based on the expressions 1-22.

These data have been derived from the Varna Medicinal university group respectively for 2011 and are presented in Tables 1S-3S in the Supporting Information. The results from the calculations are illustrated with calculated values for 3 fishes in Figure 1.

After each calculation of the influence of any heavy metal of a fish we have estimates of the percentage of aggregation of all the elements included and column *All elements to fish*" which takes into account the influence of all considered toxic metals and their mutual accumulates in the fish from both the sea water and the surface-sediments. We found that these values from sea water ranged from 30.217% in *horse mackerel* to 40.365% at *sprat*, and values for sediment ranged between 6.188% of *clamshell (wild)* (*Mytilus edulis*) and *Kefal (M.cephalus) South* 1.785%, and for Combination If water + sediments in the range: 1.641% - 6.686%.

We present in Figure 1 results from two fishes to illustrate the pollution in percentage according the formulas above.

WATER "Black sea-Krapets (North)
BG2BS00000MS001 43°36'60.0"" / 28°35'60.0"
========================descriptors =========
Elements Cr, [μg/L]=0.4 Mn, [μg/L]=1.0 Ni, [μg/L]=0.6 Cu, [μg/L]=1.
1 Zn, [μg/L]=18.0 As, [μg/L]]=1.5 Cd, [μg/L]=0.06
Hg, [μg/L],=0.05 Pb, [μg/L]=1.5
================
FISH Карагьоз (A. pontica) North
FISH / ELEMENT RESULTS
Element Cr [μg/g] water-> Xfw= 12.5%-- sediment= Xfs=2.501%-
--avrg water= XavrgfW = 7.99%----avrgSediment= XavrgfS 0.905%
-----water+sediment value= 2.084%
Element Mn [μg/g] water-> Xfw = 22%----- sediment= Xfs =0.043%
---avrg water= XavrgW = 6.986%----avrgSediment= XavrgS 0.024%
-----water+sediment value= 0.043%
Element Ni [μg/g] water-> Xfw = 11.667%----- sediment= Xfs =0.351%-
-----avrg water= XavrgW = 7.778%----avrgSediment=XavrgS 0.212%
-----water+sediment value= 0.34%
Element Cu [μg/g] water-> Xfw = 75%----- sediment= Xfs =1.801%
---avrg water= XavrgW = 33.906%----avrgSediment= XavrgS 0.826%
-----water+sediment value= 1.758%
Element Zn [μg/g] water-> Xfw = 29.033%----- sediment= Xfs =17.308%
---avrg water= XavrgW = 41.079%----avrgSediment= XavrgS 10.297%-----water+sediment value= 10.844%
Element As [μg/g] water-> Xfw = 34.546%----- sediment= Xfs =9.269%
---avrg water= XavrgW = 16.866%----avrgSediment= XavrgS 5.957%
-----water+sediment value= 7.308%
Element Cd [μg/g] water-> Xfw = 14.001%----- sediment= Xfs =7.778%
---avrg water= XavrgW = 8.457%----avrgSediment= XavrgS 4.713%
-----water+sediment value= 5.001%
Element Hg [μg/g] water-> Xfw 160%----- sediment= Xfs =160%-
--avrg water= XavrgW = 124.445%----avrgSediment= XavrgS 106.706%
-----water+sediment value= 80%
Element Pb [μg/g] water-> Xfw = 14.706%----- sediment= Xs=0.173%-
--avrg water= XavrgW = 5.158%----avrgSediment= XavrgS 0.113%
-----water+sediment value= 0.171%

All elements from water to fish = 29.438%
All elements from sediments to fish = 2.6%
All elements from water and sediments to fish = 2.389%
Time spent in sediments in % = 1.008%
Time spent in water in % = 98.993%

FISH Кая (N. melanostomus) North

Results

Element Cr [μg/g] water-> Xfw = 12.5%----- sediment= Xfs =2.501%
---avrg water= XavrgW = 7.99%----avrgSediment= XavrgS 0.905%
-----water+sediment value= 2.084%
Element Mn [μg/g] water-> Xfw Xw= 14.001%----- sediment= Xfs =0.027%
---avrg water= XavrgW = 4.446%----avrgSediment= XavrgS 0.015%-----water+sediment value= 0.027%
Element Ni [μg/g] water-> Xfw = 1.334%----- sediment= Xfs =0.04%-
----avrg water= XavrgW = 0.889%----avrgSediment= XavrgS 0.025%
-----water+sediment value= 0.039%
Element Cu [μg/g] water-> Xfw = 126.667%----- sediment= Xfs =3.041%
---avrg water= XavrgW = 57.262%----avrgSediment= XavrgS 1.395%-----water+sediment value= 2.969%
Element Zn [μg/g] water-> Xfw = 29.033%----- sediment= Xfs=17.308%
---avrg water= XavrgW = 41.079%
----avrgSediment= XavrgS 10.297%-----water+sediment value= 10.844%
Element As [μg/g] water-> Xfw = 60%----- sediment= Xfs=16.098%
-----avrg water= XavrgW = 29.293%
----avrgSediment= XavrgS 10.345%-----water+sediment value= 12.693%
Element Cd [μg/g] water-> Xfw = 12%----- sediment= Xfs=6.667%
---avrg water= XavrgW = 7.249%
----avrgSediment= XavrgS 4.039%-----water+sediment value= 4.286%
Element Hg [μg/g] water-> Xfw = 100%----- sediment= Xfs=100%
---avrg water= XavrgW = 77.778%----avrgSediment= XavrgS 66.691%
-----water+sediment value= 50%
Element Pb [μg/g] water-> Xfw = 8.824%----- sediment= Xfs=0.104%
---avrg water= XavrgW = 3.095%----avrgSediment= XavrgS 0.068%
-----water+sediment value= 0.103%

All elements from water to fish = 30.699%
All elements from sediments to fish = 2.712%
All elements from water and sediments to fish = 2.492%
Time spent in sediments in % = 1.008%
Time spent in water in % = 98.993%

Fig. 1. Listing with the results for 2 fishes in in Black sea-Krapets water.

In Figure 1 Xw is the percentage of pollution calculated on the local water only, Xs - the percentage of pollution calculated on the local sediments only. The same values are averaged for waters of all locations, XavrgW, sediments XavrgS, averaged from all locations and the percentage of pollution Xws by using both water and sediment values in the calculations.

One can see from Figure 1 that in the case of Hg for both fish and shell the Xw result is higher than 100%. This indicates that there is another source of pollution, which are obviously sediments. The result Xs show clearly that we have increase pollution of Hg from sediments. When we use the joint pollution of water and sediments we obtain normal value less than 100%. Our calculations show that that the great part of pollution of Hg comes from the sediments.

The data in Figure 1 show that in the case of combined action of the two factors (sea water and surface sediment) data extracting normal appearance. As an example we can cite the estimated value of Hg fish shad caught by region Krapec (North):

Hg [µg / g] value = 0.08-> Xw = 160% ----- Xs = 160% ------ XavrgW = 124.445% ---- XavrgS 106.706% ----- Xws = 80%

Here, the value of Xws is equal to 80% (by comparing with XavrgW=124.445% and 106.706% XavrgS-). Then, a question arises, why a toxic element percentage of the combined influence of marine water and sediment on fish decreases the contamination of the sea organisms. The explanation is logical. Our data for the contamination of fishes are constant. We haven't got data to form a function that shows how the contamination of marine organism increases with the pollution of the water and when combined we have influence of both factors (sea water and sediment), the percentage that each component introduced into combined value decreases, i.e. it shows that owing to the rich contamination of the sediments a smaller amount of sediment and water pollution is needed in order the same value of the contamination of the fish to be reached.

The time values of the stay in water and sediments show the same trend. Thus, the fish stays very little time in the sediments, but because they are rich of heavy metal pollution the fish absorbs much more contamination. The remaining time the fish is in the waters which are shorter of pollution.

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Electronic Supplementary Data available here.

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МАТЕМАТИЧЕСКО ОПИСАНИЕ НА ЗАВИСИМОСТТА МЕЖДУ ЗАМЪРСЯВАНЕТО НА МОРСКАТА ВОДА И НА МОРСКИТЕ ОРГАНИЗМИ

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(Резюме)

Урбанизираните и индустриални активности допринасят за големи количества замърсители в морската среда, причинявайки значителни и постоянни смущения в морските системи и като следствие екологична деградация на околната среда. Настоящата статия изучава тежките метали, като замърсители. Нашата цел е да се развие математическо описание на зависимостта на морските води и седименти и замърсяването на морските организми.