IOSR Journal of Mathematics (IOSR-JM)
e-ISSN: 2278-5728, p-ISSN: 2319-765X. Volume 12, Issue 3 Ver. VI (May. - Jun. 2016), PP 01-06
www.iosrjournals.org

Mathematical Approach to Describe Metal Concentration and Toxicity Growth by Laplace Transform

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Abstract: *Heavy metals are the most hazardous pollutants because they are non-degradable and get accumulate to the toxic level in both plants and animals. An environmental mathematical model to describe toxicity growth and metal concentration.*
Keywords: *Heavy metals, Toxicity, Laplace Transform, and Gate function.*

I. Introduction

Natural and anthropogenic activities are responsible for global pollution throughout the world. The big impact can be seen of global pollution on various terrestrial and aquatic water ecosystems, i.e., already contaminated with heavy metals, inorganic, organic compounds and radionuclides. The type of waste produced varies with the type of human activities, which are affected by various factors such as climate conditions, seasons, standard of living etc. (Patil *et. al*., 1991). The role of environmental pollutants has been well established to produce various types of effect on diverse living system.

Different kind of waste creates environmental problems to increasing pollution. The discharge of heavy metals into aquatic ecosystem has been a matter of concern in the world (Ahalya *et. al*., 2003). Due to color, high COD (Chemical Oxygen Demand), organic and inorganic contents, possibility of toxicity and carcinogenicity, effluent discharging from textile and dyes stuff industries and city waste (liquid), has raised a number of points of concern, such as initial adverse effects on the natural ecosystems and long term health effects (Mc-Mullan *et. al*., 2001).

Waste water showed highly contamination dissolved organic and inorganic components. Sorption and transport of many organic chemicals, pesticides and other contaminations by DOM (Dissolved Organic Matter) or soluble humic substances were extensively investigated (Cox *et. al*., 2000; Seol and Lee, 2000, 2001; Kopinke *et. al*., 2001; Kulikova and Perminova, 2002 and Mackenzie *et. al*., 2002). Dissolved organic matter is highly heterogeneous in size and in chemical composition. The molecular masses of the dissolved organic matter are ranged from 500 to 5000Da (Imai *et. al*., 2002).

Resin adsorbents are used for determination of chemical structure of dissolved organic matter is difficult due to of this complex composition i.e., hydrophobic and hydrophilic fractions and acid, neutral and base sub-fractions. This preparative dissolved organic matter (DOM) fractionation appears to be useful for the characteristics determination of effluent in waste water, lake, soil, sludge and composts (Raber *et. al*., 1998 and Imai *et. al*., 2002). It is important to understand that how microorganisms are affected by this pollution, because they control mostly biogeochemical processes and ecosystem productivity (Hinojosa, 2005).

The pollutants are aggravated by the presence of free chlorine. Toxic heavy metals cause rapid depletation of dissolved oxygen, leading to "Oxygen Sag" in the receiving water (Ademorotti *et. al*., 1992). The increase of metal concentration in living body along with food chain that has human at its top through different trophic level is referred as bio-magnification (Gadd *et. al.*, 1993 and Paknikar *et. al*., 2003).

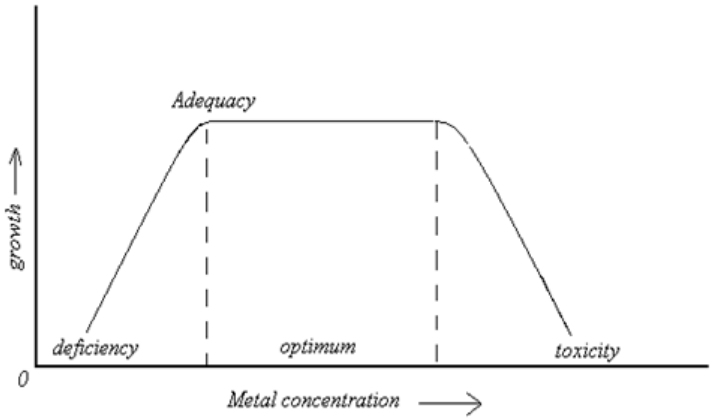
II. Heavy metals as pollutants

Heavy metals are the most hazardous pollutants because they are non-degradable and get accumulate to the toxic level in both plants and animals. Selwood (1959) defined the heavy metals, based on its high density and comparatively low chemical activity. According to Sharma and Sobti (1989), heavy metals are heavier than water. Blum (1992) and Bishop (2002) emphasized that heavy metals have high density large than $5gm/cm^3$.

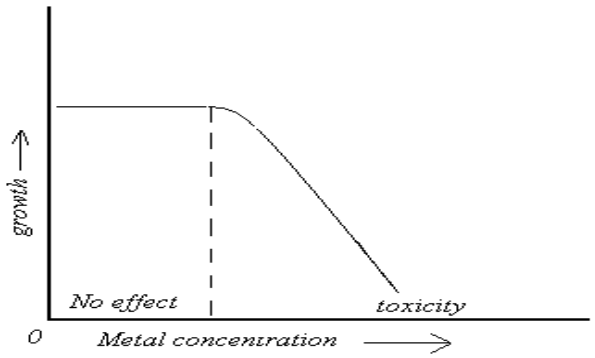
As, Cr, Cu, Hg, Mn, Ni, Sb and Se are more frequently present in household wastes, coal fed power stations and metal smelters. Out of these metals 25% are through to enter in rivers, lakes and their surrounding soils (Markert, 1998 and Brunis *et. al*., 2000). Certain water especially those in moorland areas contain considerable amounts of humic substance and organic matter in the soil environment which can be bound metals including zinc, cobalt and mercury (Bucheda, 1974 and Benes, 1976).

Zinc is one of the most important heavy metals widely used in the electroplating industries. It is an essential element for activation of enzyme in human but become toxic at levels of 100 to 500µg/day and is a known as carcinogen (Senthilkumar *et. al*., 2006).

Living organism both fauna and flora contain different heavy metals in different body parts e.g., Iron in hemoglobin and Mg, Cu, Fe in chloroplast. Elements not participating in biochemical reactions or in building of molecular structure of the body are called as 'Non-essential elements' and also known as toxic element. The optimum range is called adequate; lower and higher than it is referred as deficient & toxic zone. Such non essential elements cause toxicity in concentration that exceed to the tolerance of the organism but do not cause deficiency disorder at low concentrations as by essential micronutrients (Fig-1). When the optimum range for a particular heavy metal is narrow, the risk of toxicity increases thus even a minor increase in environment increase can be highly effective (Mido *et. al*., 1995).



(a)



(b)

Fig-1: Typical dose-response curve for (a) Micronutrient (b) Non- essential trace metal

In general, heavy metals produce their toxicity by forming complexes with biological molecules of the body like cellulose, protein, fats, enzyme etc. The modified biological molecules lose their ability to function properly and results in malfunction or death of the affected cells. They combine with enzymes and affect the biochemical pathway of the living cells and also cause disease. The most common groups involved in formation of complexes with heavy metals are amino (-NH2), Imino (-NH), Sulphydryl (-SH) and Hydroxyl (-OH) group. Metals bind theses groups; inactivate important enzyme system by affecting protein structure. Saxena (2002) introduced the two type of toxicity (1) Acute toxicity also termed as lethal toxicity (2) Chronic toxicity (Delayed toxicity) which is toxicity from long-term exposure.

According to the "World Health Organization" (1984), the metals of most immediate concern are Cd, Cr, Co, Cu, Pb, Ni, Hg and Zn. Some metals such as Cu, Fe and Zn are essential at low concentrations and are toxic at higher levels (Hare, 1992 and Tiina, 2002). Heavy metals also occur in immobilized form in sediments and as ores in nature (Alluri *et. al*., 2007). High concentration of heavy metals in soil, have an adverse effect on living organism. Mycorrhizal fungi are the only ones providing a direct link between soil and roots and can therefore be of great importance in heavy metal availability and toxicity to plants (Leyval *et. al*., 1997)

One of the most important factors that determine the biological availability of a metal in a system is its binding to other environmental constituents. If a metal is partially or wholly removed by binding, a decrease or complete disappearance of toxic effects may result (Gadd, 1978).

III. Heavy Metals

Metals found in the environment can be divided into two classes: Bioavailable (soluble, Sorbed and mobile) and non-bioavailable (precipitated complexes, non-sorbed and non-mobile). Bioavailable metal concentration is toxic to biological systems (Roane *et. al.*, 1996). Shyamala and Rao (1999) have discussed the emission of heavy metals as particulate and gasses from volcanoes, forest fires, crusted material and continental dust have always been a natural input to soil and ecosystem.

There is little information on interactions between heavy metals and microorganisms (fungi) in the natural microbial habitats and the toxicity of heavy metals to the micro biota in natural habitats is expected to be dependent on the environment into which the pollutants are deposited. Babich and Stotzky (1977) reported Cd, K, Ca, Mg, Na, Mn, Fe, Zn, Pb and Cu from contaminated soil of Japan. It has also been reported that the waste water contains varying level of heavy metals (Mc-Grath, 1998; Hayat *et. al.*, 2002 and Koroute *et. al.*, 2002) and higher concentration of suspended particles. Kelly and Tate (1998) and Kelly (2003) have reported the effects of heavy metal (Zn) contamination and remediation on soil microbial communities.

Hetrick *et. al.* (1994) studied the area of North-Eastern Oklahoma and South - Western Missouri in the United States, where Zn and Pb mining and smelting ceased more than 60 years ago, but the soil is still seriously contaminated with Cd, Cu, Zn and Pb. Soil characteristics of the Chat (μg/g) were Zn 750, Pb 19 and Cd 5.48. Kovalick (1991) reported that in the United State 37% of the tested sites polluted with organic compounds, were found to be also polluted with metals such as As, Hg, Pb and Zn.

Chaudhry *et. al*. (1997) assessed the trace metal contamination (Cu, Zn, Pb, Cd, Ni, Fe and Mn) in soil at four sites. Creek site-1, located near mine, contained much higher levels of DTPA extractable metals, as compared to site 4, which was a further 3 km down stream. The concentrations (μg/g) for various metals at the site-1 and 4 respectively, were Cu (2347 and 725), Zn (1550 and 705), Pb (627 and 3002), Cd (8.9 and 2.6), Ni (0.26 and 4.5). Cr was only present at site-1, with a concentration of 0.94 μg/g.

Berlekamp *et. al.* (1998) investigated that heavy metal pollution from various German states and region in the sediment, which were Al, Ca, Ti, V, Cr, Fe, Ni, Cu, Zn, As, Cd, Pb and SO^{4-}. Goncalves *et. al.* (1994) have reported concentration (μg/g) of Cd, Cr, Cu, Ni, Pb and Zn to be 36, 700, 88400, 360, 6000 and 4780 respectively in sediment. Tobin and Roux, 1998 has been found carcinogenic hexavalent chromium in the effluents of a leather tanning industry. They analyzed industrial tanning effluent that had deep blue colour, high conductivity, pH 4.0 and Cr content of 1.77 g/L. Selho and Este rivers was contaminated with heavy metals, coming from leather tanning, metal plating and textile industries and this river was reported to contain highest concentrations of Cr, Cd, Cu and Zn (Goncalves *et. al.*, 1992.)

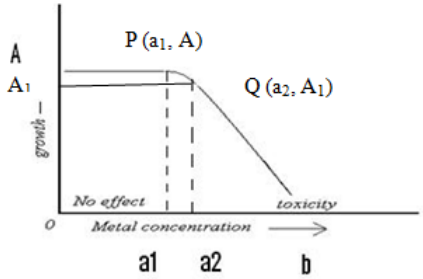
Ahamad *et. al.* (2005) have analyzed the concentration of Pb, Cd, Cr, Cu, Zn and Fe from agricultural soil field which received long term application of waste water. Water and soil of Moghogha river were examined for Cr, Pb, Cd, Cu and Zn concentrations by Ezzouhri *et. al.* (2009) observed that the concentrations of heavy metals in soil sediments were higher to the permissible limits.

Kakati *et. al.* (2007) studied drinking water of the Lakhimpur, Assam for Na, K, and Ca content. Goswami and Sharma (2007) have studied the pond water for contamination of K, Ca, Mg, Cl, Na and Fe which comes from municipal solid waste. Cu, Ni, Zn, Cr, Fe, Pb, Cd, Mn and Co was noted from municipal waste (Syvokiene *et. al.*, 2003) and sewage (Indra and Sivaji, 2006.

IV. Mathematical Model

The graph between metal concentration & growth includes two parts one is constant value (adequate region) and other is the region of decreasing value (toxic region).

Let us divide the graph using Gate function such as-

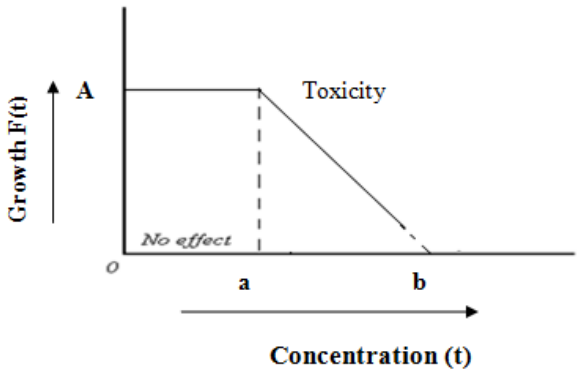


Since toxic region starts from the decrement of growth and there is no critical (transition) point so we can neglect the region between a_1 & a_2 or we can say A_1 & A are representing on same point similarly a_1&a_2 are representing same point {$a_1 = a_2 = a$ (say)}

Where

$$f(t) = \begin{cases} A[u(t) - u(t-a_1)] & for\ 0 < t < a_1 \\ Neglecting & for\ \alpha_1 < t < a_2 \\ \{\dfrac{A1}{a_2 - b}(t-b)\}[u(t-a_2) - u(t-b)] & for\ \alpha_2 < t < b \end{cases}$$

Since the toxic region starts from the decrement of growth and there is no critical point so we can neglect the region between a_1 and a_2, that is we can say A_1 and A are representation the same point this holds for a_1 and a_2.if we take A_1 = A and $a_1 = a_2 = a$ (say), since the function between a_1 to a_2 is {$u(t-a_1)-u(t-a_2)$}, the negligible function $f_1(t)$ then the new generating function can be written as



The new function defined as:

$$f(t) = A[u(t) - u(t-a)] + \frac{A}{(a-b)}(t-b)[u(t-a) - u(t-b)] + f_1(t)[u(t-a) - u(t-a)]$$

$$\Rightarrow f(t) = A[u(t) - u(t-a)] + \frac{A}{(a-b)}(t-b)[u(t-a) - u(t-b)]$$

Taking Laplace both side

$$L\{f(t)\} = L\{A[u(t)-u(t-a)] + \frac{A}{(a-b)}(t-b)[u(t-a)-u(t-b)]\}$$

$$where, u(t)-u(t-a) = \begin{cases} 1 \ for \ 0 < t < a \\ 0 \ \ otherwise \end{cases}$$

$$and, u(t-a)-u(t-b) = \begin{cases} 1 \ for \ a < t < b \\ 0 \ \ otherwise \end{cases}$$

$$L\{f(t)\} = L\{A[u(t)-u(t-a)]\} + \frac{A}{(a-b)} L\{(t-b)[u(t-a)-u(t-b)]\}$$

$$L\{f(t)\} = \int_0^a A.e^{-st}dt + \int_a^\infty 0.e^{-st}dt + \frac{A}{(a-b)}\left[\int_0^a 0.e^{-st}dt + \int_a^b (t-b).e^{-st}dt + \int_b^\infty 0.e^{-st}dt\right]$$

$$L\{f(t)\} = \int_0^a A.e^{-st}dt + \frac{A}{(a-b)}\int_a^b (t-b).e^{-st}dt$$

$$L\{f(t)\} = A\left[\frac{e^{-st}}{-s}\right]_0^a + \frac{A}{(a-b)}\left[(t-b)\left(\frac{e^{-st}}{-s}\right) - (1)(\frac{e^{-st}}{s^2})\right]_a^b$$

$$L\{f(t)\} = -\frac{A}{s}\left[e^{-as}-1\right] + \frac{A}{(a-b)}\left[(0-\frac{e^{-bs}}{s^2}) - \{(a-b)\left(\frac{e^{-as}}{-s}\right) - (\frac{e^{-as}}{s^2})\}\right]$$

$$L\{f(t)\} = A\left[\frac{1}{s} + \frac{1}{s^2(a-b)}(e^{-as}-e^{-bs})\right]$$

Since the equation has a pole at s = 0 so the ROC does not contain the origin**.**
Then

$$f(s) = A\left[\frac{1}{s} + \frac{1}{s^2(a-b)}(e^{-as}-e^{-bs})\right] ...(1)$$

V. Results and Discussion

From equation (1) we have

$$\lim_{s\to\infty} sf(s) = sA\left[\frac{1}{s} + \frac{1}{s^2(a-b)}(e^{-as}-e^{-bs})\right] = A\left[1 + \frac{1}{s(a-b)}(e^{-as}-e^{-bs})\right]$$

$$\lim_{s\to\infty} sf(s) = A$$

$$\Rightarrow \lim_{t\to 0} f(t) = A$$

Here by initial value theorem it is clear that for low value of concentration the growth is constant which support the graph also from final value theorem say for t = ∞ growth will be negative quantity which is not possible. Hence the mathematical expression gives appropriate values which are shown by above graph.

VI. Conclusion

In general, heavy metals produce their toxicity by forming complexes with biological molecules of the body like cellulose, protein, fats, enzyme etc. The modified biological molecules lose their ability to function properly and results in malfunction or death of the affected cells. They combine with enzymes and affect the biochemical pathway of the living cells and also cause disease.

This mathematical expression separates the constant growth region and toxic region. If the value of concentration at all the points is defined, the effect of toxicity can be predicted and the tolerable range of concentration can also be defined according to the expected growth**.**

If there are three sites and one of them chosen for a given value of growth? This mathematical expression helps us by providing the value of concentration at given growth so that the one of three sites can be chosen according to growth restriction.

This paper attract that one should deal with individual concentration of each element even the total concentration of every element is the effective factor for the growth. However the beneficial element behaviover according to the concentration is not describe separately so if any site contains the increasing concentration of beneficial element should be avoided in growth point of view. This idea focuses on growth and cannot suggest the concentration range of individual element for example zinc becomes toxic at the level 100 to 500 µg/day. So if effects the growth considerable but this cannot be found out by the observation of the growth. So the role of particular element should be tested separately.

Since$f(t) = A[u(t) - u(t-a)] + \left\{\frac{A}{a-b}(t-b)\right\}[u(t-a) - u(t-b)]$, hence we can say that when $t \leq a$ the growth f(t) = A

Which shows maximum growth over a range of concentration? This is adoptable range of concentration for maximum growth.

In future we develop, a technique to define t in the region 0<t<a.

Acknowledgement

This paper includes the area of environment & mathematics. The Guidance of Professor& Head A.K.Jaitly, Department of Plant Science, MJP Rohilkhand University Bareilly As well as Our Sincere thanks to Er Prem Prakash Gupta Chairman of the Institute at Bareilly and Dr.M.K.Singh Department of Mathematics FGI at Bareilly UP India for the instruction and facilities at my work place are provided to us.

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