Environ Monit Assess (2007) 130:173–185
DOI 10.1007/s10661-006-9387-2

ORIGINAL ARTICLE

Mathematical Modeling of Leachates from Ash Ponds of Thermal Power Plants

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Received: 12 February 2006 / Accepted: 28 June 2006 / Published online: 21 October 2006

Abstract The present study describes the development of empirical models for the prediction of various trace metals i.e., Mn, Cu, Fe, Zn and Pb found in the leachates generated from the ash ponds of various thermal power plants. The dispersion phenomenon of these trace metals followed first order reaction rate kinetics. The empirical models for individual trace metals derived from the lab scale models data correlate well with the real field data with regression coefficients varying from 0.93 to 0.98. The predicted concentrations of the trace metals varied within ±3% of the observed values in the leachates generated from the ash ponds of four thermal power plants with standard deviation varying from 0.001 to 0.032. The empirical models derived from the study can be applied for prediction of trace metals in leachates generated from similar thermal power plants.

Keywords Fly ash · Trace metals · Runoff · Leaching · Dispersion coefficients · Empirical models · Ground water pollution

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1 Introduction

Coal accounts for about 70% of power generation and its dominance as prime energy source will continue in the future due to abrupt increase in the cost of crude oil specially during the last few years. Combustion of coal to generate electricity produces huge amounts of fly ash, the disposal of which has now become a prime concern of various countries generating electricity through coal based thermal power plants. At present, India generates about 120 MT/year of fly ash through various thermal power plants which is expected to further increase to 170 MT/year by the end of Eleventh Five year Plan in year 2012 (FAUP, 2005). In view of disposal and proper utilization of fly ash; Govt. of India constituted “Fly Ash Mission” (FAM) in 1994 towards development, scale-up and field demonstration of fly ash utilization technologies in order to enhance its adoption by various user agencies (Singh et al., 2005). FAM has further been upgraded to Fly Ash Utilization Programme (FAUP) in view of the considerable utilization (41%) of fly ash from a mere 3% in 1997.

Presently, fly ash generated from the thermal power plants is disposed in the form of slurry in the ash ponds within the plant called Coal Combustion Residues (CCRs). The leachates generated from these ash ponds contains various trace elements such as Na, K, Ca, Mg, Mn, Cu, Fe, Zn and Pb etc., which on accumulation can pose serious environmental problems and hazards to human health (Singh & Kumar, 2004). Zn and Cu are reported to cause toxicity to fish and brain damage in mammals, respectively (DWAF, 1996b; Skidmore, 1964; Spear, 1981). Pb causes neurological disorders and picca-picca disease especially in the foetus and in children leading to behavioral changes and impaired performance in IQ tests (Lansdown, 1974; Huel et al., 1987). Similarly, the presence of Fe and Mn in water poses taste and aesthetic problems. Owing to significant concentration levels of these trace metals in the leachates, studying the behavior of these trace metals becomes imperative and hence is of prime concern and area of current research. Hower et al. (2005) have studied the temperature dependent behaviour of the Hg in fly ash generated from the Kentucky Power Plant. Akira et al. (2006) have studied various trace metals in coal fly ash and the effect of pre-treatment conditions on the determination of trace metals. Several researchers (Hassett, 1994; Liu, Yang, & Wang, 2000b; Liu, Yang, & Wang, 2003; Liu, Yang, Zhang, Wang, 2000a; Marcal et al., 1997) have studied the leaching behavior of various trace metals found in the leachates generated from the ash ponds of different thermal power plants. However, the studies on mathematical modeling of these trace metals to predict the behaviors of the leachates are very limited. Owing to the above facts, studying the behavior and dispersion phenomenon of these trace metals in the leachates generated from the ash ponds of various thermal power plants were undertaken as the prime objective of the study. An attempt has been made to develop the empirical models for few trace metals using laboratory scale models and correlating it with the real field data.

2 Objective

The prime objective of the study is to develop a mathematical model to predict the concentration of various trace metals present in the leachates generated from thermal power plants. The specific objectives of the study are as under:

- Assess the concentration of various metals in the leachates;
- Develop empirical models to predict the concentration of most frequently occurring trace metals in leachates.

3 Theoretical Concepts

3.1 Development of mathematical model

When the water flows through a porous media it follows diversified set of paths. However, certain set of paths may occur more frequently to yield a uniformly declined concentration profile in the continuously leaching water, which are known as the most probable set of paths. Figure 1 shows the diversified and most probable set of paths followed by water during its flow through the porous media.

These sets of flow paths do not only vary with respect to the variation in the flow rate but the continuous deformation phenomenon occurring in the particulate matter may also cause diversified paths. For example, the water initially flows through the path P_1, may be leached out through two paths; P_{11} and P_{12}, which later leached out through either P_{11} or P_{12}, or even entirely a new path P_{13} (Figure 1). If we assume that $\{P_{11}, P_{12}, P_{13}, ... P_{1n}\}$, where n = any natural number is the set of diversified paths of P_1 at any time, then path of flow of leaching metals can be expressed by Equation (1).

$$P_1 = P_{11} + P_{12} + P_{13} + ... + P_{1n} = \sum_{i=1}^{n} P_{1i} \tag{1}$$

As the set of paths vary with respect to time, the concentration profile of the leachates also varies. Figure 2 shows the concentration profile of Sodium

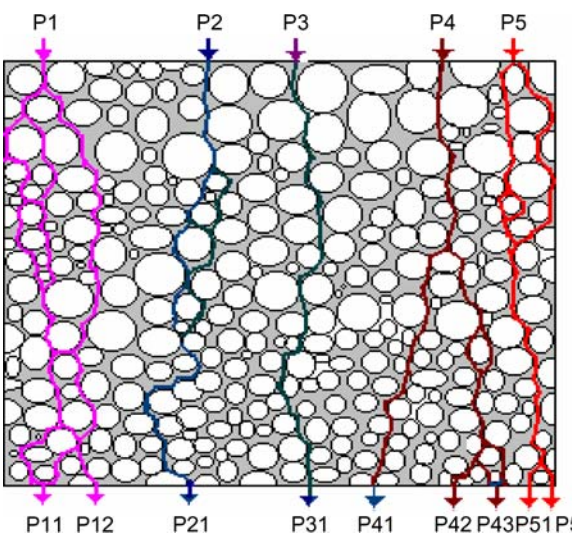

Figure 1 Pictorial view of water flow through the most probable paths.

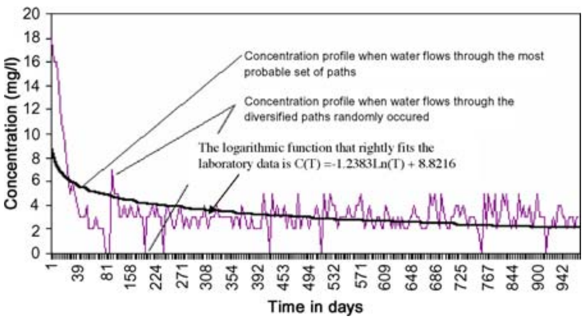

Figure 2 Concentration profile of sodium (Na) when water flows through the set of most probable paths and randomly diversified paths.

(Na) when water flows through the set of most probable paths and randomly diversified paths. From Figure 2 it is evident that though the variation in the concentration is non-uniform, however, it essentially decreases with increase in time. Thus, the rate of change in the dissolved contaminants can be reasonably assumed to be inversely proportional to the time 't' when the water flows through the most probable set of paths.

Further, if the initial time be zero and the time taken to pass through the porous media is 't', then it can be assumed that the concentration profile declines at the end of the successive time series i.e., $t = h$, $t + h$, $t + 2h$, $t + 3h$, $t + 4h$, ... etc., where $h > 0$ and as much as small (Sunderarajan, Chakraborty, & Loveson, 1994). Based on the above facts concentration of the trace metals in the water successively passing through the porous media can be theoretically drawn and is shown in Figure 3.

Based on these assumptions the governing equation describing the dispersion phenomena of the trace metals can be expressed as a first order differential equation (Chattterji, 2000).

$$\frac{dc(t)}{dt} \alpha \frac{1}{t} \tag{2}$$

$$\Rightarrow \frac{dc(t)}{dt} = k \cdot \frac{1}{t} \tag{3}$$

Where, $c(t)$ = concentration at time 't'
k = dispersion coefficient

Now, integration of Equation (3) over the time interval (t, $t + h$) can be expressed as under:

$$\begin{aligned} &\Rightarrow c(t+h) - c(t) = k \cdot \int^{+h} \frac{1}{t} \cdot dt \\ &\Rightarrow c(t+h) = k \ln\left(\frac{t+h}{t}\right) + c(t) + a \end{aligned} \tag{4}$$

Where, 'a' is a constant, and at $h = 0$, the value of constant $a = 0$. Hence, the general solution for Equation (4) can be expressed by Equation (5):

$$c(t+h) = k \ln\left(\frac{t+h}{t}\right) + c(t) \tag{5}$$

Again, at $t = 1$ and $h = 0$, the Equation (5) results a valid solution and the time series t, $t + h$, $t + 2h$, $t + 3h$, ... ∞ can be constituted by assuming initial time $t = 1$ day with an increment of 1 and the general solution of the Equation (5) can be expressed by Equation (6) as under:

$$c(1+h) = k \ln(1+h) + c(1) \tag{6}$$

In Equation (6), if we replace c (1) which is the concentration of trace metals on the first day) by c_0 (initial concentration) and $1 + h$ by the time 'T', then the Equation (6) can be transformed as Equation (7).

$$c(T) = k \ln(T) + c_o \tag{7}$$

Where, T = days
$c(T)$ = concentration at time 'T'
c_o = initial concentration
k = dispersion coefficient

Thus the Equation (7) can be used to find the concentration profile of the trace metals in the leachates. However, a correction factor needs to be incorporated in order to simulate the laboratory experimental data with the field conditions due to the following facts:

- Laboratory experiments were conducted with continuous flow of water under static head whereas the rainfall does not take place continuously in the real world.
- Moreover, as the intensity of rainfall varies with time, the flow may not be in steady state condition.

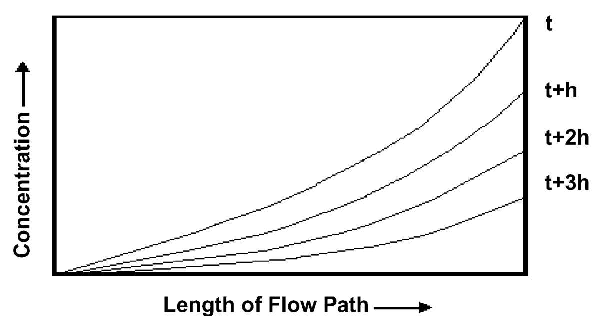

Figure 3 Hypothetical concentration profile of trace metals at successive series of time when the water flow passes through the ash sample.

3.2 Estimation of rainy days

The empirical model derived through laboratory experiments cannot be applied to the real field unless the data on the rainfall and its duration are available. In addition, the rainfall in a region is not uniform and varies both monthly and annually. Hence, in order to consider these variations, a statistical analysis of the rainfall data is essential to find the monthly and yearly rainfall and their flow durations. In the present case, the rainfall data for the past few years were available in the form of monthly total hence, the intensity factor (F) was calculated individually for every month using Equation (8) and The number of rainy days in a particular month was statistically found out by converting the duration of total rainfall hour of a year into number of rainy days and distributing it statistically in proportion to rainfall intensity factor of a particular month:

$$F = R_m / R_a \tag{8}$$

Where, R_m = monthly average rainfall
R_a = average total annual rainfall

It is assumed that the duration of the rainfall in a particular month is directly proportional to the intensity factor. In addition, a proportional constant (k_p) was estimated using Equation (9) for considering the annual variation of rainfall in estimation of average rainy days of the individual months.

$$R_{est}(T_m) = k_p \cdot R_{act}(T_m) \tag{9}$$

Where, R_{est} (T_m) = estimated average rainy days of month T_m
R_{act} (T_m) = actual average rainy days of month T_m
K_p = proportional constant

3.3 Experimental set-up and methodology

The open percolation column used for studying behavior and characteristics of leachates generated is shown in Figure 4. The set up consists of PVC columns of 10 cm diameter and 75 cm height, open at the top and fitted with an outlet at the bottom to collect the leachates. The columns are filled up into layers with the fly ash collected from ash ponds of different thermal power plants. Sufficient ramming and scratching was done during the addition of each new layer to ensure proper interlocking and packing of fly ash into the column. All the columns were packed up to 60 cm height with fly ash collected from the ash ponds of various thermal power plants, leaving a 15 cm space at the top as per standard guidelines and procedure adopted for design in the Open Percolation Column Experiments. The guidelines were followed in order to maintain a constant head of 15 cm water and to simulate the solid liquid ratio of the Ash ponds in the real field conditions (Singh & Kumar, 2004). Leachates were collected in polypropylene beakers placed below the outlet of the column. The top of the column and the beakers were covered with common zip-lock plastic bags to prevent dust and other contamination of the water.

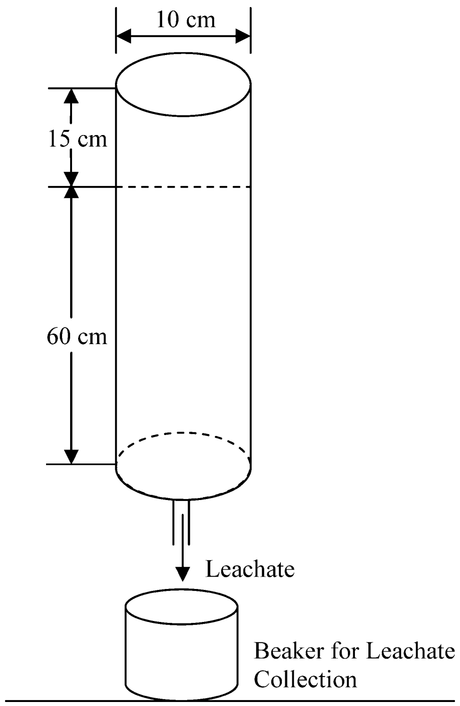

Figure 4 Open column experimental set-up for leaching study.

The physical properties of the fly ash collected from various thermal power plants are given in Table I. It can be seen from the table that the properties of fly ash generated from the thermal power plants varies from plant to plant which can be attributed to the many factors i.e., inherent properties of the coal, combustion efficiency, method of combustion etc. The particle size analysis shows that fly ash collected from various ash ponds are uniformly graded (Cu varying from 0.871 to 1.008). The specific gravity of the fly ash varied from 1.74 to 2.60. The surface area

Table I Physical properties of the fly ash collected from the ash ponds of various thermal power plants

Parameters	Fly ash characteristics of various thermal power plants			
	BTPS	DTPS	FBCP	FCI
Size (μm)				
• D60	143.24	143.57	158.73	136.26
• D10	43.27	50.99	50.99	41.51
Uniformity coefficient, C_u	0.871	1.008	0.949	0.898
Bulk density (g/cc)	0.960	0.73	0.55	0.81
Specific gravity	2.60	1.74	2.02	2.01
Surface area, (m^2/kg)	2	4.20	6.70	8.5
Permeability (10^{-4} cm/s)	2.12	1.6	2.02	2.01
Porosity (%)	50.16	58.04	72.77	59.70
Water holding capacity, WHC (%)	75.59	50.91	78.25	63.90
Optimum moisture content, OMC (%)	20.68	437	42.50	40.5
Maximum dry density, MDD (g/cc)	1.27	1.12	1.067	0.96

Table II Characteristics of the leachates collected from ash ponds of various thermal power plants (all values except pH are in mg/l)

Parameters	Ash pond effluents from various thermal power plants			
	BTPS	DTPS	FBCP	FCI
pH	6.97–8.97	7.20–8.30	7.36–9.17	6.27–7.52
Conductivity	0.549–0.897	0.824–1.260	0.216–1.876	0.523–0.638
TDS	275–449	355–510	108–688	261–319
Iron	0.133–3.634	0.086–3.974	0.026–0.687	0.375–0.592
Lead	BDL–0.158	BDL	0.033–0.069	BDL
Magnesium	0.077–55.00	11–31	0.086–181.65	40.54–59.62
Calcium	3.265–117.30	17–63	0.058–176.30	48.64–56.96
Copper	BDL–0.107	BDL–0.063	0.031–0.086	BDL–0.048
Zinc	0.765–1.754	0.769–1.131	0.029–0.096	0.128–0.165
Manganese	BDL–0.083	BDL	0.023–0.059	0.043–0.072
Sodium	5.00–37.00	4.00–28.00	18.00–66.00	28.00–45.00
Potassium	4.00–53.00	6.00–39.00	15.00–47.00	10.00–24.00
Chromium	BDL	BDL	BDL	BDL–0.481
Nickel	BDL	BDL	BDL	BDL
Cobalt	BDL	BDL	BDL	0.067–0.095
Cadmium	BDL	BDL	BDL	BDL
Selenium	BDL	BDL	BDL	BDL
Aluminium	BDL	BDL	BDL	BDL
Silver	BDL	BDL	BDL	BDL
Arsenic	BDL	BDL	BDL	BDL
Boron	BDL	BDL	BDL	BDL
Barium	BDL	BDL	BDL	BDL
Vanadium	BDL	BDL	BDL	BDL
Antimony	BDL	BDL	BDL	BDL
Molybdenum	BDL	BDL	BDL	BDL
Mercury	BDL	BDL	BDL	BDL

Table III Empirical models for predicting the trace metals concentration in leachates generated from ash ponds of various thermal power plants

Parameter	Empirical models			
	BTPS ash pond	FBCP ash pond	FCI ash pond	DTPS ash pond
Mn	$C(t) = -0.0029\ln(t) + 0.0366$	$C(t) = -0.0045\ln(t) + 0.0446$	$C(t) = -0.0155\ln(t) + 0.0942$	–
Cu	$C(t) = -0.0019\ln(t) + 0.0355$	$C(t) = -0.0053\ln(t) + 0.0526$	$C(t) = -0.0013\ln(t) + 0.0314$	–
Fe	$C(t) = -0.1986\ln(t) + 1.2468$	$C(t) = -0.0751\ln(t) + 0.482$	$C(t) = -0.0218\ln(t) + 0.1961$	$C(t) = -0.078\ln(t) + 0.4519$
Zn	$C(t) = -0.0158\ln(t) + 0.1036$	$C(t) = -0.0101\ln(t) + 0.0653$	$C(t) = -0.0129\ln(t) + 0.0691$	$C(t) = -0.0034\ln(t) + 0.0271$
Pb	$C(t) = -0.0891\ln(t) + 0.5349$	$C(t) = -0.0038\ln(t) + 0.0696$	–	–

of the fly ash varied significantly i.e., from 2 m^2/kg to 8.5 m^2/kg. The permeability and porosity of the fly ash were found to be varying from the 1.6×10^{-4} cm/s to 2.12 cm/s and 50.16% to 78.25%, respectively.

The samples of the leachates were collected bi-weekly from the lab-scale Open Column as well as from the ash ponds of four thermal power plants i.e., BTPS (Bokaro Thermal Power Station), DTPS (Durgapur Thermal Power Station), FBCP (Fluidized Bed Combustion Plant) of TATA STEEL and FCI (Fertilizer Corporation of India); for the duration of five years since the commencement of the experiments. Potentiometric and elemental analyses of leachates were carried out using Atomic Absorption Spectrophotometer (AAS), coupled with hydride generator, computer data station, Systronics (Model GBC-902), and Flame Photometer (Model-128) as per the procedure mentioned in the Standard Methods for Examination of Water and Wastewaters (APHA, 1995).

4 Results and Discussion

4.1 Characteristics of the leachates from various thermal power plants

The chemical characteristics of leachates of the ash ponds were found to be varying from time to time as well as from plant to plant which can be attributed to

Table IV Monthly rainfall data and estimation of rainy days

Years/months	Monthly rainfall record in mm						R_m (mm)	$F = R_m / R_a$	T_m (days)
	1999	2000	2001	2002	2003	2004			
January	14	0	0	24	12.8	11.2	10.33	0.008	0.25
February	0	11.2	6.2	23.4	27.2	13.7	13.62	0.011	0.31
March	0	0	7.4	3.4	21.4	15.6	7.97	0.006	0.19
April	0	5.4	33.6	46.4	0	30.8	19.37	0.015	0.45
May	4.4	49.4	94.6	55.6	42	50.8	49.47	0.039	1.21
June	200	185	302	153.2	0	213.8	175.67	0.138	4.14
July	371	213	194	295.8	272.8	277.1	270.58	0.213	6.60
August	254	426	296	422.4	220.4	302.2	320.07	0.252	7.81
September	24.4	239.8	436.2	188.8	541.8	302.8	288.97	0.228	6.84
October	24.4	45.2	52.4	91.4	59.8	79.6	58.80	0.046	1.43
November	0	4.2	65.4	0	153	31.8	42.40	0.033	0.99
December	62.4	0	0	0	0	9.1	11.92	0.009	0.279
Total	954.6	1,179.2	1,487	1,304.4	1,351.2	1,338.5	R_a = 1,269.15	1	30.55

Table V Correction factors of various empirical models for prediction of trace metals for different thermal power plants

Trace elements	Thermal power plants			
	BTPS	DTPS	FBCP	FCI
Mn	0.933401	–	1.200584	0.958979
Cu	1.086426	–	1.227135	1.111397
Fe	0.899233	1.071618	1.275410	0.966553
Zn	0.983615	1.055069	1.347616	1.249598
Pb	1.060761	–	0.999414	–

the variations in the sources of the coal used in various thermal power plants. However, typical characteristics of leachates from various thermal power plants are worked out and given in Table II. It can be seen from the table that leachates are generally alkaline in nature with pH values varying from 6.97 to 8.97 in all the three samples (ash ponds of BTPS, DTPS and FBCP) while it varies from 6.27 to 7.52 in case of FCI ash ponds. In general, nine elements such as Na, K Ca, Mg, Mn, Cu, Fe, Zn and Pb were observed in the leachates from the ash ponds of various thermal power plants. However, their concentration levels differ from plant to plant. Mn and Cu are found to be BDL (Below Detection Limit < 0.001 mg/l) in leachates of DTPS ash ponds. While, Pb is found to be nil in leachates of both DTPS and FCI. Na, K, Ca and Mg were found to be present in the leachates of all four thermal power plants, which are mainly responsible for alkalinity nature of leachates. Martinez-Tarazona and Spears (1995) reported high concentration of As, Cu, Mo, Pb and Zn in the fly ash from pulverized coal combustion Power Plant. Many researchers (Akira et al., 2006; Ashokan, Saxena, Asokan, 2003; Praharaj, Powell, Hart, & Tripathy, 2002) have observed varying composition of the trace metals in leachates, which can be attributed to variations in the coal and fly ash characteristics, employed in various studies.

4.2 Development of empirical models

As per Equation (7), five year experimental data of the concentrations of individual trace metals were plotted on the *y*-axis against the logarithm of time periods in days on the *x*-axis and a suitable logarithmic functions of the best fit curves were found which yielded a good correlation with regression coefficients (R^2) varying from 0.93 to 0.98. The equations governing the best fit of the experimental data, thus, were taken as the empirical models for predicting the concentrations of these trace metals and are given in Table III. In order to calibrate these empirical models for the field conditions a suitable correction factor needs to be incorporated in the models in order to consider the variations in lab and field conditions.

4.3 Calibration and validation of empirical models

The empirical model that has been derived through laboratory experiment cannot have harmony with the real world. The number of rainy days in a certain month of a year varies year to year. Therefore, the

Table VI Standard deviation of the predicted data for various thermal power plants

Trace elements	Thermal power plants			
	BTPS	DTPS	FBCP	FCI
Mn	0.002	–	0.006	0.002
Cu	0.009	0.007	0.008	0.001
Fe	0.047	0.012	0.074	0.004
Zn	0.002	0.001	0.013	0.002
Pb	0.011	–	0.008	–

models have to be tuned or calibrated with the real field conditions. The following two factors were considered in the calibration of these empirical models:

- Tuning the trend of overall annual variation
- Tuning the cyclic trend of monthly variation

In order to analyze the monthly and annual cyclic variations of the rainfall the rainfall data of the study area of the past five years duration were collected from the District Statistic Department and Centre of Mining Environment, ISM, Dhanbad and the intensity factor and the number of rainy days for every month

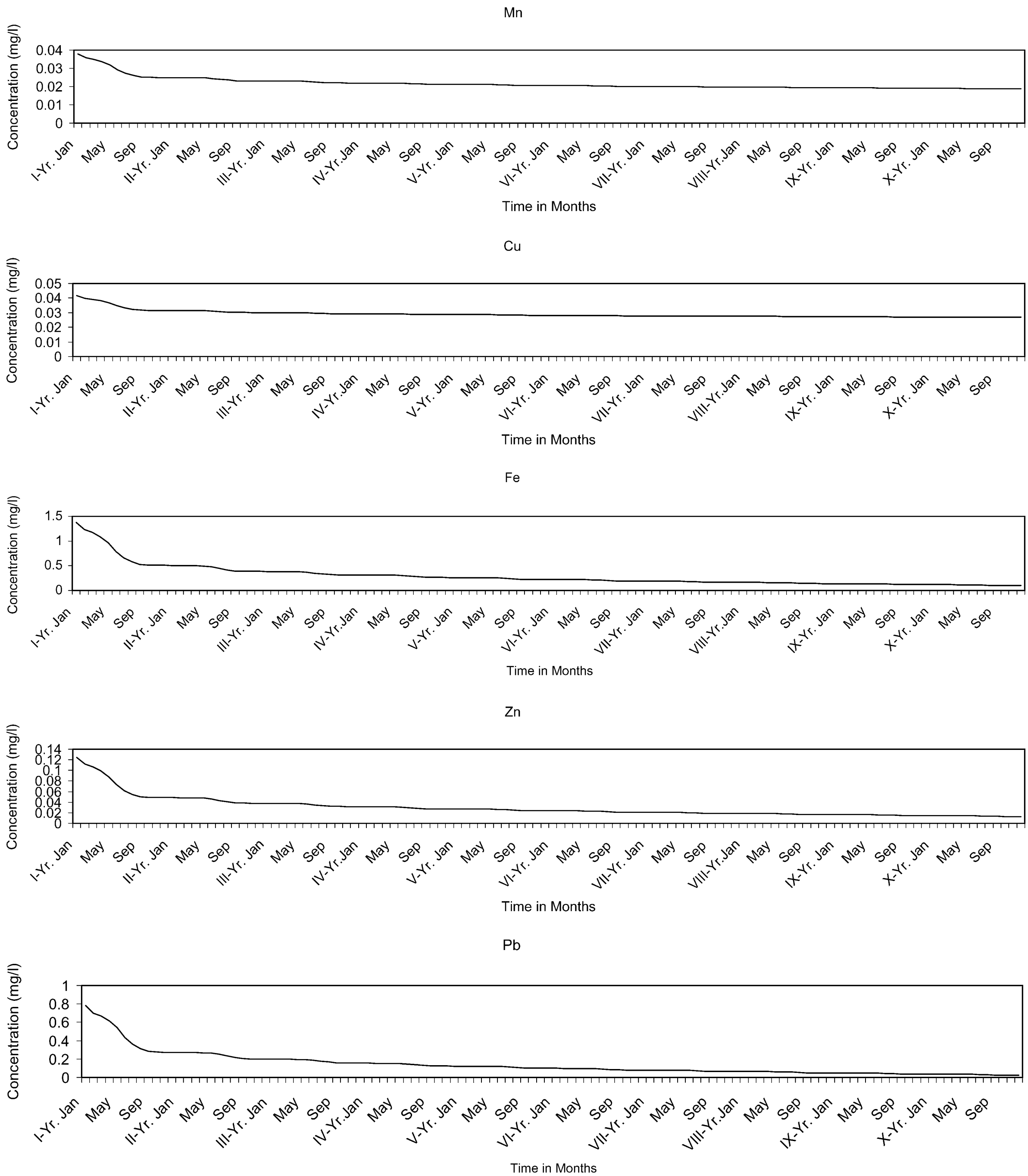

Figure 5 Predicted concentration of trace metals in the leachates of BTPS.

was estimated and are given in Table IV. It can be seen from the table that the total number of rainfall days in a year is 30.55 days with a maximum rainfall being found in normal rainy season of study region during the months of July, August and September.

Now, if the number of rainy days in different months in particular year be the random variables X_i, $i = 1, 2, 3 \ldots, 12$; then the number of rainy days 'T' of the random variable for mth month of nth year, can be computed using Equation (10) (Sunderarajan & Loveson, 1998; Sunderarajan et al., 1994).

$$T_m = (n-1)\sum_{i=1}^{12} X_i + \sum_{i=1}^{m} X_i \tag{10}$$

Using Equation (10), the number of rainy days for every month in the coming decades have been calculated and used in Equation (7) for the prediction of the trace metals concentrations for the future. Accordingly, the duration of five hundred days of continuous laboratory experiments equals to approximately 16 ½ years in the real world as 30.55 days of laboratory analysis covers one year in the real world.

The correction factor 'C' for various trace metals were calculated by comparing the results of the Equation (7) with observed concentrations of these trace metals in the leachates generated from the ash ponds of different thermal power plants and the empirical models derived from the lab scale data were accordingly modified by incorporating the correction factors as expressed by Equation (11):

$$c(T_m) = C[k \ln(T_m) + c_o] \tag{11}$$

Where, $c(T_{\mathrm{m}})$ = concentration at time 'T_m'
c_{o} = initial concentration
k = dispersion coefficient
C = correction factor
T_m = time length in days

Using Equation (11) the correction factors for various trace metals in leachates generated from different Thermal Power Plants have been estimated, which are given in Table V. It can be seen from the table that the correction factor for various trace metals varied from 0.9 to 1.35 showing the derived empirical models from lab scale data can be well used to describe the dispersion phenomenon of these trace metals in leachates of various ash ponds of the field.

4.4 Validation of models

For validation of these models the concentrations of trace metals i.e., Mn, Cu, Fe, Zn and Pb found in the leachates of various thermal power plants for the five-year period in the field have been compared with the predicted data and the standard deviations were estimated. Table VI shows the standard deviations of predicted data of various trace metals i.e., Mn, Cu, Fe, Zn and Pb for different thermal power plants. The

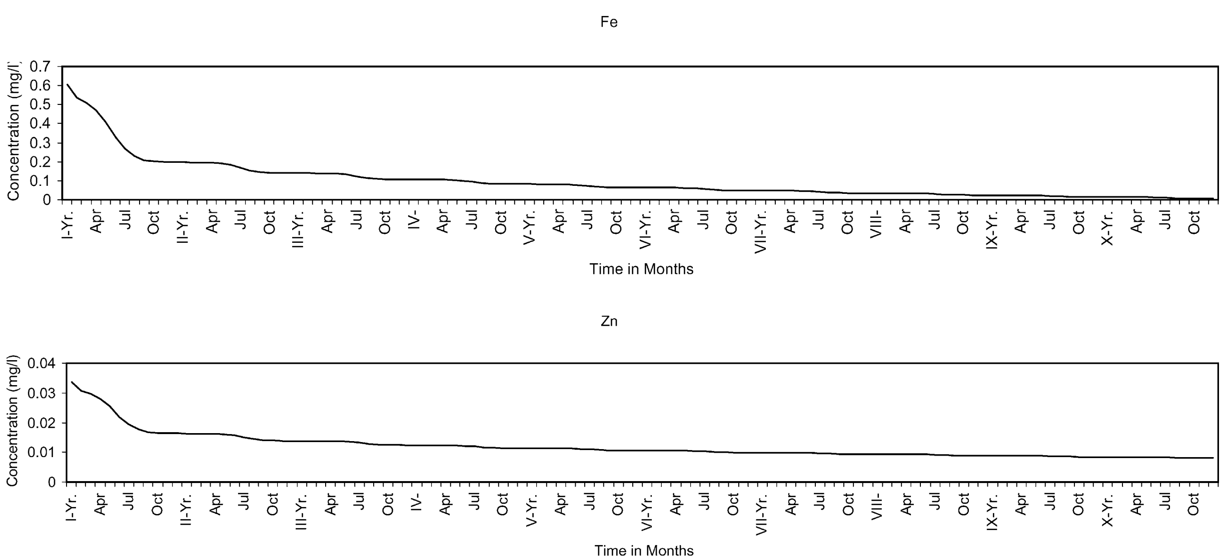

Figure 6 Predicted concentration of trace metals in the leachates of DTPS.

analysis of data demonstrated that the predicted results follow the same trend of real time field data with the standard variations varying from 0.001 to .074. David et al. (2005) studied the leaching behaviour of trace elements for over 25 years and observed the decreasing concentration of various trace elements in the leachates with respect to the time.

4.5 Application of model

The derived empirical models after incorporating appropriate correction factors were used to predict the concentration of trace metals in leachates of various thermal power plants for the period of ten years. Figures 5, 6, 7 and 8 show the plots of predicted trace metals

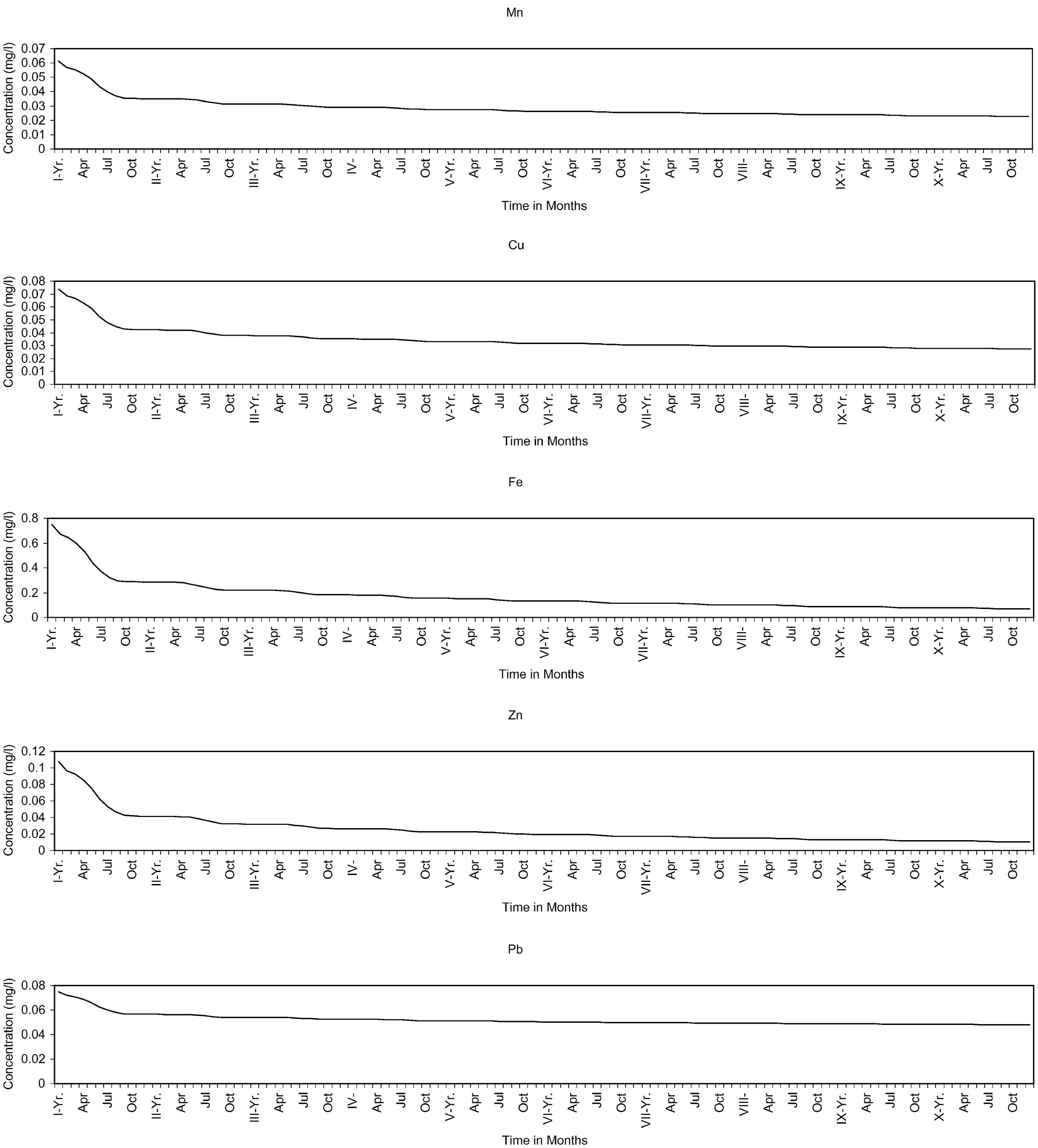

Figure 7 Predicted concentration of trace metals in the leachates of FBCP.

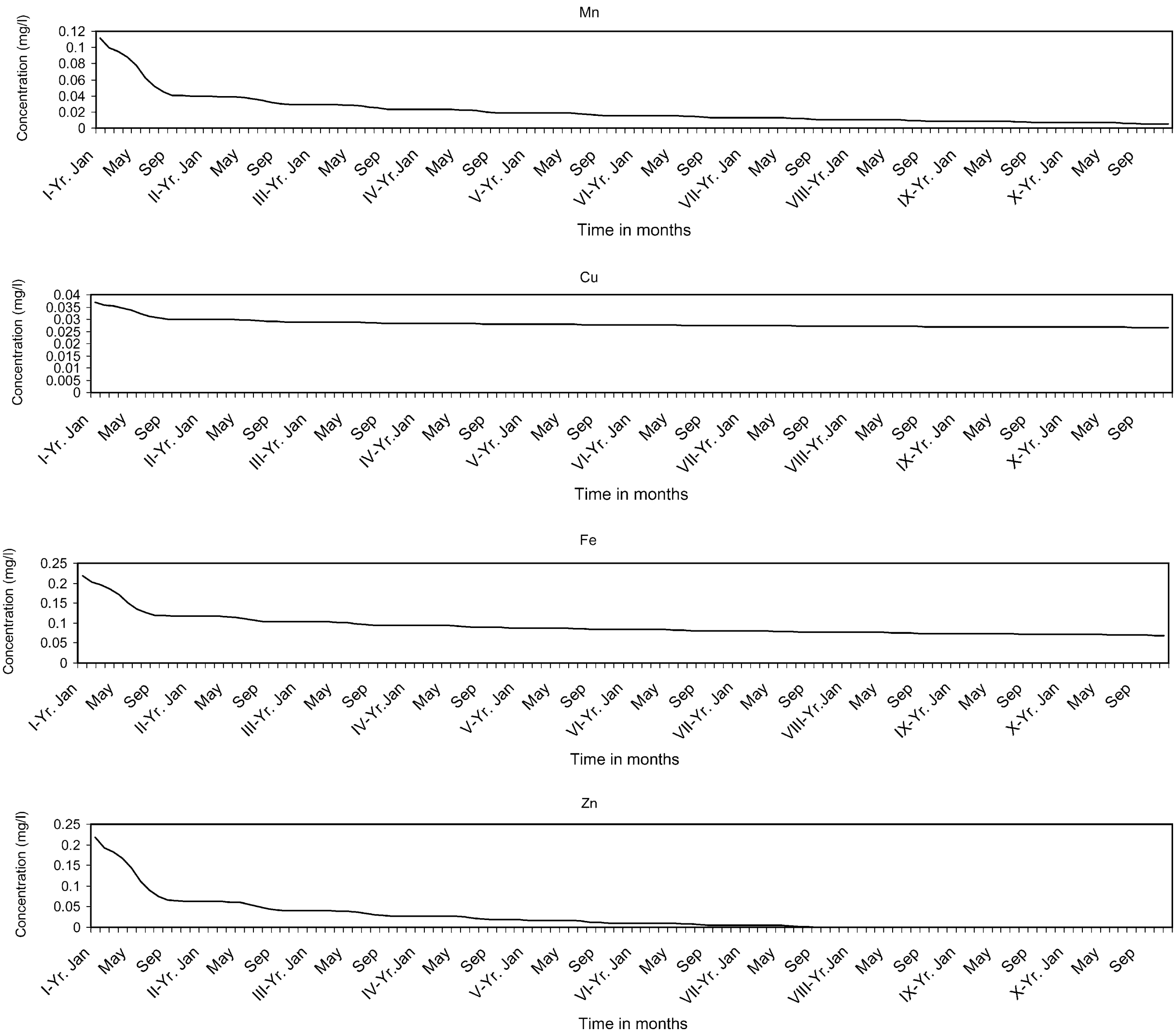

Figure 8 Predicted concentration of trace metals in the leachates of FCI.

concentration for the period of ten years in the leachates of BTPS, DTPS, FBCP and FCI, respectively.

It can be seen from Figure 5 that the concentration of Mn, Cu, Fe, Zn and Pb in the leachates from BTPS ash ponds were initially to be 0.037 mg/l, 0.036 mg/l, 1.247 mg/l, 0.104 mg/l and 0.540 mg/l, respectively which reduced to 0.022 mg/l, 0.026 mg/l, 0.250 mg/l, 0.024 mg/l and 0.094 mg/l at the end of fifth year and are predicted to be as 0.016, 0.020 mg/l, 0.110 mg/l, 0.013 mg/l and 0.024 mg/l, respectively at the end of tenth year. Jankowski, Ward, French, and Groves (2006) performed Batch leaching tests on fly ashes collected from four Australian power stations and reported the diminishing behaviour of As, B, Mo and Se. Leaching of trace elements occurs under different conditions and over different leaching times.

Figure 6 shows that Fe (0.452 mg/l) and Zn (0.027 mg/l) were predominant while Mn, Cu and Pb were almost nil in the leachates of DTPS ash pond. Hence, the prediction of these metals was not attempted for this plant. The concentration of Fe and Zn, however, was found to decrease to 0.059 mg/l and 0.010 mg/l after five years and predicted to be 0.0056 mg/l and 0.008 mg/l, respectively at the end of ten years. Figure 7 shows that the concentrations of Mn, Cu, Fe, Zn and Pb in the leachates of FBCP ash ponds were initially found to be 0.045 mg/l, 0.053 mg/l, 0.482 mg/l, 0.065 mg/l and 0.069 mg/l and decreased to 0.022 mg/l, 0.026 mg/l 0.104 mg/l, 0.015 mg/l and 0.051 mg/l, respectively at the end of the fifth year. The predicted concentration of these trace metals were found to be 0.012 mg/l, 0.022 mg/l, 0.052 mg/l, 0.007508 mg/l and 0.047 mg/l, respectively after ten years. The concentrations of trace elements found in case FBCP pond varies from the reported concentration of trace metals for PFBC and AFBC processes (Benito, Ruiz, Cosmen, & Merino, 2001). This can be attributed to the variation in the coal and the combustion processes used in the study.

Figure 8 shows that the Pb was almost nil (<0.001 mg/l) in the leachates from the ash ponds of FCI while the Mn. Cu, Fe and Zn were predominant (0.094 mg/l, 0.031 mg/l, 0.196 mg/l and 0.069 mg/l, respectively). The concentrations of these trace metals decreased to 0.016 mg/l, 0.025 mg/l, 0.086 mg/l and 0.004 mg/l, respectively at the end fifth year and predicted to further decreased to 0.006 mg/l, 0.024 mg/l, 0.071 mg/l and BDL (0.001 mg/l), respectively. Thus Zn vanishes from the leachates at the end of ninth month of sixth year.

The decrease in the concentration of these trace metals i.e., Mn, Cu, Fe, Zn and Pb can be easily visualized from the plot of the predicted concentrations of these trace metals with respect to time periods for different thermal power plants. It can further be seen that diminishing behavior (concentration profiles) of Cu in the leachates from the ash pond of DTPS and FCI were almost the same while Fe, Zn and Pb have shown different behaviors in the leachates of various thermal power plants. The variations in the diminishing behaviors of various trace metals can be attributed to variations in the coal and inherent properties of different metals (Hower et al., 2005; Marcal & Xavier, 2004; Mardon & Hower, 2004; Praharaj et al., 2002; Tripathy & Gambhir, 1999). Further, the leaching of metals i.e., Na, K, Ca and Mg was found to be throughout the study period as they were always present in the leachates while other metals i.e., Fe, Cu, Pb, Fe and Zn, disappear from the leachates with the increase in time periods.

5 Conclusions

The following conclusions can be drawn from the present studies:

- Amongst various trace metals mere nine metals i.e., Na, K, Mg, Ca, Fe, Pb, Mn, Cu, Zn are predominant in the leachates of various thermal power plants.
- The concentrations of various trace metals in leachates vary significantly from plant to plant which entirely depends on the inherent properties of the coal used in the individual thermal power plants.
- Fe, Cu, Pb, Fe and Zn do not show a regular trend of leaching. However, Na, K, Ca and Mg were found to be leached throughout the study period, which are responsible for the alkaline nature of the leachates.
- Dispersion of the trace metals in the leachates of various thermal power plants can be described by first order differential equation with a regression coefficient of 0.93 to 0.98. The decrease in the concentrations of these trace metals in leachates was found to be proportional to the logarithm of the time period.
- The developed empirical models can be used to predict the concentration of various trace metals in leachates generated from a few select thermal power plants.

Notations

P_{1i}	Pathways of leaching
$c(t)$	Concentration of trace metal at time t
t	Time period
k	Dispersion coefficient
$c(T)$	Concentration of trace metal at any time T after the first day
c_o	Initial concentration of trace metal (on first day)
R_m	Monthly average rainfall
R_a	Average total annual rainfall
F	Intensity factor
$R_{est}(T_m)$	Estimated average rainy days of month T_m
$R_{act}(T_m)$	Actual average rainy days of month T_m
K_p	Proportional constant
C	Correction factor
T_m	Time length in days of an mth month

Acknowledgements This work was financially supported by a grant from Ministry of Environment and Forest Government of India, New Delhi.

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