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LONG-TERM PREDICTION OF THE POTENTIAL IMPACT OF HEAVY METALS ON GROUNDWATER QUALITY AS A RESULT OF FERTILIZER USE

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ABSTRACT

In the context of the programme of action of the European Communities on the environment directed to prevent and reduce pollution, a study on the potential impact of heavy metals (HM) on groundwater as a result of fertilizer use has been undertaken at JRC-Ispra. The prediction of the increase of HM in soil as a result of long-term use of phosphatic fertilizers, based on the estimated global mobilization of the elements, suggests significant potential groundwater pollution for Cd, Se, Mo and U. In order to predict time-dependent migration of HM through soil to groundwater, a system analysis method involving the development of a mathematical dose prediction model was applied. The application of the dynamic model to the migration of Cd-fertilizer taken as a reference case, indicates the possibility for this element to reach really the groundwater system through the soil-compartments.

INTRODUCTION

Phosphate minerals used for the production of fertilizers contain variable amounts of heavy metals (HM) ranging from few to hundreds of ppm (ref.1) which remain in the final products after the chemical treatment of the mineral rocks for the preparation of fertilizers (ref. 2-3).

Some of these elements are essential nutrients for plants (ref.4) while others are considered toxic agents. HM of concern include, among others, As, Cd, Cr, Cu, Ni, Pb, U and V. Following fertilizer application, HM are released to soil and potentially can have an impact not only on plants but also on surface and groundwater after percolation through the soil compartments. This may result in hazardous exposure of living organism because HM can reach drinking water supplies through hydrological transport or enter the food chain (ref.5-6).

While the studies of the effects that HM from fertilizer can have on plants are relatively numerous, very little attention has been surprisingly posed to their possible impact on groundwater, probably due to the difficulty to describe the mobility of HM in soil which is the basis to quantify the transfer through soil components up to groundwater.

Evidence exists that HM entering the soil are cumulated both in the organic matter zone with formation of stable chelating complexes as well as in mineral zone through complicated hydrolytical and redox processes existing in natural conditions which can convert HM to insoluble compounds. Although these findings would indicate a little mobility of HM in soils in-field studies show that infiltration of HM into groundwater from fly ash disposal sites is possible suggesting that re-mobilization of the elements chelated on immobilized in soil may occur (ref.7).

The objective of this paper is to illustrate the studies carried out at the JRC-Ispra on the long term prediction of the potential impact that HM may have on groundwater as a result of the use of phosphatic fertilizer on the territory of the European Communities.

LONG TERM PREDICTIONS OF THE RELEASE OF HM - FERTILIZERS TO SOIL

The prediction of the total amounts of HM - fertilizers released to soil of each country of the EC, is the basis for assessing the long term increase of the endogenous level of HM in soil which can be used to identify what HM may have a significant impact on groundwater. The knowledge of fertilizer consumption for each Member State and the average values of HM in fertilizers applied are the two parameters which must be known for such prediction.

Table 1 reports the mean values of the HM content as taken to estimate the total release of HM-fertilizers to soils. The same table reports also the calculated amounts of HM mobilized for the year 1978 in each country of the EC.

TABLE 1 - Heavy metals added to the soils of the EC countries during 1978 as a consequence of phosphatic fertilizer use

Element	Concentration in phosphorites (ppm)	Amount of heavy metals mobilized (ton/y)								
		F	I	FRG	UK	Ir	DK	N	B/L	EUR-9
B	35	49	27	28	13	6	4	2.4	3.5	133
V	400	373	209	156	142	41	31	26	28	1006
Cr	350	518	290	312	116	57	42	28	21	1384
Mn	60	45	25	65	102	5	4	5.5	3	254
Ni	70	89	50	54	20	11	7	4	4.5	240
Cu	100	117	66	56	26	13	10	5.5	6.5	300
Zn	400	581	326	146	108	64	47	15	13	1300
As	30	49	27	17	11	4.5	3.3	2	3	117
Se	22	34	20	34	9	4	9	2	1.5	108
Mo	80	85	48	80	26	10	7	5.5	3	264
Cd	80	102	57	39	25	11	8	5.5	3.5	251
U	340	405	227	53	67	45	33	12	13	855
Fertilizer consumption (t/1978) x 10^3:										
		1621	909	690	356	179	132	75	61	4023

From the data of Table 1, the long term effects of the exogenous amounts of HM-fertilizers on the endogenous level of HM in soil can be assessed (Table 2).

Three different categories of metals with regard to their potential groundwater pollution can be observed:

- element with high significant potential pollution such as Cd since it is sixfold increased over the normal concentration expected in soil;
- HM with moderate potential pollution such as Se, Mo, U with increasing level between 0.5 and 2 times;
- metals with little potential pollution such as Cr, Zn, Cu, As, V, Ni and B showing factors of a possible increase less than 0.5 times over the endogenous level of HM in soil.

DEVELOPMENT OF THE DOSE PREDICTION MODEL (SYSTEM ANALYSIS METHOD)

The predictions of the potential impact of HM fertilizers on groundwater as calculated from their total release to soil, are little realistic from the quantitative point of view because they do not consider losses of the system. In order to quantify the impact, a system analysis method of dose prediction was developed modelling mathematically the dynamic behaviour of HM in soil column compartmentalized conceptually into soil subsystems (Fig.1). The model of the soil column takes into account only the downward vertical flow while lateral losses or inputs are neglected. The column is one of the

TABLE 2 - Long-term effect on the level of heavy metals in soil due to the exogenous amounts released from fertilizer applications

	Average concentration in phosphorites (ppm)	Average endogenous[a] concentration in soil (ppm)	Amount released to[b] soil after 20 years of fertilizer application (ppm)	Increase of total endogenous concentration (%)
B	35	10	0.15	1.5
V	400	100	1.7	1.7
Cr	350	40	1.5	3.7
Mn	60	850	0.26	0.03
Ni	70	40	0.3	0.75
Cu	100	20	0.4	2.15
Zn	400	50	1.7	3.4
As	30	6	0.13	2.2
Se	22	0.2	0.09	45
Mo	80	2	0.34	17
Cd	80	0.06	0.34	570
U	340	0.8	1.45	180

[a] From Bowen

[b] At a rate of 1 ton/ha. Soil depth: 35 cm; soil density: 1.35 g/cm^3

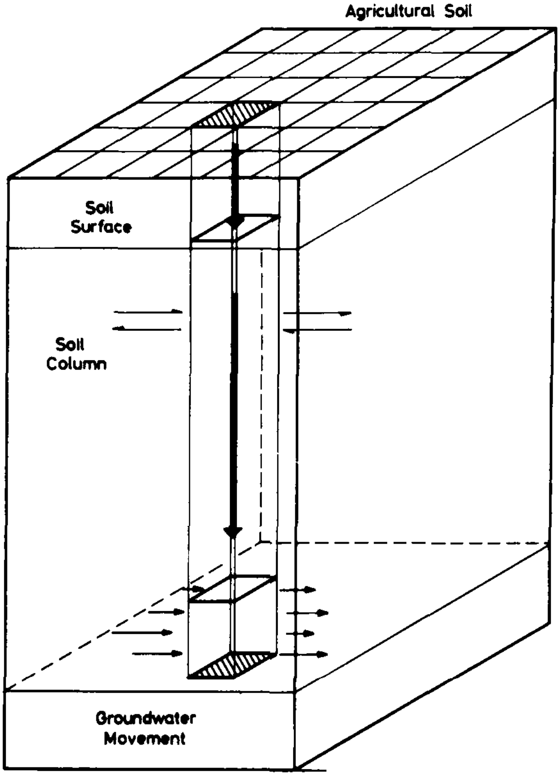

Fig. 1 - Soil column compartments

discrete elements of volume composing the soil matrix considered (Fig.2).

The dynamic variation of the quantity q(mg) of the element considered is given for each level by solving the following linear system equation:

$$
\begin{aligned}
q_s &= I_s + q_1 K_{1s} + q_3 (K_{3s} + K_{3Ms}) - q_s (K_{s1} + Kw) \\
q_1 &= I_F + q_s K_{s1} - q_1 (K_{12} + K_{1v}) \\
q_2 &= q_1 K_{12} - q_2 K_{23} \\
q_3 &= I_3 + q_2 K_{23} - q_3 (K_3 + K_{3s} + K_{3Ms} + K_{3M} + K_{3c})
\end{aligned}
\qquad (1)
$$

where I and K are the inputs and the intercompartmental rate constants of the system (Fig.1) respectively. The most important paedological rate constant have been calculated by the following equation:

$$V_i = W_w/1 + [(1 - p/p)\ \rho\ Kd_i] \qquad (2)$$

where V_i is the ionic migration velocity of the metal i in soil, W_w is the pore water velocity, ρ is the soil bulk density, p is the soil porosity and Kd_i is the distribution coefficient of element i between solid and liquid phase of soil. When Kd_i values are not known, but are available, the pedological half-times $T_{i\frac{1}{2}}$ (ref.8-9), the rate constants can be calculated as follows: $K_i = 0.693/T_{i\frac{1}{2}}$ (years^{-1}) thus is the reciprocal of the residence time in soil considered. The same approach has been used to calculate the other rate constants such as surface soil erosion and losses from groundwater due to its spontaneous movements, to irrigate or pumped as drinking water for man.

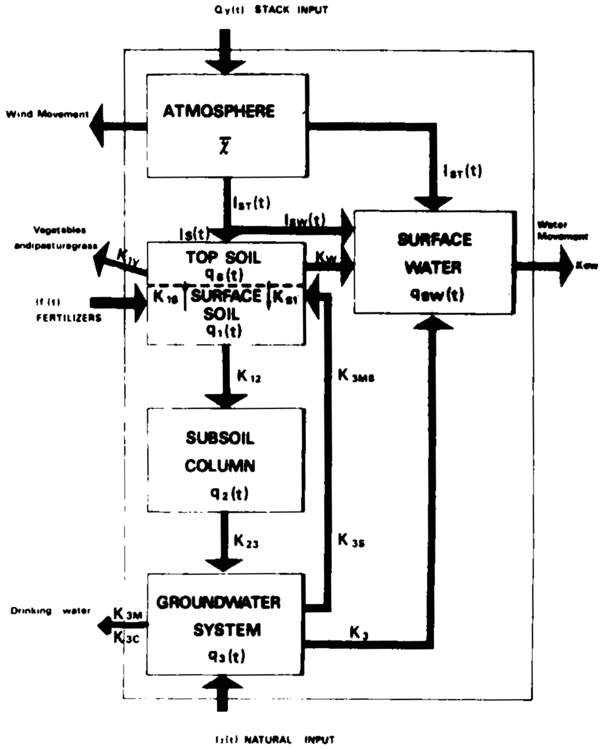

Fig. 2 - Flow of contaminant through soil column considered

The metal quantity present in the soil is able to be adsorbed by vegetables through roots. The corresponding rate constant K_{1V} (mg) during one year of agricultural practice:

$$q_{i,v} = q_{i,1}\ CR\ BIV/v_1 \rho_1\ 10^6 \qquad (3)$$

where $q_{i,1}$ is the quantity (mg) of element i in the soil surface, CR is the soil-vegetable concentration ratio, BIV is the quantity of vegetables produced per year (g/m^2 wet weight), V_1 and ρ_1 are the volume (m^3) and density (g/cm^3) of the soil compartment, while 10^6 is the conversion constant (m^3 to cm^3).

The assumption that the dissolved material in the water is in equilibrium with the material adsorbed by the soil matrix is expressed by the linear equation of the Kd_i:

$$f_{i,s} = Kd_i\ S/Kd_i\ S + 1 \qquad (4)$$

where $f_{i,s}$ is the fraction adsorbed on solid phase and $S = M/v$, where M and V are the mass of solid phase and volume of liquid phase respectively. The effective HM concentration, $C_{i,3}(t)$, in groundwater was calculated as follows:

$$C_{i,3}(t) = \frac{q_{i,3}(t)\ (1 - f_s)}{V_3 p_3} \qquad (5)$$

where $q_{i,3}$ (mg) is calculated by system equation 1, V_3 is the total volume of groundwater compartment (ℓ) and p_3 is the porosity of the material composing groundwater system.

THE IMPACT OF Cd ON GROUNDWATER AS PREDICTED BY THE SYSTEM ANALYSIS METHOD

The system analysis method has been applied to predict the time-dependent concentration of Cd in groundwater as a result of long term fertilizer application. The hypothetical reference case considered the use of 1 ton/ha/y of a fertilizer containing 80 ppm of Cd. The other input parameters have been previously reported (ref.2).

Fig. 3 shows the long term effect of Cd fertilizer on groundwater quality as a result of the computer implementation of the model in comparison to its present level (0.0007 ppm) (ref.10) and the maximum permissible level (MPC) adopted by the EC (0.005 ppm).

The following conclusions can be drawn:

i) a fraction of the total Cd released to soil is able to migrate through the soil to groundwater;

ii) the value of the normal concentration of Cd of the groundwater increases after 36 - 40 years to

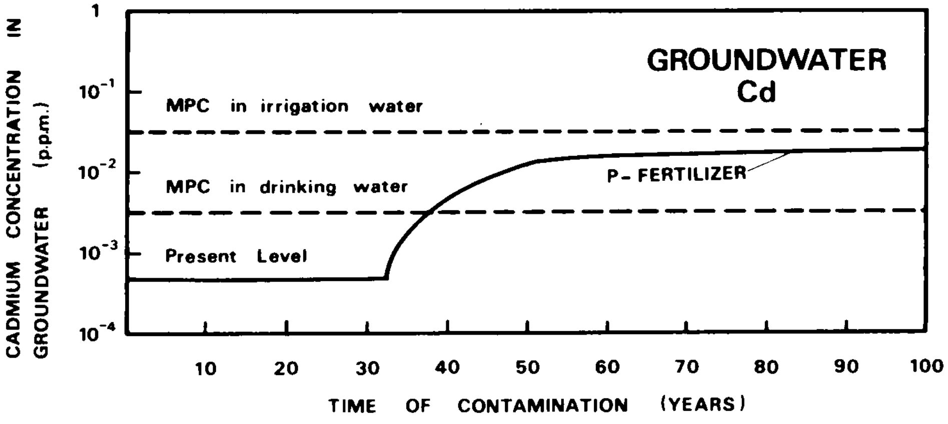

Fig. 3 - Impact of Cd on groundwater quality as a result of fertilizer use

that of the proposed MPC in drinking water (5 μg/ℓ). The same conclusion is valid when the water should be used for long term irrigation in aquifer layer was assumed;

iii) the concentration of Cd in soil over 20 years of fertilizer application increases with a factor 1.2 when predicted by the system analysis method in comparison to the sixfold increase as calculated under "static conditions" (Table 3).

TABLE 3 - Percent Cd increase over total average endogenous concentration in soil*

Time (years)	Percent increase	
	Static condition	by dynamical model
5	142.5	74
10	285	108
15	427.5	119
20	570	122

* soil depth: 35 cm; soil density: 1.35 g/cm^3

NEEDS FOR FURTHER RESEARCH

The use of the sequential path approach to assess the impact of HM-fertilizers on groundwater indicates how many areas of technical weakness are uncovered. For a more sound scientific assessment some research needs to be identified:

- better knowledge of the concentration of HM as well as their characterization as to chemical form in commercial phosphatic fertilizers is required;
- particular and urgent attention should be given to the determination of the distribution coefficients between soil organic matter and soil column components and the pedological half life for different HM because these parameters govern the mobility in soil;
- the fraction of HM released to soil and leaving the system requires delineation;
- in field studies should be conducted to validate the model;
- the influence of the different types of fertilizer on the mobility of HM in soil should also be evaluated.

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