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SLUDGE DISPOSAL IN COASTAL WATERS
Desorption of heavy metals from sewage sludge in seawater

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ABSTRACT

A basic prerequisite for the mathematical simulation of the physical dispersal of sewage sludge in coastal waters is the knowledge of the rate of desorption of heavy metals from the sludge, and the partition between the dissolved and adsorbed states in equilibrium conditions.

Results of experiments, carried out by Rohatgi and Chen (1975) on the desorption of heavy metals from digested sewage sludge particles after dilution by seawater over a period of 36 days, were analysed to determine the equilibrium partition coefficients and desorption rate constants for cadmium, zinc, copper, nickel, manganese and lead. The conditions in the early stages of the experiments are considered to approximate to conditions at sludge disposal sites in UK waters.

It was found that about 20% of the Cadmium and about 50% of the Lead dissociated itself from the sludge almost immediately once it was diluted with seawater. This initial release is probably explained by the fact that these particular metals were already partially dissolved in the water, which accounts for about 95% by weight of the sludge. About 8% of the dry weight of the sludge appeared to oxidise and lose mass within the first hour of dilution. The remaining 92% of the digested sludge appeared to be oxidised and lose mass at a rate of about 0.001 day^{-1}.

Representative values of the equilibrium partition coefficients varied from $30x10^{-4}$ for cadmium to $0.1x10^{-4}$ for copper. The experimental rates of desorption had values in the range 0.1 day^{-1} to 0.4 day^{-1} for most of the metals except for the residual fraction of the adsorbed cadmium which desorbed at a much lower rate of 0.02 day^{-1} and lead which desorbed at a very high rate of at least 10 day^{-1}.

The equilibrium partition coefficients and rate constants are considered to be accurate enough for modelling purposes. However, they should be verified by more recent experiments.

CONTENTS

1 INTRODUCTION

The physico-chemical processes of adsorption and desorption of metals to and from clay and organic particles have been defined algebraically in terms of an equilibrium theory and an equilibrium partition coefficient. The theory takes desorption into account by introducing the concept of a desorption rate constant.

Experimental observations of the desorption of heavy metals from digested sewage sludge particles after dilution with seawater made by Rohatgi and Chen (1975) (Ref 2) were anlaysed to determine the equilibrium partition coefficients and desorption rate constants, which could be used in a mathematical model.

In this analysis all concentrations are quoted in a dimensionless form of mass per unit mass unless otherwise defined. For practical purposes seawater is assumed to have a density of 1 tonne/m^3.

2 EQUILIBRIUM THEORY

The equilibrium theory is based on the assumption that the equilibrium concentration of dissolved metal is directly proportional to the concentration of metals per unit surface area of the clay or organic particles. This condition can be defined algebraically as follows.

Consider a volume of water where:-

C_m is the mass of particles in suspension per unit mass of water

α is the specific surface area of the particles (m^2/kg)

C_a is the mass of adsorbed metals per unit mass of water

It follows that the concentration of adsorbed metals per unit surface area is:-

$$\frac{C_a}{\alpha C_m} \ (kg/m^2)$$

Assume that the equilibrium mass of dissolved metal per unit mass of water, C_{de}, is a constant proportion, β, of the mass of adsorbed metal per unit surface area so

$$C_{de} = \frac{\beta C_a}{\alpha C_m} = \frac{\beta}{\alpha} C_{am} \qquad (1)$$

where

$$C_{am} = \frac{C_a}{C_m}$$

β is a constant for a given metal for specified conditions (kg/m^2)

C_{am} is the mass of adsorbed metal per unit mass of suspended particulate matter

Let $K_e = \beta/\alpha$ be a dimensionless equilibrium partition coefficient

so $C_{de} = K_e \ C_{am}$

Laboratory experiments indicate that such an equilibrium exists (Ref 2 and Ref 3). Although the value of K_e may be affected by the type of particle, temperature, the behaviour of different chemical and biochemical forms of the metal, the presence of other metals and other conditions.

3 DESORPTION

In reality it takes time to reach equilibrium following the inital dilution of sewage sludge in seawater.

Thus; if locally,

$$C_d < C_{de}$$

where

C_d is the mass of dissolved metals per unit mass of water

one would expect the metals to tend to dissolve at a rate dependent on the deviation of the dissolved concentration from its equilibrium value, so that

$$\frac{dC_d}{dt} = K_d (K_e C_{am} - C_d) \qquad (2)$$

where

K_d is the rate constant (t^{-1}) for the process of desorption

Experiments by Rohatgi and Chen (1975) performed at 15°C using digested sewage sludge diluted with oxygenated seawater (salinity approximately 35ppt), were considered to approximate to conditions at sludge disposal sites in UK Coastal Waters, where desorption takes place.

4 PROPERTIES OF SEWAGE SLUDGE

British sludge (Ref 4) has only about 4.5% solids, 30% of which is inorganic matter such as phosphates. The other 70% is organic matter, which readily adsorbs

heavy metals. Part of the organic matter is rapidly oxidised at a rate of about 0.2 day $^{-1}$ at 20°C. The remaining organic matter, which is mainly cellulose, is oxidised at a very much slower rate of about 0.004 day $^{-1}$ at 20°C (Ref 4). The two fractions may adsorb and desorb different quantities of metals.

The observed concentration of heavy metals adsorbed onto sewage sludge for Manchester (1974 to 1977) (Ref 5) and that used in the experiments by Rohatgi and Chen (Ref 2) are as follows:

Concentrations of heavy metals adsorbed on sewage sludge (ppm dry weight)

Metal	Sewage sludge*	California sludge**
Zinc	3500	3500
Copper	2000	2500
Chromium	1500	-
Lead	1000	150
Cadmium	50	200
Mercury	50	-

* Average value for Manchester sludge 1974-1977 Appendix I LBWG (78)4, Sludge disposal data, P C Head (MAFF 1982).

** Representative values of sewage sludge used in lab. experiments by Rohatgi and Chen (Ref 2)

The metal concentrations in UK sludges have decreased dramatically since 1977.

5 EXPERIMENTAL METHODS

Equilibrium partition coefficients and desorption rate constants for several heavy metals were evaluated, using the results of laboratory experiments undertaken by Rohatgi and Chen (1975) which were specifically designed to determine the extent to which heavy metals are released from sewage sludge particles upon dilution with seawater.

Samples of digested sewage sludge were diluted with seawater (salinity approximately 35ppt) at varying dilutions (1:100, 1:200, 1:50) and mixed at a constant rate and temperature of 15°C. Aerobic conditions were maintained throughout (dissolved oxygen 6-8 ppm). Periodic samples over 36 days were analysed for metals content in the liquid and solid fractions. An example of results for cadmium is shown in Figure 1. Data was availabe for the following metals: zinc, copper, lead, nickel and manganese.

The release of heavy metals was observed to occur in two stages: an inital very rapid release, followed by a much slower, long term release. The desorption was attributed to the following:

- oxidisation of organic matter or metal sulfides
- desorption from suspended solids - due to dilution ratio and seawater pH.
- complexation of metals to form soluble complexes of both inorganic and organic ligands.

The percentage of heavy metals released after 1 hour and 36 days are given in Table 1. A significant proportion, (20%) of the cadmium and 50% of the lead was observed to desorb within one hour, while the other metals were released at a slower rate.

The loss of mass of solid organic matter by oxidation will contribute to the apparent rate of desorption. The oxidation rates of the particulate matter as determined by loss of mass for the afore mentioned experiments are listed in Table 2.

The very high initial rate of about 2 day $^{-1}$ is ten times higher than would be expected for a UK sludge. On the other hand the long term rate of oxidation of the Californian sludge is about four times slower than that reported for UK sludge. However, the rate of desorption of cadmium and lead in the first hour is not accounted for by these high rates of oxidation. A significant part of the initial desorption is probably accounted for by dilution of metal laden anerobic non-saline water associated with the sludge particles.

After the sludge had been diluted with aerobic seawater it re-adsorbed part of the initial release of land.

6 EQUILIBRIUM PARTITION COEFFICIENTS

Equation 1 identifies the relationship between the equilibrium mass of dissolved metal per unit volume of water, and the mass of adsorbed metal per unit mass of suspended particulate matter.

The assumption has been made that the specific surface area of particles of digested sewage sludge used experimentally in Ref 2 is similar to that of UK sewage sludge.

Rohatgi and Chen's experimental results were used to estimate equilibrium partition coefficients for Cd, Zn, Cu, Ni, Mn and Pb, which are listed in Table 3.

The graphical method is illustrated in Fig 2. The more soluble the metal the higher the value of the partition coefficient. If the equilibrium theory were exact three experimental points for dilution of 1:50, 1:100 and 1:200 should sit on a straight line. In fact there was a tendency with most metals for the equilibrium partition coefficient to decrease with increasing dilution.

In reality, the disposal of sewage sludge in the open sea produces much higher dilutions than those in the experiments. Therefore, one should expect the actual equilibrium partition coefficient to be at the lower end of the experimental range (Table 3).

7 DESORPTION RATE CONSTANTS

Equation 2 - representing unsteady conditions that promote desorption, has been used to calculate K_d (day^{-1}) (desorption rate constants) values for the various heavy metals.

The exponential decay of organic matter has been considered when calculating Cam (the mass of adsorbed metal per unit mass of suspended particulate matter).

The rate of change of the dissolved concentration has been calculated at various intervals throughout the experiment, along with the deviation of this dissolved concentration from its theortical equilibrium value based on the relevent equilibrium partition coefficient for each experiment. Several K_d values were then calculated at varying time intervals - for both the 1:100 and 1:200 dilutions. Table 3 lists the range of K_d values for each metal analysed; there was a tendency for the desorption rate constants to increase with increasing dilution.

8 DISCUSSION AND CONCLUSIONS

The experiments by Rohatgi and Chen (Ref 2, 1975) into the desorption of heavy metals from digested sewage sludge diluted with aerobic seawater are considered to approximate to conditions at sludge disposal sites in the UK waters. The main differences appear to be the initial dilution of the sludge and the ultimate concentration of the dissolved metals at the end of the experiments, which were up to fifty times greater than the concentration of heavy metals in the waters of Liverpool Bay, for example (Ref 6).

Concentration of dissolved metals in Liverpool Bay (ppb)
(ppb = ppm/1000 dry weight)

Zn	Cu	Cr	Pb	Cd	Hg
20	2	1	2	0.2	0.1

However, the conditions for the desorption of heavy metals in the early and middle stages of the experiments were considered to approximate to conditions at sludge disposal sites in UK waters.

The experiments showed that one can expect about 20% of the cadmium and 50% of the lead in the sewage sludge to desorb almost immediately after the sewage sludge is discharged into the sea. This sudden release is probably explained by the fact that those metals were already partially dissolved in the anaerobic water associated with the sewage sludge. After the sludge had been diluted with aerobic seawater it re-adsorbed part of the initial release of lead. The residual fraction of adsorbed cadmium desorbed at a much slower rate ($0.02\ day^{-1}$) than the other apparently less soluble metals.

About 8% of the sludge appeared to oxidise and lose mass in the first hour. The remaining slowly decaying

fraction of the digested sewage sludge, which was probably mainly cellulose, appeared to oxidise and lose mass at a rate of about 0.001 day $^{-1}$.

In the case of a raw sewage rather than a sewage sludge discharge one might expect an oxidation rate and consequent loss of mass near to 0.2 day $^{-1}$, which would effectively double the observed rates of desorption, which were in the range 0.1 to 0.4 day^{-1}.

The analysis provided estimates for the equilibrium partition coefficients, K_e, and the long term desorption rates, K_d, for cadmium, zinc, copper, nickel, manganese, and lead, over a period of 36 days. (Table 3)

The equilibrium partition coefficients tended to decrease with increasing dilution. On the other hand the desorption rates tended to increase, with increasing dilution.

In reality, the disposal of sewage sludge in the open sea produces much higher dilutions than those achieved in the experiments. Therefore, one should expect the actual equilibrium partition coefficients and desorption rate constants to be at the lower and upper end of the respective experimental ranges given in Table 3.

The analysis of Rohatgi and Chen's experimental results indicates that representative values for the equilibrium partition coefficient and the long term desorption rates for sewage sludge diluted with aerobic seawater at 15°C all as follows.

	K_e Equilibrium partition coefficient	K_d Desorption rate constant (day^{-1})
Cadmium	30×10^{-4}	0.02
Zinc	1×10^{-4}	0.2
Copper	0.1×10^{-4}	0.15
Nickel	2×10^{-4}	0.1
Manganese	1×10^{-4}	0.4
Lead	1×10^{-4}	≈10

Lead appears to desorb and reach equilibrium very rapidly, and a value of 10 day^{-1} is recommended for the desorption rate constant for this metal. The above values are concluded to be accurate enough for modelling purposes. However, they should be verified by more recent experiments.

9 REFERENCES

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TABLES

Table 1 Percentage of heavy metals desorbed from sewage sludge in seawater at fast and slow rates

Metal	% Trace metals released after 1 hour		% Trace metals released after 36 days	
	1:100 dilution	1:200 dilution	1:100 dilution	1:200 dilution
CADMIUM	37.2	20.5	95.0	96.0
ZINC	9.8	14.5	24.4	38.7
COPPER	3.3	7.1	5.6	9.0
NICKEL	2.5	10.9	58.0	64.0
MANAGANESE	4.5	7.7	34.7	35.7
LEAD	45.1	53.1	35.4	35.4

Source:- Rohatgi + Chen (1975) (Ref 2)

Table 2 Oxidation rates of digested sewage sludge

	Diluted with seawater 1:100 at 15°C	Diluted with seawater 1:200 at 15°C	Sewage sludge at 20°C
	(day^{-1})	(day^{-1})	(day^{-1})
Fast rate	1.84	1.6	0.2
Slow rate	0.0011	0.0013	0.004

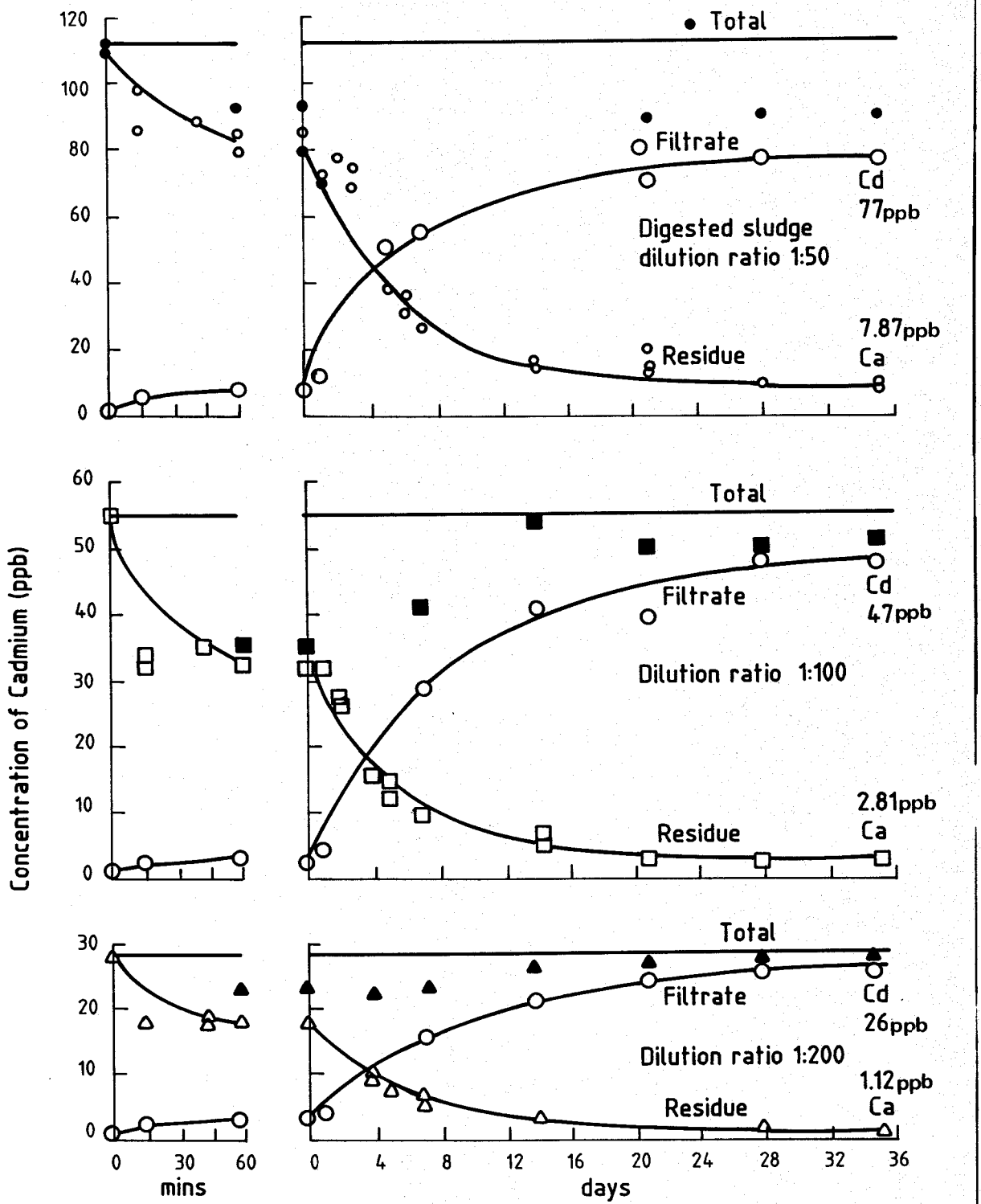
Table 3 Heavy metal equilibrium patition coefficients and desorption rate constants for sewage sludge in seawater

Metal	Dissolved metal range	Adsorbed metal range	Equilibrium partition coefficient	Desorption rate constant K_d (day^{-1})	
				1:100 dilution	1:200 dilution
	C_d (ppb)	C_{am} (ppm)	K_e		
CADIMUM	0-47	220-9	$3.9 \pm 1.0 \times 10^{-3}$	0.012 - 0.032	0.0062 - 0.015
*	0-4	218-140	-	0.27 - 0.97	0.11 - 0.67
ZINC	0-352	4333-2800	$1.0 \pm 0.2 \times 10^{-4}$	0.15 - 0.19	0.17 - 0.25
COPPER	0-40	2627-2419	$1.6 \pm 0.7 \times 10^{-5}$	0.05 - 0.13	0.09 - 0.19
NICKEL	0-93	580-228	$3.6 \pm 1.0 \times 10^{-4}$	0.045 - 0.086	0.08 - 0.12
MANGANESE	0-10	17-12	$1.6 \pm 0.9 \times 10^{-4}$	0.19 - 0.42	0.19 - 0.79
LEAD *	0-90	140-90	$1.4 \pm 1.0 \times 10^{-4}$	216.0	346.0

* Initial phase

Note:- Constant Temp 15°C
Constant salinity 35 ppt
Constant DO - always aerobic
36 day test

FIGURES



Source : Rohatgi and Chen (1975)

Notes : Temp - 15°
Salinity - 35 ppt
Cd = Equilibrium conc. of dissolved metal(ppb)
Ca = Conc. of adsorbed metal(ppb)

Fig 1 Distribution of Cadmium in solid and solution phases of digested sewage sludge in seawater

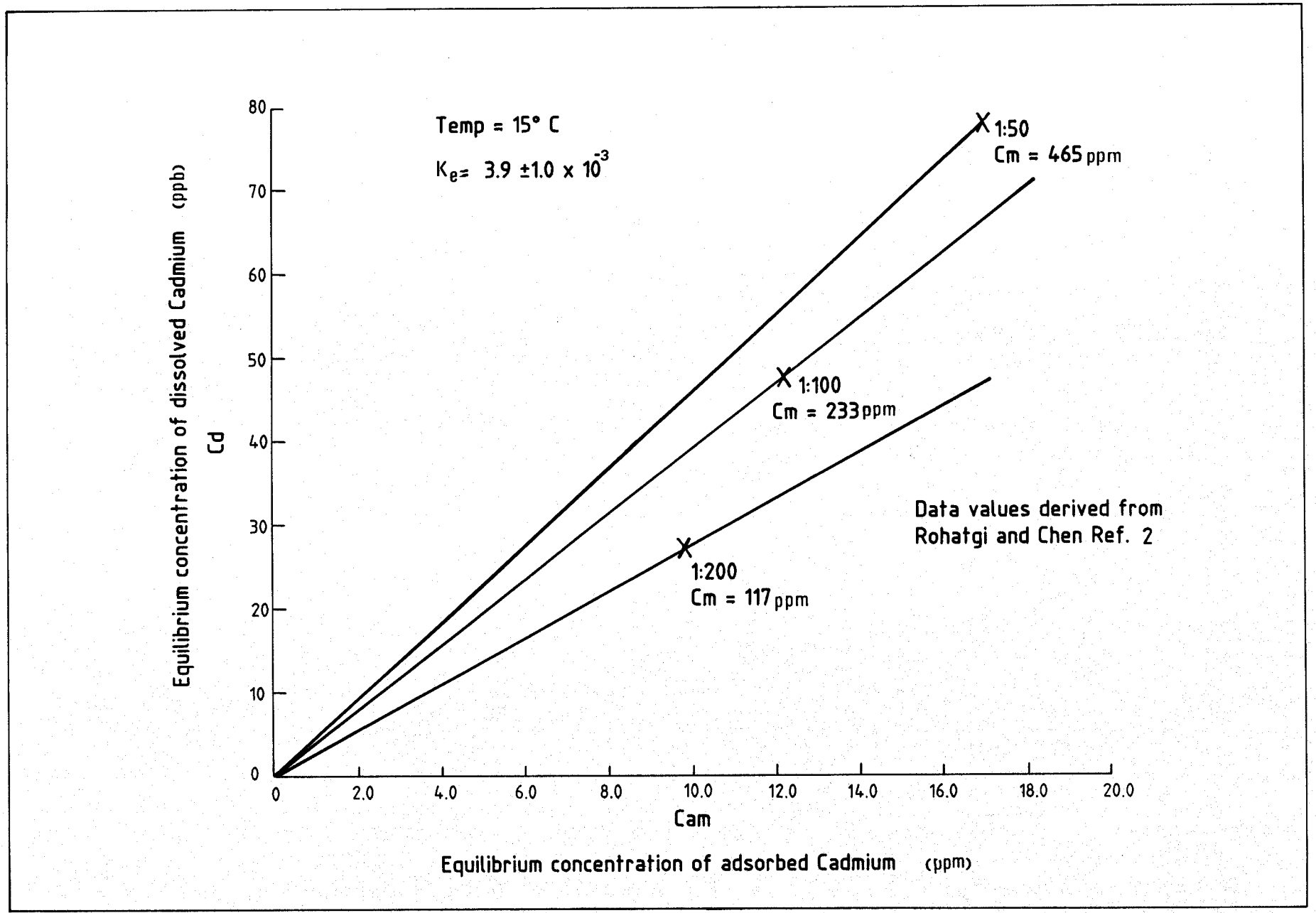


Fig 2 Adsorption of Cadmium on suspended digested sewage sludge in seawater