MOBILITY OF IRON IN THE ESTUARIES
OF THE RHINE AND THE EMS
RELEVANT TO PLANT-AVAILABILITY PROBLEMS

by R. BOXMA

Institute for Soil Fertility, Haren (Gr.), the Netherlands

ABSTRACT

   Studies were undertaken to obtain information on the iron mobilization processes in the sediments of the rivers Rhine and Ems, both located in western Europe. On their way from the fresh-water tidal area to the marine environment these sediments loose a considerable amount of their iron. The iron is released from the sediment by means of biodegradation products of the organic matter which dissolve the iron as organic iron complexes. The major functional groups of these organic compounds responsible for the iron mobilization are carboxyls and phenolic hydroxyls. From the sediments of the river Ems greater amounts of organic iron compounds are dissolved than from sediments of the river Rhine. Also fewer organic compounds are released from marine sediments than from fresh-water sediments, which indicates a diminished iron mobility in the marine area of the delta. Besides this the organic compounds from the marine sediments show an impoverishment in their functional groups. The sediments of the rivers Rhine and Ems are also distinguished by a different occupation of functional groups in the organic compounds. On account of a number of experiments the mobilization capacity of these river systems have been discussed.

   From a viewpoint of plant nutrition the mobility of iron in deposits of different ripening stages was also investigated.

INTRODUCTION

   During the movement of the sediments on their way from the rivers through the deltas to the coastal areas the sediments can undergo losses in their contents of metals, consequent on the mobilization of these elements as soluble metal compounds[5].

   Much information about the mobilization of a number of metals has been obtained by de Groot[5], who studied the changes of the total metal contents in the sediments depending on the location of deposition during the passage of the sediments to the lower courses

of the delta and the coastal areas. However, little attention has been paid to direct determinations of mobile metal fractions in sediments.

The heavy metals in the sediment are distributed over various chemical compounds and minerals (elemental partition). The metals of the lithogeneous fraction, which are incorporated in the crystal lattice of the minerals are, in general, immobile during the transport of the sediment.

The heavy metals which are not present in the lithogeneous fraction are associated with the organic matter, the hydrous manganese and iron oxides and/or occur as discrete inorganic metal compounds. The metals in these fractions are more or less mobile and can be released to the overlying water. To determine the elemental partition selective extraction procedures must be developed. From studies on availability of metals in soils to plants it is well known that the contents of available metal forms depend on the extraction procedure used and show a great variety. These values represent no absolute contents of special metal forms because a shaking procedure is founded on the establishment of a dynamic equilibrium between soil and extractant, often depending on covering soil factors.

However, differentiation of metal forms, based on different chemical reactivity with extractants, can give valuable informations in soil and sediment studies. We must realize in this respect that the contents obtained are relative values.

From a review presented by Mortensen[8] it appears to be well established that iron is made mobile in soils by its interaction with the organic matter. When it became apparent that chelation played an important role in the mobilization of iron, chelating agents able to compete with the organic matter were used as extractants for mobile iron in soils. For assessing the mobility of iron and other metals in acid soils Rauterberg[10] used EDTA as an extractant. Since at high pH competition effects of Ca^{2+} and OH^- ions decrease greatly the chelating capacity of EDTA for iron, this chelate is not a suitable extractant for mobile iron in river sediments and calcareous clay soils. Also methods involving the use of acid solutions of citrate, oxalate or acetate are unsatisfactory, because immobile forms of iron may be dissolved by these acid extractants.

On account of these considerations it is clear that the chelating agent ethylenediamine di(o-hydroxyphenylacetic acid) (EDDHA)

with a low affinity for calcium and a high affinity for iron at high pH-values offers the best perspective for extracting mobile iron from river sediments and calcareous clay soils. Also the fact that EDDHA can function simultaneously as a colorimetric reagent for iron makes it attractive to use EDDHA for the analysis of mobile iron. The aim of this investigation was to study the mobility of iron in river sediments during their way from the river to the sea and to give some experimental background on the chemical compounds which are responsible for iron mobilization. From a viewpoint of availability for plant nutrition the iron status of old and young cultivated soils, as well as of flood plains derived from river deposits, was also involved in this study.

METHODS

a. Determination of mobile iron in sediments and calcareous soils

In extracting arable soils with reagents of increasing concentration it is possible to dissolve increasing quantities of the elements present in a certain range of chemical forms. Although a high concentration of EDDHA dissolves much more iron than a low concentration the relative differences in characterizing the iron availability among the soils are greater in the range of lower concentration of the reagent [14]. Therefore a low concentration of $2.5 \times 10^{-4} M$ EDDHA was chosen as an extractant for our routine analysis of mobile iron in sediments and calcareous soils.

To adapt the extraction solution to the pH of the sediments and soils, the pH of the EDDHA solution was adjusted to 7.5 with 0.1 N KOH solution. In 1958 Underwood [12] described a method for the spectrophotometric determination of iron with EDDHA, using the intensity of the red-coloured chelate Fe-EDDHA. Later studies [13] indicated that foreign metals did not interfere with this reaction and that solutions of Fe-EDDHA followed Beer's Law over a pH range from 3 to 9.

The effect of the shaking time on the extraction of mobile iron was investigated for four calcareous soils, differing in their iron availability for crops and in their status of available iron. Samples of 2 g of dry soils were shaken with 100 ml of a $2.5 \times 10^{-4} M$ EDDHA solution for $\frac{1}{4}$, $\frac{1}{2}$, 1, 2, 3 and 4 hours on a mechanical shaker. Then the suspensions were passed through a folding filter (Macherey, Nagel & Co no. 619 eh $\frac{1}{4}$). After having removed the first 10 ml of the filtrate the absorbance was measured against a blank of the EDDHA solution at 485 nm.

Dependant on the relevant soils, highly different levels of mobile iron were found. Carrying out the extraction procedure with one type of soil, however, the amounts of extractable Fe were similar during shaking times from $\frac{1}{2}$ to 4 hours. By using shaking times of $\frac{1}{4}$ hour, the amounts of extracted Fe were

somewhat lower. Since a rapid analysis is desirable and apparently no loss of accuracy would result, half an hour shaking time was adopted for our work.

For testing the direct spectrophotometric measurement of iron in EDDHA extracts from soils, this method was controlled by the o-phenanthroline method. For this purpose the EDDHA extracts were digested with sulfuric acid and perchloric acid and the iron contents were determined according to Van Driel[2] using o-phenanthroline.

Table 1 shows for a number of EDDHA extracts that a good agreement has been found for both methods.

TABLE 1

Comparison of the spectrophotometric measurement of Fe-EDDHA with the O-phenanthroline method in determining the iron contents (ppm Fe) in EDDHA-soil extracts

Location of the soil sample	Fe EDDHA measurement	O-phenanthroline method
's-Gravenpolder	38	38
Steenbergen	17	18
Yerseke	75	73
Tholen	51	51
Hoofddorp	147	144

b. *Solubilization and fractionation of the mobile iron compounds from sediments of the aquatic environment*

The very slow rate at which in nature iron compounds are dissolved from sediments into the surrounding water, makes adequate laboratory studies extremely difficult. In soil chemistry sodiumpyrophosphate and particularly NaOH are popular extractants for organic iron compounds from soils, but decarboxylation, hydrolysis and oxidation, involved in their use, produce many artifacts and alter the properties of the extracted material. Therefore these methods are not admissible for the characterization of the organic iron compounds in sediments because almost all information on the originally natural structure of the mobile iron compounds is lost. With the intention to adopt the solubilization process as much as possible to the natural conditions, the following method has been developed. A 10-kg sample of fresh sediments, mixed with 10 l of the surrounding river water, was kept in a closed black polyethylene bottle during two weeks at 20°C. Every day the bottle was opened for some minutes and the suspension was stirred, promoting the dissolution of the organic iron compounds and preventing the development of a very low redox potential. In spite of the high pH of the water (pH 8) a part of the mobile iron dissolved under these mildly reducing conditions. Then the suspension was filtered on a Büchner funnel and the filtrate evaporated by heating at 35°C under reduced pressure. Based on solubility characteristics the extractable organic matter from soils is generally separated into three fractions: fulvic acid fraction, which is alkali and acid soluble; humic acid

fraction, alkali soluble and acid insoluble; and humin fraction, insoluble in both alkali and acid. Analogous to this separation the residue after evaporating the filtrate was extracted with 0.1 N H_2SO_4 and after centrifuging the fulvic acid fraction was poured off and filtered. After washing the remaining residue with water, extraction with 0.1 N NaOH was carried out and the humic acid fraction was obtained in the same way by centrifuging and filtration of the supernatant. The insoluble part, that cannot be dissolved by dilute acid and alkali, mainly consists of calcium sulphate. The fulvic acid and humic acid fractions were adjusted to pH 2.0 and 11.0, respectively, and used for characterizing the organic compounds. Carbon was determined in the extracts by a wet oxidation procedure according to Kurmisch[7].

The major oxygen containing functional groups responsible for metal chelation in organic substances are carboxyls and phenolic hydroxyls. Carboxyls were estimated in the fulvic acid fractions by potentiometric titration, using the inflection points corresponding to COOH- and phenolic OH-groups[11]. According to the method of Pauly[9] phenolic hydroxyls were determined with diazotized sulphanilic acid. Finally, the fulvic acid fractions were subjected to circular paper chromatography and paper electrophoresis and subsequently detected by means of specific sprays for iron, carboxyls and phenolic hydroxyls (solutions of o-phenanthroline and hydroxylamine, the indicator brom cresol green and a mixture of diazotized sulphanilic acid and Na_2CO_3, respectively).

MATERIALS

In the deltas of the rivers Rhine and Ems samples have been taken from the surface layers of the sediments, which were freshly deposited close to the low-water level. From each delta the samples were taken from both the inner part of the delta, where fresh-water conditions occur, and from the outer marine environment. All these samples were examined in the laboratory in the wet state. To determine the influence of soil ripening processes on iron mobility, more elevated parts as river flood plains and young embankments were also sampled. In both wet and dried samples mobile iron was determined.

To study the relation between chemical mobility and plant availability of the iron also soil samples of the layer 0–20 cm were collected from orchards on calcareous clay soils, representing a wide range in susceptibility to iron chlorosis. These samples were dried at 35°C, homogenized and passed through a 2-mm sieve.

RESULTS

a. Mobility of iron in the Rhine and Ems delta during the transport of the sediments by the streams

Before the execution of the Delta Plan the Rhine transported its sediments by way of the fresh-water tidal area Biesbosch via the Haringvliet into the North Sea and then they moved in a north-
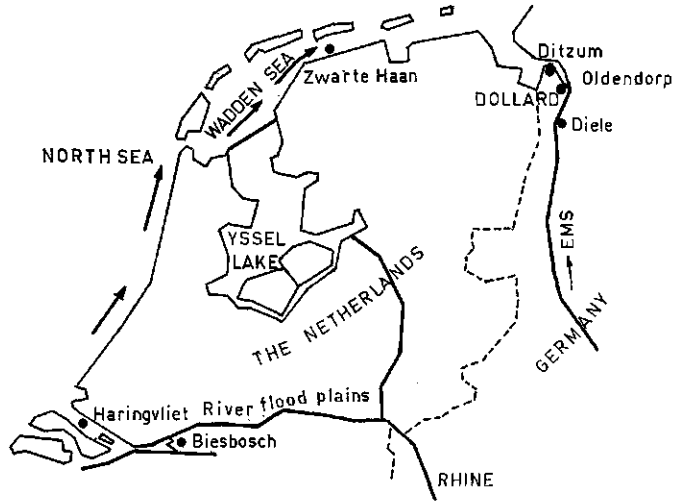
Fig. 1.   Movements of sediments originating from the rivers Rhine and Ems.

easterly direction along the coast into the Dutch Wadden Sea (Fig. 1). The Ems transports its sediments by way of the fresh-water tidal area near Diele to the Dollard[11]. From both rivers the mobile-iron contents in the sediments of the fresh-water tidal area and the marine area have been determined.

Table 2 demonstrates that the mobile iron contents decrease into the downstream direction of the delta, which indicates a diminishing mobility into the direction of the sea. Further, it is obvious that the

TABLE 2

Contents of the mobile iron in sediments from the Ems- and the Rhine delta (mean values of 10 samples per location)

Location	Mobile iron content (ppm)	Mobile iron in the sediment, expressed as a percentage of the total iron content
Ems		
Diele; fresh water sediment of the Ems	7820	17.0
Ditzum; sediment deposited in the brackish part of the Ems	459	1.7
Rhine		
Biesbosch; fresh water sediment of the Rhine	2150	5.1
Zwarte Haan; marine sediment of the Rhine	410	2.1

fresh water sediment of the river Ems contains more mobile iron than that of the Rhine.

The mobile-iron contents of the different locations are the mean values of a number of samples, which show a great variety in these contents. This is demonstrated in Table 3, where the mobile-iron content for a number of samples of one location has also been expressed as a percentage of the total iron content. The latter figures indicate which part of the total iron content of the sediment occurs in a mobile state. Probably the differences between the samples must be partly attributed to variations in the contents of the finest grain-size fractions of the sediments[1].

TABLE 3

Comparison between the mobile-iron content and the mobile iron expressed as a percentage of total iron, for a number of samples of one location

Location	Sample no.	Mobile iron (ppm)	Mobile iron expressed as a percentage of the total iron in the sediment
Oldendorp:	1	613	1.7
sediment deposited	2	526	1.6
in the brackish part	3	565	1.7
of the Ems	4	608	1.6
	5	417	1.4
	6	589	1.9
	7	473	2.0
	8	548	1.4

It is interesting to know what chemical forms of iron are extracted by EDDHA. Besides chelating properties EDDHA has a slightly reducing effect, which can be demonstrated by the discolouration of a redox dye like methylene blue. For this reason EDDHA can dissolve freshly precipitated iron oxides, but aged oxides are not attacked. In a separate investigation the dissolution of reactive iron oxides was prevented by the addition of a small quantity of H_2O_2 to the extractant. In that way it could be shown that about 20% of the mobile iron in the sediments of Diele was present as reactive iron oxides and about 80% was bound to the organic matter.

The presence of reactive iron oxides in the mobile iron fraction,

however, does not suggest that this part of the mobile iron leaves the sediments in the form of iron oxides during transportation. In all probability the fresh iron oxides are dissolved by degradation products of the organic matter like fulvic acids, which have also a reducing effect on reactive iron oxides even at high pH. Although the mobile-iron contents in question refer to insoluble iron compounds in the sediments, they are expected to reflect the contents of iron solubilizing into the surrounding river or sea water.

b. *Characterization of the soluble organic iron compounds*

According to the described method fulvic acid and humic acid fractions were isolated from the same locations as used for the analysis of mobile iron. The amounts of iron and organic C in the humic acid and fulvic acid fractions, which were extracted from 10 kg of sediment, are given in Tables 4 and 5. The contributions of the river

TABLE 4

Amounts of organic C and iron in the humic acid fractions, isolated from 10 kg of fresh-water and marine sediments of the rivers Ems and Rhine

Location	Organic C mg	Fe mg
Fresh-water sediment of the Ems	98	3.8
Sediment deposited in the brackish part of the Ems	38	0.4
Fresh-water sediment of the Rhine	80	2.0
Marine sediment of the Rhine	45	0.3

and sea water to the amounts of iron and organic C are very small and can be neglected. From these tables it is obvious that only very small amounts of the total contents of organic Fe are related with humic acids. Consequently the contribution of the humic acid fraction to the iron mobilization can be neglected. The results show, that the sediments after transport to the sea have lost a great deal of their mobile iron. In the fulvic acid fractions carboxyls and phenolic hydroxyls were determined. Phenolic hydroxyls were expressed in extinction units because the composition of the phenolic components in the extracts was unknown. The amounts of carboxyls and phenolic hydroxyls in the fulvic acid fractions show the same trend as the amounts of iron and organic C. From marine sediments much smaller quantities of organic compounds with carboxyl and phenolic hy-

TABLE 5

Amounts of organic C, iron, carboxyls and phenolic hydroxyls in the fulvic acid fractions, isolated from 10 kg of fresh-water and marine sediments of the rivers Ems and Rhine

Location	Organic C mg	Fe mg	COOH meq	Σ OH
Fresh-water sediment of the Ems	1380	622	27	143
Marine sediment of the Ems	770	20	4	50
Fresh-water sediment of the Rhine	750	290	20	31
Marine sediment of the Rhine	440	41	10	12

droxyl groups were dissolved than from fresh-water sediments. However, under marine conditions not only the quantities of organics are reduced, but also their occupation with carboxyl- and phenolic hydroxyl groups (Table 6). Finally a remarkable difference is noted between the sediments of the river Ems and those of the Rhine. By comparing the distribution of the functional groups it appears, that in the sediments of the Ems more phenolic hydroxyls are involved in iron mobilization than in the sediments of the Rhine, whereas the dissolved organic compounds of the Rhine sediments contain more carboxyls than those of the Ems.

Using salicylic acid as a standard in the analysis of phenolic hydroxyl groups the ratio of carboxyl to phenolic hydroxyl groups in the fulvic acid fraction from the fresh-water sediments of the Ems approaches the value of 3.

It is reasonable to assume that at the high pH of the sediments and the river water iron can only dissolve as organic iron complexes. This assumption was proved by subjecting the fulvic acid fractions to circular-paper chromatography and paper electrophoresis.

TABLE 6

Relative distribution of carboxyls and phenolic hydroxyls in the organic compounds of the fulvic acid fractions

Location	COOH/mg C meq	Σ OH/mg C
Fresh-water sediment of the Ems	0.020	0.104
Marine sediment of the Ems	0.005	0.065
Fresh-water sediment of the Rhine	0.027	0.041
Marine sediment of the Rhine	0.023	0.027

After drying the chromatogram, iron, carboxyls and phenolic hydroxyls were located on the same place on the chromatogram after spraying with solutions of specific colour reagents (solutions of o-phenanthroline and hydroxylamine; brom cresol green and a mixture of diazotized sulphanilic acid and Na_2CO_3 respectively). On the electrophoregrams iron moved together with phenolic hydroxyls and carboxyls with the same velocity to the anode. This means that iron is present as a chelated organic anion in the fulvic acid fractions.

However, these soluble organic iron compounds are converted into insoluble colloidal particles when they are exposed to the oxygenated river or sea water. This was demonstrated by aerating an extract, obtained by filtration of an anaerobic mud suspension. After an aeration period of half an hour approximately 98% of the iron in the extract has been precipitated, while 2% of the iron remains in solution.

The extraction by means of EDDHA dissolves much more iron from the sediments than the anaerobic solubilization process because the concentration of EDDHA is much higher than the concentration of the dissolved organic compounds. Therefore the EDDHA extraction will reflect the amount of mobile iron in the sediment. The solubilization process, however, refers in the first place to the amount of organic compounds formed by the decomposition of the organic matter in the sediment.

The ligands of the organic compounds in the fulvic acid fractions of fresh sediments are not able to bind more iron.

c. Influence of the stage of ripening on mobile-iron contents of sediments

In the Biesbosch transformations in sediments like loss of water and oxidation, summarized under the term 'ripening' may occur, when the sediments are deposited above the low-tide level of the river. After sedimentation has reached a height of 60 cm above the mean high-tide level the stage of the river flood plains with a characteristic vegetation begins. Further ripening processes take place after embankment of the river flood plains, by which procedure the usual arable soils are obtained (Fig. 2).

Table 7 shows that during the processes of ripening from deposited mud via river flood plains to arable land the mobile-iron contents undergo a sharp decrease. Also it is seen that drying of the samples at 35°C has a different effect on the mobile-iron contents. Whereas
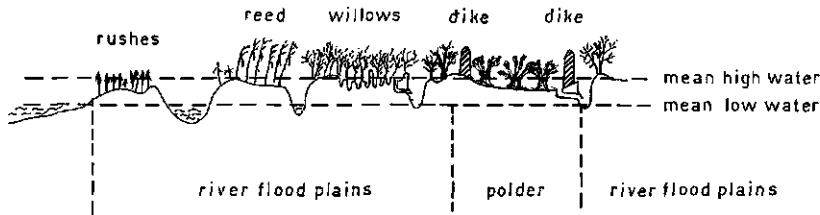
Fig. 2. The process of the accumulation of land in the Biesbosch.

TABLE 7

Effect of drying at 35°C on the mobile iron
contents (ppm Fe) of sediments, river flood
plains and arable lands in the Rhine delta

Ripening stage	Wet soil	Dried soil
Fresh mud no. 1	1976	305
2	1868	268
3	2280	353
4	2463	381
Flood plain no. 1	1140	134
2	1075	118
3	854	109
4	1179	234
Arable land no. 1	23	25
2	21	24
3	73	85
4	84	89

the mobile-iron contents of the arable lands are hardly influenced by drying, the mobile-iron contents of freshly deposited mud and river flood plains decrease to about 15% of the values in the originally wet state.

The consequences of this phenomenon with respect to the iron supply of plants have been demonstrated in a pot experiment with spinach. The plants were grown on three calcareous soil types from the Biesbosch: – an old cultivated soil, a young cultivated soil and a river flood-plain soil. Before planting, the soils were made air-dry, which results in a rapid fall of the mobile iron contents of the young cultivated soil and of the flood plain soil. The plants only received just sufficient water as needed for a healthy growth, so that the mobile-iron contents remained low and also a high bicarbonate con-

TABLE 8

Effect of drying on mobile iron in different stages of ripening in Biesbosch soils with regard to the iron supply of spinach plants

Ripening stage	Organic matter (%)	Mobile-iron content in wet condition (field condition) (ppm)	Mobile-iron content in dry condition (condition of the pot experiment) (ppm)	Degree of iron chlorosis in spinach plants
Flood plain soil	14.2	356	37	Moderate
Young cultivated soil	5.9	116	22	Mild
Old cultivated soil	1.7	15	16	Healthy

tent was prevented (high bicarbonate concentrations can prevent the uptake of iron by plants). The results of this experiment are shown in Table 8. Notwithstanding that even after drying the mobile iron contents of the flood-plain soil and the young cultivated soil are still higher than the mobile iron content of the old cultivated soil, these soils induce iron chlorosis. A possible explanation of this phenomenon may be given by the role of the organic matter in the iron uptake by plants. Both roots and ligands of the organic matter compete for the mobile iron. The drying process causes a drastic fall of the mobile-iron contents, but the contents of the organic matter remain unaltered. Probably the occurrence of iron deficiency on the flood plain and young cultivated soil in the dried state must be attributed to an unfavourable ratio between the contents of mobile-iron and organic matter. This explanation is also supported by the relation, which is found in orchards on calcareous clay soils, between the mobile-iron content, the content of organic matter and the occurrence of iron deficiency. Fig. 3 demonstrates that the occurrence of iron deficiency is not directly related with the mobile iron content of the calcareous soils. However, a distinction between healthy and iron-deficient orchards on calcareous soils could be made if the mobile-iron contents were correlated with the contents of the organic matter of the relevant soils. So the relationship between the mobile-iron content and the content of the organic matter, represented by approximatively the equation $y = 27x - 16$, can be used to predict the susceptibility of a calcareous soil to iron deficiency.
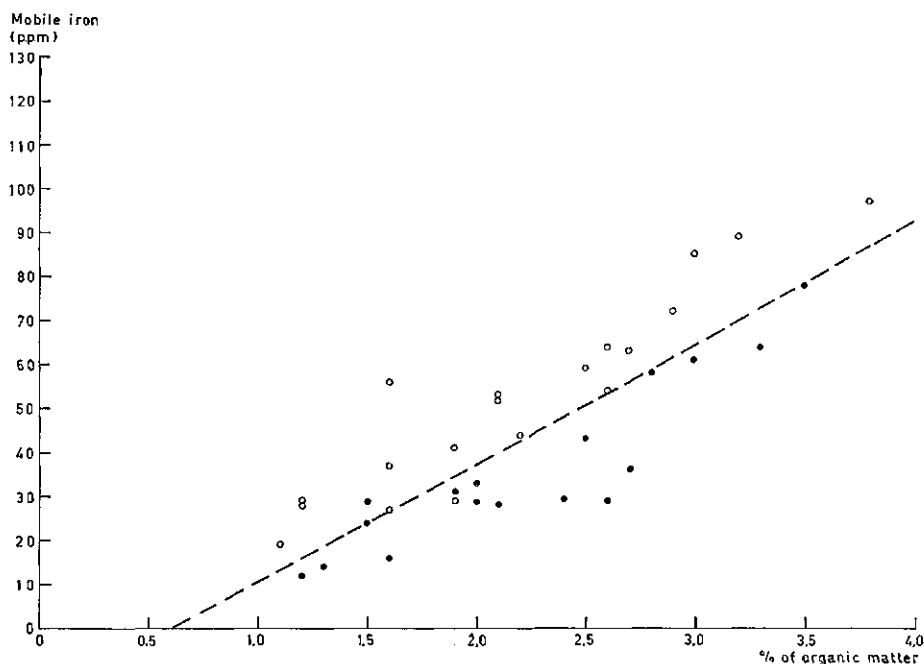
Fig. 3. Relation between mobile iron (ppm) and organic matter (%) with regard to the susceptibility of orchards to iron chlorosis.

Regression line: $y = 27x - 16$.

Legend: ● susceptible to iron chlorosis,
○ insusceptible to iron chlorosis

DISCUSSION

The iron-mobilization processes are caused by the intensive break-down of the organic matter of the sediments of the fresh-water tidal area. The decomposition products of the organic matter form soluble organometallic complexes with the iron from the sediments.

In this study these organic substances, responsible for the iron mobilization, are defined as fulvic acids, because the bulk of the components in this fraction shows a great similarity in chemical behaviour to soil fulvic acids. From Table 5 it is seen, that the amounts of organic C and iron in the fresh-water sediments of the Ems are mobilized in the ratio 2:1. This ratio approached the value, which is found by de Groot[4].

Although the mobilization of iron is not so interesting from a view-

point of pollution, its behaviour in this respect may be of great importance for the understanding of the mobilization behaviour of other metals like copper, zinc, and mercury. As a result of the high iron contents in the sediments and of the fact that ferric-iron forms the most stable organometallic complexes according to the series of Irving and Williams[6], the amount of mobilized iron is much greater than that of any other metal[5]. Therefore iron may have a strong competition effect on the mobilization of other metals and perhaps this effect can give an explanation for the difference in mobilization behaviour between the rivers Rhine and Ems. The Rhine mobilizes much less iron than the Ems, the latter river, on the other hand, shows a smaller mobilization for copper, zinc, and chromium, possible due to the competition effect of iron.

The above-mentioned consideration makes it clear that the extent to which metals are mobilized in the mouthing area of a river cannot be expressed in a single measure. Besides the quantity of decomposable organic matter and the series of Irving and Williams[6] concerning the stability of metal chelates, other considerations, like mutual competition between the metals and selective chelation of a metal by special ligands may be of importance in the regulation of the mobilization of metals.

The percentages of iron mobilization in Table 2 are small in comparison with the natural values found by de Groot[5]. This is understandable because the mobile iron contents do not represent absolute values. During the extraction with EDDHA a dynamic equilibrium is established between the mobile iron in the sediment and the iron in the extractant. In fact, if the extraction is repeated, a considerable amount of iron is released again from the sediment. For characterizing the iron mobility, however, the EDDHA extraction procedure is very useful and gives a reliable index.

The organic iron compounds were solubilized from the sediment under mildly reducing conditions. This artifact seems to be in conflict with the naturally occurring aerobic environment of the river system. But even in such an aerobic ecosystem reducing processsss take place by microbiological attack. Under the mildly reducing conditions of the experiment, however, these processes are favoured over the oxidizing processes. Transportation of sediments is a complex process and related to the circulation patterns of the water. Under the influence of the flow conditions sedimentation and subsequent

erosion of the sediments take place alternately. Probably these processes occur many times before the sediments reach the final place of deposition. As the oxygen supply in the state of deposition will be lower than in the state of movement with the stream, the state of deposition may favour the mobilization of iron.

When these soluble organic iron compounds have left the sediments, they are directly converted into colloidal particles under the oxidizing conditions of the river and sea water. Thus the mobilization of iron may be attributed to chelation, followed by processes of hydrolysis, which lead to the formation of a colloidal fraction of insoluble Fe compounds. According to Aston and Chester[1] these compounds can be adsorbed by fine, suspended clay particles and may be transported by tidal and current action.

Both ripening and drying of the sediments cause a large decrease of the mobile-iron content. Especially with respect to the empoldering of new land the effect of drying may have harmful consequences for plant nutrition. The sedimentary deposit looses a great part of its water in a relatively short period, whereas the organic matter content only decreases slowly when the deposit is ripening to arable soil. In this way an unfavourable ratio between mobile-iron and organic matter may lead to a low iron availability. The competitive action of the organic matter on iron availability has also been found in old calcareous soils. The combination of low contents of mobile-iron and high contents of organic matter implies susceptibility of these soils to iron chlorosis.

REFERENCES

1 Aston, S. R. and Chester, R. The influence of suspended particles on the precipitation of iron in natural waters. Estuarine Coastal Mar. Sci. 1, 225–231 (1973).
2 Driel, W. van, The effect of iron ethylenediaminetetraacetic acid on the growth and metabolism of tomato plants in water cultures. Plant and Soil 20, 85–104 (1964).
3 Groot, A. J. de, Origin and transport of mud in coastal waters from the Western Scheldt to the Danisch frontier, in L. M· J. V. van Straaten (Ed.), Deltaic and Shallow Marine Deposits. (Elsevier, Amsterdam), p. 91–103 (1964).

4   Groot, A. J. de, Mobility of trace elements in deltas. Trans. Comm. II and IV. Intern. Soc. Soil Sci., Aberdeen, 267–269 (1966).

5   Groot, A. J. de, Occurrence and behaviour of heavy metals in river deltas, with special reference to the Rhine and Ems river, *in* E. D. Goldberg (Ed.), North Sea Science (MIT Press, Cambridge, Mass.) p. 308–325 (1973).

6   Irving, A. and Williams, R., Order of stability of metal complexes. Nature 162, 746–747 (1948).

7   Kurmisch, B., Humusbestimmung nach dem Bichromatverfahren ohne Kalium-jodid. Z. Pflanzenernähr. Düng. Bodenk. 44, 121–125 (1949).

8   Mortensen, J. L., Complexing of metals by soil organic matter. Soil Sci. Soc. Am. Proc. 27, 179–186 (1963).

9   Pauly, H., Zur Kenntnis der Diazoreaktion des Eiweisses. Z. Physiol. Chem. 94, 284–290 (1915).

10 Rauterberg, E., Die bestimmung der verfügbaren Pflanzennährstoffe im Boden mit Chelatoren. Z. Pflanzenernähr. Düng. Bodenk. 106, 128–134 (1964).

11 Schnitzer, M. and Desjardins, J. G., Molecular and equivalent weights of the organic matter of a podzol. Soil Sci. Soc. Am. Proc. 26, 362–365 (1962).

12 Underwood, A. L., Spectrophotometric determination of iron with ethylene diamine di(o-hydroxyphenylacetic acid). Anal. Chem. 30, 44 (1958).

13 Underwood, A. L., Photometric titration of iron with EDDHA. Anal. Chim. Acta 20, 228–232 (1969).

14 Wallace, A., A Decade of Synthetic Chelating Agents in Inorganic Plant Nutrition. Ed. Wallace, Los Angeles 64, California (1962).