

## The Behaviour of Dissolved Iron and its Variability in the Keum Estuary, a Macrotidal System on the Western Coast of Korea

CHANG-BOK LEE

*Department of Oceanography, Seoul National University, Seoul 151-742, Korea*

### 금강 하구에서의 용존 철 행동과 그 변화에 대한 연구

이 창 복

서울대학교 해양학과

The behaviour of dissolved iron and its temporal variability were investigated in the Keum Estuary, a temperate and macrotidal system on the west coast of Korea, by means of laboratory mixing experiments and field surveys. Four field surveys were conducted under different tidal and fluvial conditions with an aim of understanding the effects of these two most important environmental variables on dissolved iron.

Results from the mixing experiments clearly showed an extensive removal (>90%) of dissolved iron during the early stage of estuarine mixing (<5‰ S), as was reported from many other estuaries. In the field data, however, this pattern was observed in only one survey among four, which was conducted under low river discharge and neap-tide condition. The data obtained from the other three surveys, representing either different tidal or fluvial conditions, showed scatter which in some cases obscures the iron removal in the estuary. This variability of dissolved iron was discussed in terms of various physical processes including water circulation, sediment resuspension and deflocculation.

용존 철의 행동과 시간적 변화에 대한 연구가 온대 대조차 환경인 금강 하구에서 이루어졌다. 이 지역에서 가장 중요한 환경변수인 하천배수량과 조차의 차이로 야기되는 변화를 파악할 수 있도록 4번의 현장조사를 각각 다른 배수량과 조차의 시기에 실시하였으며, 아울러 실험실 내에서 혼합실험도 행해졌다.

혼합실험의 결과 하천에 의해 운반되는 용존 철의 90% 이상이 5‰ 이하의 저염분역에서 제거되는 현상이 확인되었다. 그러나 현장조사에서 이러한 초기 혼합시의 용존 철 제거가 뚜렷이 나타난 것은 갈수기·소조기의 단 한번 뿐이었으며, 나머지 3번의 다른 환경조건 하에서는 용존 철 농도의 심한 변화가 관측되었다. 하천배수량과 조차의 변화에 따라 보여진 용존 철의 변화는 하구순환이나 퇴적물 재부유 및 응집체 해체 등의 물리적 현상과 관련시켜 해석되었다.

### INTRODUCTION

During the past two decades there has been considerable progress in our knowledge of metal behaviour during its transition through an estuarine zone. For dissolved iron, numerous field and laboratory studies have contributed in establishing

its large scale removal at an early stage of estuarine mixing (Boyle et al., 1974, 1977; Holliday and Liss, 1976; Sholkovitz, 1976; Moore et al., 1979) as well as the mechanisms involved in this removal process. These studies elucidated various mechanisms of dissolved iron removal, such as the adsorption onto particles (Aston and Chester, 19

73), the precipitation as iron hydroxide flocs (Cooney et al., 1971), and the flocculation of colloidal humic acids and iron hydroxides (Eckert and Sholkovitz, 1976; Boyle et al., 1977; Sholkovitz, 1978).

The dissolved iron content in the inflowing river waters varies greatly both spatially—within a range of two orders of magnitude from one estuary to another—and temporally for a given estuary (Figuères et al., 1978; Yeats and Bewers, 1982; Shiller and Boyle, 1985). Although the removal during estuarine mixing is now generally accepted as a global behaviour pattern of dissolved iron, the magnitude of this removal also varies greatly from one estuary to another. Moreover, on some occasions the removal of dissolved iron could not be observed (Eisma, 1975; Shiller and Boyle, 1991). Besides these variabilities, Boyden et al. (1979) also reported considerable differences in concentrations and behaviour of trace elements, including iron, on a tidal and seasonal basis from their study on two Cornish estuaries in the United Kingdom. All these facts clearly show the highly complex nature of metal geochemistry in the estuarine environment.

Therefore, it is necessary to understand the temporal variability in relation to the local environmental conditions before we estimate the chemical mass balance of trace elements in any particular estuarine system. This is especially important for a temperate macrotidal estuary where great variations in river discharge and tidal energy occur over seasonal and fortnightly time scales. The seasonal variation in river flow regime and the spring-neap tidal cycle exert great influence on the residence time of water and suspended sediment in estuaries, which in turn can affect the sediment-solution interactions in that environment.

During the last ten years numerous studies have been carried out for the Keum Estuary, located on the west coast of Korea (Chung et al., 1983; Chung and Bhang, 1984; Lee, 1985; Kim and Ki, 1987; Lee and Kim, 1987; Choi et al., 1989). As a result of these studies, the sedimentary processes and related dynamic phenomena of this estuary are now relatively well understood. Very little atten-

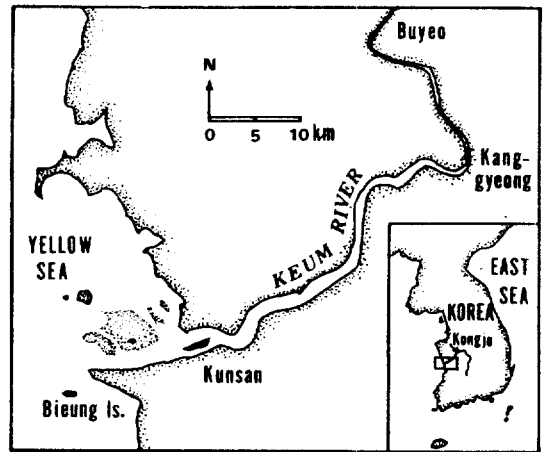


Fig. 1. The Keum Estuary.

tion, however, has been paid to the geochemical processes of trace elements in this estuary. Recently, Byrd et al. (1990) studied the behaviour of some trace metals in the Keum Estuary and reported the rapid removal of dissolved iron during estuarine mixing. Their data, however, are restricted to field samples collected during one particular hydrologic condition and the temporal variability in metal behaviour is still unknown.

The present study was conducted in order to investigate the temporal variability of dissolved iron concentration in the Keum Estuary with regard to the different dynamic conditions, principally related with the varying river discharge and tidal energy. I will discuss here the estuarine behaviour of dissolved iron under various tidal and fluvial conditions, with an emphasis on its relationship with various physical processes whenever appropriate.

## THE STUDY AREA

The Keum Estuary is a shallow macrotidal estuary which is located on the western coast of Korea (Fig. 1). The tide at the estuary mouth is a semi-diurnal type with a mean range of 4.3 m, and exhibits a large fortnightly spring-neap variation. The average spring- and neap-tidal ranges are estimated at 5.7 m and 2.8 m, respectively. This great fluctuation in the tidal energy input

into the estuary controls not only the residence time of fresh water within the estuarine zone but also the dynamics of fine sediments in this environment. Consequently, a periodic resuspension and deposition of bottom sediments occurs along with the spring-neap cycle, which results in the periodic growth and waning out of a turbidity maximum (Lee and Kim, 1987). The annual fresh water discharge is estimated at about  $6 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$ , most of which is concentrated in the summer rainy season, causing a great seasonal variation. According to Lee and Kim (1987), this seasonal fluctuation in river discharge controls mainly the seaward transport of the estuarine fine sediments through modification of the flood-ebb asymmetry in current velocity and the flushing rate of suspended sediments.

## MATERIALS AND METHODS

The estuarine waters were sampled four times during the year 1987, on different periods of tidal and fluvial conditions; the period of low river discharge and neap-tide (May 22), high river discharge and spring-tide (August 12), high river discharge and neap-tide (August 19), and medium river discharge and spring-tide (November 5). Water samples were collected along the Keum Estuary and its adjacent offshore area, covering the entire salinity range of estuarine mixing, on a small ship using a pole-type sampler. During collecting and subsequent handling of water samples every precaution was taken against possible contaminations.

The samples were stored in an ice-box and transferred to the laboratory within 24 hours. Upon arrival in the laboratory, the water samples were immediately filtered through precleaned  $0.45 \mu\text{m}$  membrane filters, acidified with redistilled HCl to pH 1.8, and stored in clean high-density polyethylene bottles with vinyl cover until the time of analysis.

Analysis of dissolved iron was made colorimetrically using ferrozine as reagent (Stookey, 1970). This colorimetric method determines only that fraction of iron species which is solubilised by storage at pH 1.8 and subsequently reduced to

Table 1. Dissolved Fe contents of the Keum River waters, measured at Kongju on five different periods during the year 1987

	River Discharge ( $\text{m}^3/\text{sec}$ )	Dissolved Fe ( $\mu\text{g}/\text{l}$ )
April 30	21.6	52.4
July 8	54.4	41.7
August 2	359.4	83.7
August 13	548.9	31.2
September 20	45.6	20.8

$\text{Fe}^{2+}$  by hydroxylamine at room temperature. Some authors termed this as 'colorimetric iron', distinguishing it from 'total dissolved iron' measured by graphite furnace atomic absorption spectrophotometry. However, Boyle et al. (1977) found that the ratio of colorimetric Fe to total Fe was constant within a given estuary. The 'colorimetric iron' was shown to comprise about 88% of the 'total dissolved iron' in the Keum Estuary. The precision of analysis was fairly good, generally within 2% for the entire concentration range analyzed.

Mixing experiments were carried out in the laboratory using aliquots of both river water and seawater endmembers. Two types of experiments were done: one with unfiltered endmembers and another with filtered ones. Aliquots of river water and seawater were mixed in varying proportions in order to obtain 12 mixtures of different salinities. After allowing 3 hours of mixing time, the mixtures were filtered, acidified and stored, as described for field samples. All the laboratory procedures were carried out in a laminar-flow bench.

## RESULTS AND DISCUSSIONS

### *Dissolved Iron in River Waters and Seawaters*

The dissolved iron content in the Keum River waters at Kongju, located at about 100 km upstream from the estuary mouth, varied between 20.8 and  $83.7 \mu\text{g}/\text{l}$ . The result of five different measurements, shown in Table 1, does not show that dissolved iron content has any relationship with the river discharge. Instead, the dissolved iron content

in September was reduced to less than half of that observed in spring under the same discharge condition, suggesting an apparent seasonal variation in riverine iron content. This decreased content in autumn, compared to spring and summer, may be expressed in terms of hysteresis effect (Whitfield and Schreier, 1981), though more detailed time series study is required in order to evaluate the seasonal pattern. However, the washout of the drainage basin during the rainy season may result in the reduced availability of dissolved iron during the subsequent dry season. In the same context, the maximum content observed in early August may be explained as a result of the exceptionally dry weather which persisted during the spring and early summer of 1987.

In contrast to the temporal variability, the dissolved iron content of the Keum River waters does not appear to vary noticeably in space. On July 8, 1987, river waters were collected at three different locations along the Keum River; at Kongju, Buyeo and Kang-gyeong, located at about 100, 60 and 40 km, respectively, upstream from the mouth. The measured dissolved iron values at the above three freshwater stations were 41.7, 35.6 and 40.0  $\mu\text{g/l}$  respectively. This result suggests that there is no significant process that affects the dissolved iron content in the upstream of the salt water intrusion. The dissolved iron level observed in the Keum River is similar to those reported from the Göta River, Sweden (Danielsson et al., 1983), the Connecticut River, U.S.A. (Hong and Kester, 1985), the Amazon (Gibbs, 1977), and perhaps the Chang-jiang, China (Chen and Zeng, 1983).

In the offshore areas, the dissolved iron values vary widely both in space and in time, with an overall range of 0.2 and 12.2  $\mu\text{g/l}$ . This may reflect, at least in part, the influence of anthropogenic inputs from localized sources. Both the frequent dredging operations in the area for the maintenance of navigation route and the construction of dams along the coastline for land reclamation can be the additional iron sources into the coastal waters. But at the same time, it may also be conceivable that such various iron contents result from the mixing of different coastal water masses by

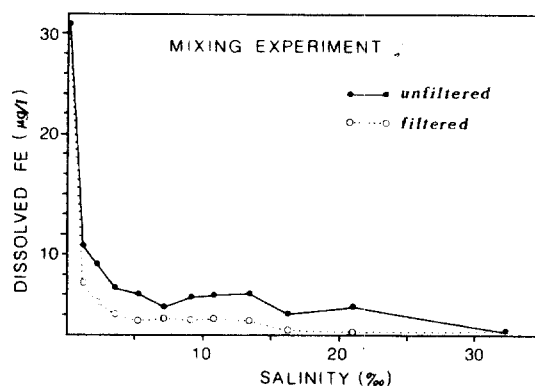


Fig. 2. Results of laboratory mixing experiments using the river water and seawater endmembers.

periodic tidal movement, most of which lies between 1-5  $\mu\text{g/l}$ . Whatever the reason, it is evident from our result that the dissolved iron content in coastal waters is highly variable and sometimes more elevated than in the estuarine waters.

#### *Behaviour of Dissolved Iron in the Mixing Experiments*

The behaviour of dissolved iron in the estuarine mixing zone was investigated by means of artificial mixing experiments using the river water and seawater endmembers. The controlled laboratory experimental conditions can allow us to characterize the processes involved in the field observations. Two types of experiments, one with unfiltered endmembers and another with filtered ones, were performed with an aim of distinguishing the two most important effects: the adsorption-desorption behaviour and the colloid flocculation. In these experiments, a river water sample containing 31.2  $\mu\text{g/l}$  of dissolved iron, collected on August 13 at Kongju, and an offshore water sample with 0.4  $\mu\text{g/l}$  of dissolved iron value were used as endmembers of mixing.

The result of these laboratory mixings, shown in Fig. 2, exhibits a similar pattern for the both types of experiments: a rapid decrease with increasing salinity in dissolved iron content in the 0-5‰ salinity range followed by a conservative dilution pattern at higher salinities. The magnitude of dis-

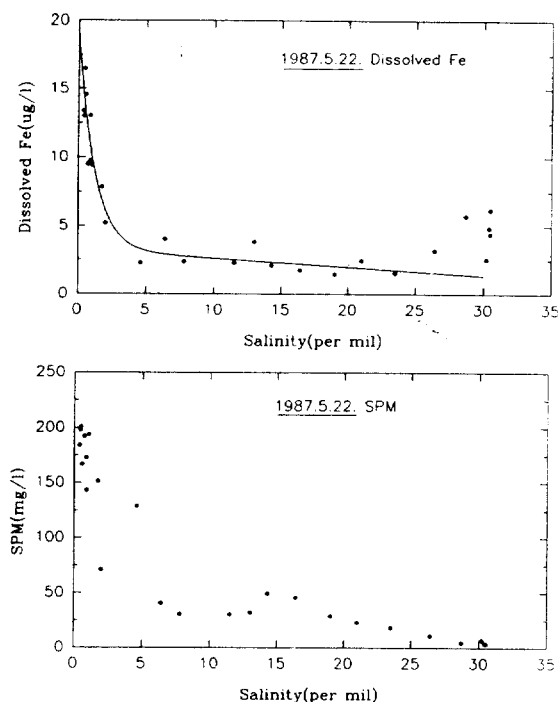


Fig. 3. Concentrations of (a) dissolved iron and (b) SPM against salinity, observed in the Keum Estuary on May 22, 1987 (low discharge, neap-tide). The best-fit regression curve:  $\text{Fe } (\mu\text{g/l}) = -0.063 S + 15.88 e^{-0.833S} + 3.23$  (for  $S < 25\text{‰}$ ),  $r^2 = 0.937$ .

solved iron removal in these experiments was estimated by the method of Boyle et al. (1974) and was shown to be 94% and 90% for filtered mixing and unfiltered mixing, respectively. The rapid and extensive removal of dissolved iron during the early stage of estuarine mixing was reported from numerous estuaries, including the Amazon (Sholkovitz et al., 1978), the Zaire (Figuères et al., 1978), the Connecticut (Hong and Kester, 1985) and the Changjiang (Chen and Zeng, 1983; Edmond et al., 1985).

The fact that there is no difference in the iron-salinity relationships between the filtered and unfiltered mixings indicates that the observed removal of dissolved iron was caused by some processes which were independent of suspended particles ( $>0.45 \mu\text{m}$ ). Numerous studies have shown that a major part of dissolved iron in river water consists of colloids ( $<0.45 \mu\text{m}$ ) stabilised by organic material, which flocculates rapidly upon encounter

with the seawater electrolytes (Boyle et al., 1977; Sholkovitz et al., 1978; Moore et al., 1979; Hunter and Leonard, 1988). Therefore, the rapid removal of dissolved iron at low salinities observed in the mixing experiments is most probably due to the flocculation of colloidal iron.

#### *Dissolved Iron and SPM in the Estuarine Mixing Zone*

##### May 22, 1987 (Fig. 3)

This was the period of low river discharge and neap-tide. The tidal range at Kunsan Harbour was 3.6 m, a value somewhat greater than the average neap-tidal range (2.8 m) but smaller than the mean tidal range (4.3 m) in this environment. The salt water intruded into the estuary up to about a 20 km upstream position from Kunsan. Water samples were collected from a distance of about 40 km along the estuary and adjacent coastal areas, and covered a range in salinities from 0.5‰ to 30.5‰.

The dissolved iron content varied between 1.5 and 16.5  $\mu\text{g/l}$ , with an overall decreasing trend with increasing salinity. The decrease in dissolved iron content, however, was most pronounced in low salinity areas, less than about 5‰. Beyond that salinity range, the dissolved iron content did not vary much and remained below 4  $\mu\text{g/l}$  along the rest of the estuary. The removal of dissolved iron was thus confined to the early stage of estuarine mixing, mainly in the 0.5-5‰ salinity range. The magnitude of this removal was about 84% of the dissolved iron introduced to the estuary by river water.

In offshore waters, the dissolved iron content varied in the range of 2.6-6.2  $\mu\text{g/l}$ . Some of these offshore dissolved iron values were higher than those observed within the estuary, suggesting a heterogeneity of offshore waters with regard to dissolved iron.

With increasing salinity, concentrations of the suspended particulate matter (SPM) also showed a decreasing trend, with a maximum value of 200.6 mg/l near the saline intrusion limit. Fluctuations in the SPM concentration near the 5‰ and 15‰ S

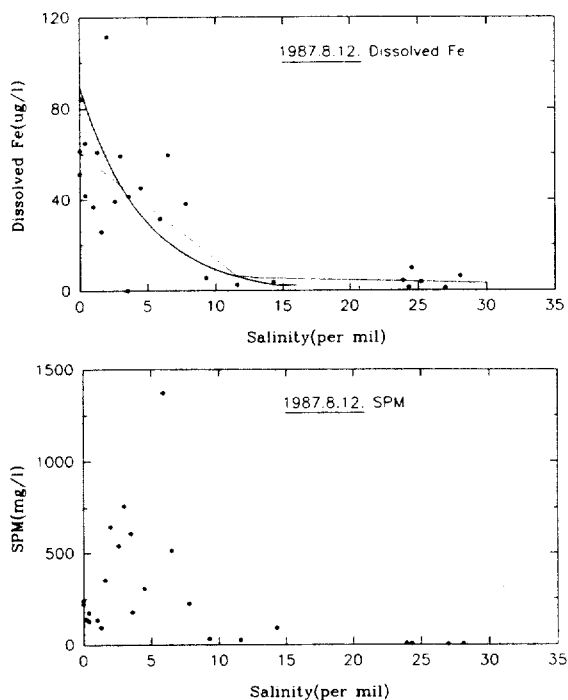


Fig. 4. Concentrations of (a) dissolved iron and (b) SPM against salinity, observed in the Keum Estuary on August 12, 1987 (high discharge, spring-tide). The best-fit regression curve:  $\text{Fe}(\mu\text{g/l}) = -0.1 S + 89.6 e^{-0.218S} + 0.014$  (for  $S < 15\text{‰}$ ),  $r^2 = 0.339$ . Dotted line represents the least-square regression line assuming conservative mixing within the salinity range of 0-12‰:  $\text{Fe}(\mu\text{g/l}) = -4.69 S + 60.5$ ,  $r^2 = 0.677$ .

were probably caused by the resuspension of bottom sediments. The SPM level in coastal waters, on the other hand, was very low and showed a range of 3.4-7.0 mg/l.

#### August 12, 1987 (Fig. 4)

This was the period of high river discharge and spring-tide. The tidal range at Kunsan Harbour was 7 m, the largest among the four periods studied. This, in spite of the extremely high river discharge, allowed salt water to intrude up to about 12 km upstream from Kunsan. However, only those waters with salinities of less than about 15‰ could be observed within the estuary proper and higher salinities were encountered in the adjacent offshore waters.

Both the SPM and dissolved iron concentra-

tions in estuarine waters were relatively high on this day, the SPM concentration varying in the range of 25.5-1370 mg/l and the dissolved iron in the range of 2.5-111.3 µg/l. Great scatters in both the SPM and dissolved iron contents were observed in the low salinity zone of less than 10‰ S. The removal of dissolved iron at low salinities, which was shown in the mixing experiment, was thus not evident in field samples during this high-discharge, spring-tidal period. Instead, the removal appeared to have occurred at an intermediate salinity area, probably near 10‰ S. However, a limited number of samples from the area covering 10-23‰ of salinity during this field study makes any definitive conclusions difficult.

The high SPM level as well as its great variability in the low salinity zone is readily explained in terms of resuspension of bottom sediments by strong spring-tidal currents. The tidal resuspension of bottom sediments are known to provide the principal mechanism in the formation of a turbidity maximum in this estuary (Lee and Kim, 1987). The variation of SPM in respect to salinity was, on the other hand, very similar to that of dissolved iron. It may thus be assumed that behind this similar trend in the behaviour of SPM and dissolved iron lie some related causes, notably vigorous resuspension of bottom sediments caused by strong spring-tidal currents.

#### August 19, 1987 (Fig. 5)

This was the period of high river discharge and neap-tide. The tidal range at Kunsan Harbour was only 1.4 m, a value far below the average neap-tidal range of 2.8 m. This extremely weak tidal condition together with the strong fluvial regime hindered the salt water intrusion mainly to the downstream part of Kunsan Harbour. The water samples were collected over a salinity range of 0.1-26.5‰, but only samples with less than about 15‰ were found within the estuary.

The dissolved iron content varied between 5.1 and 47.9 µg/l, with a maximum value occurring at the uppermost part of the estuary. A general trend of decreasing dissolved iron content with increasing salinity could be discerned. In spite of

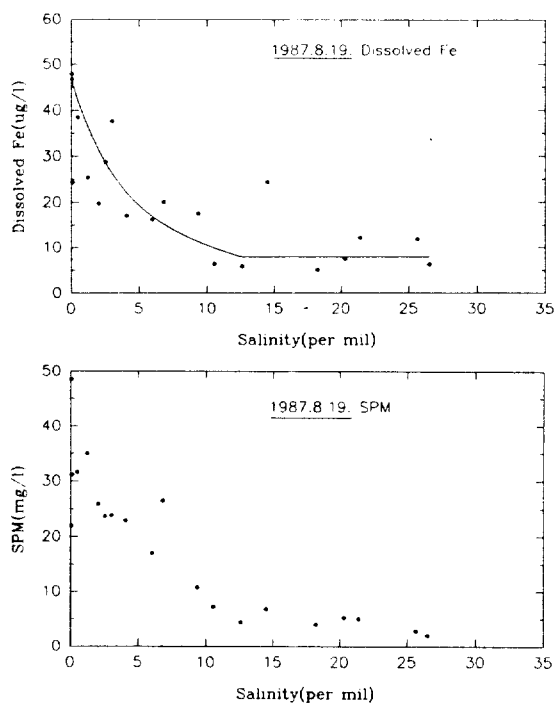


Fig. 5. Concentrations of (a) dissolved iron and (b) SPM against salinity, observed in the Keum Estuary on August 19, 1987 (high discharge, neap-tide). The best-fit regression curve:  $Fe(\mu g/l) = -0.705 S + 30.6 e^{-0.35S} + 16.0$  (for  $S < 15\text{‰}$ ),  $r^2 = 0.802$ .

the scattered data, the dissolved iron vs salinity relationship appears as a curvature which suggests a removal of dissolved iron. However, the extent of this removal was greatly reduced compared to the May data, with an estimated rate of less than 60% of the river-borne dissolved iron.

The SPM concentrations were very low compared to the other periods and showed on the whole a monotonous decreasing pattern with increasing salinity. Under the weak tidal energy condition the resuspension of bottom sediments was greatly reduced. The fluctuation of dissolved iron contents in estuarine waters was thus, unlike August 12, not accompanied with fluctuation in SPM during this period.

#### November 5, 1987 (Fig. 6)

This was the period of intermediate river discharge and spring-tide. The tidal range at Kunsan Harbour was 6 m. The salt water penetrated into

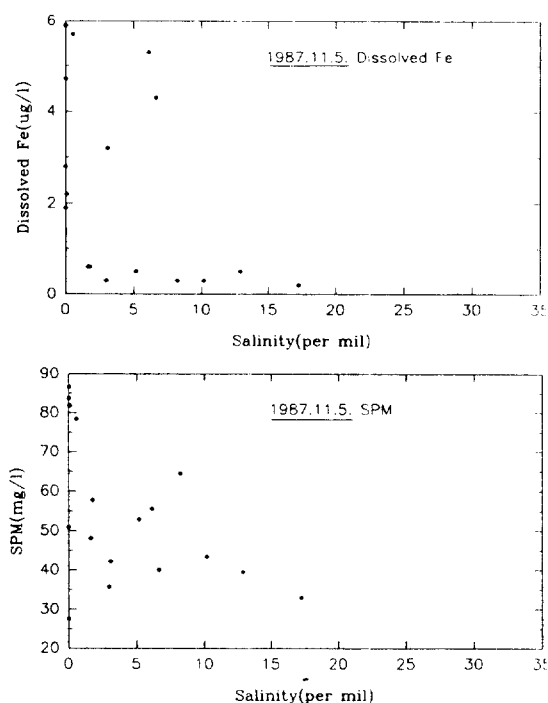


Fig. 6. Concentrations of (a) dissolved iron and (b) SPM against salinity, observed in the Keum Estuary on November 5, 1987 (medium discharge, spring-tide).

the estuary up to about 10 km upstream from Kunsan. Water samples, collected from a distance of about 36 km along the estuary, covered a range of 0.1-17.3‰ salinities.

The dissolved iron content, varying in a range of 0.2-5.7 µg/l, was lowest among the four periods studied. The data are scattered within the estuary, in an area of less than about 7‰ S, which makes it difficult to conclude that the removal of dissolved iron occurred within the estuary. However, underlying this fluctuation persisted a relatively low dissolved iron content of 0.3-0.6 µg/l in waters with salinity higher than about 3‰. It is hence probable that the removal occurred at low salinity if we assume that the three samples with relatively high dissolved iron were influenced by localized secondary inputs or contamination during handling. Byrd et al. (1990), who analyzed water samples collected on October 24, 1986 from the Keum Estuary, also found a removal of dissolved iron. The dissolved iron content reported by Byrd et

al. (1990), which was analyzed by graphite furnace atomic absorption spectrometry, was of the same range as our data. This will serve as another evidence supporting the fact that the colorimetric iron makes up the major part of the total dissolved iron in the Keum Estuary.

The SPM concentrations varied between 27.5 and 86.6 mg/l. Along with a general tendency of the decreasing SPM level with increasing salinities, some fluctuations deviating from this general trend were observed in the salinity range of 1-8‰.

#### *Temporal Variability in the Dissolved Iron Behaviour*

The above-described observations from four field studies show that a wide variability, both in time and space, of dissolved iron occurs in the Keum Estuary and its adjacent coastal waters. One conspicuous feature which emerges from this variability is the great difference in the dissolved iron content between the high and low river discharge periods. During the high river discharge, dissolved iron contents in estuarine waters were generally higher by a factor of 5-10 compared to the low discharge period, with the maximum values more elevated than in the inflowing river waters. A wide scatter in the dissolved iron content with respect to salinity could be also observed within the estuary under this enhanced river regime. During the low river discharge, on the other hand, the maximum dissolved iron values observed within the estuarine zone were much lower than the river water contents in contrast to the high discharge period.

The 'dissolved' iron, which pass through a 0.45  $\mu\text{m}$  membrane filter, is known to be present in river water mainly as colloidal iron(III) oxides stabilized by association with humic substances (Sholkovitz, 1976; Boyle et al., 1977; Moore et al., 1979; Hunter, 1983). The removal of dissolved iron during estuarine mixing may be said to result from destabilization of these colloids under the influence of seawater electrolytes. The rapidity of this flocculation reaction, reported by various authors (Boyle et al., 1977; Mayer, 1982; Hunter and

Leonard, 1988), can explain the early removal of dissolved iron, which is generally restricted within the area of less than 5‰ S, during estuarine mixing. The results from our mixing experiment and one of our field data (May 22) also clearly show this early removal pattern of dissolved iron (Fig. 2 and 3). Therefore, in order to understand the contrasting feature of dissolved iron observed between the high and low discharge periods, we should consider the possible effects of fluvial discharge upon the metal behaviour in the Keum Estuary.

It is well known that the residence time of water in an estuary, or the flushing time, is related to river discharge. Thus an increased river discharge is accompanied by a more rapid exchange of fresh water with the sea (Dyer, 1973, 1981). It also causes both a downstream movement of the salinity intrusion and a more rapid circulation of water. Through these modifications, the variation in river discharge can influence the metal behaviour in the estuary. Both the reduced flushing time and the increased water movement under the high river discharge condition will broaden the zone where the flocculation of colloidal iron occurs. When it happens, flocs of various sizes will be dispersed over a wider salinity range and in consequence a scatter in the iron-salinity relationship may be produced. But at the same time, a high level of water turbulence under the increased fluvial discharge might also be held responsible in part for the lack of any distinct removal pattern in the low salinity zone from the August field data.

The water turbulence however is influenced more by the tidal condition than by river discharge in the Keum Estuary. Lee and Kim (1987) have shown that the tidal range is the dominant factor in controlling the SPM level in this estuary since it regulates the resuspension of the bottom sediments. The sediment resuspension, which is directly related with the turbulence of overlying water, brings various particulate chemical components into the water column as well as the interstitial solution. Therefore, if an anoxic condition prevails within the bottom sediment, then a large



amount of dissolved iron could come from this source. Though such an extensive anoxic environment is not reported from the Keum Estuary, a minor contribution of dissolved iron from this source will not be fully rejected and may explain, at least in part, the elevated dissolved iron content from the August 12 data.

On the other hand, it is also imaginable that the intensified water turbulence may bring about deflocculation by breaking the aggregated flocs into much smaller sizes. If this happens, the content of 'dissolved' iron, which passes through a 0.45  $\mu\text{m}$  pore size, will be increased correspondingly. Though this deflocculation process has not yet been reported from any estuaries of the world, Yan et al. (1991) have suggested this as a probable mechanism responsible for the increased dissolved iron level observed in the coastal waters of New Jersey, U.S.A. Considering the coinciding of the period of most highly elevated dissolved iron content (Aug. 12, 1987) with the highest water turbulence under the combined influences of both the high river discharge and spring-tide (Fig. 4), the addition of dissolved iron within the estuary by deflocculation process is very probable.

Nevertheless, there still remains a possibility of anthropogenic inputs as additional dissolved iron sources. The fluctuation of dissolved iron contents in coastal waters, some of which are even higher than in the upstream estuarine waters, supports the probability of such additional sources. A dam was being constructed during the study period along the coastline near the estuary mouth, between the Outer Harbour and Bieung Island, for the reclamation of intertidal lands. Besides, the seaward part from the Outer Harbor, located in the estuary mouth, is frequently navigated by large ships. All these circumstances makes it difficult for me to ignore the pollution effect from the possible causes of scattered data in coastal waters, even though the magnitude of its influence is still to be investigated.

## CONCLUSIONS

From the present study, the following conclu-

sions can be drawn on the behaviour of dissolved iron in the Keum Estuary, a temperate macro-tidal system on the western coast of Korea.

(1) The widely reported phenomenon of dissolved-iron removal during estuarine mixing was also confirmed in the Keum Estuary by both the laboratory experiments and field data. The flocculation of colloidal iron appears to be the major mechanism responsible for this removal. More than 90% of the dissolved iron from the inflowing river waters can be removed through this process. The removal of dissolved iron occurs mostly within the low salinity zone of less than 5‰.

(2) A great temporal variation was observed both in the dissolved iron content and in its behaviour during estuarine mixing. In general, more elevated content and greater scatter occurred in estuarine waters under the high river discharge condition. During the low river discharge, on the other hand, the dissolved iron contents in the uppermost part of the estuary waters were much lower than those in the inflowing river waters measured at Kongju, which suggests that additional removal of dissolved iron had occurred in waters downstream of Kongju before it entered the estuarine zone.

(3) Different estuarine dynamics arising from the varying river discharge and tidal range affects the behaviour of dissolved iron during estuarine mixing through modifications of the various physico-chemical and sedimentary processes. The residence time of fresh water, which is dependent mainly upon river discharge in this estuary, controls both the areal extent and the time scale of interaction between fresh water and seawater, affecting distribution pattern of dissolved iron in the estuary. In addition, the turbulence of estuarine waters, which is principally related to the tidal energy in this estuary, controls the resuspension of bottom sediments and can thereby further complicate the iron behaviour in the study area. It is also suggested that the deflocculation process may also be responsible for the high iron values and the scatter observed during the extremely high energy period under the combined effect of high river discharge and spring-tide.

## ACKNOWLEDGEMENTS

The present study was supported by a grant from the Korea Science and Engineering Foundation (No. 871-0505-015-2). The author wishes to thank Mrs. H.J. Cha for her devoted field and laboratory work during the course of this study. Thanks are also due to Prof. K.H. Kim, Dr. S.H. Lee and Prof. M.W. Han for reading the manuscript and giving many helpful comments.

## REFERENCES

- Aston, S.R. and R. Chester, 1973. The influence of suspended particles on the precipitation of iron in natural waters. *Estuar. Coast. Mar. Sci.*, **1**: 225-231.
- Boyden, C.R., S.R. Aston and I. Thornton, 1979. Tidal and seasonal variations of trace elements in two Cornish estuaries. *Estuar. Coast. Mar. Sci.*, **9**: 303-317.
- Boyle, E.A., R. Collier, A.T. Dengler, J.M. Edmond, A.C. Ng and R.F. Stallard, 1974. On the chemical mass-balance in estuaries. *Geochim. Cosmochim. Acta*, **38**: 1719-1728.
- Boyle, E.A., J.M. Edmond and E.R. Sholkovitz, 1977. The mechanism of iron removal in estuaries. *Geochim. Cosmochim. Acta*, **41**: 1313-1324.
- Byrd, J.T., K.W. Lee, D.S. Lee, R.G. Smith and H.L. Windom, 1990. The behavior of trace metals in the Geum Estuary, Korea. *Estuaries*, **13**: 8-13.
- Chen, Z. and X. Zeng, 1983. Mechanism of iron and manganese transport in the Changjiang River plume. In: Proc. Intern. Symp. 'Sedimentation on the Continental Shelf, with Special Reference to the East China Sea', April 12-16, 1983, Hangzhou (China). China Ocean Press, Beijing, pp.206-214.
- Choi, B.H., K.G. Kang and S.W. Lee, 1989. Tide and sediment transport in the Keum River estuary. *J. Korean Soc. Coast. Ocean Engineers*, **1**: 31-43.
- Chung, J.Y. and I.K. Bhang, 1984. Circulation dynamics of the Keum River estuary II. Fluid dynamic characteristics. *J. Oceanol. Soc. Korea*, **19**: 141-152.
- Chung, J.Y., J.H. Lee and H.S. An, 1983. Circulation dynamics of the Keum River estuary. *J. Oceanol. Soc. Korea*, **18**: 142-148. (In Korean with English abstract)
- Coonley, L.S. Jr., E.B. Baker and H.D. Holland, 1971. Iron in the Mullica River and in Great Bay, New Jersey. *Chem. Geol.*, **7**: 51-63.
- Danielsson, L.G., B. Magnusson, S. Westerlund and K. Zhang, 1983. Trace metals in the Göta River estuary. *Estuar. Coast. Shelf Sci.*, **17**: 73-85.
- Dyer, K.R., 1973. *Estuaries: A Physical Introduction*. John Wiley & Sons, London. 140 pp.
- Dyer, K.R., 1981. The measurement of fluxes and flushing times in estuaries. In: *River Inputs to Ocean Systems*, edited by J.M. Martin et al., UNEP and UNESCO, 67-76.
- Eckert, J.M. and E.R. Sholkovitz, 1976. The flocculation of iron, aluminium and humates from river water by electrolytes. *Geochim. Cosmochim. Acta*, **40**: 847-848.
- Edmond, J.M., A. Spivack, B.C. Grant, M.H. Hu, Z. Chen, S. Chen and X. Zeng, 1985. Chemical dynamics of the Changjiang estuary. *Cont. Shelf Res.*, **4**: 17-36.
- Eisma, D., 1975. Dissolved iron in the Rhine Estuary and the adjacent North Sea. *Neth. J. Sea Res.*, **9**: 222-230.
- Figüères, G., J.M. Martin and M. Meybeck, 1978. Iron behaviour in the Zaire Estuary. *Neth. J. Sea Res.*, **12**: 329-337.
- Gibbs, R.J., 1977. Transport phases of transition metals in the Amazon and Yukon Rivers. *Geol. Soc. Am. Bull.*, **88**: 829-843.
- Holliday, L.M. and P.S. Liss, 1976. The behaviour of dissolved iron, manganese and zinc in the Beaulieu Estuary. *Estuar. Coast. Mar. Sci.*, **4**: 349-353.
- Hong, H. and D.R. Kester, 1985. Chemical forms of iron in the Connecticut River estuary. *Estuar. Coast. Shelf Sci.*, **21**: 449-459.
- Hunter, K.A., 1983. On the estuarine mixing of dissolved substances in relation to colloidal stability and surface properties. *Geochim. Cosmochim. Acta*, **47**: 467-473.
- Hunter, K.A. and M.W. Leonard, 1988. Colloid stability and aggregation in estuaries: 1. Aggregation kinetics of riverine dissolved iron after mixing with seawater. *Geochim. Cosmochim. Acta*, **52**: 1123-1130.
- Kim, K.R. and J.H. Ki, 1987. Studies on chemical and biological processes in the Keum River estuary, Korea. I. The cycle of dissolved inorganic nitrogen: general considerations. *J. Oceanol. Soc. Korea*, **22**: 191-206. (In Korean with English abstract)
- Lee, C.B., 1985. Sedimentary processes of fine sediments and the behaviour of associated metals in the Keum Estuary, Korea. In: *Marine and Estuarine Geochemistry*, edited by A.C. Sigleo and A. Hattori, Lewis Publishers, Chelsea (MI), 209-225.
- Lee, C.B. and T.I. Kim, 1987. Formation and evolution of turbidity maximum in the Keum Estuary, west coast of Korea. *J. Oceanol. Soc. Korea*, **22**: 105-118.
- Mayer, L.M., 1982. Aggregation of colloidal iron during estuarine mixing: Kinetics, mechanism, and seasonality. *Geochim. Cosmochim. Acta*, **46**: 2527-2535.
- Moore, R.M., J.D. Burton, P.J.L. Williams and M.L. Young, 1979. The behaviour of dissolved organic material, iron and manganese in estuarine mixing. *Geochim. Cosmochim. Acta*, **43**: 919-926.
- Shiller, A.M. and E.A. Boyle, 1985. Variability of dissolved trace metals in the Mississippi River. *Geochim. Cosmochim. Acta*, **51**: 3273-3277.
- Shiller, A.M. and E.A. Boyle, 1991. Trace elements in the Mississippi River delta outflow region: Behavior at high discharge. *Geochim. Cosmochim. Acta*, **55**

- 3241-3251.
- Sholkovitz, E. R., 1976. Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater. *Geochim. Cosmochim. Acta*, **40**: 831-845.
- Sholkovitz, E. R., 1978. The flocculation of dissolved Fe, Mn, Al, Cu, Ni, Co and Cd during estuarine mixing. *Earth Planet. Sci. Lett.*, **41**: 77-86.
- Sholkovitz, E. R., E. A. Boyle and N. B. Price, 1978. The removal of dissolved humic acids and iron during estuarine mixing. *Earth Planet. Sci. Lett.*, **40**: 130-136.
- Stookey, L. L., 1970. Ferrozine: a new spectrophotometric reagent for iron. *Anal. Chem.*, **42**: 779-781.
- Whitfield, P. H. and H. Schreier, 1981. Hysteresis in relationships between discharge and water chemistry in the Fraser River basin, British Columbia. *Limnol. Oceanogr.*, **26**: 1179-1182.
- Yan, L., R. F. Stallard, R. M. Key and D. A. Crerar, 1991. Trace metals and dissolved organic carbon in estuaries and offshore waters of New Jersey, USA. *Geochim. Cosmochim. Acta*, **55**: 3647-3656.
- Yeats, P. A. and J. M. Bowers, 1982. Discharge of metals from the St. Lawrence River. *Can. J. Earth Sci.*, **19**: 982-992.

---

Revision accepted April 28, 1992