POSSIBLE FUNDAMENTAL SOURCES OF DISSOLVED IRON IN TERRESTRIAL ENVIRONMENTS: THEIR MECHANISMS, PRESUMED ANTHROPOGENIC IMPACT, AND RESEARCH NEEDS.

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INTRODUCTION

Iron is essentially insoluble in lands, but there are three particular situations in the soil systems through which it is solubilized. Generating mobile and labile iron forms, they probably act as principal terrestrial agents to export the iron available to oceanic organisms. A perspective of such possible iron sources in lands, including anthropogenic impacts, is presented here chiefly from the knowledge of soil taxonomy. Based on this backgrounds, a research strategy effective to the present project is provided.

1. THE MOST FUNDAMENTAL SOURCE OF FE TO THE OCEAN

Considering terrestrial sources of Fe to the ocean, we should firstly remember that iron is not necessarily scarce at all in the earth's crust. Rather, Fe is the third most abundant component in the continental crust; its average iron content is as high as 4.3%.

A considerable amount of sediments are exported to the ocean by river flows. The flux of sediment has been measured for world major rivers, where a tendency exists that the annual flux is large in areas at lower latitude and with plentiful rain but small in higher latitudes (Fig. 1). The total mass export via suspended materials by world rivers is estimated at 16.2×10^{15} g/yr (Tamrazyan, 1989). Adopting the above Fe content in the continental crust of 4.3%, the total river export of Fe in the form of soil particles is calculated as 0.70×10^{15} g/yr.

The mass movement, largely driven by the hydrological cycle on the earth, exerts a mechanical action to make the shape of earth's surface flat. The fact that the earth's surface is nevertheless fairly rough (ranging from +9000m to -11000m against the sea level) implies that the amount of mass export due to river suspended particles as well as aeolian dust to the ocean is approximately balanced by the mass production by mountain-making activities. For instance, it is little doubt that, without this activity, the earth would have had much more flat surface. Thus, iron export through river sediments is an inevitable and the most fundamental process to provide iron to the ocean, which could be recognized to have a tectonic cause in an ultimate sense.

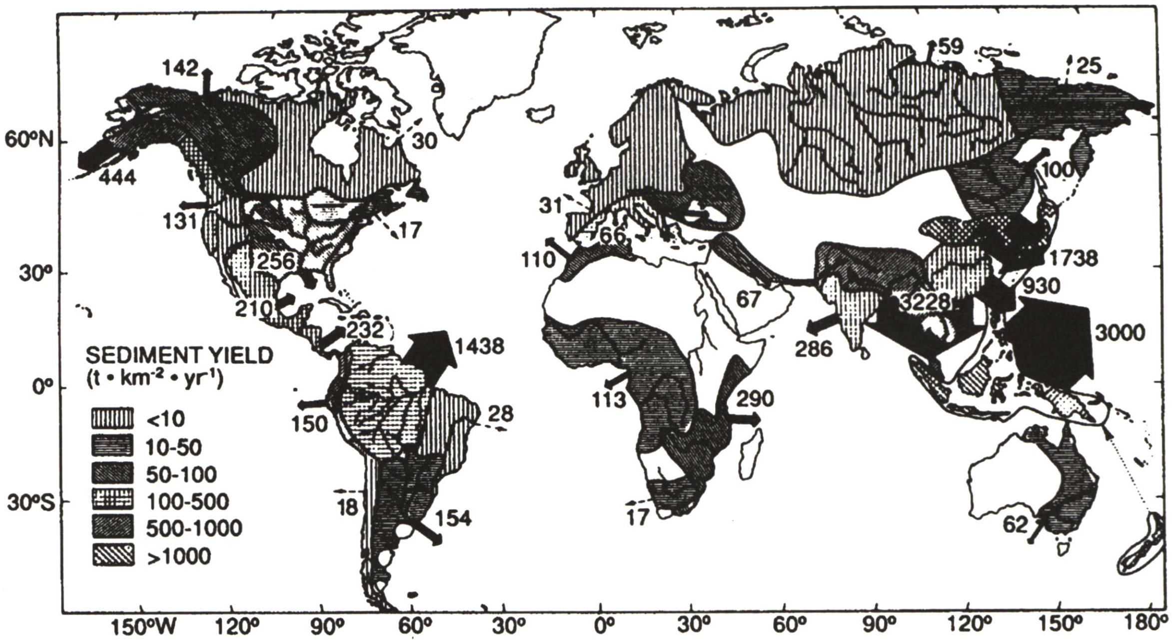

Fig. 1 Annual sediment flux from world rivers. (Milliman and Meade, 1983)

2. Presumed dissolved iron sources in lands derived from soil taxonomical knowledge

Because almost all of Fe in suspended particles should sink just as littoral and pelagic sediments, little of such particulate Fe transported through riverine sediments likely serves as "nutrient" to the oceanic ecosystems. Consequently, bio-available Fe for oceanic organisms may be mostly indebted to the iron present as dissolved (or labile) forms in river waters.

However, iron is basically the least mobile element among the major components in most soils. It is known that the elements susceptible to dissolution and leaching loss to rivers are in the following order:

$$Ca > Na > Mg > K > Si > Fe > Al.$$

Such a difference in the tendency of elemental dissolution is actually responsible for the increase in Fe content with an increase in the soil age and the degree of weathering. In contrast, three kinds of possible iron dissolution processes are suggested in lands from the knowledge of soil taxonomy. Three soil types that could be the source of dissolved iron are described in the following.

(1) HISTOSOLS

The first one is a soil type classified as Histosols in the soil taxonomy, which is characteristic of organic matter accumulation. Elevated organic matter content in this soil type, most typically known as peat, is caused by incomplete decomposition of plant debris under waterlogged conditions (wetlands).

It is often observed that the water in wetland areas has high DOC concentration derived from humic substances. Table 1 compares total iron concentrations between waters having different DOC levels (Kortelainen, 1993). The data show not only that Fe concentration is generally elevated in these wetland areas, but that its level is accompanied with DOC contents. Higher Fe concentrations associated with DOC suggests that Fe dissolution is closely linked with the formation of humic substances, in consistent with high stability of iron-organic complex. Wetland ecosystems have much higher DOC levels than any other aquatic environments (Fig. 1). 'Marsh' is a wetland type with little peat accumulation, but the mean DOC concentration amounts to 15 g/m^3, while in 'bog', where a typical peat accumulation is found, the DOC level averages as high as 30 g/m^3. It is thus highly likely that the region having Histosol soils could act as a prominent source of dissolved Fe, most of which is probably present in organic-bound forms.

Table 1 Comparison of Fe concentration in lake water between different DOC levels. (Data from the Finnish lake survey; Kortelainen, 1993)

	TOC <10g m^{-3} (n=397)	TOC >10g m^{-3} (n=580)
Total Fe (mg m^{-3})	140	740

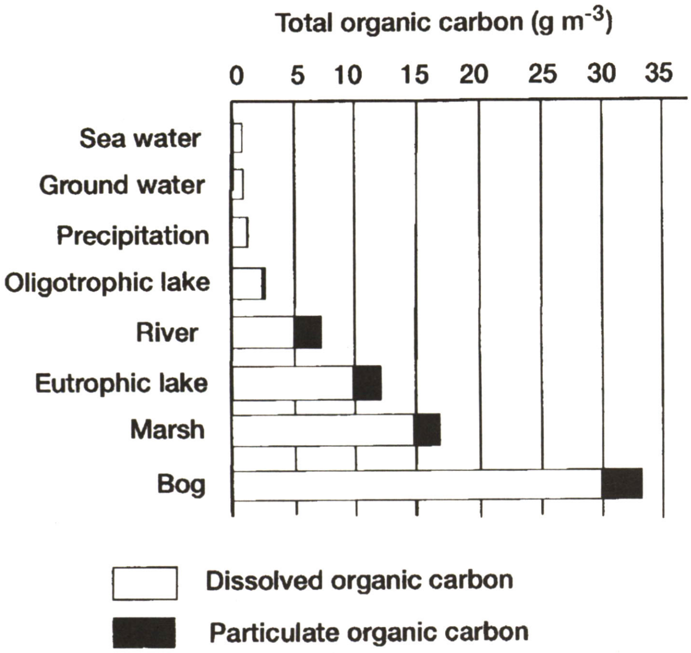

Fig. 2 Approximate organic carbon concentration in natural waters. (Thurman, 1985)

(2) GLEYSOLS

Gleysols occurs where groundwater level is high. The word "gley" is derived from Russia, having a meaning of muddy soil. Oxygen-limited condition due to water saturation allows insoluble ferric iron and manganese oxides in the soil to be reduced to soluble ferrous iron and Mn^{2+}. Part of them may be leached away from the soil to groundwater. As a result, the soil below a water-saturated depth shows blue-gley color typical of this soil type. Thus, it is likely that soluble reduced Fe^{2+} may be discharged from this type of soil. Reduced Fe^{2+} is immediately re-oxidized to insoluble iron oxides under well-oxygenated conditions. Nevertheless, this soil type is worth noting as a possible source of Fe to the ocean because labile forms of Fe at any rate are possibly discharged from the area of this soil type. Since groundwater level is an important factor, this soil type is usually found in lowlands in alluvial plain (e.g., in paddy fields). Such a topographical situation appears common in the lower Amur Basin.

(3) PODSOLS

Podsols, the word also came from Russia, is a well-known soil type which is distributed in cold regions worldwide. Two typical features exist in Podsols. One is the presence of "albic" horizon, where Fe and Al in soil are leached out to turn this horizon whitish. Second is the presence of "spodic" horizon, where Fe and Al leached from the above layer are deposited to look dark reddish-brown in color. Podzolization is particularly intense in boreal and cool temperate forests. The dissolution of Fe and Al in soil is caused by organic acids: large quantity of fulvic acids is produced through incomplete decomposition of litter from coniferous trees which are dominant in these climates. Thus, it is possible that cold climate can also be a vital factor contributing to podzolization.

As far as I aware, there appear limited data available to show dissolved Fe concentration in rivers for districts of this soil types. But the data shown in Tab. 2 indicate that river waters in Taiga forest (a typical vegetation for podosols) have a high DOC concentration of 10 g/m^3. Provided that this result is generally applicable for such regions, and DOC concentration has some relevance to iron dissolution in this case as well (e.g., via some leachate from albic horizon), it is expected that podsols could act as a source to discharge elevated concentrations of dissolved iron.

Table 2 Relatively high DOC concentration observed for rivers in "Taiga" regions. (Thurman, 1985)

Climate	DOC ($g\ m^{-3}$)
Arctic and alpine	2
Taiga (Boreal forests)	10
Cool temperate	3
Warm temperate	7
Arid	3
Wet tropics	6
Swamps and wetlands	25

3. Research needs and proposed strategy

Based on the knowledge of soil taxonomy as above, terrestrial release of dissolved (or labile) iron is expected from three kinds of situations: soil systems showing "Histozoic (peaty)", "Albic (podzolizing)", and "Gleying (Fe reducing)" features. What is important to note concerning this subject is that these soil types are just a static concept, which is established in the scope of soil classification and formation (pedology). Little information may be available regarding to their dynamic aspects at present. Thus, what is to do in this project is to understand the implications of such soil features in the context of biogeochemical cycling of Fe.

Each of the three soil types as above is formed in association to either water regimes arising from landscapes or a climatic cause. Accordingly, the research objectives also include interests in understanding a possible significance of boreal climate and topographic feature (i.e., lowlands or wetlands) for terrestrial iron biogeochemistry.

Second research need lies in the anthropogenic effects on the above matters. It is important to elucidate two aspects. Vast areas of wetlands have been and will be reclaimed by drainage for agricultural purposes especially in the China side of the Amur Basin (Sanjian Plain). It is highly likely that drying due to drainage of wetlands will result in a considerable decline of iron dissolution because of oxygenation of the soil. It is therefore needed to study both the intensity (how it has been changed) and the extent (how widely it is occurring) of such a possible suppression of Fe dissolution. Nutrients release due to organic matter decomposition is also worth noting. Second anthropogenic effect is related to temperature rise due to global warming. Pronounced increase in temperature is expected in near future, particularly in higher latitudes. According to a model adopted in Intergovermental Panel on Climate Change (IPCC, 2001), for instance, the predicted temperature rise from 1961-1990 to 2071-2100 amounts to about 8 °C around the Amur Basin. Information on the effects of such warming on ecosystem cyclings is limited and accordingly quite obscure. Nevertheless, a possibility exists that this might also exert a considerable influence on iron biogeochemistry, provided that podsolization is associated with cold climate.

The research strategy on the basis of the above information is depicted as follows (Fig. 3). Essentially, it is of prime importance in the 'terrestrial' group of the present project to relate quantitatively the dynamic property of iron biogeochemistry, which could be known from river studies, to the static property known from soil studies. The former includes an observation of river water chemistry to make clear where and how much iron is discharged. In this observation, Fe concentrations, in the forms of both particulate/dissolved and inorganic/organic, and other chemical components should be measured in an appropriate range of tributaries of the Amur basin. For the study on the static property, soil observations at several representative sites help to investigate the mechanisms by which iron concentration is controlled. The third stage is to make a scaling up by correlating these data with the GIS information on the regional distributions of soil, vegetation or else. The synthesis of these three phases could enable us to evaluate quantitatively and predict the iron export from the Amur Basin to the ocean, including anthropogenic impacts on them such as land use change due to agricultural activities and global warming.

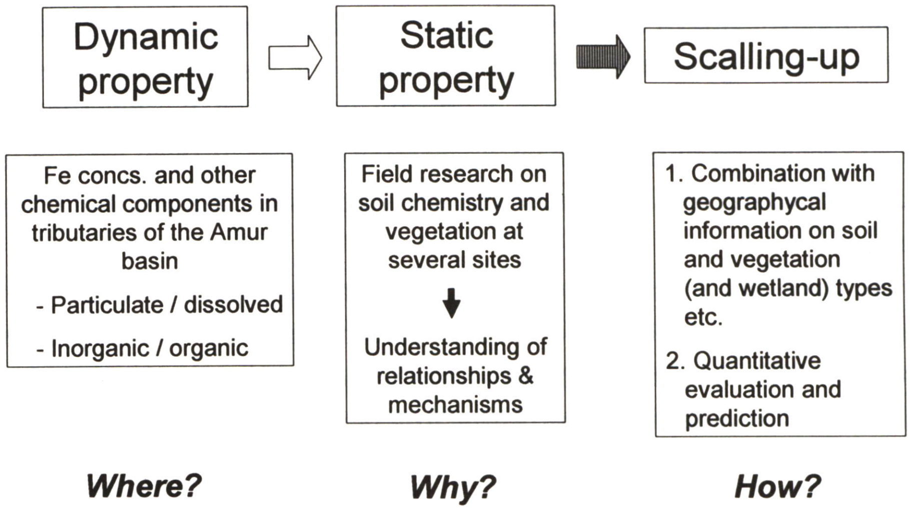

Fig. 3 Schematic diagram of proposed basic research strategy

REFERENCES

IPCC (2001): Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change, Houghton, J.T. et al. (eds.), Cambridge University Press, 881pp.

Kortelainen P.(1993): Contribution of organic acids to the acidity of Finnish lakes. PhD Thesis, University of Helsinki. Publ. Wat. Envir. Res. Inst. **13**, 1-48.

Milliman J.D. and Meade R.H.(1983): World-wide delivery of river sediment to the oceans. Journal of Geology, **91**, 1-21.

Tamrazyan G.P.(1989): Global peculiarities and tendencies in river discharge and wash-down of the suspended sediments-the Earth as a whole. Journal of Hydrology, **107**, 113-131.

Thurman E.M.(1985): Organic geochemistry of natural waters. Dordrecht, Martinus Nijihoff, 489.