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CHARACTERIZATION OF HUMIC SUBSTANCES DEPOSITED ON THE BOTTOM OF DAM RESERVOIR AND THEIR EFFECTIVE UTIILIZATION [*]

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1. INTRODUCTION

On the bottom of dam lakes, fallen leaves and timbers are input into the lake from the upper reaches of the river, and deposition of such organic materials can result in producing sediments including humic substances (HS). This leads to one of reasons for the reduction of active storage of the dam lake. However, HS that

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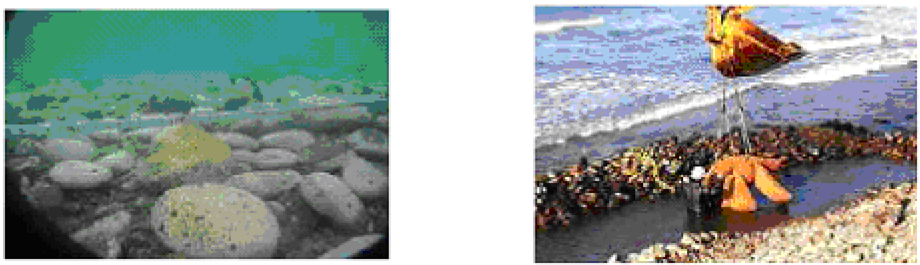
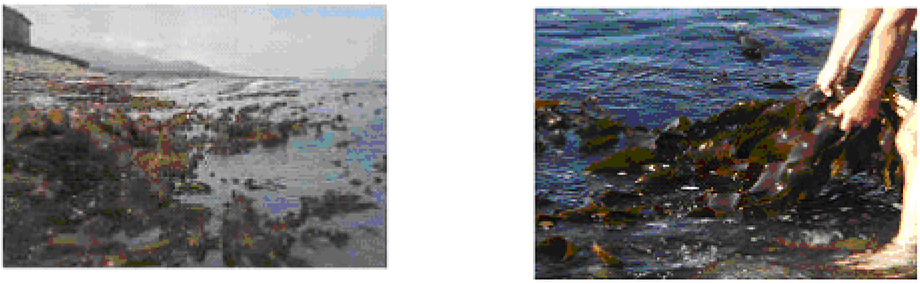
[*] *Caractérisation et utilisation efficace des substances humiques déposées sur le fond des barrages-réservoirs*

binds to Fe(II) can form stable iron-humates (Fe-HS), and those may be deposited into the bottom of dam lakes. We demonstrated that such Fe-HS were effective in recovering the vegetation on the areas of barren ground in the sea of Japan (Photo 1).



Before fertilizing (May, 2004)

Firtilization of HS and iron-containing waste (May, 2004)



Growth of the sea tangle at Shaguma coast (June, 2006)

Growth of the sea tangle at Shaguma coast (June, 2007)

Photo 1

Demonstration at Shaguma coast in Hokkaido, Japan

Expérience sur la côte Shaguma à Hokkaido, Japon

Surveys of potentiality for depositing Fe-HS in the bottom of dam lakes and development of technologies for supplying Fe-HS to rivers and coast are important from the ecological point of view. Applications of iron-humate depositing on the bottom of dam lakes to their supply in rivers and coastal areas may be a method for supplying the nutrients that can mimic natural environments, and this can be utilized to recover and increase resources of fishery. In addition, fixation of CO_2 by the growth of seaweeds can contribute to the suppression of global warming as well as increase of life-time for dams. To evaluate the potentiality for applying the sediments including Fe-HS on the bottom of dam lakes, we analyzed the contents of iron-humate in the sludge.

2. INVESTIGATIONS OF IRON-HUMATES ON THE BOTTOM OF DAM LAKES

During 2006 – 2008, the present study was carried out at Ainumanai dam (Hokkaido Electric Power Co., inc.) that was 76-ages at Hokkaido and Dorobe dam (Tokyo Electric Power Co.,Inc) that was 44-ages at Nikkou (Fig. 1).

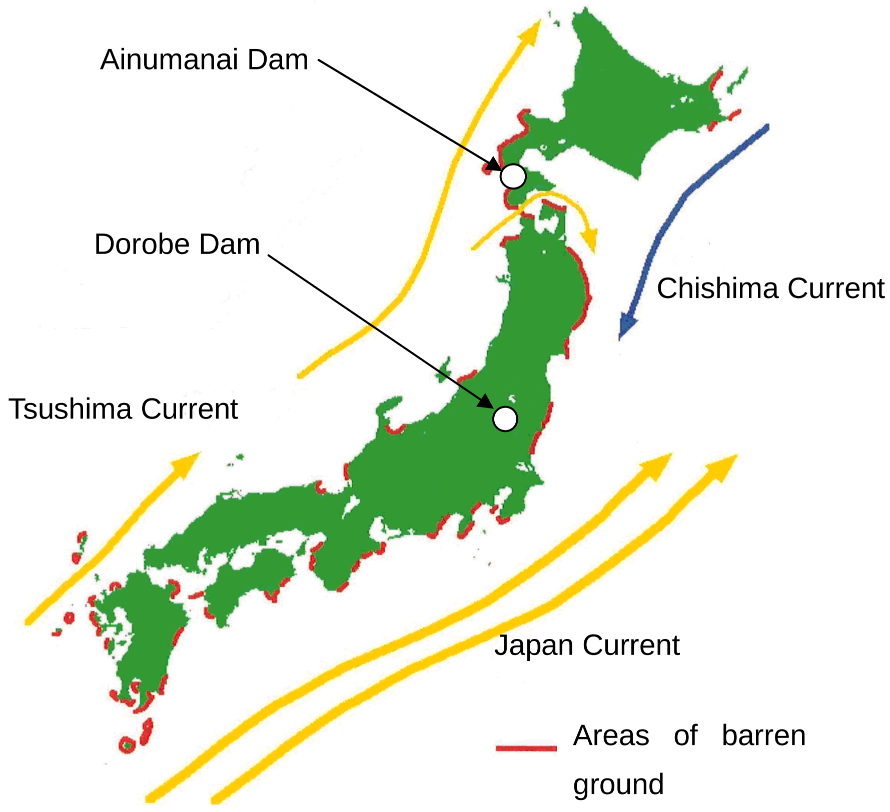


Fig. 1
Dam locations in Japan
Localisation des barrages au Japon

2.1. INVESTIGATIONS OF IRON-HUMATE AT AINUMANAI DAM IN 2006

2.1.1. Sampling and Pretreatment

In the present study, 3 sediments were sampled using a grove sampler, and sandy and organic soils near the dam lake were sampled (Fig. 2 and Table 1). Samples were stocked in freezer at –10°C and freeze-dried. The dry samples were pulverized using a pestle and motor, and filtered through a stainless-steel sieve (0.22 mm). Particles less than 0.22 mm in size were tested.

Table 1
Sampling stations at Ainumanai dam

Samples	Sampling Areas	Sampling Date
CTL-1	Sandy soil near the river	June 29, 2006
CTL-2	Organic soil on the lake side	June 29, 2006
St. 1	Sediment	July 21, 2006
St. 2	Sediment	July 21, 2006
St. 11	Sediment	July 21, 2006

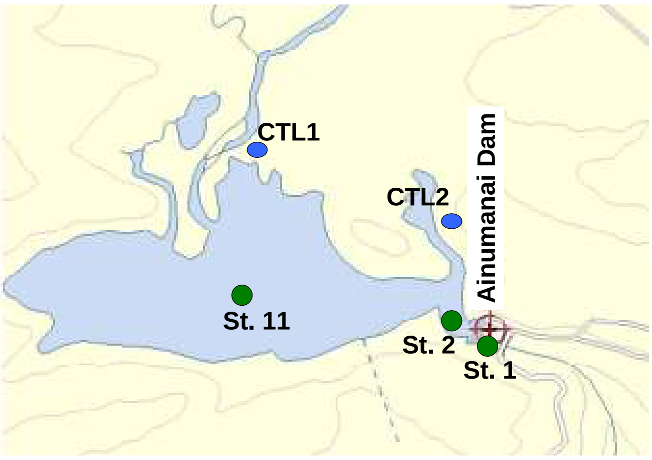


Fig. 2
Sampling stations at Ainumanai dam
Stations d'échantillonnage au Barrage de Ainumanai

2.1.2. Analyses of Samples

HS were extracted and analyzed by a method according to the International Humic Substances Society [1]. Inorganic elements in the samples (Fe, Al, Mn, Ca and Si) were determined by means of ICP-AES after the alkali fusion. The iron species in samples were analyzed using a sequential extraction method by Yuan et al. [2]. Fig. 3 shows the scheme for the sequential extraction of the sample, and the fraction of C corresponds to Fe-HS.

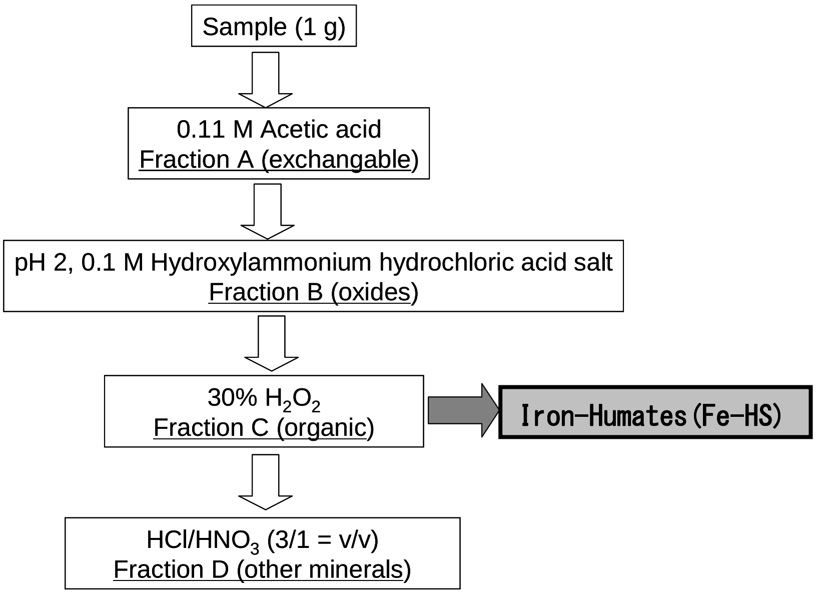


Fig. 3

Scheme for sequential extraction method

Schéma de méthode d’extraction séquentielle

The binding sites of iron in HS have been known to be carboxylic acids and phenolic hydroxyl groups. Thus, such acidic functional groups in humic acids (HA) were determined by the $Ba(OH)_2$ and $Ca(CH_3COOH)_2$ methods [3]. In addition, molecular weights of HA were measured using size exclusion chromatography [4]. Elemental composition and contents of amino acids were analyzed at the Center for Instrumental Analysis at Hokkaido University, Sapporo, Japan.

2.1.3. Results and Discussion

(1) Contents of HS in Samples

Concentrations of total organic carbon (TOC) for HS and fulvic acid (FA) fractions were determined and their subtractions corresponded to the TOC of HA. Percents carbons of HS, HA and FA fractions were calculated from contents of total organic carbon in the samples (Table 2).

Table 2
Percentages of HS carbons to total organic carbon in the samples.

Samples	%C	HS-C（%）	HA-C（%）	FA-C（%）
CTL-1	0.59	16.4±1.4	6.2±0.6	10.2±0.8
CTL-2	3.16	48.4±7.5	30.2±6.7	18.3±0.7
St. 1	6.18	45.0±1.3	30.0±1.1	15.0±0.2
St. 2	5.02	39.8±1.3	26.9±0.4	13.6±0.1
St. 11	4.95	29.6±1.1	18.9±0.9	11.0±0.5

The contents of HS were larger in CTL-2 and St. 1. The carbons as HS were smaller in CTL-1 and St. 11, because they were relatively sandy soil. The atomic ratios of FA to HA were in the range of 0.5 – 1.6, suggesting that half of HS is FA fraction. Although the FA/HA for CTL-1 was the highest value (1.6), HS carbons were the lowest.

(2) Analyses of Iron

The average content of iron in soils has been known to be 4.7%, and the iron contents in our samples(3.5 – 5.6%) were apparently similar to this value (Table 3). Although total iron contents in samples were higher in CTL-1, CTL-2 and St. 11, St. 1 and St. 2 on the vicinity of dam showed lower values. This may be attributed to the fact that iron(III) oxides or carbonates in the sediments are dissolved into aquatic environments as iron(II) form under anaerobic conditions. This hypothesis can be supported by the fact that contents of Mn in land soils (CTL-1 and CTL-2) were significantly higher than those in sediments (St. 1 and St. 2). If iron would be remained in the sediments, iron should bind to soil organic matter, such as HS. Thus, speciation analyses of iron in samples should be required. Fig. 4 shows the results of speciation analyses of iron in soils and sediments. As shown in Fig. 4, rate of fraction C that corresponds to Fe-HS increased as following order: St. 11 < St. 2 < St. 1. This suggests that Fe-HS are accumulated in the sediment on the vicinity of dam. This can be attributed to the fact that HSs can move easily and be deposited on the vicinity of dam, although heavy materials such as minerals are difficult to move. If lake would be aerobic conditions, oxidation of HS to CO_2 could result in the decrease of HS contents. Therefore, anaerobic conditions contribute to the accumulation of HS in the sediments on the vicinity of dam.

Table 3
Inorganic elemental composition of soils and sediments in 2006 (wt %)

Samples	Fe	Al	Ca	Mn	Si
CTL-1	4.89±0.29	9.79±0.20	4.42±0.31	0.10±0.01	23.9± 0.7
CTL-2	5.56±0.37	9.67±0.09	3.14±0.38	0.11±0.00	17.4± 0.4
St. 1	3.63±0.09	8.17±0.30	2.44±0.06	0.06±0.00	20.4± 0.3
St. 2	3.54±0.09	8.37±0.09	2.53±0.01	0.06±0.00	21.2± 0.6
St. 11	4.21±0.02	9.21±0.14	3.55±0.01	0.08±0.00	20.9 ±0.2

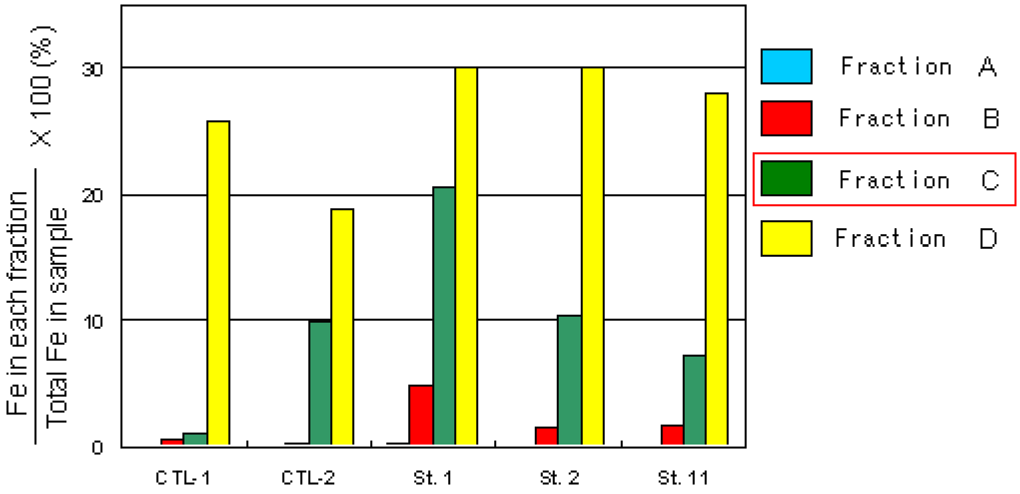


Fig. 4
Rates of Fe species to total Fe in samples collected in 2006
Taux des diverses espèces de fer par rapport au fer total dans les échantillons prélevés en 2006

(3) Analyses of HA

Elemental compositions of HA, which were extracted from soil and sediment samples, are summarized in Table 4. Carbon contents of HAs were approximately 50%, except for the sandy soil, CTL-1. In addition, contents of H, N and O of HA were not different significantly between samples. However, S content for St. 1 was the largest value of all samples. This suggests proceedings of anaerobic fermentation by sulfur bacteria at St. 1. It has been known that iron-sulfur complexes can distribute in anaerobic bacteria and algae in aquatic environments [5]. Thus, the largest value for Fe-HS (fraction C) may be due to iron-sulfur complexes in HA.

Table 4
Elemental compositions of HA

Samples	%C	%H	%N	%O	%S	%ash
CTL-1	42.89	4.21	3.44	46.28	0.58	2.65
CTL-2	51.93	5.34	4.03	36.62	0.62	1.46
St. 1	49.42	5.25	4.34	36.67	1.36	2.96
St. 2	48.74	5.17	4.22	38.83	0.46	2.58
St. 11	49.13	5.13	4.07	38.12	0.74	2.81

The weight average molecular weight (M_w) and number average molecular weight (M_n) of HA are summarized in Table 5. The HA with higher humification results in lowering the molecular size. The M_w for St. 1 was significantly smaller than those for other HA. This supports that humification processes are enhanced on the vicinity of dam.

In general, binding sites of Fe in HA are known to be carboxylic acids and phenolic hydroxyl groups. Table 6 shows the acidic functional groups in HAs. These values were not different significantly between samples. Thus, the major factor for the highest Fe-HSs in St. 1 may be attributed to the sulfur-containing groups in HA rather than acidic functional groups.

On the other hand, HS consist of amid acids and peptides as well as lignin-derived phenolic compounds [6]. Therefore, contents of amino acids were analyzed, after degrading via hydrolysis with HCl. The content of total amino acids was the largest in St. 1. Thus, such the amino acid components in HAs may serve as strong complexation sites to Fe.

Table 5
Weight average (M_w) and number average (M_n) molecular weights of HA.

Samples	M_w	M_n
CTL-1	41062±2908	2994±306
CTL-2	35490±1221	4242±330
St. 1	39855±7285	3734±189
St. 2	50820±3807	4005±170
St. 11	42966±2756	3865±138

Table 6
Results of acidic functional group analyses for HA (meq g^{-1} C).

Samples	Total acidity	COOH	Phenol-OH
CTL-1	8.1	2.6	5.5
CTL-2	13.5	4.8	8.7
St. 1	13.3	5.0	8.3
St. 2	18.7	5.0	13.6
St. 11	14.2	3.8	10.5

2.2. INVESTIGATIONS OF IRON-HUMATE AT AINUMANAI DAM IN 2007

2.2.1. Objectives of surveys

To confirm the tendency that Fe-HS are accumulated to the sediment on the vicinity of dam, speciation of Fe and HS in the soil and sediment samples were analyzed in 2007. The soils and sediments were sampled in July 6, 2007.

2.2.2. Iron complexing ability and structural feature of HS

In 2007, analysis of CTL-1 was not carried out, because HS contents were very small. Fe, Al, Mn, Ca and Si contents in the samples are summarized in Table 7. For sediment samples, Fe contents were almost similar to those analyzed in 2006, and the highest value was observed in St. 11, the center of the dam lake. Fe content in soil sample (CTL-2) was smaller than those for sediment samples (St. 1, 2 and 11).

Table 7
Inorganic elemental composition of soils and sediments in 2007 (wt %)

Samples	Fe	Al	Ca	Mn	Si
CTL-2	3.02	6.73	3.05	0.091	21.4
St. 1	3.12	7.77	2.46	0.074	19.8
St. 2	3.44	8.39	2.53	0.067	21.3
St. 11	4.30	9.61	4.44	0.084	22.3

The results of the speciation analyses of Fe are summarized in Table 8. Although fraction D was the largest in all samples, rates of fraction C corresponding to Fe-HS were in the range of 0.64 – 7.65%. Fig. 5 shows the comparison of fraction C of the samples in 2006 and 2007. Rates of fraction C in

2007 were significantly smaller than those in 2006. One of reasons of this may probably be the input of sandy soils because of the heavy rain before sampling date. However, the tendency that the highest fraction C is observed on the vicinity of dam was consistent with the results in 2006.

Table 8

Rate of Fe species to total Fe in samples collected in 2007（wt%）

Samples	Fraction A	Fraction B	Fraction C	Fraction D
CTL-2	< 0.0013	0.49	7.65	8.74
St. 1	0.19	4.10	4.77	47.81
St. 2	0.26	2.60	2.75	39.68
St. 11	0.14	1.82	0.64	50.14

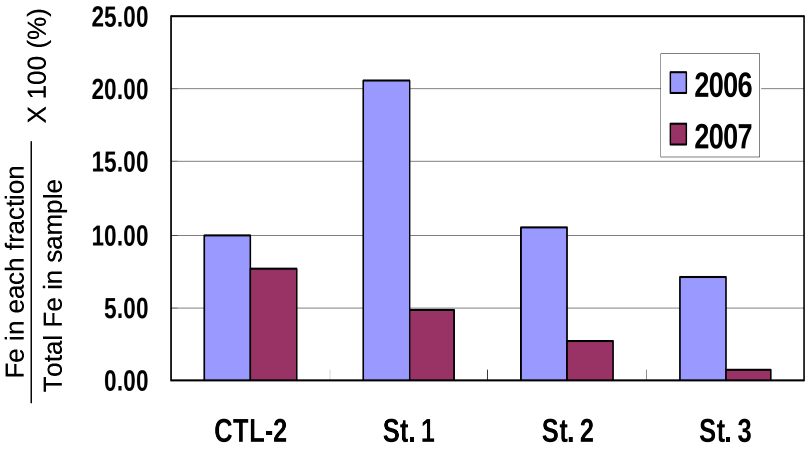


Fig. 5

Comparison of fraction C for samples in 2006 and 2007

Comparaison de la fraction C dans les échantillons de 2006 et de 2007

2.2.3. Monitoring data of lake water and sediments and analysis

The results of monitoring gas concentrations and redox condition in lake water and sediments at St. 1 to St. 11 are summarized in Table 9. In the sediments around St. 1, high concentration of H_2 and CH_4 was observed. This suggests that the activity of anaerobic microbes is relatively high in the sediments due to anaerobic condition. On the other hand, the environment at St. 11 is assumed to be more aerobic condition, because of very small concentration of H_2 and low activity of anaerobic microbes. According to the observation of water column, higher concentration of H_2 was found just above the position of bottom at St1-2.5m, although the concentrations of CH_4 did not so change in vertical direction of water column.

Table 10 represents the results of water quality and mentoring data for measuring contents of lake water and sediments at St. 1 to St.11. Monitoring contents are dissolved oxygen (DO), hydrogen-ion concentration (pH), electric conductivity (EC), oxidation reduction potential (ORP), and temperature (T). Water temperatures at surface and bottom of lake were 20.9 ^{o}C and 15.6 ^{o}C, approximately 5 ^{o}C differences between surface and bottom of water column. DO at surface of water was almost 100 %, meanwhile DO at bottom of lake water was 6.9 %, indicating the semi-anaerobic environment around bottom of water column. Therefore, ORP of pore water in sediments St.2. was –113 mV, showing a little aerobic condition compared to St. 1. The data at St. 2 were consistent with the tendency of St. 1, but much aerobic condition was observed at St. 11 as DO in the sediments was 80 %.

According to the result of macroscopic observation for three samples of sediments, large amount of organic matters was revealed at St. 1 where HS could be actively formed. The sample of sediments at St. 2 contains organic matters and sandy sediments, and small amount of organic matters was found in sandy sediments at St. 11. These results of observation support well with those of monitoring water and sediments, DO, ORP and other contents.

Table 9
Results of monitoring gas concentrations in water and sediments.

Samples \ Analyte		H_2 gas		CH_4 gas	
		Average (nmol/ml sed)	Standard deviation	Average (nmol/ml sed)	Standard deviation
Sediments	St. 1	19.9	32.2	115.7	90.3
	St. 2	14.4	22.8	5.7	1.7
	St. 11	0.4	0.1	61.9	31.9
Waters	St. 1-surface	0.3	0.1	72.2	12.6
	St. 1-2.5m	796.1	1339.4	68.1	4.4
	St. 1-bottom	32.6	16.3	74.5	4.4
	St. 2-bottom	36.8	17.6	46.7	8.8
	St. 11-bottom	20.7	—	74.7	—

The progress of HS formation was strongly suggested in the sediments of dam and around bottom of lake. The position of St. 1 where leaves and organic substances were stacked for a long while showed relatively anaerobic condition, due to microbiological activity of oxygen consumption. As the concentrations of H_2 and CH_4 are high, it can be considered that the process of HS formation is proceeding at the position.

Table 10
Results of measurement for samples of water and sediments.

Samples	Depth (m)	DO (%)	pH	EC (mS/m)	ORP (mV)	T (°C)
St. 1	0	99.0	6.47	8.6	183	20.9
	1	82.9	6.77	8.8	158	20.0
	2	75.8	7.17	8.8	164	17.3
	3	74.0	7.15	8.9	160	16.9
	4	59.5	7.16	8.7	166	16.7
	5	25.8	—	8.7	—	15.8
	5.4	6.9	7.40	8.7	168	15.6
	sediment	—	—	—	-135	—
St. 2	0	96.3	7.13	9.3	134	20.1
	1	86.3	—	9.2	—	18.4
	2	80.5	—	9.1	—	17.2
	3	73.0	—	9.0	—	16.9
	3.8	65.3	6.98	9.0	—	16.6
	sediment	—	—	—	-113	—
St. 11	0	97.4	6.87	5.4	118	20.7
	1	83.7	—	9.4	—	18.2
	1.5	80.3	6.81	9.1	124	17.6
	sediment	—	—	—	-71	—

Microbial analysis was conducted by using a method of PCR (polymerase chain reaction) and cloning for samples including HSs and microbes, based on the aspect that organic and HSs are one of the products of microbiological activity. In this analysis samples at St. 1 were used because of very low DO and more anaerobic condition. Four kinds of microbes, such as *Actinobacteria* and microbes degrading organic substances, were found. In the microbial community, anaerobic heterotrophs and *Actinobacteria* is considered to be very active to utilize organic substances, which accelerates the formation of HS in sediments.

The results of observation and monitoring of lake water and sediments reveal some evidences that the active formation of HS proceeds at the bottom of lake, especially in the sediments and high concentrations of H_2 and CH_4 are present due to the anaerobic fermentation around the bottom of lake. In addition, large amount of HA produced in the lake by the activity of anaerobic microbes might be supplied to the sediments and the environment of lake water.

2.2.4. Investigation and analysis of Fe-HS in dam

We sampled water at river and lake that flow in dam and analyzed the quantity of Fe-HS such as iron fulvates because of the understanding the relationship between the scientific character of lake sediment (Ainuma Lake) and the capability of production of iron complex compound (Fig.6).

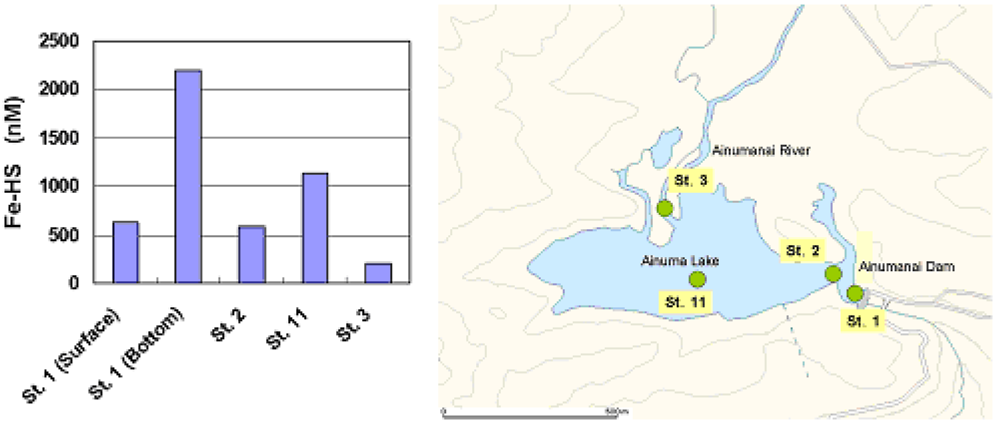


Fig. 6

Concentrations of iron-humates in river and reservoir waters at Ainumanai dam

Concentrations d'humates de fer dans les eaux de la rivière et du réservoir au Barrage de Ainumanai

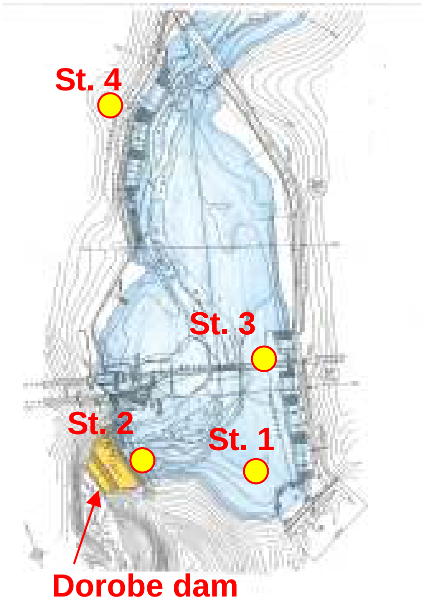
From the analysis results of the Fe-HSs concentration at each sampling point in lake (St. 1, St. 2 and St. 11), the concentration of St. 1(Surface) and St. 2 point were almost the same value and that of St. 11 was the highest value. And the Fe-HS concentration in St. 3 (Ainumanai River) was about 1/3 of that of surface water in lake. Moreover, from the analysis results of concentrations of both water surface and the bottom of lake, the latter concentration was 3.5 times as high as the former. Moreover, we confirmed that the analysis results in lake were very high value compared with the concentration (several tens of nM) of Fe-HS in water at sea desertification area.

2.3. INVESTIGATIONS OF IRON-HUMATE AT DOROBE DAM IN 2008

We investigated the characterization of Fe-HS in sediments at Ainumanai dam only. To confirm that sediments on the bottoms of dam lakes include higher levels of Fe-HS, another field should be examined. Therefore, we sampled the sediments at Dorobe dam (Nikkou, Japan) in February 1, 2008.

2.3.1. Analyses of iron humates

Fig. 7 shows the sampling stations and notes for soil and sediment samples at Dorobe dam. St. 1, 2 and 3 indicate sediments from the bottom of dam lake, and St. 4 represents the soil sample that was collected near the lake.



● : Sampling stations

St. 1: Sediment on the center of the lake.

St. 2 (upper): Sediment from upstream on the vicinity of dam.

St. 2 (down): Sediment from downstream on the vicinity of dam

St. 3: Sediment on the center of the lake

St. 4: Soil near the dam lake

Fig. 7

Sampling stations at Dorobe dam

Stations d'échantillonnage au Barrage de Dorobe

First inorganic elements in soil and sediment samples were analyzed (Table 11). Fe contents for sediment samples were in the range of 2.47 – 2.93%, and these values were lower than those for sediments in Ainumanai dam lake. However, the level of Fe content in land soil (St. 4) was similar to the Clarke number (4.70%).

Table 11

Inorganic elemental composition of soils and sediments in 2008 (wt%).

Samples	Fe	Al	Ca	Mn	Si
St. 1	2.47	7.53	1.98	0.06	27.16
St. 2 (upper)	2.58	7.17	1.94	0.07	25.18
St. 2 (down)	2.93	7.30	2.03	0.07	27.11
St. 3	2.60	6.90	1.50	0.07	22.13
St. 4	4.96	7.82	3.08	0.12	22.91

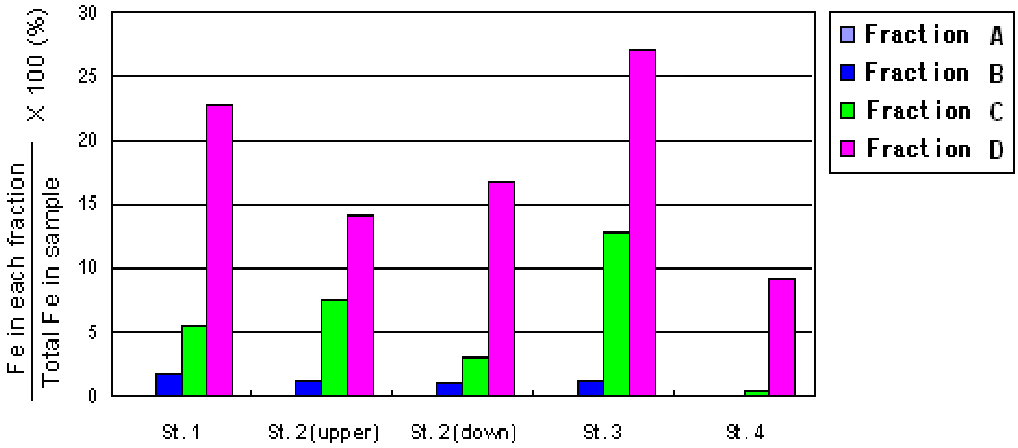


Fig. 8

Rates of Fe species to total Fe in samples collected at Dorobe dam in 2008

Taux des diverses espèces de fer par rapport au fer total
dans les échantillons au Barrage de Dorobe

Speciation analyses of Fe in the samples were carried out according to the method by Yuan et al. [2]. Fig. 8 shows the rate of Fe species to total Fe in the samples. The content of fraction C, corresponding to Fe-HS, for St. 2 (upper) was relatively larger than those for St. 1, St. 2 (down) and St. 4. However, the level of fraction C for St. 3 was the largest of all samples. The contents of HS in the samples are summarized in Table 12. It is difficult to find the relationships between levels of fraction C and contents of HS from the results in Table 12. However, amounts of HS (TOC in the sample (g) X HS-C (%)/100) were clearly higher in St.2 (upper) and St. 3, indicating that these samples include higher levels of HS. Complexation with iron in soils and sediments are depend on the structural features of HS as well as their amounts. Thus, organic functional groups in HS should be analyzed.

Table 12

Rates of HS, HA and FA in the samples at Dorobe dam.

Samples	TOC (g/10g)	HS-C(%)	HA-C(%)	FA-C(%)	FA/HA
St. 1	0.232	18.5	13.8	4.7	0.337
St. 2 (upper)	0.414	17.2	12.7	4.5	0.351
St. 2(down)	0.173	16.2	11.5	4.7	0.408
St. 3	0.855	12.5	9.6	3.0	0.309
St. 4	0.547	21.4	15.6	5.9	0.376

2.3.2. Comparison with the results in Ainumanai dam

1. In Dorobe dam, rates of Fe-HS (fraction C) to total Fe were in the range of 5 – 13%, except for St. 2 (down). These levels were somewhat lower than those observed at Ainumanai dam in 2006 (7 – 21%). Percentages of HSs to total organic carbons in samples for Ainumanai dam were in the range of 30 – 40%, but 13 – 21% for Dorobe dam. Thus, levels of HS contents may influence the levels of Fe-HS.
2. In Ainumanai dam, the level of Fe-HS was the highest on the vicinity of dam lake. However, the level of Fe-HS for St. 2 (upper) on the vicinity of dam was smaller than that for St. 3 in the center of lake. This may probably be due to the hydraulic character of rivers into Dorobe dam.

3. UTILIZATION OF IRON-HUMATES IN SEDIMENTS OF DAM LAKE

We found that Fe-HS were produced and accumulated in sediments on the bottoms of dam lakes. In future, this survey should be continued for the cases of other dam lakes. In the previous demonstration tests at Shaguma coast (Hokkaido, Japan) and Oomura Bay (Nagasaki, Japan), Fe-HS that were artificially prepared from composts and iron-containing wastes (e.g. slug) were effective in recovering the vegetation of barren grounds. Our strategy from the results in the present study is to apply the natural Fe-HS to technologies for recovering the vegetation of barren grounds. Thus, demonstration tests will be carried out at several coasts of barren grounds from 2008.

CONCLUSION

Although the treatment of sediments from dam lakes has been studied, studies on the utilization basing on the chemical analyses seem to be novel. In the present study, we selected old dams and investigated chemical characters of sediments. It was found that organic matter from forest in upstream was deposited on the bottom of dam lakes and large amounts of Fe-HS were accumulated via anaerobic fermentation. These results contribute to environmental remediation and protection as well as prolonging life of dam. Thus, the survey like the present study should be continued for other dam lakes.

Treatments of sediments from dam lakes have been studied. However, utilization of Fe-HS in sediments can be novel current for contributing to recover and protection of natural resources (seaweeds and marine animals). In addition, recovery of vegetation in barren grounds may be effective in fixation of CO_2 to biomass.

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REFERENCES

[1] http://www.ihss.gatech.edu

[2] C. YUAN, J. SHI, B. HE, J. LIU, L. LIANG, G. JIANG, Speciation of heavy metal in marine sediments from the east China sea by ICP-MS with sequential extraction, *Environ. Int.* 20, 769-783, 2004.

[3] M. FUKUSHIMA, Y. TANABE, K. MORIMOTO, K. TATSUMI, Role of humic acid fraction with higher aromaticity in enhancing the activity of a biomimetic catalyst, tetra(p-sulfonatopheny1)porphineiron(III), *Biomacromolecules* 8, 386-391, 2007.

[4] M. SCHNITZER, S.U. KHAN, *Humic Substances in the Environment*, Dekker, New York, pp 37-43, 1972.

[5] R.W. HAY, Bio-Inorganic Chemistry (Japanese version, translated by J. Oota, T. Takeuchi, K. Murofushi), Ohmu Publisher, Tokyo, pp.157-166, 1986.

[6] P.-H. HSU, P.G. HATCHER, New evidence for covalent coupling of peptides to humic acids based on 2D NMR spectroscopy: A means for preservation. *Geochim. Cosmochim. Acta* 69, 4521-4533, 2005.

SUMMARY

This study investigates the potential use of sediments from dam reservoirs, these being problematical wastes in Japan. We collected sediment samples from Ainumanai dam (Hokkaido Electric Power Co., Inc.) from 2006 to 2007. Upon chemical analysis, it was found that higher levels of iron-humates (Fe-HS) accumulate within the sediments. It is thought that such iron-humates are the product, resulting from anaerobic fermentation on the dam reservoir bottom, of organic matter from upstream forests. Furthermore, similar levels of Fe-HS were found in such sediments for another dam reservoir (Dorobe dam, Tokyo Electric Power Co.,Inc.).

On the other hand, Fe-HS can serve as nutrients for seaweed in coastal environments. Recently, we demonstrated in [pilot] experiments along the

Shaguma coast (Hokkaido, Japan) and Oomura Bay (Nagasaki, Japan) that Fe-HS are effective in recovering vegetation from barren grounds. Although artificial Fe-HS were used for these experiments, we plan to include the sediments encompassing Fe-HS from dam reservoir upon demonstration concerning restoration of vegetation (seaweed) from barren grounds in coastal areas, especially along the Sea of Japan.

RÉSUMÉ

Cette étude examine l’utilité potentielle des sédiments de barrages-réservoirs, qui sont des déchets problématiques au Japon. Nous avons prélevé des échantillons de sédiments au Barrage de Ainumanai (Hokkaido Electric Power Co., Inc.) de 2006 à 2007. À l’analyse chimique, il s’est révélé que des taux relativement élevés de humates de fer (SH-Fe) s’accumulent dans les sédiments. Ces humates de fer sont en toute probabilité le produit de la fermentation anaérobie, sur le fond du barrage-réservoir, de matières organiques provenant des forêts en amont. En outre, des taux comparables de SH-Fe ont été découverts dans des sédiments semblables prélevés dans un autre barrage-réservoir (Barrage de Dorobe, Tokyo Electric Power Company, Inc.).

Par ailleurs, les SH-Fe peuvent servir de nutriments aux algues dans les environnements côtiers. Nous avons démontré récemment lors d’expériences [pilotes] le long de la côte de Shaguma (Hokkaido, Japon) et de la Baie de Oomura (Nagasaki, Japon) que les SH-Fe sont efficaces pour rétablir la végétation sur les terres infertiles. Quoique nous ayons eu recours à des SH-Fe artificiels pour ces expériences, nous envisageons d’utiliser des sédiments de barrages-réservoirs incorporant des SH-Fe dans nos expériences futures de régénération de la végétation (algues) sur les terres infertiles des zones côtières, en particulier le long de la mer du Japon.