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Trace Metals in Water and Sediments from Ologe Lagoon, Southwestern Nigeria

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Abstract. The concentrations of trace metals in water and sediment samples from Ologe lagoon located in southwestern Nigeria were investigated. The lagoon is a source of water for domestic, transportation and fishing activities. The water quality characteristics for a period of two years (January, 1997 - November, 1998), and the speciation of metals in the lagoon sediments were evaluated. The lagoon water quality characteristics, with respect to heavy metal contamination, were compared with global averages for freshwater and international water quality standards for drinking water. All elements except iron, were well within the safety limits. Sequential extraction techniques were used to establish the association of the total concentrations of Zn, Cu, Pb, Cd and Mn in the sediment samples with their contents as exchangeables, carbonates, Fe/Mn oxides, and organic and residual fractions. The concentrations of trace metals in the whole sediments were generally below the world-wide background levels. When compared to a number of sediment quality guidelines, the concentrations of trace metals were found to be below the level considered to have the potential to cause biological effects. Pb and Cd were extracted from the residual fraction at values greater than 50%. The metals that were most easily extractable in the samples analysed were Mn and Zn, which posed the highest risk to water contamination. The low level of industrialization in the study area has kept the lagoon relatively free from heavy metal contamination.

Keywords: lagoon sediments, trace metals, water quality, lagoon, sequential extraction, Ologe lagoon, metal speciation

Introduction

Fresh water lagoons are crucial resource for drinking, irrigation, transportation, recreation, fishing, and sheer aesthetic enjoyment. The contamination of soils, sediments, water resources and biota by heavy metals has become a problem of increasing concern due to their toxicity, persistence and bioaccumulative nature (Biney, 1991).

Studies on heavy metals in rivers, lakes, and sediments have received a mojor environmental focus, especially during the last decade (Storelli and Marcotrigiano, 2001; Gray *et al.,* 2000; Grosheva *et al.,* 2000; Aucoin *et al.,* 1999; Bortoli *et al.,* 1998; Zhou *et al.,* 1998; Elbaz-Poulichet *et al.,* 1996; Johansson *et al.,* 1995; Mannio *et al.,* 1995; Biney, 1991; Kakulu and Osibanjo, 1991; Okoye, 1991). Sediments are the principal sinks for aquatic environment, but when the environmental conditions change, sediments can act as a source. The release of trace metals from sediments into the water bodies will depend on the speciation of metals (i.e., metals may be precipitated, complexed and adsorbed, or solubilized) and other factors, such as the sediment-pH and the physical and chemical characteristics of the aquatic system (Narwal *et al.,* 1999; Karczewska *et al.,* 1998; Ma and Rao, 1997; Morgan and Stumm, 1991). Metals may distribute in sediments as exchangeables, carbonate bound, iron-manganese oxide bound, organic matter bound, and residue bound species. The speciation of metals can be evaluated by carefully choosing the extracting solutions and digestion conditions. The speciation is a useful indication for determining the association of the metals in the sediments and as to what extent they may be remobilized into the environment (Forstner *et al.,* 1990), and it is also used for distinguishing the metals of the lithogenic origin from those of the anthropogenic origin. According to Rubio *et al.* (1991), metlas with an anthropogenic origin are mainly obtained in the first extractions, while in the last stage of the process, residual fraction is obtained, corresponding to metals with lithogenic origin.

The present study was undertaken due to the paucity of published data on trace metal contamination in lagoons. Since lagoons support large segments of populations, there are serious concerns regarding the quality of water of the lagoons. The main uses of water in the lagoon are domestic, agricultural (inclusive of livestocks), various industrial activities, aquatic ecosystem support, and for recreational purposes, such as swimming. The major objectives of this study included the determination of water quality characteristics of Ologe lagoon and assessment of the risks associated with the lagoon water contamination by surface sediments, determination of the levels of total extractable trace metals (Cu, Fe, Mn, Cd, Zn, Pb),

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and the fractionation of these metals in the sediments due to their environmental implications. These data may be used as the baseline for future work in the area as well as by those interested in the study of their transfer to man via the food chain.

Materials and Methods

Study area. Ologe lagoon (Fig. 1) is a natural semi-enclosed fresh water body located about 30 km west of Lagos city on the Lagos-Badagry Expressway. Owo river is the major fresh water inlet into the lagoon, which is tapped for drinking water supply by the Lagos State Water Corporation and the lagoon provides a source of living to some inhabitatnts through transportation and fishing activities. The outlet of the lagoon is on a section of the coastline which discharges into the Atlantic Ocean (25 km away). The lagoon is subjected to threats from human activities, among which are open defecation, sand dredging, domestic waste dumping by inhabitants at the banks, and discharge of effluents by Agbara Industrial Estate, housing food, beverages and pharmaceutical industries, into the lagoon, via Owo river.

Water collection and analyses. Water samples were collected from the indicated sampling spots (Fig. 1.), using open water grab sampler equipped with a pull-ring that allowed for sampling at various water depths. Samples were collected in acid-washed polyethylene plastic containers with screw caps and amber glass bottles. Washing procedure for containers was as recommended in the standard methods of analysis for waters and wastewaters (APHA, 1998). For the determination of general parameters, one litre polyethylene bottles were thoroughly washed with detergent and rinsed many times with distilled water. For the metal determination studies, bottles were washed with metal-free soap, rinsed many times and finally soaked in 50% nitric acid for 24 h before final rinse with distilled water. The collected water samples did not contain noticeable suspended materials, the samples were therefore not filtered prior to analyses for water quality constituents.

For metal determination in the lagoon water samples, standard methods for waters and wastewaters were used (APHA, 1998). Concentrated nitric acid (5 ml) was added to each 50 ml of the lagoon water samples in a digestion vessel. Metal levels in the digests were determined with Buck Scientific 200A atomic absorption spectrophotometer and air acetylene flame. All chemicals used were of analytical grade, procedural blanks were analysed under the same experimental conditions used for the water samples investigated. Procedural blanks were used for background correction and other sources of error. Accuracy was assessed by analyzing three replicates of the selected

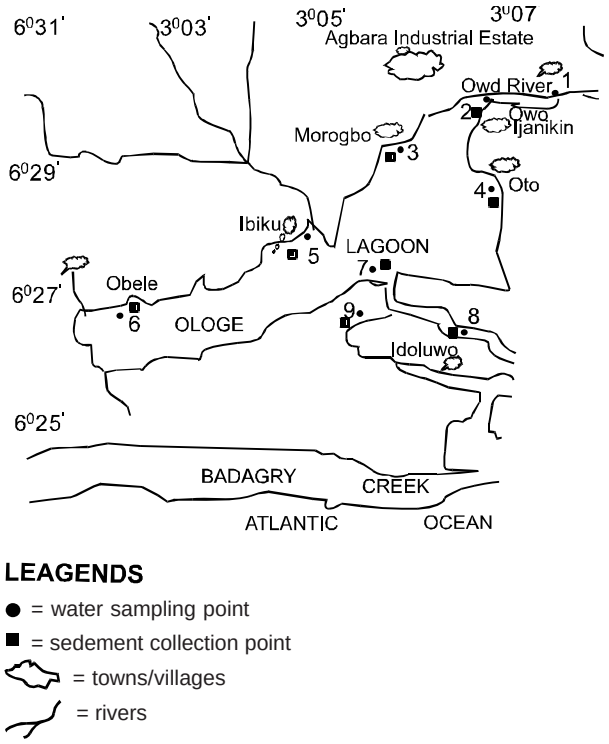

Fig. 1. Map of Ologe lagoon, southwestern Nigeria, and sampling points.

samples yielding standard devations lower than 5% for all the metals. pH of the water samples was taken using a field pH metre (Jenway model 3050 ser. N. 40131), conductivity was measured with conductivity metre (model Mc-1, Mark V). Other water quality parameters, such as chloride and total alkalinity were determined by argentometric and titrimetric procedures, respectively (APHA, 1998). Ammonia, nitrate, phosphate and sulphate were determined spectrophotometrically.

Sediment collection and analyses. Sediment samples (Fig. 1) were collected by scooping, which on collection were packed in polyvinyl chloride (PVC) until arrival in the laboratory (Thomas *et al.*, 1994). The sediment samples were air-dried in the laboratory at room temperature and sieved with a 2 mm mesh. The < 2 mm fraction was selected for chemical analysis. The pH of the sediment was measured in water with a 1: 2.5 soil/solution ratio after equilibration for 30 min (McLean, 1982). The sediment fractions were subjected to a five-step sequential extraction technique (Tessier *et al.*, 1979), with a modified final step. The final step in the sediment extraction was conducted by adopting the method of Gauthreaux *et al.* (1998). The extraction stages employed were as below.

Extraction-1: exchangeable metals. 8 ml of 1 mol dm^{-3} magnesium chloride (pH 7.0) was added to the weighed sediment

fraction in a centrifuge tube, and the sample was shaken for 1 h at a speed of 200 rpm at room temperature.

Extraction-2: metals bound to carbonates. 8 ml of 1 mol dm^{-3} sodium acetate (adjusted to pH 5.0 with acetic acid) was added to the residue from Extraction-1, and the sample was shaken for 1 h under the same conditions as in Extraction-1.

Extraction-3: metals bound to iron and manganese oxides. 20 ml of 0.04 mol dm^{-3} hydroxylamine hydrogen chloride in 25% (v/v) acetic acid was added to the residue from Extraction-2. The extraction was carried out at 96 ± 3 °C for 1 h.

Extraction-4: metals bound to organic matter. First, 1:3 ml of 0.02 mol dm^{-3} nitric acid and 5 mol of 30% hydrogen peroxide, adjusted to pH 2.0 with nitric acid, were added to the residue from Extraction-3, the sample was placed in a waterbath and heated at 85 ±2 °C for 3 h with intermittent agitation. This step was followed by the additon of 3:5 ml of 3.2 mol dm^{-3} ammonium acetate in 20% (v/v) nitric acid to the sample and continuous agitation for 30 min.

Extraction-5: residuals. The residue from Extraction-4 was subjected to digestion by adding 20 ml of 70% nitric acid and heated to near dryness. The extracts collected were analysed using Buck Scientific 200A atomic absorption spectrophotometer, to determine the concentrations of Cd, Cu, Fe, Mn, Pb and Zn.

Results and Discussion

Water quality. Results of the analysis of trace metals (Cu, Fe, Mn, Cd, Zn, Pb) and the water quality constituents of Ologe lagoon water are presented in Table 1. The average pH values reported for 210 lakes in Norway (Rognerud and Fjeld, 2000), Kaduna river in Nigeria (Ajayi and Osibanjo, 1981), and 36 lakes in Lapland, Finland (Mannio *et al.,* 1995) were comparable to the mean values observed for Ologe lagoon water samples, which was slightly acidic or near neutral (pH range: 5.7-6.7). Irrespective of the sampling sites, phenolphthalein alkalinity was zero and total alkalinity was due to bicarbonates. The mean conductivity values obtained for Ologe lagoon water samples (< 400 µS cm^{-1}) were higher than the mean conductivity values reported for the acidic Lake Success (Sprenger *et al.,* 1987), but three times lower than 36 lakes in Lapland, Finland (Mannio *et al.,* 1995). A lower conductivity concentration was recorded upstream of the Ologe lagoon due to the absence of tidal action and limited water exchange in the river. This phenomenon probably accounted for the same trend in the chloride values.

Heavy metals in the lagoon water. The average values for manganese, zinc, copper, lead, cadmium, and nickel were 35.8 µg per litre, 4.4 µg per litre, 0.05 µg per litre, and 0.03 per litre (Table 1). Iron was unusually high (704.7 µg per litre), which probably reflects the presence of a natural source due to the geology of the catchment soil. A similar observation has been reported by Ajayi and Osibanjo (1981). The present study also suggests that except for iron and cadmium, the values of manganese, zinc, copper, and lead in the Ologe lagoon water samples were consistently lower than the corresponding values reported for dissolved metal concentrations in African rivers (CIFA, 1994). The average levels of iron, manganese, zinc and copper reported for Ogun river (Udousoro, 1997) and Oyi river (Ajayi and Osibanjo, 1981) were higher than the reported mean values for the Ologe lagoon water samples. However, the concentrations of iron in the lagoon exceeded the respective values recommended for drinking water by WHO, US EPA and the Canadian drinking water standards (CCME, 1999; US EPA, 1988; CCREM, 1987; WHO, 1984). Thus, Ologe lagoon water will require chemical and biological treatment at the municipal water works in order to serve as a good drinking water source.

Ologe lagoon sediments: total metal contents from the sediment grain fractions. The mean metal concentrations from Ologe lagoon sediments and other global values for surface sediments published in literature are given in Table 2. Iron was the most abundant metal in all the sediment samples analysed. Sediment sample obtained from site 12 showed the highest enrichment of cadmium, copper, manganese and iron as compared to sites 1-11. The average values of iron, manganese, copper and zinc in this study were higher than the corresponding values obtained for Lekki lagoon, Nigeria (Ojo, 1991), Lake Victoria, Kenya (Onyari and Wandiga, 1989), Calcasieu river/ lake, USA (Berk *et al.,* 1990), Tuskegee lake, USA (Ikem *et al.,* 2003), and Latvian lakes, Latvia (Klavins *et al.,* 2000). The average levels of manganese, zinc, copper, lead and cadmium reported for Niger Delta, Nigeria (Kakulu and Osibanjo, 1988), Lake Zurich, Switzerland (von Gunten *et al.,* 1997), Swartkops river, South Africa (Watling and Emmerson, 1981), Lake Macquarie, Australia (Kirby *et al.,* 2001), and a Siberian pond, Russia (Gladyshev *et al.,* 2001) were higher than the corresponding values in the present study. Similarly, the reported average values of iron, zinc, manganese, copper, lead and cadmium in unpolluted sediments were also higher (Salomons and Forstner, 1984) than the average values obtained for these elements in Ologe sediments.

The observations on the sediments in the present study (Table 2) for manganese, zinc, copper, lead and cadmium were lower than the Ontario guidelines (Persuad *et al.,* 1993), Canadian guidelines (CCME, 1999), and the Level of adverse biological

Table 1. Some water quality parameters and heavy metals constituents of Ologe lagoon, southwestern Nigeria, as compared with global averages for freshwaters of different sources published in literature and international standards for drinking water

Source of freshwater/ standards of freshwater	pH	EC (µS/cm)	Cl (mg/l)	TA (mg/l)	Fe (µg/l)	Zn (µg/l)	Cu (µg/l)	Mn (µg/l)	Pb (µg/l)	Cd (µg/l)	Ni (µg/l)	Reference
Ologe lagoon	6.3±3.6	429.0±293	87.6±78	31.6±6.8	704.7±66.3	19.2±3.5	4.4±1.0	35.8±9.2	0.5±0.5	0.05±0.04	0.03±0.02	Present study
African rivers					40.0	20.0	7.0	7.0	3.0	0.02		CIFA, 1994
Ogun river, Nigeria					3760	470	170	310				Udousoro, 1997
Oyi river, Nigeria	7.1				1800	90	100	300				Ajayi and Osibanjo, 1981
Warri river, Nigeria					625	42.9	23.1		17.9	2.3		Kakulu and Osibanjo, 1992
Kpong headpond, Ghana					90	< 20	< 20	45	< 20	< 10		Biney Beeko, 1991
Tuskegee lake, USA	7.34	83.84	12.9	23.65	280-340	5.5-5.7	0.5-1.2	58.4-107.7	0.1-0.7	nd-0.001	nd-6.6	Ikem *et al.*, 2003
36 lakes, Lapland, Finland	5.7	1300	14 (µeq/l)		87	1.84	0.28	15	0.25	0.02	0.25	Mannio *et al.*, 1995
Lake Success, USA	4.0-5.0	22.7-30.0				21-142		103-144	0.9-5.0	0.05-0.4		Sprenger *et al.*, 1987
Scottish lakes							0.18-2.02		0.51-1.19	0.09-0.23	0.14-0.30	Yang *et al.*, 2002
16 Latvian lakes	6.5-8.1					2.87-6.80	0.32-0.96	1.50-7.90	0.03-0.85	0.01-0.08	0.15-0.85	Klavins *et al.*, 2000
Nacharam lake, India					0.07±0.009			23.0±35.9	8.8±3.6	8.9±3.5		Govil *et al.*, 1999
Siberian pond, Russia	7.7-9.5			0.29±0.06	0.02±0.02	2.29±0.43	0.06±0.01	2.26±0.15	< 1	1.86±0.2		Gladyshev *et al.*, 2001
WHO drinking water standards				300	5000	1000	100	50.0	5.0			WHO, 1984
USA drinking water standard				300	5000	1000	50	50	10			US EPA, 1988
Canadian drinking water standards				300	5000	1000	50	50	5.0			CCREM, 1987
Indian drinking water standards					500	50			10			ICMR, 1975

± = standard deviation of the mean; EC = electrical conductivity; TA = total alkalinity; Cl = chloride value; * = drinking water standards

effects (Long and Morgan, 1990), but were higher than the average values for pristine sediments (Sadiq, 1992). The relatively lower values obtained for Ologe lagoon sediments relative to unpolluted sediments, as already discussed, suggest lesser impact of anthropogenic sources of pollution in the Ologe area. The possible metal-metal relationships in water and sediments were investigated using the statistical Pearson correlation coefficient, r, at $\alpha = 0.05$ significant level. Iron, manganese, zinc, copper, lead and cadmium were significantly correlated with values of r, varying between 0.74 and 0.92. These significant correlations of metals are indicative of a common source of pollution.

Chemical fractionation of metals in the sediments. Mean distribution of the heavy metals in the five fractions obtained by sequential extraction procedure have been shown in Table 3. It was observed that all metals in the Ologe lagoon sediments existed largely in the sedimentary matrix (residual phase). According to Rubio *et al.* (1991) and Samanidou and Fytianos (1987), the residual phase represents metals largely embedded in the crystal lattice of the sediment fraction and should not be available for remobilization, except under very harsh conditions. Lead was largely associated with the residual bound fraction. No detectable amount of exchangeable lead was found in all the sediments studied. Ramos *et al.* (1994) reported similar observation. Despite the reported affinity of lead to soil organic matter (Kabata-Pendias and Pendias, 1992), non-detectable amount of oxidizable lead (organic matter forms) was extracted. Acidic pH condition is known to influence the sorption of lead by organic matter fraction in the sediments (Baruah *et al.*,1996). However, the values of lead associated with carbonates and reducible fractions were very low.

Table 2. The total heavy metal contents in sediments of Ologe lagoon, southwestern Nigeria, and the values of these metals publishd for sediments from other countries, and the sediment quality guidelines*

Source of sediments guidelines for sediments	Fe**	Mn	Zn	Cu	Pb	Cd	Reference
Ologe lagoon, Nigeria	21 ± 4.6	123.4 ± 57	35.3 ± 10	11.4 ± 3.7	11.0 ± 4.1	0.60 ± 0.08	Present study
Unpolluted sediments	41	770	95	33	19	0.11	Salomons and Forstener, 1984
Niger Delta, Nigeria	20.7	349	62	23.9	32.1	0.79	Kakulu and Osibanjo, 1988
Lekki lgoon, Nigeria	0.34	37.6		4.33	15.6	0.32	Ojo, 1991
Wiwi river, Ghana			16	4.7	13.4	0.16	Biney and Beeko,1991
Lake Victoria, Kenya	1.18 - 52.9	53.1 - 616	2.54 - 265	0.96 - 78.6	6.02 - 69.4	0.55 - 1.02	Onyari and Wandiga, 1989
Swartkops river, SA	15.5	177	35.5	10.5	17.8	1.0	Watling and Emmerson, 1981
Calcasieu river/lake, USA			35.16	6.91	9.90	0.98	Berk *et al.*, 1990
Tuskegee lake, USA	3.0	53.43	8.72	6.84	14.84	0.56	Ikem *et al.*, 2003
Latvian lakes, Latvia		14.3 - 81.2	15.32 - 78.4	1.33 - 16.34	6.64 - 83.2	0.28 - 5.3	Klavins *et al.*, 2000
Lake Zurich, Switzerland			232	37	97	1.7	von Gunten *et al.*, 1997
Lake Macquarie, Australia			152	36		2.1	Kirby *et al.*, 2001
Siberian pond, Russia	21 ± 1.1	671.5 ± 104.31	15.8 ± 63	20.5 ± 2.75	16.7 ± 1.8	< 1.0	Gladyshev *et al.*, 2001
Pristine sediments				< 10	< 31	< 1.0	Sadiq, 1992
Ontario guidelines		< 460	< 120	< 16	< 31	< 0.6	Persuad *et al.*, 1993
Canadian guidelines			123	35.7	35	0.6	CCME, 1995
Adverse biological effects			< 260	< 300	< 30	< 5.0	Long and Morgan, 1990

* = mg kg^{-1}; * * = $x10^3$; ± = standard deviation of the mean

Table 3. Amounts of heavy metals concentration, as different metal species in various fractionations of metals, in the sediments (mg kg^{-1}) from Ologe lagoon, southwestern Nigeria

Metal and metal species	Sample site number*			
	6	8	10	12
Lead				
Exchangeable	nd	nd	nd	nd
Carbonate	1.29	nd	1.5	nd
Reducible	4.4	nd	0.42	3.4
Organic	nd	nd	nd	nd
Residual	6.89	13.5	2.66	8.6
Cadmium				
Exchangeable	nd	nd	nd	nd
Carbonate	nd	nd	0.15	0.17
Reducible	nd	nd	nd	nd
Organic	nd	nd	nd	nd
Residual	0.60	0.65	0.31	0.50
Zinc				
Exchangeable	nd	nd	nd	nd
Carbonate	7.90	11.0	4.9	9.7
Reducible	7.90	11.2	3.7	5.6
Organic	4.70	6.43	3.2	3.8
Residual	19.8	22.52	5.9	11.5
Copper				
Exchangeable	nd	nd	nd	nd
Carbonate	nd	nd	3.3	nd
Reducible	nd	nd	nd	nd
Organic	3.8	3.8	3.6	nd
Residual	5.9	4.8	4.4	15.6
Manganese				
Exchangeable	11.8	5.8	7.3	12.9
Carbonate	44.2	46.5	25.5	98.0
Reducible	8.8	8.7	3.6	18.0
Organic	11.8	17.4	7.6	25.8
Residual	34.4	37.8	29.2	103.2

* = refer Fig. 1 for site numbers; nd = not detected

Cadmium was associated largely in the sedimentary matrix and its association with the carbonate phase was very poor. Zinc was concentrated in the residual fraction with moderated amounts in the carbonates and reducibles, and to a lesser extent in the organically complexed forms. Ma and Rao (1997), and Narwal and Singh (1998) also found zinc to be strongly bound in the residual fraction (even up to 98% of its total content). Copper existed mostly in the residual form and also in the organically complexed form. Under oxidizing conditions, metals present in both natural organic matter (due to complexation and peptizaiton) and living organisms (as a result of bioaccu mulation of metals) may be remobilized into the aquatic environment. Exchangeable and carbonate fractions had the greatest amounts of manganese with a decreasing contribution of manganese associated with the residual, organic and reducible forms.

According to Perez *et al*. (1991), the sum of the metals associated with exchangeable and carbonate bound fractions is extremely important as it represents the proportion of heavy metals that can be easily remobilized by changes in the environmental conditions, such as pH and salinity.

Kindler and Sevim (1990) found that the metals with the greatest values of the exchangeable and carbonate bound fractions in the Turkish rivers were Mn, Cd, Pb and Zn, in the same order. In the sediments of Ologe lagoon, the metals that were least extractable (that were not detected in the exchangeable and carbonate bound fractions) were: Cd, Pb, Cu, Zn, and Mn.

The analysed metals can be put in order, according to the sum of their exchangeable and carbonate bound fractions, at different collection sites (Fig. 1), as follows:

Mn > Zn > Pb > Cu = Cd at site 6
Mn > Zn > Pb = Cu = Cd at site 8
Mn > Zn > Pb > Cu > Cd at site 10
Mn > Zn > Cd > Pb = Cu at site 12

Conclusions

The status of Ologe lagoon with respect to water quality and risk to water column contamination by heavy metals in the lagoon sediment was investigated in this study. The lagoon water quality characteristics were mostly below the recommended international drinking water standards. From the fractionation study, the metal contents in the Ologe lagoon sediments were characteristic of unpolluted sediments; besides, the greatest amounts of the metals studied were associated with the residual fraction. The metals associated with this fraction may be remobilized under the conditions normally encountered in the nature. The metals that were mostly extracted in all the analysed samples were Mn and Zn.

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