Distribution of Trace Elements in Sediments and Biota of Songkhla Lake, Southern Thailand

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Abstract The concentrations of Co, Ni, Cu, Zn, Cd, Pb, As, Fe, Mn, and Al were determined in sediments and biota of Songkhla Lake, a shallow coastal lagoon located in southern Thailand. In June 2006, surface sediments were sampled in 44 stations in the three sections of the lake (inner-, middle-, and outer sections). Sediment cores were also sampled in 13 stations in three cross-sections of the lake. In surface sediments, trace and major elements, organic matter, sediment grain size analysis, and sulfides were determined, and in the sediment cores, redox profiles were made. Soil samples were also collected at garbage dumping sites in the vicinity of the lake. In addition, the metal accumulation in two catfish species (*Arius maculatus* and *Osteogeneiosus militaris*) and the crustacean (*Apseudes sapensis*) was also investigated. Trace element concentrations in sediments of Songkhla Lake show that, especially the Outer section of the lake, in particular the sediments at the mouths of the Phawong, U-Taphao, and Samrong Canals are significantly enriched with trace elements due to municipal, agricultural, and industrial discharges entering the lake through the canals. Aluminum-normalized enrichment factors throughout the lake vary from 0.4 to 1.7 for Ni, 0.3 to 3.3 for Cu, 0.2 to 7 for Zn, 0.1 to 14 for As, 1 to 24 for Cd, 0.7 to 6.8 for Pb, and 0.1 to 7.8 for Mn. Correlations between the elements and sediment characteristics show that Cu, Zn, Cd, and Pb are essentially associated with the sulfide fraction; that Ni and Co are predominantly bound to the clay minerals and iron oxy-hydroxides, and that As is principally bound to iron oxy-hydroxides. The accumulation of trace elements between muscle tissue and liver and eggs of *A. maculatus* and *O. militaris* is element-specific, but concentrations of trace elements in fish muscle tissue are well within the limits for human consumption.

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1 Introduction

In the aquatic environment, trace elements are distributed between the dissolved phase, colloids, suspended matter, and sedimentary phases. Sediments and soils have a high storage capacity for contaminants. In the hydrological cycle, less than 0.1% of the metals are actually dissolved in the water, and more than 99.9% are stored in sediments and soils (Salomons 1998).

Sediment-associated metals pose a direct risk to detrital and deposit-feeding benthic organisms and may also represent long-term sources of contamination to higher trophic level (Mendil and Uluözlü 2007).

Lake sediments can serve as archives of environmental changes though time (Silva and Rezende 2002). The distribution and accumulation of trace metals is influenced by sediment texture, mineralogical composition, reduction/oxidation state, adsorption and desorption processes, and physical transport (Buccolieri et al. 2006). Changes in sediment oxidation/reduction state and pH influence the solubility of both metals and nutrients (Miao et al. 2006). Direct effects of pH are (co)precipitation and dissolution phenomena of heavy-metal-bearing minerals (Herreweghe et al. 2002). To evaluate the potential environmental contamination of lagoons, the chemical analysis of the surface sediments is very important since it represents the current situation (Prudêncio et al. 2007).

Songkhla Lake, a coastal shallow lagoon located in the south of Thailand, is a very important natural resource for the people living in the surrounding provinces: Songkhla Province, Phatthalung Province, and some parts of Nakhon Si Thammarat Province. The lake is a major fishing ground for mollusks, crustaceans, and fish and is intensively used for the aquaculture of sea bass. The catchment area of about 8,020 km^2 consists mostly of lowland rice fields, rubber plantations, and forest-covered hills but contains rapidly growing cities such as Hat Yai and Songkhla. This has led to increased discharges into the lake from human activities including urbanization, industrialization, and agriculture. Recently, the Lake has faced serious problems which have been summarized in ONEP (2005) as follows: (a) a steady decline of the upstream forest and mangrove, (b) soil erosion and sedimentation in the waterways and in the lake, (c) overuse of ground water, (d) severe flooding, (e) over-fishing, (f) unsanitary drainage from urban areas, (g) industrial wastes (mainly related to rubber and food products), (h) pollution from boats and fish wastes from Songkhla harbor, (i) lack of effective management, etc.

During the past two decades, quite a number of studies concerning the area have been carried out (Baeyens Maneepong 1996; Maneepong and Angsupanich 1999; Bhongsuwan and Bhongsuwan 2002; Sirinawin and Sompongchaiyakul 2005). A limited number of studies have been made regarding the pollution of the lake by heavy metals (Sompongchaiyakul and Sirinawin 2007;

Sirinawin and Sompongchaiyakul 2005; Sirinawin et al. 1998; Sukapan et al. 2006; Maneepong 1996; Maneepong and Rakeaw 1998). The aim of the present study is to screen the current distribution of trace elements in surface sediments of the lake together with other chemical properties such as organic matter, sulfides, grain size, pH, and redox. In addition, the metal accumulation in two catfish species (*Arius maculatus* and *Osteogeneiosus militaris*) and the crustacean *Apseudes sapensis* was also investigated.

2 Study Area

Songkhla Lake, a coastal shallow lagoon, is located in the south of Thailand (7°08′–50′ N and 100°07′–37′ E) and has a total area of 1,042 km^2. The lake is divided into four sections: Thale Noi, a freshwater lake surrounded by freshwater swamps with a surface area of 28 km^2; an inner section with an average depth of 2 m and a surface area of 459 km^2; a shallow middle section with an average depth of 1 m and a surface area of 377 km^2; and an outer section (Thale Sap Songkhla) connected to the Gulf of Thailand with a surface area of 182 km^2 (Fig. 1). The salinity ranges from freshwater in Thale Noi to saline water in the outer section. Several streams are flowing into the lake. Important canals in the outer section are (a) U-Taphao canal which is the main source of freshwater draining into the outer part, with the length around 90 km, originating from the Sadao district, in the Songkhla province; the canal is flowing through a large city (Hat Yai) before entering the lake, (b) Phawong canal is a short canal with a length of around 5.5 km, and both sides of canal are densely covered with the mangrove trees, and (c) Samrong canal is a short canal and located in a densely populated area.

3 Materials and Methods

3.1 Sample Collection and Storage

3.1.1 Sediment Samples

The surface sediments were collected from 44 stations using a grab sampler, of which 40 were located in the Songkhla Lake, three in the canals (about 1–2 km from the lake), and one in the Gulf of Thailand. Sampling stations are shown in Fig. 1. The survey was carried out
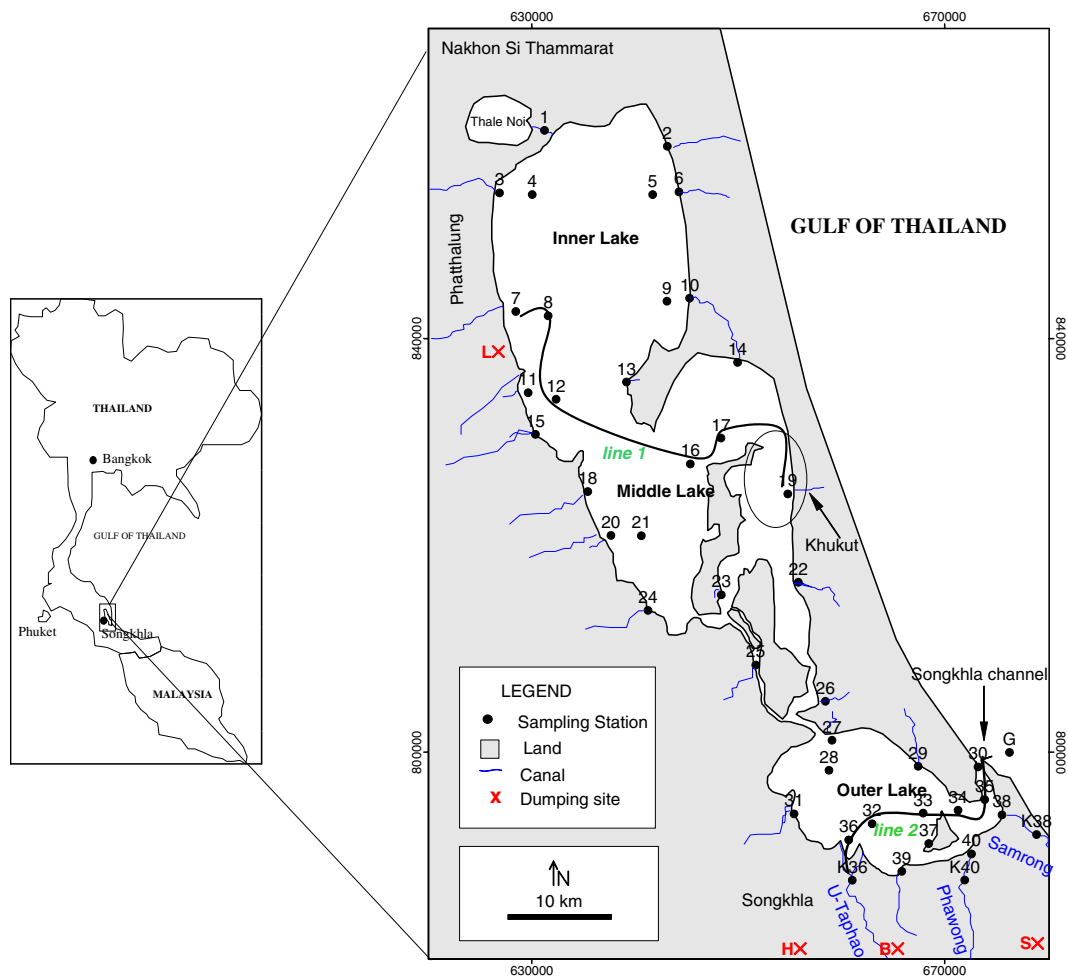
Fig. 1 Location of sampling stations in Songkhla Lake

between June 3 and June 25, 2006. In addition, sediment cores were collected from 13 stations in the upper–middle section (line 1: stations 7, 8, 12, 16, 17, and 19) and outer section (line 2: stations 30, 32, 33, 34, 35, 36, and K36) using Plexiglas tubes (5 cm diameter and 40 cm length). In addition, cores were taken in soils at four local garbage dumping sites near the lake (stations L, S, H, and B) from 20 to 21 September 2006.

3.1.2 Biological Samples

Benthos (Tanaidacea: *A. sapensis*) was sampled on 18 September 2006 in the Middle Lake (station 19) using a dredge sampler. The sample was sieved through a 5-, 1-, and 0.5-mm sieve. Tanaidacea were separated on the 0.5- and 1-mm sieves. The samples which were retained on the 1-mm size sieve were collected together

with field water and put in a plastic bag. The plastic bags were oxygenated during transport to the laboratory. Tanaid was separated again in the laboratory before being frozen at −20°C.

Two catfish species (*A. maculatus* and *O. militaris*) were collected from six stations from several areas in lake by different methods. In station 7, the fish were sampled using a fishing rod, at station 19 by fish traps, and at stations 24, 36, and 37 bought from local fishermen.

3.2 Microwave Digestion Procedure

3.2.1 Sediments

Prior to analysis, the wet sediment samples were frozen, dried in the lyophilizer, homogenized and grinded in a

mortar, and sieved through a 1-mm nylon sieve. Around 0.1 g of sediment was weighed in the Teflon digestion bomb, and 2 mL of HNO_3 (65%, Merck, Suprapur) and 6 mL HCl (30%, Merck, suprapur) were added to the samples. The bombs were closed tightly and put in the microwave oven (CEM Mars 5) for digestion. The digestion was carried out with the following procedure: ramp to 150°C during 10 min then hold at 150°C for 10 min and then cool down for 10 min. When the samples were cooled, 30 mL of Milli-Q water was added and stored in acid-cleaned polyethylene storage bottles (60 mL, Nalgene).

3.2.2 Biological Samples

Around 0.10–0.15 g of lyophilized and homogenized sample was weighed in a Teflon digestion bomb. Five milliliters of HNO_3 (Merck, 65%, suprapur) and 1 mL H_2O_2 (30%, Merck, suprapur) were added to the samples. The bombs were closed and put in the microwave oven (CEM MARS 5) and digested using the following procedure: ramp to 180°C during 15 min, hold at 180°C for 15 min, then cool down for 15 min. After that, the samples were diluted to 30 mL with Milli-Q water and stored in polyethylene storage bottle.

3.3 Analysis of Metals

A high-resolution inductively coupled plasma mass spectrometry Thermo Finnigan Element II was used to measure the concentrations of trace elements in the sediment sample. Before analysis, the digested samples were diluted ten times, and Indium was added as internal standard (final concentration 1 ppb). Major metals (Al, Fe, Mn) were analyzed with inductively coupled plasma atomic emission using Thermo SPEC/WIN (IRIS) from ThermoOptek. Quantification

of trace metal concentrations was based upon calibration curves prepared from multi-element (Merck) or single element (Johnson Matthey Specpure) standard solutions. Blanks and standard references materials were included in each digestion batch to verify the accuracy of the extraction method. For the analysis of sediment, the standard reference material LGC6139 (river clay sediment) was used. The results of analysis of reference material and the certified value are given in Table 1.

3.4 Determination of Readily Oxidizable Organic Matter

The readily oxidizable organic matter contents of the sediment samples was determined by the Walkey-Black method (1947) as described in Loring and Rantala (1992) and Schumacher (2002). Dried sediment samples were sieved through a 0.2-mm nonferrous sieve. Dried sediment (0.5 g) was transferred to a 500-mL Erlenmeyer flask. Ten milliliters of 1 N potassium dichromate was then added to oxidize organic carbon in the sample. A 20-mL mixture of H_2SO_4 and Ag_2SO_4 was added to eliminate chlorine. The mixture was left for 30 min then diluted with 200 mL distilled water. Ten milliliters of 85% H_3PO_4 and 0.2 g NaF was then added as catalyst and for the purpose of a clear end point. Finally, 15 drops of diphenylamine indicator were added. Back titration was performed with titrant 0.5 N $Fe(NH_4)_2(SO_4)_2$ (ferrous solution). During the titration, the sample color gradually changed from dull green to turbid blue and finally green. At this point, one drop is added to reach the end point. If the volume of ferrous solution used is less than 4 mL to reach the end point, then more than 8 mL of dichromate has been consumed in the oxidation, so the whole process was repeated again by using less sediment.

Table 1 Comparison of the analytical results of the reference materials with the certified data

Reference materials	Matrix	n	Mn	Co	Ni	Cu	Zn	As	Cd	Pb
LGC6139 (μg g^{-1})	Sediment	9	1,084±98	13.05	38±1.14	84±1.69	539±10.79	25±1.01	2.5±0.10	146±2.9
Certified value	Sediment		1,100±99	–	38±1.14	92±1.84	513±10.26	27±1.08	2.3±0.09	160±3.2
DORM-2 (μg g^{-1})	Dogfish muscle	3	na	0.168±0.028	17.0±2.7	1.90±0.13	25.4±2.3	16±0.9	0.046±0.009	0.076±0.008
Certified value	Dogfish muscle		3.66±0.34	0.182±0.031	19.4±3.1	2.34±0.16	25.6±2.3	18±1.1	0.043±0.008	0.065±0.007
NIST-SRM 2976 (μg g^{-1})	Mussel tissue	2	na	0.59	1.11	4.01±0.32	157±14.18	12.1±1.70	0.76±0.15	1.12±0.17
Certified value	Mussel tissue		33	0.61	0.93	4.02±0.32	137±12.33	13.3±1.86	0.82±0.16	1.19±0.18

na not analyzed

3.5 Sediment Grain Size Analysis

The particle size analysis was done using the hydrometer method (Gee and Bauder 1986). Air-dried sediments were sieved through a 2 mm nonferrous sieve. Forty grams of dried sediments was then transferred to a 600-mL beaker with the addition of 100 to 150 mL of distilled water. Hydrogen peroxide 30% was continuously added to eliminate organic matter in the sample until bubbles disappeared. The samples were heated at 90°C on a hot plate for 1 h before incubating in an oven at 105°C for 24 h. After cooling in a desiccator, the samples were weighed again. One hundred milliliters of Calgon 5% and 50 mL of distilled water were added to the sediment, and the sample was stirred on a mechanical shaker for 5 min. The samples were sieved on a 63-μm sieve until no more silt and clay remained on the sieve and the wash water was clear. The portion that passed through the sieve was transferred to a 1-L sedimentation cylinder. The volume was then adjusted using distilled water up to 1 L. The sediment was dispersed in the cylinder again by a plunger then after 50 s, density and temperature of the sample were measured using hydrometer and a thermometer, respectively. The whole system was left for 2 h without disturbance, and then at 2 h, the density and temperature were measured again. A blank was prepared using Calgon. The percent of sand, silt, and clay was calculated.

3.6 Water Content

The percentages of water content of the sediment samples will be determined by weight reduction (drying wet sediments in oven at 110°C for 24 h).

3.7 Total Acid-Volatile Sulfides

The frozen sediments were thawed, and the total acid-volatile sulfide content of the sediment was determined by acidifying the sediment with 18 N H_2SO_4 and subsequently trapping the released H_2S with an H_2S-absorbent column (Gastec, Hedrotek 201H, Kagawa Science, Japan). The reaction time is generally 2 min. This simple procedure has been used in numerous studies (Tsutsumi and Kikuchi 1983; Sasayama et al. 2007; Yodnarasri et al. 2008; Chareonpanich et al. 1993; Meksumpun and Meksumpun 1999; Moqsud et al. 2006; Chareonpanich and Seurungreong 1999).

The addition of acid to a sediment will release H_2S from dissolved sulfur species as well as metastable iron sulfide minerals (FeS, Fe_3S_4) and partially from pyrite (FeS_2) depending on the acid concentration used, temperature, and reaction time (Rickard and Morse 2005). Although often referred to as acid-volatile sulfide (AVS), we will define this sulfide fraction as total acid-volatile sulfide (TAVS) to distinguish this from the classical operationally defined AVS fraction extracted by 1 M HCl. Though the concentrations may not be completely comparable to the classical AVS extractions, this method provides a rapid screening of reduced sulfur species. The level of TAVS was expressed in milligram TAVS per gram (dry weight) of the analyzed sediments. The model of H_2S test columns that was used (Hedrotek 201H) had a quantification limit of 0.02 mg TAVS per gram dry weight sediment.

3.8 Redox Potential (Eh) and pH

The measurements of redox potential (Eh) and pH profiles were performed in the field with a combined pH/Eh meter (IQ 140 pH/mV/Temp/ORP) using Plexiglas sampling tubes in which holes had been drilled every 2 cm. The Plexiglas tube with holes was covered tightly by the plastic film before being used. Redox was measured using a Pt redox electrode combined with a Ag/AgCl, [KCl]=3 mol L^{-1} reference electrode (IQ/model ORP110-GS), and measurements of pH were performed using a combination glass electrode with a Ag/AgCl, [KCl]=3 mol L^{-1} reference electrode (IQ 140/ model pH30-GS)).

4 Results

4.1 Sediment Characteristics

Sediment texture data indicate that the sediments are mainly sand–silt–clay (percent of each component more than 20%), clayey sand, and sandy clay (Fig. 2). Distribution patterns of the sand, silt, and clay fraction, together with readily oxidizable organic matter (OM) and total acid-volatile sulfide are shown in Fig. 3. Fine grain sediments accumulate in the Outer section at the mouths of the Phawong, U-Taphao, and Samrong canals as well as in the lower Middle section.

The concentration of readily oxidizable organic matter in the surface sediment ranged from 0.68% to

Fig. 2 Sediment texture of
Songkhla Lake sediments
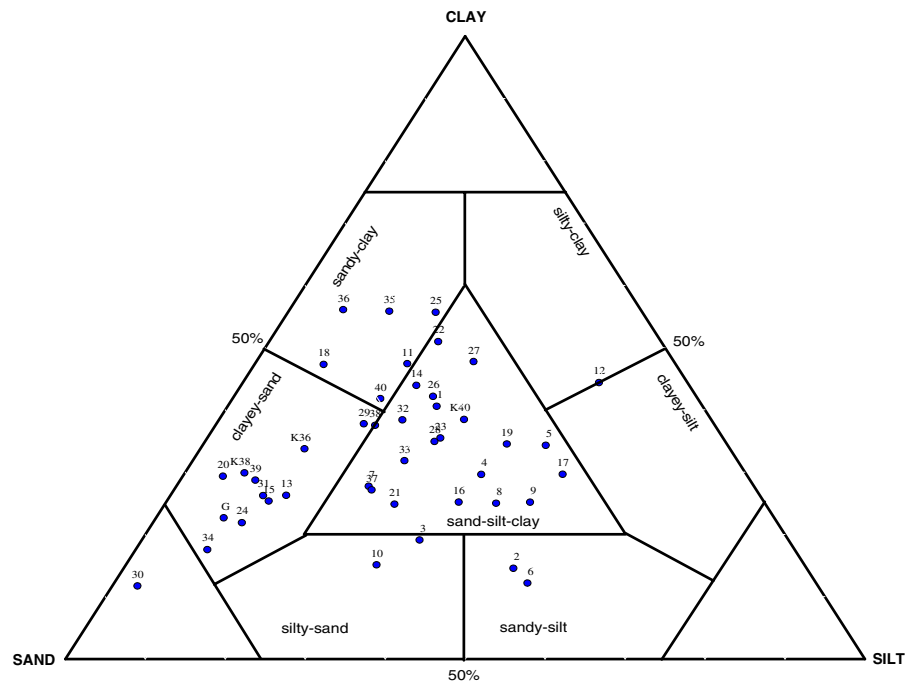
10.9%. Relatively higher concentrations were found
in the Outer section at the mouths of the Phawong and
Samrong Canals (up to 10.9% at station K40), as well
as in the southeastern part of the Middle section of the
lake (station 26 (7.71%)) located near a shrimp farm.
The higher levels in the Outer section can be
explained by riverine inputs from the Phawong,
Samrong, and U-Taphao canals transporting organic
matter from the domestic origin into the lake. In the
Middle section, higher levels were found in the area
called the nonhunting area (Khukut); an area which
consists of a shallow water body with many isles
covered with mangrove trees, sea grass, and seaweed.
This area dries out during the dry season, and the
flora can thus contribute to the organic matter loading.

The level of total acid-volatile sulfides in the
surface sediments ranged from below the detection
limit (<0.02 mg g^{-1} dry weight) to 5.7 mg g^{-1} dry
weight (average 0.57 mg g^{-1} dry weight). As for
organic matter contents, higher values were found in
the Outer section and the southeastern part of the
Inner section. The highest level was found at station
38 (5.7 mg g^{-1} dry weight), which was located at the
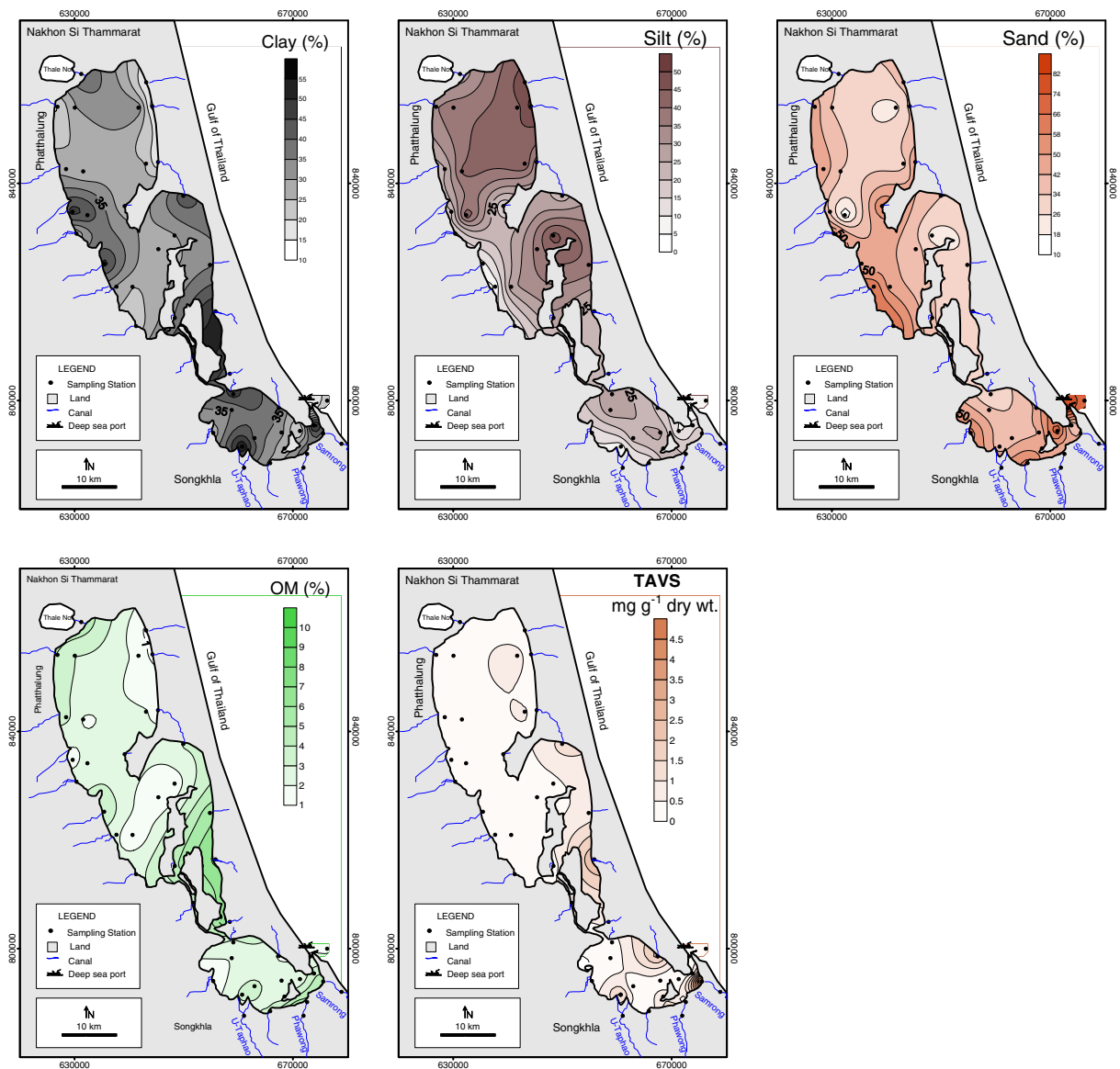mouth of Samrong canal.

In the western part of the Inner section (stations 7
and 8), the redox potential (Fig. 4) decreases from oxic
or suboxic conditions at the surface to anoxic

conditions reaching minimum concentrations at a depth
of 3–4 cm. In the Middle section, especially in the area
of high organic matter accumulation, the redox profiles
show anoxic conditions at the surface (stations 16, 17,
19). In the Outer section, the most anoxic sediments
are found at the mouth of the U-Taphao canal. Anoxic
surface sediments are found in the muddy sediments at
the outflows of the canals, whereas oxic surface
sediments and a sharp decrease in the redox potential
is observed in the more sandy station 33 as well as in
the mouth of the Outer section to the Gulf of Thailand.

4.2 Trace Element Concentrations in Sediments

The trace element concentrations in surface sediment
ranged: 48–1,820 µg g^{-1} dry weight for Mn, 1.3–
16.3 µg g^{-1} dry weight for Co, 2.5–21.9 µg g^{-1} dry
weight for Ni, 1.8–126 µg g^{-1} dry weight for Cu, 5.4–
562 µg g^{-1} dry weight for Zn, 0.8–70.7 µg g^{-1} dry
weight for As, 0.1–2.4 µg g^{-1} dry weight for Cd, and
8.2–131 µg g^{-1} dry weight for Pb. Figure 5 shows the
spatial distribution of these metals in de surface
sediments.

For all elements except Mn, concentrations are
higher in the Outer section and lower part of the
Middle section compared to the Inner section. The
highest concentrations of Cd, Pb, Cu, and Zn are

Fig. 3 Sediment grain size, organic matter, and total acid-volatile sulfides in the sediments of Songkhla Lake

found at the mouth of the Samrong canal (station 38), in the U-Taphao and Phawong canals (K36, K40), and at the outflows of these canals (stations 36, 40). Increased levels of these elements are also found in the lower Middle section (station 26), and for Cd and Pb, higher levels are also found in the Middle section at stations 18 and 15. For Co and Ni, highest concentrations are found in the lower Middle section (stations 22–26), followed by the Outer section. Arsenic concentrations are higher in the Outer section, especially the Phawong Canal and its

outflow. Mn shows a completely different distribution, with higher levels in the Inner section compared to the Middle and Outer sections.

4.3 Trace Element Concentrations in Soil Profiles at Garbage Dumping Sites

Table 2 shows the trace element content in soil profiles from four local garbage dumping sites nearby Songkhla Lake. Trace element concentrations are comparable to the levels found in the lake sediments except for As at

Redox Potential- Inner and Middle Section

Redox Potential-Outer Section
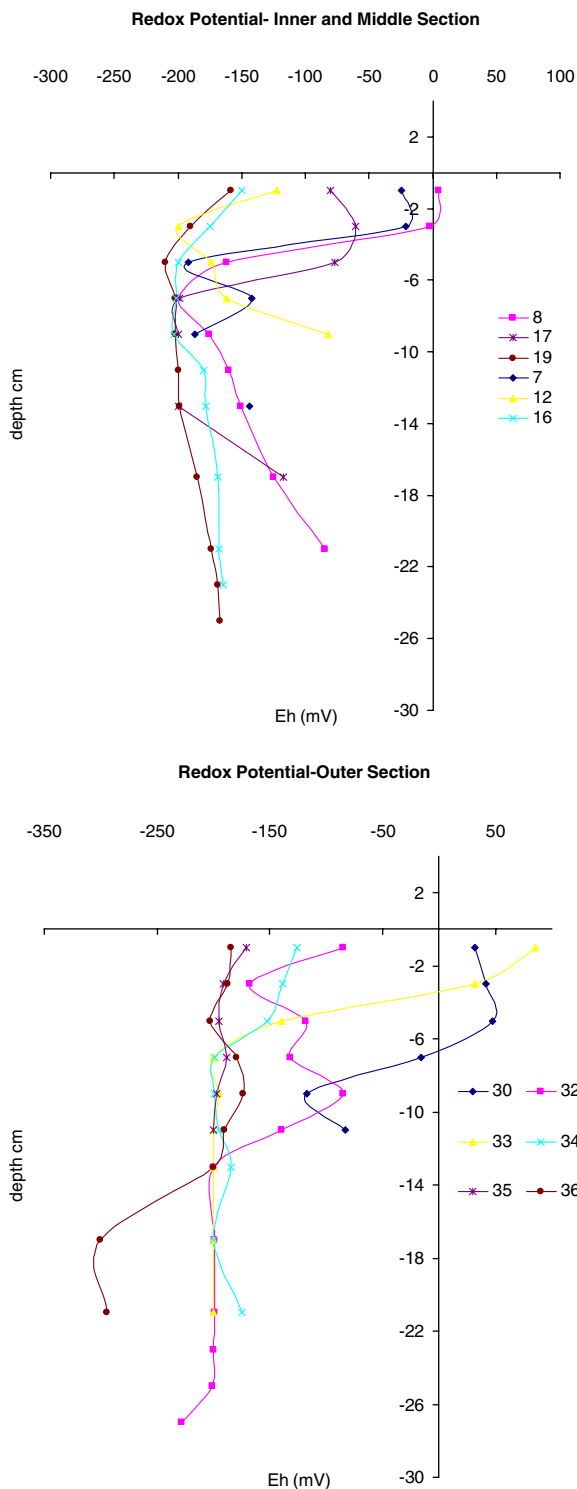
Fig. 4 Redoxpotential in the sediments

station B, where very high levels were found (up to 145 µg g^{-1} dry weight). The dumping site B is located between the U-Taphao and Phawong Canals. Cu was highest at station S (32 µg g^{-1} dry weight; located between Phawong and Samrong canals), whereas Pb was highest at station L (34 µg g^{-1} dry weight; located at the Inner Lake) and station B (30 µg g^{-1} dry weight).

4.4 Heavy Metals in Biological Samples

The concentrations of Co, Ni, Cu, Zn, As, Cd, and Pb in muscle and liver tissue as well as in the eggs of two catfish species (*A. maculatus* and *O. militaris*) caught in the different sections of the lake and the in the crustacae (*A. sapensis*) collected at station 19 are shown in Table 3.

The concentrations of Co, Ni, Cu, Zn, As, Cd, and Pb in muscle tissue of *A. maculatus* were in the ranges 0.04–0.24, 0.25–5.44, 0.98–2.08, 21–95, 0.50–7.24, <dl–0.03, and 0.06–0.40 µg g^{-1} dry weight, respectively, whereas the concentrations in liver were in the ranges 0.41–2.36, 0.14–15.4, 10.7–254, 383–998, 0.27–1.96, 0.09–1.37 and 0.24–3.44 µg g^{-1} dry weight, respectively, and in the fish eggs 0.15–0.39, 0.32–0.73, 2.14–6.53, 161–210, 0.33–1.11, 0.01–0.03 and 0.02–0.12 µg g^{-1} dry weight, respectively. The concentrations of Co, Ni, Cu, Zn, As, Cd, and Pb in muscle tissue of *O. militaris* were in the ranges 0.03–0.10, 0.06–0.66, 0.44–1.75, 13.15–51.25, 0.19–0.60, 0.00–0.01, and 0.05–0.18 µg g^{-1} dry weight, while the concentrations in the liver were in the ranges 0.39–0.92, 0.21–1.61, 21.14–99.43, 331.90–1,145.19, 0.26–0.62, 0.10–0.53 and 0.14–0.87 µg g^{-1} dry weight, respectively, and in the fish eggs 0.22, 0.89, 3.28, 171, 0.17, 0.01, and 0.01 µg g^{-1} dry weight, respectively. No significant differences in trace element concentrations between the two catfish species could be found. Co, Cu, Zn, and Cd are essentially accumulating in the liver, whereas the distribution of Ni and Pb between liver and muscle tissue is highly variable. The concentrations of As are more or less evenly distributed between muscle and liver tissue, except in the Outer section where a higher muscle-to-liver ratio is observed. For Cd, Pb, and As, the concentrations found in fish eggs are lower than the concentrations in muscle and liver tissue, whereas for Zn, Cu, and Co, the levels found in fish eggs are in between the levels in muscle tissue and in the liver. For Ni, no distinct pattern can be found.
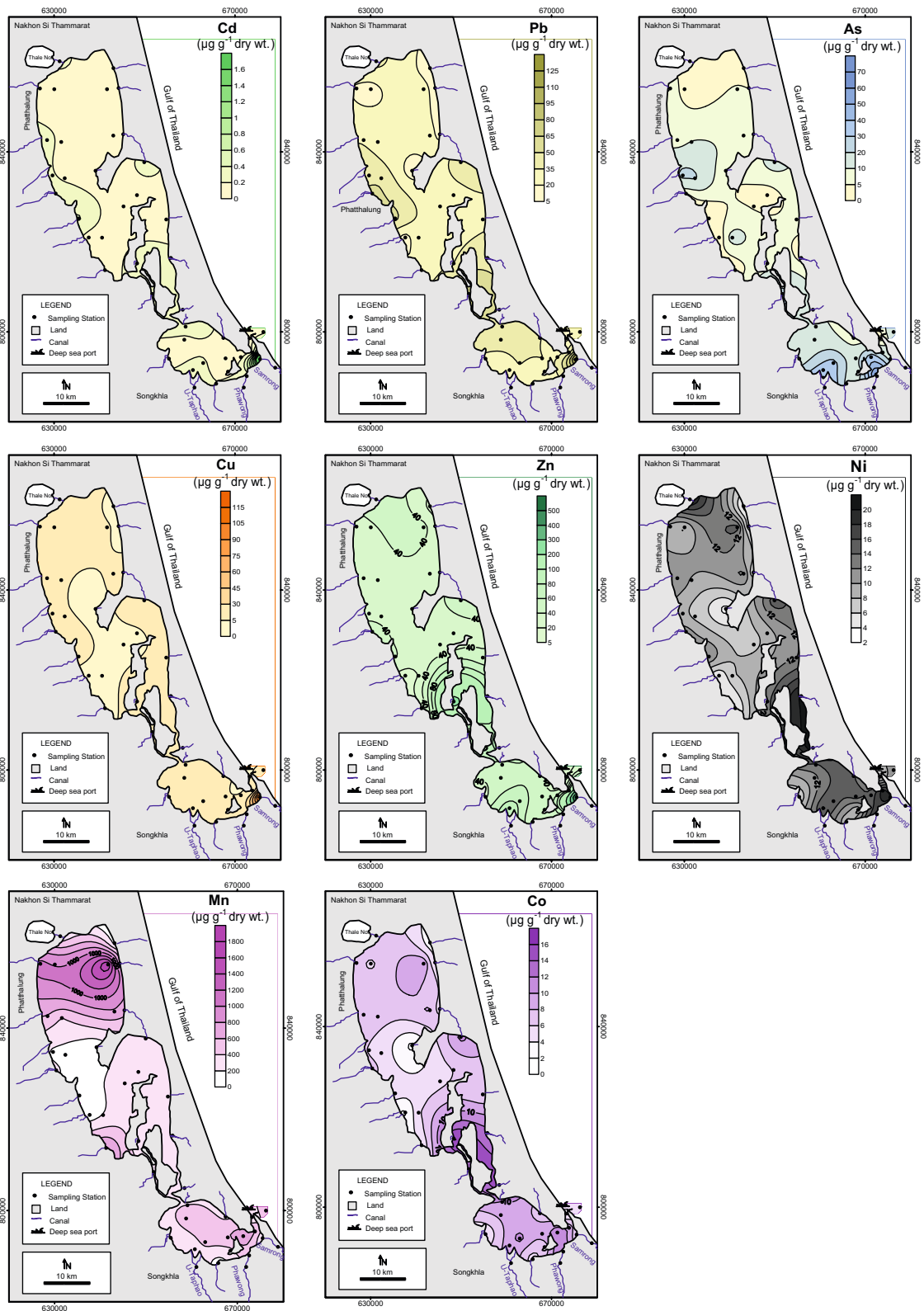
Fig. 5 Trace element concentrations in surface sediments of Songkhla Lake

Table 2 Trace element concentrations (µg g^{-1} dry weight) in soil profiles at different local garbage dumping sites nearby Songkhla Lake

Station	Depth (cm)	Concentrations (µg g^{-1} dry weight)								Remarks
		Cd	Pb	Co	Ni	Cu	Zn	As	Mn	
L	0–2	0.18	31.8	2.73	8.51	8.42	31.2	12.1	107	About 5 km from stations 7 and 11
	2–4	0.15	26.9	2.62	8.42	3.21	24.8	5.78	74.9	About 5 km from stations 7 and 11
	4–6	0.15	33.8	3.06	13.4	8.47	22.1	10.9	92.2	About 5 km from stations 7 and 11
S	0–2	1.09	11.2	3.85	9.65	28.1	29.4	4.33	226	Near station K38
	2–4	0.10	12.4	2.45	5.72	31.7	26.7	6.68	171	Near station K38
	4–6	0.31	16.1	11.8	12.5	31.5	33.7	6.09	345	Near station K38
H	0–2	0.22	13.5	1.13	6.38	3.75	14.5	4.27	31.0	About 15 km from station K36
	2–4	0.26	19.5	1.37	6.59	5.50	15.6	9.18	45.7	About 15 km from station K36
	4–6	0.24	23.5	1.95	8.52	6.60	18.1	14.0	52.0	About 15 km from station K36
B	0–2	0.31	20.1	1.77	11.2	19.9	15.0	124	75.7	About 20 km from stations K36 and K40
	2–4	0.33	30.3	3.14	10.5	21.9	12.3	146	442	About 20 km from stations K36 and K40
	4–6	0.31	20.2	2.03	12.2	21.0	27.1	120	95.3	About 20 km from stations K36 and K40

Comparison of element concentrations in the fish collected in the different sections of the lake show that the levels of Co and especially As are higher in the Outer section compared to the Inner and Middle sections. For the other elements, no significant differences can be observed between the stations.

Both fish species are carnivores, feeding mainly on benthic invertebrates which are predominantly Tanidacea (*A. sapensis*) (Angsupanich et al. 2005). Samples of *A. sapensis* were collected at station 19. The concentrations of all trace elements (Co, Ni, Cu, Zn, As, Cd, and Pb) were higher in *A. sapensis* than in the muscle of both fish species which were caught in the same area. The concentrations in the benthic invertebrates were, however, lower than the concentrations found in the sediments at that station, except for Cu and Zn, which were significantly higher, and Cd, which was at the same concentration level as in the sediments.

5 Discussion

5.1 Comparison with Regional Background Values and Sediment Quality Guidelines

Since metals are naturally occurring and distributed in the environment, distributions are a combination of both the natural background concentrations and anthropogenic inputs in the region. Background concentrations are

known to be associated with a number of sediment geochemical groupings: associations between contaminants and grain size, Fe/Mn oxides, organic carbon (OC), and carbonates. Normalization procedures attempt to compensate for the naturally occurring geochemical associations so that the anthropogenic contribution can be isolated and quantified. Normalization against grain size has been used to compensate for granulometric variations, based on either grain size analysis or normalizing with an element the acts conservatively, and is a proxy for the fine fraction (Loring and Rantala 1992). There is no consensus on the appropriate sediment constituent to be used for normalization. The most commonly used are Al, Li, OC, and clay fraction. Adjusting for grain size effects is important to distinguish the degree of anthropogenic enrichment and to compare metal data from site to site and with regional background values. Al normalization has been shown to be applicable for coastal sediments in the Gulf of Thailand (Cheevaporn and San Diego-McGlone 1997).

Regional background values assessed from core sediment samples are reported by Choi et al. (2008) and offshore sediments in the Gulf of Thailand by Shazilli et al. (1999). Background levels varied from 10 to 23 µg g^{-1} dry weight for Ni, from 10 to 25 µg g^{-1} dry weight for Cu, from 55 to 115 µg g^{-1} dry weight for Zn, from 5 to 9 µg g^{-1} dry weight for As, from 0.03 to 0.2 µg g^{-1} dry weight for Cd, from 15 to 30 µg g^{-1} dry weight for Pb, 370–720 µg g^{-1} dry weight for Mn, and

Table 3 Trace element concentrations (μg g^{-1} dry weight) in fishes and benthos of Songkhla Lake

Section	Station	Species	Length (cm)	Weight (g)	Tissue	Co	Ni	Cu	Zn	As	Cd	Pb
Fishes												
Inner section	7	A. maculatus	15	60	Muscle	0.04	5.44	0.98	20.9	0.54	0.02	0.19
					Liver	0.87	0.51	44.2	784	0.41	0.17	0.24
		A. maculatus	14.5	45	Muscle	0.06	0.44	1.30	37.5	0.53	0.01	0.36
					Liver	0.47	0.43	29.7	388	0.41	0.30	0.42
					Egg	0.15	0.32	3.94	161	0.33	<dl	0.07
		A. maculatus	14	45	Muscle	0.07	0.25	1.90	43.3	0.49	0.02	0.21
					Liver	0.54	0.14	20.7	414	0.36	0.34	0.26
					Egg	0.18	0.64	6.53	170	0.34	0.01	0.12
		A. maculatus	14.5	50	Muscle	0.11	0.35	1.74	46.7	0.70	0.01	0.15
					Liver	0.92	0.85	20.1	553	0.59	0.39	0.41
					Egg	0.27	0.73	4.34	204	0.39	0.03	0.07
		O. militaris	17.5	70	Muscle	0.06	0.36	0.77	29.4	0.25	0.01	0.05
					Liver	0.84	0.21	71.9	817	0.46	0.24	0.45
		O. militaris	19	80	Muscle	0.06	0.06	0.50	14.1	0.25	<dl	0.05
					Liver	0.43	0.58	42.8	479	0.62	0.24	0.87
		O. militaris	18	70	Muscle	0.03	0.37	0.44	33.1	0.37	0.01	0.08
					Liver	0.39	0.95	69.1	917	0.43	0.21	0.73
Middle Section	24	A. maculatus	20.5	90	Muscle	0.11	0.57	1.36	67	1.04	0.01	0.19
					Liver	0.78	0.16	26.5	753	0.78	0.09	0.41
		A. maculatus	20	90	Muscle	0.04	0.51	1.28	25.6	0.90	0.02	0.35
					Liver	0.41	0.42	84.9	382	0.43	1.37	1.49
		O. militaris	19	90	Muscle	0.08	0.26	0.57	13.2	0.19	0.01	0.18
					Liver	0.92	0.35	99.4	868	0.40	0.16	0.38
		O. militaris	20	90	Muscle	0.10	0.24	1.70	51.3	0.60	0.01	0.15
					Liver	0.51	0.37	21.1	331	0.33	0.10	0.14
					Egg	0.22	0.89	3.28	171	0.17	0.01	0.01
	19	A. maculatus	17.5	60	Muscle	0.06	0.69	1.93	53.7	0.57	0.02	0.40
					Liver	0.45	2.01	46.1	477	0.38	0.28	3.44
		A. maculatus	16	50	Muscle	0.05	0.41	1.41	43	1.02	0.01	0.09
					Liver	0.56	0.41	60.8	527	0.27	0.86	2.11
		O. militaris	19	90	Muscle	0.08	0.66	1.75	48.7	0.24	0.01	0.18
					Liver	0.74	1.61	51.0	1,145	0.26	0.53	0.69
Outer Section	37	A. maculatus	19	85	Muscle	0.21	0.38	1.88	53.8	7.25	0.01	0.13
					Liver	0.93	0.22	42.8	767	1.35	0.37	1.06
		A. maculatus	20	105	Muscle	0.12	0.94	1.64	74.4	7.20	0.01	0.19
					Liver	2.36	15.4	254	998	1.96	0.47	0.75
	36	A. maculatus	20	100	Muscle	0.24	0.38	2.08	95.0	1.86	<dl	0.06
					Liver	2.01	6.02	10.7	796	1.63	0.19	1.80
					Egg	0.39	0.68	2.14	210	1.11	0.01	0.02
Benthos												
	19	A. sapensis				2.95±0.10	6.28±0.3	46.0±1.4	94.8±4.5	4.21±0.07	0.19±0.02	11.2±0.4

4–6% for Al. Averaged values normalized to Al were used to compare concentrations found at different stations to background values (Fig. 6). Enrichment factors (EF) were calculated as EF=(Me/Al)sample/(Me/Al)background (Table 4). Figure 6 and Table 4 show that very important enrichment of trace elements in the surface sediments are found at station 38 (mouth of Samrong canal) for Cd, Cu, Zn, and Pb; for several stations in the Outer section for As and also in the Middle section at station 23 for Zn and in the Inner section for Mn. Enrichment factors vary from 0.4 to 1.7

for Ni, 0.3 to 3.3 for Cu, 0.2 to 7 for Zn, 0.1 to 14 for As, 1 to 24 for Cd, 0.7 to 6.8 for Pb, and 0.1 to 7.8 for Mn.

Several sediment quality guidelines (SQGs) for the assessment of sediment quality using chemical and biological effects databases have been established. These SQGs are summarized in Table 5. The US National Oceanic and Atmospheric Administration (NOAA) presents effects low range (ERL) and effects range median (ERM) guidelines for estuarine and marine environments which represent the tenth and

Fig. 6 Normalized trace element concentrations (Me/Al) 10^{-4} in Songkha Lake and average regional background value

Table 4 Enrichment factors EF=(Me/Al)sample/(Me/Al)background in Songkhla Lake sediments

Station	Mn	Ni	Cu	Zn	As	Cd	Pb
1	0.4	1.0	0.5	0.6	0.2	1.6	1.4
2	1.8	1.3	1.2	1.2	1.5	3.0	3.0
3	6.6	1.7	1.2	0.9	4.5	3.8	2.5
4	2.4	0.6	0.4	0.5	0.3	1.0	0.7
5	5.4	1.3	0.5	0.8	1.2	2.1	1.9
6	7.8	1.5	0.9	1.4	4.2	3.0	2.2
7	1.2	0.7	0.4	0.3	0.9	2.0	1.5
8	1.3	1.0	0.5	0.7	2.4	2.5	2.3
9	2.3	1.1	0.5	0.6	2.1	1.9	1.8
10	6.3	1.6	1.5	1.3	4.1	3.0	2.8
11	0.4	0.5	0.3	0.4	3.2	1.8	2.0
12	0.6	0.7	0.5	0.6	4.8	2.5	3.4
13	0.5	0.9	0.8	1.1	3.4	2.4	2.3
14	0.6	1.1	0.8	0.8	2.2	2.6	2.5
15	0.5	0.6	0.5	0.6	0.6	2.4	2.3
16	2.1	1.1	0.5	0.7	1.7	2.3	3.1
17	1.4	1.0	0.4	0.4	0.6	2.2	2.3
18	0.1	0.5	0.3	0.3	0.1	2.4	1.6
19	0.6	0.9	0.5	0.7	1.1	1.6	1.9
20	0.5	0.7	0.3	0.4	0.5	3.6	1.8
21	0.9	1.0	0.4	0.5	4.1	2.0	3.0
22	0.6	1.1	0.6	1.0	0.4	1.7	1.6
23	0.7	1.1	0.7	3.7	1.5	3.6	2.1
24	6.8	0.9	0.6	0.7	0.8	3.4	3.7
25	0.4	0.8	0.4	0.6	2.6	1.9	2.7
26	0.5	1.1	0.9	1.1	1.2	3.1	1.8
27	1.0	1.0	0.5	0.6	2.5	2.8	2.3
28	1.7	1.1	0.7	0.8	2.6	2.3	2.8
29	1.1	1.3	0.9	1.0	0.9	2.3	2.4
30	1.3	1.3	0.7	0.2	0.6	3.3	2.1
31	1.0	1.0	0.8	1.1	4.5	2.9	3.7
32	1.4	1.3	1.0	1.3	7.1	2.8	2.3
33	1.5	1.1	0.5	0.7	2.8	1.4	2.0
34	2.7	1.6	0.7	1.3	9.3	2.1	2.6
35	0.9	0.8	0.5	0.6	1.7	1.3	1.3
36	0.7	1.3	1.2	1.5	6.6	2.8	1.6
K36	1.1	1.2	1.2	1.6	10.1	5.0	1.6
37	1.1	0.8	0.7	0.8	3.1	1.5	1.5
38	0.4	1.3	8.3	7.7	2.8	24.6	6.8
K38	0.3	0.4	0.5	0.6	1.0	2.7	1.3
39	0.5	1.2	1.6	1.0	6.0	4.6	2.1
40	1.5	1.5	1.7	0.8	14.1	2.7	2.4
K40	0.5	0.9	1.1	1.0	1.7	4.4	1.2
G	2.3	1.4	0.9	0.9	5.0	2.2	2.5

Table 5 Sediment quality guidelines (SQGs) based on effects to benthic-dwelling species (mg kg^{-1} dry weight)

Element	US EPA Toxicity classifications			OSPAR	MacDonald et al., 2000		NOAA	
	Nonpolluted	Moderately Polluted	Heavily Polluted	EAC values	TEC	PEC	ERL	ERM
Pb	<40	40–60	>60	5–50	36	130	46.7	218
Zn	<90	90–200	>200	50–500	120	460	150	410
Cu	<25	25–50	>50	5–50	32	150	34	270
As	<3	3–8	>8	1–10	9.8	33	8.2	70
Cd			>6	0.1–1	0.99	5.0	1.2	9.6
Ni	<20	20–50	>50	5–50	23	49	20.9	51.6
Mn	<300	300–500	>500		460	1,100		

For explanation, see text

OSPAR-EAC Ecological Assessment Criteria, *TEC* threshold effect concentration, *PEC* probable effect concentration, *ERL* effects low range, *ERM* effects mean range

50th percentiles of adverse biological effects (NOAA 1999). The MacDonald et al. (2000) SQGs for freshwater environments have a lower threshold effects concentration (TEC) and an upper probable effect concentration (PEC) at which toxicity to bottom-dwelling organisms is predicted to be unlikely and probable, respectively. The Oslo and Paris Conventions for the prevention of marine pollution have also established Ecological Assessment Criteria (EAC; OSPAR 1997). EAC values are the threshold values. Lower-level EACs are derived for the protection of all marine species, also the most sensitive. Higher value EACs are the highest concentrations that are expected not to cause acute toxic effects. The US Environmental Protection Agency (US EPA) has also made classifications (nonpolluted, moderately polluted, heavily polluted based on toxicity tests (reported in Baudo and Muntau 1990 and Filgueiras et al. 2004)).

For Pb, values exceeding the TEC value were observed at 16 stations and exceeded the PEC level at one station (station 38). The levels at ten stations can be classified as moderately polluted (spread over Inner, Middle, and Outer sections) and heavily polluted at two stations (stations 38 and 25). For As, values exceeding the TEC value were observed at 22 stations (in Inner, Middle, and Outer sections) and exceeded the PEC level at four stations, all in the Outer section. For Zn, TEC values were exceeded at two stations (stations 38 and 23) and PEC levels at station 38. For Cd and Cu, the TEC values were only exceeded at station 38, and the concentrations of Ni were all below TEC values. For

Mn, values exceeding the TEC values were found at 14 stations, mostly in the Inner section.

5.2 Sources of Trace Elements to the Lake

The sediment data clearly show that the Outer section of the lake, in particular the sediments at the mouths of the rivers Samrong, Phawong, and U-Tapao are significantly enriched in trace elements. These rivers receive municipal wastes from two large and rapidly expanding cities: Songkhla City and Hat Yai as well as industrial and agricultural wastes from the growing industrial estates, the rubber plantations, and the parawood industry as well as seafood processing industries. As and Cu are used as wood preservatives, and the parawood industry has rapidly expanded in this area in the last decade (Sompongchaiyakul and Sirinawin 2007). The high levels of As found in the soils at the garbage dumping site indicate that runoff from the dumping sites into the canals and lake may also be an important source of As to the lake.

In the Middle section of the lake, the lake receives inputs from the intensive aquaculture activities which take place (shrimp farms, sea bass farms) as well as mining activities. Various kinds of mining activities have been conducted in the lagoon catchment area (e.g., tin, barite, phosphate, and lead), and therefore, contamination from mining residues is possible. Tin mining in Ronpiboon, Nakhon Si Thammarat Province has caused arsenic (a residue of the tin mining) to spread to outlying areas, resulting in high levels of As in soils and canal sediments (up to 305 µg g^{-1} dry weight), with people

living there suffering from skin cancer and increased mortality (cited in Maneepong and Angsupanich 1999).

Comparison of our data with previous data from Songkhla lake as well as other areas in the world is shown in Table 6. The levels are comparable to those reported in previous studies in the area. High levels of As at the mouth of the Phawong canal have previously been reported by Sompongchaiyakul and Sirinawin (2007), but compared to these previous studies, the levels of As are increasing. However, As levels in Songkhla Lake are much lower than those found in contaminated estuaries of the UK (50–1,000 µg g^{-1} dry weight) reported by Bryan and Langston (1992).

Mean concentrations of Co, Ni, Cu, Zn, Cd, and Pb are comparable to those found in relatively unpolluted aquatic ecosystems such as Lake Balaton (Hungary) and Laguna Lake (Philippines) and offshore sediments of the Gulf of Thailand, whereas the highest concentrations of Cd, Pb, and Zn inSongkhla Lake are comparable to those found in contaminated sediments of the Lagoon of Venice (Italy) and Izmir Bay (Turkey).

5.3 Trace Element Geochemistry in Songkhla Lake Sediments

Table 7 shows the correlation coefficients between the different metals and other sediment properties. The elements Cd, Pb, Cu, and Zn are strongly correlated and also show a strong correlation with TAVS and a positive but weaker correlation with OM. Ni shows a

Table 6 Trace element concentrations (µg g^{-1} dry weight) in sediments of Songkhla Lake and at other sites

Area	Mn	Co	Ni	Cu	Zn	As	Cd	Pb
Songkhla Lake								
This study	48.1–1,817	1.3–16.3	2.5–21.9	1.8–125	5.4–562	0.8–70.7	0.1–2.4	8.2–131
Songkhla Lake[a]	32–545	–	2.9–27.3	2.2–11.4	5.5–56.3	–	<0.1–0.7	13.0–46.3
Outer Songkhla Lake[b]	368–756	–	1.1–16.7				<2.5	24.5–59.8
Songkhla Lake Thale Noi [i]						5.7–10.8		
Songkhla Lake Inner and Middle Lake [i]						3.7–10.8		
Songkhla Lake Outer Lake [i]						5.1–25.7		
U-Tapao canal[c]	200–500	–	–	12.4–28.2	48.6–122.7	–	–	16.7–43.1
U-Tapao canal[j]						1.7–32.6		
Pawong canal						4.2–27.4		
Gulf of Thailand and East Coast of Peninsular Malaysia[d]	–	–	–	10–36	15.3–352	–	0.2–0.4	7–27.8
Sea of Japan [k]			10–23	10–25	55–115	5–9	0.03–0.2	15–30
Other areas								
Venice lagoon (Italy)[e]	–	–	–	–	101–1,115	5–25	0.2–5	38–114
Lake Balaton (Hungary)[f]	160–760	1.7–17	4.4–55	0.7–36	13–150	–	0.1–0.7	2.4–160
Laguna Lake (Philippines)[g]	–	–	9.7–18.7	86.9–116.9	10.3–18.3	–	0.02–0.09	17–23
Izmir Bay (Turkey)[h]	–	–	–	32–70	440–1,900	13.5–28.2	2.5–9.5	55.2–172

[a] Maneepong and Rakaew 1998

[b] Bhongsuwan and Bhongsuwan 2002

[c] Sirinawin and Sompongchaiyakul 2005

[d] Shazili et al. 1999

[e] Bellucci et al. 2002

[f] Nguyen et al. 2005

[g] Hallare et al. 2005

[h] Pekey 2006

[i] Sompongehaiyakul and Sirinawin 2007

[j] Maneepong and Angsupanich 1999

[k] Choi et al. 2008

Table 7 Correlation coefficients (R) at $p<0.05$ between different metals (μg/g dry weight) and other sediment property

	Co	Ni	Cu	Zn	As	Cd	Pb	Al	Fe	Mn	TAVS	% OM	% Sand	% Silt	% Clay
Co	1.00														
Ni	**0.83**	1.00													
Cu	0.13	**0.41**	1.00												
Zn	**0.30**	**0.46**	**0.93**	1.00											
As	**0.43**	**0.38**	0.19	0.15	1.00										
Cd	0.14	**0.41**	**0.98**	**0.94**	0.12	1.00									
Pb	**0.36**	**0.58**	**0.78**	**0.77**	0.19	**0.81**	1.00								
Al	**0.59**	**0.78**	0.23	0.27	0.11	**0.31**	**0.58**	1.00							
Fe	**0.81**	**0.77**	0.23	**0.34**	**0.53**	0.22	**0.51**	**0.62**	1.00						
Mn	0.21	0.10	−0.13	−0.13	0.03	−0.17	−0.18	−0.08	0.04	1.00					
TAVS (mg/g dry weight)	0.21	**0.49**	**0.82**	**0.79**	0.00	**0.81**	**0.65**	**0.33**	0.26	−0.12	1.00				
%OM	**0.52**	**0.64**	**0.34**	**0.38**	0.12	**0.38**	**0.30**	**0.58**	**0.38**	−0.15	**0.49**	1.00			
%Sand	**−0.42**	**−0.42**	−0.07	−0.13	−0.03	−0.09	−0.29	**−0.44**	**−0.45**	−0.13	−0.21	−0.22	1.00		
%Silt	0.05	−0.07	−0.10	−0.07	−0.23	−0.10	−0.11	−0.13	0.01	**0.34**	−0.03	−0.12	**−0.69**	1.00	
%Clay	**0.52**	**0.65**	0.20	0.26	**0.30**	0.23	**0.52**	**0.75**	**0.59**	−0.20	**0.33**	**0.44**	**−0.57**	−0.20	1.00

Significant results are highlighted

positive but weaker correlation with TAVS. The elements Co, Ni, Fe, and Al show a good correlation and are positively correlated with OM and clay fraction. As is correlated with Fe and shows a positive but weak correlation with the clay fraction. Mn shows no significant correlations with other elements.

Diagenetic processes involving Mn and Fe and redox conditions control the behavior of metals in the sediments. Surface enrichment of manganese in sediments where oxic surface sediments become anoxic with depth is well documented (e.g., Winterlund and Ingri 1996; Sirinawin and Sompongchaiyakul 2005). The net effect in such environments is believed to result from the upward migration of dissolved Mn^{2+} ions from the reducing sublayers and subsequent precipitation and enrichment of MnO_2 upon reoxidation in the oxygenated surface layer. The main process underlying the recycling of Mn is the microbiological decomposition of organic matter through bacterial utilization of oxygen and inorganic oxidizing agents. These changes in redox potential pore water chemistry with depth generate the dissolution, upward flux, and reprecipitation of Mn compounds. These conditions also promote the formation of metal sulfide compounds from the available metal species, which are released from the loosely bound and ion exchange sites of Mn and Fe oxy-hydroxides under reducing conditions. During this process, the behavior of Fe and Mn is different, since

Fe is much less mobile and tends to form various sulfur compounds. Enrichment of Mn in the Inner section of the Lake can thus partially be explained by the oxic conditions of the surface sediments, promoting reprecipitation of MnO_2 compared to the suboxic and anoxic conditions in the Middle and Outer sections.

The distribution of TAVS is correlated to the OM and clay content of the sediments as the TAVS are formed in the anoxic sediments receiving high organic matter inputs from riverine sources in the Outer section and decomposing plants in the Middle section. A number of the elements are associated with the TAVS fraction (Cu, Zn, Cd, Pb) and to a lesser extend Ni. These metals are thus principally bound as metal sulfides in the sediments. Differences in water exchange reaction kinetics partially explain the different behavior of the metals. Pb, Zn, Cu, and Cd have faster water exchange reaction kinetics than Fe^{2+}, resulting in the precipitation of metal sulfide phases before the formation of FeS, whereas Co and Ni, which have slower water exchange reaction kinetics, are incorporated in pyrite (Morse and Luther 1999; Billon et al. 2001).

The correlations between Co and Ni with Al, Fe, and clay suggest that these elements are essentially incorporated in the clay minerals as well as adsorbed on the iron oxy-hydroxides. Good correlations between Cu, Zn, Pb, and Co and Ni were also found in suspended matter of the Outer section of Songkhla Lake (Sirinawin et al.

1998). The close relationship between Fe and As in the sediments of Songkhla Lake have been reported in previous studies (Sompongchaiyakul and Sirinawin 2007; Maneepong and Angsupanich 1999). The behavior of As in natural waters depends on pH and redox conditions. In oxidized sediments, arsenate (As^{5+}) is the dominant species, primarily bound to iron oxyhydroxides. In reducing environments, arsenate may be reduced to the arsenite form (As^{3+}), which is more mobile and toxic than the arsenate form (Ryu et al. 2002). The Outer section of the lake is thus a vulnerable area regarding the mobility of As, combining both important riverine inputs and reduced sediment conditions promoting mobilization of As.

5.4 Arsenic and Heavy Metals in Fish and Crustacea

Aquatic organisms accumulate contaminants from the environment and therefore have extensively been used in pollution monitoring programs (UNEP 1993). The accumulation pattern of contaminants in fish and other aquatic organisms depend both on uptake and elimination rates. Uptake routes may be both through food chain and water (Mendil and Uluözlü 2007). Both mollusks and crustacea are useful species for biomonitoring studies (Ali and Fishar 2005). Good indicator species should, however, not be able to regulate tissue metal concentrations relative to environmental levels.

Bioaccumulation factors (BAF) can be calculated as the ratio of the concentration in the organism relative to the concentrations in the sediments. The BAFs for *A. sapensis* in station 19 are 0.48 for Co, 0.53 for Ni, 7.26 for Cu, 2.12 for Zn, 0.68 for As, 1.36 for Cd, and 0.33 for Pb. Differences for the different trace elements may be either due to differences in bioavailability of these elements or, for the essential elements Cu and Zn, be an indication that these species can regulate the concentrations of these elements (Langston and Spence 1995).

In fish, trace elements may be concentrated at different levels in different organs of the body and may be present in different forms (inorganic forms, organometal compounds). High levels of arsenic are encountered in marine fish, but arsenic is predominantly present in the nontoxic arsenobetaine form (De Gieter et al. 2002, Baeyens et al. 2009). Inorganic As on the other hand is highly toxic and carcinogenic.

Fish form an important part of human food, and thus, numerous studies have been carried out on metal pollution in different species of edible fish. Maximum allowable levels in fish according to the European Union regulations are only provided for Hg, Cd, and Pb (EC 2001); whereas in other countries, maximum levels for As, Ni, Cr, Cu, and Zn are also established (US EPA 1989; FAO 1983).

The EU limit for Cd is 0.25 μg g^{-1} dry weight and 2.5 μg g^{-1} dry weight for Pb. Legal limits for As vary between 0.5 and 50 μg g^{-1} dry weight. However, in some countries, this norm is related to the total As content, whereas in some countries, it expresses the inorganic fraction. The Joint FAO/WHO Expert Committee (1983) has set a limit of 0.5 μg g^{-1} dry weight for inorganic As. Limits for Cu vary from 30 to 350 μg g^{-1} dry weight; for Zn, the limits vary between 150 and 500 μg g^{-1} dry weight; for Cr, the limits vary from 1 to 13 μg g^{-1} dry weight; and for Ni, 70–80 μg g^{-1} dry weight. For all the elements, the levels observed are all well within the maximum residual levels prescribed, indicating that consumption of the fish from Songkhla Lake does not pose a threat to human health. Although the observed levels can be regarded as levels in uncontaminated fish, the values of As in the Outer section are substantially higher than in the other parts of the lake as well as the muscle-to-liver ratio of As. Speciation of As is required to distinguish between the toxic inorganic As forms and the nontoxic forms such as arsenobetaine. Future monitoring of trace element concentrations in several groups of benthic fauna and fish and speciation analysis is thus required in order to guarantee the food safety.

6 Conclusions

Trace element concentrations in sediments of Songkhla lake show that especially the Outer section of the lake, in particular the sediments at the mouths of the canals Phawong, Samrong, and U-Taphao, were significantly enriched in trace elements due to municipal, agricultural, and industrial discharges entering the lake through the canals. Large amount of organic matter is also transported by the canals, resulting in anoxic conditions in the sediments, which may in turn affect the mobility and bioavailability of the pollutants. Trace element concentrations exceeding SQGs were observed at different stations. At the mouth of the Samrong canal, values exceeding the SQGs were observed for Cd, Pb,

Cu, Zn, Ni, and As. Very high As levels were also found at a garbage dumping site located between the U-Taphao and Phawong canals.

For Pb, values exceeding the TEC value were observed at 16 stations and exceeded the PEC level at one station (station 38). The levels at ten stations can be classified as moderately polluted (spread over Inner, Middle, and Outer sections) and heavily polluted at two stations (stations 38 and 25). For As, values exceeding the TEC value were observed at 22 stations (in Inner, Middle, and Outer sections) and exceeded the PEC level at four stations, all in the Outer section. For Zn, TEC values were exceeded at two stations (stations 38 and 23) and PEC levels at station 38. For Cd and Cu, the TEC values were only exceeded at station 38, and the concentrations of Ni were all below TEC values. For Mn, values exceeding the TEC values were found at 14 stations, mostly in the Inner section.

Correlations between the elements and sediment characteristics show that Cu, Zn, Cd, and Pb are essentially associated with the reduced sulfur fraction; that Ni and Co are predominantly bound to the clay minerals and iron oxy-hydroxides and that As is principally bound to iron oxy-hydroxides. Mn has a totally different behavior than the other metals and seems to be controlled by the reprecipitation of MnO_2 in oxic surface sediments.

Although the trace element levels in the fish muscle tissue are much lower than allowable levels, the higher concentrations of As found in the fish samples caught in the Outer section compared to the Inner and Middle sections as well as the higher muscle-to-liver tissue require monitoring of these pollutants in different fish species as well as performing speciation analysis for As.

References

Ali, M. H. H., & Fishar, M. R. A. (2005). Accumulation of trace metals in some benthic invertebrates and fish species relevant to their concentration in water and sediment of Lake Qarun, Egypt. *Egyptian Journal of Aquatic Research, 31*(1), 289–301.

Angsupanich, S., Somsak, S., & Phrommoon, J. (2005). Stomach contents of the catfishes *Osteogeneiosus militaris* (Linnaeus, 1758) and *Arius maculatus* (Thunberg, 1792) in the Songkhla Lake. *Songklanakarin Journal of Science and Technology, 27*, 391–402.

Baeyens, W., Gao, Y., De Galan, S., Bilau, M., Van Larebeke, N., & Leermakers, M. (2009). Dietary exposure to total and toxic As in Belgium: Importance of As speciation in North Sea fish. *Molecular Nutrition & Food Research* . doi:10.1002/mnfr.200700533.

Baudo, R., & Muntau, H. (1990). Lesser known in-place pollutants and diffuse source problems. In R. Baudo, J. P. Giesy & H. Muntau (Eds.), *Sediment: Chemistry and toxicity of in-place pollutants* (pp. 1–14). USA: Lewis Publishers.

Bellucci, G. L., Frignani, M., Paolucci, D., & Ravanelli, M. (2002). Distribution of heavy metals in sediments of the Venice Lagoon: The role of the industrial area. *The Science of the Total Environment, 295*, 35–49. doi:10.1016/S0048-9697(02)00040-2.

Bhongsuwan, T., & Bhongsuwan, D. (2002). Concentration of heavy metals, Mn, Fe, Ni, Pb, Cr and Cd in bottom sediments of the outer Songkhla Lake deposited between the year B.E.2520–2538. *Songklanakarin Journal of Science and Technology, 24*, 89–106.

Billon, G., Ouddance, B., & Boughriet, A. (2001). Artefacts in the speciation of sulfides in anoxic sediments. *Analyst (London), 126*, 1805–1809. doi:10.1039/b104704n.

Bryan, G. W., & Langston, W. J. (1992). Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: A review. *Environmental Pollution, 76*, 9–131. doi:10.1016/0269-7491(92)90099-V.

Buccolieri, A., Buccolieri, G., Cardellicchio, N., Atti, A. D., Leo, A. D., & Maci, A. (2006). Heavy metals in marine sediments of Taranto Gulf (Ionian Sea, Southern Italy). *Marine Chemistry, 99*, 227–235. doi:10.1016/j.marchem.2005.09.009.

Chareonpanich, C., & Seurungreong, S. (1999). Some physical and Chemical Characteristics of Bottom Sediments in the South China Sea, Area I: Gulf of Thailand and East Coast of Peninsular Malaysia. *Proceedings of the first technical seminar on marine fishery resources survey in the South China Sea area I: Gulf of Thailand and East Coast of Peninsular Malaysia*, 24-26 November 1997, Bangkok, Thailand, pp.12-33.

Chareonpanich, C., Montani, S., Tsutsumi, H., & Matsuoka, S. (1993). Modification of chemical characteristics of organically enriched sediment by *Capitella* sp. *Marine Pollution Bulletin, 26*, 375–379. doi:10.1016/0025-326X(93)90184-L.

Cheevaporn, V., & San Diego-McGlone, M. L. (1997). Aluminium normalization of heavy-metal data from estuarine and coastal sediments of the Gulf of Thailand. *Thammasat International Journal of Science and Technology, 2*, 37–46.

Choi, K. Y., Kim, S. H., & Chon, H. T. (2008). Distribution and accumulations of heavy metals in the sediments of harbors and coastal areas in Korea. *Proceedings of the International Symposia on Geoscience Resources and Environments of Asian Terranes (GREAT 200!),* November 24-26 2008, Bangkok, Thailand, pp. 474-476.

De Gieter, M., Leermakers, M., Van Ryssen, R., Noyen, J., Goeyens, L., & Baeyens, W. (2002). Total and toxic arsenic levels in North Sea Fish. *Archives of Environmental Contamination and Toxicology, 43*, 406–417. doi:10.1007/s00244-002-1193-4.

EC. (2001). Comission Regulation No. 466/2001 of 8 March 2001. Official journal of European Communities 1.77/1.

FAO. (1983). Compilation of legal limits for hazardous subnstance in fish and fishery products (Food and agricultural organization) FAO fishery circular, No. 464, 5-100.

Filgueiras, A. V., Lavilla, I., & Bendicho, C. (2004). Evaluation of distribution, mobility and binding behaviour of heavy metals in surficial sediments of Louro River (Galicia, Spain) using chemometric analysis: A case study. *The Science of the Total Environment, 330*, 115–129. doi:10.1016/j.scitotenv.2004.03.038.

Gee, G. W., & Bauder, J. W. (1986). Particle-size analysis. In A. Klute (Ed.), *Method of soil analysis part 1: Physical and mineralogical methods* (pp. 383–412). Wisconsin: Madison Publisher.

Hallare, A. V., Kosmehl, T., Schulze, T., Hollert, H., Kohler, H. R., & Triebskorn, R. (2005). Assessing contamination levels of Laguna Lake sediments (Philippines) using a contact assay with zebrafish (*Danio rerio*) embryos. *The Science of the Total Environment, 347*, 254–271. doi:10.1016/j.scitotenv.2004.12.002.

Herreweghe, S. V., Swennen, R., Cappuyns, V., & Vandecasteele, C. (2002). Chemical associations of heavy metals and metalloids in contaminated soils near former ore treatment plants: A differentiated approach with emphasis on pHstat-leaching. *Journal of Geochemical Exploration, 76*, 113–138. doi:10.1016/S0375-6742(02)00232-7.

Langston, W. J., & Spence, S. K. (1995). Biological factors involved in metal concentrations observed in aquatic organisms. In A. Tessier & D. Turner (Eds.), *Metal speciation and bioavalability in aquatic systems*. West Sussex, England: John Wiley & Sons.

Loring, D. H., & Rantala, R. T. T. (1992). Manual for the geochemical analyses of marine sediments and suspended particulate matter. *Earth-Science Reviews, 32*, 235–283. doi:10.1016/0012-8252(92)90001-A.

MacDonald, D. D., Ingersoll, C. G., & Berger, T. A. (2000). Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Archives of Environmental Contamination and Toxicology, 39*, 20–31. doi:10.1007/s002440010075.

Maneepong, S. (1996). Distribution of heavy metals in sediments from outer part of Songkhla Lagoon, southern Thailand. *Songklanakarin Journal of Science and Technology, 18*, 87–97.

Maneepong, S., & Angsupanich, S. (1999). Concentration of arsenic and heavy metals in sediment and aquatic fauna from the outer Songkhla Lagoon, Phawong and U Taphao Canals. *Songklanakarin Journal of Science and Technology, 21*, 111–121.

Maneepong, S., & Rakeaw, S. (1998). Study of Chemical Properties of Sediments from Thale Noi and Thale Luang. Research report (in Thai). Prince of Songkla University, Thailand.

Meksumpun, C., & Meksumpun, S. (1999). Polychaete–sediment relations in Rayong, Thailand. *Environmental Pollution, 105*, 447–456. doi:10.1016/S0269-7491(98)00222-X.

Mendil, D., & Uluözlü, O. D. (2007). Determination of trace metal levels in sediment and five fish species from lakes in Tokat, Turkey. *Food Chemistry, 101*, 739–745. doi:10.1016/j.foodchem.2006.01.050.

Miao, S., DeLaune, R. D., & Jugsujinda, A. (2006). Influence of sediment redox conditions on release/solubility of metals and nutrients in a Louisiana Mississippi River deltaic plain freshwater lake. *The Science of the Total Environment, 371*, 334–343. doi:10.1016/j.scitotenv.2006.07.027.

Moqsud, M. A., Hayashi, S., Du, Y. J., & Suetsugu, D. (2006). Temporal variation of sulphide content, pH, salinity and oxidation-reduction potential of tidal flat mud in the Ariake Sea, Japan. *Evironmental Informatics Archives, 4*, 225–232.

Morse, J. W., & Luther, G. W. (1999). Chemical influences on trace metal–sulfide interactions in anoxic sediments. *Geochimica et Cosmochimica Acta, 63*, 3373–3378. doi:10.1016/S0016-7037(99)00258-6.

Nguyen, H. L., Leermakers, M., Osán, J., Török, S., & Baeyens, W. (2005). Heavy metals in Lake Balaton: Water column, suspended matter, sediment and biota. *The Science of the Total Environment, 340*, 213–230. doi:10.1016/j.scitotenv.2004.07.032.

NOAA. (1999). Sediment quality guidelines developed for the National Status and Trends Program. http://response.restoration.noaa.gov/book_shelf/121_sedi_qual_guide.pdf.

Office of Natural Resources and Environmental Policy and Planning (ONEP).(2005). Master Plan for Songkhla Lake Basin Development. Final Report by Prince of Songkla University, Taksin University and Songkhla Rajabhat University.

OSPAR. (1997) Contaminants in Sea Water, Biota and Sediment. Agreed Ecotoxicological Assessment Criteria for Trace Metals, PCBs, PAHs, TBT and some Organochlorine Pesticides. OSPAR Commission, meeting document No. OSPAR 97/15/1, Annexes 5 and 6.

Pekey, H. (2006). The distribution and sources of heavy metals in Izmit Bay surface sediments affected by a polluted stream. *Marine Pollution Bulletin, 52*, 1197–1208. doi:10.1016/j.marpolbul.2006.02.012.

Prudêncio, M. I., Gonzalez, M. I., Dias, M. I., Galan, E., & Ruiz, F. (2007). Geochemistry of sediments from El Melah lagoon (NE Tunisia): A contribution for the evaluation of anthropogenic inputs. *Journal of Arid Environments, 69*, 285–298. doi:10.1016/j.jaridenv.2006.10.006.

Rickard, D., & Morse, J. W. (2005). Acid volatile sulfide (AVS). *Marine Chemistry, 97*, 141–197. doi:10.1016/j.marchem.2005.08.004.

Ryu, J. H., Gao, S., Dahlgren, R. A., & Zierenberg, R. A. (2002). Arsenic distribution, speciation and solubility in shallow groundwater of Owens Dry Lake, California. *Geochimica et Cosmochimica Acta, 66*, 2981–2994. doi:10.1016/S0016-7037(02)00897-9.

Salomons, W. (1998). Biogeodynamics of contaminated sediments and soils: Perspectives for future research. *Journal of Geochemical Exploration, 62*, 37–40. doi:10.1016/S0375-6742(97)00063-0.

Sasayama, Y., Higashide, Y., Sakai, M., Matada, M., & Fukumori, Y. (2007). Relationship between the lifestile

of Siboglinid (Pogonophoran) Polychaete, *Oligobrachia mashikoi*, and the total sulfide and nitrogen levels in its habitat. *Zoological Science, 24*, 131–136. doi:10.2108/zsj.24.131.

Schumacher, B. A. (2002). Methods for the determination of total organic carbon (TOC) in soils and sediments. NCEA-C-1282, EMASC-001. USEPA.

Shazilli, N. A. M., Rashid, M. K. A., Husain, M. L., Nordin, A., & Ali, S. (1999). Trace Metals in the surface sediments of the South China Sea, Area I: Gulf of Thailand and East Coast of Peninsular Malaysia. *Proceedings of the first technical seminar on marine fishery resources survey in the South China Sea area I: Gulf of Thailand and East Coast of Peninsular Malaysia*, 24-26 November 1997, Bangkok, Thailand, 1999:73-85.

Silva, M. A. L., & Rezende, C. E. (2002). Behavior of selected micro and trace elements and organic matter in sediments of a freshwater system in south-east Brazil. *The Science of the Total Environment, 292*, 121–128. doi:10.1016/S0048-9697(02)00034-7.

Sirinawin, W., & Sompongchaiyakul, P. (2005). Nondetrital and total metal distribution in core sediments from the U-Taphao Canal, Songkhla, Thailand. *Marine Chemistry, 94*, 5–16. doi:10.1016/j.marchem.2004.07.007.

Sirinawin, W., Turner, W. S., & Kanatharana, P. (1998). Trace metals study in the Outer Songkla Lake, Thale Sap Songkla, a southern Thai estuary. *Marine Chemistry, 62*, 175–183. doi:10.1016/S0304-4203(98)00042-5.

Sompongchaiyakul, P., & Sirinawin, W. (2007). Arsenic, chromium and mercury in surface sediment of Songkhla Lake system. Thailand. *Asian Journal of Water Environmental Pollution, 4*, 17–24.

Sukapan, S., Sompongchaiyakul, P., & Khokiattiwong, S. (2006). Variation and Distribution of Mercury in the tissues of Aquatic Organisms Catching from Songkhla Lake. *Proceedings of the NIE-SEAGA Conference on Sustainability and Southeast Asia*, 28-30 November 2006, Singapore.

Tsutsumi, H., & Kikuchi, T. (1983). Benthic ecological of a small cove with seasonal oxygen depletion caused by organic pollution. *Journal of Amakusa Marine Biological Laboratory, 7*, 17–40.

UNEP. (1993). Guidelines for monitoring chemical contaminants in the sea using marine organisms (United Nations Environmental Program). Reference methods for marine pollution studies. Report 6; Athens.

US EPA. (1989). Assessing human health risks from chemically contaminated fish and shellfish. A guidance manual. EPA-503/8-89-002.

Winterlund, A., & Ingri, J. (1996). Redox cycling of iron and manganese in sediments of the Halix River Estuary, Northern Sweden. *Aquatic Geochemistry, 2*, 185–201. doi:10.1007/BF00121631.

Yodnarasri, S., Montani, S., Tada, K., Shibanuma, S., & Yamada, T. (2008). Is there any seasonal variation in marine nematodes within the sediments of the intertidal zone? *Marine Pollution Bulletin, 57*, 149–154. doi:10.1016/j.marpolbul.2008.04.016.