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# Lead and Cadmiun Concentrations in the Catfish *Pangasius Polyuranodon* (Bleeker 1852) from the Siak River, Riau Province, Indonesia

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**Abstract:** During the last decades, increasing development of industries, urban communities and agriculture near aquatic ecosystems lead to pollution, especially in the developing countries of Southeast Asia. Due to trace metal pollution through increasing development and human activities near aquatic ecosystems, there is a growing risk of toxic metal exposure to fish and through their consumption also to humans. Therefore, the investigation of the chemical quality of fish for consumption, particularly the concentrations of toxic metals, is important for human health. We investigated the trace metal concentrations of lead (Pb) and cadmium (Cd) in different tissues of the catfish *Pangasius polyuranodon* from five areas of the Siak River in order to evaluate the potential for human health hazards resulting from fish consumption. Mean concentrations of Pb and Cd in gills (0.14 and 0.22, respectively), livers (0.11 and 0.18, respectively) and muscles (0.14 and 0.15, respectively) of *P. polyuranodon* were below national and international standards. Pb levels in gills and muscles were close to the national food standard at one sampling site and Cd concentrations in the gills were found to be at the national food standard at the same site. Only at one site, Cd concentration in the liver slightly exceeded the national, but not the international food standard. The overall results indicate that the edibles parts of *P. polyuranodon* in the Siak are only slightly contaminated by Pb and Cd and do not represent a risk for human consumption in regard to the two investigated trace metals. However, the special biogeochemistry of the blackwater river Siak might enhance bioaccumulation of toxic metals and more research is needed in regard to other toxic metals, seasonal availability of these metals, other consumed fish species, as well as fish age or size dependent accumulation of toxic metals.

**Key words:** Lead and cadmium concentrations, bioaccumulation, Pangasius polyuranodon, Siak river, international food standard.

## Introduction

Fish represent an important nutritional source of high quality protein for people all over the world. They contain high amounts of essential unsaturated fatty acids and fish consumption is beneficial for human health (Daviglus et al., 2002). During the last decades, pollution of aquatic environments and therefore the possible danger of contamination of fish for human consumption have reached greater awareness. Increasing development of industries, urban communities and agriculture near aquatic ecosystems promotes their pollution, for instance an increase in trace metal concentrations in the water. Trace metals can reach aquatic ecosystems through natural processes, e.g. from the atmosphere or by erosion of soil or rock, which

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occurs usually at low levels (Alam et al., 2002; Zouh et al., 2008). The common anthropogenic sources of metal pollution are industrial discharges, traffic and utility waste, urban waste waters and agricultural runoff, e.g. from some herbicides (Olojo et al., 2005; Matasin, 2011). Some trace metals are harmful for organisms due to their perseverance, high toxicity and their tendency of bioaccumulation (Nicolau et al., 2006; Matasin, 2011). This can lead to biomagnification of trace metals along the food chain up to the higher trophic levels in the aquatic ecosystem, namely predatory fishes (Wang, 2002, Croteau et al., 2005). However, the trace metals can also be taken up constantly from the surrounding water (Gray 2002).

Despite their relatively high mobility, fish present very useful organisms for pollution monitoring in aquatic systems, because they occur ubiquitously in the aquatic environment and they are key organisms in food-webs, either between lower and higher trophic levels or as top-predators (Van de Oost et al., 2003). Trace metal uptake in fish occurs mainly through gills or intestinal walls via food (Karlsson-Norrgren and Runn, 1985). In freshwater fish, uptake of dissolved metals through the gills is high as these fish do not drink (Olsson et al., 1998). They are bound to transport proteins and distributed by circulation to different tissues of the body (Olsson et al., 1998). Trace metals are mainly accumulated in kidneys and liver of fish (Olsson and Haux, 1986; Hogstrand, 1991). Elimination of toxic metals occurs through protein binding, e.g. by metallothionein, a metal binding protein thought to detoxify, and excretion (Olsson et al., 1998). Water hardness decreases the uptake of trace metals and protects against their toxicity (Wicklund and Runn, 1988; Comhaire et al., 1994).

The Food and Agriculture Organization (FAO) of the United Nations identifies eight metals in fish, which should be monitored: mercury (Hg), cadmium (Cd), lead (Pb), arsenic (As), copper (Cu), zinc (Zn), iron (Fe), and selenium (Se) (FAO, 2005). Cd and Pb are non-essential and toxic metals, which are mainly derived from industrial activities such as mining, refining of ores, plating process, the use of phosphate fertilizers and gasoline containing lead (Pascoe and Mattery, 1977; Handy, 1994). In fish, Cd can cause kidney failure and demineralisation of the skeleton (Larsson et al., 1981) and it can reduce reproduction success (Birge et al., 1981). Pb can inhibit an enzyme in the haemoglobin synthesis and it is a neurotoxin, causing behavioural deficits (Haux et al., 1986; Hodson et al., 1984). It can reduce survival and growth rates, as well as a decrease in metabolism (Burger and Gochfeld, 2005 and references therein). In humans, Cd also causes renal deficiency and demineralisation of bones (Goyer, 1995). In 1912, the Itai-itai disease, a Cd-poisoning in Japan, caused softening of the bones and kidney failure. The Cd was released into rivers by mining companies and accumulated in the rice on agriculture fields near the river. Pb can cause damage of the nervous system including the brain, as well as blood disorders (Goyer, 1995). Due to trace metal pollution through increasing development and human activities in many aquatic ecosystems there is a growing risk of toxic metal exposure to fish and through their consumption also to humans.

Trace metal pollution of aquatic systems is increasing especially in the developing countries of Southeast Asia (Wong et al., 2006). Therefore, the investigation of the chemical quality of fish for consumption, particularly the concentrations of toxic metals, is significant for human health. Predatory fish, like catfish, are an important fishery resource of freshwater aquatic ecosystems in Southeast Asia, but they are at the top of food chains in river ecosystems and therefore likely to accumulate trace metals in their body. Twelve commonly caught catfish species belonging to the *Pangasiidae* occur in Indonesia. In 2009, 109,685 t of *Pangasius* spp. were caught in the inland fishery of Indonesia without specification of species (FishStatPlus, 2011). *P. hypophthalamus* is farmed in ponds and *P. djambal* is a promising candidate for further aquaculture development (Legrende et al., 2000). In Sumatra, *P. polyuranodon*is one of economical important catfishes, commonly caught by fishermen in estuaries and lower reaches of rivers, but it occasionally migrates in upper reaches during the rainy season (Pouyaud et al., 2002; Gustiano, 2009). *P. polyuranodon* is omnivorous with a tendency to opportunism, but mainly feeding on small gastropods, bivalves, insects, leaves, and detritus and reaches a maximum length of 800 mm (Pouyaud et al., 2002; Gustiano, 2009). *P. polyuranodon* in the Siak River in central Sumatra contributes between 6 to 40% of the fish catches in weight (Husnah et al., 2008).

The Siak River is a nutrient-poor blackwater river with high levels of dissolved organic matter (DOM), leached from surrounding, heavily disturbed peat soils, leading to its brown colour (Baum et al., 2007; Rixen et al., 2008). At least 44 industries, including pulp and paper factories, palm oil and rubber plantations and processing plants and sawmills, are based along its main body (Pusat Pelayanan Publik, 2006) and discharge waste water into the river. The Siak River receives urban sewage from the largest and capital city of the province Riau, Pekanbaru (km 180) with a population of 680,000 and from two smaller industrial cities, Perawang (km 220) and Siak Sri Indrapura (km 286). In general, fishery has a high importance as protein source in Indonesia and the fisheries of the Siak are of great importance for the population along the river. According to the impression of local fishermen, the fish catches are declining due to increasing environmental pollution during the last decade (Suhren et al., 2014). To investigate this hypothesis lies far beyond the scope of this paper, which nevertheless will try to add some important information to the subject.

The main objective of this study is to assess the magnitude of Pb and Cd contamination in three different tissues of the catfish *P. polyuranodon* from five areas of the Siak River affected by industrial and other human activities, and to evaluate the potential for human health hazards resulting from fish consumption.

## Materials and Methods

### Study Area

The Siak with a total length of 370 km is one of the major rivers of the central Sumatran lowlands. It originates at the confluence of the Sungai Tapung Kanan and the Sungai Tapung Kiri, passes through adjacent lowlands including the province capital Pekanbaru, and discharges after 370 km into the Bengkalis Strait (Figure 1). The study area is located in the middle part of the Siak River drainage area, covers approximately 2919 km$^2$ and its land area is dominated by palm oil and rubber plantation, bushes and forest, mixed plantations, open area, and small parts of agriculture. A part of the open area was categorized as mining area. The average rainfall in Pekanbaru reaches 2168 mm yr$^{-1}$. The highest rainfalls occur from October to December, while the driest season is from June to August (Rixen et al., 2008).

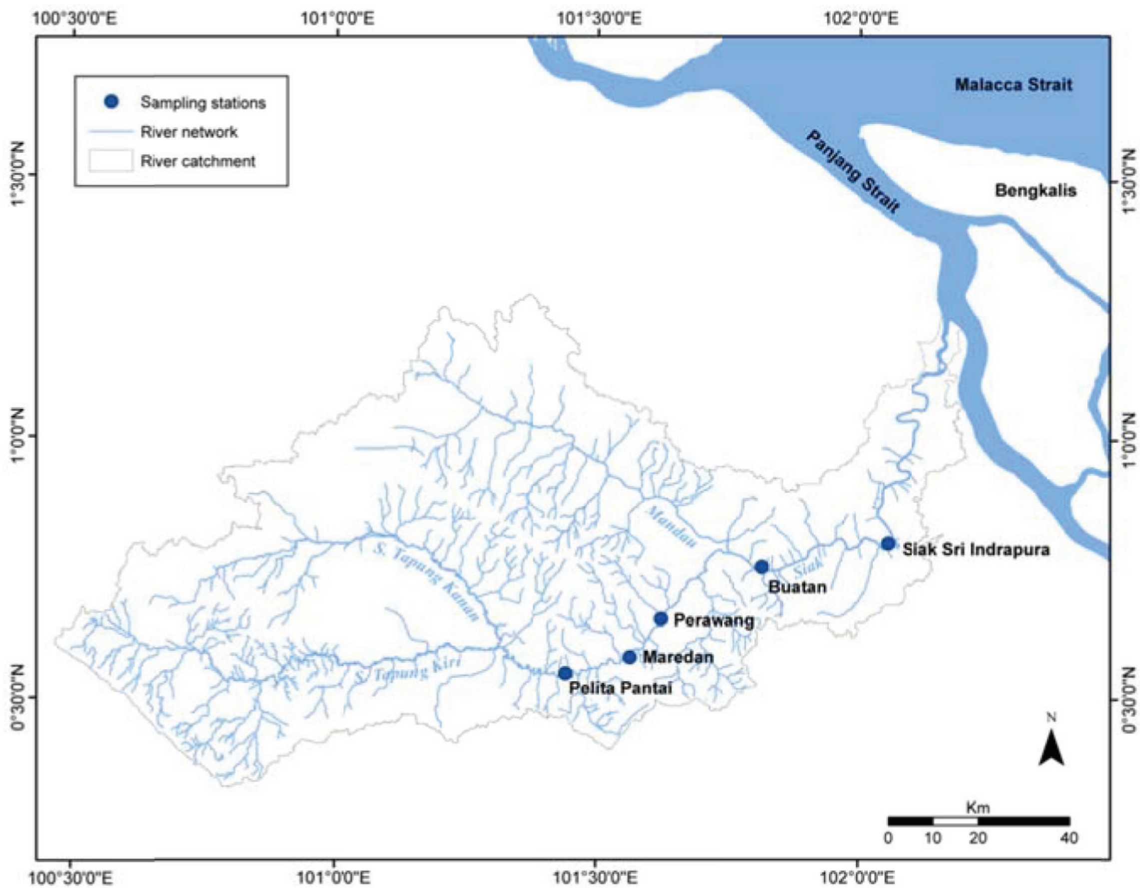


**Figure 1: Map of the study area showing the Siak River catchment area. Sampling sites are indicated by blue circles along the middle part of Siak River.**

### Sampling and Analyses

Water quality parameters, such as pH, total alkalinity, total hardness, and dissolved oxygen, were measured in situ. Water samples were collected at 1 m depth below the surface in each of sampling sites by using a 2 L Kemmerer water sampler. pH was determined by using a pH universal indicator. Total alkalinity and water hardness were measured by titration using 0.02 $H_2SO_4$, titrimetric using 0.01 EDTA, respectively. Dissolved oxygen was determined by the Winkler method (APHA, 1980).

*P. polyuranodon* were collected from fishermen in each of the five sampling sites, Pelita Pantai, Maredan, Perawang, Buatan and Siak Sri Indrapura, located in the middle part of the Siak River drainage area in November 2009 (Figure 1). Five individuals of *P. polyuranodon* of approximately 200 mm length were caught at each station. The tissue of the three organs, gill, liver and muscle, from five fish in each sampling site were composite, put into the pre-acidified plastic bottle and preserved with 70% alcohol solution. The samples were sent to the Research Center for Limnology of the Indonesian Institute of Science, and analysed with Indonesian National Standard (SNI) No. 01-2354.7-2006 for Pb analysis and No. 01-2354.5-2006 for Cd analysis. Measurement of Pb and Cd were conducted with dry digestion at temperature of 450 $^oC$. Both, Pb and Cd in the ash were dissolved firstly with 6 M of hydrochloric acid (HCl) and secondly 0.1 M of nitrate acid ($HNO_3$). A hollow cathode lamp in an electrothermal line source atomic absorption spectrophotometer (LS AAS) was used to measure Pb and Cd concentrations. Calibration was performed by analysing standards and blank samples. As it was not possible to measure samples of fish individually, statistics like ANOVA could not be applied to the data.

## Results and Discussion

From a human health perception, consumers need to know, which fish to buy based on available knowledge on the levels of contaminants. Contaminant information is generally unavailable for many fish species and many aquatic ecosystems in developing countries. In this study, levels of trace metals in the commonly consumed catfish *P. polyuranodon* from a blackwater river system were investigated.

All mean concentrations of Pb and Cd in the three organ tissues of *P. polyuranodon* from the Siak River were below the FAO/WHO limit (Nauen, 1983), Indonesia's Reg. No. 03725/B/SK/VII/89 (National drug & food standards of Indonesia, 1989) and the maximum limits for heavy metals impurities in food (National Standardisation Agency of Indonesia, 2009) (Table 1). Pb levels were close to the maximum limits for heavy metals impurities in food (National Standardisation Agency of Indonesia, 2009) in gills and muscles of fish at Meradan (Figure 2a). Cd concentrations were found to be at the limit of the maximum limit for heavy metals impurities in food (National Standardisation Agency of Indonesia, 2009) in the gills of fish at Meradan and above this limit in the livers of fish at Buatan (Figure 2b). However, all Pb and Cd concentrations in the edible parts of *P. polyuranodon* were below the recommended limits (Figure 2).

The accumulation of Pb and Cd in gills, livers and muscles of *P. polyuranodon* from thefive sampling sites varied slightly (Figure 2). Highest accumulation of Pb was found in the fish from Maredan for the gill and muscle tissue and in Buatan for the liver tissue (Figure 2a). Concentrations of Cd in fish were highest in Maredan for gill tissue, in Siak Sri Indrapura for muscle tissue and in Buatan for liver tissue (Figure 2b).

**Table 1: Mean (±sd) lead (Pb) and cadmium (Cd) concentrations (mg kg$^{-1}$) in three different organs of *P. polyuranodon* and different international and national standards for the two metals in fish tissue**

| | *P. polyuranodon gill mean (mg kg$^{-1}$)* | *P. polyuranodon liver mean 1989 (mg kg$^{-1}$)* | *P. polyuranodon muscle mean (mg kg$^{-1}$)* | *FAO/WHO (Nauen, 1983) (mg kg$^{-1}$)* | *National drug & food standards of Indonesia Reg.No. 03725/B/SK/VII/89 1989 (mg kg$^{-1}$)* | *Max. limits for heavy metals impurities in food, National Standardisation Agency of Indonesia, SNI7387:2009* |
|---|---|---|---|---|---|---|
| Pb | 0.14 (±0.14) | 0.11 (±0.11) | 0.14 (±0.18) | 0.5 | 0.2 | 0.4 |
| Cd | 0.22 (±0.17) | 0.18 (±0.19) | 0.15 (±0.11) | 0.5 | 0.5 | 0.5 |

(a)

(b)

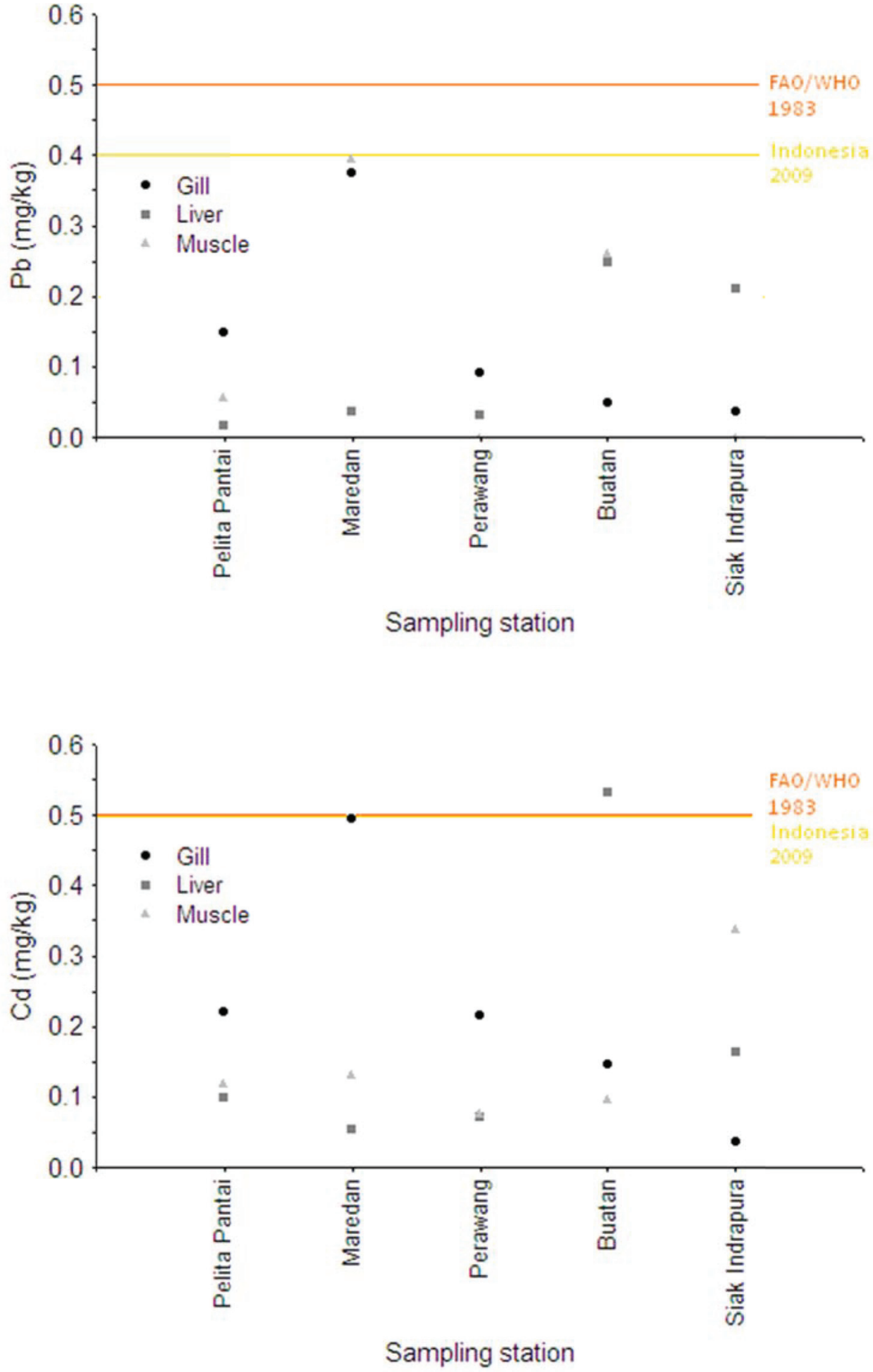


**Figure 2: Pb (a) and Cd (b) concentrations in the gills (circle), liver (rectangle), and muscle (triangle) of five *P. polyuranodon* at the five different sampling stations. The orange line indicates the FAO/WHO (1983) standard; and the yellow line indicates the maximum limits for heavy metals impurities in food (National Standardisation Agency of Indonesia, 2009).**

In general, concentrations of the two trace metals were higher in the gills than in the other tissues for the first three stations, Pelita Pantai, Maredan and Perawang, whereas the two lower stations, Buatan and Siak Sri Indrapura, metal concentrations were higher in liver and muscle tissue, except for high Pb concentration in muscle tissue at Maredan. This indicates that at the first three sampling sites, trace metal uptake occurred mainly through the gills, where the metal accumulated. This is supported by findings of Jayakumar and Paul (2006), that Cd in the surrounding water was first accumulated with a higher rate in the gills, then in the kidney, liver and finally in the muscle in lower concentration.

These concentrations of the investigated trace metals in *P. polyuranodon* gills may relate to the close distance of these sites to domestic and industrial activities, such as farms and pulp and paper industry. Higher concentrations of Pb and Cd in the liver and muscle tissue in fish from the two lower stations indicate either uptake of trace metals by feeding or accumulation over a longer time. In the latter case, trace metals might have been transported from the gills into liver and muscle tissue long after exposure of the fish to polluted water and the uptake through the gills. As fish were of the same size, we assume that they are also of a similar age indicating that the differences in metal accumulation are not a result of age or size specific accumulation. The catfish *P. polyuranodon* is known to migrate upstream in the Siak during rainy season (Gustiano, 2009) and consequently, they could have taken up Cd and Pb in the more industrialised areas.

Pb and Cd concentrations in the water were relatively low and constantly distributed along the river. Average concentrations of Pb and Cd were 0.025 ± 0.005 mg $g^{-1}$ and 0.0005 ± 0.0001 mg $g^{-1}$ respectively. The metal content of the suspended particles in the Siak varied more. Cd was again rather uniformly distributed along the Siak with an average concentration of 0.0007 ± 0.0003 mg $g^{-1}$, whereas Pb had an average value 0.029 ± 0.016 mg $g^{-1}$ and had slightly elevated levels upstream of Pekanbaru and downstream of Perawang. As oxygen concentrations in the Siak are also generally low (Table 2; Rixen et al., 2008), it can be hypothesised that fish and other mobile organisms in need of oxygen linger around the discharges, where more turbulence enhances oxygen levels of the water. At the same time, the organisms are possibly exposed to higher loads of pollutants in the waste water, which dilute in the river with distance from the discharge site. However, also exposure of the fish in the long term could have led to accumulation of trace metals in the fish tissue. In the freshwater fish tilapia (*Oreochromisniloticus*), metal levels in liver and muscle were found to be significantly higher than the levels in water, indicating bioaccumulation (Al-Kahtani, 2009).

The pH value of the river was 7 at the first station Pelita Pantai and decreased towards the most downstream station Siak Sri Indrapura, where it was only 5 (Table 2). The Siak water has a low alkalinity between 2.3 and 12 mg $L^{-1}$ $CaCO_3$ and therefore a low pH buffering capacity. Furthermore, the river water is very soft, ranging in hardness from 11 to 49 mg $L^{-1}$ $CaCO_3$ at the five sampling stations (Table 2). Blackwater rivers, like the Siak, are nutrient poor and rich in humic acids and thus dissolved organic carbon (DOC) (Baum et al., 2007). Metal toxicity and bioaccumulation are affected by all these water parameters. The pH of the river water is negatively correlated to Cd solubility and Pb bioaccumulation (Merlini and Pozzi, 1977; Galvin, 1996). In addition there is a negative relationship between alkalinity and Cd and Pb bioaccumulation, as found for Cd and Pb concentrations in the kidneys of Arctic char (*Salvelinusalpinus*) (Köck et al., 1995).

In general, bioavailability of metals increases with decreasing water hardness (Wang, 1987). Therefore, the toxicity of Pb and Cd is greater in soft water than in hard water (Pettinen et al., 1986; Galvin, 1996). However, humic substances associate with metals, e.g. the Cd-humic substance complex has a high stability and reduces its bioavailability (Cleven and van Leeuwen,

**Table 2: The water parameters pH, alkalinity, hardness and oxygen measured at the five sampling stations along the Siak river**

| *Station* | *pH* | *Alkalinity (mg $CaCO_3$ $L^{-1}$)* | *Hardness (mg $CaCO_3$ $L^{-1}$)* | *Oxygen (mg $L^{-1}$)* |
|---|---|---|---|---|
| Pelita Pantai | 7.0 | 6.5 | 11.0 | 5.17 |
| Maredan | 6.5 | 5.0 | 11.5 | 3.23 |
| Perawang | 6.5 | 12.0 | 17.0 | 0.81 |
| Buatan | 5.5 | 2.8 | 48.0 | 0.80 |
| Siak Indrapura | 5.0 | 2.3 | 49.0 | 0.65 |

**Table 3: Overview of water chemistry parameters of the Siak river and its effects on the bioavailability, toxicity and bioaccumulation of Pb and Cd**

| | *Water chemistry of the Siak* | *Effect Cd* | *Effect Pb* |
|---|---|---|---|
| pH | Low | Higher solubility and bioavailability | higher bioaccumulation |
| Alkalinity | Low | Higher bioaccumulation | higher bioaccumulation |
| Hardness | Soft | Higher bioavailability, higher toxicity, higher bioaccumulation | Higher bioavailability, higher toxicity |
| Humic substances/DOC | High | Lower bioavailability | Lower bioavailability |

1986; Wang, 1987; Galvin, 1996). All these parameters affect the bioavailability, toxicity and bioaccumulation of Pb and Cd in the Siak River (Table 3). The magnitude of these partly contradictory effects is unknown. However, based on the high number of negative effects of the special water chemistry of blackwater rivers, it can be surmised that toxic metals in the Siak River can be harmful to organisms and the ecosystem even at the relatively low concentrations found.

In conclusion, no Pb and Cd concentrations exceeding any of the recommended levels were found in the edible parts of *P. polyuranodon* from the Siak River and thus, they did not represent a risk for human consumption. Nevertheless, no universal reference for permitted levels of toxic metals in marine or freshwater fish exists to date. The uptake of a metal by humans depends on the quantity of fish consumed, and should be expressed in mg kg-body weight$^{-1}$ day$^{-1}$. Such a dose recommendation should also include levels for sensitive subgroups, such as infants. Furthermore, toxicity and bioaccumulation of toxic metals depend on the metal itself, its concentration, the uptaking organism and water parameters influencing the bioavailability of the metal. Therefore, this study investigated the possible risk of toxic metal accumulation in fish from the Siak River in a snapshot. Further research is needed in regard to other toxic metals than Pb and Cd, seasonal availability of toxic metals, other consumed fish species, as well as age or size dependent accumulation of toxic metals against the background of the special biogeochemistry of the blackwater river Siak.

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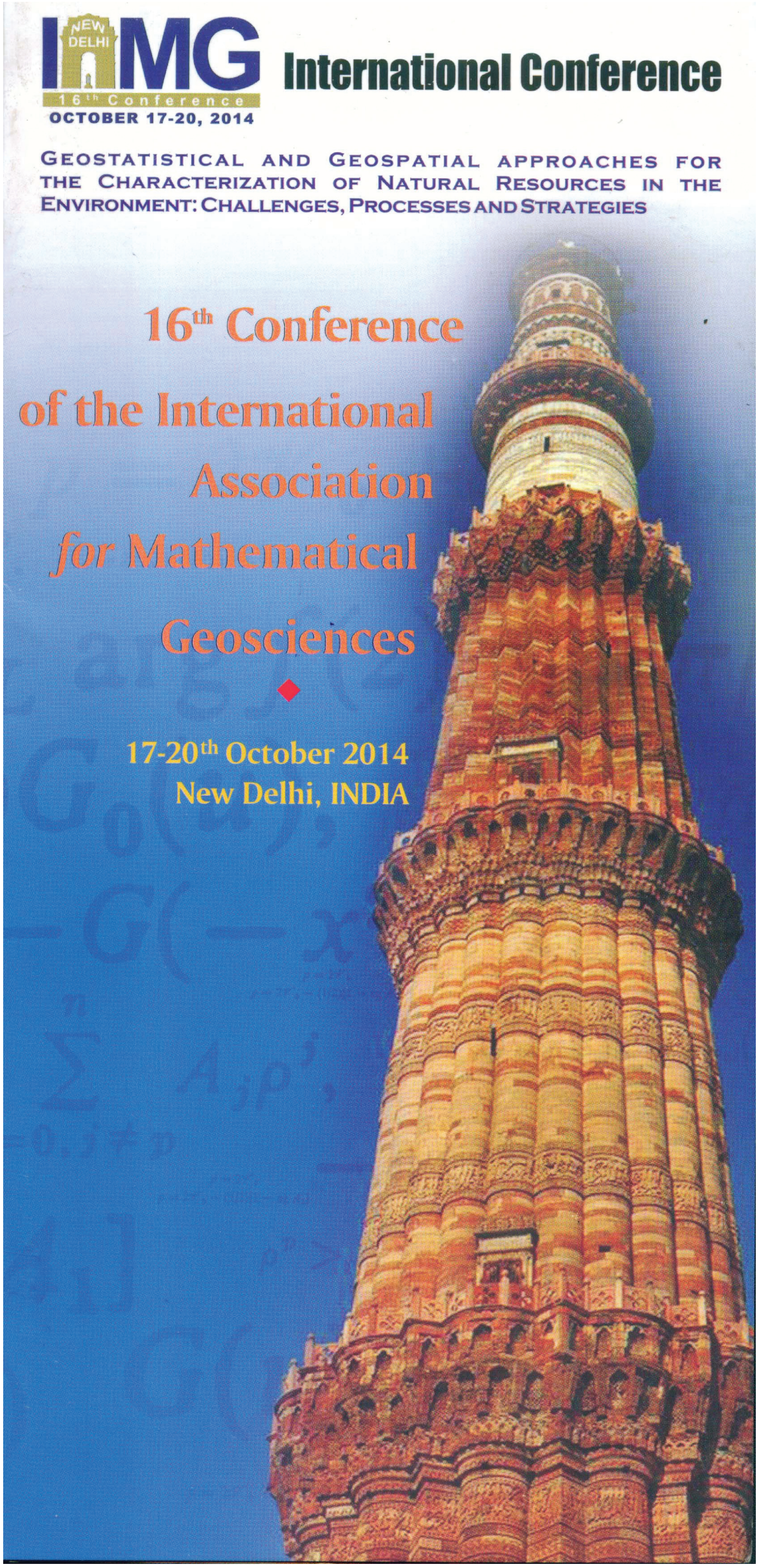


## Conference Topics

The interest areas of the conference include but are not limited to the topics related to mathematical geosciences and environmental issues like 3D visualization in geo- and environmental sciences, hydrology and time series analysis, isotope hydrology, environmental geochemistry and pollution, climate and groundwater functioning - the need for correct questions, numerical solutions in hydrogeology, geostatistics in hydrology, engineering geology and geotechnical engineering, trendy geostatistics, mathematical geosciences and planetary geology, multivariate geostatistics, medical geology, classical statistics in the earth sciences, compositional data analysis and its applications, prediction and characterization of natural disasters, fractal modelling, multiple point geostatistics, marine geology and oceanography, advances in mining assessment, petroleum systems, digital rock geophysics, mathematical morphology in geosciences and geoinformatics, remote sensing and geo-informatics for natural resources management, sedimentary basin analysis, modeling aquifer heterogeneities by means of 3D geostatistics, observed changes in Himalayan cryosphere, polar sciences, computer application in earth sciences, spatiotemporal modeling, agriculture, environment & ecosystems, new frontiers of mathematical geology for resources exploration.

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