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Effect of different organic matter composition on methyl mercury concentrations of sediments in fish ponds

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Die Komplexität unserer Umwelt aus einem subjektiven Blickwinkel begreifen und erklären zu müssen ist nicht unsere Schwäche, sondern vielleicht unsere größte Stärke.

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1. Einleitung

Die Fragestellungen und Untersuchungen dieser Arbeit beruhen auf einer Studie an sechs Karpfenteichen anthropogenen Ursprungs im Waldviertel, welche unter anderem den Anteil essentieller Fettsäuren und die Menge an Methylquecksilber (MeHg) in Fisch, zugeführtem Futter und Zooplankton analysiert. Die erhaltenen Ergebnisse weisen auf eine geringe Belastung der Fische mit MeHg hin, welche jedoch je nach Untersuchungsstandort unterschiedliche Ausmaße annimmt. Da in keinem zugesetzten Fischfutter Spuren von MeHg gefunden wurden, stellt sich die Frage nach dem Ursprung dieser Kontaminierung. MeHg ist eine hochgiftige und bioverfügbare Spezies von Quecksilber, welche das Endprodukt bakterieller Aktivität von Sulfat reduzierenden Bakterien (SRB) ist (Compeau und Bartha 1985), wobei die Nettokonzentration von MeHg ein Ergebnis von Methylierungs- und Demethylierungsprozessen darstellt (Gilmour et al. 1992, Pak und Bartha 1998). Abiotische Prozesse können ebenfalls zu einem geringen Teil an der Entstehung von MeHg beteiligt sein (Compeau und Bartha 1985). Bildung von MeHg kann sowohl in der anoxischen Wassersäule als auch im Sediment erfolgen. Studien zufolge ist dem Sediment jedoch eine größere Bedeutung beizumessen (Hammerschmidt und Fitzgerald 2006). Während anorganisches Quecksilber (Hg) sowie Dimethyl-Hg im Nahrungsnetz nicht bioakkumuliert, besitzt MeHg die Fähigkeit über trophische Stufen zu akkumulieren und birgt somit ein erhebliches ökosystemarisches Risiko. Um die Gefahr einer Kontamination erkennen und vermindern zu können, ist es notwendig Prädiktoren zu finden, welche eine Aussage zulassen, ob und wie viel MeHg in einem System zu finden ist.

Eine Aufgabe dieser Studie war es jene Faktoren zu finden und zu fragen, unter welchen Bedingungen MeHg in Sedimenten von Karpfenteichen vorkommt. Zur Beantwortung dieser Frage sind geo- und biochemische Einflüsse relevant, wie auch die Herkunft und Zusammensetzung des Sediments in Bezug auf autochthones und allochthones Material.

Viele Studien haben sich bereits mit der Suche nach Faktoren beschäftigt, welche die Bildung von MeHg beeinflussen. Großteils wurden dabei die Beziehungen zwischen MeHg, der totalen Konzentration von Hg ([Hg_{tot}]) und organischem Material untersucht (He et al. 2007), aber auch das Redoxpotential und die totale Konzentration von Sulfiden in Sedimenten (Sunderland et al. 2006) wurden mit

der Entstehung von MeHg kausal in Zusammenhang gebracht. Andere Untersuchungen beschäftigten sich mit der Beziehung zwischen MeHg und der Zusammensetzung der bakteriellen Gemeinschaft des Sediments (Batten und Scow 2003), wobei der Faktor Kohlenstoff in diesem Fall außen vorgelassen wurde, obwohl Kohlenstoff stets als Hauptquelle der Energielieferung für Bakterien dient. Die hier vorliegende Studie hingegen versucht geochemische Untersuchungen ($\delta^{13}C$, $\delta^{15}N$, $[C_{org}]$ und $[N_{org}]$) mit Fettsäureanalysen zu verbinden, um die Beziehung zwischen MeHg und bakteriellen Fettsäuren in Hinsicht auf die Qualität organischen Kohlenstoffs beleuchten zu können. Material organischen Ursprungs wird demzufolge nicht nur in seiner Gesamtkonzentration beziehungsweise Quantität betrachtet, sondern zwischen autochthonen (d.h., labilen) und allochthonen (d.h., refraktären) Kohlenstoffverbindungen unterschieden.

Die meisten Untersuchungen, die sich mit der Bildung und Verteilung von MeHg in Sedimenten beschäftigen, wurden an marinen Standorten, Ästuarien und natürlich entstandenen Seen durchgeführt. Wasserkörper anthropogenen Ursprungs und Aquakulturen wurden in dieser Hinsicht bislang vernachlässigt, obgleich ihnen eine wichtige Bedeutung zukommt, wie man an der ständig wachsenden Nachfrage nach Fisch sehen kann.

Bevor man sich mit potentiellen Faktoren beschäftigt, die den Methylierungsprozess von Quecksilber beeinflussen, stellt sich die Frage nach der Herkunft dieses Schwermetalls in einem aquatischen System. Neben vulkanischer Aktivität und natürlichen Quellen haben anthropogene Aktivitäten wie die Verbrennung von fossilen Brennstoffen den größten Einfluss auf Hg-Eintrag in die Umwelt (Schuster et al. 2002). Sowohl atmosphärischer Transport als auch Eintrag von landwirtschaftlich bedingten Altlasten aus dem Einzugsgebiet der untersuchten Teiche (Runoff) können für das Vorkommen von Quecksilber im Sediment verantwortlich sein. Ein Anteil des Eintrags kann auch direkt durch Niederschläge erfolgen, ist jedoch so gering, dass er im Vergleich zu den anderen Quellen keine große Rolle spielt (Hammerschmidt und Fitzgerald 2006). Es wäre demnach anzunehmen, dass sich die Menge an eingetragenem Quecksilber als Substrat für Methylierungsprozesse auf die MeHg Konzentration im Sediment auswirkt. Die Bedeutung der Gesamtkonzentration von Hg für das Ausmaß an gebildetem MeHg wurde jedoch bisher nicht eindeutig ermittelt. Obgleich mehrere Studien einen positiven, signifikanten Zusammenhang

zwischen sedimentärem Hg_{tot} und MeHg gefunden haben (Ethier et al. 2010, He et al. 2007, Regnell et al. 1997, Sunderland et al. 2006), ist in anderen Untersuchungen keine Beziehung zwischen diesen beiden Spezien zu erkennen (Canário et al. 2008, Kannan et al. 1998, Lambertsson und Nilsson 2006). Dies kann durch hemmende Faktoren wie beispielsweise eine erhöhte Konzentration von Sulfiden erklärt werden (Hammerschmidt und Fitzgerald 2008), welche die Bioverfügbarkeit von Hg_{tot} beeinflussen können und zu einer verminderten Konzentration von MeHg führen. Die Affinität von Hg mit organischem Material Komplexe zu bilden wird ebenfalls als Grund für eine verringerte Bioverfügbarkeit dieser Spezies angesehen (Hammerschmidt und Fitzgerald 2008). Andererseits besteht die Möglichkeit, dass die Menge von Hg_{tot} keine tragende Rolle für die MeHg Konzentration einnimmt. Sulfat-reduzierenden Bakterien und ihrer Aktivität wird hingegen eine große Bedeutung als Motor für die Entstehung von MeHg beigemessen und legt die Vermutung nahe, dass höhere Abundanzen von Bakterien zu einer vermehrten Bildung von MeHg führen. Batten und Scow (2003) konnten in ihrer Studie an Sedimentproben vier aquatischer Systeme eine positive Korrelation zwischen SRB Biomarkern und MeHg nachweisen. Die Quantifizierung dieser Bakterien erfolgt in dieser Studie durch Identifikation von Biomarkern mittels Lipidanalysen. Abundanzen bakterieller Fettsäuren (FAs) werden hier mit bakterieller Aktivität verbunden, obgleich die Menge an gefundenen Biomarkern keine genaue Aussage über physiologische Aktivität geben kann, sondern nur als Annäherung zu sehen ist.

Energielieferant für die Aktivität und das Wachstum von Bakterien ist organischer Kohlenstoff (C_{org}). Die Qualität dieser Nahrungsquelle spielt eine große Rolle für ihre Verwertbarkeit und Effizienz. Autochthon, also direkt im System gebildeter, labiler Kohlenstoff (Algen) ist leichter zur Energiegewinnung nutzbar, als allochthone Verbindungen, die von Wind und Wasser aus dem Einzugsbereich des Gewässers eingebracht werden und größtenteils aus refraktärem Kohlenstoff bestehen. Die Zusammensetzung von Sediment, beziehungsweise der Anteil an autochthonem und allochthonem Material, spielt demzufolge eine große Rolle für bakterielle Aktivität und Bildung von MeHg. Die Bedeutung des Ursprungs organischen Materials auf die Konzentration von MeHg ist einer der Hauptbestandteile dieser Studie und wird an Hand verschiedener zugesetzter Futtermittelarten an sechs Fischteichen beleuchtet.

Eine der Aquakulturen, Dürnhofteich (D), erhält im Gegensatz zu den anderen keine zusätzliche Nahrungsquelle und dient somit als Referenzsystem. Das gewählte Zufutter ist entweder marinen oder terrestrischen Ursprungs und unterscheidet sich außerdem durch seinen Fettgehalt. Karpfen der Winterbecken 1-3 (WB1-3) werden mit Pellets gefüttert, welche mit marinem Fischöl in verschiedenen Konzentrationen (6%, 10% und 18%) behandelt wurden. Das Futter der Teiche Klein Schandach (KS) und Schlägerwehr (SW) besteht hingegen aus Getreide und pflanzlichem Öl (1% und 3,3% Distelöl) und ist in seiner Kohlenstoffzusammensetzung nicht so labil wie das andere Futtermittel. Die verschiedenen Fettgehalte des zugesetzten Futters sind Bestandteil der Studie von Schultz et al und sollten in dieser Arbeit keine Auswirkung auf die zu erwarteten Ergebnisse haben. Zusammen mit dem Referenzteich sind in dieser Studie drei verschiedene Teichsysteme vertreten, welche sich in ihrer Zusammensetzung von Sedimenten unterscheiden können, nämlich Teiche mit marinem und terrestrischem Eintrag und ein mehr oder weniger natürliches System.

Die Fragestellung mit welcher sich ein Großteil dieser Arbeit beschäftigt, ist, welche Prädiktoren die Konzentration von MeHg in Sedimenten erklären können und in wie weit die Qualität des organischen Anteils dieser Sedimente die Menge an MeHg beeinflusst. Als potentielle Prädiktoren wurden einerseits Hg_{tot}, C_{org} und Abundanzen bakterieller FAs gewählt, alles Faktoren, deren Einfluss auf MeHg bereits in früheren Studien erforscht wurde. Für die Untersuchung des Einflusses der Kohlenstoffqualität wurden Biomarker verwendet, welche Aufschluss über die autochthone und allochthone Herkunft des organischen Materials geben können. Labile und refraktäre Anteile werden mit Hilfe unterschiedlicher Methoden bestimmt. Lipidanalysen ermöglichen die Identifikation und Quantifizierung von Algenbiomarkern in Sedimentproben, welche grundsätzlich durch mehrfach ungesättigte Fettsäuren (PUFA) charakterisiert sind. Langkettige (>22 C), gesättigte Fettsäuren hingegen weisen auf terrestrisches Material hin. Das Verhältnis von C:N kann ebenfalls als Indikator für die Herkunft von organischem Kohlenstoff in Sedimenten herangezogen werden. (Meyers and Ishiwatari 1993) Der Anteil von C-Verbindungen unterschiedlicher Herkunft (organisches Material allochthonen und autochthonen Ursprungs in dieser Studie) kann mit Hilfe von stabilen Isotopen ($\delta^{13}C$ Signaturen) an Hand eines mixing models bestimmt werden (Phillips and Gregg 2001). Das zugeführte Fischfutter wird in diesem Fall

als einzige Quelle allochthonen Kohlenstoffes festgelegt, unter der Annahme, dass andere Einträge vernachlässigt werden können. Drei der sechs untersuchten Stationen (Winterbecken 1-3) weisen nur eine geringe Umsäumung von begleitender Ufervegetation auf. Obgleich es nach dem Mähen der umliegenden Wiesen zu Graseintrag in die Teiche kommt, kann dieser Anteil und Einfluss im Vergleich zu dem zugeführten Futtermittel als gering betrachtet werden. Die anderen drei Teiche sind teilweise bis vollständig von Gehölzen umgeben, jedoch wird auch hier der Eintrag von terrestrischem Material als vernachlässigbar betrachtet, da die Probenahme vor dem Laubfall im Herbst durchgeführt wurde und die Teiche im Winter trocken liegen. Des Weiteren wird das Sediment zu diesem Zeitpunkt oft ausgebaggert. Die $\delta^{13}C$ Signaturen von Zooplankton wurden in der Berechnung des mixing models als Quelle für autochthones Material verwendet.

Es wird erwartet, dass die Konzentration von bakteriellen FAs und C_{org} als Mediatoren für MeHg-Bildung - beziehungsweise Energiequelle für SRB - Einfluss auf [MeHg] in Sedimenten der untersuchten Fischteiche hat. Des Weiteren wird vermutet, dass die Qualität von C_{org} sich auf die Konzentration von MeHg auswirkt. Ein höherer Anteil an autochthonem C in Sedimenten sollte demzufolge zu einer größeren Menge MeHg führen, was sich in einer positiven Beziehung zwischen [MeHg] und [PUFA] beziehungsweise einer negativen Korrelation zwischen [MeHg] und C:N widerspiegeln müsste. Möglicherweise spielt auch die Wahl des zugeführten Futters für die Konzentration von MeHg eine Rolle, da sich die verschiedenen Futtermittel in ihrer Kohlenstoffqualität unterscheiden. Ein Einfluss von Hg_{tot} auf die Konzentration von MeHg wird hingegen nicht erwartet, da zahlreiche Studien darauf schließen lassen, dass es keine oder nur eine geringe Beziehung zwischen diesen beiden Faktoren gibt. Terrestrische Biomarker als Zeichen für refraktären C sollten ebenfalls keine Korrelation mit [MeHg] aufweisen. Hingegen wird erwartet, dass die Konzentrationen bakterieller FAs mit [C_{org}] und [PUFA] in einer positiven Beziehung stehen.

Neben der Bedeutung der Sedimente für die Bildung von MeHg stellt sich auch die Frage nach ihrem Einfluss auf Organismen eines Habitats als potentielle Quelle für Kontaminationen. Ob und wie MeHg aus dem Sediment in das Nahrungsnetz gelangen kann, ist bereits Thema mehrerer Untersuchungen gewesen. Schadstoffe können durch Organismen, die direkt an der Oberfläche von Sedimenten (sediment-water interface, SWI) nach Nahrung suchen,

aufgenommen werden. Dieses Benthos wird wiederum von im Sediment wühlenden Fischen gefressen (Mason und Lawrence 1999). Eine andere Möglichkeit für MeHg in das Nahrungsnetz zu gelangen ist durch Diffusion oder Resuspension in die Wassersäule, wo es dann von Mikroseston über Zooplankton in Fische kommen kann (Mason und Lawrence 1999). Organismen aquatischer Lebensräume können MeHg aus dem Wasser (vorwiegend osmotrophe Organismen), dem Sediment oder ihrer Nahrung aufnehmen (Hammerschmidt und Fitzgerald 2006), wobei der primäre Weg bei Fischen über die Nahrung ist (Hall et al. 1997). Um die MeHg Konzentration von Fischen erklären zu können, ist demzufolge die Beantwortung der Frage wichtig, woher Fische ihre Nahrung beziehen. Dies hängt sowohl vom Lebensraum ab, den sie bewohnen (Pelagial, Benthal, Littoral) und der Ernährungsgilde, der sie angehören (piscivor, planktivor, herbivor).

Die hier vorliegende Studie befasst sich mit Aquakulturen, in denen Karpfen (*Cyprinus carpio*) gezüchtet werden. Diese Fische sind omnivor und wühlen oft im Sediment nach Nahrung, welche aus Benthos besteht. Die Möglichkeit eines direkten Transfers von MeHg aus dem Sediment in den Organismus der Fische ist somit gegeben. Ein möglicher Einfluss von Sedimenten auf die MeHg Konzentration in Fischen wurde beispielsweise von Kannan et al. (1998) untersucht. Diese Studie zeigt eine positive Korrelation ($p<0,05$) zwischen [Hg_{tot}] in Fischen und den korrespondierenden Sedimenten, während [MeHg] zwischen einzelnen Fischarten und Sedimenten keine positive Beziehung aufwies. Als mögliche Erklärung wird hierfür neben Variationen von MeHg Bioverfügbarkeit und Methylierungsraten auch die unterschiedliche Mobilität von Fischen angegeben. Im Gegensatz zu der oben genannten Studie, welche an Ästuaren in Florida durchgeführt wurde, sind die Forschungsstandorte dieser Arbeit Teiche, welche für den Fisch Systeme darstellen, denen er nicht durch Wanderbewegungen ausweichen kann. Demzufolge ist eine positive Korrelation zwischen [MeHg] in Sedimenten und dem Organismus von Fischen wahrscheinlich. Da die Konzentration von MeHg in Konsumenten entlang der Nahrungskette zunimmt, sollte sich diese Akkumulierung in der Menge an gemessenem MeHg von Sediment-, Zooplankton- und Fischproben widerspiegeln. Natürlich nur falls die beiden ersteren Kompartments von den Fischen als Nahrung genutzt werden. An den sechs Untersuchungsstandorten werden hierfür die MeHg-Konzentrationen analysiert und jene der Fische mit ihren potentiellen

Nahrungsquellen Sediment und Zooplankton verglichen. Benthos wird in dieser Studie nicht untersucht. Der Grund hierfür liegt in früheren Probennahmen von S. Schultz an diesen Teichen, welche erkennen lassen, dass sich in den Sedimenten wenig bis beinahe kein Benthos befindet.

Mit Ausnahme von D steht den Karpfen jedoch noch eine dritte Nahrungsquelle zur Verfügung, nämlich das Fischfutter. Da dieses nicht mit MeHg kontaminiert ist, kann es bei Aufnahme durch den Fisch zu Verdünnungsprozessen kommen, wodurch sich die Frage stellt, welche Nahrungsquelle die Karpfen dieser Teiche hauptsächlich beziehen. Um dieser Frage auf den Grund zu gehen, werden Isotopensignale von $\delta^{13}C$ und $\delta^{15}N$ analysiert und verglichen. Da $\delta^{13}C$ Signaturen um ca. 1 ‰ und $\delta^{15}N$ Signaturen um 2-4 ‰ mit jeder trophischen Stufe zunehmen, kann man eine ungefähre Aussage tätigen, welche Nahrung der Fisch direkt aufnimmt, beziehungsweise wie viele trophische Stufen zwischen Fisch, Sediment, Zooplankton und zugesetztem Futter liegen. Es wird erwartet, dass Zooplankton und Fische von Teichen, deren Sediment hohe MeHg Werte aufweist, ebenfalls eine höhere Belastung zeigen, wobei der MeHg-freie Faktor Futter einen verdünnenden Effekt auf die Karpfen haben kann. Ein möglicher Zusammenhang zwischen MeHg Konzentrationen von Fisch, Zooplankton und Sediment sollte sich auch in der Isotopenanalyse widerspiegeln. Falls Fische durch Sedimente oder Zooplankton mit MeHg kontaminiert werden, muss sich dies auch in einer Ähnlichkeit der $\delta^{13}C$ oder $\delta^{15}N$ Signale zeigen, wobei die Problematik darin besteht, dass potentielle Nahrungsquellen übersehen werden können.

Schlussendlich werden die 6 untersuchten Fischteiche mit einem vergleichbaren natürlichen System verglichen, um feststellen zu können, ob sich mögliche Unterschiede in der biochemischen Zusammensetzung und MeHg Kontaminierung von Sedimenten auf die Herkunft von Ökosystemen zurückführen lassen können.

2. Manuscript for submission

2.1. Abstract

We investigated the influence of biochemical organic matter composition on methyl mercury (MeHg) concentrations in sediments of 6 fish ponds in Lower Austria and explored the ecotoxicological potential of MeHg in sediments of getting directly conveyed to fish (common carp; *Cyprinus carpio*). Only 3 ponds contained MeHg concentrations in the upper sediment layers (1.1 to 3.2 ng g^{-1} dw) and Hg_{tot} concentrations could not predict MeHg concentrations in these sediments. MeHg concentrations were significantly correlated with bacterial biomarkers (bacterial fatty acids), but bacterial fatty acid concentrations of sediments did not differ significantly among the investigated ponds. Moreover, organic carbon concentrations or mostly algae-derived, labile organic matter (polyunsaturated fatty acids) of sediments could not account for differences of MeHg concentrations. Results of mixing models indicated that different sediment sources (autochthonous versus allochthonous organic matter) were not associated with MeHg concentrations. MeHg concentrations of carp were higher in ponds with no MeHg concentrations in sediments, strongly suggesting that MeHg concentrations of pond sediments cannot predict MeHg concentrations in muscle tissues of common carp.

Keywords: methyl mercury, sediment, organic matter, fatty acids

2.2. Introduction

Methyl mercury (MeHg) can be produced in freshwater and marine sediments (St. Louis et al. 2004; Gilmour et al. 2011) and subsequently introduced to benthic and pelagic organisms (Orihel et al. 2008; Wang et al. 1998) where it bioaccumulates along the aquatic food chain (Wiener et al. 2003). Methyl Hg passes through biological membranes and, contrary to other heavy metals, its excretion from organisms is very slow (Lofroth 1968; Reinfelder et al. 1998). While the uptake of most heavy metals can be regulated through excretion (Gray 2002), leading to limited bioaccumulation, MeHg is well retained in aquatic organisms (Reinfelder et at. 1998).

The main mechanism of both regional and global Hg contamination is via atmospheric transport (Schuster et al. 2002), either through direct atmospheric deposition or through leaching of earlier deposited airborne mercury from the drainage area (Anderson et al. 1990). Both natural and anthropogenic sources are responsible for the release of Hg in the atmosphere, although up to 70% of total Hg (Hg_{tot}) contribution during the last 100 years was man-made with a slight decline during the last 10 years (Schuster et al. 2002). Currently 40-60% of the amount of Hg_{tot} in the atmosphere is due to gold and silver mining, coal combustion and municipal waste incineration (Batten and Scow 2003). Atmospheric deposition is also the main pathway of Hg to aquatic systems and occurs primarily in its inorganic form (Gilmour et al. 1992).

The *in situ* formation of MeHg in aquatic ecosystems is a biological driven process (Gilmour et al. 1992) with sediments being its main production site (Benoit et al. 2003). Sulphate reducing bacteria (SRB) are the predominant mediators of this process (Compeau and Bartha 1985, Gilmour et al. 1992) with later studies suggesting that iron-reducing bacteria play a part in the formation of MeHg as well (Kerin et al. 2006). These organisms convert Hg^{2+} to MeHg under anoxic conditions (Regnell et al. 1997). Two counteracting microbial processes control net production of MeHg: Hg methylation and MeHg demethylation (Lambertson and Nilsson 2006). Due to its hazardous effects on biota it is necessary to understand which factors influence MeHg production and which factors are able to predict MeHg presence and concentration in sediments that are thought to be the starting point for MeHg entering the food web.

Studies that aim to identify factors promoting MeHg formation often provide contrasting results. While some authors found a significant positive correlation between Hg_{tot} and MeHg (Sunderland et al. 2006, Ethier et al. 2010, Regnell et al. 1997), other studies did not display this relationship (Benoit et al. 2003, He et al. 2007, Kannan et al. 1998, Lambertsson and Nilsson 2006). Moreover, it was shown that MeHg concentrations in upper sediments were related with the amount of organic carbon (C_{org}) (Hammerschmidt et al. 2008). Such C:MeHg relationships require functional explanations. While C is an energy-yielding substance for bacteria, bulk C differs in its biochemical lability and thus in providing accessible energy for MeHg-producing bacteria (e.g. Westrich and Berner 1984). For example, Hg species show a great affinity for allochthonous OM, which leads to the formation of complexes and a lower bioavailability of Hg^{2+} (Hammerschmidt et al. 2008).

However, the supply of labile C or biodegradable organic matter (OM) plays a major role in the distribution of methylation activity (Benoit et al. 2003), seeing that it is the energy-yielding source for SRB (Compeau and Bartha 1985). In addition to carbon quality, the availability of sulphate as an electron acceptor and anoxic conditions are further crucial for Hg methylation by SRB populations (Lambertsson and Nilsson 2006).

The severe consequences of MeHg accumulation for end consumers makes it important to understand how MeHg enters and is transported throughout the food web in these environments. Since the input of contaminants such as Hg or PCBs into aquatic ecosystems has decreased in the last years, the role of sediments has changed from sinks to possible sources for toxins (Moermond et al. 2004). While sediments are a buffer during times of high loading, they become a potential source when loading decreases (Anderson et al. 1990). It is therefore necessary to investigate the pollution and distribution of contaminants. Composition and stratification of sediments in respect of Hg/MeHg is a much investigated research field where both freshwater and marine environments are explored. (e.g. Ethier et al. 2010, He et al. 2007, Lambertsson and Nilsson 2006). Artificial lake systems, such as fishponds, on the other hand have been more or less neglected in this regard although their sediment may have great influence on farmed fish.

Demand and consumption of fish have dramatically increased in the last years. Salmon consumption for example rises annually at a rate of 14% in the European

Union and 23% in the United States (Engelhaupt 2007). This growing demand puts pressure on wild stocks to the point where it is not sufficient to use wild fish but also farmed fish from aquacultures (Santerre 2010). Consequently, aquaculture is one of the fastest growing food-producing sectors worldwide (Cole et al. 2009). Although aquacultures provide a good source of protein and in particular polyunsaturated fatty acids (PUFAs), which are an important part of human diet, they also pose a considerable risk for example in terms of higher amounts of toxic chemicals such as antibiotics or persistent organic pollutants in farmed fish compared to wild fish (Cole et al. 2009).

There are different possibilities for fish to be exposed to contaminants: uptake through the water (e.g. gills), through ingestion of prey and through sediments (Moermond et al. 2004). Through the process of bioaccumulation toxic substances are enhanced in the fish body and pose potential health issues for both animal and human consumers. This study is concerned with aquacultures where *Cyprinus carpio* is bred. Cyprinids are omnivorous fish which also posses the ability to consume detritus (e.g. Tolonen et al. 2000). Michelsen et al. (1994) and Russell et al. (1998) also show that benthivorous fish ingest considerable amounts of sediment which even lead to higher contaminations of pollutants in their organisms than that of pelagic feeding fish although their piscivore foraging habits and higher trophic level should imply the opposite. It was concluded that this result might be due to the fact that benthivorous fish ingest large quantities of contaminated sediment with food. Although the ingestion of sediment alone allows no conclusion about the actual amount of assimilated nutrients or contaminants, it shows a possible pathway for pollutants to enter the fish body. A study of estuarine waters of Florida which was conducted by Kannan et al. (1998) further describes the relationship between sediments and fish by observing a positive correlation between both Hg_{tot} and MeHg concentrations in sediments and fish tissue for some of the examined fish species. Seeing that sediments might not only be the primary site of MeHg production but also a possible starting point for this contaminant into the food web, it is important to identify driving forces which control its concentration.

In this study we examined six fish ponds used for farming of *C. caprio* to determine biogeochemical factors that can predict MeHg concentrations in sediments. Both analyses of lipid biomarkers and isotopic signals of $\delta^{13}C$ and $\delta^{15}N$ were used to examine the impact of biogeochemical attributes of sediments

on MeHg concentration with particular focus on the influence of labile OM. The effect of sedimentary MeHg contamination on higher trophic levels such as zooplankton and fish was furthermore investigated.

In view of this aim we ask;

a) How does carbon quantity and quality of sediments affect MeHg concentrations in sediments and which other factors influence its concentration?

b) How do sediments affect MeHg concentrations in zooplankton and fish as a potential source of both nutrients and contaminants?

We hypothesize that MeHg concentrations in sediments increase with increasing carbon quantity and biochemical lability of carbon, as determined by algal and bacterial fatty acids.

We further postulate that organisms in aquacultures with enhanced MeHg concentrations in sediments show an enrichment of MeHg due to transport and bioaccumulation processes.

2.3. Material and Methods

2.3.1. Study sites and sampling collection

This study was conducted at 6 artificial fish ponds in Lower Austria used for cultivation of *Cyprinus carpio*. Lake Dürnhof (D) is located near the small town Zwettl while two further lakes, Klein Schandacher (KS) and Schläger Wehr (SW), are situated in the vicinity of the village Litschau. The three winter basins (WB1, WB2, WB3) are located in Waidhofen an der Thaya. Like most other lakes in Lower Austria these water bodies are of anthropologic nature with a surrounding area mostly composed of agricultural fields and woodland. All ponds are lacking littoral zones due to shore stabilisation with rocks. No input through flowing waters occurs. Water levels of ponds were on average 2.5 metres. WB1, WB2 and WB3 had a slightly more artificial character attributable to their rectangular form and bare water edges. After fish harvest in autumn these basins were drained and periodically subjected to excavation events. D, KS and SW showed a more natural morphology characterised through basin heterogeneity and associated shore vegetation. Being used for fish aquaculture different kinds of supplementary feed (marine and terrestrial treatment) with different lipid content were added in all lakes but one (Tab.1). Benthic organisms were absent in sediments of all lakes.

Sediment cores were collected in September 2009 from the deepest part of the six different lake basins using a Kajak Brinkhurst corer. Redox potential depth profiles were measured in 0.5 cm steps immediately after sampling. In addition, pH values of the overlying water column were measured. The sediment-water interface (SWI) was collected using a plastic syringe. The first 5 cm of the cores were cut in 0.5 cm intervals; afterwards sediments were taken in 1cm steps. Samples were transferred in polypropylene vials and were stored on ice for a day; thereafter they were stored at -80°C. For further analyses samples were freeze dried for 3 days and homogenized with a spatula.

Tab.1. Locations and dietary treatments of all six sampling stations

pond	location	diet
Dürnhofteich (D)	48°37'N, 15°10'E	natural diet
Klein Schandacher (KS)	48°58'N, 15°05' E	1% thistle oil + wheat
Schläger Wehr (SW)	48°57'N, 15°E	3,3% thistle oil + wheat
Winterbecken 1 (WB1)	48°49'N, 15°17'E	18% fish oil
Winterbecken 2 (WB2)	48°49'N, 15°17'E	10% fish oil
Winterbecken 3 (WB3)	48°49'N, 15°17'E	6% fish oil

2.3.2. Lab analysis

For lipid analysis, 64 samples were processed, while isotopic and mercury analyses were performed with 42 samples (7 depth steps from each lake ranging from the SWI to a depth of 10cm).

Lipid analysis was performed as described in Heissenberger et al. 2010. In short, 100 to 250 mg of the homogenized sediment samples were stored in 2 ml chloroform for at least 16 hours at -80°C. After the addition of mehtanol, 2:1 chloroform-methanol and NaCl, samples were sonicated and centrifugalized. The lipid layer at the bottom was transferred into another vial and the remaining layer was washed with chloroform. After repeating this procedure two times the lipid layer was stored at -80°C until esterification. No gravimetrical analysis was performed due to avoid problems with interfering sediment particles that may have altered total lipid concentrations. For esterification, samples were completely dried under N_2. Toluene and H_2SO_4-methanol was added and the samples were stored at 50°C for 16 hours. After addition of $KHCO_3$ and BHT, samples were centrifugalized and the top layer was transferred to another vial. After repetition of this process the lipid layer was evaporated under N_2, re-

dissolved in hexane and transferred to FAME vials. For gas chromatograph (GC) analysis FAME was dried under N_2 to a know volume (1 mL).

Analysis of $\delta^{13}C$, $\delta^{15}N$, TOC and TN was performed at the University of Vienna using a continuous-flow isotope ratio mass spectrometer (Delta^{PLUS}; Finnigan MAT, Bremen, Germany), coupled to an elemental analyzer (EA 1110, CE Instruments, Milan, Italy). Before analysis was conducted, 100-200 µL 1M HCl were added to the homogenized sediment samples to remove inorganic C. This process was continued till no further sign of foaming was detected. Afterwards the samples were dried and approximately 7 mg sediment were put in tin capsules for analysis as described in Göttlicher et al. (2006) and Watzka et al. (2006). Stable isotope values are displayed in δ notation according to the following equation by Peterson and Fry 1987

$$\delta^{13}C \text{ or } \delta^{15}N = \left[R_{sample}/R_{standard} - 1\right] \times 1000$$

with R being $^{13}C/^{12}C$ and $^{15}N/^{14}N$ respectively.
Seeing as lipids are depleted in ^{13}C compared to proteins (Sweeting et al. 2007) lipid corrections for ^{13}C values were performed using the model of McConnaughey and McRoy (1979). Total lipid content was calculated using C:N ratios. Lipid corrections were performed for fish, zooplankton and fish feed samples using these formulas

$$L = 93/[1 + (0.246 \times (C{:}N) - 0.775)^{-1}]$$

$$\delta^{13}C' = \delta^{13}C + D \times [I + \frac{3.90}{1 + 287/L}]$$

with $\delta^{13}C$ being the measured and $\delta^{13}C$' the lipid corrected value of the sample. *L* is the proportional lipid content of the sample, C:N the proportion of carbon and nitrogen in the sample and *D* the isotopic difference between protein and lipid suggested to be 7 ‰ by Sweeting et al. 2007. The constant *I* has a value of -0.207.

The total amount of Hg in sediment samples was analyzed using a FIMS^{TM}-400 atomic absorption spectrometer. For sample preparation about 1 g of dried and homogenized sediment was filled in 75 mL teflon tubes. After the addition of 8 mL of a 1:1 mixture of H_2O and NHO_3 and 1 mL H_2O_2 samples were processed in a CEM MARSXpress microwave reaction system. Temperature was stepwise

increased for 15 mins until a maintenance temperature of 180°C was attained which was kept for further 15 mins. After a cooling period of approximately 90 mins the samples were transferred into 15 mL glass flasks. H_2O was added until a volume of 15 mL was achieved. To prevent the presence of coarse sediment particles during the analysis, 6 to 8 mL of the sample solution were transferred in 10 mL tubes after sedimentation of material had occurred. Analysis was performed immediately afterward using a flow injection mercury system (FIMS^{TM}-400) with 3%HCl as carrier agent and 0,2% $NaBH_4$ in 0,05% NaOH as reducing agent. During the analysis of the lake sediments it became evident, that the samples of Dürnhofteich and Schläger Wehr had to be 1:1 diluted.

MeHg analysis of sediments was performed at the Federal Environment Agency of Vienna. For sample preparation sediment (~250 mg) was filled in polypropylene test tubes and 5 mL eluate (50 mM pyridine, 0.5% L-cysteine, 5% MeOH, pH = 2.2) were added. After sonication (15 min) and centrifugation (4 min at 3500 rps in the first round, 4 min at 1500 rps in the second round) the supernatant was decanted. This procedure was repeated and the combined supernatant was filtered through 0.2 µm filters. Reference material and blanks were prepared in the same manner. For measurement of MeHg a HPLC method was applied which was combines with a ICP-MS detection using an Agilent 1100 series HPLC system. An exact description of this method is found in Vallant et al. (2007). The determination limit for this method was 1.9 ng g^{-1} dry weight (dw), the detection limit 0.6 ng g^{-1} dw.

2.3.3. Statistical analysis

Statistical analyses of most data sets were performed using IBM SPSS Statistics 19. Univariate correlations were applied to identify potential predictors for MeHg concentrations. Differences of observed factors between stations were analyzed using analysis of variance (ANOVA). Mixing models were performed to calculate proportional contributions of allochthonous and autochthonous carbon to sediment composition using stable isotope analyses in R (SIAR). No fractionation factors were applied as no trophic enrichment occurred for sedimentary samples. Isotopic signals of fish feed and zooplankton were proxies for allochthonous and autochthonous sources respectively.

2.4. Results

2.4.1. Mercury and Methylmercury concentrations

Analyses of MeHg revealed that this compound was present in five of the six investigated fish pond sediments with only traces being found at two locations. Mean MeHg concentrations of all fish ponds ranged from 3.2 to 0.2 ng g-1 dry weight (dw) and are displayed in Tab.2. Vertical distribution of MeHg concentrations was similar in sediments of WB1-WB3, where highest amounts were detected in the top layers of sediment cores (Fig.1a). Additionally a downcore decrease of MeHg was observed for each winter basin. While MeHg was present throughout the sediment core in WB3, MeHg concentrations dropped below the detection limit of 0.6 ng g^{-1}dw in the other ponds. Only traces of MeHg were found in D and KS (located near the SWI), while sediment of SW didn't feature any MeHg at all. Contrary to its methylated species, Hg_{tot} concentrations generally increased with sediment depth of the three winter basins (Fig.1b). Hg_{tot} concentrations of sediments were considerably higher at D, KS and SW than at the three winter basins (Tab.2). A Post-Hoc test also confirms significant differences between WB1-3 and the other lakes whereby a significant distinction also occurred between SW and the remaining ponds.

Tab.2. Mean concentrations and standard deviations of MeHg and Hg_{tot} (ng g^{-1} dry weight), C_{org} (mg g^{-1} dry weight), BAFA and PUFA (µg g^{-1} dry weight) and C:N.

station	MeHg	Hg_{tot}	BAFA	C_{org}	PUFA	C:N
WB1	2.61 (±2.61)	78.93 (±17.37)	287.26 (±285.38)	33.51 (±11.20)	115.84 (±93.59)	8.45 (±1.00)
WB2	1.08 (±0.93)	43.44 (±19.61)	65.39 (±31.79)	15.53 (±3.43)	36.02 (±29.55)	8.29 (±0.95)
WB3	3.23 (±1.02)	52.33 (±12.04)	140.98 (±25.50)	23.03 (±6.00)	82.65 (±21.80)	7.99 (±1.01)
D	0.20 (±0.53)	170.66 (±31.61)	203.24 (±44.88)	142.00 (±7.96)	214.78 (±98.39)	9.96 (±0.25)
KS	0.21 (±0.57)	111.70 (±17.95)	167.93 (±45.07)	85.59 (±8.08)	171.50 (±97.86)	9.66 (±0.23)
SW	0.00 (±0.00)	202.49 (±26.95)	91.42 (±31.10)	90.21 (±7.79)	67.08 (±34.52)	11.95 (±0.91)

Tab.3. Total concentrations of MeHg and Hg_{tot} (ng g^{-1}dw), BAFA, PUFA and FAME (µg g^{-1}dw) for six fish ponds and Lake Lusignan.

station	MeHg	Hg_{tot}	BAFA	PUFA	FAME
Lake Lusignan	1.6 (± 0.77)	178 (± 58)	407 (± 137)	483 (± 157)	4093 (± 1721)
WB1	4.6 (± 1.29)	86 (± 17)	464 (± 255)	174 (± 83)	4713 (± 2721)
WB2	1.7 (± 0.69)	33 (± 9)	85 (± 25)	50 (± 32)	810 (± 304)
WB3	3.7 (± 0.97)	45 (± 3)	152 (± 16)	94 (± 15)	1601 (± 192)
D	0.4 (± 0.70)	186 (± 18)	230 (± 36)	272 (± 95)	2013 (± 249)
KS	0.4 (± 0.75)	105 (± 7)	180 (± 45)	198 (± 112)	1332 (± 319)
SW	0.0 (± 0.00)	201 (± 26)	110 (± 14)	89 (± 19)	898 (± 164)

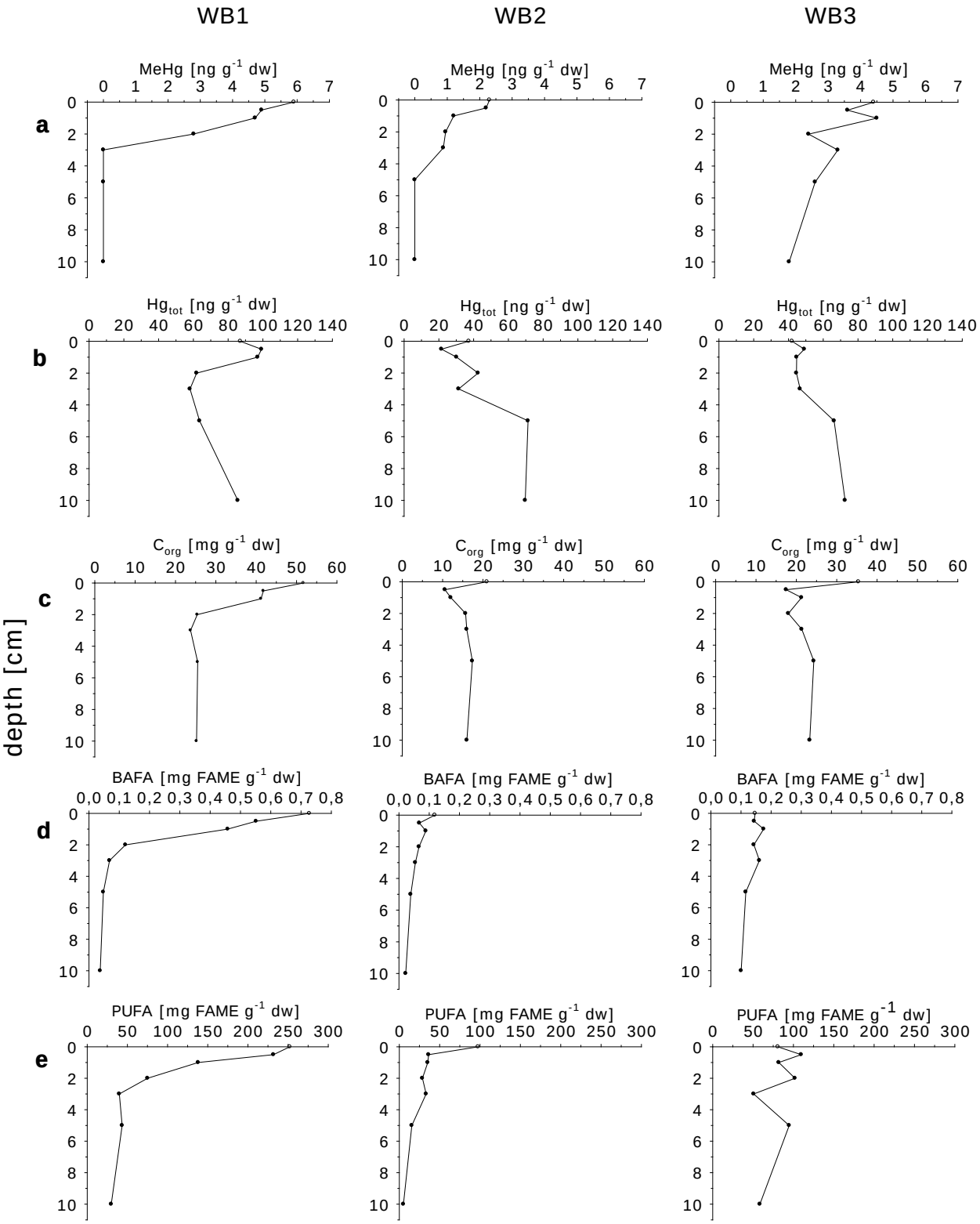

Fig.1. Sediment profiles of MeHg, Hg_{tot} and C_{org} concentrations, concentrations of total identified bacterial biomarkers (BAFA) and algal biomarkers (PUFA) in sediments of the three winter basins.

Tab.4. Correlation table of selected environmental and biotic factors with MeHg in sediments of the winter basins.

		WB1	WB2	WB3
Hg_{tot}	r	0,679	-0,827(*)	-0,741
	p	0,930	0,022	0,057
BAFA	r	0,946(**)	0,834(*)	0,800(*)
	p	0,001	0,02	0,031
iso+aiso	r	0,950(**)	0,671	0,395
	p	0,001	0,099	0,380
iso15	r	0,951(**)	0,634	0,078
	p	0,001	0,126	0,868
aiso15	r	0,952(**)	0,412	-0,023
	p	0,001	0,358	0,962
iso17	r	0,944(**)	0,840(*)	0,713
	p	0,001	0,018	0,072
C_{org}	r	0,920(**)	-0,100	0,354
	p	0,003	0,831	0,436
N_{org}	r	0,934(**)	-0,428	-0,89
	p	0,002	0,338	0,849
PUFA	r	0,930(**)	0,806(*)	0,117
	p	0,002	0,029	0,803
terrFA	r	0,916(**)	-0,470	-0,473
	p	0,004	0,288	0,284
C/N	r	-0,908(*)	0,419	0,718
	p	0,005	0,350	0,069

2.4.2. Redox potential

Results of redox potential (E_h) profiles shown in Fig.2 feature no great differences between the six sampling sites. Similar trends of steep downcore E_h decrease were observed with the exception of D which displayed a more moderate descent. The SWI was either already anoxic at four of the six ponds or showed nearly negative E_h values. KS and SW featured positive redox potentials by contrast (122 mV and 110 mV respectively) but while an immense decrease occurred in sediments of KS, those of SW remained oxic till three centimetres below the SWI. Consequently ANOVA calculations only yielded significant differences between SW and two winter basins (WB1 and WB2)

2.4.3. Biochemical composition of sediments

Down core distribution of bacterial fatty acids (BAFA) predicted MeHg profiles of sediments at WB1-3. Hence they are the only factor to show a significant relationship with MeHg at these three ponds (Tab.4). This correlation was most prominent in WB1 where BAFA concentrations were furthermore at least two times higher than in sediments of WB2 and WB3. Differences in BAFAs concentration among all six fish ponds were not as pronounced as they were with MeHg and Hg_{tot} (Tab.2). The only significant differences were found in sediments of WB1 with WB2 ($p = 0.018$) and SW ($p = 0.048$) respectively. The term BAFA comprised different bacterial FAs found in our samples which consisted of both saturated bacterial biomarkers (15:0, 17:0) and branched chain FAs (iso15, iso17, aiso15). To see if one of these branched FAs is a dominant factor for MeHg

concentration further correlations were performed. Although all bacterial biomarkers predicted the amount of MeHg found at WB1 this war not the case in sediments of WB2 and WB3 (Tab.4).

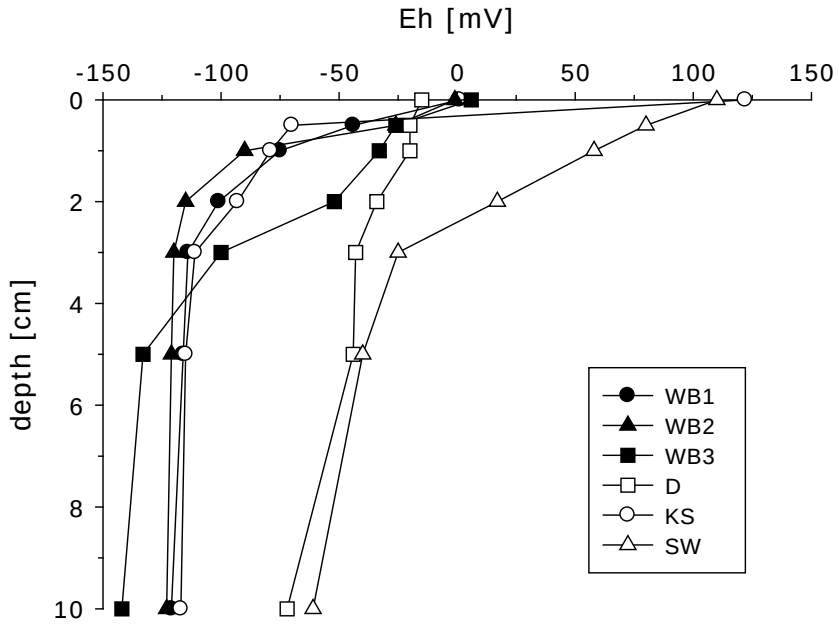

Fig.2. Redox potential profiles of investigated fish ponds

Only the total amount of BAFA yielded significant results for all winter basins. In contrast to the amount of BAFA found in sediments C_{org} concentrations showed a broader variability among all fish ponds. D, KS and SW all feature at least 2.6 times higher concentrations of C_{org} than WB1-3 and Post-Hoc tests further revealed these differences to be significant. Although C_{org} profiles of all winter basins followed a similar trend with highest concentrations found at the sediment-water interface (Fig.1c), significant distinctions occurred between WB1 and WB2 ($p = 0.001$). Only sediments of WB1 showed a significant relationship with MeHg while distributions of C_{org} and MeHg were negatively correlated in WB2. PUFAs are biomarkers, which suggest the presence of algal material (Desvilettes et al. 1997) and were used as indicators of labile autochthonous organic matter. Highest mean PUFA concentrations were found in D whereas lowest concentrations occurred in WB2 (Tab.2). Although Post-Hoc tests showed the occurrence of significant differences between some fish ponds, no clear distinctions appeared between ponds with and without MeHg. Even among the winter basins no consistent tendencies are found. Albeit both WB1 and WB2 show a distinct decrease of PUFA concentration with increasing sediment depth,

this trend is far less pronounced in WB3 (Fig.1e). A significant relationship between PUFA and MeHg concentrations occurred only in WB1 and WB2 while these two terms featured nearly no correlation at all in WB3 (Tab.4). PUFA concentrations were generally higher in WB1 than in the other two winter basins. Linear regressions were calculated for BAFA and C_{org} and BAFA and PUFA respectively to examine the importance of different carbon species on the amount of bacteria which are important mediators for Hg methylation. WB1, KS and SW displayed a more or less tight and positive relationship between the amount of BAFA and C_{org} (Fig.3). WB2-3 and D do not follow this trend. Here nearly no impact of C_{org} on BAFA was observed. Contrary to these results the relationship between BAFA and PUFA is more closely linked with only WB3 beeing the exception (Fig.4). In addition to Hg_{tot}, BAFA, PUFA and C_{org} we also tested the influence of terrestrial organic matter on MeHg concentration in sediments; i.e., long chain, saturated FAs (C>22; Kainz et al. 2003). WB2 and WB3 both feature a negative effect of these long chain FAs on the amount of MeHg while the reverse effect occurred in WB1. Additionally to terrestrial OM C:N ratios were applied as indicators for autochthonous or terrestrial input into sediments (Meyers and Ishiwatari 1993). Mean C:N ratios ranged between 7.99 and 11.95 (Tab.2). Significant differences occurred between WB1-3 (which also featured lower C:N values) and the other lakes but there were also noticeable distinctions between KS and the two other more natural lakes. In spite of the similarities among the winter basins no consistent relationship exists between C:N and MeHg in these ponds (Tab.4).

2.4.4. Geochemical composition of sediments

In addition to source-specific markers of organic matter in sediments, geochemical bulk quality of sediments was used to determine how MeHg distribution is associated with sediment composition. Therefore both isotopic signals of C and N were examined and the allochthonous and autochthonous fractions of sediments were calculated for every station using a mixing model. Fig.5 shows relative evenly down core distributions of both $\delta^{13}C$ and $\delta^{15}N$ for all fish ponds. $\delta^{13}C$ signals range from -31.5 ‰ (D) to -24.8 ‰ (WB3) with a total standard variance of ± 1.9 while $\delta^{15}N$ signals range from 2.5 ‰ (SW) to 6.6 ‰ (WB1) with a total standard variance of ± 1.3. ANOVA results show significant differences for both $\delta^{13}C$ and $\delta^{15}N$ signals among nearly all fish ponds.

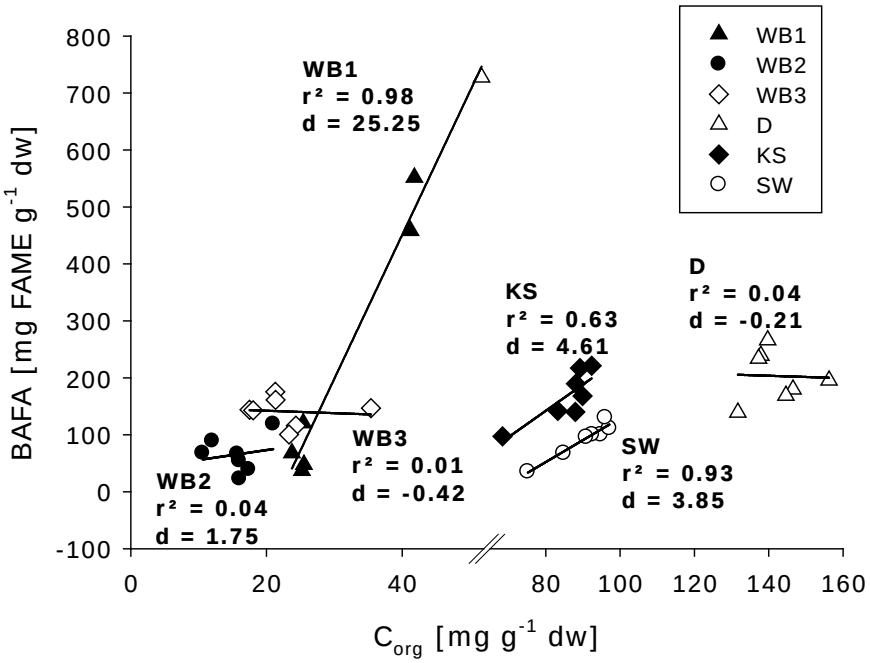

Fig.3. Linear regression between bacterial fatty acids (BAFA) and organic carbon (C_{org}) for all fish ponds. r²=regression coefficient, d=slope. WB=Winterbecken (1-3), D=Dürnhofteich, KS=Klein Schandacher Teich, SW=Schlägerwehr.

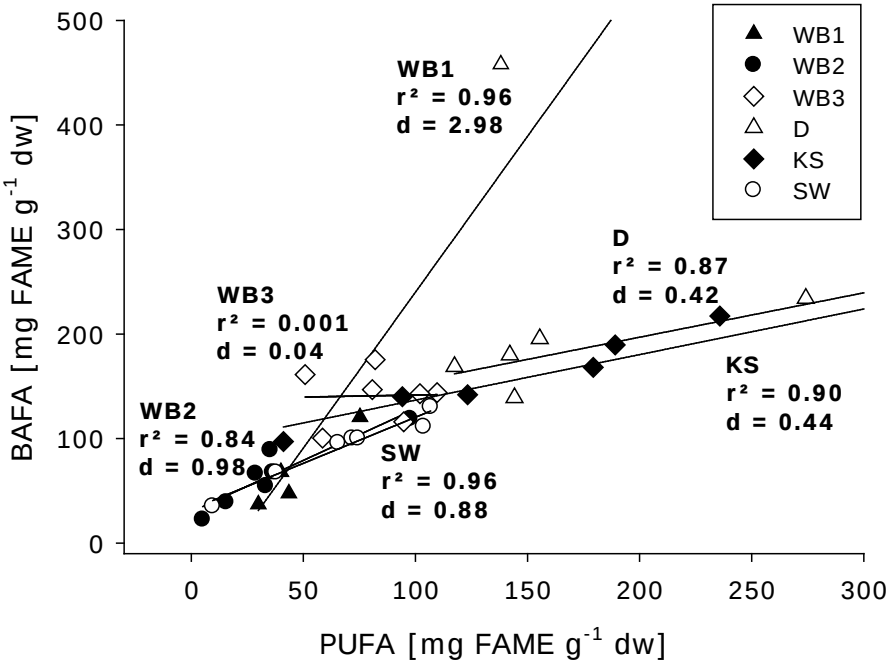

Fig.4. Linear regression between bacterial fatty acids (BAFA) and polyunsaturated fatty acids (PUFA) all fish ponds. r²=regression coefficient, d=slope. WB=Winterbecken (1-3), D=Dürnhofteich, KS=Klein Schandacher Teich, SW=Schlägerwehr.

For calculations of sedimentary composition via mixing models identification of allochthonous and autochthonous OM is necessary.

$\delta^{13}C$ signals of fish feed (allochthonous) and zooplankton (autochthonous) were used as the two main carbon sources for this calculation.

Leaf litter from surrounding vegetation was thought to have little influence due to sampling conduction before leaf fall. D was not included in mixing model calculations for lack of added fish feed.

Results shown in Fig.6 revealed enormous differences among the investigated fish ponds with no apparent tendencies existent. Highest percentages of allochthonous material was found in KS (nearly 94%) while the low value of 1.6% was calculated for SW both being lakes without MeHg present. Results for WB1-3 also lack a pronounced trend with a dominance of autochtonous material in WB1, allochthonous material in WB3 and almost equal proportions of both sources in WB2.

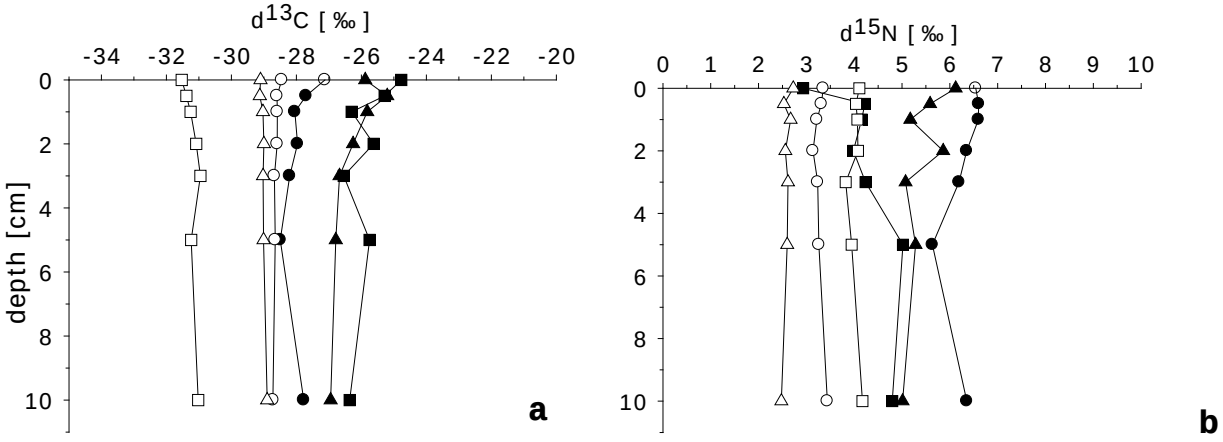

Fig. 5. Profiles of $\delta^{13}C$ (a) and $\delta^{15}N$ (b) values in sediment cores of WB1 (solid circles), WB2 (solid triangles), WB3 (solid squares), D (open squares), KS (open circles) and SW (open triangles).

2.4.5. Comparison of fish ponds with a natural ecosystem

To determine if differences between artificial and natural lakes occur, a comparison was made among the six sampling stations and Lake Lusignan (LL) representing a natural ecosystem (Tab.3). Similarities between LL and WB1 can be observed while LL showed higher concentrations of BAFA, PUFA and FAME than the five remaining fish ponds. Nearly no distinctions occurred between

MeHg concentrations of all lakes and the amount of Hg_{tot} found in LL is also within the range of Hg_{tot} values present in the fish ponds.

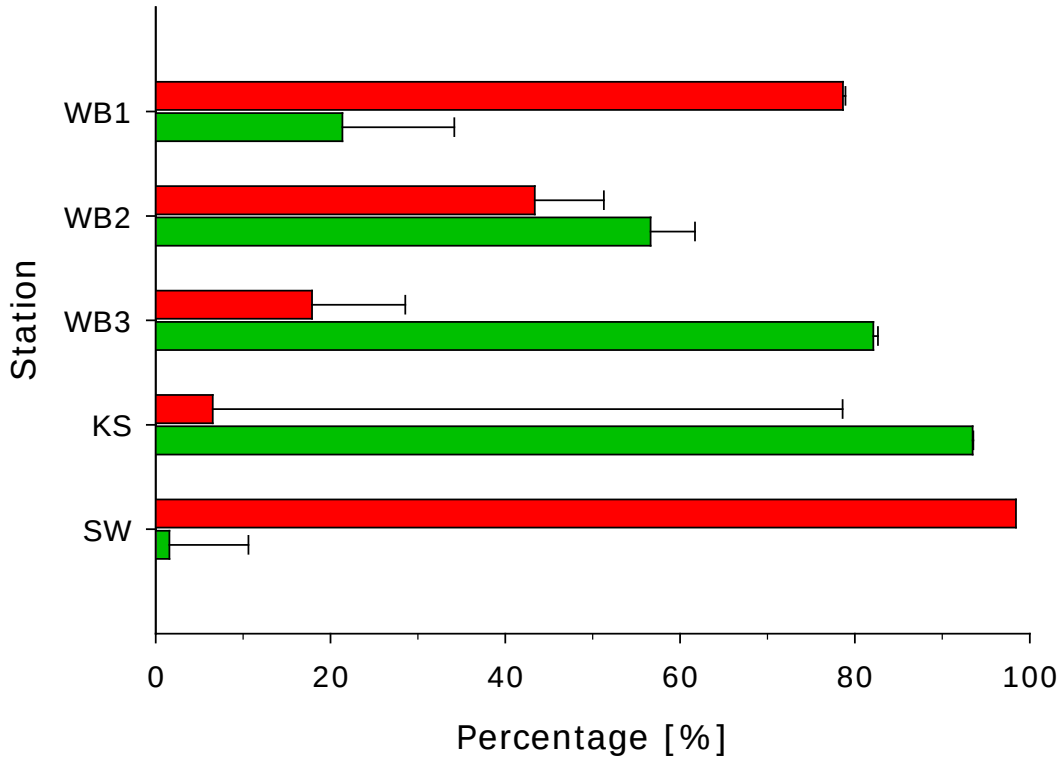

Fig. 6. Relative amounts with standard deviations of fish feed (green bars) and zooplankton (red bars) on sediment composition of all sampling stations. WB=Winterbecken (1-3), KS=Klein Schandacher Teich, SW=Schlägerwehr.

2.4.6. Sediment as source of contaminants for higher trophic levels

Mean MeHg concentrations of the first two centimetres of sediments were compared with corresponding MeHg values of zooplankton and fish tissue (data provided by S.Schultz). Mean values of zooplankton included three size classes (100, 250 and 500µm) which were collected during three campaigns in 2009. Muscle tissue of 6 fish per station was analysed and averaged (with the exception of D where n=3). Fish feed was excluded in this comparison because no MeHg was found during its analysis. Different MeHg concentrations are shown in Fig.7. Zooplankton was contaminated in all fish ponds with highest MeHg values in the winter basins (WB1 125.64 ± 98.91; WB2 170.25 ± 74.86; WB3 164.40 ± 70.11, values shown in ng g^{-1}dw respectively). MeHg concentrations of zooplankton were at least 2 times lower in D, KS and SW than those of WB1-3. The amount of MeHg found in fish tissues was 8 to 101 and that of zooplankton

27 to 139 times higher than concentrations in sediments. With the exception of KS and SW MeHg concentrations of fish showed lower values than the corresponding zooplankton.

Isotopic signals ($\delta^{13}C$ and $\delta^{15}N$) of fish tissue (muscle), zooplankton, fish feed and sediment were compared to identify major contributing feeding sources for fish and consequently ways of MeHg to pass into fish. Mean $\delta^{13}C$ and $\delta^{15}N$ values of sediments were calculated using the top two centimetres of each sediment core. Mean isotopic signals of fish tissue and zooplankton comprised the sampling set which was already used to calculate mean MeHg concentrations. Lowest $\delta^{13}C$ signals were generally found in D which is the only fish pond without feeding treatment. Different origin of feed (pellets with marine oil in WB1-3, wheat with terrestrial oil in KS and SW) caused only small differences in mean $\delta^{13}C$ values (WB1-3 -21.45 ‰ (±0.22), KS and SW -22.30 ‰ (±0.23). Fish feed also showed the highest $\delta^{13}C$ signals in all ponds where it was added. Comparison of δ13C values displayed only a weak resemblance between fish tissue and zooplankton values in WB1, WB2 and D whereas a similarity of $\delta^{13}C$ signals occurred in WB3 and KS (Fig.8). Additionally isotopic signals of sediment and zooplankton showed a certain likeness in four fish ponds. With the exception of D sedimentary signals display only a weak resemblance with $\delta^{13}C$ values of fish tissue. Literature data suggests that $\delta^{15}N$ signals increase about 3.4 ‰ with every trophic level. $\delta^{15}N$ differences between sediment and fish tissue signals range from 2.4 ‰ to 3.9 ‰ (WB1, WB2 and WB3) and from 5.1 ‰ to 6.2 ‰ (D, KS and SW) while those between fish feed and fish tissue range from 2.7 ‰ to 4.7 ‰ (WB1, WB2 and WB3). The signal differences between fish tissue and feed in KS and SW are 6.0 and 4.6 while no such value can be calculated for D due to its treatment (natural diet). No uniform character was found among investigated areas in respect of $\delta^{15}N$ differences between zooplankton and fish tissue. WB2 and WB3 both feature zooplankton values higher than their corresponding fish tissue results while other values range from 1.09 ‰ (WB1) to 2.94 ‰ (SW). $\delta^{15}N$ signals of fish feed in WB1 and WB2 display similar values while WB3 is nearly identical with isotopic signals of KS and SW (3.01, 3.07 and 3.17 ‰ respectively).

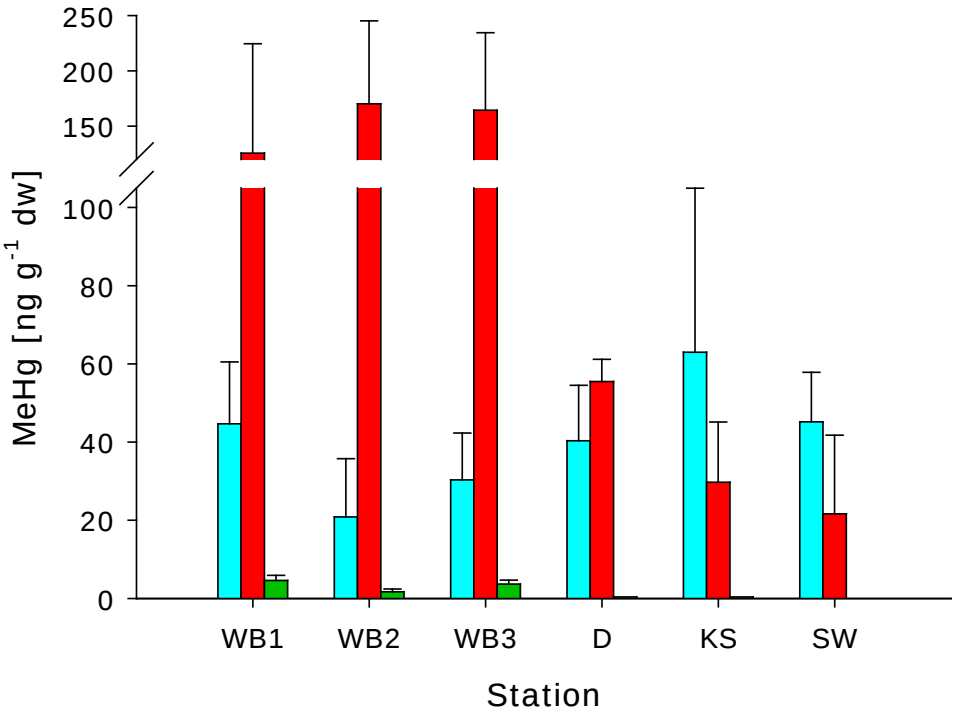

Fig.7. MeHg concentrations (± standard deviations) of sediments (green bars), zooplankton (red bars) and fish dorsal muscle tissue (blue bars). WB=Winterbecken (1-3), D=Dürnhofteich, KS=Klein Schandacher Teich, SW=Schlägerwehr.

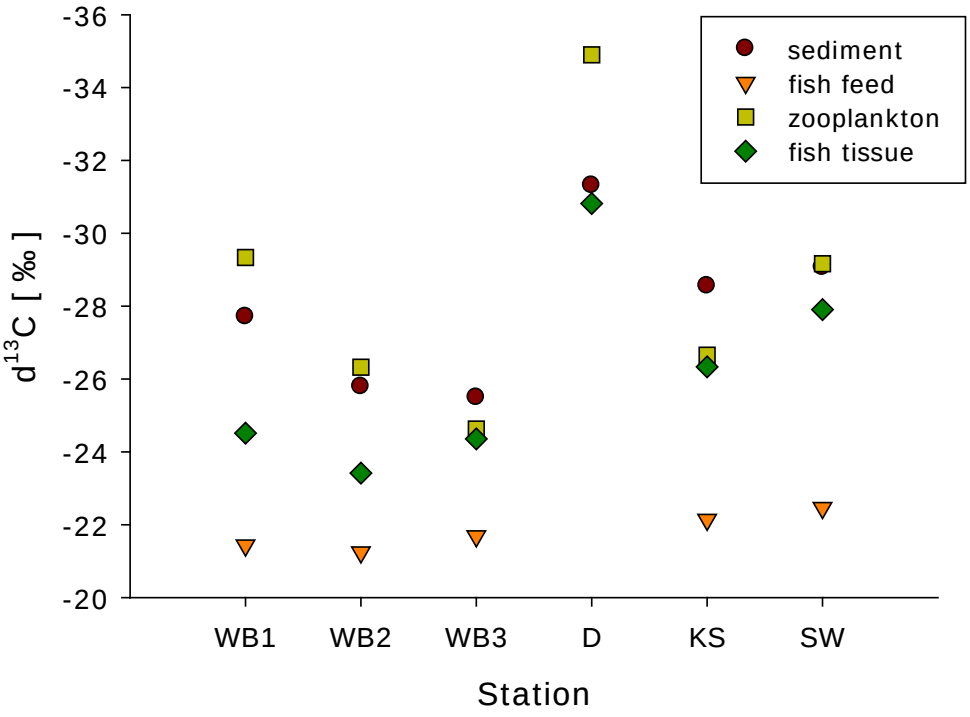

Fig.8. Mean $\delta^{13}C$ signatures of sediments, zooplankton, and fish tissue of all investigated ponds. Fish feed values are derived from a single sampling set.

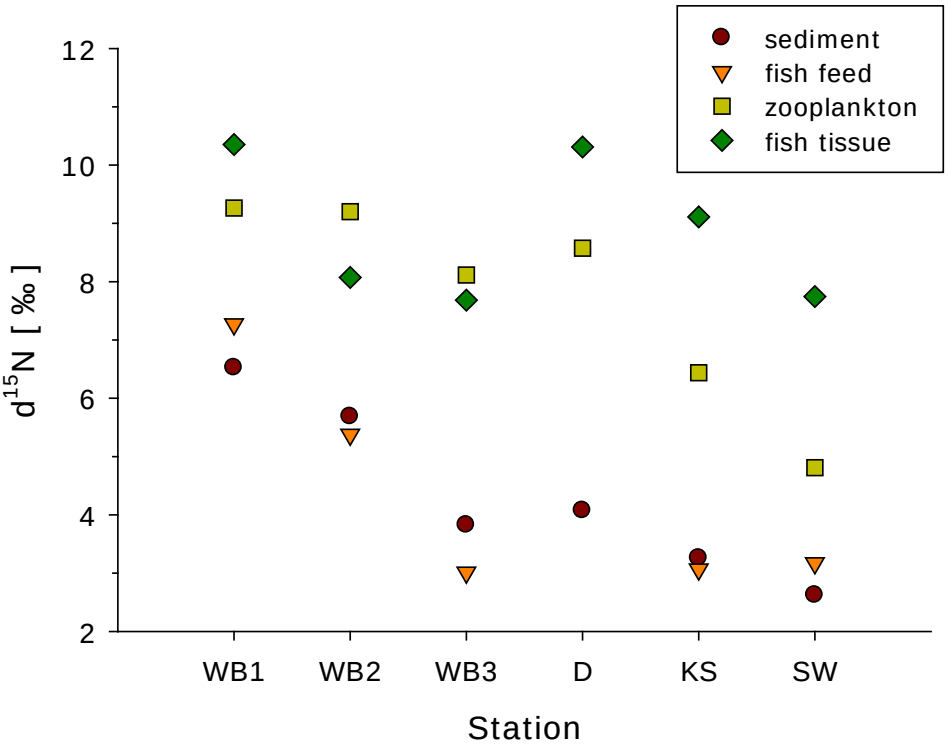

Fig.9. Mean $\delta^{15}N$ signatures of sediments, zooplankton, and fish tissue of all investigated fish ponds. Fish feed values are derived from a single sampling set.

2.5. Discussion

2.5.1. Mercury and Methylmercury concentrations

MeHg concentrations were only found in sediments of WB1-3, but not of the other, much larger fish ponds (D, KS, SW). MeHg concentrations in sediments were low, ranging from 1.1 to 3.2 ng g^{-1}. Similar sediment concentrations (1.09 to 2.32 and 1.21 to 2.30 ng MeHg g^{-1}dw for Philips Lake and George Lake, respectively) were found in a study of He et al. (2007) where relative small natural lakes north of Toronto, Canada, were examined. Sediment profiles with highest concentrations of MeHg at the SWI and a decreasing vertical distribution were in accordance with other studies (e.g. Kainz and Lucotte 2002) and suggest little or no effect of bioturbation through carp or other organisms.

The fact that MeHg was only found at three ponds raises the question about distinctive variations of biochemical and/or geochemical factors between the winter basins and the three larger fish ponds.

The amount of Hg_{tot} showed marked differences among fish ponds with up to 5X higher Hg_{tot} concentrations at D, KS and SW. It is possible that different Hg

concentrations entered these ponds due to different sources of the surrounding catchment areas that are mostly surrounded by agricultural fields where Hg runoff may occur.

Allocations of Hg_{tot} feature greater variations between all six fish ponds than those of its methylated species. While Hg_{tot} increases with depth in sediment profiles of WB2 and WB3 the opposite trend occurs in sediments of D. In WB1 a first decrease of Hg_{tot} is followed by an increase of its concentration whereas no clear trend was found in both KS and SW. These cores represent material input and sedimentation processes of just a few years because of recurring excavation events. One possible reason for the different distributions is a shifting input of mercury in these ponds. It is unlikely that diffusion processes in sediments are responsible for Hg_{tot} profiles for only one pond displayed a distinctive upward increase of mercury.

No relationship exists between the concentrations of Hg_{tot} and MeHg, which is both shown by the reverse distribution profiles of these species (Fig.1a and 1b) and their correlation values for WB1-3 (Tab.2). A significant negative correlation only occurred in WB2. The fact that most Hg_{tot} was detected in ponds where no MeHg was found further confirms that no positive relationship between MeHg and Hg_{tot} exists in sediment cores of the investigated areas. Consequently, Hg_{tot} is no predictor for MeHg in this study, which is in line with other studies (Benoit et al. 2003, He et al. 2007, Kannan et al. 1998).

2.5.2. Biochemical composition of sediments

Correlation calculations of Tab.2 show that the only factor to feature a significant relationship with MeHg in all winter basins is bacterial abundance, which consequently suggests a major predicting part of BAFA for MeHg concentrations. This trend was already indicated by sediment profiles of BAFA and MeHg (Fig.1a and 1c), which are tightly linked, in particular of WB1. Distributions of BAFA show similar trends in all ponds. Highest concentrations of bacterial biomarkers were found at the SWI or in the top centimetres (WB3) of sediment layers. A vertical decrease was also observed at all stations and was most prominent at WB1. This allocation is due to favourable conditions for bacteria at and below the SWI in terms of energy yielding substances and redox partners. Branched chain FAs, which were additionally correlated with MeHg, yielded no conclusive results. Although iso15, aiso15 and iso17 display a significant relationship with MeHg in

WB1 no such relationship was observed in WB2 and WB3, suggesting that other bacteria are responsible for Hg methylation in WB2 and WB3. The only significant differences between concentrations of bacterial biomarkers were observed between WB1 and WB2, while the other stations feature similar amounts of BAFA. This result raises the question why there is no MeHg in D, KS and SW if BAFA predicts this contaminant in the winter basins. A further complicating matter is the fact that the only pond, which shows a significantly different BAFA concentration from the other five ponds is WB2 where MeHg was found. A lipid biomarker which reflects contributions from iron and sulphate reducing bacteria is the 16:1ω7 fatty acid (Bechtel und Schubert 2009) which is present in sediments of each investigated pond, but no significant differences were detectable among them. This additionally implicates that although bacterial biomass explains MeHg in the winter basins it is not generally useable as a predicting factor. A possible explanation is that although BAFA is a proxy for the abundance of bacteria it does not predict their activity. Similar amounts of bacterial biomarkers in all ponds can allude to different activity levels.

In light of the fact that the quantity and/or quality of C_{org} as an energy yielding substrate is a possible controlling factor for the abundance and activity of bacteria the results of linear regressions (Fig.2 and Fig.3) may provide some indication for differences in MeHg concentrations. Relationships between BAFA and C_{org} are different among all fish ponds. While 3 stations feature high r^2 values, there is no close relationship between bacteria and C_{org} in the remaining ponds. C_{org} even has a negative effect on BAFA concentration at two stations (D and WB3). Results of Fig.2 show that carbon quantity is no general predictor for the amount of bacterial organism found. The quality of organic matter on the other hand seems to have a positive effect on BAFA concentrations (Fig.3). Both plots show that bacterial organisms are most influenced by the concentration of C_{org} and PUFA at WB1 (in terms of r^2 values and slopes) although other ponds feature higher amounts of these compounds. An explanation for these findings may be a higher availability of PUFA and C_{org} at WB1.

The amount of organic carbon is an important predictor for MeHg concentration in sediments whose effect on this heavy metal was observed in many studies. Surprisingly no significant influence of C_{org} on MeHg quantity was found at two winter basins with WB1 constituting the exception. Correlation coefficients even rendered a negative relationship between MeHg and C_{org} in WB2 and 3 (Tab.3). A

pronounce distinction occurred among all six fish ponds. Highest C_{org} concentrations were present in lakes where no MeHg was found, in other words there was no effect of C_{org} on MeHg concentrations. There are two possible ways for C_{org} to influence MeHg concentrations. The first is via bacteria, the main production site of MeHg, while the other affects the bioavailability of Hg_{tot}. Although the effect of C_{org} on bacterial abundance was discussed earlier it must be expanded with regard to MeHg. With 0.63 and 0.93 respectively, linear regressions yielded high r^2 values for KS and SW, two ponds where no MeHg was found in sediments. So even if a highly positive connection occurrs between BAFA and C_{org} it does not result in presence of MeHg by default. The availability of Hg_{tot} or the lack thereof poses a conceivable explanation for the effect of C_{org} on MeHg. Although the amount of Hg_{tot} shows no significant relationship with MeHg in this and other studies, it is important to note that Hg^{2+} availability is a fundamental requirement for the methylation process (Lambertsson and Nilsson 2006). If the availability of this species is reduced or non-existing due to inhibiting factors, the concentration of MeHg will be influenced. The presence of C_{org} can decrease the bioavailability of Hg^{2+} that tends to form complexes with OM due to the strong affinity of MeHg and Hg^{2+} for organic matter (Regnell et al. 1997). The part of C_{org} as a major influence on methylation processes is controversially discussed in many studies While a significant relationship is often observed (Regnell et al. 1997, Sunderland et al. 2006, Lambertsson and Nilsson 2006, Pak and Bartha 1998), other data doesn't agree with these results (He et al. 2007). Kainz and Lucotte (2002) found a significant correlation between OM and MeHg at the sediment-water interface (SWI), but not below this layer.

The predicting factor in these examinations always consisted of C_{org} concentrations. Seeing as the factor C_{org} contains the total amount of organic carbon compounds found in sediment cores, a greater distinction is essential. This was obtained with the help of lipid biomarkers for PUFA and terrestrial fatty acids. Fresh or labile C_{org} is found in the upper layers of sediments where also the greatest microbial activity occurs (Benoit et al. 2003).

With the exception of WB3, PUFA concentrations were highest at the SWI. At WB3, no relationship was found between MeHg and PUFA. In sediments of the other winter basins the amount of MeHg can be predicted by PUFA concentration. ANOVA results show that the MeHg containing winter basins and the other ponds are not clearly segregated by PUFA concentrations. D for example is significantly

different from WB2, WB3 and SW, but not from WB1 and KS, while WB1 features no significantly differences to other ponds at all. Mean concentrations of PUFA show that the highest value (at station D) doesn't cause the presence of MeHg while it is found and significantly correlated with PUFA in sediment of WB2, which is characterized by the lowest amount of PUFA found in this study. Like the concentration of C_{org} before also the relationship between bacterial organisms and the amount of PUFA was investigated by means of linear regressions. Given the fact that refractory compounds are excluded from this calculation it was assumed that a marked difference occurred between results of these two regression groups. Comparison of Fig.2 and Fig.3 show that the relationship between BAFA and PUFA is by far tighter linked than that of BAFA and C_{org}. PUFA influences the presence of bacterial biomarkers positively at every station. WB3 is the only pond where no relationship between these two factors was observed. If the amount of bacteria is dependent on PUFA in five of the six investigated lakes the question arises again why there was no MeHg present in D, KS and SW. Contrary to our expectations, PUFA are no predictor for MeHg or although it may predict the amount of BAFA it cannot serve as a proxy for MeHg alone. PUFA as a proxy for labile carbon was complemented by another factor, namely the C:N ratio, which is often used to describe the autochthonous or allochthonous nature of sediments in connection with carbon lability. Mean C:N values of the studied lakes nearly all correspond with ratios characterizing a predominance of aquatic plants (Meyers and Ishiwatari 1993) which suggests a major influence of autochthonous production or input of labile allochthonous carbon sources (fish feed) on sediment features. It further supports the assumption that input of allochthonous sources via surrounding vegetation is negligible. Although significant differences occur between the winter basins and the other lakes concerning their C:N values this factor has no powers to predict MeHg concentrations. Lower C:N values were thought to promote or enhance MeHg production since it would indicate the presence of more labile compounds. However, only WB1 features a significant and negative relationship between C:N and MeHg concentration while a positive correlation occurs at the other winter basins suggesting that C:N ratios as a proxy for carbon quality cannot explain MeHg presence in the fish ponds. Other factors must be taken into account for example the inhibition of methylating processes. Beside the possible restraint of C_{org} on Hg^{2+} availability redox potentials and sulphat concentrations can be an

issue. Negative redox potentials lead to anoxic conditions in the sediment which promote the formation of MeHg given the fact that methylating organisms are found among anaerobic bacteria (Compeau and Bartha 1984, Regnell et al. 1997, Pak and Bartha 1998). Although the lack of MeHg and the E_h profile with its oxic conditions throughout the first two centimetres of the sediment core at SW is in accordance with these observations, the similarities cease to exist at the other fish ponds. Beside the significant differences between SW and two winter basins, no other distinctions could be observed among the five remaining stations. In fact the E_h profile of KS nearly matches those of the winter basins. Therefore although the redox potential might explain the lack of MeHg at SW it cannot predict its presence at the other lakes.

So if neither the amount and quality of C_{org} nor anoxia are factors responsible for MeHg presence and concentration at the investigated stations in this study, the influence of sulphate may play the driving role for MeHg concentrations in these sediments. Seeing that SRB are the main methylators of Hg^{2+} the concentration of sulphate plays an important role in this process. If sulphate is abundant in the sediment bacteria are capable to utilize organic substrates more efficiently (Compeau and Bartha 1985). Gilmour et al. (1992) observed in their study that the concentration of MeHg increases with enhanced sulphate concentrations while a depletion of sulphate leads to a stop in MeHg production. They postulated furthermore that if the amount of available sulphate exceeds a certain level, inhibition of MeHg formation will occur due to high concentrations of sulphide. This observation is in accordance with Hammerschmidt et al. (2008) where dissolved sulphide is thought to be responsible for attenuation of MeHg production. As the measurement of sulphate concentrations was not included in this study its influence on MeHg levels can only be presumed. In the light of the fact that none of the investigated factors can explain the presence and/or absence of MeHg in lake sediments alone we suggest that sulphate concentrations are too low in D, KS and SW for methylation processes to commence. The blocking of methylation processes due to too high a concentration of sulphite can be disregarded firstly because contrary to marine environments sulphate availability is normally limited in terrestrial and freshwater habitats (Lambertsson and Nilsson 2006). Hence it is unlikely that the necessary amounts of sulphate needed for an inhibition to occur are present in sediments of the ponds. Furthermore, if a restraint due to sulphide

concentrations had appeared this fact would have indicated a foregone event of Hg methylation meaning that a certain level of MeHg should be present in all fish ponds. Although the possibility of too low a sulphate concentration might explain the differences of the amount of MeHg in sediments of the investigated ponds the question remains if the observed differences are really only attributable to the amount of sulphate. Mason and Lawrence (1999) for example observed that little relationship exists between MeHg and both AVS (acid volatile sulfide) and %S concentrations in sediments although a correlation was expected. As the influence of sulphate on MeHg was not included in this study no reasonable assumptions can be made concerning its part in MeHg allocation among sediments of the six fish ponds.

2.5.3. Geochemical composition of sediments

Depth profiles of both $\delta^{13}C$ and $\delta^{15}N$ signals are very evenly distributed indicating that little to none source changes happened in the time frame from the last excavation event to the date of the sampling. Sediments of the winter basins generally have higher $\delta^{15}N$ values than the other ponds, which can be explained by the enrichment of their added feed with fish oil being high trophic level material. This difference can be seen in the division of the winter basins represented by solid symbols from the other lakes represented by open symbols in Fig.4b. A similar separation occurs for $\delta^{13}C$ signals representing different sources of carbon input. Despite this seemingly assembly of winter basins and the three other lakes these visual differences cannot explain MeHg distribution in view of ANOVA results. Although the winter basins are mostly significantly different from D, KS and SW, they also display the same differences among themselves for both $\delta^{13}C$ and $\delta^{15}N$ values. D and WB3 are for example the only ponds with similar $\delta^{15}N$ signals so no conclusion with regard to MeHg concentration is possible beside that sediment composition alone doesn`t seem to have a measurable effect on the amount of MeHg. The amount of autochthonous and allochthonous sources in sediments calculated by mixing models was another approach to illuminate the effect of carbon origin on MeHg concentration. Results expressed in Fig.6 are highly variable and display no regularity at all among all fish ponds. For instance, sediment composition between winter basins are characterised by marked distinctions (79% zooplankton in WB1 and only 18% zooplankton in WB3). These findings would

further indicate that sediment composition possess no influence on the amount of MeHg found in sediments. However, the question arises if these results have enough validity to draw such conclusions from them.

Although differences in sediment compositions were expected because of possible deviations in both frequency and quantity of added feed and variations in terms of primary production, the extent of these divergences even between locations with similar attributes is bewildering. Foraging of fish may be responsible for some of these differences but cannot explain results of KS and SW. While 93% of the sediment composition consists of feed at the first station, the opposite occurs at SW where over 98% of the sediment is attributable to zooplankton. Mixing model calculations were performed with $\delta^{13}C$ signals of only three compartments (sediment, feed and zooplankton) and didn't include other possible fractions in pond ecosystems like algae, bacteria, viruses and protozoa. Although allochthonous input from surrounding trees might amount to great quantities in fall and winter, its influence on sediment composition in this study is not thought to be of great importance. These fish ponds are periodically excavated and its probable that the first sediment layers are mostly influenced by production which occurred in the year of sampling. However, beside the exclusion of leafs from surrounding vegetation, the omission of other sources might distort or influence the $\delta^{13}C$ signal of sediments in which case the mixing model has no explaining powers.

2.5.4. Comparison of fish ponds with a natural ecosystem

Seeing that the investigated fish ponds are of artificial origin with noticeable differences to natural formed lakes (no littoral zone, regular excavation events, drainage in winter) it is of interest to observe if these distinctions are reflected in biochemical compositions of sediments. When Lake Lusignan (LL) were to be compared with WB1 one conspicuous difference is the total amount of PUFA which is nearly 3 times higher in sediments of LL. Other differences that occur between LL and the other stations are also present between WB1 and the remaining ponds. Therefore, the distinctions between LL and the artificial fish ponds are not explainable with differences of origin.

Although LL features nearly identical BAFA concentrations and higher amounts of PUFA than WB1 MeHg concentrations of LL are even lower than those of WB2 and

WB3 which is further evidence that PUFA and BAFA concentrations alone cannot predict the amount of MeHg found in sediments.

2.5.5. Sediment as source of contaminants for higher trophic levels

MeHg concentrations of zooplankton and fish tissue were compared with those of sediments to ascertain its influence on these higher trophic levels in the investigated ecosystems. Hammerschmidt and Fitzgerald (2006) connect MeHg contamination of sediments to MeHg concentrations of zooplankton via the mediator microseston and postulate that most of the MeHg found in higher trophic levels may be attributes to net sedimentary production. This assumption would explain the at least two times higher amount of MeHg in zooplankton at the winter basins. One problem with pinpointing sediments as the main source for MeHg contamination of zooplankton is that not every compartment that might influence zooplankton was examined like the concentration of dissolved MeHg in the water column. Beside the possibility of MeHg entering the water column by means of diffusion from the sediment, it can also be directly generated there. Although sediments are the main production sites of MeHg (Benoit et al. 2003) the formation of considerable amounts of MeHg in the water column was also noticed (Regnell et al. 1997). Despite the fact that nearly no MeHg was found in sediments of D, KS and SW, zooplankton is contaminated at all sampling sites, though with high deviations in their concentration. At least one pond (SW) in our study is likely to be influenced by methylation processes in the water column seeing that although no MeHg was found at any layers of the sediment core MeHg was found in zooplankton samples. The comparison of sediment and zooplankton concentrations of MeHg can therefore not yield reliable results to fully understand the influence of sediments on ecosystems alone but our data at least suggests a direct connection. This assumption is reinforced by the study of Mason and Lawrence (1999) that yielded strong correlations between MeHg concentrations of sediments and both benthic invertebrates and zooplankton. If sediment is at least partly responsible for zooplankton contamination than concentration differences (ranging from 27 to 139 higher a concentration) in zooplankton and its corresponding sediment of the fish ponds can be explained by means of bioaccumulation, a well known process which is partly due to the great trophic transfer of MeHg (Reinfelder et al. 1998). Naturally there are more

intermediate steps between sediment and zooplankton like for example algae or protozoa.

MeHg concentrations of zooplankton display huge variations among the six ponds, a tendency which is not reflected in the amount of MeHg found in fish tissue. In four of the six fish ponds fish have lower MeHg concentrations than zooplankton. The explanation for the lack of bioaccumulation between these two trophic levels is biodilution caused by added MeHg free fish feed. Fish of KS and SW, which receive wheat as supplementary nutrition source, are the only ponds where MeHg concentration of fish tissue is higher than that of zooplankton. This might indicate a different foraging pattern of these fish compared to those in the winter basins with both a diet comprised of added feed and zooplankton either triggered by a different frequency or quantity of input or insufficient energy coverage of the chosen feeding type. Direct uptake of MeHg through water is unlikely to influence these concentrations because diet is the dominant pathway for MeHg to pass into fish (Hall et al. 1997). Pond D, which is a reference point for natural conditions, poses an issue. Zooplankton was thought to be the primary nutrition source for fish given the fact that no supplementary feed was added. However, concentrations of MeHg in fish tissues was lower than that of zooplankton meaning that no bioaccumulation would have occurred if zooplankton had been the main feeding pool.

Due to their benthivorous feeding patterns carp often take up considerable amounts of sediment while foraging at lake bottoms resulting in a greater concentration of contaminants in their bodies than for example pelagic fish despite their piscivorous nature (Russell et al. 1998). A direct transfer of MeHg from sediment to fish was therefore thought to be possible. If this assumption was correct it would result in higher MeHg concentrations of fish tissue in ponds where sediment features at least some contamination. This was not the case in this study where highest concentrations of MeHg occur in carp located in D. Furthermore, information gained by isotopic analyses implicate that no uptake of sediments through fish happens. Although some similarities occur between $\delta^{13}C$ values of fish tissue and sediment in D, KS and SW, great differences can be observed between their corresponding $\delta^{15}N$ values. Sediment profiles of both MeHg and BAFA with highest concentrations at the SWI and a decrease with depth seem to be undisturbed by bioturbation which also suggests that no foraging of fish occurs at the bottom of these ponds. The lack of benthos in

sediments of all six ponds explains these observations. It also means that contamination of MeHg via the benthic pathway is not possible in this study. Another pathway for MeHg into fish organisms is through the pelagic food chain where both sediment diffusion and production of MeHg in the water column are important contributors (Mason and Lawrence 1999) strongly suggesting that zooplankton might be a major factor controlling contamination of fish.

$\delta^{13}C$ values of fish tissue and added feed are better matched at the winter basins than those at KS and SW where differences up to 5.4 ‰ occur. These similar $\delta^{13}C$ values suggest that fish in the winter basins mainly use added feed as nutritional source, which is in accordance with $\delta^{15}N$ results of WB1 and WB2 with WB3 constitutes the exception. KS and SW are defined by a $\delta^{15}N$ much higher than the suggested 3.4 ‰ difference between two trophic levels. It can therefore be assumed that fish in KS and SW don't mainly feed on added feed.

Contrary to fish feed $\delta^{13}C$ values of zooplankton and fish tissue show only small variations in KS and SW. Isotopic signals were even nearly identical in the first-mentioned pond (Fig.8). Differences of roughly 3 ‰ between $\delta^{15}N$ signals of zooplankton and fish tissue in KS and SW further supports the assumption that zooplankton is an important feeding source for fish of these two ponds. It was expected that fish foraging in the only pond without any treatment (D) would find their major nutrient source in feeding on zooplankton. Although $\delta^{15}N$ results may suggest this feeding pattern, $\delta^{13}C$ signals don't entirely agree with this assertion indicating that a second or more diet sources might be present at this station, which were omitted in our analyses. Isotopic data of the winter basins yield contradictory results concerning zooplankton as a feeding source for fish. On one hand $\delta^{13}C$ values are nearly identical at WB3, which would imply an important connection between fish and zooplankton. On the other hand $\delta^{15}N$ values suggest that zooplankton doesn't play a substantial part for fish diet. While the difference in $\delta^{15}N$ signals only amounts to 1.09 ‰ at WB1, zooplankton values exceed those of fish at the other two winter basins. However, $\delta^{13}C$ values of added feed and fish tissue are more similar at WB1 and WB2 than fish tissue and zooplankton. We conclude as a consequence that fish feed is the major diet for fish at the winter basins while zooplankton is the more important feeding source at KS and SW. These different foraging patterns can explain why MeHg concentrations are generally higher at the three natural ponds. While

bioaccumulation occurred at KS and SW via uptake of contaminated zooplankton, the preferred feeding on MeHg free food led to biodilution at the winter basins.

2.6. Conclusio

This field study demonstrates that neither organic carbon quantity nor quality of organic carbon, as measured by source-specific fatty acids, could predict MeHg concentrations of these pond sediments. Although other factors, such as sulphate concentrations, are known to be required by Hg methylating bacteria (e.g. Pak and Bartha 1998, Benoit et al. 2001) in anoxic sediments, these results strongly suggest that different carbon sources, as energy-yielding substances for such bacteria, are not significantly associated with the presence of MeHg in sediments. Finally, based on clear differences of MeHg concentrations between sediments and carp muscle tissues, we conclude that the organic matter composition of pond sediments cannot predict MeHg concentrations of carp.

2.7. Acknowledgements

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3. Zusammenfassung und Perspektiven

Der Ursprung von MeHg-Konzentrationn von Karpfen aus Aquakulturen war der Ausgangspunkt, den diese Studie zum Anlass hatte. Es wurde vermutet, dass Sedimente als Entstehungsort von MeHg Einfluss auf die MeHg Belastung von Fischen haben und Untersuchungen wurden durchgeführt, unter welchen biogeochemischen Gegebenheiten mit einer MeHg-Konzentrationen von Sedimenten zu rechnen ist.

Im Laufe dieser Studie ergaben sich einige Schwierigkeiten mit dem Forschungsdesign.

Ein Problem des Datensatzes dieser Arbeit ist, dass jeder Teich nur an einer Stelle (dem tiefsten Punkt) mit einem einzigen Bohrkern beprobt wurde. Einerseits erlaubte das Zeitmanagement keine weiteren Probenahmen, andererseits war die Sedimentsauflage an den meisten anderen Stellen durch regelmäßiges Ausbaggern der Teiche so gering ausgeprägt, dass sich die Probenahme als schwer gestaltet und nur einen geringen Ergebnisgewinn eingebracht hätte. Schwierigkeiten ergeben sich auch durch die Tatsache, dass einige Kompartments und Faktoren nicht in die Untersuchungen inkludiert werden konnten. Die Analyse der Wassersäule als möglicher Bildungsort von MeHg musste ebenso ausgelassen werden wie die Analyse von Algen und Protozoen auf ihren MeHg Gehalt als mögliche Trophiestufen mit Bioakkumulationspotential zwischen Sediment und Zooplankton. Problematisch ist auch, dass die Probenahme von Sedimenten nur einmal erfolgte, während Zooplankton und Fische mehrmals im Jahr beprobt wurden. Eine Momentaufnahme wir dementsprechend mit Beobachtungen über einen längeren Zeitraum verglichen. Ungenauigkeiten in den Ergebnissen können die Folge sein, vor allem da MeHg Konzentrationen temporären Schwankungen unterstehen (Hammerschmidt et al. 2008).

Die Ergebnisse unserer Untersuchungen ergeben, dass von 6 Teichen lediglich 3 MeHg Konzentrationen im Sediment aufweisen, während 2 Teiche nur MeHg Spuren in einer einzigen Sedimentschicht haben. Weiters gibt es keine eindeutigen Zusammenhänge zwischen den untersuchten Faktoren und der Menge von MeHg. Hg_{tot} kann in keinem der Teiche die Konzentration von MeHg erklären, bis auf WB2, wo es eine signifikante, jedoch negative Korrelation gibt. Diese Ergebnisse stimmen mit jenen früherer Studien (z.B. Benoit et al. 2003)

überein. Auch das Redoxpotential von Sedimenten konnte die unterschiedlichen MeHg Konzentrationen zwischen den Teichen nicht erklären. Im Gegensatz zu diesen beiden Faktoren hat die Konzentration von bakteriellen Fettsäuren in den Winterbecken einen signifikanten und positiven Einfluss auf MeHg. Trotzdem kann die Konzentration von BAFA nicht als Prädiktor angesehen werden, da die Menge dieses Faktors nicht insoweit zwischen allen 6 Teichen variiert, dass sie die Abwesenheit von MeHg in Sedimenten der anderen Standorte erklären kann. Hinzu kommt, dass ein Teich ohne MeHg Kontaminierung die größte Konzentration an BAFA aufweist. Es muss allerdings festgehalten werden, dass die untersuchten bakteriellen Fettsäuren die Summe aller in Bakterien gefundenen Fettsäuren sind, und nicht den Hg-methylierenden Bakterien spezifisch zugeschrieben werden können.

Der Qualität von C_{org} wurde in dieser Studie große Bedeutung als Prädiktorvariabel für die Konzentration von MeHg beigemessen und an Hand mehrerer Faktoren zu ermitteln versucht (PUFA, C:N, allochthoner vs. autochthoner Einfluss). Obgleich eine höhere Konzentration an labilen Komponenten in Form von PUFA in 2 Teichen (WB1, WB2) einen signifikanten Zusammenhang mit MeHg aufweist, war dies in keinem der übrigen Seen der Fall und zeigt, dass die Konzentration von labilen PUFA alleine, die jedenfalls leicht abbaubare Energie für Bakterien liefern, nicht die Konzentration von MeHg erklären kann. Das C:N Verhältnis ist als Prädiktor ungeeignet, da es als Verhältnis von Gesamtkohlenstoff zu Gesamtsticktoff keinen relevanten Aufschluss auf die spezifische Kohlenstoffqualität zulässt und in dieser Studie ebenfalls keine Erklärung für die unterschiedlichen MeHg Konzentrationen der verschiedenen Teiche liefert.

Der Versuch die Herkunft von organischem Material in Hinsicht auf seinen allochthonen und autochthonen Ursprung mit Hilfe eines Mixing models zu ermitteln, um mit diesen Ergebnissen den Grund für das Fehlen von MeHg in Sedimenten dreier Teiche erklären zu können, war nicht zielführend. Die erhaltenen Resultate zeigen gewaltige Unterschiede sogar zwischen Teichen ähnlicher MeHg Konzentration, welches entweder bedeutet, dass die Herkunft von C_{org} keine Auswirkung auf MeHg hat oder dass andere Fehlerquellen aufgetreten sein müssen. Eine davon ist, dass sich das allochthone Material (Futtermittel) de facto in 2 Gruppen gliedert. Einerseits wurden die Fische der Winterbecken mit Pellets und Fischöl gefüttert, während Getreide und Distelöl für

KS und SW als Futtermittel verwendet wurde. Obwohl diese beiden Gruppen allochthonen Ursprungs sind, weisen sie eine unterschiedliche Qualität auf, was in dem mixing model nicht berücksichtigt wurde. Ein weiterer Punkt, der zu Beeinträchtigungen führen kann ist der Eintrag von anderem Material aus dem Einzugsgebiet, der in diesem Model vernachlässigt wurde. Der Anteil dieses Inputs ist im Gegensatz zu den zugeführten Futtermenden nur gering, kann jedoch für die Beeinflussung von Isotopensignaturen verantwortlich sein. Jedoch können selbst unterschiedliche Futterquellen und eine möglicherweise unterschiedliche Menge an Futterzufuhr nicht die extremen Unterschiede in der Sedimentzusammensetzung erklären, wie sie das Mixing model in Fig.6 anzeigt. Dies legt den Schluss nahe, dass die Daten dieses Models keine Erklärungskraft haben und für diese Studie nicht geeignet sind. Zusammengefasst ist zu sagen, dass die Quantität von C_{org} nicht für die Konzentration von MeHg ausschlaggebend ist und dass BAFA und PUFA zwar in allen 3 beziehungsweise 2 kontaminierten Teichen signifikant mit MeHg korrelieren, diese Beziehung jedoch nicht auf alle Untersuchungsgebiete zutrifft.

Die Frage nach dem Grund der unterschiedlichen MeHg Konzentrationen in den Sedimenten der 6 Teiche bleibt somit bestehen. Obgleich weder PUFA noch BAFA alleine eine Erklärung hierfür liefern, ist ihre Beziehung zueinander von Interesse. In allen Teichen (bis auf WB3) hat PUFA einen positiven Einfluss auf die Konzentration von BAFA mit einem $r^2 \geq 0{,}84$. Demzufolge ist die Aktivität der Bakterien oder die Hemmung derselben durch beispielsweise Temperatur oder Sulfatkonzentration ausschlaggebend. Temperaturmessungen an der SWI zeigten geringe Variationen zwischen den Teichen, jedoch sind sie anders als Sedimente nur eine Momentaufnahme. Langfristige Schwankungen, die in dieser Studie nicht erfasst werden konnten, können auf die Konzentration von MeHg Einfluss genommen haben. Obwohl alle 6 Teiche in derselben Region liegen und ähnlicher Witterung und Sonneneinstrahlung ausgesetzt sind, kann es durch die verschiedenartige Beschattung und Größe der Wasserkörper zu ausschlaggebenden Temperaturunterschieden kommen. Zum Klären dieser Frage wäre ein umfassenderes Monitoring notwendig. Die Konzentration von Sulfat, welches sowohl für den Start des Methylisationsprozesses als auch in Form von Sulfiden für seine Hemmung verantwortlich sein kann, ist möglicherweise auch für die unterschiedliche MeHg Konzentration der Sedimente verantwortlich. Da die Konzentration von Sulfat in Süßwasserökosystemen oft begrenzt ist

(Lambertsson und Nilsson 2006), ist in unserer Studie möglicherweise der Mangel an Sulfat ausschlaggebend, jedoch können aufgrund fehlender Messungen nur Vermutungen angestellt werden.

Das Vorkommen und die Konzentration von MeHg in Sedimenten ist so gesehen nicht alleine von einem bestimmten Prädiktor abhängig, sondern ist das Ergebnis eines weitaus komplexeren Prozesses, der unterschiedliche Faktoren umfasst. Weitere Studien, welche sich mit MeHg Konzentrationen beschäftigen, sollten neben der Qualität von C_{org} und bakteriellen Abundanzen auch Konzentrationen von Sulfat umfassen, um feststellen zu könne unter welchen Umständen MeHg in Sedimenten auftritt.

Diese Studie wirft auch Fragen über den Einfluss von MeHg fördernden und hemmenden Faktoren auf. BAFA und PUFA sind signifikante Prädiktoren für MeHg in WB2, obwohl sie hier von allen 6 Teichen die geringsten Konzentrationen aufweisen. D hingegen hat die zweithöchsten beziehungsweise höchsten Konzentrationen an BAFA und PUFA ohne dass sich MeHg im Sediment befindet. Es hat somit den Anschein, als ob hemmende Faktoren einen größeren Einfluss auf die Konzentration von MeHg haben als fördernde Faktoren. Falls dieser Umstand zutrifft, hätte beispielsweise die Kohlenstoffqualität eine sekundäre Bedeutung, sie erst nach dem Wegfallen des hemmenden Faktors einen Effekt bewirken würde. Mangel an Sulfat und Überschuss an Sulfid sind zwei mögliche hemmende Faktoren, die in dieser Studie angesprochen wurden, jedoch konnte nicht festgestellt werden, ob sie tatsächlich zu derart geringen Konzentrationen von MeHg führen können. Zukünftige Forschung muss ihren Blickpunkt stärker auf diese und weitere hemmende Faktoren richten, um die Gefahr von MeHg Konzentrationen in Sedimenten besser einschätzen zu können.

Die Frage, ob MeHg Konzentrationen im Sediment Auswirkungen auf die Fische in Aquakulturen haben, ist schwer zu beantworten. Einerseits zeigen Vergleiche von Zooplanktondaten, dass diese Organismen in Teichen mit MeHg im Sediment bedeutend höhere Belastungen aufweisen als Zooplankton der anderen Teiche. Andererseits gibt es keine eindeutige Tendenz in der MeHg Belastung von Fischen. Diese Tatsache im Zusammenhang mit den Ergebnissen der Isotopensignaturen zeigen, dass zugeführtes Futtermittel zu Verdünnungseffekten führt. Fische der Winterbecken scheinen ihren Energiebedarf mehr aus der Ressource Futter als aus Zooplankton zu beziehen im Gegensatz zu jenen der anderen Teiche, wodurch es zu einer geringeren

MeHg Belastung kommt. Diese Beobachtung wirft die Frage auf, warum gerade Fische der Winterbecken mehr auf das Fischfutter zurückgreifen als jene der anderen Teiche. Dies kann beispielsweise an unterschiedlichen Quantitäten der Zufuhr liegen, was leider nicht nachzuvollziehen ist, da diese Daten nicht zur Verfügung stehen. Auch die Ergebnisse des mixing models können zur Aufklärung dieser Frage nicht herangezogen werden, da einerseits an der Richtigkeit der Resultate an sich gezweifelt werden muss und da diese andererseits nur Auskunft geben würden, wie viel Futter ohne Interferenz der Fische den Teichgrund erreicht. Möglicherweise jedoch ist der Fettgehalt des Futters der Grund für dessen vermehrten Konsum durch Fische in den Winterbecken. Mit 18, 10 und 6% im Gegensatz zu 3,3 und 1% haben die Winterbecken Futter mit einem höheren Fettgehalt und möglicherweise wird dieses Zooplankton als Nahrungsquelle vorgezogen. In diesem Fall kann durch den Fettgehalt des Futters die Kontaminierung der Fische mit MeHg verringert werden.

Das Sediment kann in dieser Studie nicht der einzige Ort der MeHg Bildung sein, da auch Zooplankton von Teichen ohne MeHg Kontamination eine Belastung mit MeHg aufweist. Methylierung von Hg kann auch in der Wassersäule erfolgen, jedoch wurde dieses Kompartment nicht in unsere Untersuchungen einbezogen, sodass unklar bleibt, wie sehr dieser Anteil die Konzentration in Zooplanktonorganismen beeinflusst. Trotz dieser Tatsache legt der Vergleich von MeHg Konzentrationen in Sedimenten und Zooplankton der sechs Untersuchungsstandorte nahe, dass die Kontamination von Sediment einen Einfluss auf die Menge von MeHg in Zooplankton hat.

In dieser Studie wurden zum ersten Mal Teichsedimente von Aquakulturen anthropogenen Ursprungs untersucht, um mögliche Unterschiede zu natürlich entstandenen Seen zu analysieren und das Gefahrenpotential der Sedimente für die Fischpopulation zu ergründen. Es wurden keine bedeutenden Unterschiede in MeHg Verteilung und Konzentration im Sediment zu anderen oligotrophen Seen gefunden, was darauf schließen lässt, dass unterschiedliche Entstehungsgeschichten von Ökosystemen nicht zwangsläufig zu unterschiedlichen MeHg Konzentrationen führen. Die Fischzucht ist ein wichtiger Wirtschaftszweig, der in den kommenden Jahren noch weiter wachsen wird. Somit ist die Wichtigkeit gegeben, Aquakulturen auf ihr Gefahrenpotential zu untersuchen und Wege zu finden dieses zu verringern.

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5. Appendix

5.1. Zusammenfassung

Der Einfluss der biochemischen Zusammensetzung und Kohlenstoffqualität von Sedimenten auf die Konzentration von Methylquecksilber (MeHg) wurde in Sedimentproben von sechs künstlich angelegten Fischteichen untersucht. Zusätzlich wurde überprüft, ob MeHg Konzentrationen von Sedimenten die MeHg Konzentrationen im dorsalen Muskelfleisch von gezüchteten Karpfen (*Cypriunus carpio*) vorhersagen können. Die Aufbereitung der Proben erfolgte mittels Lipidanalyse von Biomarkern und Isotopenanalyse ($\delta^{13}C$ und $\delta^{15}N$). Nur in 3 der 6 Teiche wurde MeHg mit mittleren Konzentrationen von 1,1 bis 3,2 ng g^{-1} Trockenmasse gefunden. Hg_{tot} Konzentrationen hatten keinen Einfluss auf die Menge von MeHg in Sedimenten. MeHg kontaminierte Teiche wiesen eine signifikante Beziehung zwischen MeHg und der Konzentration von bakteriellen Fettsäuren auf, jedoch unterschieden sich alle sechs Teiche nicht signifikant in ihrer Konzentration von bakteriellen Biomarkern. Weder Menge noch Qualität (PUFA) von organischem Kohlenstoff konnte Unterschiede in der MeHg Konzentration erklären. Die Durchführung von mixing models zur Überprüfung, ob MeHg Konzentrationen mit der biochemischen Zusammensetzung (Material autochthoner und allochthoner Herkunft) von Sedimenten im Zusammenhang stehen, lieferte keine eindeutigen Ergebnisse.

Höchste MeHg Konzentrationen in Muskelgewebe von Karpfen wurde in Teichen ohne MeHg Belastung des Sediments gemessen und sind vermutlich Ergebnisse von Verdünnungseffekten, ausgelöst durch zugeführtes Fischfutter.

5.2. Summary

We investigated the influence of biochemical organic matter composition on methyl mercury (MeHg) concentrations in sediments of 6 fish ponds in Lower Austria and explored the ecotoxicological potential of MeHg in sediments of getting directly conveyed to fish (common carp; *Cyprinus carpio*). Only 3 ponds contained MeHg concentrations in the upper sediment layers (1.1 to 3.2 ng g^{-1} dw) and Hg_{tot} concentrations could not predict MeHg concentrations in these sediments. MeHg concentrations were significantly correlated with bacterial biomarkers (bacterial fatty acids), but bacterial fatty acid concentrations of sediments did not differ significantly among the investigated ponds. Moreover, organic carbon concentrations or mostly algae-derived, labile organic matter (polyunsaturated fatty acids) of sediments could not account for differences of MeHg concentrations. Results of mixing models indicated that different sediment sources (autochthonous versus allochthonous organic matter) were not associated with MeHg concentrations. MeHg concentrations of carp were higher in ponds with no MeHg concentrations in sediments, strongly suggesting that MeHg concentrations of pond sediments cannot predict MeHg concentrations in muscle tissues of common carp.

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5.4. Lebenslauf

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Lebenslauf

◊ Persönliche Daten

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◊ Weitere Kenntnisse

Sprachen	Englisch (sehr gute Kenntnisse in Schrift und Sprache) Französisch (Grundkenntnisse) Latein (Grundkenntnisse)
EDV	Windows Office, SPSS, Sigma Plot, R