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Variation in methylmercury biomagnification in freshwater and terrestrial invertebrates: a critical review

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Declaration:

I declare that this document is an original work of my own authorship and that it fulfills all the requirements of the Code of Conduct and Good Practices of the Universidade de Lisboa.

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Resumo

O mercúrio é um poluente extremamente tóxico que pode ser encontrado em ecossistemas remotos devido à capacidade de dispersão do mercúrio elementar. Metilmercúrio é a forma de mercúrio com maior capacidade de bioacumulação e biomagnificação e a concentração em baixos níveis tróficos pode ter impactos em organismos de níveis tróficos superiores.

Dados sobre a concentração total de mercúrio, metilmercúrio e isótopos estáveis de C e N de vários invertebrados de água doce foram extraídos da literatura. Adicionalmente, as características físico-químicas dos ecossistemas também foram extraídas de modo a avaliar o impacto que têm na bioacumulação e biomagnificação.

Com esta análise foi possível compreender quais os invertebrados que, devido à bioacumulação de metilmercúrio, apresentam maior risco para níveis tróficos superiores. A elevada variabilidade de metilmercúrio em certas famílias indica que, em estudos de contaminação, os investigadores devem ter cuidado quando agrupam por família pois certas espécies podem ter elevadas concentrações devido à sua ecologia e devem ser tratadas separadamente. Em quatro invertebrados, foi possível concluir que a sua concentração de metilmercúrio depende do habitat. Análises mostraram também que o pH está negativamente correlacionado com a concentração de metilmercúrio nos invertebrados e que esta aumenta com o nível trófico.

Esta tese destaca a importância de análises padronizadas e quais os dados a serem recolhidos em estudos ecotoxicológicos de modo a permitir que sejam produzidos artigos de revisão a larga escala e a incorporação em avaliações de risco internacionais. São destacadas também recomendações, como incluir as características físico-químicas dos ecossistemas em artigos relacionados com bioacumulação e biomagnificação de mercúrio.

Palavras-chave: Mercúrio, bioacumulação, biomagnificação, metilmercúrio, invertebrados

Abstract

Mercury is a highly toxic pollutant that can be found in remote areas due to the atmospheric global dispersion of elemental mercury. Methylmercury is the form of mercury with highest capacity to bioaccumulate and biomagnify, such that its concentration in lower trophic levels can have impacts on a variety of higher trophic organisms.

Data on methylmercury, total mercury concentration and stable isotopes of C and N from several types of freshwater invertebrates were compiled from published peer-reviewed literature. Additionally, the physico-chemical characteristics of the ecosystems provided in the papers were also compiled to assess their predictive relationships with mercury bioaccumulation and biomagnification.

The analysis provided insight into which invertebrates pose a higher risk to upper trophic levels due to their methylmercury bioaccumulation. The high variability of methylmercury in some families of invertebrates indicates that researchers should be aware if grouping by family for contamination studies because some species may be outliers due to detail of their specific ecology and should be handled separately. In four invertebrates, it was possible to conclude that their methylmercury content was related to their habitat. Analysis also showed that pH is negatively correlated with the concentration of methylmercury in invertebrates and that this increases with trophic level.

Additionally, this research highlights the importance of standardized analyses and data to be collected in ecotoxicological studies to increase the capacity for large scale reviews and incorporation in international risk assessments. Recommendations such as including the physico-chemical characteristics of the ecosystems in papers related to mercury bioaccumulation and biomagnification are highlighted.

Keywords: Mercury, bioaccumulation, biomagnification, methylmercury, invertebrates

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List of Abbreviations

MeHg(I)	Monomethylmercury
THg	Total mercury
%MeHg(I)	Percentage of total mercury in the form in the form monomethylmercury
DOM	Dissolved organic matter
TOC	Total organic carbon
M	Mean
Mdn	Median
SD	Standard deviation
IQR	Interquartile range
CV	Coefficient of variation
BCF	Bioconcentration factor

1. Introduction

1.1. Rationale

Mercury is a pollutant with global distribution and can have serious impacts on ecosystem health (Lehnherr, 2014). The World Health Organization defines it as one of the ten chemicals of major public concern (WHO, 2019) and research shows that exposure to this pollutant can have serious effects on wildlife (Eagles-Smith et al., 2016). These impacts include, among others, the reduction of nesting success in songbirds (Edmonds et al., 2010; Jackson et al., 2011; Perkins et al., 2019) and decrease in reproduction in common loons (*Gavia immer*; Schoch et al., 2014). The global dispersion of mercury is mainly due to atmospheric transport and allows for mercury accumulation in remote ecosystems such as areas of eastern Canada (O'Driscoll et al., 2005; Wyn et al., 2009), the Arctic (Braune et al., 2015; Lindberg et al., 2002; Ruus et al., 2015) and Antarctica (Bargagli et al., 2007).

Dietary consumption is the primary vector of mercury bioaccumulation and biomagnification in organisms due to the ability of organic mercury (predominantly methylmercury; MeHg(I)) to be retained on tissues through protein binding mechanisms (Lemes and Wang, 2009). Organisms that occupy low trophic levels, such as some invertebrates, are key prey organisms for many fish and birds and are therefore key entry points of mercury in both the aquatic and terrestrial food webs (Buckland-Nicks et al., 2014).

Mercury bioaccumulation and biomagnification depend on several variables that can be related to the environmental conditions of the ecosystem, such as pH and the concentration and composition of dissolved organic matter (Paranjape and Hall, 2017; Ullrich et al., 2001), but also the characteristics of the organisms such as their type of diet (Kahilainen et al., 2016) and life stage (Buckland-Nicks et al., 2014). A lot of focus has been put on higher trophic level organisms, such as fish (Lavoie et al., 2013), but the organisms that occupy the low end of food webs may be a key factor in mercury biomagnification in the ecosystems.

A systematic review of the published peer-reviewed literature related to mercury bioaccumulation in freshwater and terrestrial invertebrates may provide insight into what type of invertebrates pose a higher risk to upper trophic levels of the food web. It may also help to clarify what types of ecosystems are more susceptible to bioaccumulation at these lower trophic levels and the associated physical and chemical conditions.

1.2. Research Gaps and Objectives

Extensive research shows that mercury methylation is affected by several different environmental conditions such as pH, dissolved organic matter and oxygen availability (Paranjape and Hall, 2017; Ullrich et al., 2001). It is also known that MeHg(I) is a pollutant with the capacity to bioaccumulate and biomagnify through food webs and that the concentration in the organisms also depends on biotic factors, such as life stage and diet (Buckland-Nicks et al., 2014; Kidd et al., 2011). The present review aims to address a research gap related to mercury accumulation in lower trophic levels of the food web, more precisely, in freshwater and terrestrial invertebrates. To do this, this thesis focuses on a systematic literature review related to invertebrates in freshwater ecosystems and aims to obtain information on the most relevant conditions that affect biomagnification in these systems.

Based on these objectives, several questions were developed.

1. MeHg(I) biomagnification will lead to a higher MeHg(I) concentration and higher percentage of total mercury in the form of MeHg(I) in aquatic and terrestrial invertebrates that feed on higher trophic levels (organisms with higher $\delta^{15}N$);

2. The ecology of some organisms may result in increased MeHg(I) exposure, which will result in outliers in the MeHg(I) concentration than concentrations predicted by $\delta^{15}N$ alone;

3. Due to high levels of dissolved organic matter, low pH and low dissolved oxygen availability in wetlands, this type of ecosystem is a hot-spot for mercury methylation. As such, it is predicted that MeHg(I) concentrations in aquatic and terrestrial invertebrates in wetlands would be significantly higher ($P<0.05$) when compared to lakes;

4. Multiple regression analysis of the sites physico-chemical parameters will indicate key variables that explain the MeHg(I) concentration in the invertebrates.

1.3. Thesis Organization

This thesis is divided into six chapters. In the first is presented the thesis rationale, briefly presenting the topic in research and its relevance, the research gaps and objectives of the study. The second focuses on the literature review of research on mercury, especially on speciation in aquatic ecosystems and bioaccumulation and biomagnification in invertebrates. In the third chapter, the methods of analyses used in this research are described. In the fourth, the results of the research are showed, which are then discussed on the fifth chapter. The sixth chapter is the conclusion and has the final remarks of the research of this thesis.

2. Literature Review

2.1. Mercury Sources

Mercury is a pollutant that can be transported globally due to its high residence time in the atmosphere, which is the main transport pathway (Driscoll et al., 2013). Therefore, remote places can be affected by this pollutant due to emissions from distant locations.

2.1.1. Global Sources

Mercury can be emitted to the atmosphere by natural or anthropogenic sources and the sources can also be divided into primary and secondary, the former being the emissions that release mercury from its geological origin, while the latter come from re-emissions of previously deposited mercury (Driscoll et al., 2013; UN Environment, 2019a). Using global mercury models, is possible to trace the fate of the emissions and establish where they will be deposited (Chen et al., 2014), which has high relevance in terms of policy making (UN Environment, 2019a).

In the 2018 Global Mercury Assessment (UN Environment, 2019a), the emphasis was placed on the anthropogenic sources of mercury emissions. These include the majority of the emissions released globally and the sector with the bigger percentage is artisanal and small-scale gold mining, followed by the industry sectors and coal and other fuels combustion. It was estimated that natural sources, like volcanoes, are responsible for 10% of the emissions. There is still uncertainty regarding the magnitude of natural and secondary sources of mercury (Sundseth et al., 2017; UN Environment, 2019a).

2.2. Mercury in Aquatic Environments

Mercury is a persistent chemical that can be found in various chemical forms, the most common being: elemental (Hg(0)), divalent (Hg(II)) and methylmercury (MeHg(I)) (Driscoll et al., 2013). Mercury chemical forms have different residence times in the atmosphere which influences the distance to where they can be transported and afterwards deposited in the landscape. Elemental mercury is the chemical form with longer atmospheric residence time, that varies between 9 months to almost 2 years (Ariya et al., 2015), which means it can be transported globally (Lyman et al., 2020). In the atmosphere, once Hg(0) is oxidized to Hg(II), a more soluble form of mercury, it can be rapidly removed through wet or dry deposition (Liu et al., 2011).

When deposited in aquatic environments, mercury can undergo several different chemical and biological reactions. Under the influence of solar radiation, Hg(II) can be photochemically reduced to Hg(0), which is highly volatile (O'Driscoll et al., 2005). Reduction of Hg(II) can also occur due to microbial activity but photo-reduction is the dominant process of formation of Hg(0) (Zhu et al., 2018). In freshwater, the majority of Hg(II) is in the form of complexes with dissolved organic matter (DOM) (Vost et al., 2011), which deposit and accumulate in the sediments (Liu et al., 2011). In aquatic environments with low DOM, Hg(II)-DOM complexes enhance Hg(II) bioavailability due to the easier uptake of the complex by methylating bacteria (Klapstein and O'Driscoll, 2018; O'Driscoll et al., 2005). Methylation of Hg(II) produces MeHg(I) and it is mainly a biological process carried out by sulfate and iron-reducing bacteria that highly depend on the environmental conditions like pH, organic matter and oxygen availability (Paranjape and Hall, 2017). Research shows that the concentration of sulfate in water also stimulates methylation (Hoggarth et al., 2015) and low sulfite concentrations allow the formation of complexes able to pass through cells and increase mercury bioavailability (Benoit et al., 2001). To be able to link mercury chemistry in aquatic environments to mercury in food webs it is first essential to understand some concepts such as bioavailability, bioaccumulation and biomagnification.

2.3. Bioavailability, Bioaccumulation and Biomagnification of Methylmercury

The most concerning form of mercury in food webs is MeHg(I), due to its capacity to bioaccumulate and biomagnify (Driscoll et al., 2013). The bioavailability of this mercury form depends on the presence of ligands in aquatic environments, which influence the way and speed at which the complexes created are absorbed through membranes (Kidd et al., 2011). The ligands can be dissolved organic matter complexes and inorganic ions like sulfides, Cl^- and OH^-. The presence of these ligands in the water also affects bioconcentration, which is the process that allows a higher concentration of mercury in an organism than the concentration in the water due to dermal absorption (Kidd et al., 2011; Mackay et al., 2018).

At the base of the food web, in organisms such as phytoplankton, bioconcentration is the main mechanism of uptake of mercury and the cells of these organisms can have MeHg(I) concentrations over 10,000 times higher than the water (Lee and Fisher, 2016; Pickhardt and Fisher, 2007). Additionally, studies show that the bioconcentration of MeHg(I) from the water column to the pelagic food web, such as algae, is important for MeHg(I) accumulation at subsequent trophic levels of the food web (Wu et al., 2019).

As the trophic level increases, the main mechanism of mercury uptake becomes dietary consumption (Kidd et al., 2011). The process by which an organism has a higher pollutant concentration compared to its prey it is defined as biomagnification, only considering the dietary sources. MeHg(I) has the capability to biomagnify through food webs because it binds to amino acids, such as cysteine, and it is not excreted efficiently (Lemes and Wang, 2009).

Bioaccumulation includes the bioconcentration and biomagnification processes and its defined as the accumulation of a pollutant concentration in an organism relative to the surrounding environment, taking into consideration both water and dietary sources (Borgå et al., 2012; Kidd et al., 2011).

Through these processes, mercury reaches higher trophic-levels, where it can have diverse negative effects, like influencing bird migration (Seewagen, 2018), and ultimately can negatively affect human health (Ha et al., 2017; Sundseth et al., 2017).

Recognizing the serious threat that this metal represents to the well-being of humans and ecosystems, the United Nations joined and developed a global treaty, the Minamata Convention on Mercury (UN Environment, 2019b). The treaty was agreed to and adopted in 2013 and entered into force in August of 2017.

2.4. Factors that Influence Methylmercury Bioaccumulation and Biomagnification in Invertebrates

Methylmercury concentration in a food web is affected by abiotic and biotic conditions (Kidd et al., 2011; Lavoie et al., 2013). The former influence mercury methylation and availability to the organisms and the latter regard the characteristics of the organisms that make them more susceptible to the pollutant. In Figure 2.1, some of these factors are illustrated in a freshwater ecosystem.

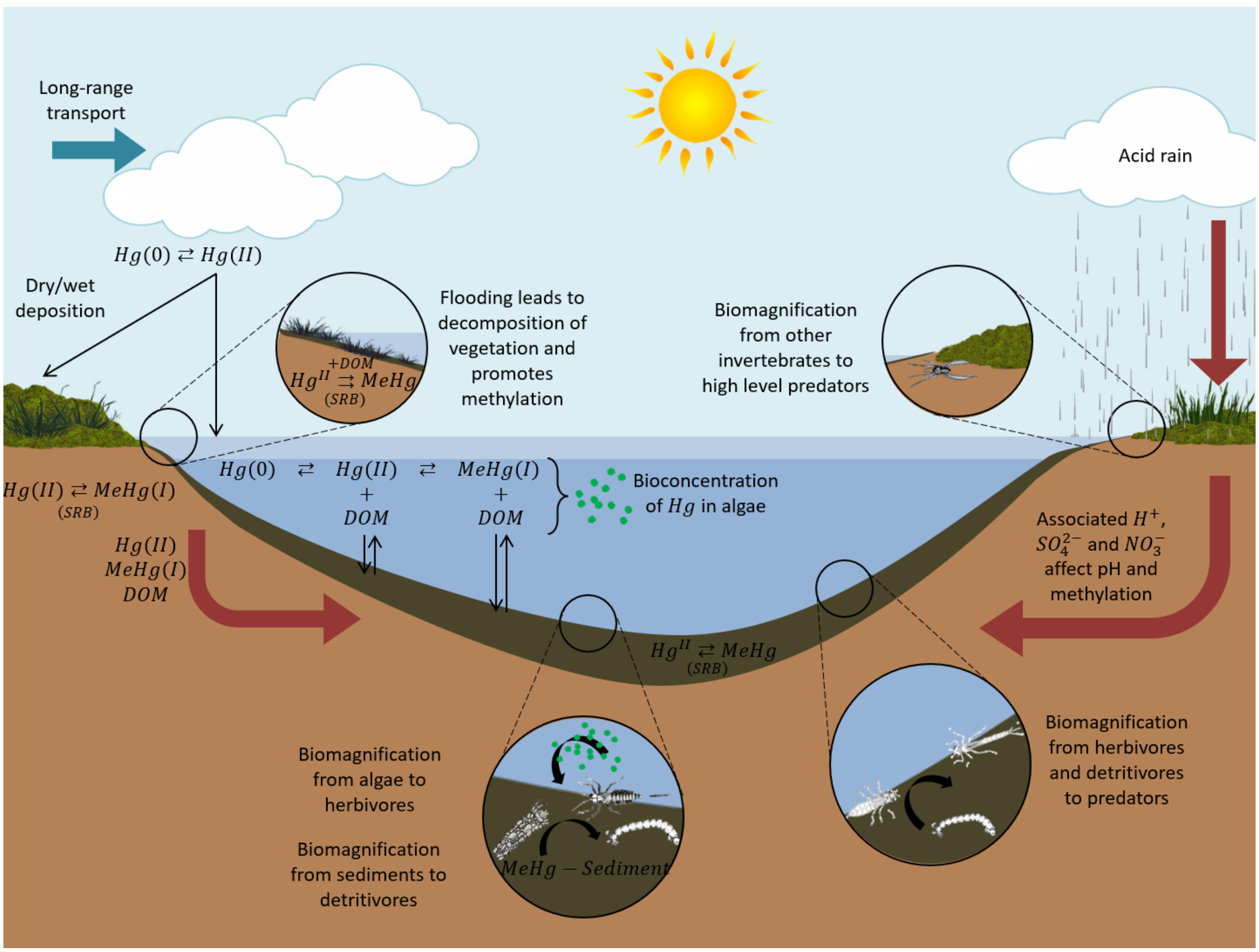

Figure 2.1: Conceptual diagram illustrating biomagnification in the invertebrates' food web from detritivores to high level predators, and some of the physico-chemical conditions that affect it such as pH and dissolved organic matter.

2.4.1. Abiotic Factors

Several abiotic factors affect mercury methylation and can have combined effects. In wetlands, the specific abiotic conditions of this type of environment make it a hot-spot for methylation (Hall et al., 2008). Low levels of oxygen, low pH and high levels of organic matter are characteristic of these environments, which are ideal conditions to enhance Hg(II) methylation by anaerobic microbes like sulfate-reducing (SRB) and iron-reducing bacteria (FeRB) (Benoit et al., 2003; Ma et al., 2019). These bacteria are the main contributors to methylation, but others like methanogens and syntrophic bacteria are also capable of producing MeHg(I) (Gilmour et al., 2013). In lakes, the concentration of dissolved organic carbon is also an important variable that affects mercury bioavailability and bioaccumulation in these systems (French et al., 2014). Some of the abiotic factors that are relevant to mercury methylation are the input of nutrients, dissolved organic matter, pH and flooding effects.

i. Effects of Nutrient Inputs

The input of nutrients can affect mercury speciation (Driscoll et al., 2012; MacMillan et al., 2015) and can come from many sources. Birds are important biovectors because they can transport and deposit previously bioaccumulated contaminants (Blais et al., 2007) and their guano has a variety of nutrients that will influence the ecosystem where they nest (Mallory et al., 2015). One example of a place that was significantly impacted by this is the Big Meadow Bog, a wetland located in Brier Island, Nova Scotia, that was ditched for agricultural purposes in the 1950s, which altered the ecosystem (Hill et al., 2019). The water level dropped and the new conditions attracted thousands of gulls (Spooner et al., 2017). Kickbush et al., (2018) showed that the colonization by herring gulls (*Larus argentatus*) and great black-backed gulls (*L. marinus*) was spatially correlated with high levels of phosphate (PO_4^{3-}) in shallow groundwater, which might have an indirect influence on the microbial populations controlling MeHg(I) production.

The over-enrichment of nutrients in an aquatic environment can also lead to eutrophication, which is defined as the rapid growth of certain organisms such as algae. Algae blooms lead to a decrease of mercury concentration per cell which results in lower bioaccumulation from these organisms to their consumers (Pickhardt et al., 2002). Additionally, the degradation of algae leads to an increase of dissolved organic matter (Zhou et al., 2018), which also affects mercury methylation and its bioavailability (Klapstein and O'Driscoll, 2018; Ullrich et al., 2001).

ii. Dissolved Organic Matter

Dissolved organic matter (DOM) is a mixture of several compounds like carboxylic acids and humic substances (Ravichandran, 2004) and the fact that it can have different compositions may be a reason why its effect on mercury speciation in aquatic ecosystems is hard to define (Jiang et al., 2018; Ma et al., 2019). Mercury preferably binds to halides with low electronegativity, like sulfur, so when it forms complexes with DOM is mostly found linked to its functional groups containing sulfur (Haitzer et al., 2002;

Ravichandran, 2004). The presence of this type of chemical elements in the environment can affect the possible associations and transport of mercury (Ravichandran, 2004).

Extensive research shows that organic matter stimulates bacterial activity (Creswell et al., 2017; Hall et al., 2005, 2004) but the effects on mercury speciation are not as straightforward because it also affects mercury's complexation with ligands such as DOM and associated photochemical processes (Klapstein and O'Driscoll, 2018; Ravichandran, 2004; Ullrich et al., 2001).

DOM can form complexes with MeHg(I) and Hg(II). In ecosystems with low DOM, the Hg(II)-DOM complexes may increase Hg(II) bioavailability by facilitating bacterial uptake (Klapstein and O'Driscoll, 2018; Mazrui et al., 2016). On the contrary, at high DOM concentrations, the Hg(II)-DOM complexes can potentially decrease Hg(II) bioavailability for methylating microbial communities (Chiasson-Gould et al., 2014; French et al., 2014). Complexes formed by MeHg(I) and DOM can increase MeHg(I) solubility and transport and also limit its uptake in biota (Paranjape and Hall, 2017; Ravichandran, 2004; Ullrich et al., 2001).

DOM has also the capacity to interact with the available wavelengths of radiation and influences photochemical processes, like photodemethylation, which is the demethylation of MeHg(I) due to solar radiation (Klapstein and O'Driscoll, 2018).

As mentioned above, DOM has several different functional groups and their chemical form depends on pH conditions (Ravichandran, 2004). For this reason and others explained afterwards, pH is also an important factor to have into consideration when assessing mercury bioavailability in an aquatic system.

iii. pH

The pH conditions affect mercury speciation in different ways. Most studies show an inverse relation between pH and mercury methylation (Allen et al., 2005; Chételat et al., 2011; Douglas et al., 2012). In acidic environments, DOM is less negatively charged so there is more competition between Hg(II) and MeHg(I) and other elements, such as H^+, which makes Hg(II) more bioavailable for methylation and MeHg(I) for biouptake (Amirbahman et al., 2002; Kelly et al., 2003; Ullrich et al., 2001). The fact that at low pH conditions there is a higher concentration of free mercury forms can also lead to a higher mercury transport in the watershed (Ullrich et al., 2001).

The pH of freshwater ecosystems can be related to the geology of the region but it can also be affected by acid precipitation (Clair et al., 2007). Acid rain is associated with the increase of H^+, which leads to acidification of the ecosystems, and also the increase of sulfate and nitrate (Clair et al., 2007; Driscoll et al., 2001). The addition of sulfate influences the activity of sulfate-reducing bacteria, that are mercury methylators, and can also increase MeHg(I) in the ecosystem (Jeremiason et al., 2006).

iv. Flooding

Flooding can also have an impact on the MeHg(I) concentrations of an aquatic environment, and wetlands and reservoirs are more susceptible to its effects (Evers et al., 2007). Research shows that flooding can increase the production of MeHg(I) within an aquatic ecosystem in the long term (Coleman Wasik et al., 2015; St. Louis et al., 2004) and lead to increased concentrations of this toxic pollutant in associated food webs. In reservoirs, the maximum concentration of MeHg(I) in water is reached in few years after the flooding (Hall et al., 2005; St. Louis et al., 2004) but in biota, such as fishes, peak values of MeHg(I) can take more than 10 years to peak (Bilodeau et al., 2015; Bodaly et al., 2007) which may be related to the slow release of MeHg(I) from the soil (Rolfhus et al., 2015). In the first years after a flood, the increase of production of MeHg(I) occurs due to the decomposition of vegetation, which increases the levels of organic carbon that lead to an increase of mercury methylation (Hall et al., 2005, 2004).

In sites where regular floods occur, such as intertidal sediments, a study by Cesário et al. (2017) shows that during the flooding period these areas act as a source of MeHg(I) to the water column and suggests that this occurs due to a rapid export of MeHg(I) from the sediments to the water column.

2.4.2. Biotic Factors

Mercury accumulation in biota depends not only on the concentration of the pollutant but also on several physico-chemical variables of the environment that affect its bioavailability (Lavoie et al., 2013). However, the bioaccumulation of mercury is also affected by the ecological characteristic of organisms', such as life stage and dietary habits (Kidd et al., 2011).

i. Life Stage

Several studies show that MeHg(I) concentration depends on the life stage of the organisms (Buckland-Nicks et al., 2014; Chételat et al., 2008; Mason et al., 2000). Chironomids are part of the lowest levels of several food chains and Chételat et al., (2008), concluded that its different development stages bioaccumulate MeHg(I) distinctly, being that adults were the ones with higher concentrations. Therefore, predators that feed on these different stages will also be affected by different MeHg(I) uptakes. Buckland-Nicks et al. (2014, p. 2) showed that mercury in dragonflies, that are "key biovectors of mercury to aquatic and terrestrial food webs", varies not only with life stage but also body region. Some predators, like beetles and spiders, selectively consume the regions of their prey that are richer in energy (Chen et al., 2004), so the mercury uptake from their diet could also expose them to different mercury concentrations. The transition between life stages can be related to a shedding process and this could be an important mechanism for mercury removal (Buckland-Nicks et al., 2014).

ii. Type of Diet

As suggested above, bioaccumulation is also correlated with the type of diet of the organisms. Generally, the higher in the food chain the greater the mercury concentration (Clayden et al., 2014; Cremona et al., 2008; Edmonds et al., 2012). Therefore, detritivores tend to be the feeding group with lower mercury levels followed by herbivores, omnivores and piscivores (Kidd et al., 2011). Diet shifts, which generally occur due to a change of season or due to a high diversity of prey, could also have implications for mercury concentrations and potentially reduce the efficiency of mercury transfer in the food web (Lavoie et al., 2013). Kahilainen et al. (2016) found lower levels of total mercury (THg) in the liver of Arctic charr (*Salvelinus alpinus* (L.)) in spring and early summer than in autumn, which corresponded to a shift from a diet of benthic macroinvertebrates towards a zooplankton diet. These results are consistent with the observations by Chételat et al. (2011) in 52 mid-latitude lakes in North America, that suggest that pelagic zooplankton constitutes a larger source of MeHg(I) than benthic invertebrates. Dietary shifts and concomitant changes in mercury concentrations have also been found in a variety of bird species (Braune et al., 2014; Fife et al., 2015).

iii. Ecology

Although the tendency is for mercury concentration to increase at higher trophic levels (Clayden et al., 2014; Lavoie et al., 2013), there are exceptions. The ecology of the organisms can also influence its MeHg(I) bioaccumulation and in some cases be more important than the differences in trophic level. An example is polychaete worms, where studies show that, although considered a primary consumer, they present high levels of MeHg(I) (Coelho et al., 2008; Sizmur et al., 2013). These organisms live in intertidal sediments and are ecosystem engineers, meaning that they create their own habitat. They create oxygenated burrows walls in anoxic sediments that accumulate dissolved organic matter, which leads to higher MeHg(I) concentrations. Sizmur et al. (2013) also showed that the worms decreased sulfide concentrations in the sediments, which can increase mercury bioavailability to sulfate-reducing bacteria (Benoit et al., 2001). Therefore, the concentrations of MeHg(I) in polychaete worms did not match with stable isotope predictions of bioaccumulation of mercury.

2.5. Stable Isotopes and Assessment of Methylmercury Biomagnification

Research has been done in MeHg(I) biomagnification through food webs in freshwater ecosystems (Clayden et al., 2017; Lescord et al., 2015; Zhang et al., 2012). As an example, Bates and Hall (2012) showed that in grassland wetlands MeHg(I) concentration increased from 14.6±8.6 ng/g dw in scrapers, to 84.2±28.7 ng/g dw in omnivores and 80.9 ± 24.6 ng/g dw and 119.6±28.7 ng/g dw in predators.

To be able to link an organisms' diet and trophic position with its mercury concentration, many authors use stable isotopes (e.g., Clayden et al., 2017; Kidd et al., 2012; Wyn et al., 2009). Isotopes are different forms of the same chemical element; they have the same atomic number, which means that they have the same number of protons but differ in the number of neutrons. When an isotope does not decay over a period of geological time and persists in nature in the same form after they are formed, it is defined as a stable isotope (Fry, 2006). Some isotopes contain more neutrons so are denominated as heavy, in contrast to other isotopes with fewer neutrons that are denominated as light. For example, ^{13}C contains more neutrons than ^{12}C so the former is a heavy stable isotope and the latter a light isotope. The most common notation for isotopes is the δ-notation, which represents the difference of the ratio between the heavy and light isotopes (R) in a sample and the international standard value (Fry, 2006). The results are expressed as parts per thousand (‰).

$$\boldsymbol{\delta = \left(\frac{R_{sample} - R_{standard}}{R_{standard}}\right) \times 1000 = \left(\frac{R_{sample}}{R_{standard}} - 1\right) \times 1000} \qquad \textbf{Equation 1}$$

The most common isotopes to understand food web structures are carbon and nitrogen isotopes, $\delta^{13}C$ and $\delta^{15}N$ respectively (Lavoie et al., 2013). Organisms tend to retain ^{15}N and excrete ^{14}N, so as the trophic position increases $\delta^{15}N$ values also tend to increase. The mean difference between $\delta^{15}N$ in a consumer and its diet is 3.4‰ (Post, 2002). Due to its characteristics, MeHg(I) tends to biomagnify through the food web, so its quantification can be estimated by a linear relationship between MeHg(I) and $\delta^{15}N$ values in organisms (Lavoie et al., 2013). This relation can be calculated using the equation:

$$\boldsymbol{log_{10}[MeHg] = \delta^{15}N \times b + a} \qquad \textbf{Equation 2}$$

In Equation 2, b is the slope and it is called the Trophic Magnification Slope (TMS) (Lavoie et al., 2013). The slope can vary due to several factors like geographic location and physico-chemical parameters.

The source of dietary carbon and its evolution through the food web can potentially be assessed by analysis of $\delta^{13}C$ (Fry, 2006). The difference of the heavy stable isotope of carbon, $\delta^{13}C$, between two trophic levels is substantially lower than $\delta^{15}N$ and has a mean value of 0.4‰ (Post, 2002).

In order to complement this information, some authors also use a stable isotope of sulfur ($\delta^{34}S$) to study the food web structure. As with $\delta^{13}C$, the difference of $\delta^{34}S$ between two trophic levels is very low (McCutchan et al., 2003). Studies suggest that $\delta^{34}S$ could be helpful to determine if members of the food chains inhabit the water column or the sediment (Croisetière et al., 2009). Also, habitats with high sulfate, which contain high $\delta^{34}S$, can lead to an increase of activity of sulfate-reducing bacteria, one of the major groups of methylating bacteria (Jeremiason et al., 2006). The concentration of total mercury in high trophic level organisms, such as birds, has shown to be well predicted by the content of $\delta^{34}S$ at the base of the food web (Elliott and Elliott, 2016).

2.6. Food Web Structure in Freshwater Ecosystems

Freshwater ecosystems are highly biodiverse, which reflects in the quantity of terrestrial and aquatic invertebrate species that can be found there. Some of the most common are midges, dragonflies, caddisflies, mayflies, damselflies, beetles, true bugs and spiders (Cooper et al., 2009; Edmonds et al., 2012; Sinclair et al., 2012).

Midges belong to the family Chironomidae from the order Diptera. These organisms have four life stages (egg, larval, pupal and adult) and live in the water except as adults (Thorp and Rogers, 2011). Larvae from this family include species of different functional feeding groups such as collector-filterers, scrappers, predators and mixed feeders, which means that they are not restricted to one single feeding method (Pinder, 1986). Collector-filterers feed on living algae cells and decomposing organic matter, while scrapers feed on attached algae and predators on living preys (Cummins, 1973). Collector-filterers are part of the functional feeding group designated collectors, that include all organisms that consume detrital particles (Cummins, 1973). As adults, most species of midges do not feed, or consume nectar or other liquids (Thorp and Rogers, 2011).

Dragonflies and damselflies belong to the suborder Anisoptera and Zygoptera, respectively, from the order Odonata. Their life is divided into three stages: egg, larva (nymph in Odonata) and adult (Thorp and Rogers, 2011). The egg develops on water and in the final larval stage it emerges. Larvae reach a large size and are predators, as adults, which makes them high-level predators in the invertebrate community (Hilsenhoff, 2001). Insects are the most common prey for these organisms (Hilsenhoff, 2001). Some of their predators are other insects from the order Odonata and various vertebrates and invertebrates like predaceous bugs and beetles (Thorp and Rogers, 2011).

Mayflies are insects of the order Ephemeroptera. Their life is divided into three stages: egg, nymph and adult (Thorp and Rogers, 2011). The nymph is aquatic until it reaches adulthood, upon which it crawls out of the water (Thorp and Rogers, 2011). Almost all nymphs are scrapers or collectors and the adults do not eat (Cummins, 1973; Thorp and Rogers, 2011). In North America, it is possible to find several families of mayflies such as Leptophlebiidae, Ephemerellidae and Heptageniidae (Edmonds et al., 2012; Naimo et al., 2000).

Caddisflies belong to the order Trichoptera. These insects have four stages in their development that are egg, larva, pupa and adult (Thorp and Rogers, 2011). Generally, larvae and pupae are aquatic and adults are terrestrial (Hilsenhoff, 2001). Some of the families of caddisflies that can be found in North America are Limnephilidae, Odontoceridae and Phryganeidae (Edmonds et al., 2012). The larvae of these families are mostly herbivores or detritivores but there are some cases of omnivores and predators (Hilsenhoff, 2001). Caddisflies are prey to several vertebrates and invertebrates like odonates and other trichopterans (Thorp and Rogers, 2011).

Predaceous diving beetles belong to the order Coleoptera. In almost all species, larvae and adults are aquatic and most are predators in both life stages (Thorp and Rogers, 2011). Other invertebrates, like dragonflies and damselflies, are their most common prey (Thorp and Rogers, 2011). In North America, some of the beetles' families that can be found are Dytiscidae and Hydrophilidae (Edmonds et al., 2012; Sinclair et al., 2012).

The insects from the order Hemiptera are commonly called true bugs. In freshwater ecosystems of North America, some of the insects that can be found are backswimmers and water boatmen (Edmonds et al., 2012; Sinclair et al., 2012). Their life develops in three stages that are egg, nymph and adult and all of them are aquatic (Thorp and Rogers, 2011). Backswimmers belong to the family Notonectidae and, generally, adults and nymphs are predators that can feed on other invertebrates or even small vertebrates (Hilsenhoff, 2001). Water boatmen belong to the family Corixidae and resemble backswimmers (Hilsenhoff, 2001). Both nymphs and adults are generally herbivorous, feeding on algae, but can also consume detritus and extremely small animals (Hilsenhoff, 2001; Thorp and Rogers, 2011).

Spiders are arthropods that belong to the order Araneae of the class Arachnida. In wetlands and especially in peatlands, spiders can be abundant and very diverse (Scott et al., 2006). Some of the families of the order Araneae that exist in North America are Agelenidae, Araneidae and Gnaphosidae (Edmonds et al., 2012). These animals are generalists predators and can be preyed by birds (Batzer and Wu, 2020).

3. Methods

3.1. Data Acquisition

To identify published literature related to mercury bioaccumulation in freshwater and terrestrial invertebrates, Google Scholar and Web of Science™ were used, searching with specific keywords such as "mercury", "bioaccumulation", "biomagnification, "invertebrate" and "freshwater". The timespan was not specified. The selection criteria included only studies that provided the values of MeHg(I) or THg in freshwater and terrestrial invertebrates. Some papers did not display the raw values of THg and MeHg(I) in the tissues of the invertebrates so they could not be used. Also, to prevent redundancy some studies were excluded due to the use of MeHg(I) or THg in the invertebrates from previous studies, that were already selected.

Ultimately, it was possible to obtain data from 25 papers that met the selection criteria, that studied freshwater ecosystems such as lakes, rivers, streams, reservoirs and wetlands (Allen et al., 2005; Bates and Hall, 2012; Buckland-Nicks et al., 2014; Chételat et al., 2013; Chumchal et al., 2011; Clarke, 2018; Clayden et al., 2013; Cremona et al., 2008; Edmonds et al., 2012; Finley et al., 2016; Gorski et al., 2003; Haines et al., 2003; Hall et al., 1998; Kidd et al., 2012; Lescord et al., 2015; Razavi et al., 2013; Reinhart et al., 2018; Sinclair et al., 2012; Tavshunsky et al., 2017; A. Tremblay et al., 1996; Alain Tremblay et al., 1996; Tweedy et al., 2013; van der Velden et al., 2013; Wyn et al., 2009; Zhang et al., 2012). The term "reservoir" used in this review refers to impoundments built for energy production or for water supply. Lakes are still water bodies and wetlands are considered transitional between terrestrial and aquatic ecosystems and can be covered in water or saturated permanently or only seasonally (Lehner and Döll, 2004).

Papers that studied locations near sites impacted by anthropogenic activities (such as reservoirs and chemical waste dump sites) or by natural phenomenon (such as forest fires and flooding) were kept in the analysis. It was also included two articles that study controlled environments, one in an experimental pond (Tweedy et al., 2013) and one in experimental wetlands (Sinclair et al., 2012), because it was considered that the conditions created were similar to a natural environment. Studies that approached the same location were also kept. Some of the studies presented several temporal mean values for the groups of invertebrates, for example, for one specific month of sampling and for all the analysis and, in these cases, the data chosen was always the one referred to the smallest timespan.

From the papers that reported THg or MeHg(I) in invertebrates, it was also extracted the percentage of THg in the form of MeHg(I) (designated as %MeHg(I)) of the invertebrates, information regarding the water characteristics such as pH, total organic carbon (TOC), dissolved organic carbon (DOC), total nitrogen, total phosphorus and the aqueous concentration of MeHg(I) and THg. If available, the concentration of MeHg(I) and THg in sediments was also recorded. In some papers that studied different sites, the water characteristics were presented as the mean of the several sites. In these cases, it was only extracted the mean value if the standard deviation was low.

When available, information on the stable isotopes $\delta^{15}N$ and $\delta^{13}C$ was also extracted in order to link the mercury concentration in the invertebrates to its trophic position.

3.2. Data Treatment and Analysis

After the data collection, it was necessary to select the variables that could be used for the analysis taking into consideration the amount of data that was possible to collect. The selected variables were the mean values of MeHg(I) and %MeHg(I) in the homogenized dry tissues of invertebrates of each article used. The selected physico-chemical characteristics of the ecosystems were pH and TOC. The stable isotope $\delta^{15}N$ was also used for the analysis. In Table 3.1 is possible to observe all the papers collected and used for the analysis and the parameters that each one provided regarding the characteristics of the environment and the stable isotopes.

For the analysis, it was necessary to make some assumptions. For example, some papers only presented the data on graph bars so in these cases WebPlotDigitizer (Rohatgi, 2020) was used to extract an approximate value of the data. This software is free and it was developed to extract data from a variety of graphs. Another assumption made was the value of %MeHg(I) when MeHg(I) and THg were available on the paper but not the %MeHg(I) (Cremona et al., 2008). In this case, the value was estimated by dividing the concentration of MeHg(I) per THg and multiplying by 100. In one of the studies used (Zhang et al., 2012), the concentrations of THg were provided in wet weight but the water content was provided as 80%, so the value was multiplied by five to obtain an estimation of the concentration in dry weight. Also, some articles adjusted $\delta^{15}N$ to a common baseline of the food web, so to use these values it was assumed that the baseline was the same. Finley et al., (2016) provided the raw data per sample so it was calculated the mean value per type of invertebrate in each site.

Statistical analyses conducted on the data collected from the literature were performed in the software *IBM® SPSS® Statistics*, version 26. Three major analyses were performed in this study. The first one had as the objective to provide insight regarding the general patterns of MeHg(I) concentration in invertebrates, the second one was to compare the MeHg(I) concentration in invertebrates in two types of ecosystems and the final was to assess the combined influence of different variables in MeHg(I) bioaccumulation in invertebrates.

Table 3.1: Table with all the papers collected for the analysis and the physico-chemical parameters of the studied environment and stable isotopes of the invertebrates, that each one provided. The parameters are the pH value, MeHg(I) concentration in water samples (MeHg(I) in water), stable isotope $\delta^{15}N$, THg concentration in water samples (THg in water), total phosphorus concentration (Total P), MeHg(I) concentration in sediment samples (MeHg(I) in sed.), dissolved organic carbon (DOC), concentration of sulphate ($[SO_4^{2-}]$), stable isotope $\delta^{13}C$, concentration of calcium ($[Ca^{2+}]$), total nitrogen concentration (Total N), THg concentration in sediment samples (THg in sed.), total organic carbon (TOC), concentration of chlorine ($[Cl^{+}]$), dissolved oxygen (DO_2), concentration of nitrate/nitrite ($[NO^{3-}/NO^{2-}]$).

Papers	pH	MeHg(I) in water	$\delta^{15}N$	THg in water	Total P	MeHg(I) in sed.	DOC	$[SO_4^{2-}]$	$\delta^{13}C$	$[Ca^{2+}]$	Total N	THg in sed.	TOC	$[Cl^{+}]$	DO_2	$[NO^{3-}/NO^{2-}]$
Lescord et al., 2015	■	■		■	■		■	■		■	■			■		■
Chételat et al., 2013	■	■	■	■	■	■	■		■		■					
Clayden et al., 2013	■	■	■	■	■			■		■	■		■			
Finley et al., 2016	■		■		■			■	■	■			■	■		
Kidd et al., 2012			■		■		■	■	■	■	■			■		
Sinclair et al., 2012	■	■		■		■		■				■			■	
Clarke, 2018	■	■		■		■	■					■				
Bates & Hall, 2012	■	■	■	■												
Razavi et al., 2013		■		■		■						■				
Wyn et al., 2009	■		■		■								■			
Buckland-Nicks et al., 2014	■	■					■									
Edmonds et al., 2012	■	■		■												
Gorski et al., 2003	■	■		■												
Reinhart et al., 2018		■	■			■										
Alain Tremblay et al., 1996	■					■						■				
Allen et al., 2005	■		■													
van der Velden et al., 2013			■						■							
Chumcal et al., 2011			■													
Zhang et al., 2012									■							
Cremona et al., 2008																
Haines et al., 2003																
Hall et al., 1998																
Tavshunsky et al., 2017																
A. Tremblay et al., 1996																
Tweedy et al., 2013																

3.2.1. Patterns of MeHg(I) Concentration in Invertebrates

The first analysis done was to check to general pattern of MeHg(I) bioaccumulation in the dry tissue of freshwater and terrestrial invertebrates. To do this, the mean values obtained for each type of invertebrates were used to create a boxplot and make a graph with all the invertebrates. An identical data analysis was made using the mean values of %MeHg(I) in each type of invertebrate.

3.2.2. Comparison Between Wetlands and Lakes

During the data acquisition, it was possible to extract information on several types of ecosystems. To make a comparison between them, a smaller data set of MeHg(I) concentrations was used by selecting only caddisflies, mayflies, dragonflies and damselflies (because these were well-represented across studies). It was possible to obtain information for these four types of invertebrates in wetlands and in lakes. The mean values for each type of invertebrate were plotted in a boxplot and divided by type of ecosystem.

Afterwards, Mann-Whitney *U* tests were conducted to determine if there was statistical significance that the mean value of MeHg(I) concentration in the one type of invertebrate was significantly different in the two different ecosystems.

3.2.3. Combined Influence of Different Variables in MeHg(I) Bioaccumulation

Multiple regression analyses were conducted to examine the combined influence of different physico-chemical variables on MeHg(I) bioaccumulation in freshwater and terrestrial invertebrates. To do this, the MeHg(I) concentration in the invertebrates was log-transformed and regressed against selected variables regarding the water characteristics of the sites and the $\delta^{15}N$ value. The data across species approximated normality and the log-transformed concentration of MeHg(I) provided a better distribution for the analyses. As a verification of the modelling approach, model selection was made using the Akaike Information Criterion (AIC), which allows choosing the best model. This last part was conducted in collaboration with one of the supervisors of this thesis.

4. Results

4.1. Results from the Literature Search

As previously mentioned, data was extracted from 25 scientific, peer-reviewed papers. From those, 23 contained information on MeHg(I) in the tissue of invertebrates (more than 600 individual values), 13 contained data on the %MeHg(I) (more than 270 individual values). Almost all the research gathered was from North America (United States and Canada) but there was also one study from Sweden (Alain Tremblay et al., 1996).

4.2. Patterns of MeHg(I) Concentration in Invertebrates

After the data collection and selection, it was possible to plot the MeHg(I) concentration and the %MeHg(I) in the dry tissue of several invertebrates. The MeHg(I) concentration in each type of invertebrates is represented in Figure 4.1, that shows the median value (Mdn) marked by a black bar and ordered from lowest to the highest mean value (M). The *SPSS* software also differentiates the outliers (marked with circles) and extreme outliers (marked with asterisks). The former includes the values outside the range of the third/first quartile plus/minus 1.5 times the interquartile range (IQR) and the further the ones outside the range of the third/first quartile plus/minus 3 times the IQR. In Figure 4.1, the outliers are labeled with the value of MeHg(I). The Canadian MeHg(I) tissue residue guideline for the protection of wildlife consumers of aquatic biota is also plotted, which is 33 μg/kg ww (that is the same as 33 ng/g ww) (CCME, 2000). Because the MeHg(I) concentrations represented in the graph are in dry weight it was necessary to convert the guideline value to dry weight too. To do this, it was considered an interval of 80 to 90% of water content in the invertebrates, which leads to an interval between 165 and 330 ng/g dw.

The type invertebrate with the highest mean value of MeHg(I) concentration is the grass shrimp (M=435 ng/g dw, N=1) followed by backswimmers (M=382.9 ng/g dw, Mdn=242.0 ng/g dw, N=15), water boatmen (M=339.5 ng/g dw, Mdn=210.0 ng/g dw, N=16) and water scorpions (M=306.4 ng/g dw, Mdn=350.0, N=6). It is important to take into consideration that the number of individual data points of each type of invertebrate (referred as "N") varies significantly, from only one to 102 cases for dragonflies. In Table A1, in the Annexes, it is summarized the number of individual values of MeHg(I) and %MeHg(I) of each type of invertebrate that was extracted from the literature. These values represent the number of mean values of each type of invertebrate that was possible to extract from the literature and not the number of samples that were used to calculate the mean values in each article.

To measure the dispersion between the mean values extracted from the literature for each type of invertebrate, it was calculated the coefficient of variation (CV) that is defined as the quotient between the standard deviation and the mean multiplied by 100, so it is expressed as a percentage. Among all invertebrates reported, caddisflies showed the greatest variation in mean values of MeHg(I) (CV=133.7%, N=76) followed by water boatmen (CV=114.6%, N=16) and beetles (CV=112.8%, N=49).

The %MeHg(I) in the invertebrates is displayed in Figure 4.2 and a total of 272 individual data points were used for the graph. The invertebrates are sorted from lowest to the highest mean value of %MeHg(I) and the outliers are labeled with the value of %MeHg(I). Backswimmers had the highest mean value of %MeHg(I) (M=97.2%, Mdn=96.0%, N=5) followed by water treaders (M=Mdn=94.8%, N=2) and water scorpions (M=93.1%, N=1). The type of invertebrate with higher variability regarding the mean values of %MeHg(I) were mussels (CV=92.5%, N=3), midges (CV=80.4%, N=21) and mayflies (CV=57.8%, N=31).

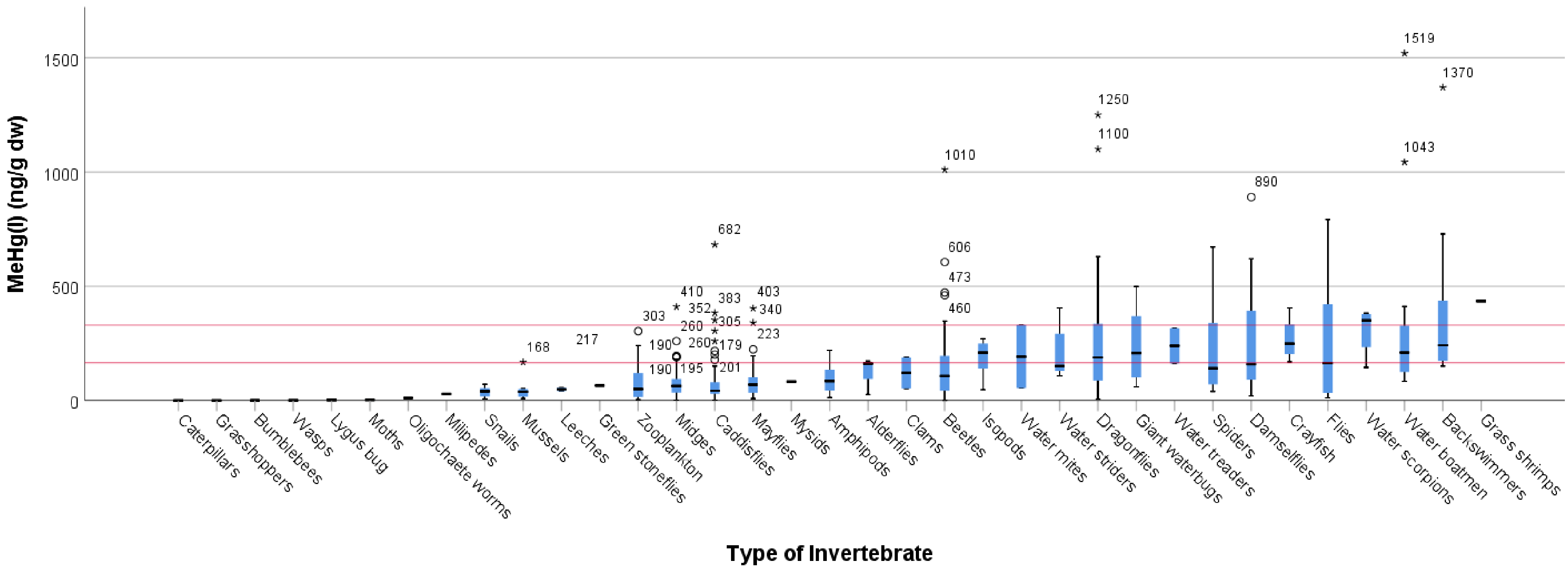

Figure 4.1: Boxplots of MeHg(I) concentration in the dry tissue of invertebrates separated by common name. In each boxplot the median is represented with a black bar, the outliers marked with circles and extreme outliers marked with asterisks. The boxplots are ordered from lowest to highest mean value and the outliers are labeled with the MeHg(I) concentration. The red lines represent the Canadian methylmercury tissue residue guideline for the protection of wildlife consumers of aquatic biotas, which is 33 µg/kg in wet weight. The MeHg(I) concentration in the invertebrates is in dry weight so the guideline value was transformed by assuming an 80% to 90% water content, which corresponds to 165 ng/g dw and 330 ng/g dw, respectively.

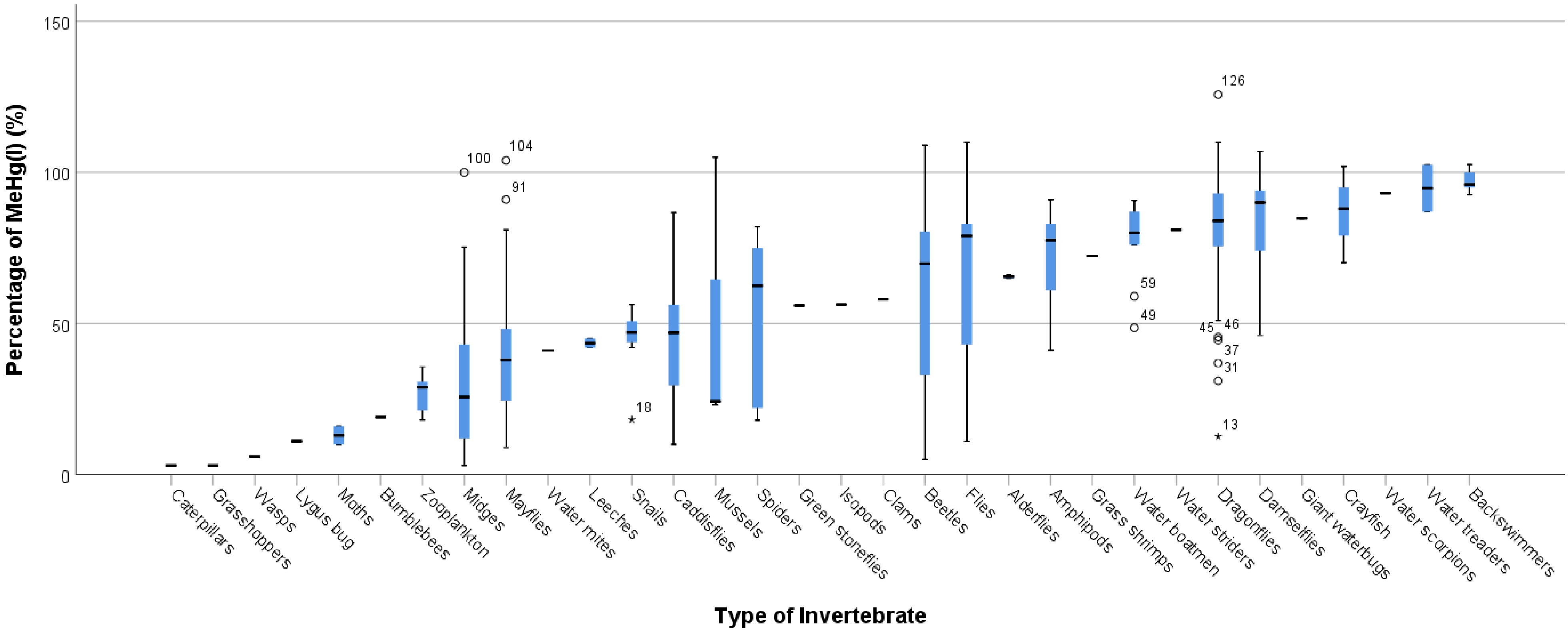

Figure 4.2: Boxplots of percentage of total mercury in the form MeHg(I) in the dry tissues of the invertebrates. In each boxplot, the median is represented with a black bar, the outliers marked with circles and extreme outliers marked with asterisks. The invertebrates are separated by common name and ordered from lowest to highest mean value and the outliers are labeled with the %MeHg(I).

4.3. Comparison Between Wetlands and Lakes

To compare MeHg(I) bioaccumulation and biomagnification in different ecosystems, a smaller data set was selected containing information on only caddisflies, mayflies, dragonflies and damselflies. From the literature collected, it was obtained data on these four types of invertebrates in only two types of ecosystems: lakes and wetlands. In total, fourteen studies presented this data in lakes and only three in wetlands, but one collected data from seven different wetlands (Sinclair et al., 2012) and the other from nineteen different wetlands (Edmonds et al., 2012). In Figure 4.3, it is possible to see the results from the analysis, in which the types of invertebrates are sorted from lowest to highest MeHg(I) concentration in each ecosystem.

In lakes, caddisflies were the group of invertebrates with the lowest mean value (M=54.3 ng/g dw) and median (Mdn=40.0 ng/g dw) but were the group that showed the highest variation between the mean values obtained from the literature (CV=94.3%). Dragonflies were the group with the highest mean (M=177.5 ng/g dw) and median (Mdn=122.0 ng/g dw) and the lowest variation (CV=75.7%).

In wetlands, mayflies were the group with the lowest mean value, 137.2 ng/g dw (and a median value of 94.1 ng/g dw). Caddisflies showed the lowest median value, of 47.7 ng/g dw, and the highest variation between values (CV=129.3%). Damselflies were the group with the highest mean (M=385.3 ng/g dw) and median value (Mdn=340.0 ng/g dw) and the lowest variation between values (CV=70.8%).

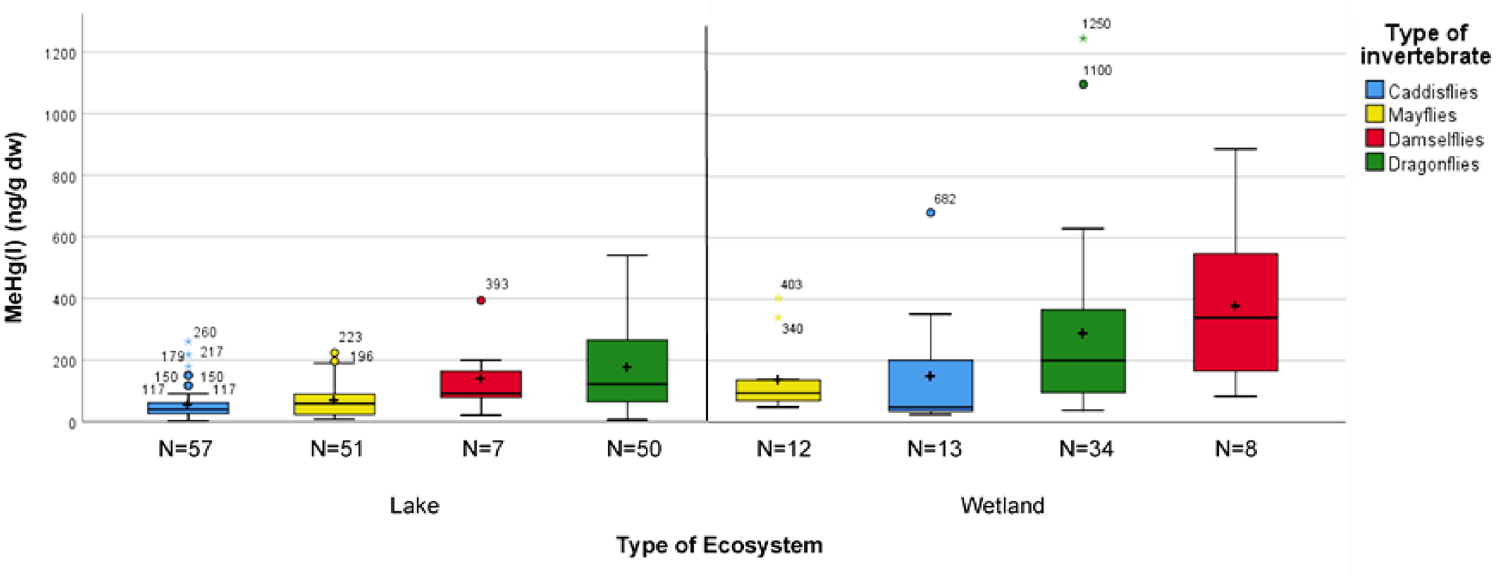

Figure 4.3: Boxplots of mean values of MeHg(I) extracted from the literature of caddisflies, mayflies, dragonflies and damselflies separated by type of ecosystem (lakes and wetlands). In each boxplot the median is represented with a black bar, the outliers marked with circles and extreme outliers marked with asterisks. The mean value is marked with a plus sign in each boxplot. The invertebrates are sorted from lowest to highest mean value in each type of ecosystem and the outliers are labeled with the MeHg(I) concentration. The number of individual data points used for each boxplot (N) is also displayed.

The descriptive analyses of the four groups of invertebrates in the two types of ecosystems are summarized in Table 4.1. In this table, the mean and standard deviation are presented and also the coefficient of variation and the median. The range between the first and third quartile, which represents the range where 50% of the values are included, the IQR and the number of individual data points used for each boxplot are also shown.

Table 4.1: Descriptive analysis of MeHg(I) in caddisflies, mayflies, dragonflies and damselflies in lakes and wetlands. In the table are presented the mean (M) and standard deviation (SD), the coefficient of variation (CV), median (Mdn), the first (Q1) and third (Q3) quartile and the interquartile range (IQR) and also the number of values used for the analysis (N). The units of M, SD, Mdn, Q1, Q3, IQR are ng/g of dry weight and CV is %.

	Lakes					Wetlands				
Invertebrate	**M [SD]**	**CV**	**Mdn**	**Q1-Q3, IQR**	**N**	**M [SD]**	**CV**	**Mdn**	**Q1-Q3, IQR**	**N**
Caddisflies	54.3 [51.2]	94.3	40.0	23.8-61.7 37.9	57	150.0 [194.0]	129.3	47.7	33.9-253.0 73.3	13
Mayflies	67.3 [54.2]	80.5	58.0	21.6-90.0 68.4	51	137.2 [114.0]	83.1	94.1	63.5-136.8 219.1	12
Damselflies	140.8 [124.2]	88.2	91.0	70.0-200 130	7	385.3 [272.8]	70.8	340.0	154.0-584.3 430.3	8
Dragonflies	177.5 [134.3]	75.7	122.0	63.2-273.8 210.6	50	290.1 [272.3]	93.9	200.7	94.7-370.0 275.7	34

After analyzing the shape of the boxplots in Figure 4.3 and concluding that in the majority of the data sets the data was skewed, it was decided to do a non-parametric test in order to determine if there was a significant difference between the mean concentration of MeHg(I) in the invertebrates in lakes and wetlands. It was run a Mann-Whitney *U* test for each type of invertebrate and for this was chosen a significance level of α=0.05.

For caddisflies, the higher mean rank was obtained in wetlands, with a value of 45.4, comparing to 33.3 in lakes. The output of the test was U=242.0 and p=0.05. Because p is equal to the significance level chosen, α=0.05, it was possible to conclude that the mean value of MeHg(I) in caddisflies in wetlands is significantly higher than caddisflies in lakes.

For mayflies, the higher mean rank was obtained in wetlands, with a value of 44.7, comparing to 29.0 in lakes. The output of the test was U=154.0 and p=0.008. Since p is lower than the significance level, α=0.05, it is possible to conclude that the mean value of MeHg(I) in mayflies in wetlands is significantly higher than mayflies in lakes.

For dragonflies, the higher mean rank was obtained in wetlands, with a value of 49.5, comparing to 37.8 in lakes. The output of the test was U=613.0 and p=0.031. Since p is lower than the significance level,

$\alpha=0.05$, it is possible to conclude that the mean value of MeHg(I) in dragonflies in wetlands is significantly higher than dragonflies in lakes.

For damselflies, the higher mean rank was obtained in wetlands, with a value of 10.3, comparing to 5.4 in lakes. The output of the test was $U=10.0$ and $p=0.037$. Since p is lower than the significance level, $\alpha=0.05$, it is possible to conclude that the mean value of MeHg(I) in damselflies in wetlands is significantly higher than damselflies in lakes.

Parametric tests were also conducted, specifically, independent samples t-test, and only for dragonflies and damselflies it was showed a significant difference between the MeHg(I) mean value in wetlands and lakes.

4.4. Combined Influence of Different Variables in MeHg(I) Bioaccumulation

Multiple regression analyses were conducted to test the influence of different physico-chemical variables on MeHg(I) bioaccumulation in invertebrates. From the available variables, which are shown in Table 3.1, the only variable that was common in numerous studies was pH. It was also included in the analysis the $\delta^{15}N$ value of the invertebrates to analyze the MeHg(I) concentration with the position of the invertebrates in the food web.

To do this first analysis, data on all invertebrates was used. The MeHg(I) concentration in the invertebrates was log-transformed and regressed against pH of the study sites and $\delta^{15}N$ value of the invertebrates. The multiple regression method selected was the stepwise method, which removes the weakest correlated variable from the model. The descriptive analysis of the variables is presented in Table 4.2.

Table 4.2: Descriptive analysis of variables used in the first multiple regression analysis: logarithm of MeHg(I) in invertebrates, stable isotope $\delta^{15}N$ and pH. For this analysis, it was used the data for all the invertebrates.

Variables	Mean	Std. Deviation	N
Log(MeHg(I)) in invertebrates	1.98	0.35	172
$\delta^{15}N$ (‰)	6.05	1.02	172
pH	3.14	2.26	172

The data was selected on *SPSS* and the program created two different models. The first one has as predictor only pH and the second one had pH and the $\delta^{15}N$ value. The summary of the models created is presented in Table 4.3.

Table 4.3: Results of the first multiple regression models explaining log(MeHg(I)) concentration in all invertebrates.

Model	Predictors	R	R^2	Adjusted R^2	Std. Error of the Estimate	ANOVA		
						F	p	df (Regression, Residual)
1	pH	0.459	0.211	0.206	0.316	45.487	<0.001	1, 170
2	pH, $\delta^{15}N$	0.511	0.261	0.252	0.306	29.841	<0.001	2, 169

On the first model, pH showed a negative partial standardized regression coefficient (b'=-0.459, $p<0.001$). On the second model, pH also showed a negative partial standardized regression coefficient (b'=-0.541, $p<0.001$) and $\delta^{15}N$ showed a positive partial standardized regression coefficient (b'=0.238, $p=0.001$).

The procedure above suggests that the inclusion of both pH and $\delta^{15}N$ produces a better model, as the R^2 was higher in model 2 (as seen in Table 4.3). However, to choose the model that had the best fit, a collaboration with one of the supervisors of this thesis was made to try a model fit approach (Burnham et al., 1998), which reduces biases associated with significance testing. It was compared how well three different models explained log(MeHg(I)) using the Akaike's Information Criterion (AIC_c) corrected for small sample size. Models were constructed using the variables shown in Table 4.4.

Table 4.4: Variables used in the 3 models of the first multiple regression analysis to choose the best fit according to the AIC.

Dependent Variable	Independent Variables
Log(MeHg(I))	pH
Log(MeHg(I))	$\delta^{15}N$
Log(MeHg(I))	pH, $\delta^{15}N$

Only one model had ΔAIC_c values less than 2 (considered better fit; Burnham et al., 1998); the best fitting model was that with pH and $\delta^{15}N$, which had a weight of 0.98. Thus, this result was consistent with the selection of this model by stepwise multiple regression.

The previous multiple regression analysis was made using data provided by six articles because those were the only ones that were extracted from the literature that provided information on the concentration of MeHg(I) in invertebrates and also the pH of the study site and the $\delta^{15}N$ of the invertebrates.

To study the effect of other parameters, it was selected a smaller data set, containing information on only caddisflies, mayflies, dragonflies and damselflies, and a second multiple regression analysis was made. For this analysis, the logarithm of MeHg(I) concentration in the invertebrates was used as the dependent variable and pH and TOC of the study site and $\delta^{15}N$ value of the invertebrates as the independent variables. TOC was added because organic matter has shown to have a significant effect on mercury methylation and bioavailability to organisms (Lavoie et al., 2019). The multiple regression method selected was the stepwise method. The descriptive analysis of the variables is presented in Table 4.5.

Table 4.5: Descriptive analysis of variables used in the second multiple regression analysis: logarithm of MeHg(I) in invertebrates, stable isotope $\delta^{15}N$, pH and TOC. For this analysis, it was used the data for caddisflies, mayflies, dragonflies and damselflies.

Variables	Mean	Std. Deviation	N
Log(MeHg(I)) in invertebrates	2.06	0.36	65
$\delta^{15}N$ (‰)	2.42	1.75	65
pH	5.79	0.86	65
TOC (mg/L)	5.49	3.14	65

The data was selected on *SPSS* and the program created two different models. The first one has as a predictor only $\delta^{15}N$ and the second one had pH and the $\delta^{15}N$ value. So, in both models, the TOC concentration was removed. The summary of the models created is presented in Table 4.6.

Table 4.6: Results of the second multiple regression models explaining log(MeHg(I)) concentration in caddisflies, mayflies, dragonflies and damselflies.

Model	Predictors	R	R^2	Adjusted R^2	Std. Error of the Estimate	ANOVA		
						F	p	df (Regression, Residual)
1	$\delta^{15}N$	0.479	0.229	0.217	0.323	18.741	<0.001	1, 63
2	pH, $\delta^{15}N$	0.788	0.622	0.610	0.228	50.950	<0.001	2, 62

On the first model, $\delta^{15}N$ showed a positive partial standardized regression coefficient (b'=0.479, p<0.001). On the second model, $\delta^{15}N$ also showed a positive partial standardized regression coefficient (b'= 0.770, p<0.001) and pH showed a negative partial standardized regression coefficient (b'=-0.691, p<0.001).

The procedure above suggests that the inclusion of both pH and $\delta^{15}N$ produces a much better model, as the R^2 was nearly three times higher in model 2 (as seen in Table 4.6). However, to choose the model that had the best fit, a collaboration with one of the supervisors of this thesis was again made to try a model fit approach (Burnham et al., 1998), which reduces biases associated with significance testing. It was compared how well seven different models explained log(MeHg(I)) using the Akaike's Information Criterion (AIC_c) corrected for small sample size. Models were constructed using the variables shown in Table 4.7.

Table 4.7: Variables used in the 7 models of the first multiple regression analysis to choose the best fit according to the AIC.

Dependent Variable	Independent Variables
Log(MeHg(I))	pH
Log(MeHg(I))	TOC
Log(MeHg(I))	$\delta^{15}N$
Log(MeHg(I))	pH, TOC
Log(MeHg(I))	pH, $\delta^{15}N$
Log(MeHg(I))	TOC, $\delta^{15}N$
Log(MeHg(I))	pH, TOC, $\delta^{15}N$

Two models had ΔAIC_c values less than 2, and hence considered to provide a similar, good fit (Burnham et al., 1998). The best-fitting model was the one with pH and $\delta^{15}N$ as predictors, which had a weight twice as strong (0.67) as the model that included those variables plus TOC (0.33; ΔAIC_c = 1.39). This approach supported the use of stepwise multiple regression.

The previous multiple regression analysis was made using data provided by only three articles because those were the only ones that were extracted from the literature that provided information on not only the concentration of MeHg(I) in the four groups of invertebrates chosen, but also the pH and TOC content of the water and the $\delta^{15}N$ of the invertebrates.

5. Discussion

5.1. Patterns of MeHg(I) Concentration in Invertebrates

It was found that the type of invertebrate with the highest mean MeHg(I) in tissue was the grass shrimp, followed by backswimmers, water boatmen and water scorpions. Grass shrimps (*Palaemonetes kadiakensis*) belong to the family Palaemonidae of the order Decapoda and are generally predators (Thorp and Rogers, 2011). The next invertebrates with highest MeHg(I) concentration are all from the order Hemiptera, which are commonly designated as true bugs (Thorp and Rogers, 2011). Both backswimmers and water scorpions are predators but water boatmen are generally non-predaceous and instead are collector-gatherers that feed on algae and detritus (Thorp and Rogers, 2011).

Due to the capacity of MeHg(I) to biomagnify through the food web (Lemes and Wang, 2009), it was expected that organisms that occupy higher trophic levels would have higher MeHg(I) concentration (Lavoie et al., 2013). As shown in Figure 4.1, most invertebrates with predatory diets, such as the ones already mentioned and damselflies (M=254.5 ng/g dw, Mdn=159.0 ng/g dw, N=17), spiders (M=254.0 ng/g dw, Mdn=141.0, N=9), dragonflies (M=237.2 ng/g dw, Mdn=188.6 ng/g dw, N=102) and water striders (M=215.6 ng/g dw, Mdn=151.0 ng/g dw, N=7), also occupy higher positions in the graph. Nevertheless, some invertebrates showed unexpected positions in the graph such as water boatmen (M=339.5 ng/g dw, Mdn=210.0 ng/g dw, N=16).

The type of invertebrate that showed the highest variation in mean values of MeHg(I) were caddisflies (CV=133.7%), followed by water boatmen (CV=114.6%) and beetles (CV=112.8%). Water boatmen presented high variation between mean values and, as discussed before, it also occupies a high position in the graph, Figure 4.1. The high mean and median values of MeHg(I) and variation of these values could be related to the fact that this family has species with significantly different types of ecology and types of diet. These organisms belong to the family Corixidae, which is the largest family from the insect order Hemiptera (Hilsenhoff, 2001). Most true bugs are predators but “corixid adults and nymphs feed primarily on detritus, algae, protozoans, and other extremely small animals” (Hilsenhoff, 2001, p. 684). In other studies, some species of water boatmen showed to be predatory and some also scavenge dead organisms, which may increase their MeHg(I) content (Hädicke et al., 2017; Pajunen and Pajunen, 1992). In a study made by Sarica et al., (2005) it was found that leeches, a necrophagous invertebrate, increased its MeHg(I) concentration five times when in contact with a fish carcass, which did not occur with other studied invertebrates that do not have this type of diet. Scavengers can therefore have significant importance in returning the MeHg(I) of dead organisms to other trophic levels of the food chain.

In Figure 4.1, it was observed that a large portion of the invertebrates has values that exceed, for example, the Canadian methylmercury tissue residue guideline for the protection of wildlife consumers of aquatic biotas, which is 33 µg/kg in wet weight (CCME, 2000). Assuming 80 to 90% water content in the invertebrates it was possible to convert this guideline value to dry weight, giving a range between 165 ng/g dw and 330 ng/g dw, which allowed the comparison with the values of MeHg(I) in the invertebrates. By analyzing Figure A1, that is the same plot as the one in Figure 4.1 but with the outliers labeled with the type of ecosystem, it is possible to observe that in wetlands and reservoirs the invertebrates show higher levels of MeHg(I) which poses a risk to higher trophic organisms, such as birds and fishes, that feed on these invertebrates. Jackson et al. (2014) assessed the THg concentration in the blood of songbirds that inhabit the eastern part of North America and concluded that there is a correlation between the type of diet and habitat with the concentration of mercury. Invertebrate-eating species had significantly higher concentrations when compared to omnivores, especially the ones that inhabited wetland habitats. So, a specific type of diet or a change in diet due to external reasons can pose a risk to these organisms and lead them to feed on invertebrates with higher MeHg(I) concentration.

Regarding the mean values of %MeHg(I), backswimmers were the type of invertebrate that showed the highest mean value (97.2%, Mdn=96.0%, N=5), followed by water treaders (M=Mdn=94.8%, N=2) and water scorpions (M=93.1%, N=1). These three groups of invertebrates are predatory which matches with previous studies that found an increase of %MeHg(I) with trophic position (Gorski et al., 2003; Mason et al., 2000; Riva-Murray et al., 2020). Backswimmers not only showed a high mean and median value of %MeHg(I) but also a low variation between the values collected (CV=4.1%). This could potentially indicate that the MeHg(I) concentration in this type of invertebrate could be estimated by measuring THg, which is a simpler laboratory analysis and significantly less expensive.

The type of invertebrate with more variation regarding the mean values of %MeHg(I) were mussels (CV=92.5%, N=3), midges (CV=80.4%, N=21) and mayflies (CV=57.8%, N=31). These three types of invertebrates are mostly primary consumers, which can influence their high variability. Riva-Murray et al. (2020) findings suggest that the %MeHg(I) of aquatic primary consumers, specifically caddisflies and mayflies, is strongly correlated with the aqueous MeHg(I) concentration that is available for uptake into periphyton. Therefore, because the MeHg(I) concentration in aquatic ecosystems is influenced by several environmental conditions (Paranjape and Hall, 2017), the higher susceptibility of primary consumers to MeHg(I) concentration of the surrounding environment may explain their high variability.

The high variation registered in MeHg(I) concentration and %MeHg(I) in some of the invertebrates could potentially be a consequence of the decision of identifying them by common name, which implies that some groups of invertebrates include several families and others only one. For example, dragonflies encompass families like Aeshnidae, Libellulidae and Gomphidae but water scorpions only include organisms from the Nepidae family. But even the groups of invertebrates that only include one family showed high variability, which is the case of the water boatmen, that are organisms from the Corixidae family. This type of invertebrate presented one of the highest variabilities in the mean values of MeHg(I) and to this family belong several species with vastly different types of ecology. In this family, species of *Cymatia* tend to be predators and even have morphological adaptations that help them catch their prey and species of *Micronecta* generally feed by scraping biofilm from the surface of the particles (Hädicke et al., 2017).

It is plausible to ponder if this variability could possibly be reduced if all sampled organisms were identified as species, because grouping invertebrates by a higher taxonomic level could mask the utility of having species-specific values. However, the identification of invertebrate species requires time and expertise and, in fact, Gerwing et al. (2020) showed that in ecological studies there was no significant difference in the conclusions taken when identifying organisms by species or grouping them by family, in coastal ecosystems. Nevertheless, the results obtained in this review could be an indication that, for contamination studies, certain individual species behaviors may create outliers in the bioaccumulation data. In these specific cases, the identification of the invertebrates by species could provide useful information.

5.2. Comparison Between Wetlands and Lakes

With the data extracted from the literature, it was possible to compare the MeHg(I) bioaccumulation and biomagnification between lakes and wetlands by comparing the concentration of MeHg(I) in caddisflies, mayflies, dragonflies and damselflies in both ecosystems. For the four types of invertebrates, it was possible to conclude that the concentrations of MeHg(I) were significantly higher in wetlands than in lakes. Several studies have concluded that wetlands are hot-spots for mercury methylation due to their high content of dissolved organic matter, anoxia, and low pH (Hall et al., 2008; Rencz et al., 2003). Eagles-Smith et al. (2020) conducted a project that allowed the assessment of mercury bioaccumulation in aquatic ecosystems in the United States, in more than 450 locations, by using larvae of dragonflies as biosentinels. In this study, it was possible to collect dragonflies from different types of ecosystems and the concentration of THg in dragonflies that inhabit wetlands was higher, but not significantly, than the ones that inhabit lakes. For this national assessment, it was chosen to analyze THg concentration in the dragonflies because a subset of individuals (652 samples) showed a strong correlation between the concentration of MeHg(I) and THg and the %MeHg(I) was also high (79.9% and standard error of 0.5%). Nevertheless, however, the fact that the concentration of mercury in dragonflies did not show a significant difference between lakes and wetlands may be related to the decision of analyzing the concentration of THg and not MeHg(I) in the invertebrates.

In the two ecosystems, caddisflies and mayflies showed the lowest mean and median values of MeHg(I) and dragonflies and damselflies showed the highest. Caddisflies larvae are mostly herbivores or detritivores but there are some cases of omnivores and predators (Hilsenhoff, 2001). Mayflies nymphs are mostly scrappers or collectors and the adults do not eat (Cummins, 1973; Thorp and Rogers, 2011). From the group of four, dragonflies and damselflies are the ones that occupy higher levels on the trophic chain because the majority are predators that feed on other insects, such as caddisflies and mayflies (Hilsenhoff, 2001). The results obtained also show a correlation between the MeHg(I) concentration and the feeding habits of these organisms because in, both ecosystems, the predators (damselflies and dragonflies) showed higher concentrations of MeHg(I).

Additionally, caddisflies were the type of invertebrates with the highest variation between mean values of MeHg(I) in both ecosystems (CV=94.3% in lakes and CV=129.3% in wetlands). In lakes, dragonflies were the invertebrates with the lowest variation (CV=75.7%) followed by mayflies (CV=80.5%) and in wetlands were damselflies (CV=70.8%) followed by mayflies (CV=83.1%). The results in Table 4.1 also demonstrate that in wetlands the variation is almost always higher than in lakes, with the exception of damselflies.

As referred to in the section before, caddisflies had the highest variation between mean values of MeHg(I) in the literature. Clarke (2018) findings show that the MeHg(I) concentration in caddisflies might be correlated with the concentration of MeHg(I) in sediments. The caddisflies sampled in the research were all case-makers, that use natural materials to build protective cases, and the correlation that was seen between MeHg(I) concentration in sediments and the invertebrates may be influenced by this characteristic (Clarke, 2018). Additionally, caddisflies biosynthesized silk to use in the construction of their cases and this fact can be important to remove Hg(II) from their body (Clarke, 2018).

In this analysis, several families of caddisflies were used, for example, Limnephilidae, Odontoceridae, Phryganeidae and Hydroptilidae. The ones referred are all case-making caddisflies (Hilsenhoff, 2001) but some of the data used was reported in the studies only by the order Trichoptera, so it is not possible to conclude that all the data of caddisflies used in this research was from families that construct these protective cases. Therefore, the high variability seen in this group of invertebrates can be related to their susceptibility to the concentration of MeHg(I) in the sediments and also due to the variability of the organisms' ecologies in the order Trichoptera.

Another relevant outtake from this part of the results was the understanding of the clear underrepresentation of wetland invertebrates in studies when compared to lakes. For this analysis, fourteen studies presented this data in lakes and only three in wetlands. Regarding the complete set of data, with all types of invertebrates, seventeen studies presented data on lakes and only five on wetlands. In this review, it was possible to verify that wetlands seem to pose a higher risk to organisms due to their elevated content of MeHg(I), so further research is needed to identify what factors have higher influence on MeHg(I) bioaccumulation in this type of ecosystem.

5.3. Combined Influence of Different Variables in MeHg(I) Bioaccumulation

Bioaccumulation and biomagnification of MeHg(I) is known to be significantly impacted by the physico-chemical characteristics of the ecosystem (Clayden et al., 2013; Lavoie et al., 2013; Sumner et al., 2020). In the first multiple regression analysis, the full data set of invertebrates was used and their value of $\delta^{15}N$ and also the pH of the study sites, because this was the chemical parameter that appears in more articles (as seen in Table 3.1). The software provided two models, one with only pH and other with pH and $\delta^{15}N$ as independent variables. Both were significant and pH showed a negative partial standardized regression coefficient (b'=-0.459, p<0.001 and b'=-0.541, p<0.001) and in the second $\delta^{15}N$ showed a positive partial standardized regression coefficient (b'=0.238, p=0.001). Both the variables had expected effects in the concentration of MeHg(I) in the invertebrates. Because MeHg(I) has the capacity to biomagnify in a food web, MeHg(I) tends to increase with $\delta^{15}N$. Additionally, studies show that acidic waters, with low pH, are generally correlated with an increase in MeHg(I) concentration in the organisms (Clayden et al., 2014; Edmonds et al., 2012), which can be related to the fact that low pH appears to favor methylation (Ullrich et al., 2001).

A smaller data set of invertebrates was used for the second analysis and the ones chosen were caddisflies, mayflies, dragonflies and damselflies. In this analysis, $\delta^{15}N$, pH and TOC were chosen as independent variables. The software provided two models, one with only $\delta^{15}N$ and other with $\delta^{15}N$ and pH as independent variables. Both were significant and $\delta^{15}N$ showed a positive partial standardized regression coefficient (b'=0.479, p<0.001 and b'=0.770, p<0.001) and in the second pH showed a negative partial standardized regression coefficient (b'=-0.691, p<0.001). The results from the multiple regression analysis showed that MeHg(I) concentration in caddisflies, mayflies, dragonflies and damselflies was significantly affected by $\delta^{15}N$, however, by adding pH to the model, the correlation between MeHg(I) and the combined effect of $\delta^{15}N$ and pH was much higher.

Analyzing the two models with pH and $\delta^{15}N$ as independent variables is possible to observe that when using the full set of data, 25.2% of the variance of the dependent variable is explained by the independent variables and when using the smaller set, with the four types of invertebrates, this percentage increases to 61.0%. These values are expressed in the column of "Adjusted R^2" in Table 4.6 and Table 4.3. The smaller set of data compromised four types of invertebrates with known types of diet and ecology. By adding all the invertebrates in the multiple regression analysis, the relation between MeHg(I) concentration and trophic position can be not so linear and the effect of other physico-chemical characteristics of the environment can be more significant to other invertebrates.

The second multiple regression analysis also included TOC, but it was removed from the model because it was the variable with the weakest correlation. The organic matter content of an aquatic ecosystem can have several effects on mercury speciation that also depend on other chemical characteristics (Ravichandran, 2004). Organic matter can have different functional groups and their chemical form depends on the pH which also affects the complexes made with the mercury forms present in the environment, affects its transport and mobility (Ravichandran, 2004; Ullrich et al., 2001) and can also influence photochemical processes, such as photodemethylation (Klapstein and O'Driscoll, 2018). Due to the variety of effects that DOM can have on mercury speciation, which depend not only on its concentration and composition but also on the characteristics of the ecosystem, research shows some contradictory results regarding its effects (Jiang et al., 2018). Therefore, the weak correlation obtained in the analysis between MeHg(I) and TOC can be associated with this complexity of effects that organic matter can have. Additionally, in aquatic environments, DOM is always in excess when compared to MeHg(I), so in ecosystems with high content of DOM it may be possible to see variation in MeHg(I) concentration but not in DOM.

The first multiple regression analysis was made using the logarithm of MeHg(I) in invertebrates as dependent variable and pH of the site and $\delta^{15}N$ of the invertebrates as independent variables, and was executed with the data of six different articles because only these reported all the information needed.

For the second multiple regression analysis, it was used the logarithm of MeHg(I) in caddisflies, mayflies, dragonflies and damselflies as the dependent variable and pH and TOC of the site and $\delta^{15}N$ as independent variables, and only three articles provided the information needed. These studies all analyzed lakes and two of them studied the same location, the Kejimkujik National Park in Nova Scotia. Consequently, the strength of the analysis was not as rigorous as desired.

An important take away message from the research of this thesis was the understanding that there is essential information missing in many of the articles examining bioaccumulation and biomagnification of MeHg(I). The variables used to assess the ecosystems' physico-chemical characteristics are one of them. Variables such as pH, the content of organic matter (for example DOC or TOC), the concentration of important nutrients such as phosphorus and nitrogen. This information can be unnecessary for some studies but will enable further and deeper analysis of the topic, such as systematic reviews of the literature.

5.4. Application to Risk Assessment

In 2017, the Minamata Convention entered into force and the Parties agreed to tackle the anthropogenic emissions of mercury (UN Environment, 2019b). Although the agreement refers to the importance to address atmospheric, land and water releases, a lot more attention has been put on atmospheric emissions (You, 2015), which has a separate article in the Convention report (UN Environment, 2019b). The article where water releases are referred to also compromises the land releases and the requirements on these are weaker than the ones for atmospheric emissions (You, 2015). The countries should identify the relevant point source categories, take measures to control releases and do an inventory of releases from relevant sources (UN Environment, 2019b). The coverage of the article is narrow and does not define specific relevant point sources and requirements for controlling them (You, 2015).

In the literature, it is also possible to see the discrepancy between the mercury inventories that have been made regarding global atmospherics emissions and direct releases to aquatic systems, that have been widely understudied (Kocman et al., 2017). The research of this thesis also supports the importance of assessing mercury releases to aquatic systems due to their susceptibility to being affected by MeHg(I), that bioaccumulates and biomagnifies through the food webs of these systems.

Additionally, although a large decline in atmospheric mercury over the past years has been registered (Zhang et al., 2016), research shows that a discrepancy exists between this trend and the one seen in mercury in aquatic biota (Wang et al., 2019). Wang et al. (2019) studied several cases where this divergence is evident and concluded that it is an indication that the mercury concentration in aquatic biota is not only influenced by the mercury influx to the ecosystem, but also by the processes that occur specifically in that ecosystem. These include the biogeochemical processes that occur in the ecosystems, the type of diet of the organisms and the climate (Wang et al., 2019). This thesis also supports the importance of internal processes that occur in the ecosystems that makes the organisms that inhabit there more susceptible to MeHg(I) bioaccumulation. The significant difference in MeHg(I) concentration in the four selected invertebrates when comparing the ones that were collected in wetlands and the ones collected in lakes, shows that there are certain processes that are dependent on the type of ecosystem that influence this problem.

In Europe, the risk assessment of substances of high concern is regulated by the REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) Regulation (EC 1907/2006). This regulation entered into force in 2007 and aims to ensure the protection of human health and the environment of hazardous substances. One of the key aspects of this regulation is the assessment of the bioaccumulation potential of the substances. In the Annex XIII (EC 1907/2006), a substance is defined as bioaccumulative if the bioconcentration factor (BCF) is superior than 2000 and very bioaccumulative if the BCF is superior than 5000. The BCF in aquatic biota is defined as the ratio between the concentration of a substance in the tissue of an organism divided by the concentration of the same substance in water and only considers the pollutant uptake from dissolved water sources.

The bioconcentration potential of the substances is traditionally assessed using fish (ECHA, 2017a). In addition, the bioaccumulation factor (defined as the ratio of the concentration of a substance concentration in an organism and the concentration in the surrounding medium), that takes into account both water and dietary sources of the pollutant, and the biomagnification factor (defined as the ratio of the concentration of a substance in a predator and in their prey) can be used as supplementary information to indicate if the substance has bioaccumulative potential or not (ECHA, 2017b). Therefore, the assessment of the substances as bioaccumulative is decided primarily using the BCF.

Mercury risk assessments could potentially be performed using monitoring data of mercury concentration in invertebrates, from field studies. Certain families of invertebrates are distributed globally and inhabit several types of ecosystems. Furthermore, the sampling of these organisms is much simpler than sampling fishes. It is relevant to note that bioconcentration of MeHg(I) from the water column to plankton can be a good predictor of the vulnerability of the ecosystems to MeHg(I) biomagnification (Wu et al., 2019) and also that upper trophic level organisms can be a better indicator of mercury in certain ecosystems. Nevertheless, it is important to mention that invertebrates are a key linkage in food webs and are important for biomagnification in the ecosystems.

Consequently, using invertebrates as biomonitors could be a good way to track mercury in aquatic environments. If the monitoring included the analysis of the physico-chemical parameters of the study sites where they were collected, a lot of information could be added to the assessment and improve the knowledge on what type of characteristics are more relevant to mercury bioaccumulation and biomagnification. Other studies also show the importance of considering the differences between ecosystems in risk assessments and biomonitoring programs (Evers et al., 2016; Wang et al., 2019), and the research of this thesis confirms the need for this type of information.

As such, the best practices for the analysis of bioaccumulation and biomagnification of mercury in the invertebrates' food web are assessing the concentration of MeHg(I) and THg, the %MeHg(I) and the stable isotopes of the invertebrates and physico-chemical characteristics of the ecosystems, such as the pH value, the MeHg(I) and THg concentration in water, the concentration of organic matter, the concentration of dissolved oxygen, the concentration of phosphorus and nitrogen and the sulfur concentration.

And the best practices to report these studies include providing the raw data of MeHg(I), THg and %MeHg(I) in the invertebrates (mean, median, standard deviation and number of samples). The lowest taxonomic level possible of each type of invertebrate should also be provided or data on stable isotopes, such as $\delta^{15}N$, because it allows better differentiation between organisms and might reduce the variability. As mentioned before, in contamination studies is also essential to be aware of specific invertebrates that due to their behavior can be outliers in the dataset. For these organisms, it would be important to identify them by species and not by family in order to handle them separately.

Additionally, the reports should also include data regarding the physico-chemical characteristics of the ecosystem. Some important parameters are the pH value, the content of organic matter (for example DOC or TOC), the concentration of dissolved oxygen, the concentration of nutrients such as phosphorus and nitrogen, the concentration of ions and also the MeHg(I) and THg concentration in water. These last two variables are harder to work in further researches because there still needs to be a consensus on reporting THg and MeHg(I) concentration from filtered or unfiltered water samples (Bravo et al., 2018). In addition, if the study includes the analysis of different sites, these parameters should be reported individually and not present a mean value of all sites.

5.5. Sources of Error and Potential Improvements

This thesis had as a focal point a systematic analysis of the published peer-reviewed literature related to mercury bioaccumulation in freshwater and terrestrial invertebrates. To do this, data was extracted from the articles, in particular, the mean values of the concentration of MeHg(I), THg and %MeHg(I) and stable isotopes in the invertebrates and also the mean values of the physico-chemical variables of the study sites. So, by not using the standard deviation associated with these values, some of the error was not accounted for. In order to use the data from the papers selected it was also reviewed the published quality assurance/quality control (QA/QC) of these papers. To do this, it was verified if quality controls were described in the papers, such as replicated sampling, blanks, matrix spikes, calibration standards, certified and standard reference materials. After this review and accepting the QA/QC, it is assumed that the studies have similar errors in the methods.

By accepting the QA/QC of the data in the papers used for this analysis, it is also accepted that all data is real and not measurement errors. Consequently, all the outliers that are seen in Figure 4.1, Figure 4.2 and Figure 4.3 were kept in the analysis. It was assumed that these values were a consequence of external conditions. For example, a lot of the outliers are from invertebrates collected in wetlands (Figure A1), therefore the high concentration of MeHg(I) that they showed can be associated with that. These outliers prove to be an excellent source of information for this review, which highlights the importance of researchers including outliers in their datasets.

Some authors adjusted $\delta^{15}N$ to a common baseline of the food web, so to use these values it was assumed that the baseline was the same, which may not be true.

Additionally, the number of mean values that were possible to collect for each invertebrate varies significantly, as it is possible to observe in Table A1 of the Annexes. Due to this disparity, the comparison of values obtained for each type of invertebrate possibly does not reflect the reality.

To improve the analysis made in this thesis, some changes could be made. Adding more articles to this review would enhance the strength of the analyses. Furthermore, some of the studies used did not have data on the chemical characteristics of the study site and this information could potentially be found in other articles that analyzed the same site. Some of the articles were excluded because they did not provide the raw data needed, so the authors could have been contacted to obtain the information that was unavailable in the paper.

6. Conclusion

This research found that predatory tendencies are a key influence on the general patterns of MeHg(I) concentration in invertebrates, using the information available in the literature.

A large percentage of the invertebrates included in the analysis exceeded the Canadian guideline value for the protection of wildlife consumers of aquatic biota. This confirms that MeHg(I) in the lower trophic levels of the food web is a key consideration in ecological risk assessments of higher organisms for mercury toxicity.

The grouping of invertebrates at the family level is a common practice in both ecological and contamination studies. However, the high variability in mercury content for some species indicates that grouping at the family level may not be appropriate in contamination studies and that more research is needed to identified key species outliers. In this review, it was found that water boatmen, that are organisms from the Corixidae family, showed high variability and the diversity of species' ecologies reflects the need to identify the organisms by species and not by family.

The analysis also confirmed that certain types of ecosystems pose a higher risk for MeHg(I) bioaccumulation and biomagnification. Wetlands, specifically, have been identified as hot-spots for mercury methylation and bioaccumulation in higher trophic levels. This research further identifies that the concentration of MeHg(I) in invertebrates is elevated in these ecosystems and likely drives accumulation in higher trophic levels. Nevertheless, it was evident that in the literature there is a large discrepancy between the number of articles regarding MeHg(I) bioaccumulation in invertebrates in lakes and in wetlands, being that the latter have been understudied. This review shows the need for further controlled research to specify what factors have the greatest influence on MeHg(I) bioaccumulation in wetlands due to the risk that this ecosystem can pose to the organisms that inhabit there.

The multiple regression analyses allowed for the assessment of the importance of some physico-chemical characteristics of the ecosystems in MeHg(I) bioaccumulation in freshwater and terrestrial invertebrates. The pH value of the aquatic system had a negative correlation with the MeHg(I) concentration and $\delta^{15}N$ showed a positive correlation with MeHg(I). This was expected since most of the invertebrates with highest mean concentration of MeHg(I) have predatory diets. In further research, it would be important to assess the combined contribution of more environmental parameters such as oxygen availability and the concentration of important nutrients (for example, phosphorus and nitrogen) in the bioaccumulation and biomagnification of MeHg(I) in the invertebrates' food web.

The results of this thesis can also be applied to risk assessment analyses. A lot of attention has been put on the atmospheric emissions of mercury in the recently developed Minamata Convention, but there is a need to look further into direct releases to aquatic systems due to their high susceptibility to be affected by mercury. This research shows the importance of the physico-chemical characteristics of the ecosystems on the accumulation of MeHg(I) in the biota. Therefore, this type of data should also be included in risk assessment analyses.

Invertebrates can be used as biomonitors of MeHg(I) in the ecosystems because they are easy to sample (when compared to fishes and birds, for example) and a significant increase of knowledge of MeHg(I) bioaccumulation and biomagnification is possible to achieve when adding to the assessment the information on the chemical and physical characteristics of the studied ecosystem.

This systematic analysis of published peer-reviewed literature related to mercury bioaccumulation in freshwater and terrestrial invertebrates also provided the possibility to evaluate which are the best practices for analysis and reporting on this topic, to enable further research and risk assessments. For the analysis, it is considered essential to assess the concentration of MeHg(I), THg, %MeHg(I) and the stable isotopes of the invertebrates and the physico-chemical characteristics of the ecosystem, such as the pH value of the water, the concentration of organic matter, the concentration of dissolved oxygen, the concentration of phosphorus and nitrogen and the sulfur concentration.

To report this information, the best practices include providing the raw data of MeHg(I), THg and %MeHg(I) in the invertebrates (mean, median, standard deviation, and the number of samples) and the lowest taxonomic level possible. Due to their ecology, some organisms, such as water boatmen, can be identified as outliers in the data set and, in these cases, it is important to identify them by species and handle them separately to reduce the variability. Additionally, the reports should also include the raw data regarding the physico-chemical characteristics of the ecosystem. If field collections were made in several study sites, the data should be presented individually for each of them.

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Appendix

Table A1: Table with the mean value (M) of MeHg(I) and %MeHg(I) of all values extracted from the literature of each type of invertebrate, the standard deviation (SD), the coefficient of variation (CV) and the median (Mdn) of the and the mean of the percentage of MeHg(I) and the standard deviation. The table is ordered by lowest to highest mean value of MeHg(I) concentration.

	MeHg(I) concentration (ng/g dw)				Percentage of MeHg(I) (%)			
Type of Invertebrate	M [SD]	CV	Mdn	N	M [SD]	CV	Mdn	N
Grass shrimps	435.0			1	72.4			1
Backswimmers	382.9 [333.3]	87.0	242.0	15	97.2 [3.9]	4.1	96.0	5
Water boatmen	339.5 [389]	114.6	210.0	16	76.3 [13.9]	18.2	80.0	9
Water scorpions	306.4 [96.3]	31.5	350.0	6	93.1			1
Flies	276.1 [285.4]	103.4	164.0	9	64.4 [34.1]	53.0	79.0	9
Crayfish	268 [99.2]	37.1	249.0	4	87 [13]	15.0	88.0	4
Damselflies	254.5 [233.6]	91.8	159.0	17	82.7 [20.1]	24.3	90.0	7
Spiders	254 [234.7]	92.4	141.0	9	53.6 [27.3]	51.0	62.5	6
Water treaders	239.5 [108.1]	45.2	239.5	2	94.8 [10.9]	11.6	94.8	2
Giant waterbugs	239.4 [167.5]	70.0	207.5	8	84.8 [0.2]	0.3	84.8	2
Dragonflies	237.2 [202.8]	85.5	188.6	102	81.8 [19.8]	24.2	84.0	56
Water striders	215.5 [130.7]	60.7	151.0	7	81			1
Water Mites	192.5 [194.4]	101.0	192.5	2	41			1
Isopods	180.4 [81]	44.9	210.0	9	56.3			1
Beetles	161.1 [181.7]	112.8	107.3	49	60.3 [29]	48.1	69.8	25
Clams	121 [96.1]	79.5	121.0	2	58			1
Alderflies	120.3 [81.8]	68.0	162.0	3	65.5 [0.7]	1.1	65.5	2
Amphipods	91.9 [56.6]	61.6	85.0	39	71.1 [19.4]	27.3	77.6	7
Mysids	82.5			1				
Mayflies	80.2 [72]	89.8	69.4	66	39.7 [22.9]	57.8	38.0	31
Caddisflies	76.9 [102.8]	133.7	42.9	76	46 [19.5]	42.4	47.0	36
Midges	76.9 [65.4]	85.0	63.6	81	31.9 [25.6]	80.4	25.7	21
Zooplankton	76.3 [75.9]	99.4	50.2	56	26.9 [6]	22.4	28.9	8
Green stoneflies	65.0			1	56			1
Leeches	48.5 [10.6]	21.9	48.5	2	43.5 [2.1]	5.0	43.5	2
Mussels	48.4 [51]	105.4	37.8	8	50.7 [46.9]	92.5	24.2	3
Snails	38 [19]	50.1	40.5	16	44.3 [12.4]	28.0	47.1	7
Milipedes	29.0			1				
Oligochaete worms	11.0			1				
Moths	2.5 [0.7]	28.3	2.5	2	13 [4.2]	32.6	13.0	2

Lygus bug	2.0			1	11			1
Bumblebees	1.0			1	19			1
Wasps	1.0			1	6			1
Grasshoppers	0.4			1	3			1
Caterpillars	0.2			1	3			1

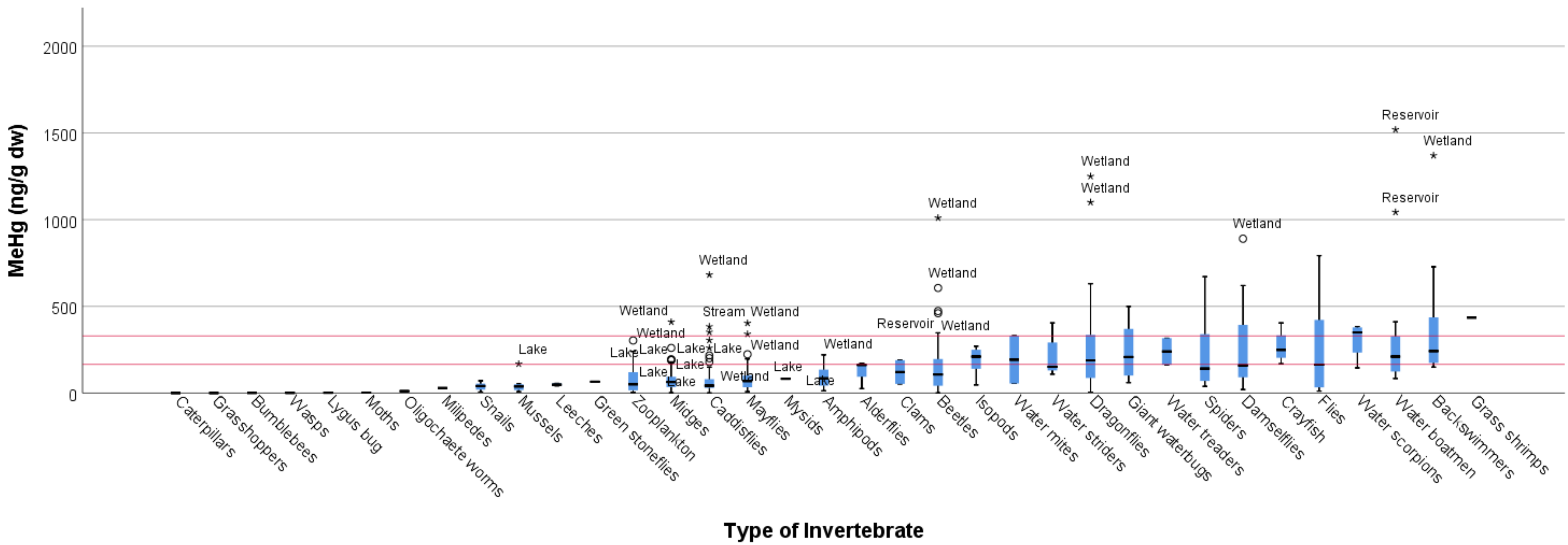

Figure A1: Boxplots of MeHg(I) concentration in the dry tissue of invertebrates separated by common name and ordered from lowest to highest mean value. In each boxplot the median is represented with a black bar, the outliers marked with circles and extreme outliers marked with asterisks. The red lines represent the Canadian methylmercury tissue residue guideline for the protection of wildlife consumers of aquatic biotas, which is 33 µg/kg in wet weight. The MeHg(I) concentration in the invertebrates is in dry weight so the guideline value was transformed by assuming a 80% to 90% water content, which corresponds to 165 ng/g dw and 330 ng/g dw respectively. In this graph, the outliers and extreme outliers are labelled with the type of ecosystem from where the invertebrates were collected.